

P2P [Phenylacetone] via aldol & Bayer Villager

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fan of zwitterion Ok,

Bio and two dogs posted awhile back, what I think would be one of the most overlooked synthesis of Phenylacetone's

An acid catalysed Aldol Condensation, followed by a Bayer-Villager, peracid, eventully gives yield of P2P.

The literature is well documented, and verified by many former researchers.

MEK+Benzaldehyde--->MethylPhenylButanone

I vaguely remember Bio saying that is also could be achieved with Acetone and benzene, respectfully

1) An acid catalysed Aldol condensation of Benzaldehyde and Methyl Ethyl Ketone to give Methyl Phenyl Butenone ie C6H5CHO + CH3CH2COCH3 + dryHCL ---> C6H5CH=C(COCH3)CH3

2) The unsaturated ketone undergoes the Baeyer-Villiger oxidation with peroxy acids to give the enol ester of Phenyl propanone ie C6H5CH=C(COCH3)CH3 + RCO3H ----> C6H5CH=C(OCOCH3)CH3

3) The enol ester is then saponified with 10% NaOH solution to give Phenyl Propanone in about 35% yield based on the unsaturated ketone.
&--1050;&--1086;&--1085;&--1076;&--1085;&--1089;&--1072;&--1094;&--1080;&--1103; Aldol.

200 gms Benzaldehyde &--1080; 300 gms Methyl Ethyl Ketone &--1089;&--1084;&--1077;&--1096;&--1080;&--1074;&--1072;&--1102;&--1090;&--1089;&--1103; &--1074; &--1083;&--1080;&--1090;&--1088;&--1086;&--1074;&--1086;&--1084; &--1093;&--1080;&--1084;&--1080;&--1095;&--

1077;&--1089;&--1082;&--1086;&--1084; &--1089;&--1090;&--1072;&--1082;&--1072;&--1085;&--1077; &--1080; &--1086;&--1093;&--1083;&--1072;&--1078;&--1076;&--1072;&--1102;&--1090;&--1089;&--1103;&--1085;&--1080;&--1078;&--1077; 5C.&--1052;&--1077;&--1076;&--1083;&--1077;&--1085;&--1085;&--1086; &--1085;&--1072;&--1089;&--1099;&--1097;&--1072;&--1077;&--1084; &--1093;&--1083;&--1086;&--1088;&--1086:&--1074:&--1086:&--1076:&--1086:&--1088:&--1086:&--1076:&--1086;&--1084; &--1087;&--1086;&--1082;&--1072; &--1089;&--1084;&--1077;&--1089;&--1100; &--1085;&--1077; &--1091;&--1074;&--1077;&--1083;&--1080;&--1095;&--1080;&--1090;&--1089;&--1103; &--1074; &--1074;&--1077;&--1089;&--1077; &--1085;&--1072; 40 &--1075;. &--1042;&--1085;&--1072;&--1095;&--1072;&--1083;&--1077; &--1089;&--1084;&--1077;&--1089;&--1100; &--1087;&--1088;&--1086;&--1079;&--1088;&--1072;&--1095;&--1085;&--1072;&--1103; &--1087;&--1086;&--1090;&--1086;&--1084; &--1085;&--1072;&--1095;&--1080;&--1085;&--1072;&--1077;&--1090; &--1082;&--1088;&--1072;&--1089;&--1085;&--1077;&--1090;&--1100; &--1080; &--1089;&--1090;&--1072;&--1085;&--1086;&--1074;&--1080;&--1090;&--1089;&--1103; &--1084;&--1091;&--1090;&--1085;&--1086;&--1081; &--1085;&--1072;&--1089;&--1090;&--1086;&--1083;&--1100;&--1082;&--1086; &--1095;&--1090;&--1086; &--1085;&--1077;&--1074;&--1080;&--1076;&--1085;&--1086; &--1085;&--1072;&--1089;&--1082;&--1074;&--1086;&--1079;&--1100;. &--1057;&--1084;&--1077;&--1089;&--1100; &--1074;&--1099;&--1076;&--1077;&--1088;&--1078;&--1080;&--1074;&--1072;&--1077;&--1084; &--1085;&--1086;&--1095;&--1100; &--1080; &--1086;&--1085;&--1072; &--1089;&--1090:&--1072;&--1085;&--1086;&--1074;&--1080;&--1090;&--1089;&--1103;&--1082;&--1086;&--1088;&--1080;&--1095;&--1085;&--1077;&--1074;&--1086;&--1081;. &--1052;&--1086;&--1077;&--1084; &--1074;&--1086;&--1076;&--1086;&--1081; &--1080; &--1079;&--1072;&--1090;&--1077;&--1084; 10% &--1088;&--1072;&--1089;&--1090;&--1074;&--1086;&--1088;&--1086;&--1084; NaOH, &--1086;&--1088;&--1075;&--1072;&--1085;&--1080;&--1095;&--1077;&--1089;&--1082;&--1080;&--1081; &--1089;&--1083;&--1086;&--1081; &--1086;&--1090;&--1076;&--1077;&--1083;&--1103;&--1077;&--1084; &--1080; &--1076;&--1080;&--1089;&--1090;&--1080;&--1083;&--1083;&--1080;&--1088;&--1091;&--1077;&--1084;. &--1044;&--1080;&--1089;&--1090;&--1080;&--1083;&--1103;&--1090;&--1085;&--1072;&--1075;&--1088;&--1077;&--1074;&--1072;&--1077;&--1084; &--1087; &--1088; &--1080; 240C &--1085; &--1072; &--1095; &--1080;&--1085;&--1072;&--1077;&--1090; &--1086;&--1073;&--1088;&--1072;&--1079;&--1086;&--1074;&--1099;&--1074;&--1072;&--1090;&--1100;&--1089;&--1103; &--1078;&--1077;&--1083;&--1090;&--1086;&--1077; &--1084; &--1072; &--1089; &--1083; &--1086;, accross &--1080; &--1090;&--1077;&--1084;&--1087;&--1077;&--1088;&--1072;&--1090;&--1091;&--1088;&--1091; &--1087;&--1086;&--1089;&--1090;&--1077;&--1087;&--1077;&--1085;&--1085;&--1086; &--1087;&--1086;&--1074;&--

1099;&--1096;&--1072;&--1077;&--1084; &--1076;&--1086; 260C. &--1052;&--1072;&--1089;&--1083;&--1086;&--1084;&--1086;&--1078;&--1085;&--1086; &--1082;&--1088;&--1077;&--1089;&--1090;&--1072;&--1083;&--1080;&--1079;&--1086;&--1074;&--1072;&--1090;&--1100; &--1074;&--1099;&--1076;&--1077;&--1088;&--1078;&--1080;&--1074;&--1072;&--1085;&--1080;&--1077;&--1084; &--1074; &--1084;&--1086;&--1088;&--1086;&--1079;&--1080;&--1083;&--1082;&--1077; &--1085;&--1072; &--1087; &--1088; &--1086; &--1090; &--1103; &--1078; &--1077; &--1085;&--1080;&--1080; &--1089;&--1091;&--1090;&--1086;&--1082;. &--1057;&--1072;&--1084;&--1072; &--1087;&--1086; &--1089;&--1077;&--1073;&--1077; &--1082;&--1088;&--1080;&--1089;&--1090;&--1072;&--1083;&--1080;&--1079;&--1072;&--1094;&--1080;&--1103; &--1085;&--1077; &--1087; &--1088; &--1086; &--1080; &--1079; &--1086; &--1081; &--1076;&--1077;&--1090;, &--1073;&--1077;&--1088;&--1077;&--1090;&--1077; &--1083; &--1086; &--1078; &--1082; &--1091; &--1083; &--1086; &--1078;&--1080;&--1090;&--1077; &--1074; &--1084;&--1086;&--1088;&--1086;&--1079;&--1080;&--1083;&--1082;&--1091; &--1082;&--1086;&--1075;&--1076;&--1072; &--1086;&--1085;&--1072; &--1073;&--1091;&--1076;&--1077;&--1090;&--1086;&--1081;&--1078;&--1077;&--1090;&--1077;&--1084;&--1087;&--1077;&--1088;&--1072;&--1090;&--1091;&--1088;&--1099; &--1095;&--1090;&--1086; &--1080; &--1088;&--1072;&--1089;&--1090;&--1074;&--1086;&--1088; &--1086;&--1087;&--1091;&--1089;&--1082;&--1072;&--1077;&--1090;&--1077;&--1077;&--1077; &--1074; &--1085; &--1077; &--1075; &--1086; , &--1101; &--1090; &--1086; &--1074; &--1099; &--1079; &--1086; &--1074; &--1077; &--1090; &--1085;&--1072;&--1095;&--1072;&--1083;&--1100;&--1085;&--1091;&--1102; &--1082; &--1088; &--1077; &--1089; &--1090; &--1072; &--1083; &--1080;&--1079;&--1072;&--1094;&--1080;&--1102; &--1080; &--1087;&--1086;&--1090;&--1086;&--1084; &--1086;&--1085;&--1072; &--1087;&--1088;&--1086;&--1076;&--1086;&--1083;&--1078;&--1080;&--1090;&--1089;&--1103;. &--1055;&--1088;&--1086;&--1080;&--1089;&--1093;&--1086;&--1076;&--1080;&--1090; &--1087;&--1077;&--1088;&--1077;&--1093;&--1086;&--1076; &--1086;&--1090; &--1086;&--1088;&--1072;&--1085;&--1100;&--1078;&--1077;&--1074;&--1086;&--1075;&--1086; &--1084;&--1072;&--1089;&--1083;&--1072; &--1082; &--1082;&--1088;&--1080;&--1089;&--1090;&--1072;&--1083;&--1072;&--1084; &--1089;&--1077;&--1088;&--1085;&--1086;&--1075;&--1086; &--1094;&--1074;&--1077;&--1090;&--1072; &--1084;&--1072;&--1089;&--1089;&--1086;&--1081; 180 &--1075; Methyl Phenyl Butenone.

&--1054;&--1082;&--1080;&--1089;&--1083;&--1077;&--1085;&--1080;&--1077; Baeyer-Villiger.

The reaction of the above unsaturated ketone with peracetic acid was first done by Boesken reported in Rec. Trav. Chim. 55, 786 (1936). There is some discussion of this also in US patent 3980708. Also see Organic Reactions Vols 9 & 43 I think. By following the directions in US Patent 5670661 you will get about 35% ketone based on the weight of the unsaturated ketone used. In that patent it is suggested that by recycling a higher percentage can be achieved.

&--1042; &--1083; &--1080; &--1090; &--1088; &--1086; &--1074; &--1091; &--1102; &--1082; &--1086; &--1083; &--1073; &--1091; &--1076; &--1086; &--1073;&--1072;&--1074;&--1083;&--1103;&--1077;&--1084; 625 ml &--1083;&--1077;&--1076;&--1103;&--1085;&--1086;&--1081; &--1091;&--1082;&--1089;&--1091;&--1089;&--1085;&--1086;&--1081; &--1082;&--1080;&--1089;&--1083;&--1086;&--1090;&--1099; &--1080; 143 grms &--1053;&--1072;&--1090;&--1088;&--1080;&--1103; &--1087;&--1077;&--1088;&--1073;&--1086;&--1088;&--1072;&--1090;&--1072;. &--1050; &--1101;&--1090;&--1086;&--1084;&--1091; &--1076;&--1086;&--1073;&--1072;&--1074;&--1083;&--1103;&--1077;&--1084; 100 grms methyl phenyl butenone &--1089; &--1087; &--1086; &--1084; &--1077; &--1096; &--1080; &--1074;&--1072;&--1085;&--1080;&--1077;&--1084; &--1080; &--1085;&--1072;&--1075;&--1088;&--1077;&--1074;&--1072;&--1077;&--1084;&--1076;&--1086; 50C. &--1050;&--1086;&--1075;&--1076;&--1072; &--1073;&--1091;&--1076;&--1077;&--1090;&--1077;&--1085;&--1072;&--1075;&--1088;&--1077;&--1074;&--1072;&--1090;&--1100; &--1089;&--1090;&--1072;&--1088;&--1072;&--1081;&--1090;&--1077;&--1089;&--1100; &--1085; &--1077; &--1087; &--1077; &--1088; &--1077; &--1075; &--1088;&--1077;&--1090;&--1100;, &--1086;&--1076;&--1085;&--1072;&--1082;&--1086;, &--1077;&--1089;&--1083;&--1080; &--1089;&--1084;&--1077;&--1089;&--1100; &--1073;&--1091;&--1076;&--1077;&--1090; &--1089;&--1083;&--1080;&--1096;&--1082;&--1086;&--1084; &--1093;&--1086;&--1083;&--1086;&--1076;&--1085;&--1072;&--1103; &--1086;&--1085;&--1072; &--1085;&--1072;&--1095;&--1080;&--1085;&--1072;&--1077;&--1090; &--1079;&--1072;&--1090;&--1074;&--1077;&--1088;&--1076;&--1077;&--1074;&--1072;&--1090;&--1100;. &--1055;&--1086;&--1084;&--1077;&--1096;&--1080;&--1074;&--1072;&--1085;&--1080;&--1077; &--1080; &--1085; &--1072; &--1075; &--1088; &--1077; &--1074; &--1087;&--1088;&--1086;&--1076;&--1086;&--1083;&--1078;&--1072;&--1077;&--1084; &--1087;&--1088;&--1080;&--1073;&--1083;&--1080;&--1079;&--1080;&--1090;&--1077;&--1083;&--1100;&--1085;&--1086; 6 &--1095;&--1072;&--1089;&--1086;&--1074;. &--1055;&--1086;&--1089;&--1083;&--1077; &--1095;&--1077;&--1075;&--1086; &--1086;&--1093;&--1083;&--1072;&--1078;&--1076;&--1072;&--1084; &--1074;&--1083;&--1080;&--1074;&--1072;&--1085;&--1080;&--1077;&--1084;&--1074; 1 &--1083; &--1080; &--1090; &--1088; H2O &--1080; &--1080; &--1079;&--1074;&--1083;&--1077;&--1082;&--1072;&--1077;&--1084; &--1089; &--1090; &--1086; &--1083; &--1091; &--1086; &--1083; &--1086; &--1084; &--1080; &--1083; &--1080; &--1076; &--1080; &--1093; &--1083; &--1086;&--1088;&--1084;&--1077;&--1090;&--1072;&--1085;&--1086;&--1084;. &--1056;&--1072;&--1089;&--1090;&--1074;&--1086;&--1088;&--

1080;&--1090;&--1077;&--1083;&--1100; &--1076;&--1080;&--1089;&--1090;&--1080;&--1083;&--1083;&--1080;&--1088;&--1091;&--1084;, &--1086;&--1089;&--1090;&--1072;&--1074;&--1083;&--1103;&--1103;&--1078;&--1077;&--1083;&--1090;&--1086;&--1077; &--1084;&--1072;&--1089;&--1083;&--1086;, &--1082;&--1086;&--1090;&--1086;&--1088;&--1072;&--1103; &--1080;&--1084;&--1077;&--1077;&--1090; &--1087;&--1088;&--1080;&--1103;&--1090;&--1085;&--1099;&--1081;&--1079;&--1072;&--1087;&--1072;&--1093;. &--1045;&--1075;&--1086; &--1076;&--1086;&--1073;&--1072;&--1074;&--1083;&--1103;&--1077;&--1084; &--1082; 500 mls 10% &--1088;&--1072;&--1089;&--1090;&--1074;&--1086;&--1088;&--1072; NaOH (50/50 H20 EtOH) &--1080; &--1087;&--1086;&--1084;&--1077;&--1096;&--1080;&--1074;&--1072;&--1077;&--1084;&--1074; &--1090; &--1077; &--1095; &--1077; &--1085; &--1080; &--1077; 1-2 &--1095;&--1072;&--1089;&--1086;&--1074;, &--1080;&--1079;&--1074;&--1083;&--1077;&--1082;&--1072;&--1077;&--1084; &--1089; &--1090;&--1086;&--1083;&--1091;&--1086;&--1083;&--1086;&--1084; &--1080;&--1083;&--1080; &--1076;&--1080;&--1093;&--1083;&--1086;&--1088;&--1084;&--1077;&--1090;&--1072;&--1085;&--1086;&--1084; &--1080; &--1076;&--1080;&--1089;&--1090;&--1080;&--1083;&--1083;&--1080;&--1088;&--1091;&--1077;&--1084; &--1089;&--1086;&--1073;&--1080;&--1088;&--1072;&--1103; &--1092;&--1088;&--1072;&--1082;&--1094;&--1080;&--1102; &--1084;&--1077;&--1078;&--1076;&--1091; 210-220C, &--1089;&--1086;&--1073;&--1088;&--1072;&--1085;&--1086;&--1077; &--1060;&--1077;&--1085;&--1080;&--1083; 2 &--1055;&--1088;&--1086;&--1087;&--1072;&--1085;&--1086;&--1085; (&--1054;&--1082;&--1086;&--1083;&--1086; 35 gms).

In the Organic Reactions review of the Baeyer-Villiger there is a reference to the oxidation of alpha Methyl Cinnamaldehyde using H2O2 catalysed by a nitrobenzene selenic acid or something like that to give the same enol ester as above but in 90% yield.

(&--1090;&--1072;&--1084; &--1074;&--1086;&--1086;&--1073;&--1097;&--1077; &--1076;&--1086;&--1089;&--1090;&--1072;&--1090;&--1086;&--1095;&--1085;&--1086; &--1083;&--1102;&--1073;&--1086;&--1087;&--1099;&--1090;&--1085;&--1099;&--1081; &--1090;&--1086;&--1087;&--1080;&--1082;)

RCHO (R = Me, Et, Pr, Me2CH, MeOC6H4, PhCH:CH, Ph) - &--1082;&--1072;&--1082;&--1080;&--1077; &--1101;&--1090;&--1086; &--1088;&--1077;&--1072;&--1075;&--1077;&--1085;&--1090;&--1099;, &--1087;&--1086;&--1084;&--1086;&--1075;&--1080;&--1090;&--1077; &--1087;&--1086;&--1085;&--1103;&--1090;&--1100;

This a russion translation of what Bio and 2dogs were up to.

Below is a similar synthesis, but a slightly different route.

Experimental

The details of preparation of the dl-â-phenylisopropylamine and its 4-methoxy derivative differ only in the aldehyde used and the intermediate and final products isolated.

Condensation of Aldehyde and Nitroethane

0.2 Mole of aldehyde, 0.2 mole of nitroethane and 0.02 mole of n-amylamine were mixed and set aside at room temperature in the dark. After a day water began to separate from the mixture; after several days the mixture became quite solid. After two weeks, the mixture was dissolved to a homogeneous solution by warming with 50 ml of ethanol and then on cooling a fine crystal product was obtained. From benzaldehyde, 0.15 mole of phenylnitropropylene melting at 65-66°C was obtained. The melting point of this compound has been reported as 64°C2. From anisaldehyde, 0.15 mole of 4-methoxyphenylnitropropylene melting at 43-44°C was obtained. The melting point of this compound has been reported as 48°C3.

Reduction of Phenylnitropropylenes

0.1 Mole of phenylnitropropylene dissolved in a catholyte of 100 ml of ethanol, 50 ml of acetic acid and 50 ml of 12 N sulfuric acid was placed above a 40 cm2 mercury cathode in a porous cell surrounded by a 3 N sulfuric acid anolyte with a water-cooled lead anode. Four amperes was passed for twenty hours and the temperature in the catholyte was kept between 30-40°C.

The resultant catholyte was partially evaporated, then made strongly alkaline and the separated basic layer taken up with benzene. The desired amine was then extracted from the benzene by just neutralizing with dilute hydrochloric acid and separating the aqueous layer. This was then evaporated and the product crystallized. From phenylnitropropylene, 0.02 mole of dl-âphenylisopropylamine hydrochloride melting at 144-145°C was obtained. The melting point of this compound has been reported as 145-147°C4. From 4methoxy-phenylnitropropylene, 0.02 mole of dl-â-4methoxyphenylisopropylamine hydrochloride melting at 205-209°C was obtained. The melting point of this compound has bees reported as 210°C2.

