317. *Geraniolenes. The Decomposition of 2 : 6-Dimethylhept-5-en-2-ol and Some Derivatives thereof.*

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The mixtures obtained by dehydration of 2 : 6-dimethylhept-5-en-2-ol, by equivalent dehydrohalogenations, and by decarboxylation of geranic acid have been analysed. The first process usually yields olefins containing tetrahydro-2 : 2 : 6 : 6 : tetramethylpyran. Pure 2 : 6-dimethylhepta-2 : 5-diene has been isolated and characterised. Spectroscopic data on this diene, its $\Delta^{2:6}$-, $\Delta^{2:4}$-, $\Delta^{1:3}$-, and cyclic isomers, and on the above mentioned pyran are reported.

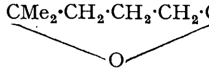
The nature of the identical or very similar olefinic materials ("geraniolene") obtained by the dehydration of dimethylheptenol (I; X = OH), by decarboxylation of geranic acid, and by other related procedures has remained in doubt from the time of Tiemann

$$\text{(I)}\quad \mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}X} \qquad\qquad \mathrm{CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}Me}\quad \text{(II)}$$

and Semmler's original preparation nearly sixty years ago (summarised in Simonsen and Owen, "The Terpenes," Cambridge Univ. Press, 2nd Edn., 1947, pp. 7—9). Difficulty arises because the elimination of HX from (I) can lead to (III), (IV), and alkylated *cyclo*-hexenes, and the identification, separation, interconvertability, and proneness to secondary reactions of these isomers have been subject to uncertainty. The possibilities of isomeric

$$\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH{:}CMe_2} \qquad\qquad \mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2}$$

(III) (IV)



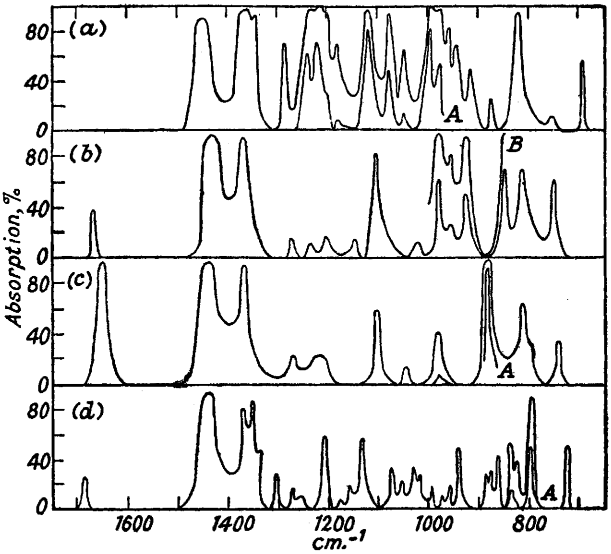
(V)

complexity are further increased if the acyclic monoterpenes are more or less inseparable mixtures of *iso*propylidene and *iso*propenyl structures, *e.g.*, if geranic acid consists of $\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CO_2H}$ and $\mathrm{CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CO_2H}$, and the methylheptenone which is the precursor of (I) is admixed with (II) (Simonsen and Owen, *op. cit.*, pp. 2—4; cf. also Grignard and Doeuvre, *Bull. Soc. chim.*, 1929, [iv], **45**, 809). The latter complication, however, can now be disregarded as physico-chemical investigations have recently established that no detectable proportion of the *iso*propenyl form occurs in the natural compounds of present interest (Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland, *J.*, 1950, 915). Furthermore, the infra-red spectroscopic method of structure analysis, soundly based in the acyclic terpene field, now provides a more direct and unequivocal means of recognising and estimating isomeric olefins than the older methods involving oxidative degradation (Barnard *et al.*, *loc. cit.*). By this means, the compositions of several geraniolene preparations have been determined approximately quantitatively, and earlier inferences (Auwers and Moosbrügger, *Annalen*, 1912, **387**, 183; Simonsen and Owen, *op. cit.*, pp. 8—9) that these are invariably heterogeneous are confirmed. Our primary purpose of isolating pure (III) has been realised; its particularly interesting autoxidation characteristics will be described elsewhere.

