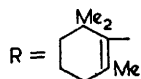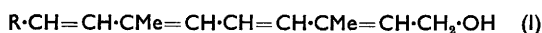# OXIDATIONS BY MANGANESE DIOXIDE IN NEUTRAL MEDIA

By R. M. Evans, B.Sc., Ph.D., D.I.C., F.R.I.C.

(Glaxo Laboratories Ltd., Greenford, Middlesex)

Manganese dioxide occurs in many minerals, the purest forms being pyrolusite, MnO_2, and psilomelane, MnO_2,H_2O. Both these substances have been known from ancient times, and manganese dioxide has been used as a decolorising agent in glass manufacture for the past two millennia. Accounts of its properties are met in early chemical literature and since the beginning of the last century its use as an oxidising agent in chemical reactions has been established. In organic chemistry it has found many applications, being used most frequently in the presence of mineral acids, as in the well-known oxidation of methyl-substituted aromatic compounds to the corresponding aldehydes, though acetic acid and aqueous solutions of alkalis have also been used as reaction media. These well-known reactions, in general applicable only to compounds with stable nuclei, will not be described here; attention will rather be centred on applications of the recent discovery that a suspension of manganese dioxide (prepared by oxidation or pyrolysis of manganese salts) can act as an oxidising agent in neutral non-aqueous media. This heterogeneous system is often effective at room temperature; under these conditions certain groups may be oxidised selectively in compounds that would be destroyed by more vigorous reagents.

This new type of reaction was discovered ten years ago by Ball, Goodwin, and Morton,[1] who found that concentrates of vitamin A (I), when dissolved in light petroleum and shaken with acidified aqueous potassium permanganate, gave products whose ultraviolet absorption was similar to that of retinene (II), the highest yields of aldehyde being associated with

$$R \cdot CH{=}CH \cdot CMe{=}CH \cdot CH{=}CH \cdot CMe{=}CH \cdot CH_2 \cdot OH \quad \text{(I)}$$
$$R \cdot CH{=}CH \cdot CMe{=}CH \cdot \overset{\downarrow}{CH}{=}CH \cdot CMe{=}CH \cdot CHO \quad \text{(II)}$$
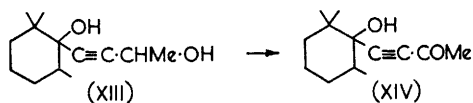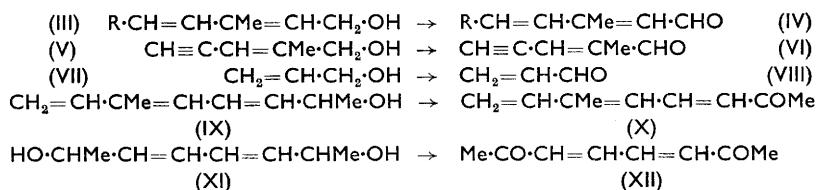
the formation of hydrated manganese dioxide during the reaction. Further experiments proved that hydrated manganese dioxide was the agent responsible for the dehydrogenation and that vitamin A in light petroleum solution was converted efficiently into retinene on being shaken at room temperature with a suspension of precipitated manganese dioxide (prepared by the oxidation of manganese sulphate with potassium permanganate in aqueous solution). Under similar conditions benzyl, cetyl, and *iso*propyl alcohol were unaffected, and other common oxidising agents, including chromic acid, barium dioxide, lead dioxide, and silver oxide, were found useless as substitutes.

[1] Ball, Goodwin, and Morton, *Biochem. J.*, 1948, **42**, 516.

Oxidations at room temperature

αβ-Ethylenic and -Acetylenic Alcohols.—After publication of these discoveries, the possibilities inherent in this type of reaction were rapidly exploited; it proved of particular value for the synthesis of vitamin A and in exploring the chemistry of polyenes and polyenynes. During the next 4—5 years, precipitated manganese dioxide became established as a convenient and efficient reagent for the oxidation of ethylenic and acetylenic αβ-unsaturated primary and secondary alcohols to the corresponding carbonyl compounds, a procedure frequently superior to the alternative Oppenauer reaction.[2] Usually the unsaturated alcohol was shaken at room temperature in a neutral organic solvent, such as light petroleum, chloroform, acetone, or ether, with finely divided precipitated manganese dioxide, or the solution was allowed to percolate through a column packed with the oxidant.[3] The necessary time of reaction varied from 1 hour to 10 days or more, undoubtedly owing to the different methods used to prepare the dioxide, to the effect of different solvents, and to the use of different ratios of oxidant to substrate. The lack of standardisation of these important factors in the early experiments gave rise to divergent views on the utility of the reagent, some of them later found to be erroneous. In this Review the applications will be considered before the influence of these factors and their control.

