475. *Hydroxylations with Potassium Manganate.*

By W. RIGBY.

cis-Hydroxylation of double bonds can be brought about by potassium manganate. Though the procedure has some advantages over that involving permanganate, the reagent is sometimes capable of oxidising the glycol produced. The reaction is not simple and is catalysed by manganese dioxide.

THE reagent formerly most used for hydroxylation of ethylenic bonds was potassium permanganate in dilute solution, *cis*-hydroxylation occurring. The yields were rarely good, often very poor, and the reagent has to a large extent been superseded by the more efficient osmium tetroxide. A plausible supposition would be that permanganate is reduced first by one valency unit and then by two, and that only the second stage is effective in the hydroxylation—the first merely producing unwanted products, or even destroying the desired product. Two successive stages can be isolated experimentally: many instances are known where the first is rapid in alkaline solution, and the second slow, *e.g.*, reduction with citrate or formate. Using a large excess of permanganate in strongly alkaline solution, Stamm [1] was able to use the first stage for the analytical determination of some organic substances by destructive oxidation. Alternatively, when oxidations are carried out with permanganate in alkaline solution in the presence of barium ions manganate is removed from the system as sparingly soluble barium manganate (solubility product $2{\cdot}46 \times 10^{-10}$;

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[1] Stamm, *Angew. Chem.*, 1934, **47**, 791.

Schlesinger and Siems [2]). This principle has been applied by Stamm [1] to the analytical determination of formate. The second supposed stage of the permanganate reaction, reduction of manganate to manganese dioxide, can be investigated directly.

Potassium manganate has been little used in organic chemistry: for example, Tcherniac [3] used it for oxidation of naphthalene to phthalonic acid, the yield being one-third greater than when permanganate was used; and Tursin and Rusakova [4] oxidised di*iso*propylidene-L-sorbose, the outcome being similar to that with permanganate.

Potassium manganate is very easily prepared by heating potassium permanganate with aqueous potassium hydroxide and is quite stable. Since it is most conveniently used in alkaline aqueous solution, alkali salts of unsaturated acids have been mainly used in this investigation of the hydroxylation reaction. The expected *cis*-hydroxylation took place with cinnamic, crotonic, oleic, and *bicyclo*[2 : 2 : 1]hept-5-ene-2 : 3-dicarboxylic acid; the yields were moderate (*threo*-β-phenylglyceric acid 40%, *threo*-αβ-dihydroxybutyric acid *ca.* 25%, *erythro*-9 : 10-dihydroxystearic acid 32%, 5 : 6-dihydroxy*bicyclo*[2 : 2 : 1]heptane-2 : 3-dicarboxylic acid 50%). No 9 : 10-dihydroxyundecanoic acid was isolated from the reaction between undecenoic acid and potassium manganate: some sebacic acid was produced. An emulsion of *cyclo*hexene in aqueous alkali was rapidly oxidised by potassium manganate but the yield of *cyclo*hexane-*cis*-1 : 2-diol was very small; this diol is itself rapidly oxidised by potassium manganate under the same conditions.

The yield of glycols from manganate oxidation of olefins is no doubt influenced strongly by the experimental conditions : Tcherniac [3] found that the oxidation of naphthalene by manganate is slow and the yield poor if the solution is not dilute enough, but rapid and giving a good yield when dilute solutions are used. The hydroxylation is usually slow to start, but when some manganese dioxide has been formed it goes rapidly. Potassium manganate can therefore act as a hydroxylating reagent, but the experiments do not prove that manganate is the active agent in hydroxylations with permanganate; and while it is possible to formulate the hydroxylation with the manganate ion performing a function analogous to that of the osmium tetroxide molecule, the marked catalytic effect of manganese dioxide indicates that the reaction course is not so simple. A surface reaction could account for the *cis*-hydroxylation.

EXPERIMENTAL

Potassium Manganate.—A solution of potassium hydroxide (85%) (1 kg.) in water (500 ml.) was heated at 120—140° and crystalline potassium permanganate (700 g.) was added in 40—50 g. portions, the effervescence being allowed to subside between additions. Heating was continued throughout the reaction, and the suspension of crystalline potassium manganate was stirred with a steel spatula, water being added occasionally to compensate for evaporation; this required $\not>$1 hr. The cooled product was filtered through a sintered-glass filter, and the solid was drained well by drawing through it a stream of carbon dioxide-free air by way of an inverted funnel luted to the filter; a mechanical pump was desirable for efficient draining. The product was an almost dry mass of fine purple crystals, very similar to potassium permanganate in the same state of subdivision; it contained *ca.* 88% of K_2MnO_4. The yield was *ca.* 1000 g. It was quite stable under ordinary conditions, even in a frequently opened bottle. By centrifugation at 2000 r.p.m. for 10 min. the purity was raised to over 96%, but the 88% material was used for all the oxidations described and is more stable to air.

Analysis.—The sample (0·12 g.) was added with rotation to 0·1N-oxalic acid (25 ml.) and dilute sulphuric acid. When the manganese dioxide had dissolved, the excess of oxalic acid was titrated with potassium permanganate.

Although the solid is stable, solutions, even moderately alkaline ones, are not : disproportionation into manganese dioxide and potassium permanganate takes place. A solution which contained initially 14·1% of K_2MnO_4 and which was 1·5N with respect to potassium hydroxide contained 9·4% after 28 days and 7·6% after a further 66 days.