Dehydration of (I; X = OH) with a number of reagents yields products which after repeated distillation from sodium fail to give analyses accurate for C_9H_{16} and contain 0·5—2·0% of oxygen; iodine is exceptional in giving a figure as high as 6% (see Experimental). The infra-red spectra show strong absorption at 885 and 1650 cm.$^{-1}$, indicating the presence of $CR_2{:}CH_2$ groups (Barnard *et al.*, *loc. cit.*) and thus that (IV) is a major constituent, and weaker absorption at 815 cm.$^{-1}$ (associated with $CR_2{:}CHR$ groupings); they fail to specify any functional groups attributable to the oxygenated material. This material must therefore be either bismethylheptenyl ether or tetrahydro-2 : 2 : 6 : 6-tetramethylpyran (V). The pyran is the known "methylcinene" (Rupe and Schlochoff, *Ber.*, 1905, **38**, 1498); it has almost the same boiling point as the dehydration product and was virtually proved to be the contaminant by elementary analysis and unsaturation data. Rigorous proof was provided by infra-red spectral comparisons (cf. Fig. 1*a* for the pure compound). Its formation finds analogies in other terpenoid and *pseudo*-terpenoid systems (see Clemo and Davison, *J.*, 1951, 447), but was overlooked in the present example by the earlier workers.

Infra-red absorption spectra. Path-length, 0·05 *mm., except where indicated A* (0·01 *mm.*) *or B* (0·1 *mm*).

a, 2 : 2 : 6 : 6-*Tetramethyltetrahydropyran.*
b, 2 : 6-*Dimethylhepta*-2 : 5-*diene.*
c, 2 : 6-*Dimethylhepta*-2 : 6-*diene.*
d, cyclo*Geraniolene.*



Sometimes, and inexplicably, a non-oxygen containing olefin C_9H_{16} was obtained on dehydration with anhydrous oxalic acid; this was found to consist largely of *cyclo*geraniolene (possibly α- and β-) admixed with acyclic heptadienes (cf. Harries and Weil, *Ber.*, 1904, **37**, 848).

Differing from the above, pyrolysis of geranic acid and of dimethylheptenyl acetate (I; X = OAc) and dehydrohalogenation of the corresponding chloride or bromide (I; X = Cl or Br), yield mixtures of (III) and (IV). The product from geranic acid consists almost entirely of (IV) (contrast Grignard and Doeuvre, *loc. cit.*) whereas more nearly equal quantities result from the other reactions. The infra-red spectra of, for example, the dehydrohalogenation products are distinctly "cleaner" than those of the dehydration products. The pure components were isolated by fractionation of such mixtures through a 40-plate column, and were characterised by their infra-red spectra (Figs. 1*b* and *c*) and by the following properties: (III), b. p. 150—151°/756 mm., n_D^{20} 1·4490; (IV), b. p. 141—142°/756 mm., n_D^{20} 1·4388; those of (IV) were in excellent agreement with Henne and Chanan's data for a synthetic specimen (*J. Amer. Chem. Soc.*, 1944, **66**, 392). The difference in n_D affords the simplest means of analysing the composition of a binary mixture: when (V) or similar substances are present, the proportion of (IV) may be determined from the absorption intensity at 885 cm.$^{-1}$, or (III) may be estimated from the amount of conjugated diene produced by hot alkali, as discussed below.

When (III) is heated with potassium hydroxide in methyl alcohol at 165°, isomerisation occurs and light absorption properties are finally developed ($\lambda_{max.}$ 2370 Å, $\varepsilon = 26{,}100$) which empirical reasoning associates with the 1 : 1 : 4-trialkylbutadiene (VI) (Booker, Evans, and Gillam, *J.*, 1940, 1453; Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72).* This extensive conjugative change is to be contrasted with the equlilibrium $Ph{\cdot}CH_2{\cdot}CH{:}CMe_2$ (43%) $\rightleftharpoons$ $Ph{\cdot}CH{:}CH{\cdot}CHMe_2$ (57%) prevailing under the same conditions (Bateman and Cunneen, *J.*, 1951, 2283), and reflects the substantially greater resonance energy of the butadienoid compared with the styryl unit. It is of interest that (VI) could not be obtained from the alcohol (VII), which on dehydration yields an olefinic mixture consisting largely of (VIII), this behaviour simulating that of the quaternary salts of analogous bromides (Bateman, Cunneen, and Koch, *J.*, 1950, 3051). A concentrated fraction of (VIII) showed maximum ultra-violet light absorption at a wave-length (2300 Å, $\varepsilon = 23{,}000$) significantly shorter than that of (VI) but in the region typical of 1 : 3-dialkylbutadienes (Booker *et al.*, *loc. cit.*). The structural distinction between (VI) and (VIII) is further indicated by their infra-red spectra (see Experimental).

$CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CHMe_2$ (VI)

$CMe_2{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CHMe_2$ (VII)

$CH_2{:}CMe{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CHMe_2$ (VIII)

The compounds (IV), (V), and any cyclic mono-olefins are inert under the isomerisation conditions described, and hence the percentage of (III) in a mixture containing one or more of these is readily obtained as $100E^{1\%}_{1\,cm.}/2100$, where $E^{1\%}_{1\,cm.}$ expresses the absorption intensity as 2370 Å developed on the isomerisation treatment. Several synthetic mixtures were tested to check the validity of this procedure.

EXPERIMENTAL

Dehydration of 2 : 6-*Dimethylhept*-5-*en*-2-*ol* (I; X = OH).—This structurally homogeneous alcohol, b. p. 75°/12 mm., n_D^{20} 1·4492 (Found: C, 75·9; H, 12·7. Calc. for $C_9H_{18}O$: C, 76·0; H, 12·7%), was heated at 140° with the dehydrating agent (at 180° with boric acid) under nitrogen, and the product isolated by ether-extraction, and finally distilled at least twice from sodium (b. p.'s 139—145°/760 mm.). Details of the experimental conditions and of the products are given in the table. The amount of (IV) present varied in the different preparations, but was always of the order of 50% (as indicated by the absorption intensity at 885 cm.$^{-1}$). On fractionation through a 15-plate column, (IV) and (V) tended to concentrate in the lower-boiling fractions, but these ternary mixtures proved unsuitable for separation of the pure components.

			Found				
Dehydrating agent	Time (hours)	n_D^{20}	C, %	H, %	O, % (diff.)	O, % (direct)	Content of (V) (%)
Oxalic acid * ...	1·5	1·4445	85·8	12·9	1·3	1·2	11
Boric acid	3	1·4438	86·8	12·5	0·7	0·5	5
$NaHSO_4$	1	1·4456	86·0	12·8	1·2	—	11
$CuSO_4$	2·5	1·4440	85·6	12·6	1·8	—	16
Ac_2O–$ZnCl_2$ ...	3	1·4449	86·8	12·9	0·3	0·3	3
Iodine †	3	1·4415	81·3	12·7	6·0	—	53

* Irreproducible; see text.
† Product contained approx. 20% of (III), 10% of (IV), and 20% of (VI).

A fractionated specimen from the boric acid treatment, b. p. 142·5—143·0°/757 mm., n_D^{20} 1·4414 (Found: C, 84·8; H, 12·6; O, 2·2%) was hydrogenated over Adams's catalyst: 35·2 mg. absorbed 10·35 ml. of hydrogen at N.T.P. The oxygen content is indicative of a methylcinene (V) content of 20%, the hydrogenation data of a value of 18·8%.

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* Previous data on this type of conjugated diene appear to be lacking. Following Ruzicka and van Veen (*Annalen*, 1929, **468**, 143), Booker *et al.* quoted zingiberene as an example, although they were at a loss to explain its low intensity ($\epsilon = 5300$ at $\lambda_{max.}$ 2355 Å). This sesquiterpene is now known, however, to be quite different in type, *viz.*, an alkenylated *cyclo*hexa-2 : 4-diene (Eschenmoser and Schinz, *Helv. Chim. Acta*, 1950, **33**, 171).

Tetrahydro-2 : 2 : 6 : 6-tetramethylpyran (" *Methylcinene* ").—Prepared according to the directions of Rupe and Schlochoff (*loc. cit.*), this compound had b. p. 143°/762 mm., n_D^{20} 1·4287 (Found : C, 76·0; H, 12·7. Calc. for $C_9H_{18}O$: C, 76·0; H, 12·7%).

