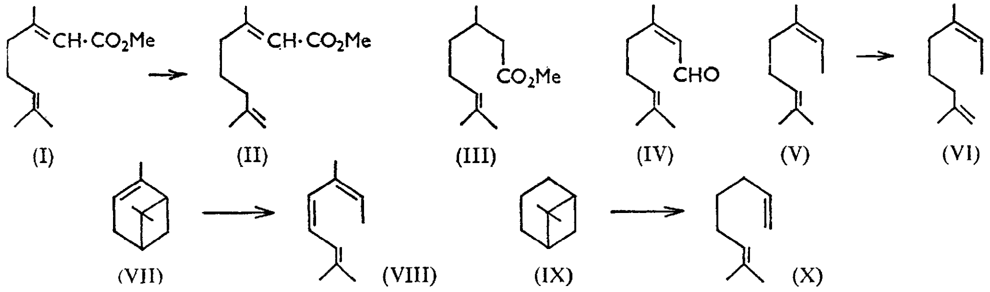
31. *The Thermal Isomerisation of Methyl Geranate and Dihydromyrcene.*

By G. A. Howard and R. Stevens.

When heated at 530° for 2 seconds, methyl geranate and dihydromyrcene undergo conversion of the isopropylidene into an isopropenyl group. Methyl citronellate is unaffected under these conditions.

Spectroscopic investigations [1] have shown that, contrary to earlier chemical evidence, the common natural alicyclic terpenes and their derivatives exist almost exclusively in the isopropylidene form. In these laboratories we have found that isopropylidene groups in alicyclic terpenoids are sometimes thermolabile (contrast Egloff *et al.*[2]).

During other work, information was sought about the infrared spectrum and gas-chromatographic behaviour of methyl geranate (I). Commercial citral which appeared by gas chromatography to be a mixture of two forms,[3] was accordingly oxidised with moist silver oxide,[4] and the resulting mixed acids were esterified with diazomethane and distilled. Gas chromatography then disclosed two esters, presumably the *cis*- and the *trans*-form (I), a comparison of its infrared absorption with those of other derivatives of geranic acid [1a] supporting this assumption. Separation on a preparative scale afforded two esters having infrared spectra such as were to be expected for these *cis*- and *trans*-forms.[5] The spectra, however, differed from that of the material before gas chromatography: the absorption bands at 5·78 (ester C=O) and 6·03 μ (C=C) were unaffected, but the samples isolated from the column had bands at 5·58 and 11·12 μ whereas the original mixed esters had no absorption at these wavelengths but showed bands at 11·50 and 11·66 μ. These facts are consistent [5] with the presence of isopropenyl and αβ-unsaturated ester groupings in the separated esters and of the isopropylidene grouping in the ester (I). Passage through the gas-chromatography equipment had thus brought about the isomerisation (I) ⟶ (II) and since this change has not been encountered before its cause was sought.



(I) (II) (III) (IV) (V) (VI)

(VII) (VIII) (IX) (X)

During gas chromatography, the sample passed through (*a*) an inlet flash-heater, (*b*) a column maintained at temperatures varying from 137° to 188°, (*c*) the detector, and (*d*) an exit heater. Passage through sections (*a*), (*b*), and (*c*), alone or together, failed to

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[1] (*a*) Thompson and Whiffen, *J.*, 1948, 1412; Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland, *J.*, 1950, 915; (*b*) Carroll, Mason, Thompson, and Wood, *J.*, 1950, 3457; (*c*) Naves, *Bull. Soc. chim. France*, 1951, 505.

[2] Egloff, Hulla, and Komarewsky, "Isomerisation of Pure Hydrocarbons," Reinhold, New York, 1942.

[3] Liberti and Cartoni, "Gas Chromatography 1958," Butterworths, London, 1958, 321; Naves and Odermatt, *Bull. Soc. chim. France*, 1958, 377.

[4] Bernhauer and Forster, *J. prakt. Chem.*, 1936, **147**, 199.

