The Synthesis and Reactions of Branched-chain Hydrocarbons. Part V.* Oxidation of 2 : 2 : 4-Trimethylpentane and of 2 : 2 : 4 : 6 : 6-Pentamethylheptane by Chromic Oxide.

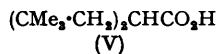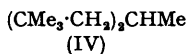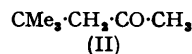## By D. P. ARCHER and W. J. HICKINBOTTOM.

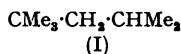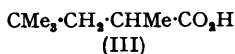The oxidation of 2 : 2 : 4-trimethylpentane and of 2 : 2 : 4 : 6 : 6-pentamethylheptane by chromic oxide in acetic anhydride has been studied. The results are discussed in relation to observations on the oxidation of *iso*-camphane and *cyclo*hexane under similar conditions.

THE description of the oxidation of 2 : 2 : 4-trimethylpentane by chromyl chloride (Hobbs and Houston, *J. Amer. Chem. Soc.*, 1954, **76**, 1254) has prompted the publication of our results on the oxidation with chromic oxide in acetic anhydride.

2 : 2 : 4-Trimethylpentane (I) in acetic anhydride with insufficient chromic oxide for complete oxidation gives acetone, trimethylacetic acid, and 4 : 4-dimethylpentan-2-one (II) as the expected fission products. There is also formed some α-*neo*pentylpropionic acid (III). Under similar conditions, 2 : 2 : 4 : 6 : 6-pentamethylheptane (IV) gives di*neo*pentylacetic acid (V) as the only recognisable product.

$$CMe_3 \cdot CH_2 \cdot CHMe \cdot CO_2H \qquad CMe_3 \cdot CH_2 \cdot CHMe_2 \qquad CMe_3 \cdot CH_2 \cdot CO \cdot CH_3$$
$$\text{(III)} \qquad\qquad\qquad \text{(I)} \qquad\qquad\qquad \text{(II)}$$

$$(CMe_3 \cdot CH_2)_2 CHMe \qquad\qquad (CMe_3 \cdot CH_2)_2 CHCO_2H$$
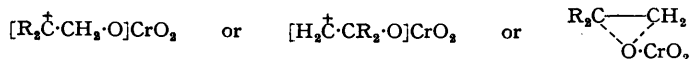$$\text{(IV)} \qquad\qquad\qquad\qquad \text{(V)}$$

It is significant that the products of the oxidation of these two paraffins in acetic anhydride are substantially the same as those from the oxidation of the corresponding olefins with chromic acid in aqueous sulphuric acid (Butleroff, *Annalen*, 1877, **189**, 44; Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 4211; 1941, **63**, 2200; Byers and Hickinbottom, *J.*, 1948, 1334). This resemblance suggests a common intermediate. An obvious choice is a carbonium ion derived from the paraffin by abstraction of H⁻ by the oxidising agent, or from the olefin by addition of H⁺ under the influence of acid. A serious objection to this view arises from an examination of the oxidation of *iso*camphane. If a carbonium ion were formed during the oxidation, rearrangement should occur with the subsequent formation of camphor. It was found, however, that *iso*camphane, when oxidised in acetic anhydride by chromic oxide, gives camphenilanic acid and camphenilone with no detectable indications of camphor.

From other work in this laboratory it seems probable that the oxidation of an olefin by chromic acid in aqueous sulphuric acid proceeds through a chromic acid complex which may undergo oxidative fission or be rearranged, if the conditions are favourable and the structure permits, to a carbonylic compound. The translation of these ideas to
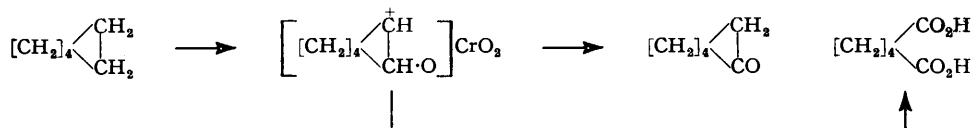
the oxidation of paraffins in acetic anhydride by chromic oxide can be effected if it is assumed that the initial stage is the abstraction of hydrogen from two adjacent carbon atoms with the subsequent formation of a complex with chromic oxide. Provisional formulations for such a complex might be

$$[R_2\overset{+}{C}\cdot CH_2\cdot O]CrO_2 \quad \text{or} \quad [H_2\overset{+}{C}\cdot CR_2\cdot O]CrO_2 \quad \text{or} \quad \begin{array}{c} R_2C\text{------}CH_2 \\ \diagdown\diagup \\ O\cdot CrO_2 \end{array}$$

On treatment with water oxidative fission to R_2CO may occur with the reduction of Cr^{IV} to Cr^{III}; alternatively, rearrangement may occur to $CHR_2\cdot CHO$ with subsequent oxidation to $CHR_2\cdot CO_2H$.