Formation of cyclo*Geraniolene during the Dehydration of Dimethylheptenol* (I; X = OH).—The heptenol (5 g.) was heated with anhydrous oxalic acid (2 g.) at 140° for 1·5 hours. The isolated product (3·5 g.) had b. p. 138—141°/761 mm., n_D^{20} 1·4476 (Found : C, 86·9; H, 12·9%); 45 mg. absorbed 10·8 ml. of hydrogen at N.T.P., corresponding to $|^{=}$ 1·33 for C_9H_{16}. Its infra-red spectrum was very similar to that of a mixture of *cyclo*geraniolene prepared as below (70%) and equal proportions of the dimethylhepta-2 : 5- and -2 : 6-diene; (V) was absent. The reason for the variable dehydrating action of oxalic acid remains obscure; traces of moisture in the acid do not appear to be reponsible.

Pyrolysis of 2 : 6-Dimethylhept-5-enyl Acetate (I; X = OAc).—Prepared from the corresponding alcohol by acetic anhydride and zinc chloride, this acetate had b. p. 89—91°/13 mm., n_D^{20} 1·4382 (cf. Escourrou, *Bull. Soc. chim.*, 1926, **39**, 1121). On passage in a stream of nitrogen through a 75-cm. tube packed with glass wool at 480° during 15 hours, it yielded an olefin with b. p. 140—142°/757 mm., n_D^{20} 1·4412 (Found : C, 86·9; H, 12·9%). Infra-red spectroscopic examination confirmed the absence of methylcinene and indicated a 2 : 6-diene content consistent with the refractive index (77%; see p. 1715).

Decarboxylation of Geranic Acid.—The acid (30 g.), b. p. 108°/0·1 mm., n_D^{20} 1·4886 (containing <3% of $CR_2{:}CH_2$ groups, probably nil), was heated at atmospheric pressure so that a distillate passed over at <150°. After being dissolved in ether, washed with water, dried, freed from solvent, and distilled from sodium, the product (20 g.) had b. p. 141—143°/759 mm., n_D^{20} 1·4392 (Found : C, 87·1; H, 12·9%). The refractive index indicates a mixture of 96% of (IV) and 4% of (III) (see p. 1715), and consistently the infra-red spectrum was practically identical with that of pure (IV) (Fig. 1*c*).

cyclo*Geraniolene.*—A portion of the above specimen of geraniolene (essentially IV) was shaken with sulphuric acid for 8 hours (Wallach and Franke, *Annalen*, 1902, **324**, 114). The resulting *cyclo*geraniolene had b. p. 136—137°/765 mm., n_D^{20} 1·4457 [Found : C. 86·5; H, 12·9%; $|^{=}$ (hydrogenation), 0·97]. Its infra-red spectrum (Fig. 1*d*) is in accord with the α- or β-structure.

Dehydrochlorination of 6-Chloro-2 : 6-dimethylhept-2-ene (I; X = Cl).—This *chloride*, prepared in 42% yield from the corresponding alcohol by Hatch and Nesbitt's procedure (*J. Amer. Chem. Soc.*, 1950, **72**, 729), had b. p. 71—72°/15 mm., n_D^{20} 1·4493 (Found : C, 67·2; H, 10·6; Cl, 22·4. $C_9H_{17}Cl$ requires C, 67·3; H, 10·6; Cl, 22·2%). Its infra-red spectrum confirmed the absence of other than trisubstituted ethylene groupings. Some spontaneous dehydrochlorination occurred during this preparation, yielding as a forerun an olefin mixture (13%) rich in (III), b. p. 144—147°/753 mm., n_D^{20} 1·4463 (Found : C, 86·9; H, 13·0%). Deliberate dehydrochlorination was effected by heating the chloride (156 g.) with purified pyridine (350 ml.) at 140° for 20 hours. The crude olefinic product (108 g.) was distilled from sodium (Found : C, 86·9; H, 13·0%; $|^{=}$ (hydrogenation), 1·98. Calc. for C_9H_{16} : C, 87·0; H, 13·0%; $|^{=}$, 2·00) and then fractionated through a 40-plate column to yield : (i) 2 : 6-dimethylhepta-2 : 6-diene (37 g.), b. p. 141—142·0°/756 mm., n_D^{20} 1·4388 (Found: C, 86·9; H, 12·9%); (ii) (24 g.), b. p. 142·1—147·5°/754 mm., n_D^{20} 1·4414; (iii) (8 g.), b. p. 147·6—148·2°/754 mm., n_D^{20} 1·4472; (iv) (6 g.), b. p. 148·3°/754 mm.; (v) (20 g.), residue. The 2 : 5-diene contents of fractions (ii), (iii), and (iv) were 73, 12, and 3% respectively, as determined by infra-red analysis. On distillation of (v) from a small flask, *2 : 6-dimethylhepta-2 : 5-diene* was obtained, of b. p. 150—151°/758 mm., n_D^{20} 1·4490 (Found : C, 86·9; H, 12·9%; $|^{=}$, 2·01); contamination with its $\Delta^{2:6}$-isomer was <0·1%.

