457. *Isopropenyl and Isopropylidene Groups: The Terpene Problem.*

By T. OLIVER.

Dehydration of 2-methylnonadecan-2-ol and 2-methylnonan-2-ol gave, in each case, a mixture of the isopropylidene and isopropenyl isomer. The isopropylidene form always predominated. A chemical separation of the isopropylidene isomers was developed and the isopropenyl isomers were synthesised. The C_{10} olefin mixture was separated by gas–liquid chromatography.

THE structural problem of the simple natural acyclic monoterpenes[1] has recently been solved[2] with the aid of infrared spectra,[3] which showed that they exist almost entirely in the isopropylidene form. As the two isomers have not been studied side by side, attention was directed first to 2-methylnonadec-1-ene and 2-methylnonadec-2-ene and later to the corresponding C_{10} compounds.

Messer[4] regarded the dehydration product of 2-methylnonadecan-2-ol as 2-methylnonadec-1-ene alone, whereas other workers[5] found it to be solely 2-methylnonadec-2-ene. In the present study, dehydration of this tertiary alcohol was found to give a mixture of the two isomers. Quantitative infrared-absorption measurements on the carbon disulphide solution indicated that mixtures prepared by different routes contained more than 50% of the isopropylidene form.

Attempts to use physical methods to effect separation all failed as did several chemical methods. However, a chemical method of separation was developed based on the action of mercuric acetate.[6] The mixture was heated to 50—70° in propionic acid containing a small amount of mercuric acetate. The isopropenyl isomer was preferentially attacked, the course of the reaction being followed by the diminution of the strong 890 cm.$^{-1}$ infrared band. 2-Methylnonadec-1-ene was prepared by the action of hexadecylmagnesium iodide on 2-methylallyl chloride. Neither of the pure olefins showed any tendency towards interconversion when treated with cold dilute acid or alkali, or passage over alumina and distillation at 190°/10 mm. On the other hand, fairly rapid polymerisation occurred when thin layers of the olefins were exposed to air.

Dehydration of 2-methylnonan-2-ol with iodine gave a mixture, containing 70% of the isopropylidene isomer. It was not possible to prepare a sample containing more than 93% of the isopropylidene form because, in this case, it also reacted with the mercuric acetate. 2-Methylnon-1-ene was prepared in 40% yield by the Wittig–Schöllkopf reaction.[7] Again, no tendency towards interconversion was noticed. A gas–liquid chromatographic investigation of the $C_{10}H_{20}$ mixture showed that a sharp separation could be achieved by using a column of benzylbiphenyl (15%) on Embacil at 60°. The isopropylidene isomer was eluted first; the relative retention times were 85 : 89. As Howard and Stevens[8] found evidence of thermal isomerisation of some terpenoid compounds during gas–liquid chromatographic investigations, several runs were carried out with different temperatures of the inlet heater. Even with a temperature of 300°, however, there was no evidence of isomerisation.

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[1] Simonsen and Owen, " The Terpenes," University Press, Cambridge, 1947, Vol. I.

[2] Caldwell and Jones, *J.*, 1946, 599; Thompson and Whiffen, *J.*, 1948, 1412; Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland, *J.*, 1950, 915.

[3] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 34.

[4] Messer, *Chem. News*, 1929, **138**, 292; *Chem. Zentr.*, 1929, II, 1645.

[5] (*a*) Grimshaw, Guy, and Smith, *J.*, 1940, 68; (*b*) Boelhouwer, Tien, and Waterman, *Rec. Trav. chim.*, 1954, **73**, 143.

[6] Balbiano and Paolini, *Ber.*, 1903, **36**, 3575; Balbiano, *ibid.*, 1909, **42**, 1502.

[7] Wittig and Schöllkopf, *Ber.*, 1954, **87**, 1318; Levisalles, *Bull. Soc. chim. France*, 1958, 1021; Schöllkopf, *Angew. Chem.*, 1959, **71**, 260.

[8] Howard and Stevens, *J.*, 1960, 161.

