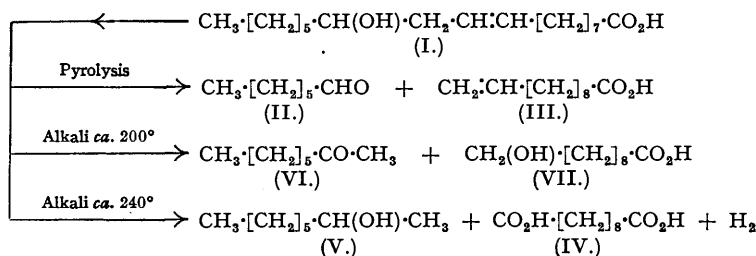## 143. Reactions of Carbinols in the Presence of Alkali. Part II. The Scission of Ricinoleic Acid.

By G. H. HARGREAVES and L. N. OWEN.

It has been confirmed that the alkaline scission of ricinoleic acid does not occur below 180°. The initial products are probably methyl *n*-hexyl ketone and 10-hydroxydecanoic acid; at higher temperatures (*ca.* 240°) these interact to give methyl-*n*-hexylcarbinol, sebacic acid, and hydrogen (cf. Part I), only one mechanism thus being necessary to explain both the "ketone-producing" and the "carbinol-producing" scissions. Sebacic semialdehyde has been obtained in pure crystalline form; it undergoes dehydrogenation to sebacic acid on treatment with alkali at 240°.

THE scission of ricinoleic acid (I) on heating was apparently first observed in 1827 by Bussy and Lecanu (*Compt. rend.*, 21, 84; *J. Pharm. Chim.*, 1845, 8, 321); by pyrolysis of ricinoleates they obtained "oenanthol," subsequently identified as *n*-heptaldehyde (II) (cf. Bouis, *Ann. Chim. Phys.*, 1855, 44, 77). It was shown by Krafft (*Ber.*, 1877, 10, 2034; 1878, 11, 2018) that undec-10-enoic acid (III) was also formed in this reaction. Bouis (*Compt. rend.*, 1851, 33, 143; 1859, 41, 603) had also investigated the pyrolysis of castor-oil, which is mainly glyceryl triricinoleate, in the presence of excess alkali, and by vigorous heating had obtained sebacic acid (IV) and a volatile "capryl" alcohol, which was eventually shown to be methyl-*n*-hexylcarbinol (V). The scission was extensively investigated during the next few years (cf. Neison, *J.*, 1874, 27, 507, 837) and although the results obtained, owing to insufficient attention to experimental conditions, were somewhat conflicting, it was shown that the alkaline scission gave methyl *n*-hexyl ketone (VI) in addition to the carbinol, though the yield of ketone diminished with increase of reaction temperature; this last observation, as will be seen subsequently, is of considerable importance. Much later, Lee (*Chem. Abstr.*, 1917, 11, 3027) reported the evolution of hydrogen during the production of carbinol, and it was only in 1941 that Houpt (U.S.P. 2,217,515) showed that the ketone is accompanied by 10-hydroxydecanoic acid (VII). Attention has also been paid in recent years to the determination of the optimum conditions for the production of either ketone or carbinol (B.PP. 534,321, 534,322; U.S.PP. 2,182,056, 2,217,516, 2,318,762; Houpt, *loc. cit.*; Adams and Marvel, *Org. Synth.*, Coll. Vol. I, 2nd ed., p. 366) and it is clear that ricinoleic acid in the presence of alkali undergoes scission to ketone and hydroxy-acid at *ca.* 200°, whilst the carbinol and sebacic acid are the main products at temperatures above 240°.

Three types of scission are therefore known, which may be summarised according to the scheme below :

$$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CH_2 \cdot CH:CH \cdot [CH_2]_7 \cdot CO_2H$$
$$(I.)$$

Pyrolysis
$$CH_3 \cdot [CH_2]_5 \cdot CHO \quad + \quad CH_2:CH \cdot [CH_2]_8 \cdot CO_2H$$
$$(II.) \qquad\qquad\qquad (III.)$$

Alkali *ca.* 200°
$$CH_3 \cdot [CH_2]_5 \cdot CO \cdot CH_3 \quad + \quad CH_2(OH) \cdot [CH_2]_8 \cdot CO_2H$$
$$(VI.) \qquad\qquad\qquad (VII.)$$

Alkali *ca.* 240°
$$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CH_3 + CO_2H \cdot [CH_2]_8 \cdot CO_2H + H_2$$
$$(V.) \qquad\qquad (IV.)$$

Other products, which have occasionally been reported, result from secondary reactions; octene, for example, is derived by dehydration of the carbinol.

