

THE OXIDATION OF ALLYL AND BENZYL ALCOHOLS TO THE ALDEHYDES¹

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The use of manganese dioxide suspended in petroleum ether to oxidize vitamin A alcohol to its aldehyde (1), to convert β -ionylidene- β -ionylidene-ethanol to β -ionylidene-acetaldehyde (2), and to oxidize 4-cyclopent-1'-enylbut-3-en-2-ol (3), vinyl cyclohept-1-enyl carbinol, and propenyl cyclohept-1-enyl carbinol (4) to their corresponding ketones has been described.

The mild conditions under which these reactions were carried out, either by shaking a slurry of the manganese dioxide with a solution of the alcohol in petroleum ether or by passing the solution through a column of the oxidant, has led us to investigate the method in order to determine and to extend its scope. In particular, since all of the compounds previously reported as oxidizable have had two or more double bonds in a position to conjugate with the carbonyl group which is formed, it was thought of interest to test the utility of this method as a means of preparing substituted acroleins, vinyl ketones and aromatic aldehydes². Both ordinary and a specially prepared precipitated manganese dioxide were reported to oxidize vitamin A alcohol to the aldehyde readily, but to be ineffective with a number of other alcohols (1). We have also found this lack of effectiveness of a number of commercially available manganese dioxides, which gave a low yield of benzaldehyde, and essentially no citral, on attempted oxidations of benzyl alcohol and of geraniol respectively. A commercial carbon monoxide oxidation reagent³ gave a low yield of benzaldehyde from benzyl alcohol.

It has been found that manganese dioxide prepared by heating a manganous salt such as the carbonate or oxalate at about 220–280° in air (called "MnO₂ A") will oxidize representative benzyl alcohols to the aldehydes, in general in good yield. When the manganese dioxide prepared by this method is washed with dilute nitric acid and then washed acid-free and redried, it gives a slightly better yield of aromatic aldehydes, and also gives fair to good yields of substituted acroleins and of the one vinyl ketone, whose preparations from the allylic alcohols were attempted. This acid-washed MnO₂ is called "MnO₂ B". Manganese dioxide prepared by treatment of nitric acid-acidified manganous sulfate with

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² The use of manganese dioxide prepared from manganous sulfate and potassium permanganate in oxidations similar to some of those described here was reported essentially simultaneously with our first report¹ by Attenburrow, *et al.*, *J. Chem. Soc.*, 1094 (1952). See also Sondheimer, *et al.*, *J. Am. Chem. Soc.*, **75**, 5930 (1953).

³ Hopcalite, listed as "Job No. 21225-2, Lab. Report No. 4293," from the Mine Safety Appliance Co., Pittsburgh, Pa.

TABLE I
OXIDATION OF BENZYL ALCOHOL TO BENZALDEHYDE

Run	MnO ₂	Solvent	Time, Hours	Assay, %	Yield, %
1	A	Ether	94	54	80
2	B	Ether	137	74	80
3	B	Ether	24	60	65
4	B	Hexane	64	59	60 ^a
5	H ^b	Ether	46	38	54
6	2H ^{b, c}	Ether	87	53	52
7	F ^d	Ether	47	84	73
8	B	Ether-5% BuOH- <i>t</i>	47	69	76

^a Conversion. ^b See footnote 3 in text. ^c Twice the "Standard" (See Experimental section) amount of Hopcalite was used. ^d MnO₂ prepared by the method of Frazer (5).

potassium permanganate (5) gave a good yield of benzaldehyde in one of the two trials in ethereal solution (Table I, line 7), but spontaneous combustion occurred during the duplicate run, and was narrowly averted in a third trial, so no further work was carried out with this oxidant. It might well be useful in cases where an especially active reagent is required, and would probably be safe in petroleum ether suspension.

Table I shows the effect of variations in conditions on the yield and purity of benzaldehyde produced by oxidation of benzyl alcohol. It is evident that excellent yields are obtained with either "MnO₂ A" or "MnO₂ B", but that the more active "MnO₂ B" yields a product containing less starting material.

