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PERACID OXYDATION OF A DOUBLE BOND NEXT TO A CARBONYL By Mr J.BOESEKEN et J.JACOBS.

One of us, (Boeseken) showed, with Mr A.Kremer's(1°) and A.L.Soesman's(2°) collaboration, that Benzalacetone, an unsaturated substance, is attacked by peracid with formation of an oxyde. But unlike alkenes and unsaturated acids, there isn't formation of an epoxide, but the actif oxygen places itself between the double bond and the carbonyl: -C=C-O-CO-

Benzalacetone forms phenylacetaldehyde enol acetate: C6H5CH:CHOCOCH3 who has two forms, one is solide and the other is liquide, and they are probably cis/trans isomers:

Н	Н		Н	OCOCH3
C====C		and	C====C	
C6H5	5 OCOCH3		C6H5 H	

We have continued this study with two homologues of the benzalacetone:

C6H5CH:CCH3COCH3 (I) and C6H5CH:CHCOC2H5 (II) (they made a typo here, it's not CO2CH5)

When mixing (I), a-methyl-a-benzalacetone, with a molecule of peracetic acid in acetic acid solution, the solution containing aprox. 20% of oxydant, we must cool to maintain the temperature under 30°C. After eight hours all the oxydant is consumed. We evaporate the acetic acid under reduced pressure and obtain a partially solid mass(3°), which is distilled under "cathodic" vacuum (very strong vacuum) and passes at 41-42°C. After recrystalizing in alcohol, the m.p. is 131°C

Analysis: 65.1mg gave 38.7mg H2O and 178.2mg CO2 69.4mg gave 43.0mg H2O and 188.9mg CO2 Found 6.6 and 6.8%H, 74.6 and 75.0%C Calculated for C11H22O2 6.8%H and 75.0%C

Next to the solide product, was formed an oil passing under 3mmHg between 100-103°C, Nd= 1.5503.

When heating 5g of this substance in a sealed tube with some methanol and hydrochloric acid at 80°C for 8 hours and distilling the tube's contents, we obtained 1g of a liquid boiling at 57°C with an methyl acetate smell. When saponificating it with KOH, the obtained salt gave all the reactions of an acetate.

The tube's residu, after evaporating the methanol, passed at 83°C/4mmHg and gave a semicarbazone of mp=184-185°C which gave no difference with the mp of the a-methyl-abenzalacetone. The obtained oxyde is thus the acetate of this enolized ketone: C6H5CH:C(CH3)OCOCH3

To prove it, we have synthetized this substance. At first we tried obtaining it as an acetate of enolized phenylacetaldehyde, by heating the ketone with acetic anhydride in presence of pyridine, but without success. Then we have applied Freer's method(4°), which means we heated the ketone(5°) in a ethereal solution with finely pulverised sodium. The metal slowly transforms itself with hydrogen release into an orange powder. This powder gave with CH3COCI some NaCl and an oil passing at 105-114°C/3mmHg. However, the yield was very low, and we had to repeat this operation a few times in order to obtain enough substance and to be able to compare it with the product from the benzalmethylketone oxydation.

Each time we took 10g of the methylbenzylketone for 1.5g of Na divided in 300cc of dry

ether. After formation of C6H5CH:CONaCH3 we added the calculated quantity of acetylchloride diluted in ether. The orange powder changes itself in NaCl with release of heat; we filter and evaporate the ether; what is left is an oil wich is mainly unchanged ketone (bp 84°C/4mmHg) with a little fraction passing at 105-114°C/3mmHg.

These lasts products comming from numerous operations were fractionned: we then obtain an oil distilling under 1-3mmHg vacuum at 98-100°C and who partially cristallizes in the recipient.

Analysis:

66.5mg gave 40.3mg H2O and 181.6mg CO2 60.3mg gave 36.4mg H2O and 164.9mg CO2 Found 6.7 and 6.8%H and 74.5 and74.6%C Calculated for C11H12O2 6.8%H 75.0%C

1g was heated in a sealed tube for 16H at 80°C in a methanol with hydrochloric acid. After this treatment the tube's content gave a little methylacetate (cacodyle (??) reaction after saponification) and some methylbenzylketone (the semicarbazone, mp=185°C didn't give any difference with the semicarbazone of pur ketone).

Therefore, we have succeded in preparing the acetate of an enolized ketone. The only difference between the synthetic acetate and the product of the a-methyl-a-benzalacetone oxydation, is that the last contains a bigger quantity of a solid substance (mp=131°C) and the former is nearly entirely liquid. We could suppose that the sodium salt of the ketone is an mix of alot of C6H5CH2C(ONa)=CH2 and a little C6H5CH=C(CH3)ONa giving with CH3COCI mainly a liquid acetate C6H5CH2C(=CH2)OCOCH3 and very little C6H5CH=C(CH3)OCOCH3, identical to the solid product of the a-methyl-a-benzalacetone oxydation. However, seeing the results we obtained with the benzalacetone, we are convinced that we have incountered two cis/trans stereoisomers:

Н	CH3		Н	OCOCH3
C===	==C	and	C===	=C
C6H5	OCOCH3		C6H5	CH3

The solid form is obtained next to it's liquid isomer by peracetic acid oxydation of a-methyl-abenzalacetone; the liquid isomer forms itself near-exclusively by methylbenzylketone acetylation

Oxidation of the ketone (II) C6H5CH=CHCOCH2CH3

The ketone was obtained by agitating some methylethylketone with benzaldehyde in a slightly alcaline solution during 8 days(6°), bp 109-117°C/3mmHg.