These ideas were tested on *cyclo*hexane, which should give two main products, *cyclo*hexanone by rearrangement, and adipic acid as the final product of oxidative fission :

$$[CH_2]_4\diagup^{CH_2}_{\diagdown CH_2} \longrightarrow \left[[CH_2]_4\diagup^{\overset{+}{C}H}_{\diagdown CH\cdot O}\right]CrO_2 \longrightarrow [CH_2]_4\diagup^{CH_2}_{\diagdown CO} \quad [CH_2]_4\diagup^{CO_2H}_{\diagdown CO_2H}$$

Both the expected products were obtained and it was established by comparative qualitative measurements that *cyclo*hexanone is oxidised more slowly than *cyclo*hexane, and is therefore not the main source of adipic acid.

Hobbs and Houston (*loc. cit.*) by a different line of reasoning have tentatively suggested a hypothesis to account for the oxidation of paraffins by chromyl chloride which in essentials is similar to the one we now propose. The products of the oxidation of 2 : 2 : 4-trimethylpentane by chromic oxide and chromyl chloride are so strikingly similar as to suggest that in both oxidations, the essentials of the mechanism are the same. Slack and Waters (*J.*, 1949, 594, 599) have come to a similar conclusion from the consideration of other evidence, and their views have provided a useful background for the development of the ideas now expressed. It is suggested as an addendum to our hypothesis that the chloro-ketones observed by Houston and Hobbs in the chromyl chloride oxidation arise from the addition of a chloride ion to the carbonium ion centre of the hydrocarbon residue on dilution with water.

In arriving at our hypothesis, consideration has been given to other possible explanations. The abstraction of one hydrogen atom as the initial stage of oxidation to give a free radical is an attractive alternative hypothesis capable of explaining qualitatively the formation of an olefin as an intermediate and also the formation of fission products. But at no stage during this work was there any evidence of the formation of succinic acid, which might reasonably be expected to be formed if the free-radical hypothesis were valid. Furthermore, there was no evidence of the formation of free olefin in any of these oxidations such as would occur if a free radical were formed; a particularly favourable example for testing this is di*neo*pentylethane which should give di*neo*pentylethylene, an olefin which is comparatively resistant to oxidation.

Fieser and Szmuskovicz's suggestion (*J. Amer. Chem. Soc.*, 1948, 70, 3355) that the oxidation of phenyl*cyclo*hexane goes by way of a tertiary alcohol cannot be applied to *iso*camphane. The tertiary alcohols derived from *iso*camphane, *viz.*, camphene hydrate and methylcamphenilol, are more resistant to oxidation than *iso*camphane and they give camphenilone as the only product of oxidation; *iso*camphane under similar conditions gives camphenilanic acid and camphenilone. By implication this objection must apply to the oxidation of all other hydrocarbons which yield tertiary alcohols relatively resistant to oxidation.

The present hypothesis makes no provision for small amounts of the esters of alcohols which are formed when *sec.*-butylbenzene or *cyclo*hexane is oxidised in acetic anhydride. It seems possible in this oxidation that two mechanisms may operate or, more probably if the hypothesis is a sound one, that the initial dehydrogenation is not of one stage but two, leading to the possibility of side reactions.

EXPERIMENTAL

The hydrocarbons were refluxed over sodium and distilled before use; they had been freed from last traces of olefin by passage through silica gel.

The general conditions for carrying out these oxidations consisted in adding a solution of chromic oxide in acetic anhydride to an excess of the hydrocarbon in acetic anhydride. The temperature of the mixture was kept at about 0°; efficient stirring was maintained throughout the oxidation and a slow stream of nitrogen was passed through the vessel to remove volatile products. Carbon dioxide was estimated from the weight of barium carbonate precipitated in a trap containing baryta solution; for volatile aldehydes a trap containing 2 : 4-dinitrophenylhydrazine was used.

