42. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part XII.* The Oxidation of 2,3-Dimethylbutane and Some Other Hydrocarbons by Chromium*(VI) *Oxide.*†

By G. FOSTER and W. J. HICKINBOTTOM.

2,3-Dimethylbutane with chromium(VI) oxide in acetic anhydride gives acetone, 3-methylbutan-2-one, and 2,3-dimethylbutanoic and 2,3-dimethylbutenoic acid. The latter acid is not derived from the former directly by oxidation. Methylcyclohexane afforded cyclohexanone, 2-methylcyclohexanone, 1-methylcyclohexanol, 6-oxoheptanoic and adipic acid and unidentified ketones. 3,3-Dimethylbutan-2-one is produced from 2,2-dimethylbutane. Neopentane and hexamethylethane are almost unaffected. 2,3-Dimethyl-2,3-diphenylbutane is oxidised very slowly to acetophenone.

IT was shown earlier [1] that oxidation of 2,2,4-trimethylpentane and of 2,2,4,6,6-pentamethylheptane by chromium(VI) oxide in acetic anhydride gave substantially the same products as did oxidation of the corresponding olefins, 2,2,4-trimethylpent-1-ene and dineopentylethylene, by chromic acid in aqueous sulphuric acid. This suggested that an intermediate stage involves dehydrogenation to the olefin, which finds support in observations by Roček [2] and Sager *et al.*[3] that oxidation of methylcyclohexane and 3-ethylpentane by chromic acid and aqueous sulphuric acid proceeds by way of the tertiary alcohol to olefin.

In the work described in this paper we examined qualitatively the oxidation of some hydrocarbons by chromic oxide in acetic anhydride; these conditions do not permit

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[1] Archer and Hickinbottom, *J.*, 1954, 4197.

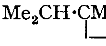
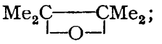
[2] Roček, *Chem. Listy*, 1957, **51**, 1838.

[3] Sager and Bradley, *J. Amer. Chem. Soc.*, 1956, **78**, 1187; Sager, *ibid.*, p. 1838.

formation of alcohols as intermediate products, and cannot be considered as the cause for any dehydrogenation observed.

Neopentane and hexamethylethane, which cannot be dehydrogenated to olefins without rearrangement, are almost indifferent to chromium(VI) oxide in acetic anhydride or acetic acid; the greater part of the hydrocarbon was recovered even after several weeks. However, hydrocarbons whose structures permit dehydrogenation to olefin are oxidised at a measurable rate. Of these, 2,3-dimethylbutane is of special interest in that the oxidation products of two olefins related to it are known.

From 2,3-dimethylbutane oxidation with chromium(VI) oxide in acetic anhydride gave acetone and 3-methylbutan-2-one as fission products, together with 2,3-dimethylbutanoic and 2,3-dimethylbut-2-enoic acid. This unsaturated acid might conceivably arise from 2,3-dimethylbutanoic acid by attack at the tertiary carbon atom and subsequent elimination. This was excluded when we found that 2,3-dimethylbutanoic acid with chromic(VI) oxide in acetic acid and acetic anhydride gave only fission products (acetone, 3-methylbutan-2-one and isobutyric acid). The annexed Table shows the oxidation products of 2,3-dimethylbutane and of the two related olefins.[4] Apart from the formation of epoxide from each olefin in acetic anhydride, there are some significant coincidences which, however, will be discussed in the light of other results to be presented later.