The reactions illustrated (III—XIV) are representative of the synthesis of polyene and polyenyne carbonyl compounds by the use of hydrated manganese dioxide. In addition to the oxidation[1,3] of vitamin A (I) to retinene (II), similar efficient dehydrogenations of vitamin A_2,[4] 8,9-dihydrovitamin A,[5] and neovitamin A[6] were obtained, and the mild nature of the reaction was illustrated particularly well by Robeson *et al.*[7] in their dehydrogenation

(III) $R \cdot CH = CH \cdot CMe = CH \cdot CH_2 \cdot OH \rightarrow R \cdot CH = CH \cdot CMe = CH \cdot CHO$ (IV)

(V) $CH \equiv C \cdot CH = CMe \cdot CH_2 \cdot OH \rightarrow CH \equiv C \cdot CH = CMe \cdot CHO$ (VI)

(VII) $CH_2 = CH \cdot CH_2 \cdot OH \rightarrow CH_2 = CH \cdot CHO$ (VIII)

$CH_2 = CH \cdot CMe = CH \cdot CH = CH \cdot CHMe \cdot OH \rightarrow CH_2 = CH \cdot CMe = CH \cdot CH = CH \cdot COMe$

(IX)   (X)

$HO \cdot CHMe \cdot CH = CH \cdot CH = CH \cdot CHMe \cdot OH \rightarrow Me \cdot CO \cdot CH = CH \cdot CH = CH \cdot COMe$

(XI)   (XII)

(XIII)   (XIV)

[2] Oppenauer, *Rec. Trav. chim.*, 1937, **56**, 137; Djerassi, "Organic Reactions", John Wiley and Son Inc., New York, 1951, Vol. VI, p. 207.

[3] Wald, *J. Gen. Physiol.*, 1948, **31**, 489.

[4] Farrar, Hamlet, Henbest, and Jones, *J.*, 1952, 2657; Cama, Dalvi, Morton, Salah, Steinberg, and Stubbs, *Biochem. J.*, 1952, **52**, 535.
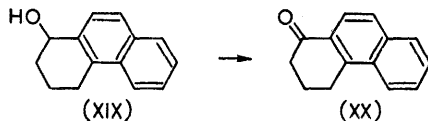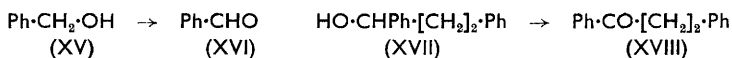
[5] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.

[6] Dalvi and Morton, *Biochem J.*, 1952, **50**, 43.

[7] Robeson, Blum, Dieterle, Cawley, and Baxter, *J. Amer. Chem. Soc.*, 1955, **77**, 4120.

of the four geometrical isomers of vitamin A to the corresponding retinenes without any isomerisation. Wendler, Slates, Trenner, and Tishler[8] likewise succeeded in oxidising the *cis-* and the *trans*-form of the C_{14} alcohol [III; R as for (I)] to the C_{14} aldehyde (IV) without interconversion. The oxidation[9] of the methylpentenynol (V) to the aldehyde (VI) shows that a free acetylenic group is unaffected and, contrary to the observation in the Glaxo Laboratories,[5] does not inhibit the reaction. The dehydrogenation[5] of the simplest ethylenic compound, allyl alcohol (VII), to acraldehyde (VIII) indicates that a single ethylenic bond provides sufficient activation to bring about the reaction; oxidation of the C_9 alcohol (IX) to the ketone[5] (X), and of the dienediol (XI) to the dienedione[10] (XII), illustrate the value of the reaction for the oxidation of $\alpha\beta$-unsaturated secondary alcohols. The final example[11] (XIII→XIV) proves the adequacy of a single $\alpha\beta$-acetylenic bond to activate the hydroxyl group.