The "Assay" column in this and in subsequent tables indicates the percent of aldehyde present in the alcohol-aldehyde mixtures obtained after oxidations, by removal of solvent and distillation of the entire residues, excepting that the *p*-nitrobenzyl alcohol oxidation product was not distilled. The "Yield" values represent essentially yields corrected for recovered starting alcohol. "Yield" values are calculated as:

$$\frac{(\text{Weight of distillate}) \times (\text{Assay})}{(\text{Weight of starting alcohol} - \text{Weight of alcohol in distillate})}$$

Where they are given, as in Tables II and VII, the "Conversions" are yields based on starting alcohol taken, with no allowance for recovery.

When the amount of MnO₂ is increased relative to the other components, the yield of benzaldehyde soon reaches a constant value, but the purity of the aldehyde produced increases. The unoxidized alcohol is apparently adsorbed on the excess MnO₂. Table II shows this when "MnO₂ A" is used. This effect should be especially useful when the alcohol and the carbonyl compound are not readily separable by other means.

Table III gives the yields of various aryl aldehydes obtained using 4 g. of MnO₂/g. of aryl carbinol. The oxidation of alcohols bearing substituents so different electronically as hydroxyl and nitro, the clean oxidation of the *o*-hy-

TABLE II
EFFECT ON YIELD AND PURITY OF BENZALDEHYDE OF CHANGES IN
MnO₂/BENZYL ALCOHOL RATIO

Run	MnO ₂ ^a /ROH		Time, Hours	Conv., %	Yield, %	Assay, %
	Grams	Moles				
1	0.89	1.1	64	12	33	16
2	1.4	1.7	70	23	69	25
3	4.0	5	68	43	—	51
4	8.0	10	66	56	57	96

^a MnO₂ A was used.

TABLE III
OXIDATION OF SOME ARYL CARBINOLS

Run	Alcohol	MnO ₂	Solvent	Time, hours	Assay, %	Yield, %
1	Furyl	B	Hexane	119	100	56
2	Furyl	B	Ether	88	100	69
3	<i>o</i> -OH-Benzyl	B	Hexane	91	97	27
4	<i>o</i> -OH-Benzyl	A	Ether	47	59	87
5	<i>o</i> -OH-Benzyl	B	Ether	93	88	78
6	<i>p</i> -NO ₂ -Benzyl	A	Ether	89	74	70
7	<i>p</i> -NO ₂ -Benzyl	B	Ether	93	85	36
8	Veratryl	B	Hexane	113	100	17
9	Veratryl	B	Ether	113	100	80

droxybenzyl alcohol, and the better yields obtained in most cases when ether⁴ rather than hexane is used as solvent are especially noteworthy.

The result of the oxidation of some aliphatic carbinols is shown in Table IV.

The results of these and of other runs not tabulated indicate that only "MnO₂ B" is sufficiently active to give adequate yields of substituted acroleins, and that, for these oxidations, use of hexane as solvent results in higher yields than does the use of ether. The slight but definite oxidations of the two saturated carbinols (runs 9 and 10) are noteworthy.

The oxidation of the "C₁₄ Alcohol", compound I (6) to the C₁₄ aldehyde (7) is of interest in connection with the question of the structure of the aldehyde. Ozonization to geronic acid suggests that the structure IIB is correct (8) while the ultraviolet absorption and the Raman spectrum of the aldehyde indicate (9) that it contains a conjugated aldehyde group as shown in structure IIA. The ease of oxidation by means of MnO₂ can be considered as chemical evidence favoring structure IIA, provided that it can be assumed, as seems reasonable, that no rearrangement took place during the lithium aluminum hydride reduction by which the alcohol was prepared.

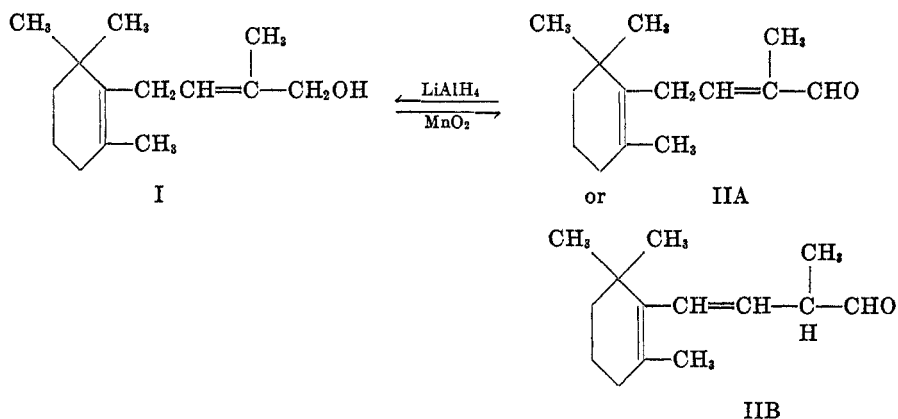
⁴ Note precaution in Footnote 8 when ether is to be used as solvent with highly active manganese dioxides.