The outstanding exception to the above conclusions is to be found in a claim by Svetlov and Vulfson (*J. Appl. Chem. Russia*, 1936, 9, 1613) for the preparation of methyl-*n*-hexylcarbinol in 90% yield by the alkaline scission of castor-oil at a reaction temperature of only 112—117°. We have been unable to repeat these results, and have shown that no appreciable reaction occurs below 180°; there would appear to be little doubt that the reaction observed by the Russian workers occurred at the surface of the gas-heated copper vessel, the temperature of which would be considerably higher than the main bulk of the semi-solid reaction mixture.

Little has hitherto been known of the mechanisms by which ricinoleic acid undergoes the above types of fission. Barbot (*Bull. Soc. chim.*, 1935, 2, 895, 1438; *Ann. Chim.*, 1939, 11, 519; cf. Isikawa *et al.*, *Chem. Abstr.*, 1940, 34, 3240) postulated the intermediate formation of an

oxide (VIII) or a hydrogen-bonded structure (IX), followed by scission, in the direction shown, to give *n*-heptaldehyde and undec-10-enoic acid. These suppositions, however, in reality offer

$$CH_3 \cdot [CH_2]_5 \cdot CH \underset{O}{\overset{CH_2}{<}} CH \cdot [CH_2]_8 \cdot CO_2H \qquad \text{(VIII.)}$$

$$CH_3 \cdot [CH_2]_5 \cdot CH \underset{O \cdots H}{\overset{CH_2 - CH}{<}} CH \cdot [CH_2]_7 \cdot CO_2H \qquad \text{(IX.)}$$

little explanation of this neutral pyrolytic scission, and, furthermore, shed no light on the more difficult problem of the scission under alkaline conditions.

It has been recognised for some time that the ethylenic linkage in ricinoleic acid is capable of migration towards the hydroxyl group; barium ricinoleate, for instance, on being heated is transformed into barium 12-ketostearate, a change which involves a double migration of the ethylenic linkage :

$$\cdot CH(OH) \cdot CH_2 \cdot CH \vdots CH \cdot \longrightarrow \cdot CH(OH) \cdot CH \vdots CH \cdot CH_2 \cdot \longrightarrow \cdot C(OH) \vdots CH \cdot [CH_2]_2 \cdot \longrightarrow \cdot CO \cdot [CH_2]_3 \cdot$$

This isomerisation may also be brought about by heating esters of ricinoleic acid with metal catalysts (Belopolski and Maximov, *Chem. Zentr.*, 1937, II, 1694; Hanford, Schreiber, and Gray, U.S.P. 2,340,745). Isomerisation to the intermediate acid (X), followed by scission at the ethylenic linkage, was considered probable by Noorduyn (*Chem. Zentr.*, 1920, I, 731) and by Verkade (*Rec. Trav. chim.*, 1927, **46**, 200) in order to explain the formation of the C_8 alcohol and ketone; Panjutin (*J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1) unsuccessfully sought evidence for the presence of (X) by examination of the residues from partly pyrolysed ricinoleic esters.

If double-bond migration from the $\beta\gamma$- to the $\alpha\beta$-position is the first step in the alkaline scission, it would be anticipated that $\alpha\beta$-ethylenic carbinols in general would also undergo fission with alkali; this is indeed the case, for it has now been shown that such carbinols undergo both types of fission when heated with concentrated alkali to the appropriate temperature (see Part III, following paper). There is therefore little doubt that preliminary isomerisation occurs with ricinoleic acid, but it is still possible to envisage several routes for the succeeding reactions. In Scheme A, hydrolytic fission of the ethylenic linkage in the rearranged acid (X) to give the carbinol (V) and sebacic semialdehyde (XI), followed by conversion of the latter into sebacic acid (IV), explains the formation of the products obtained above 240°. Furthermore, since aldehydes can be reduced by aluminium alkoxides, a similar reaction may well occur in the presence of alkali-metal alkoxides, so that the primary products (V) and (XI) would be capable of transformation into the ketone (VI) and hydroxy-acid (VII), thus accounting also for the products obtained at the lower temperature.