[5] Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 1954, pp. 31—46, 156—163.

effect rearrangement when the temperature of the inlet flash-heater was 275°. Rearrangement took place, however, during the two seconds taken by the material to pass through the exit heater, the temperature of which was found to be 530°. No detectable change took place when chromatography was carried out with this heater at 250° or when methyl geranate was heated for 20 minutes at 180° in a sealed tube. The transformation (I) $\longrightarrow$ (II) thus occurs rapidly at 530° but not at 275°, irrespective of the stereochemistry of the $\alpha\beta$-unsaturated ester groupings.

Methyl citronellate (III) was unaffected by the conditions which caused isomerisation of methyl geranate, the infrared absorption of all the samples examined indicating substantial absence of the isopropenyl form [1c] (the ester was prepared by oxidising citronellal and esterifying the acid with acidified methanol). The spectroscopic evidence suggests that neither citronellic acid not its ester is as readily isomerised by acid as is citronellol.[1c] The infrared spectrum of citral (IV) was unaffected by gas chromatography when the exit heater was at 230°, but when the heater was at 530° the carbonyl absorption at 6 μ was markedly reduced, so the product was not further examined. Reduction of technical myrcene by sodium and alcohol gave a mixture of five compounds from which the preponderant constituent, dihydromyrcene, was isolated by gas chromatography, the exit heater being at 230°. The infrared absorption of this product was consistent with structure (V). Further chromatography with the exit heater at 530° altered the absorption: bands at 5·6, 6·08, 6·25, 11·0, and 11·2 μ were much stronger than in the original dihydromyrcene, new bands had appeared at 12·05, 12·4, 12·95, 13·7, and 14·4 μ and those at 5·95, 9·6 and 12·6 μ disappeared. These facts again suggest isomerisation (V) $\longrightarrow$ (VI) although rearrangement of the other double bond in (V) is not rigidly excluded.

Thermal rearrangements of an isopropylidene to an isopropenyl group in alicyclic terpenoids has not apparently been previously reported although this transformation can take place under acidic conditions.[1c] The available evidence [2] points to thermal, as distinct from catalytic, conversion of isopropenyl into isopropylidene groups rather than the reverse, as, for example, of ocimene into allo-ocimene and 2,5-dimethylhexa-1,5-diene into the 2,4-diene, *i.e.*, to a tendency to proceed towards the conjugated diene form. Cyclic terpenes, however, are converted by heat into compounds containing an isopropenyl group: thus α-pinene affords limonene,[6,7] pinane and norpinane afford isopropenylcyclopentanes,[8] and the stability of the isopropenyl group to heat is indicated by the stability of 1-isopropenyl-4-methylcyclohexane at 600°.[9] In general, however, thermal isomerisation of cyclic hydrocarbons to unsaturated acyclic hydrocarbons gives substances with isopropylidene rather than isopropenyl groups, as, for example, the conversion of α-pinene (VII) into allo-ocimene (VIII) and neoallo-ocimene,[7] and of 6,6-dimethylnorpinane (IX) into 7-methylocta-1,6-diene (X).[10] The results reported now show, however, that it cannot be assumed that the isopropylidene will always be more stable to heat than the isopropenyl group.

EXPERIMENTAL

Gas Chromatography.—The apparatus (Gas Chromatography Ltd., London) contained a column 180 cm. long, 1·5 cm. in internal diameter, having 84 g. of a mixture of Celite (60—80 B.S.S. mesh) and Apiezon M grease (15%; *i.e.*, 10·95 g. of grease in column) and was used at temperatures ranging from 137° to 188° (vapour-jacket). The eluting gas was hydrogen, usually at 180 ml. per min. and inlet pressures of 25 cm. A current of 120 mA. was passed through the katharometer detector wire (80 ohms resistance at 188°). The input flash-heater

[6] Goldblatt and Palkin, *J. Amer. Chem. Soc.*, 1941, **63**, 3517; Fuguitt and Hawkins, *ibid.*, 1945, **67**, 243.

[7] Alder, Dreike, Erpenbach, and Wicker, *Annalen*, 1957, **609**, 1.

[8] Pines, Hoffman, and Ipatieff, *J. Amer. Chem. Soc.*, 1954, **76**, 4412.

[9] Frank and Berry, *ibid.*, 1950, **72**, 2988.

