144. *Reactions of Carbinols in the Presence of Alkali.   Part III.   The Scission of αβ-Ethylenic Carbinols.*
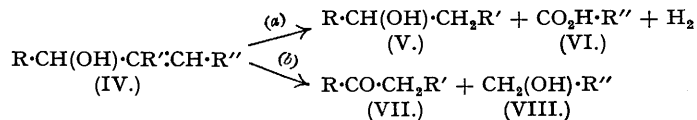
By G. H. Hargreaves and L. N. Owen.

Oct-2-en-4-ol and 6-*ethyldec-6-en-5-ol* have been found to undergo both the " ketone-producing " and " carbinol-producing " types of fission, shown by ricinoleic acid, on treatment with alkali at 180—240° (cf. Part II).

The mechanism for the alkaline scission of ricinoleic acid, discussed in Part II (preceding paper), involves a preliminary isomerisation of the ethylenic linkage from the βγ- to the αβ-position (with reference to the carbinol group).   Since the carboxyl group in the acid does not take any essential part in the reaction, it would be anticipated that simple ethylenic carbinols would also undergo fission under similar conditions.   The literature contains one well-known example of such a reaction, *viz.*, the treatment of geraniol (I) with concentrated alcoholic alkali at 150° to give methylheptenol (III) (Barbier, *Compt. rend.*, 1898, **126**, 1423; Tiemann, *Ber.*, 1898, **31**, 2991).   According to Doeuvre (*Bull. Soc. chim.*, 1929, **45**, 351; cf. Tiemann, *loc. cit.*) the scission actually gives methylheptenone (II) as primary product, which is then reduced by the ethanol :
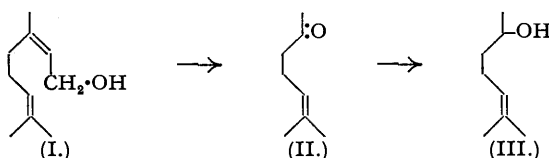
This example, however, is not strictly comparable with ricinoleic acid, since geraniol contains a primary alcoholic group, and oct-2-en-4-ol (IV; R = *n*-Bu; R′ = H, R″ = Me) was therefore chosen for the investigation.   This compound was unaffected by 60% potassium hydroxide solution at temperatures up to 175°, but treatment with the same reagent in a rocking autoclave at 240° resulted in the evolution of hydrogen (40%), and the formation of methyl-*n*-butyl-carbinol (V; R = *n*-Bu, R′ = H) (38%) and acetic acid (VI; R″ = Me) (4%), the low recovery of acid being partly due to the difficulty of its isolation.   The products of this reaction correspond precisely with those expected from a carbinol-producing scission (*a*), and the isolation of a small amount of methyl *n*-butyl ketone (VII; R = *n*-Bu, R′ = H) (4%) indicates the occurrence also of the ketone-producing scission (*b*), though it was impracticable to confirm the presence of the traces of ethanol (VIII; R″ = Me) which should also have been formed.   The comparatively low yields of degradation products, which were accompanied by a considerable amount of

$$\begin{array}{c} \xrightarrow{(a)} \quad \text{R·CH(OH)·CH}_2\text{R′} + \text{CO}_2\text{H·R″} + \text{H}_2 \\ \qquad\qquad\quad \text{(V.)} \qquad\qquad \text{(VI.)} \\ \text{R·CH(OH)·CR″:CH·R″} \\ \text{(IV.)} \qquad \searrow^{(b)} \quad \text{R·CO·CH}_2\text{R′} + \text{CH}_2\text{(OH)·R″} \\ \qquad\qquad\qquad\quad \text{(VII.)} \qquad\quad \text{(VIII.)} \end{array}$$

high-boiling material, are probably due in part to the necessity of carrying out the reaction on the ethylenic carbinol (b. p. 175°) in a closed system, with consequent facilitation of side reactions; with the non-volatile sodium ricinoleate, the neutral products can be removed by distillation during the course of the reaction.   It was therefore of interest to use an ethylenic carbinol of higher boiling point, on which the scission could be investigated at atmospheric pressure.   The choice of such a carbinol is restricted not only by availability but also by