$$CO_2H \cdot [CH_2]_8 \cdot CO_2H + H_2$$
$$\text{(IV.)}$$

Scheme A
$$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CH_3 + CHO \cdot [CH_2]_8 \cdot CO_2H$$
$$\text{(V.)} \qquad\qquad \text{(XI.)}$$

$$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CH \vdots CH \cdot [CH_2]_8 \cdot CO_2H$$
$$\text{(X.)} \qquad\qquad\qquad - H_2$$

Scheme B
$$CH_3 \cdot [CH_2]_5 \cdot CO \cdot CH_3 + CH_2OH \cdot [CH_2]_8 \cdot CO_2H$$
$$\text{(VI.)} \qquad\qquad \text{(VII.)}$$
$$+ H_2O$$

$$CH_3 \cdot [CH_2]_5 \cdot CH(OH) \cdot CH \vdots + \vdots CH \cdot [CH_2]_8 \cdot CO_2H$$

An obvious difficulty about Scheme A is this fact that the ketone-producing scission occurs at a temperature appreciably lower than that required for the production of the carbinol, since it is possible, by careful control of the temperature, to obtain the ketone practically free from carbinol. This strongly suggests that the primary products are the ketone and hydroxy-acid, the formation of which may perhaps be visualised as though occurring by scission at the ethylenic linkage, followed by rearrangement of one fragment to give the ketone, and hydration of the other to give the hydroxy-acid, according to Scheme B. The production of the carbinol, sebacic acid, and hydrogen at the higher temperature can then be explained in a simple manner as a direct reduction of the ketone by the primary alcoholic group present in the acid; the generality of this type of reaction for aliphatic ketones and primary alcohols has already been demonstrated (Part I, preceding paper), and it has now been shown to apply to the case under discussion, since the treatment of a mixture of methyl *n*-hexyl ketone and 10-hydroxydecanoic acid with 60%

sodium hydroxide solution at 240° resulted in the formation of methyl-*n*-hexylcarbinol, sebacic acid, and hydrogen.

Sebacic semialdehyde, a postulated intermediate in both of the above schemes, has now been obtained in a pure crystalline form, m. p. 56—57° (cf. Braun and Keller, *Ber.*, 1933, **66**, 215), by ozonisation of undec-10-enoic acid. In agreement with the suggested mechanisms, it is converted into sebacic acid when heated with concentrated aqueous alkali at 240°.

A probable side reaction, represented by the broken line in the diagram, is the direct conversion of the hydroxy-acid into sebacic acid (cf. Part I). This would account for the observation that the carbinol is never obtained completely free from small amounts of ketone.

Account must still be taken, however, of an early observation, due to Marckwald and McKenzie (*Ber.*, 1901, **34**, 469), which we have confirmed, that the methyl-*n*-hexylcarbinol obtained by the alkaline fission of ricinoleic acid shows slight optical activity ($[\alpha]_D^{20°} - 0 \cdot 1°$). This may be due to a trace of impurity, since commercial ricinoleic acid was used in these experiments,* or it may indicate that, if the temperature is raised rapidly to 240°, scission can also occur to some extent according to the first mechanism, in which case the asymmetric character of the carbinol group would be maintained.

<div align="center">Experimental.</div>

(Light petroleum refers to the fraction of b. p. 40—60°.)

Minimum Scission Temperature of Ricinoleic Acid.—Treatment of either ricinoleic acid (20 g.) or castor oil (20 g.) with 30% aqueous sodium hydroxide (18 c.c.) was carried out in a "Pyrex" flask under reflux, heated in an oil-bath maintained at 125—130° for 3 hours. The proportions of materials were those used by Svetlov and Vulfson (*loc. cit.*). Neither ketone nor carbinol could be detected in the reaction products, which yielded only unchanged ricinoleic acid. The addition of copper bronze to the reactants did not affect the result.

The experiments were then repeated, the condenser being arranged for distillation, and the contents of the flask vigorously stirred whilst the temperature of the oil-bath was gradually raised. Water was added to the reaction mixture at a rate equal to that at which it was lost by distillation. The minimum bath temperature at which scission occurred, as indicated by the appearance of methyl *n*-hexyl ketone in the distillate, was 180—200°, the corresponding internal temperature being 175—195°. The presence of a small quantity of copper bronze accelerated the scission, the effect probably being due to increased heat conductivity.