References Piness, Miller and Alles, J. Am. Med. Assn. 94, 790 (1930) Mannich and Jacobsohn, Ber. 43, 189 (1910) Knoevenagel and Walther, Ber. 37, 4502 (1904) Hey, J. Chem. Soc. 18 (1930)

Also here is a link for the basic schematics of the aldol

http://www.miracosta.edu/home/dlr/211exp5.htm

IndoleAmine I (and surely many others) would appreciate it if you would complete what you announced. 8)

But its an **acid-catalysed** aldol condensation (usually they are done with NaOH, not acid), and the perborate/peracetic oxidation of the resulting unsaturated ketone intermediate is called **Baeyer-Villiger**

Links now part of Synthetika

fan ofI think these are great reference experiments, I get permission, and have themzwitterionuploaded the Watcher link Depository,

I just got a pm for the admin, and all the old hive files are starting to be indexed, Yippe

zitt

Experimenters report in

bio Experimenters report in, you know who you are.

There is a pretty good thread on Wet Dreams with some valuable info on this reaction that some of you may already know about. I was thinking maybe the new stuff could be pasted here in this thread (possibly edited). I would do it if the moderator has no objections although it could be a little rough as notepad is my only forte in word processing, LOL.

.....I vaguely remember Bio saying that is also could be achieved with Acetone and benzene, respectfully

I am not sure what was meant by this statement but it could be a little misleading to some.

Phenylacetone from benzene and acetone can only be done one way as far as I know, the free radical reaction between the two utilizing Mn3OAc. Problem with this reaction is really not the yield so much but the dilution. I found regeneration of the Mn2 back to Mn3 works best electroliticly insitu using waaay less in the soup (about 20:1). Still have a bucket of perborate to use up so will be a while before doing more experimentation on this.

I read in the general forum something about an anonymous testing organization. What a great idea! My testing org. (sic) fell apart when the Hive

dissolved.

The other two ways, if you count Halo derivatives, would be the Freidel/Crafts with haloacetone or the enol reaction with halobenzene.

Oh btw fan of zwitterion; did a google search a few weeks ago on Baeyer/Villiger and what do I stumble on but an article in Russian with the twodogs procedure transliterated from the Hive. Must be yours, good going. **Bio**

synthetika We would love that excerpt, from wet dreams, Copy and paste away,∖

syn

IndoleAmine The original thread from the Hive:

Subject: Benzaldehyde + MEK acid catalyzed aldol

Posted by: bio (Stranger) Posted on: 08-03-03 07:28 Post No: 451381

I am prepared to do the subject reaction with Bayer Villager oxidation to P2P. Where I am now I have no access to a library only the internet for references. Does anyone have anymore details on this procedure? I feel the sketchy details in Post 245942 (twodogs: "New method for P2P", Novel Discourse) are fraught with pitfalls and I sure don't want to waste my analytical grade \$80 a liter PhCHO. Also I have been searching the internet for other catalysts other than Hydrogen Chloride which would be suitable for this type reaction to no avail. Any references or pointers would be highly appreciated. The Organic Reactions

volumes referenced don't seem to be available on-line and the Patents referenced aren't very helpful. Anyway I will try it on a small scale soon and will let you all know how it turns out.

Subject: Benzaldehyde + MEK Posted by: twodogs (Newbee) Posted on: 08-03-03 22:49 Post No: 451488

Sketchy details?? Jesus Christ ...how much detail do you want? If you follow the procedure exactly as I have mentioned you will get a result.

Subject: Benzaldehyde + MEK Posted by: bio (Stranger) Posted on: 08-05-03 03:07 Post No: 451702

OK, Two Dogs thanks for the encouragment. Perhaps sketchy was a poor choice of

words. So I assume you have had success with this reaction. It does seem fairly simple to do. Apparently a little H2O is not detrimental to the condensation product yield as they performed it in an open beaker at freezing temperature. This puzzled me somewhat as water is eliminated and usually I used a Dean Stark tube or at least a drying tube in a sealed system for similar PhCHO condensations. Also I wonder if the relatively low yields are partly due to doing atmospheric distillation. At those high temps it seems a lot of decomposition could occur. I will try a test batch tomorrow and see if it will crystallize after removing the excess MEK. If you have done this reaction could you share some more thoughts? I want to scale it up and think the oxidation step could get by with way less MeCOOH.

Rated as: good read Subject: Benzaldehyde + MEK acid catalyzed aldol Posted by: twodogs (Newbee) Posted on: 08-05-03 04:19 Post No: 451718

Bio...yes I have had sucess with this reaction but I felt that 35% was too low for me. The aldol condensation part is very easy and as I mentioned can be done with refluxing conc. HCl or with H2SO4 but you get the best result with dry HCl. With the oxidation part, I would use peracetic acid or performic acid if I were you as the perborate makes for a messy workup. If you use less Acetic with the perborate you will end up with such a solid mass that you won't be able to stir it. I don't do this shit any more but have a look at this site from time to time but I know two another ways to the ketone from the unsaturated ketone that is formed from the aldol condensation. The unsaturated ketone can be oxidised with NaOCl to give the alpha- methyl cinnamic acid. This can be decarboxylated to give phenyl propene that can be worked up with performic etc or the methyl cinnamic can be oxidised with oxone and the resulting epoxy acid decarboxylated to give the ketone. I was looking at these reactions when I figured out that the Baeyer-villager worked as well and that seemed easier. It is a pity you don't have a library handy as I think that the Baeyer-Villager would work much better with a catalyst.

Subject: peracetic oxidation Posted by: viki (Stranger) Posted on: 08-05-03 05:49 Post No: 451737

question for two dogs.what strength peracetic would you recommend for the oxidation?would 30-35 %work? viki

Subject: Benzaldehyde + MEK acid catalyzed aldol

Posted by: twodogs (Newbee) Posted on: 08-05-03 06:17 Post No: 451739

Viki, yes that would work. Have a look at all the patents under Baeyer-Villager and you will see all the different oxidisers used. Boesken used peracetic.

Subject: Benzaldehyde + MEK acid catalyzed aldol

Posted by: bio (Stranger) Posted on: 08-06-03 05:32 Post No: 451987

Yea, twodogs the peracetic makes sense. I bought some 30% H2O2 intending to

try it or even regenerate the Na Perborate. Can the peracetic or performic be made insitu? and would the same molar ratios be used. Also I have the perborate tetrahydrate a monohydrate is also available, the 4 hydrate which is NaBO3.H2O2.3H2O is ca. 10% O2. What is the actual mole ratio needed of O2 for

the Baeyer Villiger?

Again thanks for your assistance as the library here is in the wrong language and only goes to the 10th grade (sic).

Subject: Baeyer-Villager Posted by: twodogs (Newbee) Posted on: 08-06-03 07:11 Post No: 452010

Bio

I am sorry but this was a while ago and I don't have any notes. I would have

thought that you would need at least 50% H2O2 to make a strong enough peracetic. Performic pretty much has to be made on the spot as it deteriorates quite quickly. Peracetic needs a catalyst like H2SO4 to form and that may need to be neutralised before use. I had alot of difficulty in figuring out the percentage of peracetic formed by combining H2O2 and acetic acid. A lot of posts on the topic here at the Hive I think are wrong in that they assume too high a percentage of peracetic in the final product. It is one of those reactions where 1+1 doesn't equal 2. I couldn't buy peracetic and this is the main reason why I went with the perborate as the quantities needed are easier to work out. Have a look at US Patent 4988825 where I got the idea of using perborate.

Rated as: good read Subject: Peracid concentrations Posted by: Rhodium (Chief Bee) Posted on: 08-06-03 11:16 Post No: 452068

See J. Am. Chem. Soc. 907 (1946) (https://www.rhodium.ws/pdf/peracid.pdf)

Subject: Peracid concentrations

Posted by: twodogs (Newbee) Posted on: 08-06-03 11:39 Post No: 452069

Thanks Rhodium. That is what I had read.. if you use 90% H2O2 with acetic acid you can get the high concentrations of peracetic but 30% H2O2 only gives about 8%. I don't believe that you can buy 90% H2O2 any more. 35% peracetic seems to be the reaction grade.

Subject: Peracid concentrations

Posted by: bio (Stranger) Posted on: 08-07-03 06:33 Post No: 452240

OK, twodogs and Rhodium, thanks for the references. Doing my research now. By the way Rhodium can P2P be distilled at atmospheric without decomposition (or only minimal)? I always used about 10 torr and it stayed water white for days.

Subject: P2P distillation Posted by: Rhodium (Chief Bee) Posted on: 08-07-03 08:21 Post No: 452251

Yes, P2P can be distilled without vacuum, but you might get 10% better yield by using vacuum. 10 mmHg is excellent in this case.

Subject: Benzaldehyde + MEK acid catalyzed aldol

Posted by: bio (Stranger) Posted on: 08-09-03 06:16 Post No: 452559

Hi twodogs and Rhodium. The condensation went quite smoothly I added about

half the HCL gas before the color change started and it was just as you said the next morning. I will try to crystallize my little test batch tonight without distilling. Did you ever have any luck with this? When I crystallized phenyl nitropropene w/o distillation it worked but only by seeding with a grain or two of fine sand and this without removing the solvent or chilling. I presume not as you mention the freezer trip. Anyway I will try it as it would save a lot of work especially when scaled to the proportions planned. PhCHO is

sold as bacteriacide around here so it's about as common as formaldehyde.

Subject: Benzaldehyde + MEK acid catalyzed aldol

Posted by: bio (Stranger) Posted on: 08-09-03 22:57 Post No: 452657

OK, It crystallized after freezing with scratching and seeding. Now trying to determine a suitable recrys solvent. Any ideas. Will try abs IPA and Hexane or Benzene first.

Subject: Post 208702 Post 451381 I've seen MEK (methyl...

Posted by: Herr_Ovalmeister (Stranger) Posted on: 08-15-03 02:28 Post No: 453611

Post 208702 (Antoncho: "The easiest synth of benzaldehyde from toluene", Chemistry Discourse)

I've seen MEK (methyl ethyl ketone) sold at one hardware store OTC.

Subject: CeMolybdate Posted by: bio (Stranger) Posted on: 09-09-03 03:36 Post No: 457817

The CeMolybdate vapor phase method is INMHO the best. See my other posts.

Subject: tried this... Posted by: chilly_willy (Hive Bee) Posted on: 09-25-03 03:40 Post No: 460868

Someone I know tried this reaction a while back. Seemed too good to be true! Was it? During the condensation he found it impossible to weigh the gassed liquid to determine any amount of absorbed HCl. Digi(good one) weighed NO appreciable weight change. <--missing something here??.. He just kept gassing and gassing until everything got blood red brown. It was left overnight..washed, extracted, and distilled...a yellow oil was left over that still smelled like cherries. What the hell?? Instinct told him something went wrong. Anyway. for shits and giggles he left everything in some ice.. and to his surprise the whole lot of yellow oil solidified the next day..still smelled like cherries..but crystals..yea! The cherry-smelling sulfur crystals were added to the perborate w/ gaa..and heating started...a little too fast. Whoops..a little boil-over. Shit! vinegar smell all over..oh well..fan took care of that. Heating was properly maintained..crap...the crystasls werent dissoving. Kept heating. Left for a couple hours...seemed as though perborate and cherry xtals didnt dissove at all. That cant be right since the p2p comes from the cherry xtals...? Dumped the whole mess. What the hell happened? Bio please post as to what happened during your oxidation step. Ne1 else please enlighten as to what happened/went wrong....

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<=====>

Subject: Or you could steam distill the p2p.

Posted by: placebo (arrogant bee of the day) Posted on: 09-25-03 12:26 Post No: 460953

Or you could steam distill the p2p.

I'm not fat, I'm just too short for my weight. http://www.whatreallyhappened.com

Subject: sodium perborate tetrahydrate

Posted by: bio (Stranger) Posted on: 10-08-03 04:54 Post No: 463310

two dogs......Please could you clarify for me if the ca. 8% peracetic from 30% H2O2 will oxidize the ester we discussed, given the perborates ca. 10% H2O2? I did get the unsat ketone to crys w/o distill.

Subject: it worked Posted by: bio (Stranger) Posted on: 10-21-03 07:08 Post No: 465882

just like you said twodogs, thankyou very much. Only thing is I got a slightly better yield

Subject: gassing MEK Posted by: viki (Stranger) Posted on: 11-06-03 05:23 Post No: 469038

If one were scaling this reaction up would it work if one were to gas say 3 litres of MEK first a la Argox, then add the MEK to the benzaldehyde say at a litre a time?Cheers Viki

Subject: gassing MEK Posted by: bio (Newbee) Posted on: 11-06-03 19:23 Post No: 469174

Seems like it should work but I don't see the point here(storage maybe?) The gassing took me over 3 hours for a 360g MePhBuO in a 2 liter RB using an ice salt bath to keep the temp about 5 deg +/-. Then it would probably heat up again when you add to the PhCHO. Maybe a colder bath would speed it up if it wouldn't get too cold.

The left over MEK goes into the water wash. I was surprised to learn that MEK holds 24% water........... To recycle do you know if distilling this MEK/HCL solution would damage the ketone?............ Or you could mix with the NaOH wash to neutralize as some is in there too. I only use AR chems and hate throwing it out but have been to busy to experiment with this idea. Also do a 1/2 vol sat salt wash to clear up the organic layer. This helps a lot.

Once you have some seeds the MePhBuO crystallizes nicely at room temp if properly distilled. It's instantaneous.

Subject: The left over MEK goes into the water wash

Posted by: bio (Newbee) Posted on: 11-08-03 03:07 Post No: 469564

Should have said a lot of it. You will get a small 74-84 deg fraction when distilling the MePhBuO (196ml of 750ml) in the last run. It is full of HCl even after washing with a 20% excess of lye.

Subject: baeyer-villiger catalyst

Posted by: chilly_willy (Hive Bee) Posted on: 11-15-03 04:06 Post No: 470971

I just finished searching at the library for possible baeyer-villiger catalysts and have come up with one that might seem promising. Ferric chloride. Would using this alone with H2O2 stirring like mad do the job any better? Yield-wise I mean. What about adding it in with the perborate in twodogs original procedure. I am still trying to understand the dynamics of the lewis-acid here so please correct me or point out why either suggestion will or wont work. Thx...

----->

Subject: I haven't memorized the entire literature

Posted by: Rhodium (Chief Bee) Posted on: 11-15-03 04:59 Post No: 470981

Post the procedures/references you have found, so that we have something to work with. It is a little hard to give critique on something we haven't read...

Subject: baeyer-villiger catalysts

Posted by: bio (Newbee) Posted on: 11-15-03 05:25 Post No: 470993

Would using this alone with H2O2 stirring like mad do the job any better?

The oxidation is done by the per acid; acetic in this case.

What about adding it in with the perborate in twodogs original procedure.

This sounds feasible, would probably want the anhydrous ferric chloride as water is a product of the condensation. What molar proportions were used in the examples you found? I would think very little as FeCl3 is a good Friedel Crafts reactant, not quite as strong as Aluminum chloride which might also work.

Subject: Perborate oxidations of ketones

Posted by: bio (Newbee) Posted on: 11-17-03 23:55 Post No: 471446

SPC/SPB Post 446838 (GC_MS: "SPC/SPB", Novel Discourse)Read this

Chilly Willy and if you or anyone else has acess to

Tetrahedron 1987,43,1753-1758

It is from the above article and is on room temp perborate oxidation of ketones to ketones in acetic acid at room temperature in good to excellent yields.

I'm still searching for a an oxidation catalyst to try and have seen MnSO4 a couple times in .01-.1 molar ratio but it's not clear if this won't also oxidise the ketone itself.

Rated as: excellent Subject: Benzaldehyde + MEK acid catalyzed aldol Posted by: bio (Newbee) Posted on: 11-24-03 23:24 Post No: 472943

I don't have a lot of time to spend on this so if anyone sees any obvious boo boos please let me know. Just trying to repay my debt to the Hive. And clear my bad karma, how the hell did that happen?

Results of latest twodogs reaction.

1) Methyl Phenyl Butanone (MePhBuO)...... 400g PhCHO and 600g MEK (both RA

grade) were mixed in a 2L flask placed in an ice salt bath and cooled to -5 degrees. 80 grams of DRY HCL gas was passed over about 3 hours keeping the temp below 5-7 degrees. Stirring with the thermometer. (This is about a 1 to 2.2 mole ratio as given by twodogs. Rhodium has posted an apparent improvement

of yield to 94% with 1 to 1 mole which has not been tried yet.) A saturated solution is what is strived for here. Previous results indicated about 85% of the calculated HCl was absorbed. An additional 15% was partly added to compensate and the solution was saturated before it was all added. Flask stoppered and left in bath to warm up overnight ca. 10 hours. The Vogel method of dripping 37% HCl into 98% H2SO4 was used with a H2SO4 dryer. Trap

also used but not needed this time. Vogel says 31-33g HCl per 100ml.

2) The resulting deep reddish brown reaction mix was washed with an equal volume of water separated then washed with a 20% excess of 10% NaOH separated

then washed with 1/2 volume of brine separated and filtered to give 845ml Ph

7-8 solution. This was distilled at atmospheric collecting most of the first fraction 74-84 degrees PH1 and the second fraction at aspirator pressure most was collected 119-140 degrees. MePhBuO clear yellow fruity smelling oil 506.7

gram includes the forerun and after run. This was allowed to cool to ambient, then seeded causing immediate crystalization. Let set up in frig with stirring for a couple hours. Filter on buchner wash with 95% EtOH dried for 430 grams total very clean and dry light yellow (almost white) pleasant smelling crystals. These initially set up as long transparent light yellow needles. Happy now as had expected only 360 grams. Even returned to the vac dessicator

to insure they were dry. Recrys of a little test resulted in very little improvement. This stuff is easy to crys in a relatively pure form. No GC/MS sorry.

3) Baeyer-Villiger Oxidation...... To a 6 liter FB flask on the mag stirrer hotplate in a water bath was added 2.3L Glacial Acetic Acid (RA) 615g NaPerborate 4H2O and 430g MePhBuO with stirring. This starts endothermic and

mag stirring is inadequate until heat is added and the stuff dissolves. Added the crystals over ca. 1/2 hour while heating to about 45 deg. After the induction period added ice and or heating periodically to keep the solution temp 55-65 deg. Can get into this more later if anyone actually is ready to do it. Stir vigorously keeping the temp as above for 6 hours. If it gets hotter as long as controllable it's OK. Be very carefull here I already had a near runaway...... Proceed slowly and carefully....... Cool to ambient then either dilute with water or recover the NaBO2 and acid first. Now extract with toluene or DCM. I used DCM this time and wish I didn't. Anyway extracted with

1.2L DCM washed with water and brine then removed solvent to leave the enol ester.

4) Hydrolysis and P2P..... enol ester added to 2.25L 10% NaOH in 50/50 w/w EtOH/H2O and stirred 2 hours. Extracted with DCM 300/200/200ml (again wish I

had used PhMe) washed with water and brine removed solvent and collected 162g

P2P at aspirator pressure (almost all between 119-140 deg). OVER

Subject: collected 162g P2P Posted by: bio (Newbee) Posted on: 11-25-03 01:02 Post No: 472961 correction.....collected 169.5g..... did not drain completely...takes time you know

Subject: Benzaldehyde + MEK acid catalyzed aldol

Posted by: twodogs (Newbee) Posted on: 11-25-03 11:20 Post No: 473050

Nicely done Bio. One thing that should be mentioned is that in the condensation step, over gassing leads to some sort of polymerisation...evidently. There is a paper mentioning this somewhere. This is why I stated the weight of dry HCl in my original post of the set of reactions instead of just saying gas the shit out of it.

Subject: polymerization Posted by: bio (Newbee) Posted on: 11-25-03 19:36 Post No: 473129

Well there is certainly a lot of the tarry polymer created using the 1 to ca.2 mole ratio. Perhaps going slower this time and watching temp more carefully and not taking out of the ice right away helped the yield. Also there could be a clue hidden in the reference to the gassing procedure (not given) which is the key to the 94% yield with only a trace of tar. The statement regarding saturation was gleaned from the JACS 65,1824(1943) article Rhodium posted. I

did notice that following your weights of HCL that saturation (or somewhere close) was reached very near the end. What was not stated in the synthesis part was the procedure or temp used when HCL gasing. There is a footnote to this article saying they followed this procedure.,,,,(5) Muller and Harries, Ber., 36, 9BG (1902).,,,,if anyone could find this it would be very helpfull.

Surely somebee has access to Ber. (berliner I think) and could dig it up to assist.

Rated as: good read Subject: Making this reaction more OTC . . . Posted by: psychokitty («») Posted on: 10-11-04 08:41 Post No: 535306 I think the value of the following patent speaks for itself. If it's already been posted before, please accept my apologies in advance. I tried to use TFSE.