Oxidations.—The oxidations were conducted at about 0°, the bath-temperature being only a

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[2] Schlesinger and Siems, *J. Amer. Chem. Soc.*, 1924, **46**, 1965.

[3] Tcherniac, G.P. 86,914; cf. *J.*, 1916, **109**, 1236.

[4] Tursin and Rusakova, *Zhur. priklad. Khim.*, 1945, **18**, 564; *Chem. Abs.*, 1946, **40**, 5704.

few degrees lower, otherwise crusts of potassium salts tended to form. To start the reaction it was in some cases necessary to stir the solution with a small amount (0·5 g.) of the manganate at room temperature until it was reduced, before cooling to 0°. A stirrer capable of dealing with a thin sludge was necessary. The oxidations were usually carried out at the highest concentration practicable, although it is probable [3] that these are not the best conditions.

threo-β-*Phenylglyceric Acid.*—Cinnamic acid (29·6 g.) was dissolved in water (250 ml.) with potassium hydroxide (85%; 14 g.), and a solution of potassium hydroxide (14 g.) in water (80 ml.) was then added. Potassium manganate (0·2 mole) was added in portions, with stirring at 0° to $-3°$, during 1 hr. and the mixture was stirred at 0° for a further ¼ hr. Sulphur dioxide (30 g.) was added, the stirred suspension was acidified by dropwise addition of a mixture of sulphuric acid (70 g.) and water (40 ml.) and was then heated to boiling. The cooled solution, after filtration, was extracted continuously with ether for 12 hr. and the ether was evaporated. The residue, which contained a little oxalic acid, was washed with benzene and crystallised from 2N-hydrochloric acid and then from water. The yield was 14—15 g., and the m. p. 141—142°; individual crystals melted at 166° (cf. ref. 5) (Found: equiv., 184. Calc. for $C_9H_{10}O_4$: equiv., 182).

threo-αβ-*Dihydroxybutyric Acid.*—Crotonic acid (25·8 g.), potassium manganate (0·3 mole), potassium hydroxide (42 g.), and water (300 ml.) were used: the mixture consistently set suddenly to a gel 50—55 min. after the start of the oxidation, so that it was important to have added all the manganate before then. After removal of the manganese dioxide, oxalic acid was removed by addition of barium chloride (14 g.) to the neutralised solution, and salts were removed by extraction of the acidified, evaporated liquor with alcohol. The *threo*-dihydroxybutyric acid, m. p. 73—74°, was extracted with acetone and crystallised from propyl acetate. Isolation of the acid through its potassium hydrogen salt [6] was not found satisfactory; acid salts of variable composition and m. p. tended to be formed.

erythro-9 : 10-*Dihydroxystearic Acid.*—Oleic acid (28 g.), potassium manganate (0·15 mole), potassium hydroxide (14 g.), and water (400 ml.) were allowed to react for 2 hr. Addition of sulphur dioxide (15 g.) and acidification yielded *erythro*-9 : 10-dihydroxystearic acid, m. p. 130—131° (from ethyl acetate–alcohol) (9—10 g.).

5 : 6-*Dihydroxy*bicyclo[2 : 2 : 1]*heptane*-2 : 3-*dicarboxylic Acid.*—Potassium manganate (0·11 mole) was added with stirring during ½ hr. at $-3°$ to a solution of *cyclo*pentadiene–maleic acid adduct (18·2 g.) in water (150 ml.) containing potassium hydroxide (15 g.). Sulphur dioxide (15 g.) and 1 : 1 (w/w) sulphuric acid–water (50 g.) were added; the mixture was heated, cooled, and filtered and the filtrate was extracted continuously for 50 hr. with ether. The ether was removed and the residue was recrystallised from 96% alcohol, to give 5 : 6-*dihydroxy*bicyclo[2 : 2 : 1]*heptane*-2 : 3-*dicarboxylic acid* (10 g.), needles, m. p. depending on the conditions of heating; when introduced into the bath at 150—180° the substance loses vapour and melts at *ca.* 185° (decomp.); if the substance is introduced at 185° the m. p. is above 190° (Found, in material dried at 140—170°: C, 50·1; H, 5·8. $C_9H_{12}O_6$ requires C, 50·0; H, 5·6. Found, in material dried at 30°: C, 48·1; H, 5·9%; equiv., 118. $C_9H_{12}O_6,\frac{1}{2}H_2O$ requires C, 48·0; H, 5·8%; equiv., 112·5). The dimethyl ester (prepared by diazomethane) did not crystallise.

A solution of *cyclo*pentadiene–maleic acid adduct (1·82 g.) in water (25 ml.) was left overnight with 1% osmium tetroxide solution (1 ml.) and 30% hydrogen peroxide (0·5 ml.) and then evaporated. The residual solid, after recrystallisation from 95% alcohol, had the same m. p. and mixed m. p. as that prepared by the manganate oxidation.

CHEMISTRY DEPARTMENT, BIRKBECK COLLEGE, LONDON, W.C.1. [*Received, January 26th,* 1956.]

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[5] Furberg and Hassel, *Acta Chem. Scand.*, 1950, **4**, 1020.
[6] Braun, *J. Amer. Chem. Soc.*, 1929, **51**, 228.