TABLE IV
 OXIDATION OF SOME ALIPHATIC ALCOHOLS

Run	Alcohol	MnO ₂	Solvent	Time, Hours	Assay ^a	Yield, %
1	Geraniol ^b	H ^c	Hexane	66	51 u	31 ^d
2	Geraniol ^b	A	Hexane	60	15 u	23 ^d
3	Geraniol ^c	B	Hexane	96	64 u	61-79
4	Crotonyl	B	Ether	73	66 u	45
5	Cinnamyl	B	Ether	188	99 d	77
6	Ph(CH ₂) ₃ OH	B	Hexane	115	14 d	9 ^d
7	beta-Ionol	B	Ether	136	83 u	41
8	C ₁₄ Alcohol (6)	B	Hexane	113	93 u	61
9	Capryl	B	Ether	95	18 o	15 ^d
10	2-Butyl	B	Pentane	115	15 o	7 ^d

^a Method of assay: u, ultraviolet absorption; d, dinitrophenylhydrazone (gravimetric); o, oximation (acidimetric). ^b Commercial geraniol used. Yields corrected for geraniol content. ^c Geraniol was purified *via* the calcium chloride adduct. ^d Conversion, i.e. not corrected for recovered alcohol. ^e See footnote 3 in text.

A number of examples in the literature indicate that ozonization of α,β -unsaturated carbonyl compounds yields rearranged products and so is unreliable as a method of structure proof for those compounds (10).



EXPERIMENTAL

Preparation of "MnO₂ A." One pound of C.P. powdered manganous carbonate (manganous oxalate was equally satisfactory)⁵ was spread in a one-inch thick layer in a Pyrex glass or porcelain dish, and heated at 220-280° for about 18 hours in an oven in which air circulated by convection. The initially tan powder turned darker at about 180°, and black when maintained at over 220°. No attempt was made to determine lower temperature or time limits, nor the upper limit of temperature. The black powder was cooled in air.

Preparation of "MnO₂ B." "MnO₂ A" prepared as above was stirred with about 1 l. of a solution made up of 15% of concentrated nitric acid in distilled water. The slurry was

⁵ Salts purchased from either Eimer and Amend or from Merck and Co., Inc. were used.

TABLE V
THE RATE OF OXIDATION OF BENZYL ALCOHOL^a

Time, hours	Conversion, %
1	28
4	44
7	44
24	68
48	71
73	73

^a The standardized procedure was used, with hexane as solvent and "MnO₂ B".

TABLE VI
THE RATE OF OXIDATION OF GERANIOL^a

Time, Hours	Conversion, %
0.5	16
1	23
2	26
6	29
24	38
48	40
97	45

^a The standardized procedure was used, with hexane and "MnO₂ B". The geraniol was purified *via* the calcium chloride adduct.

filtered with suction, the solid was washed on the Buchner funnel with distilled water until the washes were at about pH 5, and finally was dried at 220–250°. The friable caked black solid was readily crushed to a powder which retained its oxidizing ability even after having been stored for several months in a loosely stoppered container.

Carbinols. The carbinols to be oxidized were purchased unless otherwise noted, and were distilled or recrystallized to acceptable values of the melting or boiling point. All were tested for the presence of carbonyl groups by the method of assay to be used after oxidation, and for peroxides with iodide-acetic acid. The solvents used were petroleum ether fractions boiling about 55–67°,⁶ commercial C.P. absolute ether, and, in a few runs, 2,2,4-trimethylpentane.⁷

Oxidations. The oxidations were all carried out by a standardized procedure: 100 g. of the manganese dioxide was placed in a 500-ml. flask, and about 300 ml. of the solvent was added in one portion. The flask was immediately swirled and, if necessary, stoppered and shaken vigorously to wet all of the MnO₂.⁸ The alcohol to be oxidized was added (25 g.),

⁶ Skellysolve B., from the Skelly Petroleum Co., Inc. and C. P. hexane, from Eimer and Amend, Inc.