(1 of 1) United States Patent 4,673,766 Buck , et al. June 16, 1987 Method of producing benzaldehyde

Abstract

A method is disclosed for producing benzaldehyde by fractionally steam distilling benzaldehyde from cinnamaldehyde in the presence of hydroxide catalyst and at a pH on the order of about 11 to about 13. Conversions of cinnamaldehyde to benzaldehyde can be achieved on the order of about 75% or more.

Inventors: Buck; Keith T. (Cincinnati, OH); Boeing; Anthony J. (Cincinnati, OH); Dolfini; Joseph E. (Cincinnati, OH) Assignee: Mallinckrodt, Inc. (St. Louis, MO) Appl. No.: 856595 Filed: April 25, 1986

Current U.S. Class: 568/433; 568/458 Intern'l Class: C07C 045/51 Field of Search: 568/433,458 References Cited

Other References

Guthrie et al., Can. Jour. Chem., vol. 62 (1984), 1441-1445.

Primary Examiner: Helfin; Bernard Attorney, Agent or Firm: Wood, Herron & Evans Claims

What is claimed is:

1. A method of making benzaldehyde com- prising

dispersing cinnamaldehyde in water,

converting the cinnamaldehyde to benzaldehyde under the action of heat in the presence of a catalytic amount of hydroxide ion and at a pH of about 11 to

about 13,

fractionally steam distilling benzaldehyde and acetaldehyde from the cinnamaldehyde, and

recovering benzaldehyde from the distillate.

2. The method of claim 1 which is conducted at a pH in the range of about 12 to about 12.5.

3. The method of claim 1 wherein the benzaldehyde distillate resulting from the steam distillation is fractionally distilled for separation of the benzaldehyde in substantially pure form.

4. The method of claim 1 wherein the acetaldehyde is vaporized during the course of the conversion while the benzaldehyde is condensed.

5. The method of claim 1 conducted in the presence of an anionic surfactant.

6. The method of claim 1 conducted under shearing agitation to facilitate the dispersion of the cinnamaldehyde in the water.

7. A method of making benzaldehyde com- prising

dispersing cinnamaldehyde in water in the presence of an anionic surfactant,

agitating the dispersion under the action of heat in the presence of a catalytic amount of hydroxide ion and at a pH of about 12 to about 12.5 for the conversion of cinnamaldehyde to benzaldehyde,

fractionally steam distilling benzaldehyde and acetaldehyde from the cinnamaldehyde in a still having a pot temperature of about 105.degree. C. and a column temperature of about 99.degree. C., and

fractionally distilling the benzaldehyde from the distillate for the separation of substantially pure benzaldehyde to obtain a yield of at least about 75% based upon the cinnamaldehyde.

8. The method of claim 7 wherein cassia oil is employed as a natural source for the cinnamaldehyde employed in the conversion. Description

BACKGROUND OF THE INVENTION

The retroaldol reaction of cinnamaldehyde is well known. In this reaction, cinnamaldehyde is converted to benzaldehyde and acetaldehyde with various potential side reactions. Recently, for example, an investigation of the kinetics of the retroaldol reaction of cinnamaldehyde has been reported by J. Peter Guthrie, et al, Can. J. Chem., Vol. 62, pp. 1441-1445 (1984). While the conversion of the cinnamaldehyde to benzaldehyde has been long known and well

studied, it has not been heretofore known to produce benzaldehyde from cinnamaldehyde in substantial yields and favorable reaction conditions for production of such yields have not been reported.

SUMMARY OF THE INVENTION

This invention is directed to a method of making benzaldehyde by conversion of

cinnamaldehyde in the presence of water with surprisingly high yields heretofore unachieved. The invention involves the dispersion of cinnamaldehyde

in water and, in the presence of an effective catalytic amount of hydroxide ion, fractionally steam distilling benzaldehyde from the cinnamaldehyde. The reaction is conducted at a pH on the order of about 11 to about 13 and, unexpectedly, within this pH range it has been discovered that a substantial conversion of cinnamaldehyde to benzaldehyde can be achieved on the order of about 75% or more. It has also been found that the conversion may be achieved at such a high pH without adverse side reactions.

In a preferred mode of conducting the method, the cinnamaldehyde is dispersed in the water in the presence of shearing agitation and a surfactant. In another aspect of this invention, it is preferred to employ an anionic surfactant such as sodium lauryl sulfate. Preferably, the hydroxide ion is furnished by means of sodium hydroxide which also achieves the pH in the range

of about 11 to about 13. It has critically been determined that the fractional steam distillation of benzaldehyde from the cinnamaldehyde must be conducted

at a pH within the range of about 11 to about 13, preferably about 12 to about 12.5. Below and above this pH range, very poor conversions are obtained of 50%

or far less and competing reactions interfere with the production of benzaldehyde. Outside of this critical pH range, side reactions,

polymerization and other adverse reactions prohibit any significant yield of benzaldehyde. Yet, within the pH range of about 11 to about 13, especially about 12 to about 12.5, significant yields on the order of 75% or greater are achieved and benzaldehyde is recoverable in substantially pure form free of side reaction products. These results are considered to be unexpected especially at the high pHs of the reaction where it may have been expected that side reactions would have significantly lessened or prevented the yield for the desired product.

During the course of the fractional steam distillation of benzaldehyde from the cinnamaldehyde, acetaldehyde is also vaporized and removed. The removal of

acetaldehyde thus prevents the forward polymerization reaction which otherwise

competes in the presence of the catalyst. The benzaldehyde which has been steam distilled is then subsequently fractionally distilled for separation of the benzaldehyde from other components in the distillate such as minor amounts

of acetaldehyde, terpenes and orthomethoxybenzaldehyde. It has also been found

that a natural source for the cinnamaldehyde such as cassia oil may be employed containing a substantial amount of the natural cinnamaldehyde. Thus,

a natural product such as cassia oil may be employed in the fractional steam distillation method of this invention and still the significant yields on the order of about 75% or more are achieved.

DETAILED DESCRIPTION

The following detailed operating example illustrates the practice of the invention in its most preferred form, thereby enabling a person of ordinary skill in the art to practice the invention. The principles of this invention, its operating parameters and other obvious modifications thereof will be understood in view of the following detailed procedure.

OPERATING EXAMPLE

A solution was made up from 38.6 lbs. sodium hydroxide, 4 lbs. sodium lauryl sulfate and 10 liters antifoam agent in 760 gallons of water. The solution was stirred until a homogeneous solution was obtained. Then, 1320 lbs. of cassia oil were placed in a 1150 gallon still. The oil contained approximately 72% by weight of cinnamaldehyde. The still had a pot volume of about 1150 gallons onto which was mounted a 4 foot fractionating column containing 1".times.1" ceramic tubes and a water cooled condenser was thereafter connected in series for condensing the benzaldehyde-water azeotrope.

The above prepared sodium hydroxide solution was then added to the cassia oil and introduced into the pot of the still. The pot was equipped with a stirrer. Using pressurized steam and vigorous stirring, the pot was heated to reflux with a pot temperature of 105.degree. C. Reflux was established with a column head temperature of about 99.degree. C. Once reflux was established, it was continued for about 1 hour. During the course of the conversion of the cinnamaldehyde in the cassia oil to benzaldehyde, pH was monitored and was maintained at about 12 to about 12.5. In the event the pH fell below about 12, sodium hydroxide was added to bring the pH back up to the range of about 12-12.5. After refluxing for about 1 hour, take-off of the water-benzaldehyde azeotrope was initiated. The water cooled condenser was operated at 100.degree. F. thereby enabling the water-benzaldehyde azeotrope to be condensed and collected in a chilled receiver. The acetaldehyde by-product was

principally vaporized at the temperature of the condenser and was taken off as vapor. The distillate principally containing benzaldehyde in an amount of about 75% or more with minor amounts of cinnamaldehyde, terpenes, orthomethoxybenzaldehyde and acetaldehyde was obtained. The crude benzaldehyde

was thus collected in a chilled receiver and, in a continuous feed operation the condensed water was continuously fed back to the still to replace what had been taken off and the distillation of the azeotrope continued. The fractional steam distillation of the crude benzaldehyde continued until about 670 lbs. of crude benzaldehyde were obtained. The crude distillate containing benzaldehyde

was then dried under vacuum and fractionally distilled under vacuum of about 29" thereby providing a boiling point for the benzaldehyde at about 70.degree. C. in order to obtain a substantially pure benzaldehyde free from residual terpenes and other impurities.

Thus, by means of practicing the above process, the objectives of this invention are achieved in that cinnamaldehyde is converted into benzaldehyde in substantially pure form even from the natural source of cassia oil. Surprisingly, it has been found that substantial yields in excess of 75% or more of substantially pure benzaldehyde are achieved by this method. Moreover,

it has been found that there is a surprising window of high pH at which the conversion may take place in a fractional steam distillation column in order to separate the benzaldehyde and acetaldehyde from the reaction mixture and still avoid the adverse side reactions from occurring.

Having described this invention and its operating parameters, variations may be achieved without departing from the spirit and scope hereof.

Rated as: good read Subject: The surprises never end, do they? . . . Posted by: psychokitty («») Posted on: 10-11-04 08:45 Post No: 535307

And here's yet another good and useful patent:

(1 of 1)
United States Patent 4,766,249
Buck , et al. * August 23, 1988
Method of catalytically hydrolyzing alpha, beta-unsaturated carbonyl compounds

Abstract

Alpha, beta-unsaturated carbonyl compounds are hydrolyzed under alkaline conditions in the presence of water to produce additional carbonyl-containing compounds. High yields are obtained when the alkaline catalyst contains hydroxide ion and the pH is maintained in the range of about 11 to about 13. Inventors: Buck; Keith T. (Cincinnati, OH); Boeing; Anthony J. (Cincinnati, OH); Dolfini; Joseph E. (Cincinnati, OH); Glinka; Jerome (Cincinnati, OH) Assignee: Mallinckrodt, Inc. (St. Louis, MO) + Notice: The portion of the term of this patent subsequent to June 16, 2004 has been disclaimed.Appl. No.: 942491 Filed: December 24, 1986

Current U.S. Class: 568/433; 568/458 Intern'l Class: C07C 045/42 Field of Search: 568/426,433,435,437,440,458 References Cited

Other References

Guthrie et al., "Can. J. Chem.", vol. 62, pp. 1441-1445, (1984).

Primary Examiner: Lone; Werren B. Attorney, Agent or Firm: Wood, Herron & Evans Parent Case Text

RELATED APPLICATION

This is a continuation-in-part of application Ser. No. 856,595, filed Apr. 25, 1986, invented by Keith T. Buck, Anthony J. Boeing and Joseph E. Dolfini, and assigned to the assignee of this application, now U.S. Pat. No. 4,673,766. Claims

What is claimed is:

1. A method of producing a carbonyl-containing compound which comprises

hydrolyzing by dispersing in water an alpha, beta-unsaturated carbonyl compound of the formula ----STR3---- to produce a carbonyl-containing compound and

by-product according to the following formulas ----STR4---- wherein R' and R" are

hydrogen, aliphatic or aromatic hydrocarbon groups or substituted derivatives thereof, and R''' is an aliphatic or aromatic aldehyde- or ketone-containing group having the carbon to oxygen double bond of said aldehyde or ketone conjugated with the alpha, beta double bond between C and R''' of alpha, beta-unsaturated alpha,beta-unsaturated carbonyl compound, and

conducting said hydrolysis of the alpha, beta-unsaturated carbonyl compound under the action of heat in the presence of a catalytic amount of hydroxide ion and at a pH of about 11 to about 13.

2. The method of claim 1 which is conducted at a pH in the range of about 12 to about 12.5.

3. The method of claim 1 wherein the individual carbonyl-containing compounds

obtained from said hydrolysis reaction are fractionally distilled for separation in substantially pure form.

4. The method of claim 1 conducted in the presence of an anionic or non-ionic surfactant.

5. The method of claim 1 conducted under shearing agitation to facilitate the dispersion of the alpha, beta-unsaturated carbonyl compound in the water.

6. The method of claim 1 wherein said alpha, beta-unsaturated carbonyl compound is citral and the carbonyl-containing compounds produced are 6-methyl-5-hepten-2-one and acetaldehyde.

7. The method of claim 1 wherein said alpha, beta-unsaturated carbonyl compound is pulegone and the carbonyl-containing compounds produced are acetone and 3-methylcyclohexanone.

8. A method of producing a carbonyl-containing compound which comprises

hydrolyzing by dispersing in water under shearing agitation in the presence of

an anionic surfactant an alpha, beta-unsaturated carbonyl compound of the formula ----STR5---- to produce a carbonyl-containing compound and by-product

according to the following formulas ----STR6---- wherein R' and R" are hydrogen,

aliphatic or aromatic hydrocarbon groups or substituted derivatives thereof, and R"' is an aliphatic or aromatic aldehyde- or ketone-containing group having the carbon to oxygen double bond of said aldehyde or ketone conjugated

with the alpha, beta double bond between C and R'' of said alpha, beta-unsaturated carbonyl compound, and

conducting said hydrolysis of the alpha, beta-unsaturated carbonyl compound under the action of heat in the presence of a catalytic amount of hydroxide ion and at a pH of about 12 to about 12.5. Description

BACKGROUND OF THE INVENTION

The retroaldol reaction of cinnamaldehyde is well known. In this reaction, cinnamaldehyde is converted to benzaldehyde and acetaldehyde with various potential side reactions. Recently, for example, an investigation of the kinetics of the retroaldol reaction of cinnamaldehyde has been reported by J. Peter Guthrie, et al, Can. J. Chem., Vol. 62, pp. 1441-1445 (1984). The conversion of the cinnamaldehyde to benzaldehyde has been long known and well

studied. However, it has not been heretofore known to produce benzaldehyde from cinnamaldehyde in substantial yields, and favorable reaction conditions for production of such yields have not been reported. Similarly, citral has been hydrolyzed via the retroaldol reaction to produce 6-methyl-5-hepten-2-one

and acetaldehyde. Again, however, product yield is low. Up to now, it has not been known how to obtain carbonyl-containing reaction products in substantial yields through the retroaldol hydrolysis of any of the alpha,beta-unsaturated carbonyl compounds, of which cinnamaldehyde and citral are examples.

SUMMARY OF THE INVENTION

The invention disclosed in the above application Ser. No. 856,595 is directed to a method of making benzaldehyde by conversion of cinnamaldehyde in the presence of water with surprisingly high yields heretofore unachieved. The invention involved the dispersion of cinnamaldehyde in water and, in the presence of an effective catalytic amount of hydroxide ion, fractionally steam distilling benzaldehyde from the cinnamaldehyde. The reaction was conducted

at

a pH on the order of about 11 to about B 13 and, unexpectedly, within this pH range it has been discovered that a substantial conversion of cinnamaldehyde to benzaldehyde could be achieved on the order of about 75% or more. It has also been found that the conversion may be achieved at such a high pH without adverse side reaction.

It has also been found that members of the class of compounds known as alpha,beta-unsaturated carbonyl compounds, of which cinnamaldehyde is an example, can be hydrolyzed via the retroaldol reaction to produce carbonyl-containing compounds in substantial yields.

In a preferred mode of conducting the method, the alpha, beta-unsaturated carbonyl compound is dispersed in water in the presence of shearing agitation. It will be understood that other water soluble or dispersible cosolvents such as alcohols, ethers or the like may be used in the aqueous reaction medium. An anionic surfactant such as sodium lauryl sulfate or a non-ionic surfactant such as polyethylene glycol having a molecular weight in the range of 400 to 600 may be used. Preferably, the hydroxide ion is furnished by means of sodium

hydroxide which also achieves a pH in the range of about 11 to about 13. After the starting materials have been charged to the flask, reaction is initiated with the addition of heat. Once reaction has begun, separation of the products is achieved through the production of water-product azeotropes which are isolated by fractional distillation. It has been critically determined that the fractional distillation must be conducted at a pH within the range of about 11 to about 13, preferably about 12 to about 12.5. Reactions conducted outside this pH range exhibit very poor conversion to desired product because side reactions, polymerization and other adverse reactions occur.

Reactions conducted within the pH range of about 11 to about 13, and especially between about 12 and about 12.5, produce significant yields on the order of 75% or greater and are substantially free of side reaction products. These results are considered to be unexpected especially at the high pH levels of the reaction where it may have been expected that side reactions would have significantly lessened or prevented the yield for the desired product.

The reaction products isolated by fractional distillation may be further purified by means of additional separation techniques. The separation technique employed may vary with the degree of purity sought. Pure alpha,beta-unsaturated carbonyl compounds may be used as starting materials for the reaction. However, product yield percentage is not adversely affected when natural products containing the desired starting materials are used in the reaction. Thus, a natural product such as cassia oil containing substantial amounts of cinnamaldehyde may be used successfully in this invention. Similarly, lemon grass oil containing citral may be used successfully. Also, pennyroyal oil may be utilized under the teachings of this invention as a source of pulegone, an alpha,beta-unsaturated carbonyl compound.

DETAILED DESCRIPTION

The method in its broader aspects is practiced by hydrolyzing after dispersing in water an alpha,beta-unsaturated carbonyl compound having the formula ----STR1---- to produce a carbonyl-containing compound and a by-product having the

general formulas ----STR2---- The substituents R' and R" are hydrogen, aliphatic

or aromatic hydrocarbon groups or substituted derivatives thereof, and R"' is an aliphatic or aromatic aldehyde- or ketone-containing group having the carbon to oxygen double bond of the aldehyde or ketone conjugated with the alpha,beta double bond between C and R"' of the alpha,beta-unsaturated carbonyl compound. The hydrolysis reaction proceeds under the action of heat and is catalyzed by hydroxide ion having a concentration level sufficient to maintain the solution pH between about 11 and about 13.

A large number of alpha, beta-unsaturated carbonyl compounds may be hydrolyzed

according to the teachings of this invention. The compounds in the following non-comprehensive list are included under the description of hydrolyzable alpha,beta-unsaturated carbonyl compounds: cinnamaldehyde to produce benzaldehyde and acetaldehyde; citral to produce 6-methyl-5-hepten-2-one and acetaldehyde; pulegone to produce 3-methylcyclohexanone and acetone; 3-decen-2-one to produce heptanal and acetone; 2-dodecenal to produce decanal

and acetaldehyde; 2-heptenal to produce pentanal and acetaldehyde; 2-hexenal to produce butanal and acetaldehyde; ionone to produce cyclocitral and acetone; irone to produce 2,5,6,6-tetramethyl-cyclohex-1-ene-1-carboxaldehyde

and acetone; 1-(4-methoxyphenyl)-1-penten-3-one to produce paramethoxybenzaldehyde and methyl ethyl ketone; 5-methyl-3-hexen-2-one to

produce isobutyraldehyde and acetone; alpha-methyl-iso-ionone to produce citral and methyl ethyl ketone; 5-methyl-2-phenyl-2-hexenal to produce phenyl acetaldehyde and 3-methylbutanal; 4-phenyl-3-buten-2-one to produce benzaldehyde and acetone; and ortho-methoxy cinnamaldehyde to produce ortho-methoxy benzaldehyde and acetaldehyde.

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(to be continued . . .)
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Subject: Continued from above . . .

Posted by: psychokitty («») Posted on: 10-11-04 08:47 Post No: 535308

OPERATING EXAMPLE I

A solution was made up from 38.6 lbs. sodium hydroxide, 4 lbs. sodium lauryl sulfate and 10 liters antifoam agent in 760 gallons of water. The solution was stirred until a homogeneous solution was obtained. Then, 1320 lbs. of cassia oil were placed in a 1150 gallon still. The oil contained approximately 72% by weight of cinnamaldehyde. The still had a pot volume of about 1150 gallons onto which was mounted a 4 foot fractionating column containing 1".times.1" ceramic tubes and a water-cooled condenser was thereafter connected in series for condensing the benzaldehyde-water azeotrope.