consideration of the ease of separation of the possible degradation products, but a suitable substance was found in 6-*ethyldec*-6-*en*-5-*ol* (IV; R = *n*-Bu, R' = Et, R'' = *n*-Pr) which was synthesised by the condensation of 2-ethylhex-2-en-1-al with *n*-butylmagnesium bromide. The ketone-producing scission was brought about by treatment of this carbinol (b. p. 225°) with 60% aqueous potassium hydroxide at a bath temperature of 190—200°. Slow distillation occurred, but no gas was evolved, and the distillate yielded unchanged carbinol (25%), *n*-propyl *n*-butyl ketone (VII; R = *n*-Bu, R' = Et) (22%), and *n*-butanol (VIII; R'' = *n*-Pr) (19%). The temperature at which this scission took place compared well with that required for the production of methyl *n*-hexyl ketone from ricinoleic acid (180—200°). No trace of products corresponding to the carbinol-producing scission (*a*) could be detected.

6-Ethyldec-6-en-5-ol was then shaken with 60% aqueous alkali in an autoclave at 240°. Scission (*a*) was shown to have occurred by the formation of hydrogen (45%) and the isolation from the reaction products of *n*-propyl-*n*-butylcarbinol (V; R = *n*-Bu, R' = Et) (31%), identified as the α-naphthylurethane, and *n*-butyric acid (VI; R'' = *n*-Pr) (21%); small amounts of *n*-butanol (2%) and *n*-propyl *n*-butyl ketone (17%), which were also present, were evidently formed from scission (*b*).

An attempt was made to prepare an αβ-ethylenic carbinol from 2-ethylhex-2-en-1-al and *n*-octylmagnesium bromide, but dehydration occurred on distillation of the product, to give a 70% yield of a compound which was probably *di*-(5-*ethyltetradec*-4-*en*-6-*yl*) *ether*, [*n*-C$_8$H$_{17}$·CH(CEt:CH·CH$_2$·CH$_2$·CH$_3$)]$_2$O; it was unaffected by aqueous alkali at 250°. n-*Propyl*-n-*octylcarbinol*, which would have been one of the fission products from the expected ethylenic carbinol, was synthesised by the condensation of *n*-octylmagnesium bromide and *n*-butaldehyde.

The mechanism of the alkaline scission of αβ-ethylenic carbinols is clearly similar to that of ricinoleic acid (Part II), and this has been confirmed by the reductions, described in Part I, of methyl *n*-butyl ketone with ethanol to give methyl-*n*-butylcarbinol, and of *n*-propyl *n*-butyl ketone with *n*-butanol to give *n*-propyl-*n*-butylcarbinol, the primary alcohols being simultaneously converted into acetic and *n*-butyric acids, respectively, and hydrogen being liberated. The ketone (VII) and primary alcohol (VIII) would thus appear to be the primary products, which at the higher temperature interact to give carbinol (V), acid (VI), and hydrogen, the overall mechanism corresponding to Scheme B (Part II, p. 754).

With regard to the scission of geraniol, to which reference was made above, since this is a primary alcohol and carries a substituent in the β-position, the " ketone-producing " scission would give acetaldehyde and methylheptenol (III) (corresponding to the ketone and primary alcohol, respectively, from the ethylenic carbinols previously considered) whereas from a " carbinol-producing " scission ethanol and methylheptenone (II) would be obtained. If, therefore, the scission of geraniol is comparable with that of the other ethylenic carbinols, methylheptenol may be a *primary* product of the scission, not derived by reduction of methylheptenone; the formation of the latter as a primary product would involve the mechanism of Scheme A rather than Scheme B.

Reference must also be made to the action of alkali on the βγ-ethylenic alcohol, *iso*pulegol (IX), which gives 3-methyl*cyclo*hexanol (XI) (*Ber. Schimmel*, 1913, October, p. 91). This evidently proceeds by initial isomerisation into pulegol (X); the formation of (XI) can then be

(IX.)   (X.)   (XI.)
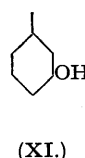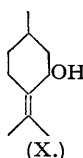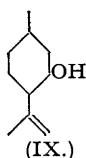
explained either by a direct scission of Type A, or by a scission of Type B, in which case the primary products, 3-methyl*cyclo*hexanone and *iso*propyl alcohol, would interact to give 3-methyl*cyclo*hexanol and acetone.

