473. *Oxidation by Manganese Dioxide of Some Unsaturated Alcohols.*

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Oxidation of 1-phenylbut-2-yn-1-ol, the *cis*- and the *trans*-form of the corresponding ethylenic analogue, and 4-*cyclo*hex-1′-enylbut-3-en-2-ol to their respective ketones by manganese dioxide is described. The procedure is also utilised for the conversion of quinol into benzoquinone.

THE ability of manganese dioxide to oxidise primary and secondary alcohols to the corresponding carbonyl compounds was first shown by conversion [1] of vitamin A_1 alcohol into vitamin A_1 aldehyde (retinene$_1$). It is particularly valuable for the oxidation of "activated" alcohols, though activation of the allylic or benzylic type is not a prerequisite, since even saturated alcohols (*e.g.*,, butan-2-ol and octan-1-ol) undergo oxidation,[2] albeit with difficulty and in poor yields.

Some unsaturated alcohols, made available by other work, have been subjected to the reaction but without efforts to obtain optimum yields.

1-Phenylbut-2-yn-1-ol [3] in acetone readily gave an 80% yield of phenyl propynyl ketone, the structure of which was confirmed by catalytic hydrogenation to butyrophenone; it is noteworthy in this connection that Oppenauer oxidation fails with αβ-acetylenylcarbinols.[4] The *cis*- and the *trans*-form of 1-phenylbut-2-en-1-ol in acetone similarly yielded phenyl propenyl ketone in *ca.* 70% yields. An attempt to establish the stereochemical course of the oxidation by characterisation as solid derivatives was frustrated by the isolation of a semicarbazinosemicarbazone, in place of the expected semicarbazone, on treatment of the ketone derived from the *cis*-alcohol with semicarbazide under the usual conditions. However, in view of the earlier work,[5] it appears that geometrical configuration is preserved if stereomutation is precluded during the isolation.

4-*cyclo*Hex-1′-enylbut-3-en-2-ol in light petroleum gave the corresponding diene-ketone, isolated as its 2 : 4-dinitrophenylhydrazone, and quinol in acetone gave a 54% yield of *p*-benzoquinone.

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

[2] Harfenist, Bavley, and Lazier, *J. Org. Chem.*, 1954, **19**, 1608.

[3] Braude and Coles, *J.*, 1951, 2078.

[4] Heilbron, Jones, Lewis, Richardson, and Weedon, *J.*, 1949, 742.

[5] Dalvi and Morton, *Biochem. J.*, 1951, **50**, 43; Curtin, Johnson, and Steiner, *J. Amer. Chem. Soc.*, 1955, **77**, 4566.

EXPERIMENTAL

Ultraviolet absorptions refer to EtOH solutions unless otherwise stated. Distillations were carried out in nitrogen. Acetone was purified by distillation over potassium permanganate and dried (K_2CO_3). Manganese dioxide was selected from commercial sources, according to the procedure of Weedon and Woods,[6] and dried over P_2O_5 in a vacuum-desiccator.

Phenyl Propynyl Ketone.—A solution of 1-phenylbut-2-yn-1-ol [3] (3·0 g.) in acetone (120 c.c.) was shaken at 20° for 6 hr. with manganese dioxide (30 g.), then filtered, and the residue washed well with acetone. Evaporation of the combined filtrates *in vacuo* gave the crude ketone (2·99 g.), n_D^{18} 1·5618, whose absorption indicated a purity of *ca.* 90%. Distillation gave *phenyl propynyl ketone* (2·47 g.), b. p. 79—80°/0·7 mm., n_D^{20} 1·5638 (Found : C, 83·45; H, 5·9. $C_{10}H_8O$ requires C, 83·3; H, 5·6%). Light absorption : max. 2580 Å (ε 14,000); infl. 2630 Å (ε 13,500). The 2 : 4-*dinitrophenylhydrazone* (from 0·2 g. of ketone) crystallised from chloroform in orange prisms (0·1 g.), m. p. 232—233° (Found : N, 16·75. $C_{16}H_{12}O_4N_4$ requires N, 17·3%). Light absorption in $CHCl_3$: main max. 3940 Å (ε 31,000). The *semicarbazone* crystallised from aqueous ethanol in needles, m. p. 185—186° (decomp.) (Found : N, 21·2. $C_{11}H_{11}ON_3$ requires N, 20·9%). Light absorption : max. 2260 and 2980 Å (ε = 21,000, 20,000).