The above prepared sodium hydroxide solution was then added to the cassia oil and introduced into the pot of the still. The pot was equipped with a stirrer. Using pressurized steam and vigorous stirring, the pot was heated to reflux with a pot temperature of 105.degree. C. Reflux was established with a column head temperature of about 99.degree. C. Once reflux was established, it was continued for about 1 hour. During the course of the conversion of the cinnamaldehyde in the cassia oil to benzaldehyde, pH was monitored and was maintained at about 12 to about 12.5. In the event the pH fell below about 12, sodium hydroxide was added to bring the pH back up to the range of about 12-12.5. After refluxing for about 1 hour, take-off of the water-benzaldehyde azeotrope was initiated. The water-cooled condenser was operated at 100.degree. F. thereby enabling the water-benzaldehyde azeotrope to be condensed and collected in a chilled receiver. The acetaldehyde by-product was

principally vaporized at the temperature of the condenser and was taken off as vapor. The distillate consisted principally of benzaldehyde in an amount of about 75% or more with minor amounts of cinnamaldehyde, terpenes, orthomethoxybenzaldehyde and acetaldehyde. The crude benzaldehyde was thus

collected in a chilled receiver and, in a continuous feed operation the condensed water was continuously fed back to the still to replace what had been taken off and the distillation of the azeotrope continued. The fractional steam distillation of the crude benzaldehyde continued until about 670 lbs. of crude benzaldehyde was obtained. The crude distillate containing benzaldehyde

was then dried under vacuum and fractionally distilled under vacuum of about 29" thereby providing a boiling point for the benzaldehyde at about 70.degree.

C. in order to obtain a substantially pure benzaldehyde free from residual terpenes and other impurities.

OPERATING EXAMPLE II

Into a 5-liter, 3-neck flask was charged 1012.5 g of pennyroyal oil, containing a substantial portion of pulegone, 3.5 liters water and 30 g sodium hydroxide having a minimum 90% purity. The initial charge of hydroxide produced a pH of about 12. The pH was monitored during the subsequent reaction, and additional sodium hydroxide was added as needed to maintain a pH

of about 12. The flask was equipped with a mechanical stirrer/drive motor apparatus and a fractionating column. After agitation was initiated, heat was applied to the mixture in the flask by means of a heating mantle.

As the agitated mixture of pennyroyal oil, sodium hydroxide and water was heated, the pressure in the flask was maintained at atmospheric by permitting the fractionating column to remain uncapped. At a pot temperature of approximately 100.degree. C. and a head temperature of approximately 56.degree. C., distillation occurs and an azeotropic mixture of 96% acetone and 4% water is collected off the top of the fractionating column. The azeotrope was collected by means of the fractionating column.

The co-distillation of acetone occurred over a period of about six days. Agitation and heating were discontinued when no additional distillate was generated. The oil layer remaining in the flask was separated from the sodium hydroxide solution and then water-washed to remove traces of sodium hydroxide.

The washed oil contained the hydrolysis product 3-methylcyclohexanone (b.p. 168.degree.-9.degree. C.), minor amounts of unhydrolyzed pulegone (b.p. 224.degree. C.), and other trace components attributable to the starting pennyroyal oil. The acetone was subsequently assayed for purity, including a determination of water content. The yield of acetone was approximately 73%.

OPERATING EXAMPLE III

Approximately 500 ml water, 5 g (90% active) sodium hydroxide, and 88 g terpeneless lemon grass oil containing approximately 95% citral were charged into a one-liter round bottom flask. The round bottom flask was equipped additionally with a trap having means of permitting removal of the lower density liquid while recirculating the higher density liquid, a fractionating column, and a means for stirring.

The stirred contents of the flask were heated to reflux by means of a heating

mantle. The pH of the contents was set at 12 and maintained at that level during the remainder of the run by addition of sodium hydroxide when necessary. The contents were refluxed for one hour, after which time the steam distillate was slowly collected. The distillate take-off was regulated so that little or no citral distilled over. The distillation was continued until no additional oil was collected.

The oil phase distillate was separated from the steam condensate. The separated oil was then short-path vacuum distilled. The main cut yielded 72 g of the citral hydrolysis product, 6-methyl-5-hepten-2-one. The other reaction product, acetaldehyde, was vented from the flask through the fractionating column during the reaction. The yield of 6-methyl-5-hepten-2-one was approximately 90% under the above conditions.

Thus, by means of practicing the preferred processes listed above, the objectives of this invention are achieved in that desirable products can be obtained in good yield from alpha,beta-unsaturated carbonyl compounds. Pure starting materials may be used, but good results are obtainable even from natural sources of the alpha,beta-unsaturated carbonyl compounds. It is critical to the teachings of this invention that reaction take place in an alkaline hydroxide environment wherein the pH is maintained within a window of

about 11 to about 13. Unexpectedly, not only are products obtained in yields exceeding 70 to 75%, but the reaction proceeds with a low level of competitive side reactions, polymerization or other adverse reactions.

Having described this invention and its operating parameters, variations may be achieved without departing from the spirit and scope hereof.

Rated as: good read Subject: Another retroaldol cleavage of cinnamaldehyde? Posted by: psychokitty («») Posted on: 10-12-04 01:05 Post No: 535419

Here's another way to get benzaldehyde using a variation of the retroaldol reaction. 4-Phenyl-3-buten-2-one is oxidized to the epoxide via basic H2O2 and then cleaved by the NaOH to benzaldehyde and acetone. The yields are supposedly higher that the then-utilized base-catalyzed "retrograde aldol reaction" (retroaldol reaction) and the products of the reaction appear to be cleaner. All in all, the method seems pretty simple and just as OTC as the aforementioned retroaldol reaction using cinnamaldehyde as a precursor to benzaldehyde.

The Epoxidation and Cleavage of a,B-Unsaturated Ketones with Alkaline Hydrogen Peroxide ROBERT D. TEMPLE The Journal of Organic Chemistry Vol. 35, No. 6, May 1970

Abstract:

The kinetics of the reaction between 4-phenyl-3-buten-2-one and aqueous alkaline hydrogen peroxide were studied. Four reactions occur in this system : epoxidation by hydroperoxide ion to form 4-phenyl-3,4-epoxy-2-butanone, oxidative cleavage of the epoxide by hydroperoxide to give benzaldehyde, retrograde aldol reaction, and cleavage of the epoxide by hydroxide. The rates of these reactions in water at 25 are 0.22,0.05,0.00016, and 0.0032 1. molsec-l, respectively. The influence of substituents in the phenyl ring on reaction rates and the relative reactivities of hydroperoxide and hydroxide ions are discussed in terms of the reaction mechanisms. The oxidative cleavage of a,p-epoxy ketones is mechanistically similar to several recently reported fragmentation reactions. The cleavage reaction was shown to have general synthetic utility in preparing diacids, keto acids, and ketones from +-unsaturated ketones, alp-unsaturated aldehydes, and p diketones.

Preparative Oxidation Procedure:

To a solution of 0.01 mol of the a,B-unsaturated carbonyl compound in 50 ml of

methanol,12 ml of 30% aqueous hydrogen peroxide and then 30 ml of 1 N aqueous

sodium hydroxide solution were added with cooling. The mixture was then stirred overnight at 40-50" (1 hr at 40" for the reaction with citral). The resulting solution was evaporated to about half the original volume on a rotary evaporator and then washed with ether. The aqueous solution was made acidic with sulfuric acid, saturated with sodium sulfate, and extracted thoroughly with ether. The extract was treated with FeSO4 or Na2SO3 to destroy

peroxides, dried (MgSO4), and evaporated. The residue, which was essentially pure product, was recrystallized, distilled, or converted into a suitable derivative as outlined below.

Note: 4-Phenyl-3-buten-2-one is not listed in the experimetal section of the article.

Rated as: excellent Subject: Baeyer-Villiger reaction using Oxone as oxidant Posted by: psychokitty («») Posted on: 10-12-04 02:11 Post No: 535428

Maybe this might work to effect a more OTC Baeyer-Villiger transformation.

Facile Oxidation of Aldehydes to Acids and Esters with Oxone Benjamin R. Travis, Meenakshi Sivakumar, G. Olatunji Hollist, and Babak Borhan* ORGANIC LETTERS 2003 Vol. 5, No. 7 1031-1034

Abstract:

A highly efficient, mild, and simple protocol is presented for the oxidation of aldehydes to carboxylic acids utilizing Oxone as the sole oxidant. Direct conversion of aldehydes in alcoholic solvents to their corresponding ester products is also reported. These reactions may prove to be valuable alternatives to traditional metal-mediated oxidations.

Description of the art:

As a fortuitous extension of the solvent study, the oxidation of aldehydes with Oxone in alcoholic solvents cleanly provided high conversion to esters. Thus, the oxidation of benzaldehyde in methanol did not yield the expected carboxylic acid, but instead the methyl ester was obtained. The present strategy complements other known methods that directly convert aldehydes to esters such as oxidation in the presence of alcohol with Br2 or I2, NBS/AIBN, PDC, HCN/MnO2, or performed electrochemically.21-25 Additionally, we found

that other alcohols such as ethanol, n-propanol, and 2-propanol also provide their corresponding esters in excellent yields, although oxidation in tert-butyl alcohol furnished the carboxylic acid as the sole product (Table 3, entries 1-9). It is important to note that the esters are not obtained as the result of the oxidation of aldehydes to carboxylic acids followed by Fischer-type esterification of the acids in alcoholic solvents. Incubation of benzoic acid in methanol with Oxone for a prolonged period did not result in the isolation of methyl benzoate, but in fact the starting acid was re-isolated quantitatively.

The direct oxidation of a variety of aryl and alkyl aldehydes to their corresponding methyl esters is also illustrated in Table 3 (entries 10-19).

Oxidation of aryl aldehydes with electron-withdrawing substituents showed slow

conversion to the esters (Table 3, entries 10 and 11) initially providing dimethyl acetals in addition to the ester products. This was overcome by heating the reactions to reflux overnight, which provided clean conversion to the desired methyl esters 1b and 2b. Oxidation of 6 and 9 (electroneutral aromatics aldehydes) and 19-23 (aliphatic aldehydes) proceeded smoothly at rt to furnish the desired methyl esters in excellent yields. In the case of electronrich aromatic substrates, as with the oxidations to carboxylic acids in DMF, the Dakin products were observed. thus, 4-hydroxybenzaldehyde, 12, and

p-anisaldehyde, 13, provided primarily phenols 16 and 17 in 77% yield for both

(Scheme 3), along with small amounts of the corresponding sters (Table 3, entries 14 and 15). Additionally, oxidation of 27 provided 75% yield of the c-ketomethyl ester product 30 (methyl ester of 29).

Noteworthy, is the fact that isopropyl esters are made with ease in high yields. However, as mentioned above, tert-butyl esters cannot be accessed, most probably due to the sterics of the bulky alcohol. Although at this time conversion of aldehydes to esters proceed best if the reaction is performed in the alcoholic solvent (in order to circumvent the formation of carboxylic acids), studies are underway with mixed solvents and show promising indications that the oxidation to carboxylic acids could be retarded in favor of esterification. Thus, it could be possible to lessen the amounts of alcohol used in the oxidation.

Although any mechanistic discussion is speculative at this point, we believe that the oxidation proceeds via a Baeyer-Villiger process. As depicted in Scheme 4, the proposed intermediates in the oxidation of aldehydes to carboxylic acids and esters are mixed peroxyacetals A and B. Rearrangement of

intermediates A and B would yield the products by expelling bisulfate. Corroboration for the proposed mechanism is based on the well-understood oxidation of aldehydes to carboxylic acids with peroxyacids.26 Also, recently it has been demonstrated that acetals are oxidized to their corresponding esters with Oxone,10 and thus, intermediate B could be derived from either the hemiacetal or acetal (Scheme 4). It should be pointed out that Oxone is slightly acidic and, therefore, could catalyze the formation of the presumed peroxyacetals. Presently, mechanistic studies including use of 18O-labeled aldehydes and NMR experiments to observe transient intermediates are underway.

In conclusion, we have demonstrated a simple and effective one-pot protocol to oxidize aldehydes directly to acids or esters. These reactions are facile,

high-yielding, and easy to work up (most do not require chromatography) and should provide a mild oxidative alternative for organic chemists. The mechanism of these transformations is being investigated and will be reported in due course.

Experimental:

(A bit too simple.)

Aldehyde (1 equiv), Oxone (1 equiv), ROH (0.2 M), 18 h, rt.

Subject: Baeyer-Villiger reaction recycling

Posted by: bio (Hive Bee) Posted on: 10-12-04 08:37 Post No: 535485

Some nice articles you found psychokitty.

Assuming you have a basic understanding of the procedure of this thread (Rhodium posted some dwgs somewhere) I wanted to ask you if you have any input on the following:

In the patent twodogs cited where he got the idea of using perborate it states(paraphrased)near quantitative yields of the B/V product can be achieved in the oxidation by appropriate recycling......

That's it no experimental, examples, discussion, nothing. Will be making a few more runs with the MePhBuO soon and will try some recycling ideas at small test scale. Ah.... so many reactions so little time...

Now I suppose that the simplest and easiest way to do this would be to simply filter, add more perborate and run it again. Maybe removing some water (dessicant) would be helpful. Hopefully the selectivity is such that the ketone enol ester would not be damaged. Another place would be after the isolation before the hydrolysis or even after the hydrolysis itself.

Any thoughts on this?????? I have various improvements on the overall procedure but nobody seems to be interested enough in this method (except one

bee I know of) to

actually do it. So I don't waste my time but I do thank you and the Hive for all the great stuff, especially Rhodium for finding several of the key references for this and similar reactions.

IndoleAmine and the second part...

Subject: United States Patent 4,988,825

Posted by: psychokitty («») Posted on: 10-13-04 07:28 Post No: 535611

In the patent twodogs cited where he got the idea of using perborate it states(paraphrased)near quantitative yields of the B/V product can be achieved in the oxidation by appropriate recycling......

That's it no experimental, examples, discussion, nothing. Will be making a few more runs with the MePhBuO soon and will try some recycling ideas at small test scale. Ah.... so many reactions so little time...

Actually, the segment in the patent to which you refer goes like this:

The present invention provides a safe and economical process for oxidizing aldehydes and ketones using an alkali metal perborate, such as sodium perborate, as the oxidant. Alkali metal perborates are safe and economical to use, and the sodium borate by-product thus formed is safely handled and is a valuable product that can be sold in its own right. In addition, the oxidation is carried out under easily maintained reaction conditions and provides selectivities approaching 100% so that all of the starting aldehydes or ketones can be converted to final product by appropriate recycling. It can be seen that the use of the alkali metal perborate provides a substantial advance in the oxidation of aldehydes and ketones.

All the authors are trying to say is that because the use of sodium perborate is so exceptionally selective, there won't be any byproducts to the reaction, and whatever starting materials are left over--in this case, the intermediate aldol condensation product of benzaldhyde and MEK--can be reused in another sodium perborate Baeyer-Villiger reaction.

Anyway, that's my interpretation. I could be wrong.

Here's the a text copy of the patent in question, for all those who would like to read it:

(1 of 1)United States Patent 4,988,825Bove January 29, 1991Oxidation of aldehydes and ketones using alkali metal perborates

Abstract

Aldehydes and ketones, other than acetone, are oxidized with an alkali metal perborate in the presence of an acid. Inventors: Bove; John L. (Ridgewood, NJ) Assignee: Cooper Union Research Foundation, Inc. (New York, NY) Appl. No.: 910615 Filed: September 23, 1986

Current U.S. Class: 549/272; 549/273; 549/295; 560/231; 562/528 Intern'l Class: C07D 313/18; C07D 313/04 Field of Search: 549/272,273,295 562/528 560/231 **References** Cited U.S. Patent Documents 3122586 Feb., 1964 Berndt et al. 3154586 Oct., 1964 Bander et al. 3483222 Dec., 1969 Sennewald et al. 3716563 Feb., 1973 Brunie et al. 549/524. 3833613 Sep., 1974 Field 549/272. 4160769 Jul., 1979 Higley. 4213906 Jul., 1980 Mares et al. 549/272. 4286068 Aug., 1981 Mares et al. 549/272. 4338260 Jul., 1982 Schirmann 260/502. Foreign Patent Documents 1096967 Dec., 1967 GB 549/272.

Other References

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A. Baeyer et al., Ber., 1899, 32, 3625-3633.
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Ogata et al., Chem. Abst. 90:167685, (1979).
McKillop et al., Tetrahedron Letters, 24, No. 14, (1983), 1505-1508.
McKillop et al., Tetrahedron, 43, pp. 1753-1758 (1987).
A. Rashid et al., J. Chem. Soc. (C) (1967), pp. 1323-1325.

Description

The present invention is directed to the oxidation of aldehydes and ketones to the corresponding acids and esters, respectively using an alkali metal perborate as the oxidant.

The oxidation of ketones, including cyclic ketones, to esters through the use of peracids is known as the Baeyer-Villager Reaction (A. Von Baeyer and V. Villager, Ber., 1899, 32, 3265; 1900, 33, 858) While widely applied, particularly for the oxidation of cyclohexanone to epsilon-caprolactone, nevertheless the use of a peracid presents problems of safety and disposal and/or recycling of organic compounds.

The present invention provides a safe and economical process for oxidizing aldehydes and ketones using an alkali metal perborate, such as sodium perborate, as the oxidant. Alkali metal perborates are safe and economical to use, and the sodium borate by-product thus formed is safely handled and is a valuable product that can be sold in its own right. In addition, the oxidation is carried out under easily maintained reaction conditions and provides selectivities approaching 100% so that all of the starting aldehydes or ketones can be converted to final product by appropriate recycling. It can be seen that the use of the alkali metal perborate provides a substantial advance in the oxidation of aldehydes and ketones.

In particular, the present invention provides a method of preparing acids or esters, which comprises oxidizing an aldehyde (other than acetone) or a ketone with an alkali metal perborate in the presence of an acid.

With the exception of acetone, the present invention is applicable to the oxidation of aldehydes and ketones to form the corresponding esters and/or acids. Aromatic and aliphatic aldehydes and ketones may be used, such as benzaldehyde and methylethyl ketone and the like, as well as cyclic ketones, such as cyclohexanone and the like. Aliphatic and cycloaliphatic aldehydes and ketones containing olefinic unsaturation may likewise be employed to form the

corresponding unsaturated ester and/or acid. When ketones are oxidized according to the present invention, the product obtained will be the corresponding ester, but in some cases a mixture of the ester and acid will be produced.

In a preferred embodiment, the present invention may be used for the preparation of esters and/or acids of the formula (I) ----STR1---- which comprises

reacting an aldehyde or ketone of the formula (II) ----STR2---- wherein R.sup.1 is

alkyl or aryl, R.sup.2 is hydrogen, alkyl or aryl, or R.sup.1 and R.sup.2 are both hydrogen, or R.sup.1 and R.sup.2 together represent alkylene, provided that R.sup.1 and R.sup.2 may not both be methyl. When R.sup.1 and R.sup.2 is alkyl, R.sup.1 and R.sup.2 may be straight or branched chain alkyl, suitably straight or branched chain alkyl of from 1 to about 15 carbon atoms, such as from 1 to about 10 carbon atoms. When R.sup.1 or R.sup.2 is aryl, R.sup.1 and R.sup.2 may be aryl of from 1 to about 4 rings, including fused rings, and may suitably contain from about 6 to about 30 carbon atoms. Suitably, R.sup.1 or R.sup.2 maybe phenyl, naphthyl, biphenyl and the like. When R.sup.1 and R.sup.2 together represent alkylene, the alkylene may suitably be straight or branched chain alkylene of from 1 to about 1 to about 15 carbon atoms in the carbon-to-carbon chain, such as from 1 to about 10 carbon atoms in the carbon-to-carbon chain. Usually when R.sup.1 and R.sup.2 together represent alkylene, there will be from about 1 to about 30 carbon atoms in total, preferably from about 3 to about 15 carbon atoms in total.

In the above formulas (I) and (II), alkyl and alkylene may be unsubstituted or substituted by aryl, halogen, nitro or the like, while the aryl may be substituted by alkyl, preferably lower alkyl, i.e. from about 1 to about 6 carbon atoms, halogen, nitro or the like.

Preferably, R.sup.1 may represent alkyl of from about 1 to about 10 carbon atoms, phenyl, or alkylene of from about 3 to about 15 carbon atoms with from about 3 to about 9 carbon atoms in the carbon-to-carbon chain, said alkyl, phenyl or alkylene being unsubstituted or substituted by halogen, cyano or nitro or, in the case of phenyl, lower alkyl. Further, R.sup.2, or both R.sup.1 and R.sup.2 may represent hydrogen.