[10] Pines and Hoffmann, *ibid.*, 1954, **76**, 4417.

used to vaporise the sample was at 230°, and the heater at the exit from the katharometer chamber at various temperatures as reported above. The exit heater was a " Pyrex " glass tube, 1 cm. in diameter, 5 cm. long, heated externally by a resistance winding. Specific retention volumes (*Vg*) were calculated by the method recommended by Ambrose *et al.*[11]

Methyl Geranate.—Citral (20 g.; B.D.H.; redistilled; b. p. 107—110°/10 mm.) was oxidised with moist silver oxide,[4] and the resulting crude geranic acid (19·5 g.) converted by ethereal diazomethane into the methyl ester, b. p. 122—125°/17 mm., n_D^{20} 1·4696 (lit.,[12] b. p. 117°/14 mm., n_D^{20} 1·4714). Gas chromatography showed the presence of two components (*Vg* 476 and 650, respectively, at 137°, 99 and 126 at 170°, and 59 and 71 at 188°).

Methyl Citronellate.—Citronellal (Hopkins and Williams Ltd.; redistilled; b. p. 114—116°/27 mm.) was oxidised as for citral, to citronellic acid which with methanolic sulphuric acid gave methyl citronellate, b. p. 116—128°/11 mm., n_D^{20} 1·4360. Gas chromatography indicated the presence of one compound (*Vg* 156 at 170°).

Dihydromyrcene.—Reduction of technical myrcene (A. Boake, Roberts, & Co. Ltd.) with sodium and alcohol [13] afforded material from which dihydromyrcene (*Vg* 23 at 170°) was isolated by gas chromatography.

Infrared Spectra.—The mixture of methyl *cis*- and *trans*-geranate isolated by preparative gas chromatography under conditions avoiding isomerisation had absorption bands in carbon tetrachloride solution at 3·41s, 3·50infl.,m, 5·82s, 6·09m, 6·99m, 7·28w, 7·38w, 7·56w, 7·82infl.,w, 8·19s, 8·64s, 8·72s, 9·03w, 9·80w, 10·16w, 10·82w, 11·50infl.,w, and 11·66m μ.

After passage through the preparative gas-chromatography column and the heater at 530° the bands were at 3·38s, 3·45infl.,m, 5·58s, 5·70infl.,m, 5·78s, 6·04m, 6·92m, 7·22w, 7·34w, 7·62w, 7·80infl.,w, 8·0infl.,m, 8·11s, 8·34m, 8·64s, 9·0w, 9·48w, 9·61w, 9·86w, 10·05w, 10·80w and 11·12m μ.

Methyl citronellate, examined as the liquid, had bands at 3·42s, 5·78s, 6·87 and 6·99m, 7·27 and 7·35m, 7·79m, 8·0m, 8·25infl.,m, 8·40s, 8·50 and 8·60infl.,s, 9·20s, 9·85m, 11·31m, 11·85m, and 13·55m μ.

Dihydromyrcene, examined as the liquid, had bands at 3·35s, 3·65w, 5·6w, 5·95m, 6·08m, 6·25w, 6·9s, 7·25s, 8·25w, 8·65w, 9·0m, 9·6w, 10·05m, 11·0m, 11·2s, 11·9infl.,m, 12·05m, 12·6m, and 13·45w μ.

After passage through the gas-chromatography apparatus with the exit heater at 530°, the recovered " dihydromyrcene " (examined as the liquid) had bands at 3·35s, 3·65w, 5·6s-m, 6·08m, 6·25m, 6·9s, 7·25s, 8·25w, 8·65w, 9·0w, 10·05m, 10·35w, 11·0infl.,s, 11·2s, 11·9infl.,m, 12·25infl.,m, 12·35m, 12·96w, 13·45w, 13·68m, and 14·4w μ.

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[11] Ambrose, Keulemans, and Purnell, *Analyt. Chem.*, 1958, **30**, 1582.
[12] Auwers and Eisenlohr, *J. prakt. Chem.*, 1911, **84**, 25.
[13] Semmler, *Ber.*, 1901, **34**, 3126.