Benzylic Alcohols.—Although Morton and his colleagues[1] could not oxidise benzyl alcohol (XV) to benzaldehyde (XVI), more active forms of the dioxide (see below) achieved this in high yield.[12,13]

$$Ph \cdot CH_2 \cdot OH \quad \rightarrow \quad Ph \cdot CHO \qquad HO \cdot CHPh \cdot [CH_2]_2 \cdot Ph \quad \rightarrow \quad Ph \cdot CO \cdot [CH_2]_2 \cdot Ph$$

(XV)　　　　　　(XVI)　　　　　　(XVII)　　　　　　(XVIII)

(XIX)　　　　　(XX)

Good conversions of α-substituted benzyl alcohols such as (XVII) and (XIX) into the ketones (XVIII) and (XX) respectively,[14] together with many other examples in the literature, further illustrate the general applicability of the reaction to this type of compound.[12–15]

Alicyclic $\alpha\beta$-Unsaturated Alcohols.—In 1953 workers at the Syntex Laboratories extended the use of this dehydrogenating system to syntheses in the steroid field, showing that $\alpha\beta$-unsaturated hydroxyl groups in ring A, B, or C were converted efficiently into ketone groups[16,17] and that, in contrast to what happens with the Oppenauer reagents, ketol side chains were in general unaffected. They used the selective action with particular

[8] Wendler, Slates, Trenner, and Tishler, *ibid.*, 1951, **73**, 719.
[9] Ahmad and Weedon, *J.*, 1953, 3286.
[10] Ahmad, Sondheimer, Weedon, and Woods, *J.*, 1952, 4089.
[11] Attenburrow *et al.*, unpublished results.
[12] Harnfeist, Baveley, and Lazier, *J. Org. Chem.*, 1954, **19**, 1608.
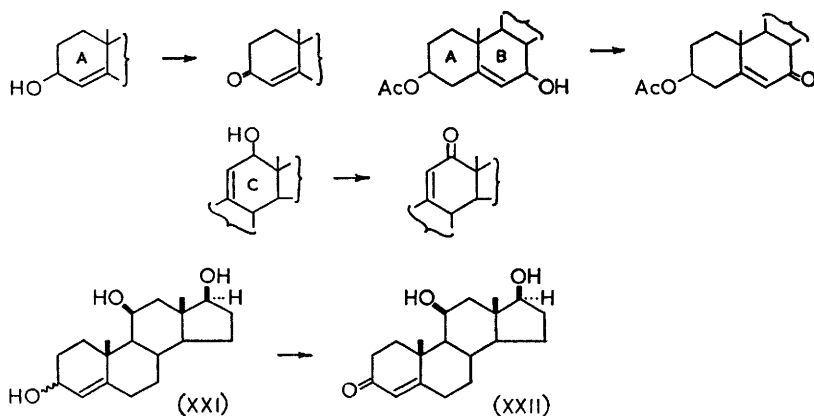[13] Highnet and Wildman, *J. Amer. Chem. Soc.*, 1955, **77**, 4399.
[14] Turner, *ibid.*, 1954, **76**, 5175.
[15] Rappaport and Masamune, *ibid.*, 1955, **77**, 4330.
[16] Mancera, Rosenkranz, and Sondheimer, *J.*, 1953, 2189.
[17] Sondheimer, Amendolla, and Rosenkranz, *J. Amer. Chem. Soc.*, 1953, **75**, 5930.

advantage to prepare 11β-hydroxytestosterone (XXII) in good yield from androst-4-ene-3ξ,11β,17β-triol (XXI).[16]

Saturated Alcohols.—The earliest experiments indicated that active manganese dioxide at room temperature had no effect on primary and secondary saturated alcohols,[1] but Harnfeist and his co-workers[12] have shown that this is not strictly true, although the rate of oxidation is small compared with that of αβ-unsaturated alcohols.

