391. *Reactions of Unsaturated Compounds. Part X.* The Oxidation of Camphene by Chromic Oxide.*

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(±)-Camphene is oxidised by chromic oxide in acetic anhydride, to give camphene oxide as the first product. Camphene oxide is reduced by lithium aluminium hydride in ether to 2-methylcamphenilol.

TREIBS and SCHMIDT (*Ber.*, 1928, **61**, 464) reported that oxidation of camphene by chromium trioxide in acetic anhydride gave camphenilone, camphenilanic acid, and probably camphenilanaldehyde. Our experience of this type of oxidation with 2 : 4 : 4-trimethylpent-1- and -2-ene and with di*neo*pentylethylene (*J.*, 1948, 1334; 1951, 1600) suggests that neither the acid nor the aldehyde is a primary product of the oxidation, but that they result from the initial formation of an epoxide which isomerises under the conditions used by Treibs and Schmidt to an aldehyde and thence by oxidation to the acid.

Oxidation of camphene by chromic oxide in acetic anhydride, with such modification of Treibs and Schmidt's technique as was considered necessary to prevent isomerisation of the epoxide, gave camphene oxide and a high-boiling complex mixture.

The satisfactory identification of camphene oxide by comparison of melting points is difficult owing to the existence of stereoisomeric forms. The recorded melting points for (±)-camphene oxide are 86—88° (Arbusov, *J. Gen. Chem. Russia*, 1939, 255) and 96—104° with semi-solid and liquid products (Hückel and Kirschner, *Chem. Ber.*, 1947, **80**, 46). Crude (±)-camphene oxide, prepared from (±)-camphene by oxidation with perbenzoic acid, gave on sublimation at 25 mm., two batches, (*a*) m. p. 84—86° and (*b*) m. p. 78—92°, resolved by chromatography into fractions, m. p. 84—86° and 96—98°, but no further separation could be obtained. It is unlikely that these differences in melting point can be due to partial isomerisation to camphenilanaldehyde, m. p. 76°, during the separation, since no detectable amount of camphenilanol could be obtained from the reduction of the epoxide (see below).

Each of the fractions isomerised to camphenilanaldehyde under the influence of acids. Attempts to hydrate the epoxides by boiling aqueous alcohol for 24 or 60 hr. gave no glycol but only camphenilanaldehyde. The camphene oxide was identified by reduction in ether with lithium aluminium hydride. A mixture of tertiary alcohols was obtained from which only 2-methylcamphenilol could be characterised (as *p*-nitrobenzoate). The presence of camphene hydrate was inferred from the melting point of some of the fractions resulting from chromatography of the crude alcohol, but attempts to isolate it were unsuccessful. The preparation of crystalline esters of camphene hydrate is difficult and gives poor yields (cf. Hückel, *Annalen*, 1941, **549**, 201). In the reduction product, no camphenilanol could be detected, although this alcohol forms a *p*-nitrobenzoate readily and with ease. The

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absence of noticeable amounts of this alcohol excludes the presence of an appreciable amount of camphenilanaldehyde in the camphene oxide.

A search was made for camphenilone among the oxidation products. It was first established that the 2 : 4-dinitrophenylhydrazones of camphenilone and camphenilanaldehyde could be separated by chromatography on alumina. These fractions of the oxidation product which might be expected to contain camphenilone were converted into 2 : 4-dinitrophenylhydrazones in acid aqueous alcohol, any epoxide present being thus isomerised to camphenilanaldehyde. Camphenilone could not be detected.

EXPERIMENTAL

Preparation of (±)-*Camphene Oxide.*—Reaction of (±)-camphene (15·6 g.) in chloroform (20 ml.) with a solution of perbenzoic acid (23·1 g.) in chloroform (430 ml.) at 0° was substantially complete in 45 min. The crude epoxide, b. p. 87—96/25 mm., was separated by sublimation at 25 mm. into fractions, (a) m. p. 84—86° (3·6 g.) and (b) m. p. 78—92° (5·4 g.), which on chromatography on alumina from 1 : 1 benzene–light petroleum (b. p. 40—60°), with elution by ether, gave fractions, m. p. 94—98°, 96—98°, 92—100°, 94—96°, and 84—86°, respectively. Each fraction, with a warm aqueous acid solution of 2 : 4-dinitrophenylhydrazine, gave the 2 : 4-*dinitrophenylhydrazone*, yellow needles (from alcohol), m. p. 151°, of camphenilanaldehyde (Found : C, 57·7; H, 6·5; N, 16·9. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·1; N, 16·9%).

Aqueous mineral acid isomerised the epoxide to aldehyde, with no evidence of hydration.