Hydrocarbon	Oxidant	Products
$\mathrm{Me_2CH{\cdot}CHMe_2}$	$\mathrm{CrO_3{-}Ac_2O}$	$\mathrm{Me_2C{:}CMe{\cdot}CO_2H}$; $\mathrm{Me_2CO}$ $\mathrm{Me_2CH{\cdot}CHMe{\cdot}CO_2H}$; $\mathrm{Me_2CH{\cdot}CO_2H}$
$\mathrm{Me_2CH{\cdot}CMe{:}CH_2}$	$\mathrm{CrO_3{-}Ac_2O}$	 $\mathrm{Me_2CH{\cdot}}\underbrace{\mathrm{CMe{-}CH_2}}_{\mathrm{O}}$; $\mathrm{Me_2CH{\cdot}COMe}$ $\mathrm{Me_2C{:}CMe{\cdot}CHO}$
	$\mathrm{H_2SO_4{-}H_2CrO_4}$	$\mathrm{Me_2CH{\cdot}COMe}$; $\mathrm{Me_2CH{\cdot}CHMe{\cdot}CO_2H}$
$\mathrm{Me_2C{:}CMe_2}$	$\mathrm{CrO_3{-}Ac_2O}$	 $\underbrace{\mathrm{Me_2C{-}{-}CMe_2}}_{\mathrm{O}}$; $\mathrm{Me_2C{:}CMe{\cdot}CHO}$
	$\mathrm{H_2SO_4{-}H_2CrO_4}$	$\mathrm{Me_3C{\cdot}COMe}$; $\mathrm{Me_2CO}$

Oxidation of methylcyclohexane in acetic anhydride–acetic acid afforded cyclohexanone, 2-methylcyclohexanone, and adipic and 6-oxoheptanoic acid (there is also good presumptive evidence that other methylcyclohexanones were present although the methods available did not permit us to establish their identity or proportions). It seems then that oxidation of methylcyclohexane is not confined exclusively to attack at the tertiary carbon atom, which is the view now generally accepted.[2,3,5] Some analogous examples are reported by Fieser and Szmuskovicz[5] in the oxidation of some 2-acetyl-3-alkyl- and 2-acetyl-3-cyclohexyl-naphthaquinone, but it is possible here that the naphthaquinone residue deactivates the adjacent tertiary $\geqslant$C linkage to favour attack elsewhere.

EXPERIMENTAL

Oxidation of Saturated Hydrocarbons.—The following general procedure was used: a solution of chromium(VI) oxide in acetic anhydride containing some acetic acid was added gradually and regularly to the hydrocarbon diluted with acetic anhydride or acetic acid, with stirring and temperature-control, under nitrogen. Light was excluded by covering the reaction vessel with tinfoil except in those oxidations which were complete within a few hours. The volatile products (A) were distilled out at 20° under reduced pressure into cold traps until acetic acid began to distill in quantity. The residual solution was diluted with ice-water and extracted exhaustively with ether. From this extract, acetic acid and acid products (B) were removed by sodium carbonate solution. The residual ether solution (C), containing only neutral products, was dried and distilled through an efficient column.

The aqueous solution of chromium salts remaining after ether-extraction was distilled to

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[4] (*a*) Hickinbottom, Hogg, Peters, and Wood, *J.*, 1954, 4400; (*b*) Hickinbottom, Peters, and Wood, *J.*, 1955, 1360.

[5] Fieser and Szmuskovicz, *J. Amer. Chem. Soc.*, 1948, **70**, 3352.

remove any other volatile compounds: the remaining solution was then extracted continuously with ethyl acetate in order to isolate any acids not previously removed by ether. In no oxidation did this procedure give any indication of the presence of succinic acid (cf. Slack and Waters [6]).

(a) 2,3-*Dimethylbutane.* A pure commercial sample (Phillips, " Pure grade, 99·5% pure ") was distilled from sodium and freed from possible unsaturated impurities by passage through a column of activated silica. Before use, it was again distilled from sodium; it had b. p. 58°, n_D^{20} 1·3748—1·3749.