When adding to 15g of ketone the calculated amount of peracetic acid in acetic acid solution, taking care not that the temperature doesn't exceed 35°C, the reaction was finished after 24H. We distilled the solvant at aspirator pressure, and then the obtained product at 1-3mmHg.

The main fraction (11.5g) (Note: 70% molar yield!) then passes at 90-92°C; it's an slightly coloured oil, containing a few crystals.

Main Fraction Analysis:

72.8mg gave 43.9mg H2O and 199.8mg CO2 68.4mg gave 43.3mg H2O and 187.9mg CO2 Found 6.8 and 7.0%H; 74.8 and 74.9%C Calculated for C11H12O2 6.8%H and 75.0%C Molar mass (in C6H5OH) found 170 and 172 calc.176 Nd20°C=1.5541

M.Soesman had found, next to an oil, a solid melting at 33°C who melted after a few days; at the

beggining, this oil had a refraction Nd20°C=1.5243; the liquid having Nd20°C=1.5525 is thus identical to the substance we obtained.

The benzalmethylethylketone (II) has thus captured an oxygen atom. If we consider that the reaction proceeds like with the other benzalacetones, the obtained product must be the phenyacetaldehyde enol proprionate:

C6H5CH:CHCOC2H5 + CH3CO3H --> C6H5CH:CHOCOC2H5 + CH3CO2H

To verify this supposition, we have saponified the substance with methanol in presence of HCl and distilled the obtained product while adding Ag2SO4(2°). The propionic ether was collected in alcoholic KOH of know concentration; we have thus found 80% of the theoritical quantity.

Another sample was saponified the same way; we evaporated the propionic ether and the methanol and added to the remaining oil an alcoholic solution of hydroxyamine; we have thus obtained a little phenylacetaldehyde oxime (mp=97°C).

We have then synthetized this propionate by boilling for 3 hours 1/8mol of phenylethanol with 1/4mol of propîonic anhydride and a little pyridine. By fractionating we obtained as main fraction an oil boilling at 92-96°C/0mmHg

Analysis:

53.5mg gave 32.7mg H2O and 146.9mg CO2 60.5mg gave 37.3mg H2O and 165.9mg CO2 Found 6.8 and 6.8%H; 74.9 and 74.8%C Calculated for C11H12O2 6.8%H and 75.0%C MM (in C6H5OH) 168 and 171, Calc. 176 Nd20°C=1.5371

We saponified this product as we have described for the benzalmethylethylketone oxyde et retrieved 85% of the principal group, while isolating the phenylacetaldehyde as its oxime (mp=98°C).

Even if in the both cases the product is the phenylacetaldehyde enol proprionate, the two substances are not identical; they differ notably by their refraction: Nd20°c= 1.5541 and 1.5371.

Besides M.Soesman had obtained a unstable solid product. That's why we suppose that it's a mixture of the cis/trans isomers:

Н	Н		Н	OOCC2H5
C====C		and	C===C	
C6H5	OOCC2H5		C6l	45 H

Both substances react with a brome molecule.

With this research, former observations on peracetic acid oxydation of benzalacetone are confirmed; the actif oxygen places itself between the two unsaturated systems -C=C- and C=O. In the first communication, one of us showed that it isn't an secondary action of the type: epoxide---> ester; because the cyclic oxyde (epoxide), obtained by Weitz and Scheffer(7°) by action of hydrogen peroxyde in presence of alcali on benzalacetone, is stable in the conditions of peracetic acid oxydation. This remarquable oxydation can be compared to the action of peracetic acid on fural(8°), that displace the aldehyde group as formic acid(9°), action that can be formulated as this:

O:C4H3CHO + O --> O:C4H3OCHO + H2O --> HCOOH + decomposition products and hydroxyfurane polymerisation. The furanic ring can be thought of as an unsaturated system.

Besides, p.hydroxybenzaldehyde has be scindered in hydroquinol and formic acid HOC6H4CHO + O --> HOC6H4OCHO HOC6H4OCHO + H2O --> HOC6H4OH + HCOOH It's from this idea that one of us (B), in collaboration with MM W.D.Cohen and J.C.Kip, has made us regain our efforts in trying to synthetize sesamol from piperonal:

H2CO2C6H3CHO + CH3CO3H --> H2CO2C6H3OCHO + CH3CO2H H2CO2C6H3OCHO + CH3CO2H --> H2CO2C6H3OCOCH3 + HCOOH

We have succeeded and manadged to thus obtain approx. 60% of sesamol acetate.

NOTES: 1° Rec.trav.chim. 50, 827 (1931) 2° Rec.trav.chim. 52, 875 (1933) 3° M.Soesman had already prepared this oxyde 4° Ann. 278, 116 (1893) 5° The ketone was prepared by action of benzylmagnesium chloride on acetonitrile and decomposition of the magnesium. 6° Harries and Muller, Ber. 35, 968, 971 (1902) 7° Ber. 54, 2372 (1921) 8° Rec.trav.chim. 50, 1024 (1931) 9° Dakin, Am. Chem. J. 42, 490 (1916)