From the foregoing examples it appears that only the αβ-unsaturated hydroxyl groups in polyhydroxy-compounds are oxidised to an appreciable extent, but an exception is the oxidation of both hydroxyl groups in (XXIII) to give the keto-aldehyde (XXIV) as the major product,[18] and Dr. L. Crombie[19] has found that a cyclopropane ring will also activate an α-hydroxyl group and cause it to undergo oxidation by manganese dioxide.
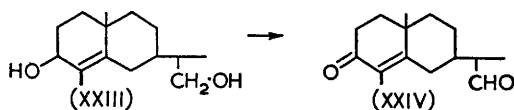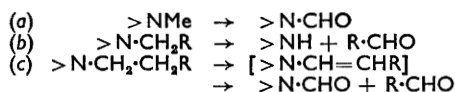

It may therefore be concluded that, in non-aqueous inert organic media at room temperature, hydrated (or "active") manganese dioxide efficiently oxidises αβ-unsaturated primary and secondary alcohols to the corresponding carbonyl compounds whether the unsaturation is part of an olefinic, acetylenic, aromatic, or alicyclic system, whereas tertiary and saturated hydroxyl groups are generally little affected. The exceptions have not so far proved numerous, and the reagent has been used with success on several occasions to detect the presence of αβ-unsaturated

[18] Bruderer, Arigoni, and Jeger, *Helv. Chem. Acta*, 1956, **39**, 858.
[19] Dr. L. Crombie, personal communication.

primary and secondary hydroxyl groupings, the resulting conjugated carbonyl compounds being readily detected by their ultraviolet spectra or as derivatives.[12,13,20]

N-*Alkyl- and* NN-*Dialkyl-anilines.*—A further interesting type of dehydrogenation by hydrated manganese dioxide was provided recently by Henbest and Thomas[21] in the ready oxidation of N-alkyl and NN-dialkyl-anilines. Three types of reaction were discerned:

$$
\begin{aligned}
&(a) && >\text{NMe} && \rightarrow && >\text{N·CHO} \\
&(b) && >\text{N·CH}_2\text{R} && \rightarrow && >\text{NH} + \text{R·CHO} \\
&(c) && >\text{N·CH}_2\text{·CH}_2\text{R} && \rightarrow && [>\text{N·CH}=\text{CHR}] \\
& && && \rightarrow && >\text{N·CHO} + \text{R·CHO}
\end{aligned}
$$
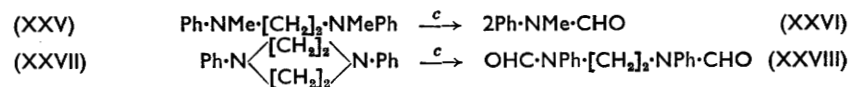
With several amines the reaction took essentially a single course, NN-dimethylaniline gave N-methylformanilide in 80% yield, and N-methyl-aniline was oxidised even more efficiently to formanilide according to route (a). The oxidation of NN-dimethylaniline was facilitated by the introduction of a *p*-methyl group but a *p*-nitro-substituent completely inhibited the reaction.

The oxidation of diethylaniline proved more complex. The predominant initial reaction was by route (b) to give acetaldehyde (54%), the monoethyl-aniline thus formed then probably undergoing further oxidation by route (c) to formanilide which was isolated in 65% yield. Small quantities of N-ethylformanilide and azobenzene were also detected. As would be expected, N-ethyl-N-methylaniline gave N-ethylformanilide and formanil-ide as follows:

$$\text{Ph·NEt·CHO} \xleftarrow{a} \text{Ph·NMeEt} \xrightarrow{b} [\text{Ph·NHMe}] \xrightarrow{c} \text{Ph·NH·CHO}$$
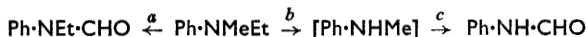
The expectation that reaction (c) would be promoted by a second amino-group in the β-position was confirmed by the efficient conversion of (XXV) and (XXVII) into (XXVI) and (XXVIII) respectively.

(XXV) $\text{Ph·NMe·[CH}_2]_2\text{·NMePh} \xrightarrow{c} 2\text{Ph·NMe·CHO}$ (XXVI)

(XXVII) $\text{Ph·N}\underset{[\text{CH}_2]_2}{\overset{[\text{CH}_2]_2}{<}}\text{N·Ph} \xrightarrow{c} \text{OHC·NPh·[CH}_2]_2\text{·NPh·CHO}$ (XXVIII)

Miscellaneous Reactions.—In addition to the types of reaction mentioned above, all exemplified by a group of related compounds, the following illustrate more limited applications of the reagent. Like the related alcohols, primary and secondary benzylamines are oxidised by hydrated manganese dioxide, but the Schiff's bases were only obtained in small yield and the reaction was slow.[13] A tetrahydroquinazoline (XXIX) has been converted

[20] Braude and Forbes, *J.*, 1951, 1756; Cross, Grove, MacMillan, and Mulholland, *Proc. Chem. Soc*, 1958, 221.
[21] Henbest and Thomas, *J.*, 1957, 3032.

into the dihydro-derivative (XXX);[22] and oxidation[13] of the hemiacetal (XXXI) to the lactone (XXXII) is also of interest in indicating a further type of application.