While sodium perborate tetrahydrate will normally be used, both in terms of economy and convenience, other alkali metal perborates may be employed of the

formula (III)

MBO.sub.3.nH.sub.2 O (III)

wherein M is an alkali metal, preferably sodium or potassium, and n is 1 to 4, usually 4. Suitably, the oxidation is carried out with the perborate (III) in the presence of an acid that hydrolyzes in water to form hydronium ions, such as mineral acids, sulfonic acids, organic acids, and the like, but a Lowry-Bronsted acid or Lewis acid may also be used, such as BF.sub.3. Glacial

acetic acid is safe and economical and hence is presently preferred. Other useful organic acids include trifluoroacetic acid and formic acid.

When an organic acid is employed, it may also serve as a solvent. If a solvent or co-solvent is required, any suitable inert solvent may be employed, such as acetone, halogenated hydrocarbons, such as methylene chloride, chloroform and

the like, aliphatic and aromatic esters, benzene and the like. It is noted that acetone, while a ketone, is nevertheless not oxidized by the perborate (III) and hence may be used as a solvent, if desired.

Usually, the oxidation will be initiated at a temperature of from about 30.degree. to about 70.degree. C., usually from about 40 to about 60.degree. C. While lower temperatures can be used, reaction rates will necessarily be slower. Temperatures higher than about 70.degree. C. may be used, if required or desired, depending upon the desired reaction rate. However, the reaction is exothermic and hence external cooling may be needed to control the reaction temperature, even at the lower temperatures employed.

The present invention is illustrated in terms of its preferred embodiments in the following Examples. In this specification and the appended claims, all parts and percentages are by weight, unless otherwise stated.

EXAMPLE 1

Preparation Of Epsilon-Caprolactone

To a 200 ml roundbottom flask was added 4.9 grams (0.05 mole) of cyclohexanone, 50ml of glacial acetic acid, and 11.4 grams (0.075 mole) of sodium perborate tetrahydrate. The mixture was heated to 50.degree. C. using a water bath. The reaction temperature was maintained in the range of 50-55.degree. C., while stirring the mixture with a magnetic stirrer for four hours, after which the reaction mixture was cooled to room temperature, and the solid sodium borate was separated from the mixture using section filtration. The acetic acid was stripped from the remaining liquid residue using a rotary evaporator, and the remaining epsilon-caprolactone was purified by vacuum distillation. Yield: 91% theoretical.

EXAMPLE 2

Preparation of Benzoic Acid

The procedure of Example 1 was followed using 5.3 grams (0.05 mole) of benzaldehyde as the starting material. Crude benzoic acid formed was purified by recrystallization. Yield: about 50% theoretical.

EXAMPLES 3-6

Following the procedure of Example 1, the ketones set forth below were oxidized with sodium perborate at a temperature of about 55.degree. C. to provide the esters and acid set forth in Table 1 below.

TABLE 1

Example **Starting Material** End Product Yield ----STR3----------STR4----- 75% 4 ----STR5---------STR6---- 74% 5 ----STR7--------STR8---- 68% 6 ----STR9----------STR10----- 24% HOOC(CH.sub.2).sub.5COOH 38% The most current patent detailing this reaction process, which has links to the relevant patent history of the prior art, is as follows: http://patft.uspto.gov/netacgi/nph-Parser? Sect1=PTO2t2=HITOFF=1=/netahtml/searc hbool.html=2=G=50&co1=AND&d=ptxt1=%27sodium+perborate%27=Baeyer-Villiger=%22so dium+perborate%22+AND+Baeyer-Villiger=%22sodium+perborate%22+AND+Baeyer-Villige

r

Rated as: good read Subject: Methyl-(a-alkyl-)-styryl ketones Posted by: psychokitty («») Posted on: 10-13-04 09:35 Post No: 535629

Information in this post relevant to this thread taken from the PDF documents found in Post 531053 (psychokitty: "Propenylbenzenes anyone?", Chemistry Discourse):

SOME ALPHA-ALKYLCINNAMIC ACIDS AND THEIR DERIVATIVES BY MARSTON TAYLOR BOGERT AND DAVID DAVIDSON J.A.C.S. v. 54 pp.334-338 (1939)

The phenomenal success of a-amylcinnamic aldehyde and other a-alkylcinnamic

aldehydes as perfume bases, led us to prepare several of the corresponding methyl ketones (methyl- (a-alkyl-)-styryl ketones) (111). These were synthesized by condensing benzaldehyde with alkyl acetones (11) by means of hydrogen chloride. . . .

... Ethyl, n-propyl, n-butyl and n-amyl derivatives are reported in this paper. The attempt to prepare the isopropyl derivatives by starting with isopropyl acetone, (CH3)2CHCH2COCH3, gave an anomalous result, since it was

not found possible to prepare a solid oxime from the supposed methyl (a-isopropyl-)-styryl ketone, nor to oxidize it to a-isopropylcinnamic acid. .

Experimental:

One-half mole of benzaldehyde was mixed with one mole of the alkyl acetone and

one-fourth mole of hydrogen chloride gas passed into the cooled mixture. The mixture, which soon became red, was then shaken for sixteen to twenty hours. At the end of this time the water formed in the reaction had separated as aqueous hydrochloric acid and was removed. Without further treatment, the oil was distilled under diminished pressure (about 20 mm.). Somewhat more than half of the alkyl acetone was recovered and a small residue, probably consisting of dibenzal-alkyl acetone (styryl-(a-alkyl-)- styryl ketone), remained in the flask. The principal fraction, consisting of crude methyl (a-alkyl-)-styryl ketone, was obtained in a yield of about 90% based on the alkyl acetone consumed, or about 75% based on the benzaldehyde employed. The

crude alkyl acetone fraction was treated with one-half mole of benzaldehyde and sufficient alkyl acetone to replace that consumed in the first reaction. Hydrogen chloride was then added and the reaction carried out as before. The process was repeated three times but could probably be carried on indefinitely. By using two moles of alkyl acetone to one of benzaldehyde and reworking the recovered alkyl acetone in this way, the amount of dibenzal derivative formed was greatly reduced, with consequent improvement in the yield of the desired product. The crude methyl (a-alkyl-)-styryl ketone may be used directly for the preparation of the a-alkylcinnamic acids. To purify it, the crude product was washed with saturated sodium bisulfite, followed by water and then treated with alcoholic potassium hydroxide, thrown into water, acidified with acetic acid, extracted with benzene, dried over sodium sulfate and distilled. A middle fraction was taken for analysis. The methyl (a-alkyl-)-styryl ketones are liquids having a greenish-yellow tinge, with a floral odor which resembles, but is much weaker than, that of the a-alkylcinnamic aldehydes.

Physiologically Active Phenethylamines. I. Hydroxy- and Methoxy-alpha-methyl-beta-Phenethylamines (beta-Phenylisopropylamines) E. H. WOODRUFF AND THEODORE W. CONGER J.A.C.S. Feb 1938 v. 60 pp. 465-467

... An excellent preparation for a-alkylcinnamic acids is that recently carried out by Bogert and Davidson" who oxidized with hypohalite methyl (a-alkyl styryl) ketones prepared by condensing benzaldehyde with a methyl alkyl ketone in the presence of dry hydrogen chloride gas. With modification this was found to give excellent yields of the methoxy-a-methylcinnamic acids The other steps in the synthesis follow essentially experimental procedures already appearing in the literature...

... When condensing the methoxy aldehydes with methyl ethyl ketone it was necessary to cool the aldehyde-ketone mixture in an ice salt bath during the addition of the hydrogen chloride gas and to allow the reaction to proceed in an electric refrigerator at 0-5 °C or in the freezing chamber at -10 to -5 °C for twenty-four to forty-eight hours, instead of at room temperature. It was found further that a practical grade of methyl ethyl ketone could be used. In this case instead of recovering the unused ketone the reaction mixture was taken up in ether, neutralized with solid sodium carbonate and washed thoroughly with water before drying with anhydrous magnesium sulfate and distilling.

These changes were found to be of particular value in the case of the m-methoxy compound.

Rated as: excellent Subject: Two great articles Posted by: psychokitty («») Posted on: 10-13-04 10:55 Post No: 535634

100 Years of Baeyer-Villiger Oxidations Michael Renz, Bernard Meunier European Journal of Organic Chemistry Volume 1999, Issue 4 , Pages 737 -750

Abstract:

In the present review, we report the discovery of the formation of esters and lactones by oxidation of ketones with a peroxide derivative, namely the Baeyer-Villiger reaction. This reaction was first reported by Adolf von Baeyer and Victor Villiger a century ago in 1899, just one year after the oxidant they used (KHSO5) has been described. Furthermore, Baeyer and Villiger established the composition of this new inorganic peroxide and showed that its instability was the reason of a controversy between several European chemists between 1878 and 1893. For the first 50 years the mechanism of the Baeyer-Villiger reaction was a matter of debate. A side product, 1,2,4,5-tetraoxocyclohexane, was ruled out as an intermediate in the ester formation by Dilthey. Criegee postulated a nucleophilic attack of the oxidant on the carbonyl group. This mechanism was confirmed by von E. Doering by a labeling experiment with benzophenone. The rearrangement step occurs with retention of the stereochemistry at the migrating center. The competitive migration and the rate-determining step are also discussed in this review.

Chemistry: How green was my ester GIORGIO STRUKUL Nature 412, 388 - 389 (26 July 2001); DOI:doi:10.1038/35086670

Introduction:

Hydrogen peroxide is an ideal oxidant. It cannot yet be used widely, because viable catalysts aren't available for many industrially important processes. But there are encouraging indications of progress.

Chemistry has turned green. The increased awareness of environmental

problems

has generated an overly simplistic division, however, especially in the media, between bad chemistry which first pollutes and then (sometimes) cleans up

and good , green chemistry. Chemists themselves are partly responsible for

setting up this misleading contrast. But they are nonetheless among the leaders in trying to find less wasteful or damaging ways to handle the planet s resources.

Subject: B/V recycling Posted by: bio (Hive Bee) Posted on: 10-14-04 06:05 Post No: 535753

Another good batch of reading material you found, psychokitty.

I have been intending to try the "distill direct" method for the MePhBuO, after mechanical HCl removal, from the article you posted. Also extracting with PhMe or Hexane from the start helps minimize emulsions and the washings

go fast. But why even wash if it's not needed.

I've gone straight to the oxidation w/o crystallizing (fractionate only) but yields suffered somewhat. You can crystallize w/o distilling with good results but it is much easier and faster to just distill it. Also it does help to keep the condensation mixture cold to avoid tar formation and process it right away if it sets solid faster than usual. Had one batch setup in 6 hours (11 hours from gassing).

Regarding your statement.....

All the authors are trying to say is that because the use of sodium perborate is so exceptionally selective, there won't be any byproducts to the reaction, and whatever starting materials are left over--in this case, the intermediate aldol condensation product of benzaldhyde and MEK--can be reused in another sodium perborate Baeyer-Villiger reaction.....

Yes, this is also my understanding. My request for suggestions was >>>>WHERE>>>>> do you think would be the best place in the procedure? The

unreacted unsaturated ketone could be isolated before the hydrolysis step in pure form by fractionating, but perhaps this would not be necessary. The ester made it through once (the oxidation) why not just run it again. Water removal might be the sticking point here though.

Ever wonder why they call them LABORatories? I think you know what I mean. Not enough hours in the day, without the technicians and assistants, to do it all.

Subject: how about replacing the perborate with percarbonat

Posted by: Mendeleev (Stranger) Posted on: 10-27-04 05:05 Post No: 538031

Sodium percarbonate has been known to form peracids as well: Post 415088 (GC_MS: "The synthesis of peracids", Chemistry Discourse)

However there are few details in this post. Could you use percarbonate instead of the perborate? Not that obtaining sodium perborate is difficult, it's just that sodium percarbonate happens to be OTC and obscenely cheap.

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Trogdor was a man. A dragon man. Or maybe just a dragon...

Subject: Na Percarbonate Posted by: bio (Hive Bee) Posted on: 10-27-04 10:30 Post No: 538078

The percarbonate should also work but I would suggest perhaps keeping the active O2 content equal or better than the perbotate and any hydrated or insipient water to a minimum.

The reaction conditions are somewhat different though. See the Percarbonate/Perborate review article on Rhodiums site. It offers many references and insights, one of which is that the perborate tetrahydrate is just as effective as the monohydrate, which is unexpected, and suggests a reaction mechanism which is only postulated.

The percarbonate I saw in the store was only 10% and would surely be a real pain in the ass to separate from all the other crap. Most dry bleaches have one or the other. Never checked but the straight stuff may be available at industrial cleaning suppliers. I just can't see spending days to separate a little from soap powder etc. that is so cheap and easily available as

perborate although the percarbonate is cheaper.

If, for whatever reason, you must make or extract the stuff OTC I would suggest just getting borax and H2O2 as being much easier and the product would

be clean and fresh. Sounds like a soap commercial, lol.

Subject: The temperature of the reaction may be the problem

Posted by: psychokitty («») Posted on: 10-28-04 05:12 Post No: 538243

If the temperature of the perborate reaction--forming, as I understand it, peracetic acid in situ--is above 30°C, that may in fact be the problem with the low 35% yields as the peracetic acid oxidation of 2-acetyl-propenylbenzene is recommended to take place well below that temperature.

For example:

https://www.rhodium.ws/chemistry/dillapiole.analogs.html

This compound was quantitatively methylated to 9 in preparation for the Baeyer-Villiger and subsequent hydrolysis of the formate ester to form 10. The conversion of 9 to 10 was carried out using 1 equiv. of MCPBA in CHCl3 at 0° C

for 18 h and afforded the formyl intermediate in 71% isolated yield, saponification of which gave 10. Under these conditions competition by the alkene moiety for the peracid to give an epoxide was minor; at room temperature the rates of desired Baeyer-Villiger and the epoxidation were quite comparable. Finally, methylation of 10 with CH3I-K2CO3 in acetone afforded pure dillapiol.

For the buffered peracetic acid reaction as per Chromic's instruction, see all the relevant posts in the following thread: Post 250788 (Chromic: "Peracetic in DCM - dreams of success", Methods Discourse)

For an example of the diluted buffered peracetic acid Baeyer-Villiger oxidation of a,B-unsaturated ketones, see the following thread (EDIT; SORRY MOO!): Post 504867 (moo: "Baeyer-Villiger on unsaturated ketones", Novel Discourse)

Can anybee speak french? I wonder what the exact details are to the 1936 french article listed in Post 487934 (Rhodium: "Peracid oxidation of

unsaturated ketones", Novel Discourse)

Also, using aqueous HCl might be a better way to carry out the hydrolysis of the phenylacetone enol acetate as use of aqueous NaOH may be contributing to the polymerization of the final product.

For more details about NaOH polymerization, see Post 336996 (Rhodium: "Base-catalyzed polymerization of P2P", Chemistry Discourse); for an example

of HCl hydrolysis, see Post 476334 (Chromic: "HCl is so good it's GOLDEN!", Chemistry Discourse).

It would appear that the advantages to the peracid oxidation of alkenes to epoxides or diols is comparable to the peracid oxidation of a,B-unsaturated ketones to enol esters.

I'll bee back soon with more information.

Subject: Posted already. Post 504867

Posted by: moo (Hive Addict) Posted on: 10-28-04 18:36 Post No: 538339

Posted already, also see Rhodium's on the subject. Post 504867 (moo: "Baeyer-Villiger on unsaturated ketones", Novel Discourse)

fear fear hate hate

Subject: Oxidation time and temperature

Posted by: bio (Hive Bee) Posted on: 10-29-04 13:59 Post No: 538513

You may have hit on the key here, psychokitty!

Reviewing the Boeseken relative article (Rec Trav Chim 55,786-790, 1936) on page 788 where the oxidation of interest experimental is described I can make out 35 degrees and terminee (terminate?) 24 hours. I would paste it up but can't do it from that PDF. It also appears they did hydrolyse with HCl at 80 deg. If somebee could please do a quicky translation of a couple paragraphs on Page 788. It is under the heading "Oxydation de la cetone II" see Post 487934 (Rhodium: "Peracid oxidation of unsaturated ketones", Novel Discourse)

Somebee I know is running a few more batches and wants to try it and I'm sure he would report back the findings to me.

The part on the HCl hydrolysis is on the first page and mentions the time, temp but no strength for a similar compound.

Anyway keep them cards and letters coming psychokitty

Rated as: excellent Subject: A better way with MEK Posted by: bio (Hive Bee) Posted on: 11-02-04 06:21 Post No: 539173

Here I go again ing to my own post. CW you are going to love this, 80% of the work is now eliminated in the MePhBuO prep.

The method below with slight modifications was tried at 1M test scale with great results. 77% molar yield or 124.4g from 106g PhCHO.

The HCl was passed slowly keeping the temp < minus 5 deg (all absorbed) and stirred for 16 hours at ice bath temp. Immediate when stopped stirring into sep funnel. This shit loves to form emulsions with the oily phase trapping below the water in gobs when washing. After 3 hours no water separated (not surprised) so just proceded anyway.

Now let me ask anyone who actually might be paying attention. How is this possible???......."The mixture...shaken for sixteen to twenty hours. At the end of this time the water formed in the reaction had separated as aqueous hydrochloric acid and was removed." I guess I don't know how to shake. What probably really happened was 2 days later the water separated, from my experience.

The one to one method was not what it was cracked up to be. Sat too long and way more tar and labor to separate the crap.

from JACS 54, 336

.....One-half mole of benzaldehyde was mixed with one mole of the alkyl acetone and one-fourth mole of hydrogen chloride gas passed into the cooled mixture. The mixture, which soon became red, was then shaken for sixteen to twenty hours. At the end of this time the water formed in the reaction had separated as aqueous hydrochloric acid and was removed. Without further treatment, the oil was distilled under diminished pressure (about 20 mm.). Somewhat more than half of the alkyl acetone was recovered and a small residue, probably consisting of dibenzal-alkyl acetone (styryl-(a-alkyl-)-styryl ketone), remained in the flask. The principal fraction, consisting of crude methyl (a-alkyl-)-styryl ketone, was obtained in a yield of about 90% based on the alkyl acetone consumed, or about 75% based on the benzaldehyde employed. The crude alkyl acetone fraction was treated with one-half mole of benzaldehyde and sufficient alkyl acetone to replace that consumed in the first reaction. Hydrogen chloride was then added and the reaction carried out as before. The process was repeated three times but could probably be carried on indefinitely. By using two moles of alkyl acetone to one of benzaldehyde and reworking the recovered alkyl acetone in this way, the

amount of dibenzal derivative formed was greatly reduced, with consequent improvement in the yield of the desired product. from JACS 54, 336.....

Anyway back to the grind.

Subject: Calling all Peracid Guru's

Posted by: bio (Hive Bee) Posted on: 11-02-04 08:36 Post No: 539184

Chromics method for 15% peracetic from ca.35% H2O2 is about to be tried.

Now Bio had an idea that if he used the perborate 4hydrate (same moles peroxide) instead of the Hydrogen Peroxide, which is mostly water, he should end up with an almost equal peracetic concentration with wayyyy less water, which if I understand correctly is detrimental to peracid oxidations.

The perborate doesn't like to dissolve too well in the GAA so a lot must be used (10:1 ratio per the Perborate/Percarbonate review article. The little Oxygen bubbles just seem to bubble right on out. So......what if the room temp moderated mixture was sealed and allowed to develop a few atmospheres of

pressure? Thoughts anyone?

Bio loves his new low pressure bomb, it makes things so easy and he gets more too!

Sulfuric Acid catalyzed Peracetic acid with NaPerborate 1:10M SPB:GAA @ 40deg (20deg??) Required for 100g,624mm MePhBuO per twodogs procedure!

1)500-625ml Glacial acetic acid ca 10M CH3COOH 60.05 g/m x 10 = 600.5g x .995 = 597.5g/1.05d = 569ml

2)143g 929mm Na Perborateca 1M 34.0g/m H2O2 NaBO2.H2O2.3H2O = 153.8 g/m

3)AcOH 597.5g + H2O2 34g/m = 631.5 x .01 = (6.31g x .98)/1.84d = 3.36ml H2SO4

Rhodium if you get a chance, please look this over. Will try it insitu the normal way and also premade peracetic (modified Chromic method as above)It is

supposed to be sulfuric acid 1% weight of total contents that you referenced for me.(JACS,907,1946, Greenspan F.P.)