The investigations described in the present paper are being extended to simple βγ-ethylenic carbinols.

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

Oct-2-*en*-4-*ol*.—To a stirred ethereal solution of butylmagnesium bromide (from 24 g. of magnesium), freshly distilled crotonaldehyde (70 g.), in ether, was added dropwise during 1 hour, with ice cooling. After being stirred for a further hour at 0°, the complex was decomposed by the addition of ammonium chloride (120 g.) and ice, and dilute sulphuric acid was added to break the emulsion. The ethereal layer

was removed, the aqueous portion was extracted with fresh ether, and the combined extracts were washed, dried, evaporated, and distilled to give oct-2-en-4-ol (85 g., 66%) as a mobile oil, b. p. 83°/20 mm., 175°/760 mm., $n_D^{15°}$ 1·4435 (Hurd, Greengard, and Pilgrim, *J. Org. Chem.*, 1937, **2**, 381, obtained a 55% yield; cf. also Karasev and Khabarova, *J. Gen. Chem. Russia*, 1940, **10**, 1641). No phenylurethane could be obtained from the carbinol, which appeared to dehydrate on standing with phenyl *iso*cyanate, but it gave a 3 : 5-*dinitrobenzoate*, which crystallised from aqueous alcohol in plates, m. p. 54° (Found : N, 8·25. $C_{15}H_{18}O_6N_2$ requires N, 8·7%).

Alkaline Degradation of Oct-2-en-4-ol.—(i) The alcohol was recovered almost quantitatively after refluxing, with vigorous stirring, with 40% sodium hydroxide or 60% potassium hydroxide for 3 hours. Scission therefore does not occur below 175°.

(ii) Oct-2-en-4-ol (50 g.), potassium hydroxide (220 g.), water (150 c.c.), and stearic acid (0·5 g., emulsifier) were heated in a rocking autoclave at 240° for 3 hours. After cooling, hydrogen (3·5 l.) was released, and the contents of the autoclave dissolved in water. The neutral products, isolated by ether extraction, gave a fraction (16·5 g.), b. p. 134—148°, $n_D^{18°}$ 1·4170, consisting mainly of methyl-*n*-butyl-carbinol, identified as the α-naphthylurethane, m. p. and mixed m. p. 61°; it also contained 8% of methyl *n*-butyl ketone, estimated as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 106° (for method of estimation, see Part I, p. 752). The yield of carbinol was thus 15 g.(38%), agreeing well with the 40% yield of hydrogen. A high-boiling fraction (10 g.), b. p. 150—220°/20 mm., was not further investigated. The aqueous residues, acidified with sulphuric acid, and extracted with ether, gave a fraction (1 g.), b. p. 100—120°, consisting largely of acetic acid, identified as the *p*-bromophenacyl ester, m. p. 85°.

6-Ethyldec-6-en-5-ol.—To a stirred ethereal solution of *n*-butylmagnesium bromide (from 24 g. of magnesium), cooled to 10°, was added freshly distilled 2-ethylhex-2-en-1-al (126 g.) in an equal volume of ether, during 1 hour. The mixture was stirred for a further hour and then refluxed for ½ hour, cooled to 0°, and the complex decomposed by the addition of ammonium nitrate (180 g.) and ice. After acidification with dilute sulphuric acid, ether extraction yielded 6-*ethyldec-6-en-5-ol* (122 g., 66%), b. p. 120—122°/10 mm., 225°/760 mm., $n_D^{16°}$ 1·4563 (Found : C, 78·1; H, 12·95. $C_{12}H_{24}O$ requires C, 78·2; H, 13·1%). No phenylurethane could be obtained, dehydration occurring on treatment with phenyl *iso*cyanate.