To 2,3-dimethylbutane (400 g.) in acetic anhydride (600 c.c.) at 5° was added chromium(VI) oxide (120 g.) in acetic anhydride (500 c.c.) during 6 hr. and oxidation completed at room temperature in 56 hr. The neutral and volatile products were resolved into 2,3-dimethylbutane (250 g.; b. p. 50°, n_D^{20} 1·3740—1·3750), acetone (22·5 g.; 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 125—126°), 3-methylbutan-2-one (2·1 g.; 2,4-dinitrophenylhydrazone, m. p. and mixed m. p., 120—121°), and some higher-boiling material. Examination of the fractions of b. p. 100—130° failed to reveal t-butyl methyl ketone. From a fraction of b. p. 130—145°, a 2,4-dinitrophenylhydrazone, m. p. 145—155°, was obtained but it could not be completely freed from impurities. The fraction from which it was isolated was aldehydic and unsaturated: the b. p. and the colour of its dinitrophenylhydrazone suggest that 2,3-dimethylbut-2-enal was present (Prevost [7] gives b. p. 146°/760 mm.) but the m. p. of the 2,4-dinitrophenylhydrazone reported by Hickinbottom *et al.*[4a] is 195°. From the neutral material of b. p. 76—128°/25 mm. some carbonylic material was isolated by using Girard T reagent (semicarbazone, m. p. 247—249°) to leave a neutral solid (0·2 g.) which after distillation, sublimation, and recrystallisation from light petroleum melted at 177—178° (Found: C, 58·6; H, 8·2%). The acid products were concentrated into fractions of b. p. 160—187° (1·75 g.). A solid, deposited on cooling, was collected and added to the residue in the distillation flask, which had also crystallised; crystallisation from light petroleum (b. p. 40—60°) gave the pure acid, m. p. 70—70·5° (Found: C, 62·9; H, 8·8. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·8%), identified as 2,3-dimethylbut-2-enoic acid by comparison with a genuine sample and by its dibromide, m. p. and mixed m. p. 188—189°. The liquid portions from the crystallisation of 2,3-dimethylbut-2-enoic acid were chilled to −15° to remove as much as possible of the solid acid. From the remaining liquid portions 2,3-dimethylbutanoic acid was isolated as 4-phenylphenacyl ester, m. p. and mixed m. p. 71—72° (Found: C, 77·5; H, 7·1. Calc. for $C_{20}H_{22}O_3$: C, 77·4; H, 7·1%).

(b) 2,2-*Dimethylbutane.* This hydrocarbon was prepared in 11% yield by reaction of methylmagnesium bromide with t-pentyl chloride in dibutyl ether at 50°, and purified by fractionation after being washed with concentrated sulphuric acid. It had b. p. 49—49·5°, n_D^{20} 1·3690 (Whitmore *et al.*[8] give b. p. 49·5°, n_D^{20} 1·3688). The paraffin (50 g.) in glacial acetic acid (50 c.c.) was oxidised at 7° by chromic(VI) oxide (20 g.) in acetic acid (50 c.c.) and acetic anhydride (20 c.c.), added in 4 hr. When the mixture was kept overnight a black tar (A) separated (49 g.). From the soluble portion of the reaction mixture, 2,2-dimethylbutane (7·5 g.; b. p. 48—49°, n_D^{20} 1·3687) and 2,2-dimethylbutan-3-one (3·6 g.; b. p. 101—103°, n_D^{20} 1·3982; 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 125°) were obtained. The tar (A) dissolved slowly in water, to give a dark green solution which liberated iodine from potassium iodide. It afforded 2,2-dimethylbutane (13·5 g.; b. p. 48—49°, n_D^{20} 1·3691) and 2,2-dimethylbutan-3-one (1 g.; 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 125°).

(c) *Neopentane.* The hydrocarbon (175 g.) was kept with chromium(VI) oxide (100 g.) in acetic acid (175 c.c.) and acetic anhydride (100 c.c.) for 5 weeks. Then 155 g. of neopentane were distilled off. The remaining solution gave a trace of acetone (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 126—127°) and a tar.

(d) 2,2,3,3-*Tetramethylbutane.* This was prepared by reaction of t-butylmagnesium chloride with a mixture of t-butyl chloride and bromide in ether containing suspended cuprous bromide and had m. p. 102° (sealed tube) [9] (Found: C, 84·55; H, 15·3. Calc. for C_8H_{18}: C, 84·25; H, 15·75%). This hydrocarbon is not attacked appreciably by chromic(VI) oxide in acetic acid at room temperature.

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[6] Slack and Waters, *J.*, 1948, 1666.
[7] Prevost, *Bull. Soc. chim. France*, 1944, **11**, 218.
[8] Whitmore, Bernstein, and Mixon, *J. Amer. Chem. Soc.*, 1938, **60**, 2539.
[9] Calingaert, *ibid.*, 1944, **66**, 1394.