(XXIX)

(XXX)

(XXXI)

(XXXII)

(XXXIII) $(CH_2=CH \cdot CH_2)_2S$ → $(CH_2=CH \cdot CH_2)_2SO$ (XXXIV)
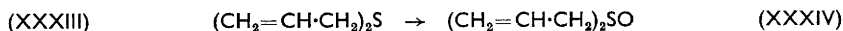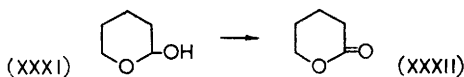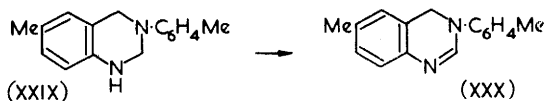
Most of the reactions described so far may be classed as dehydrogenations, but this is not so in the oxidation of diallyl sulphide (XXXIII) to the sulphoxide (XXXIV).[23] No oxidising agent other than hydrated manganese dioxide yields any of the desired product, and the mild nature of the system is also well illustrated in the successful preparation of a number of β-amino-aldehydes from β-amino-alcohols.[24]

Oxidations at higher temperatures

At temperatures between 70° and 120°, the range of reactions brought about by manganese dioxide increases, but the selectivity and the yields of polyene-carbonyl compounds are less. In refluxing benzene, there is much more dehydrogenation of $\alpha\beta$-unsaturated oxo-steroids and $\beta\gamma$-unsaturated hydroxy-steroids, such as (XXXV and XXXVI), to the dienone (XXXVII).[25]

(XXXV)   (XXXVII)   (XXXVI)
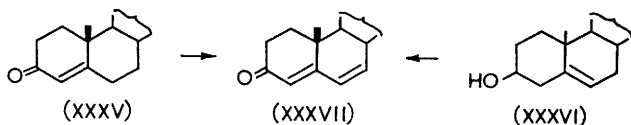
Oxidations involving fission of a C–C bond may also be brought about: α-ketols and vicinal glycols yield the corresponding ketones and aldehydes, as exemplified by the cleavage, in boiling chloroform, of the steroid dihydroxyacetonyl side-chain to yield a 17-oxo-steroid, and of 9,10-dihydroxystearic acid to pelargonic and azelaic aldehydes.[26] Under the same conditions mandelic and benzilic acid give benzaldehyde and benzophenone respectively.[26]

[22] Fales, *J. Amer. Chem. Soc.*, 1955, **77**, 5118.
[23] Edwards and Stenlake, *J.*, 1954, 3272.
[24] Birkofer and Erlenbach, *Chem. Ber.*, 1958, **91**, 2383.
[25] Sondheimer, Amendolla, and Rosenkranz, *J. Amer. Chem. Soc.*, 1953, **75**, 5932
[26] Padilla and Herran, *Bol. Inst. Quim. Univ. nac. auton., Mexico*, 1956, **8**, 1096.

An extensive study of other reactions at higher temperatures has been made by Barakat, Abdel-Wahab, and El-Sadr,[27] who described some fifty different oxidations by manganese dioxide, many of them in aqueous media. Several saturated primary and secondary alcohols were oxidised to carbonyl compounds, aromatic aldehydes gave the carboxylic acids,
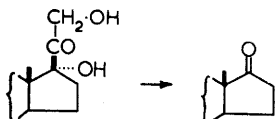
and α-hydroxy-acids and α-amino-acids readily formed the aldehydes or ketones with one carbon atom less. Aromatic primary amines gave azo-compounds, and hydrazones yielded the symmetrical diarylketazines. The efficient oxidation of triphenylphosphine to the oxide was a further application of the reagent.

Reagent and conditions

Preparation of Active Manganese Dioxide.—Despite its selective action and the efficiency of many of the reactions described, the use of manganese dioxide has as yet been somewhat restricted, possibly because difficulty has been encountered in obtaining suitable active material and in predicting the optimum reaction conditions. Unfortunately hydrated manganese dioxide is difficult to define,[28] and material of consistent activity is obtained only when the method of preparation has been carefully controlled.