Alkaline Degradation of 6-Ethyldec-6-en-5-ol.—(i) The compound (20 g.), potassium hydroxide (24 g.), water (16 c.c.), and stearic acid (0·3 g.) were heated in a "Pyrex" flask immersed in an oil-bath maintained at 190—200°. The flask was fitted with a mercury-sealed stirrer, inlet tube, and condenser, receivers being arranged to collect both liquid and gaseous products. After 10 c.c. of water had distilled, water was allowed to enter the reaction flask at a rate equal to that at which it was collected. Heating was maintained for 4 hours, after which the distillate, consisting of water (60 c.c.) with an upper immiscible liquid (15 c.c.), was extracted with ether. The extracts were washed and dried, and, after careful evaporation of solvent, distillation yielded 3 main fractions : (a) 1·5 g., b. p. 100—130°, $n_D^{17°}$ 1·4035; (b) 3 g., b. p. 166—168°, $n_D^{17°}$ 1·4184; (c) 5 g., b. p. 113—121°/13 mm., $n_D^{19°}$ 1·4518. Fraction (a) consisted largely of *n*-butanol, identified as the α-naphthylurethane, m. p. and mixed m. p. 71°. Fraction (b) was *n*-propyl *n*-butyl ketone, and gave the 2 : 4-dinitrophenylhydrazone, m. p. 38°, not depressed on admixture with an authentic specimen, m. p. 41° (cf. Part I, p. 752). Fraction (c) was unchanged ethyldecenol. The yields of *n*-butanol and *n*-propyl *n*-butyl ketone were thus 19% and 22% respectively, uncorrected for recovered ethylenic carbinol. The residue in the reaction flask was acidified with dilute sulphuric acid and extracted with ether, which yielded a small quantity of unchanged ethyldecenol, but no trace of acid products; the complete absence of the "carbinol-producing" scission was also indicated by the observation that no hydrogen was evolved during the reaction.

(ii) 6-Ethyldec-6-en-5-ol (50 g.), potassium hydroxide (220 g.), water (150 c.c.), and stearic acid (0·5 g.) were heated in a rocking autoclave for 3 hours at 240°. Hydrogen (2·75 l.) was then released from the cooled vessel, after which the neutral and acid products were isolated as previously described. The former, on distillation, gave (a) 0·5 g., b. p. 100—140°, containing *n*-butanol, identified as the α-naphthylurethane, m. p. 71°; (b) 17 g., b. p. 168—178°, $n_D^{18°}$ 1·4250, a mixture of *n*-propyl-*n*-butyl-carbinol (α-naphthylurethane, m. p. 61—62°) with 35% of *n*-propyl *n*-butyl ketone, estimated as the 2 : 4-dinitrophenylhydrazone, m. p. 41°; (c) 20 g. of high-boiling residue, b. p. > 200°, which was not further investigated. The acid products on distillation gave *n*-butyric acid (5 g.), b. p. 71—78°/16 mm., identified as the *p*-bromophenacyl ester, m. p. and mixed m. p. 62°. The yields of *n*-propyl-*n*-butyl-carbinol, *n*-butyric acid, and hydrogen were thus 31%, 21%, and 45% respectively.

Attempted Preparation of 5-Ethyltetradec-4-en-6-ol.—*n*-Octylmagnesium bromide was prepared from *n*-octyl bromide (97 g.) and magnesium (12 g.) in ether, the reaction being completed by refluxing for ½ hour. 2-Ethylhex-2-en-4-al (63 g.) was added to the cooled solution, and the product isolated by the procedure already described. On distillation it yielded a liquid (79 g., 68%), b. p. 166°/23 mm., $n_D^{18°}$ 1·4682, which showed unsaturation towards bromine water and neutral permanganate, and was recovered unchanged after treatment at 250° with concentrated sodium or potassium hydroxide solution. It was probably di-(5-ethyltetradec-4-en-6-yl) *ether* (Found : C, 83·45; H, 13·5. $C_{16}H_{32}O$ requires C, 79·9; H, 13·4; $C_{32}H_{62}O$ requires C, 83·05; H, 13·5%).

n-*Propyl*-n-*octylcarbinol.*—To a stirred ethereal solution of *n*-octylmagnesium bromide (from 2·3 g. magnesium) was added *n*-butaldehyde (7 g.) in ether, during 10 minutes. After being stirred for 2 hours, the mixture was refluxed for ½ hour, cooled to 0°, and decomposed with ice and ammonium chloride (15 g.). Isolation with ether gave n-*propyl*-n-*octylcarbinol* (6 g., 35%), b. p. 130—132°/19 mm., $n_D^{18°}$ 1·4365 (Found : C, 77·2; H, 13·8. $C_{12}H_{26}O$ requires C, 77·35; H, 14·05%).