The ketone (1·04 g.) was shaken in ethyl acetate (30 c.c.) under hydrogen with 10% palladium chloride–calcium carbonate catalyst (0·1 g.) (H_2 absorbed, 340 c.c. at 14°/762·7 mm.; 2 molar proportions). Removal of the catalyst and solvent, followed by distillation, gave butyrophenone (0·82 g.), b. p. 90—100° (bath)/0·7 mm., n_D^{19} 1·5190. The 2 : 4-*dinitrophenylhydrazone* (from 0·2 g. of ketone) crystallised from ethyl acetate in prisms (0·2 g.), m. p. and mixed m. p. 192—193° (Evans [7] gives m. p. 190°).

cis-1-*Phenylbut*-2-*en*-1-*ol*.—The alcohol was prepared in 73% yield by the partial hydrogenation of the acetylenic analogue as described by Braude and Coles [3] (except that a 10% palladium chloride–calcium carbonate catalyst was used), and had b. p. 79—80°/0·7 mm., n_D^{22} 1·5371.

Phenyl Propenyl Ketone.—(*a*) A solution of the preceding *cis*-alcohol (3·5 g.) in acetone (150 c.c.), shaken at 20° for 6 hr. with manganese dioxide (35 g.), yielded phenyl propenyl ketone (2·61 g.), b. p. 56—57°/0·2 mm., n_D^{20} 1·5471 (Found: C, 82·4; H, 7·55. Calc. for $C_{10}H_{10}O$: C, 82·15; H, 6·9%). The semicarbazinosemicarbazone crystallised from water in prisms, m. p. 191—192° (Found: N, 29·6. Calc. for $C_{12}H_{18}O_2N_6$: N, 30·2%) (von Auwers [8] gives m. p. 195—197°). Light absorption : max. 2690 Å (ε 13,000); infl. 2780 Å (ε 11,000).

(*b*) *trans*-1-Phenylbut-2-en-1-ol [9] (3·5 g.) similarly gave phenyl *trans*-propenyl ketone (2·4 g.), b. p. 71—72°/0·6 mm., n_D^{23} 1·5591 (Found: C, 81·5; H, 7·25%) (Dufraisse and Demontvignier [10] give b. p. 111—112°/9 mm., n_D^{18} 1·5626).

4-cyclo*Hex*-1′-*enylbut*-3-*en*-2-*one*.—4-*cyclo*Hex-1′-enylbut-3-en-2-ol [11] (0·5 g.) in light petroleum (b. p. 40—60°; 50 c.c.) was shaken at 20° for 3 hr. with manganese dioxide (5 g.). Isolation as usual gave the crude ketone (0·4 g.), n_D^{30} 1·5370, whose 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in dark red prisms (0·32 g.), m. p. and mixed m. p. 199° (Heilbron *et al.*[12] give m. p. 196°).

p-*Benzoquinone*.—Quinol (5 g.) in acetone (200 c.c.) was shaken for 30 min. at 20° together with manganese dioxide (50 g.). Isolation as usual gave a dark solid, which was extracted with benzene. The resulting reddish-yellow solution was dried ($CaCl_2$), filtered, and treated with charcoal (1 g.). The golden-yellow filtrate was concentrated *in vacuo* and chilled at 0°, whereby benzoquinone (2·7 g.; 54%; m. p. and mixed m. p. 112—114°) was obtained.

The author thanks Dr. B. C. L. Weedon for his interest. Analyses and light absorption measurements were carried out in the microanalytical (Mr. F. H. Oliver) and spectrographic (Mrs. A. I. Boston) laboratories of this Department.

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[*Received, November* 28*th*, 1955.]

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[6] Weedon and Woods, *J.*, 1951, 2687.
[7] Evans, *J.*, 1936, 785.
[8] von Auwers, *Ber.*, 1921, **54**, 987.
[9] Braude, Jones, and Stern, *J.*, 1946, 396.
[10] Dufraisse and Demontvignier, *Bull. Soc. chim. France*, 1927, **41**, 843.
[11] Chanley and Sobotka, *J. Amer. Chem. Soc.*, 1949, **71**, 4140.
[12] Heilbron, Jones, Richardson, and Sondheimer, *J.*, 1949, 737.