The chemical method of separation here developed, together with the chromatographic separation, should prove to be of value in studies of the natural terpenes.

EXPERIMENTAL

The alumina was "Activated Alumina Type 'H'" supplied by Peter Spence and Sons Limited. All infrared spectra (except those of carbon disulphide solutions) were recorded on a Perkin-Elmer "Infracord" model 137; carbon disulphide solutions were measured on a Perkin-Elmer model 21 double-beam spectrophotometer.

Preparation of 2-*Methylnonadecan*-2-*ol*.—Stearic acid (m. p. 67·5—69·5°) and pure methanol yielded the ester which, after fractional distillation and recrystallisation from acetone, had m. p. 38—39°. In the preparation of the alcohol,[9] it was advantageous to use 4 mol. of methylmagnesium iodide to 1 mol. of ester. Recrystallisation from light petroleum (b. p. 40—60°) at −8° gave 2-methylnonadecan-2-ol (81%), m. p. 45·5—46·5° (Smith [5a] gave m. p. 45·5°; Ryan and Dillon,[9] 44—45°).

Preparation of the Mixture of Eicosenes.—(*a*) 2-Methylnonadecan-2-ol (33 g.) and resublimed iodine (0·17 g., 0·5%) were heated for 2 hr. under dry carbon dioxide at 150°. The reaction product distilled at 186—192°/9·3 mm. and was refluxed with excess of acetic anhydride for 30 min. Excess of anhydride was distilled and the residue boiled at 192—196°/9 mm. The olefin mixture had m. p. 12·5—13·3°, n_D^{20} 1·4515, iodine no. 90·4 (theory 90·5), $\nu_{max.}$ 890s and 833m cm.$^{-1}$. The infrared spectrum of a solution in carbon disulphide indicated 65% of the isopropylidene form.

(*b*) 2-Methylnonadecan-2-ol (4 g.) was heated to 115—120° and hydrogen bromide was then passed through for 30 min. The mixture was cooled and extracted with ether. The extracts were dried (Na_2SO_4) and evaporated. Recrystallisation of the residue from hexane afforded 2-bromo-2-methylnonadecane (84%), m. p. 20·0—20·7°. 2-Bromo-2-methylnonadecane (2·6 g.) and redistilled quinoline (2·3 ml.) were heated for 1 hr. at 160° ± 5° under nitrogen. Excess of quinoline was removed and the residue allowed to cool. The upper layer was poured into water and the whole extracted with ether. The extracts were washed with 2N-hydrochloric acid, and water, dried (Na_2SO_4), and evaporated. The residue distilled at 190—194°/10 mm. to give the olefin mixture, m. p. 13·4—14·1°, n_D^{20} 1·4508, $\nu_{max.}$ 890s and 833m cm.$^{-1}$. The infrared spectrum of a solution in carbon disulphide indicated 52% of the isopropylidene isomer.

Separation of 2-*Methylnonadec*-2-*ene*.—The olefin mixture (2·2 g.; m. p. 12·5—13·3°) and mercuric acetate (0·13 g., 5% stoicheiometric weight) in propionic acid (40 ml.) were heated for 30 min. at 65—70°. 10 ml. of the hot solution were poured into water (30 ml.), and the upper layer was extracted with light petroleum (b. p. 60—80°). After being dried (Na_2SO_4), the ether extracts were passed through alumina, and yielded an olefin mixture which after distillation had m. p. 11·9—12·4°. The peaks at 890 and 833 cm.$^{-1}$ showed the same percentage absorption. This procedure was repeated twice (0·03 g. of acetate; 65—70°; 30 min.) giving an olefin mixture of m. p. 11·5—12·3°. The peak at 833 cm.$^{-1}$ was now stronger than that at 890 cm.$^{-1}$. The remaining 10 ml. with the usual procedure (0·02 g. of acetate; 50—55°; 30 min.) gave a mixture, m. p. 10·5—11·3°. This mixture was taken up in propionic acid (10 ml.), and the separation procedure (0·02 g. acetate; 50°; 30 min.) gave 2-methylnonadec-2-ene, m. p. 9·0—10·2°, n_D^{20} 1·4524, $\nu_{max.}$ 833 cm.$^{-1}$. The infrared spectrum of a solution in carbon disulphide showed no peak at 890 cm.$^{-1}$.