Also the unreacted MePhBuO will be fractionated prior to the hydrolysis (HCl instead NaOH) although the concentration and time is still not clear per your excerpt from the 1936 Boeseken article.Phenylacetone by Bayer-Villiger Oxidation of 2-acetyl-1-phenylprop-1-ene Boeeseken &Jacobs Recl. Trav. Chim. Pays-Bas 55, 786 (1936)

Peracetic acid treatment of 2-acetyl-propenylbenzene

(3-methyl-4-phenyl-but-3-en-2-one) below 30°C resulted in the formation of phenylacetone enol acetate (2-acetoxy-1-phenylprop-1-ene), mp 131°C and bp 103°C/3mmHg. Heating the crude reaction mixture with aqueous HCl at 80°C gave phenylacetone

phenylacetone.

Subject: heres my results Posted by: abacus (Hive Bee) Posted on: 11-06-04 09:18 Post No: 540001

Bio,

Swim has been carrying out a few experiments of his own and seeing how you are

still interested in this procedure, like me, i may as well share some results.

360g distilled benzaldehyde was mixed with 260g MEK in a 1L FBF and stirred in an ice bath (around equimolar amounts).

HCL gas was slowly added over two hours so that the weight of benzaldehyde/MEK mix increased by 75g.

The flask was stoppered, removed from the ice bath and the blood reddish solution was then allowed to sit for 2-3 days at room temperature.

The HCL was then removed by dissolving the resulting methyl phenyl butanone in DCM and washing with NaOH solutions, brine, then clean water.

The DCM was removed by distillation, residual water stripped off under vacuum,

and then MPB vacuum distilled to give 360g.

btw, no tar or polymerisation was ever observed.

Not too bad.

Baeyer Villager oxidation using sodium perborate then proved quite successful with similar results to your posts.

Steam distillation was employed to seperate the resulting P2P.

The down side is the use of large amounts of GAA, so experiments involving recycling the GAA and unreacted MPB are currently on the drawing board.

Subject: ? Posted by: indole_amine (Hive Bee) Posted on: 11-07-04 16:14 Post No: 540201

What was the final yield of purified propanone with the described procedure?

indole_amine

- Astrum SWIM tried this reaction recently. After distilling the final product (fraction 210-220C, no suitable vacuum was present at the time) SWIM got a brownish liquid that smells like P2P, obviously has roughly the same BP. The yield was high though, expected ~28g and got 38.2g. SWIM must have made an error somewhere and will be doing it a second time, we'll see how that turns out.
- IndoleAmine astrum: you should redistill under vacuum and see if you get cleaner product? Most likely your ketone is contaminated and therefore the "high yield"...

Does anyone know about using standard peracetic acid (Chromic method, 35% H2O2, GAA & H2SO4, let stand for 12-16h) for this "Baeyer/Villiger"-oxidation of an unsaturated ketone?

In other words, is the perborate essential or can standard peracids be used; and if this is the case: are additional solvents needed (like DCM or acetone), or does the methylphenylbutenone dissolve equally bad in aequous performic solutions, with or without solvent?

I_A

peracetic

bio

Net's been giving me a fit so might be a day or two before I post the edited WD stuff.

.....Does anyone know about using standard peracetic acid (Chromic method, 35% H2O2, GAA & H2SO4, let stand for 12-16h) for this "Baeyer/Villiger"-oxidation of an unsaturated ketone?.....

This is on the experiment list also the buffered version sans the carbonate. I believe chromics procedure calls for standing the mix 3-5 days. If you look at the previous posts on perborate w/ 1% H2SO4 you will see the max peracid concentration is in only 2-3 hours versus something like 80 hours w/ aqueous H2O2. I did use the 1% SA last run but can't tell how much of the yield increase was from this as also the reaction at RT was done simultaneously for the first time. Boeseken used 20% peracetic so it obviously will work although no yield is given in the original article or any other one that I can find.

I'll get around to it sooner or later but it sure would help if the experiments were split up. Where is CW and A when I need them. My sense is that the perborate MAY actually give better yield as there is only water of hydration present

4H2O versus using 35% H2O2. Haven't done the calcs but is probably equal to around 80% hydrogen peroxide water equivalent. How about run the calcs Indole, also for the monohydrate.

Look in the JACS article in the posts mentioned above. The peracetic concentration versus time matches the 80 or 90% fairly close.

.....In other words, is the perborate essential or can standard peracids be used; and if this is the case: are additional solvents needed (like DCM or acetone), or does the methylphenylbutenone dissolve equally bad in aequous performic solutions, with or without solvent?.....

The MPB dissolves just fine in acetic acid and no solvent should be needed. More acid could be used I suppose but the MPB melts so low that it doesn't really matter although a healthy excess of acid should of course be used. One bee actually dripped in the liquid MPB with good results. Have never tried this as I have my own pet theories about why portionwise SPB is better. Maybe somebee could prove me wrong. That would be nice. Chromic used DCM, I think, just to try and achieve a more homogeneous solution.

Astrum, IA is correct. You are weighing contamination although 46g is my best yield (per 100g) so far of clear product collected over 6 deg at 6mm. If you expect a pure product it must be slowly fractionated correctly. Aspirator vac is OK even 50mm works fine as long as it's steady. Take fractions over about 20-40 degrees to get it all if your vac is unstable. Make sure to cut the fractions say 10 deg above and below.

Anyway back to work, this place looks like a disaster zone, reduced iron and rusty electrodes everywhere. That red shit is a bitch to get off the labware.

IndoleAmine Rust everywhere? Hmm - did you maybe use a bit much HCl gas lately? :lol:

As I understand the peracid formation, the acid catalyst is for dehydration purposes, and more than 1% H2SO4 can be used if the peracid is either vac distilled or buffered. In both cases, the sulfuric is removed; and in case of using a buffer, salts are formed which bind even more water in their crystal structure/when dissolving, so the peracid should form even more readily once any buffer is added (see patent US2802025 for details).

Thinking this, SWIA takes 800ml GAA, adds 190ml H2O2 30% and 10ml H2SO4 97% and lets it stand overnight (16h). The next day, he adds some 10ml more H2SO4 (temperature rise of +1°C noted :D) and lets it stand another 10 hours (24 hours total). He places the supposed-to-be peracetic in a 2000ml RBF and starts stirring, while slowly adding 25g NaHCO3 to mostly neutralize the sulfuric (CO2 evolution). He thinks "well some sodium acetate and/or sulfate should've formed now; they can form hydrates - good thing, less water available in there", and adds 85g MePhBuO dissolved in 75ml CHCl3... ...and then starts to wonder if sodium tetraborate (borax) would help in any way, since it normally is present when using perborate.

So, he adds some few grams of borax to the reaction - somewhat seems to get it going, temp. rise to 24°C. Maybe just neutralization heat. Placed in 10°C water bath. Maybe more salts were formed, accelerating peracid formation, SWIA thinks - and is remembered that not all peracid is formed already and some still will be made during rxn. As he wants to recycle his GAA, he doesn't want any residual peracid during distillation. So what to do? Peracid formation will still take some hours, it was not really old peracid...

So SWIA adds some more 75g PhBuO dry and in portions, to make sure all peracid becomes consumed in the oxidation of the PhBuO. Temperature is still 24°C; ca. 1,5h have elapsed. The mePhBuO dissolution is endothermic, so the temp. can be somewhat kept down adding it in portions.

"Since one can recycle the unreacted a,b-unsaturated ketone prior to ester hydrolysis, not much is lost here - I can as well add a healthy excess of it", SWIA thinks. And then he realizes that this excess may in fact even drive the reaction forward, similar to using excess GAA for peracid formation.

After 3 hours, the temp. had dropped to 21°C (=ambient) again - before, it had climbed to 24°C, even with external cooling. The thermometer has a fruity smell (somewhat similar to P2P) when dipped into the rxn (and afterwards being rinsed with a little H2O to remove the peracid), SWIA thinks this may well be the desired ester. Its not MPB, for sure...

He told me he was planning to let it stir for 18h total, and that he would report back as soon as he would get to know anything about the outcome.

UPDATE: after 5 hours reaction time, 10ml H2O2 30% were added, followed by 5ml H2SO4 97% dropwise. The sulfuric caused a reddish coloration with every drop, wchich quickly disappeared on stirring. Slight exothermic reaction, caused temp rise to 24°C.

After 7 hours, 4.5g anhydrous Na2CO3 were added to mostly neutralize the additional H2SO4, resulting in much CO2 evolution. Reaction cleared up from milky-white to clean again within 5 minutes. Again rise in temp. from 21°C to 24°C. After 9 hours, the whole thing had heated up to 31°C and had to be placed back into the cooling water bath.

This is were SWIA left it. He almost can smell the ketone already, now definately (a few drops of the rxn mixture dripped into 20ml of pH 8 water gave an oily film smelling very familiar, and absolutely not like the starting material. Good old nose chromatography... :lol:)

EDIT 2: after almost 17h reaction time, the rxn had warmed up to 27°C again. still something going on there. Replaced the cooling bath with a fresh one, and will let stir until no exotherm rxn can be seen anymore (and five more hours from that point on).

Any comments?

i_a **B/V oxidation**

bio

Well, you've certainly added enough variables to the equation. I hope you get a 90% yield, then I will follow it verbatim, lol.

Good going. More later, there are some good ideas in your post.

Maybe you could take part of the ester and run an acid hydrolysis. Boeseken used HCl (I suggest large excess 15%) only aqueous given in article. 80deg for 8hours in MeOH is all I can make out from the french. Dammit why won't somebody translate this fxxxx article from 1936? I' ve asked for over a year and the words have so many meanings I finally gave up trying from a dictionary going word by word for hours.

If it's possible to post an image I would paste the hydrolysis paragraph here. but you probably have the articles. Rhodium found them and put them up on the Hive.

IndoleAmine Yeah maybe Indole tweaking too much again here, probably... :lol: (the whole shebang is still brawling along with a slight exotherm at 24°C, this after 33h rxn time: maybe the additional peroxide/sufuric wasn't that good either. We'll see...)

About the articles: I don't have them, sadly. (Java hope you read this) :cry: Give me the article in question (and the others too please), and I will translate it as good as possible (although mon francais est pas si bon peut-être anymore, by now... :wink:), you could send them to my hushmail account if the size is <2MB...

About acid hydrolysis: I am familiar with a procedure calling for 10% HCl and EtOAc at 80°C for 5 hours, but I prefer the basic one - it makes for a simpler workup, since no traces of acid have to be removed after distillation when NaOH is used. What about NaOH/H2O with some additional EtOAC (which of course would immediately become hydrolyzed to EtOH and GAA anyway, giving some sodium acetate, buffering the harsh lye conditions and maybe reducing polymerization of product)?

(SWIA is planning to maybe steam distill directly after hydrolysis, he hates aspirator noise)

About diagrams: I found this one in a patent yesterday - looks like some original hand drawing from Boeseken himself... :lol:

	http://www.shroogle.org/synthetika/files/mephbuo_oxidation_989.gif
	Greets
	i_a
Astrum	Well SWIM redistilled it under vacuum and got a light yellow liquid, 17.7g. That was from 75g of MePhBuO. SWIM still has another 75g of MePhBuO so SWIM will try it out again.
	good to gogo
bio	That's about 70% of the minimum you should have gotten and would be due to decomposition during the atmospheric distillation (see any smoke in the flask) and excessive manipulation; everything else being perfect. Holdup can also be a problem with small amounts if you don't have the mini setup.
	Light yellow is OK and should be good to gogo if the product was collected under say 15deg or so
	Aldol
synthetika	That's great work, ~18g doesn't sound too bad, considering your just getting the hang of it,
	Tremendous work,
	I don't as yet fully understand all the mechanics of the various Aldol reactions, mixed, acid catalysed, basic, etc,
	But somewhere I do remember a post replacing The dry Hcl, with another acid,
	Sulphamic, or something, oh well,
	Astrum, You are welcome to do a full write up, with any media, if you have it.
	Good to see this method, getting the attention it deserves,.
	Benzaldehyde is readily made in many.many different ways, This is a great route for PMK(p2p)
	syn

aldol acid catalyst

bio Twodogs the person that introduced this method to the Hive some years ago said in the original thread that he tried aqueous sulfuric acid and also concentrated HCl acid but did not get the results he did with the HCl gas. There was no further elaboration on the difference in yields.

This is most likely due to adding water to the reaction which has an equimolar amount of water produced along with the condensation product. This would drive the equilibrium in the wrong direction. Some aldols are quite sensitive to water contamination and require standard precautions such as drying tube etc. This reaction does not seem very sensitive to small amounts of water and no particular precautions are needed. An inert dessicant might work to improve yields if using aqueous acid but it hardly seems worth the effort HCl gas being so easy to make. One person who had very good sucess told me that he didn;t even dry his gas and his results were on par with the best.

Some of the original aldol type condensations (knoevenagle for example) used a very small amount of catalyst and let the mix sit for a couple of weeks in the dark at ambient temperature. This might work with concentrated H2SO4 using only a few drops or one of the newer solid super acids.

maybe super-acids aren't well suited here

IndoleAmine Most of the old aldol condensations need either a water-miscible solvent (like alcohols), a dessicant like silica/mol.sieves, and/or some way of mechanical water removal (dean-stark trap) to work properly and to give good results (Knoevenagel for example). :oops:

When gassing with HCl, the two important factors are time and temperature. If the benzaldehyde/MEK mix isn't cold enough, more tar will be formed due to self-condensation of the starting materials. Same thing applies for going too fast during the gassing stage (gassing should take 4-5 hours MINIMUM), and (of course) over-gassing has the same polymerization effects..

I don't think that adding stronger acids directly to the rxn would solve this problem; although they can in fact "dehydrate" the reaction effectively (especially sufuric), they also can make great red tar quite quickly..

(SWIA once had a suck-back accident during gasssing, and the MEK/benzaldehyde was sucked into a H2SO4 bubbler. The reaction occured under heat evolution, and the result was much tar and little product. But then again, this was probably waaay to much H2SO4 and much too high of a reaction temperature...)

Oh, and last but not least: most acids (especially solid super-acids :wink:) cannot be distilled, so there is no option for recycling the molar excess of MEK - you have to wash with bicarb (or similar) to neutralize the acid pre distillation, and this removes the MEK too quite effectively. With HCl gas, the MEK can be recovered very easily before distilling the a,b-unsaturated ketone...

i_a

IndoleAmine Did I mention that this was one of the most frustrating days SWIA had lately? :cry:

The peracetic B/V oxid. was allowed to run for 36h total, after this time no exotherm rxn could be detected anymore.

The acetic was distilled at 100 mmHg - almost 700ml recovered, but didn't solidify upon freezing. Not pure...

The remainder solidified upon cooling and was diluted with 300ml of hot water. This was extracted 3x with toluene (450ml total), the emulsions were dealt with by washing with copious amounts of hot, dilute brine and bicarb solutions.

The combined toluene extracts were dried over Na2SO4 and the solvent stripped to leave a nice yelow oil with a very fruity smell (definately ester, together with unreacted MePhBuO). The unreacted phenylbutenone was fractionated (at least most of it), came over at $<130^{\circ}$ C/aspirator vac.

Then SWIA decided to do something stupid - and dropped the receiver flask containing at least 70g unreacted, solidifed MePhBuO into a hot oil bath accidentally. The "nature-identical cherry aroma" was immense and overpowering, the oil bath was dumped, and SWIA had wasted lots of solvent, energy and time on recovering something which was lost now. :evil: :? :x :(:cry: ...

To the remaining slightly orange-colored oil was added 80ml EtOAc and 350ml 10% aequ.NaOH, and the whole thing was stirred at 80°C for 1,5h. The color changed from orange to red/brown.

Then, the reflux condenser was replaced with a distillation setup, the mixture diluted with 120ml hot water and heated to a vigorous boil to steam distill the BMK. It came over as an almost colorless oil, with a slight tint of green to it, and the typical smell.

Steam distillation is still in progress, and the product will be recovered by extracting 2-3x with toluene, followed by drying the combined extracts and solvent removal at the rotovap at full aspirator vacuum (currently 6mmHg due

to good weather and cold, cold 4°C tap water, in these winter daze 8))

I don't think the yield will approach 90% this time :lol: , but we're working on that... (will report back if I get to know the results)

i_a

Astrum SWIM pretty much followed bio's post (No: 472943) from the-hive. A few minor differences, for instance I used toluene for extraction instead of DCM.

This method really is easy, it just takes a lot of time to complete.

not good

IndoleAmine Fuck. Could it be that aequous workup conditions can cause partial hydrolysis of the ester before separating anything (before fractionating and hydrolysis)?

Because SWIA isolated not more than 5ml of ketone... :shock:

I think the reason is that he added 300ml hot water during workup, and tried to properly recover the unused MPB. The ester was partially hydrolyzed before separation of starting material and product was attempted, and the P2P was mostly removed with the unreacted MPB (which was then dumped into a hot oil bath. :x).

Disappointed, SWIA decided to try it again with performic and not with so many buffer/dehydration tweaks this time. Should result in a different ester, but give the same ketone after hydrolysis (SWIA will try hydrolyzing with dil.HCl only this time).

300ml of 85% HCOOH were mixed thotoughly with 77ml 30% H2O2 and cooled to 10°C in the fridge. Then 81 g MPB were weighed out and added to the performic with stirring in small increments, so that it all dissolved nicely.

After some minutes of stirring, a white coloration was noted, and then the reaction started exothermic and heated to more than 40°C while the white cloudiness was replaced with a clear yellow. A cold water bath took care of the heat, and the rxn became cloudy and white again.

Apparently the white color is caused by the decreasing solubility of the MPB in the rxn medium - it crashes out as a yellow oil floating on top, and redissolves upon heating up. (Above 40°C, the rxn looks clear yellow, as said before). I guess the ester is waaaay more soluble in formic acid than the unsaturated

ketone, and therefore the MPB crashes out as soon as any ester is formed - the ester replaces it, and MPB is insoluble in water.

(BTW steam distillation doesn't separate P2P and MPB correctly - MPB can be steam distilled just like MDP2P, if one wants to wait forever... :lol:)

EDIT: the rxn is still exothermic after 4.5h; but the temp. above which the milkyness disappears is now not 40°C but rather 24°C, and below that, not much of any yellow oil floats on top anymore. Looks better than the peracetic. This one will be left stirring until 18h have elapsed, and worked up using straight forward vacuum distillation of

a) first the remaining formic/performic along with some water

b) most probably some unreacted MPB

then the remaining formate ester and MPB remains will be hydrolyzed with 8% aequ. HCl at 80°C for 2 hours, followed by extraction with Et2O and vac.distillation at aspirator pressure to (hopefully) recover more than5ml of ketone...

EDIT2: after 12h reaction time, the cooling bath isn't needed anymore, internal temp. is noted as being 23°C (21°C=ambient), and color has changed to a nice, clear yellow. Looks good, definately better than the peracetic run. Probably the peracetic wasn't formed already, this and the wrong workup conditions made for the bad yield SWIA doesn't even want to calculate. And the ester formed with performic is also "acetoxy-", due to the very nature of thr Baeyer-Villiger (it just inserts one oxygen and changes R1-C=O-R2 into R1-O-C=O-R2, no matter which peracid is used).

cheers

i_a **hydrolysis** **bio**I think the reason is that he added 300ml hot water during workup, and tried to properly recover the unused MPB. The ester was partially hydrolyzed before separation of starting material and product was attempted, and the P2P was mostly removed with the unreacted MPB......

I don't know how hot the water was or how long it was in contact but I do know that RT water is OK for the ester.

My hunch is that the hydrolysis conditions damaged the ketone by not using enough solvent and heating. With no heat added and the 50/50 EtOH mix with the given amount of NaOH causes about a 20deg rise and I always add it slowly and stop after about 2 hours. Apparently BMK is sensitive to too strong of base but what that is empirically I don't know. One run when the hydrolysis was run at 60deg returned about 20% less than usual but I couldn't completely attribute that only to the hydrolysis as some other variables had been introduced. It's important imho that only one condition at a time be varied to get some kind of meaningful experimental results.

Also using slightly stronger base with less solvent works OK. Although I have always stayed with the original molar proportions one bee did this with less NaOH with the same results. How much excess is required is hard to say.

strange...

IndoleAmine Strange things happened.

The performic was allowed to run 16 hours, with gentle heat being applied during the last 0.5h, resulting in no more noticeable exotherm upon returning to room temp.

Vacuum distillation was then commenced, almost 300ml of water/formic were recovered, followed by a small fraction consisting of some benzaldehyde(:?:), formic and phenylacetone.