When the oxidation was complete, and this usually required 24 hr., the reaction mixture was diluted with water (3 vol.) and extracted with ether (B) after most of the anhydride had hydrolysed. The aqueous portion (A) after ether extraction was steam-distilled to remove volatile carbonyl compounds and carboxylic acids; the aqueous solution remaining after steam-distillation was extracted with ethyl acetate for the removal of succinic acid and other non-volatile acids. The ether extract B was freed from volatile carboxylic acids by washing with aqueous alkali, and then distilled to separate unchanged hydrocarbon from the neutral products of oxidation.

(1) *Oxidation of 2 : 2 : 4-Trimethylpentane* (isoOctane).—isoOctane (b. p. 99—99·5°, n_D^{20} 1·3915) (175 g.) in a mixture of acetic acid (400 ml.) and acetic anhydride (25 ml.) was oxidised by a solution of chromic oxide (52 g.) in a mixture of acetic anhydride (250 ml.) and acetic acid (120 ml.). 2·1 g. of carbon dioxide were obtained and no volatile carbonyl compounds were detected. The oxidation product contained acetone, unchanged isooctane (109 g., b. p. 96—99°, n_D^{20} 1·3910—1·3915), and methyl neopentyl ketone (9·8 g., b. p. 124°, n_D^{20} 1·4030; semicarbazone m. p. and mixed m. p. 175—176°). There was also a further small amount of this ketone in fractions of b. p. 110—124° (2·1 g., n_D^{20} 1·4000—1·4015). The product boiling above 124° weighed 1·8 g. but nothing homogeneous could be obtained from it.

The acid products of the oxidation consisted of trimethylacetic acid, b. p. 164—165° (0·9 g.; *p*-bromophenacyl ester, m. p. mixed m. p. 75—76°), some intermediate fractions containing more trimethylacetic acid, and a fraction, b. p. 98—107°/9 mm. (1·1 g.), n_D^{20} 1·4115—1·4125, consisting largely of α-neopentylpropionic acid (2 : 4 : 4-trimethylpentanoic acid); *p*-toluidide, m. p. and mixed m. p. 137—138°.

(2) *Oxidation of 2 : 2 : 4 : 6 : 6-Pentamethylheptane* (as-Dineopentylethane).—Dineopentylethane (75 g., b. p. 71—72°/24 mm., n_D^{20} 1·4186—1·4188) in acetic anhydride (300 ml.) was oxidised by a solution of chromic oxide (33 g.) in acetic anhydride (200 ml.). The acidic product was dineopentylacetic acid (2 : 2 : 6 : 6-tetramethylheptane-4-carboxylic acid) (9·4 g.), m. p. 85—86° not depressed by admixture with an authentic specimen (Found : C, 71·6; H, 11·6. Calc. for $C_{12}H_{24}O_2$: C, 71·9; H, 12·0%). The m. p. of the amide, 139—140°, was not depressed by admixture with a genuine specimen of dineopentylacetamide.

The neutral material from the oxidation contained unchanged hydrocarbon (48 g., b. p. 70—72°/24 mm., n_D^{20} 1·4172—1·4188) and some higher-boiling material (2·5 g.) not resolved into any homogeneous product.

(3) *Oxidation of isoCamphane.*—A solution of isocamphane (100 g., m. p. 63—64°) in carbon tetrachloride (600 ml.) and acetic anhydride (500 ml.) was oxidised by chromic oxide (50 g.) in acetic anhydride (300 ml.). The acid product was camphenilanic acid (4·7 g., m. p. and mixed m. p. 62—63°) (Found : C, 71·4; H, 9·3. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·5%); amide, m. p. and mixed m. p. 170—171°. The acid is reduced by lithium aluminium hydride to isocamphanol [*p*-nitrobenzoate, m. p. and mixed m. p. 90° (Found : C, 67·3; H, 7·0; N, 4·5. Calc. for $C_{17}H_{21}O_4N$: C, 67·3; H, 7·0; N, 4·6%)].