Preparation of 2-*Methylnonadec*-1-*ene*.[10]—Cetyl iodide (12 g.; m. p. 24·0—24·6°) in dry ether (70 ml.) was added slowly to magnesium turnings covered with dry ether (60 ml.) under normal Grignard conditions. Some white solid separated (later shown to be dotriacontane). 2-Methylallyl chloride (6·2 g.; b. p. 71·7—72·2°; 100% excess) in dry ether was then added and the mixture stirred for 5 hr. at room temperature. The complex was decomposed with water and then with dilute hydrochloric acid, and the whole extracted with ether. After the dotriacontane had been filtered off, the extracts were washed with 2N-hydrochloric acid, water, and 2N-sodium carbonate, dried (Na_2SO_4), and evaporated. The residue was repeatedly fractionally distilled until the higher-boiling fractions gave a negative Beilstein halogen test. These fractions were then adsorbed on alumina, and elution with light petroleum (b. p. 60—80°) gave 2-methylnonadec-1-ene (5%), m. p. 12·7—13·1°, n_D^{20} 1·4495, $\nu_{max.}$ 890s cm.$^{-1}$.

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[9] Ryan and Dillon, *Proc. Roy. Irish Acad.*, 1912, **29**, *B*, 235.

[10] Tiffeneau, *Bull. Soc. chim. France*, 1903, **29**, 1157; *Compt. rend.*, 1904, **139**, 481.

Preparation of 2-Methylnonan-2-ol.—Pure methanol and octanoic acid (m. p. 14·5—16·7°) yielded the ester which, after fractional distillation, had b. p. 90°/20·3 mm. (lit.,[11] 83°/15 mm.). Methyl octanoate (50 g.) in ether (40 ml.) was added dropwise to a solution of methylmagnesium iodide in ether under normal Grignard conditions. The complex was decomposed with water, then with 2N-sulphuric acid, and the whole extracted with ether. The combined extracts were washed with 2N-sodium carbonate and with water, dried (Na_2SO_4), and evaporated. The residue in ethanol was then refluxed with potassium hydroxide (10 g.) in water (70 ml.) for several hours, poured into water, and extracted with ether. After being washed with water, the extracts were dried (Na_2SO_4) and evaporated. Fractional distillation of the residue gave 2-methylnonan-2-ol (70%), b. p. 101·0—101·8°/21·6 mm. (lit.,[12] 96—98°/13·5 mm.), n_D^{20} 1·4320, $\nu_{max.}$ 725s, 769s, 909s, 952s, 1075m, 1105m, 1149s, 1190s, 1370s, 1460s, 2857s, 2924s, and 3333s cm.$^{-1}$ (Found: C, 75·7; H, 13·7. Calc. for $C_{10}H_{22}O$: C, 75·9; H, 14·0%). The α-*naphthylurethane* (after 432 hr. at room temperature), recrystallised from aqueous alcohol, had m. p. 70·0—70·8° (Found: C, 77·1; H, 9·0; N, 4·4. $C_{21}H_{29}NO_2$ requires C, 77·0; H, 8·9; N, 4·3%).

Preparation of the Mixture of Decenes.—2-Methylnonan-2-ol (26 g.) and resublimed iodine (0·15 g., 0·5%) were heated for 2 hr. at 150° under nitrogen. An ethereal solution of the distilled crude mixture was washed with 2N-sodium hydroxide and with water, dried (Na_2SO_4), and evaporated. The residue distilled at 64·7—66·5°/20 mm. to give the olefin mixture, n_D^{20} 1·4272, $\nu_{max.}$ 890s and 833m cm.$^{-1}$. The infrared spectrum of a solution in carbon disulphide indicated 70% of the isopropylidene isomer.