⁷ Eastman Kodak Co., Spectro grade.

⁸ Local hot spots may develop when ether is used as solvent, especially when it is added slowly or in small portions. Cooling the flask in running water is advisable should this occur, as in one oxidation of the nearly 100 performed, spontaneous combustion of the ether occurred when this precaution was omitted. Later experiments have shown that the addition of 1 ml. of water to the MnO₂ before addition of the solvent will minimize the possibility of this occurrence without lowering the yield of aldehyde.

and the flask was stoppered and shaken in a shaking machine at a rate sufficient to keep the MnO_2 suspended for the times given, in general about 3 days. The solid then was separated from the solution by suction filtration, using an inorganic filter-aid when necessary, and the solid was washed with more solvent. The combined solvent portions were concentrated, and the residues distilled at the water pump, and identified and assayed by the procedures indicated. Table V gives yields of benzaldehyde found when aliquots were removed from an oxidation and assayed for aldehyde at the times given. Table VI shows the yields at various times in a similar oxidation of geraniol to citral.

A number of oxidations were carried out by passing a petroleum ether solution of the alcohol through a column of MnO_2 , but this procedure (11) seemed to offer no advantage over the batchwise method for the oxidations considered here.

Analytical methods. The identity of most of the reaction products was established by preparation of 2,4-dinitrophenylhydrazones of the correct melting point, not depressed on admixture with known samples. Citral was identified by preparation of its β -naphthocinchoninic acid (12), and by comparison of the infrared absorption of the citral-geraniol mixtures produced by the oxidations with that of synthetic mixtures.

Assays to determine the amount of the conjugated carbonyl component were carried out, in general, by comparing the ultraviolet absorption of the ethanolic solutions with those of known concentrations of the aldehydes. This method was not readily applicable to oxidations of *p*-nitrobenzyl alcohol. In the case of citral, where extraneous absorption was not negligibly small at the absorption maximum, the formula: Citral = $(3.41/c) (2d_{240} - d_{230} - d_{220})$ was used⁹ in which c = conc. of sample in g./l., and d_x = optical density measured at x μ .

In a few cases, a weighed amount of the oxidation product was treated with a slight excess of a saturated solution of 2,4-dinitrophenylhydrazine in acetone-free methanol containing 0.01 ml. of conc'd hydrochloric acid/ml., and the resulting dinitrophenylhydrazone was washed with methanol, dried, and weighed. Results obtained by this method were similar to those obtained by the absorption method and, in the case of the oxidation of *p*-nitrobenzyl alcohol, to results of assays performed by using a melting point curve of synthetic mixtures of alcohol and aldehyde.

DISCUSSION OF RESULTS

The value of the method of oxidation described here would seem to lie in its ability to oxidize allyl and benzyl alcohols at room temperature under neutral and essentially anhydrous conditions, in good yield. Water is, of course, produced by the oxidation, but could undoubtedly be removed by addition of an appropriate desiccant if this were necessary. The oxidation is also controllable with respect to the type of alcoholic function oxidized. The oxidation of benzyl alcohol to the aldehyde in good yield in the presence of 5% of *tert*-butyl alcohol in the ether used as solvent (Table I, line 8) suggests that hydroxyl groups present elsewhere in a molecule would not interfere with the oxidation of susceptible hydroxyl groups by this method.

To determine why the oxidations stopped when unoxidized alcohol still remained, despite the use of a large excess of MnO_2 , artificial mixtures were made up corresponding in all but one product to the results of completed oxidations of benzyl alcohol. Additional benzyl alcohol was added to each in turn, and oxidation was allowed to continue. The results of these oxidations are shown in

⁹ The authors are indebted to Mr. G. Hess who suggested this method and determined the parameters of the equation. For the derivation and limitations of this type of equation, see Morton and Stubbs, *Analyst*, **71**, 348 (1946).

TABLE VII
THE EFFECT OF ADDED REACTION PRODUCTS ON THE YIELD OF BENZALDEHYDE

Run	ROH	RCHO	H ₂ O	Conv. Based On	
				ROH + RCHO	ROH
1	+	-	-	60, 73% (std.)	60, 73% (std.)
2	+	+	+	78, 84	31, 49
3	+	-	+	60	60
4	+	+	-	81	41

+ Means component present at beginning of oxidation.