The manganese dioxide used in the reactions described above was sometimes of commercial origin, in other cases specially prepared. Probably it is for this reason that differences of opinion have arisen over the suitability of the reagent for various oxidations; thus Morton and his colleagues[1] and Turner[14] found benzyl alcohol unaffected, whereas Harnfeist and his co-workers[12] and Highnet and Williams[13] obtained an efficient conversion into benzaldehyde. Similarly, manganese dioxide prepared by the pyrolysis of the carbonate or oxalate failed to oxidise allyl alcohols, whereas good yields of aldehydes were obtained if the dioxide had been first washed with dilute aqueous nitric acid and then dried.

Pyrolusite shows low and erratic activity in the types of reaction considered, and batches of commercial hydrated manganese dioxide vary widely in their efficiency in neutral media; however, suitable material may be selected by checking against a "standard" substrate such as cinnamyl alcohol.[29] But the most reliable and highly active material is obtained by

[27] Barakat, Abdel-Wahab, and El-Sadr, *J.*, 1956, 4685.
[28] Sidgwick, "Chemical Elements and their Compounds", Clarendon Press, Oxford, 1950, p. 1272; Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1950, p. 371.
[29] Weedon and Woods, *J.*, 1951, 2687.

one of the following methods: (a) Manganese sulphate and potassium permanganate are treated in hot aqueous solution in the presence of sufficient alkali to ensure that the reaction mixture remains alkaline; after being washed with water, the slurry is dried at 100–120° [5] (b) As above, omitting the addition of alkali, the aqueous solution becoming strongly acidic.[16] (c) By heating manganese oxalate or carbonate at 250°, the product may be used directly or washed with dilute aqueous nitric acid and dried at 230° to produce a more active oxidant.[12]

The products obtained by these three methods all show high activity but differ in their relative merits for some types of oxidation; however, insufficient comparisons have been made to permit other than broad generalisations.

In our experience the product prepared by method (a) has been consistently effective in dehydrogenating $\alpha\beta$-unsaturated alcohols and in cleaving α-ketols. The hydrated dioxide prepared by method (b) proved, on the other hand, the most efficient for preparation of the steroid dienones[25] and also had the virtue of not attacking the side chain of a 17α-hydroxy-20-oxo-steroid at room temperature.[17] The dioxide prepared by method (c) seems to have been the least widely used, but the more active form is most effective in oxidising allyl and benzyl alcohols.[12] Relative efficiency of reaction is, however, not the only change brought about by varying the method of preparing the dioxide. Thus, Henbest, Jones, and Owen[30] showed that, whereas the hydrated dioxide from preparation (a) converted vitamin A quantitatively into retinene (XXXVIII; R = H), one commercial product gave 16% of 3-hydroxyretinene (XXXVIII; R = OH) and another, which had been precipitated under acidic conditions, gave a considerable proportion of 3-oxoretinene (XXXVIII; R = O). The last reaction is also of interest in being the first example of the oxidation of an allylic methylene group by an insoluble reagent at room temperature to give an unsaturated ketone and may perhaps be considered analogous to the oxidation of N-methylaniline to formanilide.

(XXXVIII)
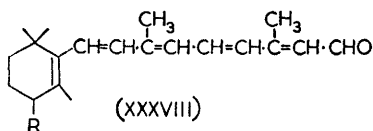
Reaction Media.—The most widely used media for the oxidations at room temperature have been saturated hydrocarbons, chlorinated hydrocarbons, benzene, lower alkyl ethers, ethyl acetate, and acetone. Solvents that compete with the substrate for adsorption on the dioxide surface are obviously unsatisfactory, and in our laboratory it has been found that primary and secondary saturated alcohols fall into this category, causing rapid and permanent deactivation of the dioxide. Acetone and

[30] Henbest, Jones, and Owen, *J.*, 1957, 4909.

ethyl acetate also bring about deactivation but much more slowly, and, in contrast to what happens with alcohols, the activity is restored by drying the dioxide in a high vacuum. A similar range of solvents has been used for reactions at higher temperatures, where water and pyridine have also proved satisfactory. As in the selection of the dioxide, an empirical approach is necessary in choosing the medium. Although many reactions proceed well in a variety of solvents, dependence of the yield on the solvent has been noted,[12,13] and Morton and his co-workers[1] showed that, whereas vitamin A in light petroleum solution was converted into retinene, the use of diethyl ether resulted in formation of anhydrovitamin A.