The neutral products of the oxidation were concentrated by passing a solution in light petroleum through a column of silica gel. Unchanged isocamphane (74·2 g., m. p. 57—58°) passed through. The oxygenated products were collected by eluting the column with ether and acetone, and on distillation, camphenilone (8·1 g.) was obtained as well as higher-boiling material (1·9 g., b. p. 210—234°, n_D^{20} 1·4672—1·4742) which could not be further resolved and contained chlorine. The camphenilone was examined particularly for the presence of camphor. A satisfactory method was found to consist in fractional sublimation from a bath at 110—115°; camphor sublimes more readily and can be recognised by its 2 : 4-dinitrophenylhydrazone. No evidence for the presence of camphor was obtained, nor was there any satisfactory evidence for the presence of camphenilanaldehyde. The camphenilone appeared to be pure, and it

was recognised by its m. p. 38°; its semicarbazone, m. p. 217—218°; and its 2 : 4-dinitro-phenylhydrazone, m. p. 159—160°.

Oxidation of Camphene Hydrate.—A solution of camphene hydrate (30 g.) in acetic anhydride was oxidised by dropwise addition of a solution of chromium trioxide (20 g.) in acetic anhydride (100 ml.). After 36 hr., the green solution was diluted with water and worked up as described above. No camphenilanic acid was found. The neutral material consisted largely of unchanged camphene hydrate (16·4 g.), a small amount of camphene, and a ketonic fraction, b. p. 178—208° (6·3 g.), consisting largely of camphenilone; no other carbonylic compound was identified.

Oxidation of Methylcamphenilol.—Methylcamphenilol (56·2 g.) in acetic anhydride (400 ml.), oxidised by chromic oxide (40 g.) in acetic anhydride (200 ml.), gave unchanged methyl-camphenilol (42 g.), crude camphene (2·2 g.), and a ketonic fraction, b. p. 180—198° (7·8 g.), containing camphenilone as the only ketone.

(4) *Oxidation of* cyclo*Hexane.*—cycloHexane (300 g.) in acetic acid (1 l.) and acetic anhydride (100 ml.) was oxidised by a solution of chromic oxide (80 g.) in acetic anhydride (700 ml.). There were obtained unchanged cyclohexane (251 g., b. p. 79—81°, n_D^{20} 1·4235—1·4265), cyclohexanone (5·8 g., b. p. 56—57°/20 mm., n_D^{20} 1·4500—1·4495; semicarbazone, m. p. 165—166°), adipic acid (4·7 g., m. p. 147—149°, di-*p*-bromophenacyl ester, m. p. and mixed m. p. 154—155°), and small amounts of cyclohexanol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 113°) and cyclohexen-3-one (2 : 4-dinitrophenylhydrazone, orange red, m. p. 157—159°, mixed m. p. with authentic specimen 160—162°; mixed m. p. with cyclohexanone 2 : 4-dinitrophenylhydrazone 145°).

(5) *Oxidation of* sec.-*Butylbenzene.*—sec.-Butylbenzene (273 g., b. p. 172—172·5°, n_D^{20} 1·4894—1·4900) in acetic anhydride (200 ml.) was oxidised by chromic oxide (100 g.) in acetic anhydride (500 ml.). There were isolated unchanged sec.-butylbenzene (143 g.), acetophenone (2·6 g.; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 246°; semicarbazone, m. p. and mixed m. p. 198°), propiophenone (1·5 g., b. p. 98—102°/11 mm.; 2 : 4-dinitrophenyl-hydrazone, m. p. and mixed m. p. 190—191°), and higher-boiling neutral material, b. p. 113—150°/15 mm. (10·4 g.), from which impure 1-methyl-1-phenylpropyl acetate was obtained (1·6 g. Found : Ac, 25·8. Calc. for $C_{12}H_{16}O_2$: Ac, 22·4%). The alcohol derived from it by alkaline hydrolysis gave a p-*nitrobenzoate*, m. p. and mixed m. p. 97—98° (Found : C, 68·3; H, 6·0; N, 4·9. $C_{17}H_{17}O_4N$ requires C, 68·3; H, 5·7; N, 4·7%). There was also present in the fractions, b. p. 136—150°/15 mm. (1·0 g.), a substantial proportion of carbonylic material from which two 2 : 4-dintrophenylhydrazones were separated : (*a*) yellow, m. p. 142—143°, and (*b*) orange, m. p. 181—183°, which were still impure and gave unsatisfactory analyses.

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