Table VII. The total aldehyde present, calculated as a fictitious conversion, is given in the next to last column, and the conversion based on added alcohol only is shown in the last column. It can readily be seen that while the total amount of aldehyde present at the end was comparable in all cases, (next to last column), the oxidation of the second portion of benzyl alcohol was low and essentially the same in the cases in which aldehyde was present at the start, whether with or without water. The addition of water and no aldehyde at the start gave much less lowering of the yield (probably about the limit of reproducibility of the yields in successive runs).¹⁰

It therefore seems obvious that the oxidations stop when the amount of carbonyl compound reaches a critical value. We presume that this represents a concentration at which the carbonyl compound can successfully displace the alcohol at some active portion of the MnO₂ surface. Any more precise discussion of the mechanism of these oxidations must be consistent with the fact that the ability of various types of MnO₂ to oxidize alcohols appears to vary: "Ordinary" MnO₂ < MnO₂ A < MnO₂ B, corresponding to the decreasing ease of oxidation: multiply-conjugated carbinols > benzyl and furyl alcohols > vinyl and ethinyl carbinols.

One obvious factor might be that of differences in adsorptive ability. The more saturated the alcohol, the less readily adsorbed it would be. The more saturated alcohol might therefore require an MnO₂ with strong adsorbing ability to adsorb and then oxidize it. The importance of this factor in the specificity of the oxidation of vitamin A alcohol to its aldehyde has been beautifully demonstrated (11). A preferential adsorption on the MnO₂ of the alcohols used here is demonstrated by the "assay" column already presented in Table II. Another example is found in one oxidation of *o*-hydroxybenzyl alcohol in which the solution after removal of solvent assayed 86% salicylaldehyde. Extraction of the residual manganese oxides with dilute aqueous alkali and acidification of the extracts gave a product which appeared by melting point to be nearly pure *o*-hydroxybenzyl alcohol.

That the relative ease of adsorption may not be the only factor governing the specificity of these oxidations is suggested by the fact that the addition of 1%

¹⁰ Other preparative runs with ether containing 1% of water as solvent gave yields comparable to those normally obtained with anhydrous ether.

of water or 5% of *tert*-butyl alcohol, which would be expected from the empirical knowledge of chromatography to change the adsorption characteristics of this system markedly, apparently affected the yields reported here only slightly, if at all. Further, it would be expected that 3-phenyl-1-propanol would be adsorbed moderately readily, and so would perhaps be intermediate in ease of oxidation between benzyl alcohol and a vinyl carbinol such as citral. This is not the case (Table IV, line 6).

The decreasing ease of oxidation by MnO_2 parallels what might be expected to be the order of increasing oxidation potentials (*i.e.* increasing stability of alcohol as compared to aldehyde at equilibrium), since it would be anticipated that the ability of a conjugated carbonyl group to distribute its partial positive charge through the conjugated system would stabilize it relative to its alcohol. Many of the pertinent oxidation potentials have been determined (13), and the aliphatic primary alcohol systems follow the expected order. Benzyl and furfuryl alcohols, however, have higher E° values than would be anticipated from their ease of oxidation by MnO_2 . Further, were the oxidation potential the major factor, it would be expected that aliphatic ketones, which have been shown to have even lower E° values than the allylic alcohols, would be readily oxidized by MnO_2 . That this is not the case is shown (Table IV, lines 9 and 10) by the attempted oxidations of *sec*-butyl alcohol and of capryl alcohol, which gave only minor amounts of ketones. This might of course be considered as due to the greater steric hindrance to the approach of a secondary alcohol function to the oxidant surface, as compared to a primary alcohol.

It seems to the authors that neither of the two obvious theories alone can serve to explain the specificity of these oxidations.

SUMMARY

Manganese dioxide prepared by heating the carbonate or oxalate in air ("MnO₂ A") will oxidize representative benzyl alcohols dissolved in petroleum ether or (preferably) in ethyl ether to the aldehydes in good yield, but will not oxidize allylic alcohols appreciably. Acid-washed "MnO₂ A", preferably suspended in petroleum ether, will also oxidize allylic alcohols to the aldehydes in good yield, while oxidizing saturated alcohols to a negligible extent. The influence of various other factors on the scope of these oxidations, and an application to a "chemical" proof of structure of the C₁₄ aldehyde, are also discussed.

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