6-Bromo-2 : 6-dimethylhept-2-ene (I; X = Br).—The action of phosphorus tribromide (73 g.) on the corresponding alcohol (56 g.) gave this *bromide*, b. p. 76—77°/11 mm., n_D^{20} 1·4711 (Found : C, 52·6; H, 8·2; Br, 38·3. $C_9H_{17}Br$ requires C, 52·7; H, 8·3; Br, 39·0%), in rather poor yield (15%). It undergoes dehydrobromination in pyridine at 140°, to give an olefinic mixture similar to that obtained from the chloride (n_D^{20} 1·4431) (Found : C, 87·0; H, 12·9%).

Isomerisation of 2 : 6-Dimethylhepta-2 : 5-diene.—When the pure 2 : 5-diene was heated with methyl alcoholic potash at 165° (Bateman and Cunneen, *loc. cit.*), light absorption at 2370 Å steadily increased and reached a maximum after about 100 hours with ε = 26,100. Various olefinic mixtures behaved as follows :

Mixture	(III) 40% + (IV) 60%	(III) 70% + (IV) 30%	(III) 25% + (IV) 55% + (V) 20%
$E_{1\,cm.}^{1\%}$ at 2370 Å	837	1520	478
2 : 5-Diene content, estimated, %	40	72	23

Isolated from a large-scale isomerisation, (VI) had n_D^{20} 1·4650, and exhibited infra-red absorption at 814 and 958 cm.$^{-1}$, attributable to the presence of $CR_2{:}CHR$ and *trans*-CHR:CHR groups respectively.

2 : 6-*Dimethylhepta*-1 : 3-*diene*.—2 : 6-*Dimethylhept*-2-*en*-4-*ol*, b. p. 74—76°/12 mm., n_D^{20} 1·4410 (Found : C, 75·6; H, 12·7. $C_9H_{18}O$ requires C, 76·0; H, 12·7%), was obtained from β-methylcrotonaldehyde (Fischer, *Ber.*, 1943, **76**, 734) and *iso*butylmagnesium bromide. Dehydration of this alcohol with sodium hydrogen sulphate at 140° afforded the slightly impure 1 : 3-diene, b. p. 66°/13 mm., n_D^{20} 1·4569, $\varepsilon_{max.}$ (unchanged in hot alkali at 165° for 100 hours) = 23,000 at 2300 Å (Found : C, 86·0; H, 13·2%). Its infra-red spectrum showed strong absorption at 888 and 961 cm.$^{-1}$ attributable to the presence of $CR_2{:}CH_2$ and *trans*-CHR:CHR groupings, respectively (contrast the $\Delta^{2:4}$-isomer).

Spectroscopic Measurements.—The infra-red absorption spectra were determined with a Grubb-Parsons single-beam instrument, with the technique previously described (Barnard, Fabian, and Koch, *J.*, 1949, 2442). The ultra-violet absorption spectra were measured in ethanolic solution with either a Hilger Uvispek photoelectric spectrophotometer or a Hilger Small Quartz spectrometer and Spekker photometer by the usual methods.

This work forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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