Separation of 2-Methylnon-2-ene.—The olefins (14 g.) and mercuric acetate (3 g.) in propionic acid (30 ml.) were heated for 30 min. at 65—70°. On cooling, black mercury and mercurous salts were deposited. The solution was poured into water (100 ml.) and the unchanged olefins extracted with light petroleum (b. p. 40—60°). The extracts were washed with 2N-sodium carbonate, and water, dried (Na_2SO_4), and adsorbed on an alumina column. Evaporation of the light petroleum eluate gave unchanged olefin mixture. This procedure was repeated 10 times, the amount of acetate being progressively reduced to 0·1 g.; a temperature of 50° was used in the last 3 separations. The final sample had b. p. 164—166°/757 mm., n_D^{20} 1·4286 [lit.,[13] n_D^{20} (calc.) 1·4289, b. p. (calc.) 169·9°/760 mm.]. The infrared spectrum of a solution in carbon disulphide showed a very small peak at 890 cm.$^{-1}$ and indicated 93 $\pm$ 2% of the isopropylidene isomer. It was found impossible to increase the percentage of the isopropylidene isomer by this procedure.

Preparation of 2-Methylnon-1-ene.[7]—Lithium (1·4 g., 0·2 g.-atom) was added gradually to bromobenzene (10 g. 0·06 mol.) in ether (100 ml.) under nitrogen. After reaction had finished, the phenyl-lithium solution was filtered into a stirred suspension of methyltriphenylphosphonium iodide (25·5 g., 0·06 mol.) in ether (200 ml.), and the whole stirred under nitrogen for 2·5 hr. at room temperature. Heptyl methyl ketone [14] (3 g.; 0·02 mol.; m. p. $-7·4°$) was added during 15 min. The mixture was then heated on a water-bath, light petroleum being added, as the ether distilled, to give a refluxing temperature of 64—66°. After refluxing for 5 hr., the solution was cooled, filtered, and passed through alumina. Evaporation of the light petroleum (b. p. 60—80°) eluate gave 2-methylnon-1-ene contaminated with bromobenzene. The crude olefin was readsorbed on alumina; elution with light petroleum (b. p. 40—60°) gave a first olefin-containing fraction which gave a negative Beilstein halogen test. The olefin had b. p. 68—70°/25·5 mm., n_D^{20} 1·4249 (lit.,[15] b. p. 66·23°/20 mm., n_D^{20} 1·42409). Further fractions afforded olefin containing 3—4 % of bromobenzene, n_D^{20} 1·4286. The yield was 40%.

Gas-chromatography Experiments.—The column was benzylbiphenyl (15% on Embacil; May and Baker Ltd.). Its length was 400 cm. and diameter 4·5 mm. The temperature of the column was 60°. The carrier gas was hydrogen, and the flow rate was 39 ml./min. The inlet pressure was 1330 mm. The detector was a flame-ionization detector [16] modified as by Thompson.[17] The recorder was a Honeywell–Brown recorder, and a flame-ionization current

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[11] Haller and Yousouffian, *Compt. rend.*, 1906, **143**, 805.

[12] Houben, *Ber.*, 1902, **35**, 3589.

[13] Mears, Fookson, Pomerantz, Rich, Dussinger, and Howard, *J. Res. Nat. Bur. Stand.*, 1950, **44**, 299.

[14] Shenton and Smith, *Chem. and Ind.*, 1958, 1510.

[15] Schuhmacher, Wibaut, and Paerels, *Rec. Trav. chim.*, 1953, **72**, 1037.

[16] McWilliam and Dewar, *Nature*, 1958, **181**, 760.

[17] Thompson, *J. Chromatog.*, 1959, **2**, 148.

of 5 × 10^{-10} amp. gave full-scale deflection. The temperature of the inlet heater was 150—200°. Under these conditions, the isopropylidene isomer was eluted after 85 min., the isopropenyl isomer after 89 min. In view of Howard and Stevens's [8] results, experiments were carried out with inlet-heater temperatures of 45°, 100°, 150°, 200°, and 300°. In all cases, the proportions of the isomers were unchanged.

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THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, October* 25*th*, 1960.]