(e) 2,3-*Dimethyl*-2,3-*diphenylbutane*. A solution of the hydrocarbon (24 g.; prepared by the dimerisation of isopropylbenzene [10]) in acetic acid (1 l.) was kept with chromium(VI) oxide (4 g.) in acetic anhydride (110 c.c.) for a week: there still remained some unreduced chromium(VI) oxide. From the mixture were isolated unchanged hydrocarbon (20 g.; b. p. 170—171°/14 mm.) and acetophenone (1·4 g.; b. p. 100—125°/20 mm.; 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 235—236°).

(f) *Methylcyclohexane*. A "pure" commercial sample, distilled from sodium, passed through silica gel and redistilled from sodium immediately before use, had b. p. 100°, n_D^{20} 1·4234. Methylcyclohexane (360 g.) in acetic acid (750 c.c.) was oxidised by chromium(VI) oxide (75 g.) in acetic anhydride (200 c.c.) for 5 hr. at $<20°$. Next morning the mixture was poured into 2½ l. of ice-water. The neutral products amounted to 17 c.c. after removal of unchanged methylcyclohexane, and were cyclohexanone [6·4 c.c.; b. p. 154—155·5°, n_D^{20} 1·4575; 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 159—160° (Found: C, 52·2; H, 5·4; N, 20·1. Calc. for $C_{12}H_{14}O_4N_4$: C, 51·8; H, 5·1; N, 20·2%)], and 2-methylcyclohexanone [0·3 g.; b. p. 111°/163 mm., n_D^{20} 1·4548; 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 136—137° (Found: C, 53·3; H, 5·2; N, 19·3. Calc. for $C_{13}H_{16}O_4N_4$: C, 53·4; H, 5·5; N, 19·4%)]. The refractive indexes of cyclohexanone and 2-methylcyclohexanone were much higher than those of the pure compounds. When the ketonic components of these fractions were removed by treatment with Girard T reagent, methylcyclohexanol was left (0·7 g.; b. p. 153—157°, m. p. and mixed m. p. 25—25·5°) (Found: C, 73·2; H, 12·6. Calc. for $C_7H_{14}O$: C, 73·6; H, 12·4%). The higher-boiling fractions were carbonylic but none afforded a pure product. From material of b. p. 90—129°, n_D^{20} 1·4590—1·4900 (0·8 g.), fractions were obtained which gave tests for aldehydes and were unsaturated, but no pure compound was isolated. From the acid products a semi-solid product, b. p. 178—181°/23 mm. (1·5 g.), was obtained, which was identified as 6-oxoheptanoic acid by its semicarbazone, m. p. 144—145° (Found: C, 47·2; H, 7·5. $C_8H_{15}O_3N_3$ requires C, 47·7; H, 7·5%), and by oxidation by hypoiodite to adipic acid, m. p. and mixed m. p. 150—151°. The aqueous solutions from the oxidation were extracted continuously with ethyl acetate; adipic acid, m. p. and mixed m. p. 149—150°, was obtained.

Oxidation of 2,3-*Dimethylbutanoic Acid*.—The acid (41 g.; b. p. 97—98°/23 mm., n_D^{20} 1·4140) in acetic acid (180 c.c.) was stirred while chromium(VI) oxide (9 g.) in acetic acid (20 c.c.) and acetic anhydride (50 c.c.) was added slowly. There was mild evolution of heat. Reaction was complete overnight. Acetone and 3-methylbutan-2-one were the neutral products, recognised by comparison of their 2,4-dinitrophenylhydrazones with authentic specimens. The acid components were separated by distillation into isobutyric acid [0·7 g.; b. p. 154—163°, n_D^{20} 1·3875; 4-phenylphenacyl ester, m. p. and mixed m. p. 88—89° (Found: C, 76·0; H, 6·3. $C_{18}H_{18}O_3$ requires C, 76·4; H, 6·4%)], and unchanged 2,3-dimethylbutanoic acid [22 g.; b. p. 189—190°; and 3·3 g. of less pure acid (4-phenylphenacyl ester, m. p. and mixed m. p. 71—71·5°)]. There was no evidence of the presence of any unsaturated acid.

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QUEEN MARY COLLEGE, MILE END ROAD,
LONDON, E.1.

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[10] Ansell, Holton, and Hickinbottom, *J.*, 1955, 349.