Reduction of Camphene Oxide.—A solution of the oxide (8·0 g.) in dry ether (50 ml.) was added dropwise to an ethereal solution of lithium aluminium hydride (1·1 g.) at such a rate that the stirred solution gently refluxed. The reduction was completed by 30 min.' further boiling. The solution was then poured on ice and sufficient dilute sulphuric acid to give two homogeneous layers. The ethereal layer was added to ethereal extracts of the aqueous solution. Evaporation of the washed ethereal solution gave a semi-solid product (8·0 g.) with a smell unlike that of the oxide. It did not react with an acid solution of 2 : 4-dinitrophenylhydrazine, showing the absence of unchanged epoxide. The alcoholic product (Found : C, 77·5; H, 12·0. Calc. for $C_{10}H_{18}O$: C, 77·9; H, 11·8%) consisted mainly of 2-methylcamphenilol. The absence of any appreciable amount of camphenilanol was shown by converting the crude alcohol into the *p*-nitrobenzoate and chromatographing this on alumina [light petroleum (b. p. 40—60°)–benzene]. The *p*-nitrobenzoate, m. p. and mixed m. p. 143°, of 2-methylcamphenilol was the only product. The presence of camphene hydrate in the product of reduction was suggested by chromatographing the crude mixture (Al_2O_3; light petroleum), which gave fractions with m. p. from 95—120° to 125—139°. But no more effective separation of the higher-melting solid could be obtained, nor could a crystalline derivative of camphene hydrate be prepared from it.

Oxidation of Camphene by Chromium Trioxide in Acetic anhydride.—(a) *Isolation of camphene oxide.* The following is typical of a number of oxidations, in which 25—75 g. of camphene were used. Chromium trioxide (19 g.) in acetic anhydride (170 ml.) was added slowly to a stirred solution of camphene (50 g.) in carbon tetrachloride (200 ml.) cooled in ice–salt. After 2 hr. the product was hydrolysed, while still in an ice-bath, by ice and aqueous sodium hydroxide (80 g. in 400 ml.). Any precipitate was removed by the addition of just sufficient acetic acid. The aqueous layer was extracted rapidly with ether. The combined carbon tetrachloride layer and ethereal extracts were thoroughly shaken with aqueous alkali before being dried. Distillation gave camphene (29 g.), crude camphene oxide (4·1 g.), b. p. 60—86/22 mm., and a high-boiling residue (A) (3·5 g.).

The crude oxide was freed from a small amount of admixed camphene by chromatography on alumina to give a specimen, m. p. 76—84° (Found : C, 79·0, 79·1; H, 10·5, 10·4. Calc. for $C_{10}H_{16}O$: C, 78·9; H, 10·6%). Its identity was established by comparison with authentic camphene oxide, by isomerisation by dilute sulphuric acid to camphenilanaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 151°), and by reduction by lithium aluminium hydride to 2-methylcamphenilol (*p*-nitrobenzoate, m. p. and mixed m. p. 143—144°).

(b) *Attempted isolation of camphenilone.* The fractions intermediate in b. p. between camphene and camphene oxide might have contained camphenilone. They were treated with 2 : 4-dinitrophenylhydrazine in aqueous-alcoholic sulphuric acid and the resulting dinitrophenylhydrazones chromatographed as described below. Only the derivative of camphenilanaldehyde was obtained.

An artificial mixture of the 2 : 4-dinitrophenylhydrazones (100 mg. each) of camphenilone and of camphenilanaldehyde was absorbed on alumina from a 2 : 1 (v/v) light petroleum (b. p. 40—60°)-benzene. Development with 19 : 1 (v/v) light petroleum (b. p. 40—60°)-ether gave two bands; the lower gave camphenilone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 161°; the upper gave the derivative, m. p. and mixed m. p. 151°, of camphenilanaldehyde.

No separation was observed on a silica column (cf. Roberts and Green, *Ind. Eng. Chem. Anal.*, 1946, **18**, 335).

Camphenilone was prepared from camphene by the method described by Snitter (*Bull. Soc. Pin.*, 1933, [2], 178. *Brit. Abs.*, 1933, 1300) and Blaise (*Bull. Soc. chim.*, 1900. **23**. 164). It gave a 2 : 4-*dinitrophenylhydrazone*, orange needles (from ethyl alcohol), m. p. 161° (Found : C, 56·6; H, 5·7; N, 17·4. $C_{15}H_{18}O_4N_4$ requires C, 56·6; H, 5·7; N, 17·6%).

(c) *The high-boiling residues.* The combined residues (A) from all the camphene oxidations were distilled at 1 mm., giving viscous unsaturated liquids boiling between 60° and 150°, which could not be separated. The fractions boiling up to 100°/1 mm. gave smaller or greater amounts of a 2 : 4-*dinitrophenylhydrazone*, needles (from aqueous acetic acid), m. p. 222—223°, almost insoluble in ether or ethyl alcohol (Found : C, 55·9; H, 5·4; N, 15·8. $C_{16}H_{18}O_5N_4$ requires C, 55·5; H, 5·2; N, 16·2. $C_{16}H_{16}O_5N_4$ requires C, 55·8; H, 4·7; N, 16·3%).

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