Then the unbelievable: a nice green oil started to flow and was collected over a range of 95-117°C at aspirator vacuum. This most surely contains some unreacted MPB, because as the flow of distillate began to cease, its color was noted to be more like that of MPB rather than BMK...

The residue had a deep brown color, but nevertheless had a clear appearance (probably some MPB - but not much, mostly ester). To it were added 60ml of 37% HCl diluted to 400ml with H2O, and hydrolysis is currently in progress, stirring at 90°C, and the upper polar layer already has taken on a greenish tint too... 8)

(this will be further worked up as follows: extraction with toluene, washing

with bicarb and brine solution, removal of solvent and then the distillate collected while separating the ester from MPB will be added and the whole thing (hydrolysis product and distillate) will be fractionated to hopefully give a killer 90+% yield of BMK... :lol:)

(to be continued)

Oh - did I mention that I suspect the formic with its low pKa being responsible for the auto-hydrolysis? :wink:

i_a

polymerization as usual ;)

IndoleAmine I think the problem with basic hydrolysis is the fact that BMK is very prone to polymerizing upon coming into contact with Na+ ions (either NaOH or Na2CO3), the red/brown coloration after steam distillation makes me think this is where some of the ketone may have gone too... :(

(the resulting tar is easily dealt with by rinsing with a wmixture of ethyl formate, formic acid and formaldehyde :P)

As I said, dilute HCl will be used next time, and workup will be straight forward, no water addition...

And while at the topic "HCl": does anyone have access to a good azeotrope database? I'm looking for an ternary azeotrope between MEK, water and HCl, could come in handy for recycling the MEK...

(and if some would be so kind and check his azeotrope book: I also need data about azeotropes between methylamine/ammonia/water in any variation, although for different reasons :wink:)

thx

i_a

This is the excerpt from WD I promised. Only that which hasn't appeared in other threads is included and has only been edited as to form NOT content.

bio Professor of P2P @ Ketone University

Just found this site today and am pleased to see so many bees here. I was running some experiments with a couple other bees and now have no way to reach them. If perhaps they read this please PM me. The catalyzed below

bio

30deg oxidation (22-26deg) was a great success with a yield increase to 55% molar. Recycling is also working out well.

So many reactions.....so little time

IndoleAmine New Dreamer

AFOAF of mine will try this very soon, he feels that more experimenting has to be done as this is a really marvelous little procedure...

psuedonymph WD Secretary of the Interior: Kung-Futon Master

Have any of you guys entertained the idea of adding a little TAED?

Astrum Starting Dreamer

SWIM has been working with this method as of late. It's a decent method and it does work well enough.

bio Professor of P2P @ Ketone University

Here is an excerpt from an interesting article I bumped into when doing a searcha year or so ago. Never tried to find the OTC stuff pure (TAED)

Another thing on the to do list. Anyone have an idea of an OTC source. Please don't say detergent!

152 JSDC VOLUME 115 MAY/JUNE 1999

If we go back some 30 years or more, consumers coped better than they donow. They probably owned a twin-tubwashing machine, had less colouredarticles and took more time to separatetheir wash loads into whites and coloureds. Whites were washed at high

temperatures and the coloureds, using the same water, were washed at lowertemperatures. The oxygen bleach (perborateor percarbonate) was

effective atthe high temperatures used for 'whites' and was relatively ineffective at the lowertemperatures used to wash coloureds(Figure 1)Times have changed; the growth in the use of synthetic fibres and fibre blends, new applied textile finishes and the increase in coloured textiles means that consumers have to wash at the lower temperatures of 40 and 50 °C. The first requirement for the wash isto remove stains and to achieve this atlow temperatures has meant the development of low-temperature bleach activators. In Europe the activator is TAED, tetra-acetylethylenediamine, while in the USA and some other countries SNOBS, sodium nonanoyloxybenzene sulphonate, is preferred. TAED is a hydrophilic bleach that, under European wash conditions of lowliquor volumes and relatively long wash times, is effective in achieving stain removalat low wash temperatures (Figure 2). SNOBS on the other hand is a hydrophobicbleach that is effective under American wash conditions of high liquor volumes and short wash times. Hydrogen peroxide is a weak bleach at low temperatures, and the function of theactivator, TAED or SNOBS, is to react chemically with the peroxide in the wash solution to produce a more activeFurther investigations have shown that 30% of cotton articles fade noticeably and irreversibly after repeated washing in a bleach-containing detergent' bleaching agent, peracetic acid orpernonanoic acid and the diacylperoxide (DAP)(Scheme 1).Hydrogen peroxide and peracetic acidor pernonanoic acid are susceptible to wasteful decomposition in the wash. The most important side reaction is the mutual decomposition of peroxide and peracetic acid or pernonanoic acid (Scheme 2). This reaction is catalysed by the presence of metal ions and can be inhibited by the inclusion in the detergent formulation of phosphonate based ethylene diamine sequestrants Additionally, the reference detergent used in these protocols is unrepresentative of market place detergents. The detergent industry workingthrough the Fastness Tests Committee of the Society has introduced a nonphosphate reference detergent to which bleach activator (TAED) and sodium perborate tetrahydrate can be added. This formulation in colour fastness testshas been shown to correlate well with marketplace heavy-duty activated bleach-containing detergents and has been adopted by the European Colourfastness Establishment (ECE).

The base formulation, TAED and sodium perborate are available through the Society.

IndoleAmine New Dreamer

I recently dreamt that both sodium perborate*4H20 and TAED are available very cheaply (and by the kilo) through professional detergent suppliers...

IndoleAmine New Dreamer

Psuedo: now that we have entertained ourselves with the idea of adding TAED to a peracid during the Bayer-Villiger oxidation of MePhBuO: For which purpose would one WANT to do something like that?

Yes, perborate and TAED go well together for washing clothes - but this doesn't mean they're good for peracid formation using NaH2BO4 and GAA, or did I miss something?

psuedonymph WD Secretary of the Interior: Kung-Futon Master

quote:Originally posted by IndoleAmine

Psuedo: now that we have entertained ourselves with the idea of adding TAED to a peracid during the Bayer-Villiger oxidation of MePhBuO: For which purpose would one WANT to do something like that?

Yes, perborate and TAED go well together for washing clothes - but this doesn't mean they're good for peracid formation using NaH2BO4 and GAA, or did I miss something?

Perborates function best at 60 Celsius, and this reaction needs to be ran at 30 C or below due to the sensitivity of 2 - acetyl - propenylbenzene.

I noticed that cold water detergents utilise TAED to activate perborates below 60 Celsius, and was wondering if TAED would be beneficial for this purpose.

AS to whether this has a benefit to dreamers, I don't know. This is purely hypothetical, just thinking out loud.

bio Professor of P2P @ Ketone University The part of the article which was the graphs I couldn't copy. Basically it shows that the TAED activates (by forming peracetic) the perborate to function at 40-50deg whereas perborate alone needs around 90deg used alone to effectively bleach out stains. The graph shows that at 80deg the TAED marginally improves stain removal (85 versus 95%) but at 40deg it is twice as effective (60 versus 30%. This is simply because peracetic is a stronger oxidizer than H2O2.

I don't think you missed anything here, IndoleAmine, as in our case we WANT the peracetic to decompose or the reaction can't proceed.

The reason the perborate4H2O is "more effective"(really just faster) above 60deg is because it "dissolves" actually melts at 63deg per CRC (melts in water of hydration to form the tri if not in solution) and loses water at 130-150deg per CRC.

One reason I remain somewhat skeptical about the 30 deg reaction being the main answer to higher yields is because in the one runaway I had (prior to adding the perborate portionwise to the substrate) the temp went to 115deg and was starting to reflux when it pooped out with me frantically putting the hose on it (I'd had wet iced towels on it from about 60deg) praying the eruption didn't happen. Good thing had a reflux condensor on it . Anyway it was all over in 2 hours and was the best yield to date at that time. About 43% I think. So you see what I mean??? I'm skeptical. My opinion is the answer lies in a catalyst. And please forget the RheniumWhateverItIs that gave the 92% yield.

The article below confirms that it works from 20deg just takes longer and really doesn't dissolve at all. One bee told me he tossed the mix out because he thought his perborate was bad cause it didn't dissolve. Poor fucker tossed his goods.

This from Ullmans.....

Physical Properties. Sodium perborate tetrahydrate, Mr 153.9, r 1.731 g/cm3, theoretical active oxygen content 10.38 wt %, melts in its own water of crystallization at 65.5 °C. distribution of 0.1 - 1.0 mm. Depending on the crystal shape, bulk densities of 0.65 - 0.9 kg/L can be obtained.

When stored under cool, dry conditions the rate of loss of active oxygen is only 1 % per year. Decomposition is accelerated at higher temperatures and moisture content.

There is a tendency for increased caking at higher temperatures caused by conversion of the tetrahydrate to the trihydrate .

The solubility in water is 0.152 mol/L at 20 °C and 0.388 mol/L at 40 °C. 23g/l 60g/l $\,$

Thermogravimetric analysis curves for sodium perborate tetrahydrate show that decomposition takes place in three stages: 20 - 150 °C, 150 - 165 °C, and 165 - 400 °C. In the first stage, the tetrahydrate is dehydrated to the monohydrate.

D. W. van Gelder, Recl. Trav. Chim. Pays-Bas 75 (1956) 117 - 126. The commercial product is a white, crystalline solid with a spherolitic or elongated particle shape, and a particle size

.....

sodium perborate hydrates are partially hydrolyzed, reforming the starting materials metaborate and hydrogen peroxide according to the following equation

t in aqueous solution the sodium perborate hydrates are partially hydrolyzed, reforming the starting materials metaborate and hydrogen peroxide according to the following equation :

OVER

madchemist Starting Dreamer

SWIM is lucky enough to have the materials/equipment involved and does have some experience with this method. Just recently found the thread and others a few months before The Hive went down. SWIM has a whole BMK compilation based on this route alone, SWIM can e-mail a zip file if any one wants (got no place to upload to, too lazy to register something right now). It's got valuable Hive posts on this route + benzaldehyde manufacture, a few pics, some patents, some MSDS sheets, basically all the info one with the knowledge could ever want to safely and properly pull this synthetic pathway off with no problems at all, and then some.

SWIM spends 80% of most of his tweek-time using it as a tool to learn about O. Chem, and also study new potential OTC methods so he can tweek even more. Screw the good book, books like Vogel and Solomons are the real holy bibles! After all life is all a result of the shitloads of never-ending always changing chemical reactions down to the subatomic particle and the energies that apply.

Anyways (so many run-ons and tangents, so little time) this is a kick-ass route, but SWIM agrees yields in both the aldol condensation and the Baeyer-Villiger can definitely use some vast improvements.

Keep in mind that this is definitely not all there is as far as the sacred lost art of coupling the holy ring with various holy hydrocarbons to get good old sundrop, rose-petal, kodak jack, prope dope or whatever your clique may have called it. Ever since SWIM

began studying all the types of coupling/condensation info he could gaze upon, so many doors leading to all sorts of kick-ass potentially OTC kitchen worthy routes for phenylacetone have come into play, and so much more are waiting to be discovered. After all, clandestined chem is all about being clever. But thats for another thread! I'm already way off subject here.

Anyways, about the aldol condensation:

Cons for SWIM with the HCl cat. MEK/PhCHO:

Distilling:

SWIM doesn't know about every one else, but a lot of precursor is destroyed upon distillation. There is tarry like shit left (in the still flask) that is a bitch and a half to remove, indicating some degredation/yeild reduction. SWIM does not currently have a vacuum source, although he does have required glass and equipment to not only build a continous aspirator, but also glass for fractionating under vacuum, complete with one of those valved manifold receiver things. You know so the vacuum doesn't have to be disturbed when switching recivers (SWIM has no cow dammit), never even been used. Right now his current living situation has put a lot of dreams on hold, and SWIM is reduced to simple lab procedures due to this situation (mainly on the factors of being detected).

He only breaks out the hand pumped auto-engine vac. line checker when he needs to use the buchner or just plain speed up filtration on the plain funnel/vac. filter flask.

So when SWIM distills the MePhButenone it's of course at normal pressures. As quoted in a lot of The Hive's threads pertaining to this, vacuum distilling will definitely raise yeilds to a worth-while degree. Plus it wouldn't be as hard to clean out the still flask hehe.

Catalysts:

SWIM always used dry HCl gas, but there was some mention from twodogs in some of his rantings that mention using H2SO4. He stated he got good yeilds by adding catalytic amount of H2SO4 to the mix and refluxing. Although that seems to me (harsher acid, higher temps) that it would actually form more by-

products but hey it could work. SWIM may try this the next time he has the chance.

There is also several patents/refs from those old posts pertaining to other things being used as catalysts also. However, they usually used more complex compounds, the types which start bringing this out of the OTC way. Got to be OTC!! No suppliers that tightly record your business and may get you caught. No hassle of making fake docs/info or company or whatever (which sometimes can get you in as much trouble as drug manufacture itself), or anything. Gotta love OTC materials!

The reaction:

It works because the acid catalyzes enolation of the MEK, causing it's alpha carbon to react with the enolized benzaldehyde. This coupling is made a condensation by the acid also catalyzing dehydration of the newly formed enol to give MePhButenone.

Now all prior attempts were done just like the posts, and the benzaldehyde and MEK were just mixed together.

Now with using HCl gas, this may not be all that bad depending on how much gas the mix can hold. My book says at least for base catalyzed crossed aldols (and SWIM's assuming this for acid ones as well, but could be wrong) that compounds with no alpha-hydrogen (aka the benzaldehyde) do not self condense. So thats good. The MEK, however does have an alpha-carbon and will self condense in a crossed aldol. There is one possible yeild reducer, esp if one were to attempt this with sulfuric which would all be in contact with all reagents (instead of being slowly introduced like HCl gas) until the end.

The book then goes on to say that the non-alpha carbon (PhCHO) and catalyst are mixed first. Then the alpha-carbon containing reagent is to be slowly added, to effectively reduce side rxns. This means higher yeilds.

SWIM is definitely gonna try using H2SO4 next, by mixing PhCHO with it and dripping in the MEK. SWIM is undecided about heating or not but twodogs did claim to reflux.

(After a quick reveiw, he stated that refluxing in conc. HCl acid, or H2SO4 worked, but not as well as dry HCl. He also states something about water that is formed as byproduct do not effect the condensation as much.)

That may be true, but it just seems highly unlikely that all the H2O from conc. HCl would not give very high yeilds. Thats another suggestion for higher yeilds, maybe adding something inert like silica-gel or using Dean-Stark or something to separate the formed H2O when using reflux with H2SO4 would make that work a lot better.

With this method,

Now as for the Baeyer-Villiger, my views and thoughts and past experiences and shit will have to wait till later on tonight. SWIM really has to get going got shit to do today. Woke up at 10am did some meth and now it's 4pm and SWIM is still sitting here trapped.

Before SWIM goes off for the day, he wants to mention another route from MePhButenone. SWIM hasn't tried it yet, but sees no reason why it shouldn't work as the rxns involved are well covered.

If the low yeilds of the Baeyer-Villiger is pissing you off, forget it entirely. If you look at the structure of methyl phenyl butenone, you begin to release it's an alpha-methyl type derivative, as well as a methyl-ketone derivative, off nothing any more special than cinnamic fucking acid! So what to do, how to convert to alpha-methcinnamic acid?

Well, right away SWIM sees the methyl-ketone group being converted back to the carboxylic acid (ex:p2p back to PAA) with a well known easy performed synthesis known as the haloform rxn.

Thats right, the same procedure using hypohalite salts (bleaching powder) to oxidise simple methyl ketones like acetone or MEK to get a haloform (CHCl3 with bleaching powder) and a carboxylic acid. Simply put, the methyl group swaps with an OH. Or R-(C=O)-CH3--->R-(C=O)-OH or better written as R-CO2H.

So basically running your basic haloform rxn on methyl phenyl butenone would give you some alpha-methylcinnamic acid.

Now if you do have access to things like Raney Nickel and sodium azide, then the procedure at Rhodiums using a-Me-cinnamic acid---(Raney/Ni)--> a-Mehydrocinnamic acid. From there you can react it with the azide and H2SO4 via the Shemidt rearangement to proceed directly to racemic amphetamine. You can always resolve if racemates aren't for you. Also one could form the Nformyl derivative and reduce that to get meth. Also as for resolution, a-Mehydrocinnamic acid (reduced double bond) can be resolved to pure dextroratory isomer before the rearangment. The result is pure dextroamph.

*****A side note about crossed aldol's: SWIM just noticed in that Rhodium doc mentioned above results are in..

IndoleAmine Well - this turned out to be a good one.

After hydrolysis (1000ml 2N HCl/reflux overnight), the MPB and ester crystallized out as brown globules and white flakes(1).

This was extracted 3x with toluene (200/200/50ml), the combined extracts were dried and added to the "auto-hydrolyzed" ketone SWIA had separated before hydrolysing the ester, and the whole thing was distilled at full aspirator vacuum.

The ketone was collected between 84-104°C and weighed at least 34 g (34ml), but the separation between BMK and MPB apparently wasn't very sharp; because as the oil bath temperature was raised, some more green distillate came over, followed by a small amount of almost white MPB(2).

Since SWIA wasn't satisfied with his result yet, he added some more 2N HCl to the remaining brown ester, refluxed for 1 hour, diluted to 1000ml with more H2O, added his not-so-pure BMK and commenced steam distillation, hoping to get a better separation this time.

At least this will make very pure ketone; vac. distilled AND steam distilled... :lol:

1) The brown ester solidified first, then the white MPB followed; selective cryst. is maybe a viable method of separating these two, since the ester melts above 80° C while the MPB does so below 60° C..

2) Since the boiling points differ only by 28°C, phenylacetone and MPB cannot be separated properly without a decent column - at least 30°C difference in boiling points is said to be the minimum requirement for a good separation through distillation....

As soon as SWIA has finished his lab work, I will post a nice short writeup of the whole aldol condensation, performic B/V and hydrolysis step.

i_a suggested alternative workup **IndoleAmine** Since a) the ester was not completely hydrolyzed and since b) the MPB seems to be not very sensitive to heating with dilute HCl, a simpler, more convenient workup is probably advised.

I therefore suggest the following route of product isolation:

After the performic has been performed :lol: , the rxn mixture is heated for 1h to mostly hydrolyze the ester and to destroy excess HCO3H. Then the residual formic acid is recovered by distillation at full aspirator vacuum. Next, hydrolysis of the remaining ester is done by adding a healthy excess of 5N HCl, refluxing for 1-2 hours and directly steam distilling the ketone part of our ester we just hydrolyzed, while the not oxidized MPB stays in the dist.flask nicely, and can be recovered through filtration after cooling to rt. (it is also said that steam distillation drives the de-esterification forward through continuous removal of product, according to the lechatelier principle :wink:) The distillate is then extracted with 2x toluene, the combined extracts washed with water and brine, and the solvent removed by distillation (first atmos, then full vac for last few ml) to leave very pure, green-yellowish benzylmethylketone with a very distinctive, sweet/flowerish odor, perfectly suitable for making SWIAs favorite eau de toilette and many other fragrant perfumery substances... 8)

The yield from the second run (using a standard performic à la Shulgin for the Baeyer-Villiger) was 48.7g btw, probably also due to using recycled solvent this time. Not bad. 8) 8)

i_a

performic

Terrific IndoleAmine. Way to go!

Is there any reason you can see that the lower acidity Peracetic would not return a similar yield? and of course peracetic made from perborate beforehand, which is my next experiment. With 1% sulfuric should give near complete conversion in 3-4 hours w/ only 4 moles water then just dump 'er in (slowly). Do NOT try this at home as it could be hazardous to your health neverminding the property.

I like the easy separation of the MPB and this is progress to the quant yields that should be attainable.

BTW you were supposed to get 95% what went wrong? :P :D **Excellent**

bio

synthetika This is excellent material, Indoleamine,

Well done,

This route needed a lift in awareness, as as you have shown, it's synthesis can be broken up into long but readily available chemicals for the hobbiest, Benzaldehyde, MEK, Formic or acetic, and you have, what I believe a pioneering method, for the chemist,

There are many good routes, now to Benzaldehyde, Toluene,Cassia Oil ,persulfate oxidation, anode/cathode,etc

This is brilliant chemistry

And a good yield too, Nice work, Bio and Indoleamine!, :wink:

syn

Hm

IndoleAmine Thanks syn! :wink:

..I just stumbled over this thread over at wd - I wonder what these guys are talking about, going via cinnamic and phenylglycidic acid to achieve a lower yield than can be had with the above procedure... :lol:

This is what I'm talking about: http://www.wetdreams.ws/forum/topic.asp?TOPIC_ID=2598

!