"*Ketone-producing*" *Scission of Ricinoleic Acid.*—Sodium hydroxide (500 g.) and water (200 c.c.) were heated in a 5-l. "Pyrex" flask immersed in an oil-bath maintained at 195—200°. The flask was fitted with a mercury-sealed stirrer, condenser, and receiver, so arranged that both liquid and gaseous products could be collected. Commercial ricinoleic acid (500 g.) was added during 3 hours, accompanied by water to replace that lost by distillation, vigorous stirring being maintained throughout. Heating, stirring, and addition of water were continued for a further 4 hours. The distillate contained an upper layer of methyl *n*-hexyl ketone (115 c.c.) containing traces of carbinol; the small amount of hydrogen evolved (2·5 l.) indicated the formation of only 7% of carbinol. The residue in the flask, after cooling, was dissolved in water (4 l.) and acidified with sulphuric acid. The oil was collected, and after standing for several days had partly solidified; the solid was obtained by filtration (36 hours at 15 mm.) and then freed from most of the remaining oil by pressing on porous tile. Recrystallisation from ether–light petroleum gave needle-clusters of 10-hydroxydecanoic acid (67 g.), m. p. 73°.

Reduction of Methyl n-*Hexyl Ketone by* 10-*Hydroxydecanoic Acid.*—The ketone (40 g.), hydroxy-acid (60 g.), sodium hydroxide (220 g.), and water (150 c.c.) were shaken in an autoclave at 240° for 3 hours. After cooling, the gas (2·5 l.) was released and shown by analysis to contain 85% hydrogen, 10% nitrogen, 1% oxygen, and *ca.* 3% hydrocarbons. (Nitrogen and oxygen are clearly derived from the air space in the autoclave.) The neutral products, isolated by ether extraction, gave, in addition to much high-boiling material, a main fraction (8 g.), b. p. 175°, $n_D^{17°}$ 1·4253. This contained 7% of unchanged methyl *n*-hexyl ketone (estimated as the 2 : 4-dinitrophenylhydrazone, m. p. 58°; cf. Part I, p. 752), but was mainly methyl-*n*-hexylcarbinol (*α*-naphthylurethane, m. p. 57—58°), the yield of which was thus 7·5 g. (18%). Acidification of the aqueous residues with sulphuric acid precipitated sebacic acid (25 g., 40%), which crystallised from water in plates, m. p. 131°.

Sebacic Semialdehyde.—A solution of undec-10-enoic acid (22 g.) in methylene dichloride (150 c.c.) was treated with ozonised oxygen at room temperature until no further absorption took place. The solution was then gradually added, with vigorous stirring and cooling, to a suspension of zinc dust (15 g.) in 30% aqueous acetic acid (200 c.c.). When the reaction had subsided, the mixture was heated on the steam-bath for 1 hour (the remaining methylene dichloride being allowed to escape through an air condenser), and then cooled, acidified to Congo-red with hydrochloric acid, and extracted with chloroform. After removal of solvent, the residual semi-solid material was distilled under reduced pressure, and gave a main fraction (12·0 g.), b. p. 150°/0·1 mm., which crystallised in the receiver as a hard white mass, m. p. 56—57°, unchanged on recrystallisation from acetone–light petroleum, from which it separated in glistening white plates (Braun and Keller, *loc. cit.*, gave m. p. 40—60°) (Found : C, 64·25; H, 9·5. Calc. for $C_{10}H_{18}O_3$: C, 64·5; H, 9·7%). The semicarbazone, recrystallised from ethanol, formed nodules, m. p. 170° (Braun and Keller, *loc. cit.*, gave m. p. 155°) (Found : N, 17·0. Calc. for $C_{11}H_{21}O_3N_3$: N,

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* The purification of ricinoleic acid is very laborious, and it is doubtful whether it has ever been obtained entirely free from traces of other acids.

17·3%). The *oxime* crystallised from methanol in prisms, m. p. 111° (Found : N, 7·1. $C_{10}H_{19}O_3N$ requires N, 7·0%).

Dehydrogenation of Sebacic Semialdehyde by Alkali—The semialdehyde (3 g.) was finely powdered and added to a hot solution of sodium hydroxide (6 g.) in water (4 c.c.). The semi-solid mass of sodium salt was thoroughly broken up, and the mixture transferred to a small autoclave and kept at 250° for 3 hours. After cooling, the product was dissolved in water, filtered, and acidified with sulphuric acid, yielding a precipitate (2·4 g.) of crude sebacic acid, m. p. *ca.* 120°, which after purification by sublimation at 100°/0·0001 mm. gave the pure acid (1·6 g.), m. p. and mixed m. p. 131°.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.