Reaction Time.—In many of the early experiments in which dioxide of low activity was used, several days were often required for complete reaction, but with the more active products prepared by methods (*a*), (*b*), or (*c*) reaction may be much more rapid. Dehydrogenation of $\alpha\beta$-unsaturated alcohols is usually complete in a few hours at room temperature,[5] but formation of steroid dienones and oxidation of alkylanilines may require 16—24 hours.[21] The time required to complete reactions at higher temperatures varies considerably; whereas at 80° a 50% yield of acetaldehyde is obtained from ethanol in 20 minutes[27] reactions involving the fission of a C–C bond often require 12—20 hours at 80—100°.[26,27]

Ratio of Oxidant to Substrate.—As the reaction is heterogeneous and takes place on the surface of the dioxide,[1] the amount required for efficient reaction depends to some extent on the particle size. A considerable excess is always necessary and ratios of dioxide to substrate ranging from 5:1 to 20:1 by weight are common in the oxidation of hydroxylic compounds; a ratio of 50:1 was used to oxidise the dialkylanilines efficiently.

Reaction mechanism

The mechanism of these reactions has not yet been elucidated, but a number of relevant observations have been made. Ball *et al.*[1] postulated that the reaction was triphasic, adsorption of the substrate being followed by oxidation and subsequent desorption of the product. On this basis the more saturated compounds would be expected to be the less readily adsorbed. This has been borne out by Harnfeist and his co-workers,[12] who observed that the order of ease of oxidation of alcohols was conjugated polyene>benzyl or furyl>vinyl or ethynyl. However, the same authors also pointed out that the addition of 5% of t-butyl alcohol or 1% of water, which would have been expected to alter appreciably the adsorption characteristics of the alcohol, did not affect the yields appreciably, nor could any relation be discerned between the ease of oxidation and the oxidation potentials of the alcohols.[12] The more readily oxidised compounds are, however, those that would be expected to form the more stable carbonium ion, which may perhaps play an important part in the reaction mechanism.

An equilibrium appears to exist on the dioxide surface between the

3

substrate and the product;[11] consequently the reactions never appear to go to completion and large increases in the amount of dioxide decrease the yield.[1]

Henbest and Thomas[21] have observed that only a small proportion of the oxygen in hydrated manganese dioxide is available for the oxidation of organic compounds and have suggested that its unusual properties may be due to the "water" being present as hydroxyl groups linked to the manganese. The hydroxyl groups in the dioxide then lead to the formation of hydroxylated amine intermediates in the dehydrogenation of the alkylanilines.

The critical effect of moisture content has been noted in unpublished work from our laboratories where it has been found that the degree of hydration had an important effect on the activity of the dioxide prepared by method (a). This is a difficult property to measure, since some of the water is so firmly bound that loss of oxygen occurs before dehydration is complete. Heating at 120° under a vacuum, however, gave a product of constant weight, and by using this as a base line it was found that an excess moisture content of ca. 4—8% (0·25 equiv.) led to the highest activity.

In the same studies it was found that available oxygen of the hydrated manganese dioxide (determined by the Bunsen method[31]) declined after an oxidation by the theoretical amount required for the reaction; the possibility of "active" oxygen adsorbed on to the dioxide surface being responsible for the oxidations was excluded, and it appeared that a portion of the manganese was reduced to a lower valency state during the reaction.

X-Ray powder photography and electron-microscopy with a 10,000-fold magnification failed to distinguish between "active" and "inactive" dioxide, but clearly indicated its amorphous structure.* It is clear that more work is necessary to elucidate the mechanism of these reactions. They do afford, however, an elegant method for carrying out a number of oxidations under extremely mild conditions in anhydrous media; although the most appropriate conditions must be determined empirically, the selectivity and efficiency of the reactions often justify the necessary exploration.

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* These determinations were kindly carried out by Mr. H. P. Rooksby and Mr. B. S. Cooper at the Research Laboratories of the General Electric Co., Ltd., Wembley.

[31] Treadwell and Hall, "Analytical Chemistry", Wiley and Sons, New York, 1942, Vol. II, p. 598.