(Picture courtesy of Ning and shamelessly ripped by me - hope you don't mind it :oops:)

...and I'm especially curious about the intermediate ning mentions as being produced in step C - maybe this (without the OH at the carboxyl of course) is the real intermediate when directly oxidizing an a,b-unsaturated ketone with peracids - and not the "O-RCOOH" ester theoretically resulting from a B/V?

At least the "ester" gotten from a "performic B/V" behaves like a glycol/epoxide, rather than like a normal ester - it looks like epoxide, changes colour like epoxide upon "thermal rearrangement" (golden->red) and can be hydrolyzed with HCl, just like the product gotten from a regular performic (or oxone) oxid. on propenylbenzenes...

(the similarity of our "B/V" to regular peracid oxidations already was pondering in my head for a while now, and then I saw this thread!

What do you think? Could this be, or is it just another crazy idea?)

i_a Using H2SO5 in the Baeyer-Villiger oxidation

Cyrax Persulfate oxidation of ketones (general procedure):

The oxidizing agent is prepared in a 500 ml flask equipped with a magnetic stirrer and cooled in as ice bath as follows: In the flask are placed 60 ml of concentrated H2SO4 and 20 ml of H2O, and the solution is cooled to 10 °C. K2S2O8 (42 g, 0,15 mole) is added slowly to the stirred solution while maintaining the temperature below 10 °C. The solution is diluted with an additional 65 ml of water maintaining the temperature below 15 °C. (EDIT: as you can see, the persulfuric acid is obtained in situ by hydrolysis of K2S2O8: K2S2O8 + H20 + H2SO4 --> H2SO5 + 2 KHSO4) The solution is now cooled to about 7 °C and 0,08 mole of ketone is added over 40 minutes. After the addition has been completed, the solution is allowed to com to room temperature and stirring has been continued for 20 hours. The solution is diluted carefully with 150 ml of water and axtracted twice with 75 ml portions of ether. The ether is washed with NaHCO3 solution, followed by water, and the ethereal solution is dried. Removal of the solvent, followed by fractional distillation (EDIT: in our case, followed by hydrolysis of the enol ester), affords the product ester.

ref.: Monson, Richard S.; Advanced organic synthesis: methods and techniques (1971), p 11

Mabey somebee should try out this reaction on 2-acetylpropenylbenzene :D

Another possibility is to prepare Baeyer-Villigers 'dry reagent' by mixing 10 g potassium persulfate with 11 g concentrated H2SO4 in a mortar, adding 30 g of K2SO4 and grinding the mixture in a dry powder. This reagent is stable in absence of moisture. Oxidations have been carried out using suspensions of dry reagent or solutions of persulfuric acid in concentrated or dilute sulfuric acid, in glacial acetic acid, in petroleum ether, and in ethanol-sulfuric acid.

IndoleAmine Hi folks!

Quote

Mabey somebee should try out this reaction on 2acetylpropenylbenzene

- definately!

As I don't like grinding oxidizing agents and conc. H2SO4 to a powder: who else wants to be the pioneer here? :wink: It really looks interesting IMO, but the techniques used simply don't appeal to me - I prefer mixing liquids..

..and might I proudly add that I seem to be the first chemist ever who successfully used performic/formic acid in a Bayer-Villiger oxidation on a,bunsatd. ketones? Or has anyone already heard of something similar being done? 8) :lol:

Quote

Oxidations have been carried out using suspensions of dry reagent or solutions of persulfuric acid in concentrated or dilute sulfuric acid, in glacial acetic acid, in petroleum ether, and in ethanol-sulfuric acid.

Performic acid & Peracetic acid

Cyrax Great work, that performic oxidation ! That reaction has also been done with peracetic acid on 2-acetylpropenylbenzene, in 1936 (Rec. Trav. Chim. vol 55 p 786) ... but not with performic acid, as far as I know.

There is some article in JACS or JOC (this bee forgot to write down the name of the journal when he copied the stuff) from 1946, p 907: "The convenient preparation of per-acids", where they reach a maximum performic concentration of 4,7 % after 2 hours:

Procedure (*): '9,2 g of formic acid (98 - 100 %) was added to a specially cleaned volumetric flask containing a catalytic amount of concentrated sulfuric acid (1 % concentration on total contents). The flask was immersed in a waterbath, agitated with an air stirrer, and maintained at about 20 °C: 33,7 g of 30 % hydrogen peroxide was then added to the flask contents. Maximum performic concentration is 4,7 %, reached within 2 hours.'

Remark: Performic acid is less stable than peracetic acid, gassing being noticeable after a few hours of standing, and the effective concentration showing a definite decline in 2 hours

The effect of ageing is nicely illustrated with a beautifull graph. The Frank P. Greenspan article rules :)

I shall elaborate further from this literature, where an example of the peracetic oxidation of 2-acetylpropenylbenzene is given:

'En mélangeant 2-acetylpropenylbenzene, avec une molécule d'acide peracétique en solution d'acide acétique glacial, la solution contenant environ 20 % de l' oxidant, il faut refroidir pour maintenir la températue sous 30 °C. Après 8 heures tout l'oxydant est consommé.'

Further in the article, they prove that the substance made is the acetate of the enolized ketone :idea: .

Discussion: 20 % concentrations of peracids aren't made easily. I rather do not dabble with 90 % hydrogen peroxide solutions, but a 8,6 % hydrogen peroxide solution is easily made by following the earlier mentioned the procedure (*) with 10 grams of glacial acetic acid (instead of the formic acid, of course :)), 28,8 g of 30 % hydrogen peroxide and 0,4 g of sulfuric acid. Maximum peracetic acid concentration is 80 to 90 hours. :idea: Now, since according to the french article the reaction takes about 8 hours, one can simply age a 30 % H202 / glacial acetic acid / drop of H2S04 for 80 - 90 hours (in the 90 - 100 hours period, the high concentration remains stable) & in that period of time, one can carefully & portionwise add the 2-acetylpropenylbenzene to a cooled (!) peracetic solution. One can do the math for the right stoichiometry.

If somebee speaks better French than me, please translate (I give it a try upon request).

More H2SO5

Cyrax Here is another example of the H2SO5 Baeyer-Villiger oxidation:

'A mixture of chalcone (i.e. Ph-CH=CH-CO-Ph) (2,08 g, 10 mmol), potassium peroxydisulfate (5,4 g, 20 mmol), conc. sulfuric acid (5 ml), and glacial acetic acid (70 ml) were kept at room temperature (~17 °C) with intermittent shaking, for 170 hours. The mixture was neutralized with potassium hydroxide solution (10 g in 60 ml of water) with ice cooling so as not to allow the temperature to exceed 20 °C. The precipitated salts were removed by filtration and the filtrate was extracted with ether. The ethereal layer was dried (MgSO4), solvent distilled off, and the residue was chromatographed on a column of silica gel. Elution with petroleum ether afforded trans1-phenyl-2-benzoyloxy-ethylene (i.e. Ph-CH=CH-O-CO-Ph) as colorless needles. Yield: 450 mg, 20 %.'

ref.: Synthesis, communications, (september 1973) p 542

Cyrax a 8,6 % hydrogen peroxide solution is easily made by following the earlier mentioned the procedure (*) with 10 grams of glacial acetic acid (instead of the formic acid, of course), 28,8 g of 30 % hydrogen peroxide and 0,4 g of sulfuric acid. Maximum peracetic acid concentration is 80 to 90 hours[/quote:a8b40d7fdd]

While playing with some numbers, my hound Fido appeared quite bored and started licking his balls. Fido does not wonder how much 2-acetyl-propenylbenzene could be eaten the Baeyer-Villiger dog, but I did.

In the article, they say that a 8,6 % CH3COOOH solution is obtained after about 90 hous. Since the total mass of the H202 (aq) / CH3COOH / H2SO4 mixture is 39,2 g, 3,37 g CH3COOOH is present (which corresponds to 0,0443 moles. After 90 hours the ratio:

Moles peracid formed / moles aliphatic used is 0,26 (which corresponds to the point on the graph)

I told Fido that the Baeyer-Villiger dog could eat about 7,098 grams of 2-acetyl-propenylbenzene, and he seemed pretty pleased.

When there is auto-hydrolysis of the enol ester, like I_A said, Fido figured that an excess of CH3COOOH could make the Baeyer-Villiger dog angry & take a bite out of the P2P (yielding Ph-CH2-O-CO-CH3 ...).

really b/v or not

IndoleAmine The percarboxylic acid article with the table comparing time vs. peracid concentration can be found here, thanks to bio: http://home.ripway.com/2005-2/264127/BV%20Ox/peracidprepsimple.PDF

(but I think they got it a bit wrong; they make performic with H2SO4 catalyst, which is wrong because it causes immediate breakdown of any (per)formic, since these acids are simply really incompatible. They further titrate aequous performic by diluting with H2O (5x the volume!), and wonder why it has a low concentration - :roll: (the equilibrium HCO2H + H2O2 <> HCO3H + H2O shifts back and forth really quick, the reason why performic is ready to use immediately after preparation - and why diluting with water will give false titration results here....)

•••

I have a little "problem" at the moment:

I'm not sure about the identity of that brown, high-boiling, VERY fruity smelling ester resulting from the B/V of our unsatd. ketone (the one which gets hydrolyzed to give the final ketone later): Boeseken said he had confirmed it as being 2-acetoxypropenylbenzene, C6H5-CH=CH(CH3)-C-O-CO-CH3, but this

was >70years ago, and in fact he didn't postulate the whole B/V mechanism correctly (as was proven later on).

And then there is Ning who is currently working on a somewhat similar route to aromatic 2-propanones - he thinks that oxidizing a,b-unsaturated ketones would create epoxides, not esters, and I would say normally he knows very well what he's talking about...

And my dog just left me a note on the table telling me he "successfully performed the performic again" - same result, works slightly better than peracetic/SPB

(not meant as competitive statement bio; I mean just SLIGHTLY better, and just enough that one notices the difference and wonders)... :wink:

And this morning, he sounded as if he had attempted to hydrolyze the brown intermediate he produced, and (at least it seemed to me) he wanted to say his intermediate behaved exactly like what Chromic has decribed as epoxide/glycol in his HCl hydrolysis writeup... (too bad my dog can't talk :mrgreen:)

And finally I just read the following a few minutes ago...

!

(taken from [url]http://home.ripway.com/2005-2/264127/BV%20Ox/peracidprepsimple.PDF[/url], if you want to read the whole thing)

.. and with all that in mind: could it be that since

a) performic from 30% H2O2 is normally inferior to peracetic from GAA/SPB when it comes to available oxygen, but still seems to work [i:2c0dd20ea4]amazingly[/i:2c0dd20ea4] well in this special case (which is quite a contradiction!)

b) performic hasn't got to do anything with any "B-containing species" like perborate, nevertheless works better than boron-containing rxns of similar nature

..the oxidation of a,b-unsatd. ketones can proceed via different intermediates, depending on which oxidant/catalyst is used - but will result in the same compound at the end?

- either an epoxidation rxn with normal peracetic acids,

- a b/v oxidation (ester formation) with persulfate/perborate etc. catalyst,

- or a mixture of both,

depending on the rxn conditions one chooses (oxidant, catalyst, amount of available oxygen as well as of free oxygen, solubility, presence of catalyst, temp. etc. etc.)?

Then we could try to optimize things by opting for either epoxidation or b/v esterification pathway, and modify the oxidation parameters accordingly, to get the maximum yield in this rxn step...

(I know, the idea of two competing rxns leading to the same compound after hydrolysis isn't very appealing; especially when the only difference is the presence of a B ion and a methyl group on the peracid - but think about persulfuric b/v, and peroxodisulfate b/v, sulfuric as b/v catalyst...

and then performic, without anything, being slightly better? Although it is normally worse than even standard peracetic, due to low peracid content?)

or maybe actually both reactions occur - epoxidation AND insertion of an additional oxygen to give an ester...

Whatever happens really inside the flask: it cannot be just a simple B/V, since it works quite well for my dog without any B/V catalyst, in fact better than with one....

..gotta go, my dog wants to promenade/urinate, maybe he tells me another story..... :wink:

i_a analysis needed IndoleAmine Hmm - I doubt we have a b/v oxidation here, really.

Just in case I could convince a friendly stranger to analyze it with common advanced analytical equipment: wouldn't a C(-O-)-C epoxide and a C=C-O ester be almost indistinguishable with most methods of analysis (since an epoxide in fact can be called a cyclic ester too, methinks), and how could one differentiate them with certainty?

i_a

Cyrax I think it is a good idea to hydrolyze the product of the BV reaction anyway, by refluxing it for 10 hours in 15 % H2SO4. If the double bond of the 2-acetoxypropenylbenzene oxidized further to the epoxide, the hydrolized product of the epoxyester would be Ph-CH(OH)-CO-CH3 whereas the hydrolysis product of the normal BV product would be P2P, of course. If an epoxyketone was formed (not by the BV, but epoxidation) hydrolysis gives benzaldehyde.

I hope this makes analysis easier.

Which procedure did you experiment with, if I may ask?

Good luck, Cyrax

IndoleAmine Upon aequous HCl hydrolysis, the compound in question does result in P2P indeed, without aldehyde or propiophenone (vac. dist. bp matches almost exactly with literature bp given for phenylacetone, and almost no forerun or residue, read almost no losses)...

What if the acetylpropenylbenzene would not become esterified at all, but only epoxidized at the double bond?? (thats what I meant with the statement that was probably no b/v, but an epoxidation)

The procedure was: oxidizing an a,b-unsaturated ketone with performic.

Just like done with a b/v, but the difference being that no b/v catalyst and/or oxidant was present at all, just plain performic, which is no b/v oxidant and/or catalyst AFAIK.

The intermediate looked and behaved like an epoxide rather than like an ester, and the resulting ketone looked exactly like expected (neo-green/yellow), smelled as expected, the bp did match, it was successfully aminated, recrystallized and bioassayed, I think the product of hydrolysis is just true "not-p2p" and nothing else..

But as said already, the citation I made above (and other facts I already depicted) make me think that an epoxidation is what really happened to the C=C bond, and no B/V oxidation.

It makes just much more sense, since the rxn conditions really were not B/Vlike - the rxn was treated & behaved much like a standard isosafrole oxidation.

And the bayer-villiger oxidation article (from which I cited a few lines above) mentions that a,b-unsatd. ketones can also be oxidized to give epoxides.

And "simple" propenylbenzenes like isosafrole for example (without acetyl present) under the same conditions (performic oxidation) are first epoxidized, then ring-opened to give a glycol, which finally results in ketone upon aequous/acidic hydrolysis - at least from my understanding...

I would be very surprised if acetylpropenylbenzenes would behave different under the same conditions, especially since the result after hydrolysis is 99% sure the same as with other proven routes to this ketone....

i_a

bio

Boeseken article

Cyrax, you said;

...... reaction has also been done with peracetic acid on 2acetylpropenylbenzene, in 1936 (Rec. Trav. Chim. vol 55 p 786) ... If somebee speaks better French than me, please translate (I give it a try upon request).....

I am hereby requesting your services as translator of subject article. :lol: :lol:

I spent a loooong time trying but finally gave up. IndoleAmine tried as well. Those f.....g french words they use have 10-20 meanings and in a chemistry context I didn't have a clue which was closest, so times and temps were about all I got out of it.

The pertinent part is quite short and there could be a real gem hiding somewhere in the Boeseken articles in general.

Interesting stuff on the intermediate ester/epoxide. Yes, Boeseken did get the mechanism wrong as the instrumentation/equipment in his day was nothing compared to today. I need to go back and read the two B/V review articles again and Cyrax if you haven't read the perborate/percarbonate review article please do and compare the peracid formation time with the JACS article.

twodogs	Aldol Bio said
	"SWIM always used dry HCl gas, but there was some mention from twodogs in some of his rantings that mention using H2SO4. He stated he got good yeilds by adding catalytic amount of H2SO4 to the mix and refluxing."
	rantings???and I never said that!
bio	Hi twodogs nice to see you're around.
	That statement from the WD thread was made by Madchemist.
	It certainly was NOT made by me.
	I have almost never used the term SWIM and recall being somewhat alarmed when I first read it. This is not the first time you have been misquoted either. Perhaps the price of fame, lol.
	What I did say recently was
	"Twodogs the person that introduced this method to the Hive some years ago said in the original thread that he tried aqueous sulfuric acid and also concentrated HCl acid but did not get the results he did with the HCl gas. There was no further elaboration on the difference in yields."
	This was to correct another misstatement by others. Just want to set the record straight and no hard feelings.
	bio Aldol
twodogs	Not a problem Bio. Have you made much progress with this procedure? I remember commenting back at the Hive that I thought what was needed was a catalyst. In the review of the B-V reaction in "Organic Reactions" someone has got a 90% result using a catalyst. Have you looked at that review? Translation

Cyrax Cyrax, you said;

...... reaction has also been done with peracetic acid on 2acetylpropenylbenzene, in 1936 (Rec. Trav. Chim. vol 55 p 786) ... If somebee speaks better French than me, please translate (I give it a try upon request).....

I am hereby requesting your services as translator of subject article.[/quote:fa9a85febb]

Hi there,

Nice to see the old folks of the hive having previous experience with this method (twodogs & bio), in this thread :D :D

I 'll give it a try to grant your request:

"While mixing 2-acetyl-propenylbenzene with a molar equivalent of peracetic acid in a solution of glacial acetic acid, one has to cool the solution (containing ~ 20 % peracid) in order to keep the temperature below 30 °C. After 8 hours, all the peracid was consumed. One evaporizes the acetic acid under reduced pressure and one obtains a partial solid mass, which was distilled 'au vide cathodique' (41 - 42 °C).

After recristalisation in ethanol, the mp = $131 \,^{\circ}$ C.

After heating 5 g of this substance in a closed tube with methanol and HCl for 8 hours at a temperature of 80 °C and after distilling the contents of the tube, we obtained 1 g of liquid that boils at 57 °C with an odour of methyl acetate. After soapification with KOH, the obtained salts gave all the reactions of an acetate. The residue of the tube, after having evaporized the methanol, distilled over at 83 °C / 4 mm and gave a semicarbazone with a mp of 184 - 185 °C that gave no mp depression when compared with the mp of phenylacetone. The obtained oxide is thus the acetate of this enolized ketone: Ph-CH=C(CH3)-O-CO-CH3. "

Have a great sunday 8)

bio Yes, twodogs, the oxidation yield is up to about 47g/100g and the workup of the aldol product is more or less eliminated with the recycle improvements. IndoleAmine proved out the peracid method you suggested but not much has really been done with the catalyst development. A couple bees from the Hive that were working together w/ me were lost touch with so progress is slooow. I am familiar with the article but need to review it again for that specific reaction which may be the tin on zeolite I think. This catalyst I have a patent on and making it is more work than the rest of the procedure put together. Other than the exotics like rutheniumwhateveritis no simple ones have been found or tried by me other than 98% H2SO4. Indicators point to MnSulfates as the one to try first. BTW recycling does work as you expected.

Cyrax; thanks for the translation. I was hoping for more at least a yield. If you need the other Boeseken articles I can send them. Perhaps you could read them over for clues as they all pertain to ketone oxidations. Even benzylideneacetone must have a use even if it is missing one carbon damnit.

Great work everyone

synthetika Vaulable chemistry- thankyou

We all are very honoured to have such chemists like IndoleAmine, Bio, and Twodogs contribute to this very exciting synthesis,

I have follwed it very closely, and can comment on a few things that i have noticed doing this type of reaction

So just a quick thankyou to all three of you for this cutting edge synthesis, I saw this synth coming a few years ago, And i saw the simple power to its beauty,

I am extremely glad to see the further progress, and am just very proud that our members, can learn so much from these our members, in this particular route

Well done, and I will make sure that members from years to come, will have access to this information

syn

IndoleAmine Further proof for my assumption that this reaction is an epoxidation can be found here, according to an article brought up by Rhodium, both SPC and SPB are known to epoxidize alkenes by releasing anhydrous hydrogen peroxide into the solvent used, in the case of acetic with H2SO4 meaning in-situ peracetic acid formation...

Both peracetic and performic have been known long time for being able to produce high purity isolated *epoxides*

- Synthetikal Forums - Main - Misc. Stimulants -