

384. *Researches in the Menthone Series. Part XVIII.**
Pyrolysis of (–)-Menthyl Acetate.

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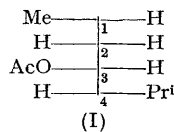
Former investigators have reported that the terpene obtained in the pyrolysis of (–)-menthyl acetate consisted of (+)-*p*-menth-3-ene unaccompanied by any (+)-*p*-menth-2-ene. It is now shown that the product consists essentially of a mixture of (+)-*p*-menth-3-ene (65.5%) and (+)-*trans-p*-menth-2-ene (34%).

VAN PELT, JUN., and WIBAUT (*Rec. Trav. chim.*, 1941, **60**, 55) reported that a (+)-*p*-menthene was formed when (–)-menthyl acetate vapour was passed through a glass tube packed with glass wool and heated externally to 425°. They assumed that this was (+)-*p*-menth-3-ene. Frank and Berry (*J. Amer. Chem. Soc.*, 1950, **72**, 2986) repeated this work and

* Part XVII, *J.*, 1952, 153. On p. 158, penultimate line of Experimental section, for “(+)-*cis-p*-menth-2-ene” read “(+)-*p*-menth-3-ene.”

examined the (+)-menthene by infra-red spectrography. They concluded that the (+)-*p*-menthene consisted of (+)-*p*-menth-3-ene with no (+)-*p*-menth-2-ene present.

This result is open to some doubt for the following reasons. It has been postulated that esters on pyrolysis break down to acids and olefins by a mechanism dependent on hydrogen bridges (Hurd and Blunck, *ibid.*, 1938, 60, 2419). This mechanism has been used in order to explain the predominance of *cis*- over *trans*-elimination in the pyrolysis of esters of cyclic alcohols (Barton, *J.*, 1949, 2174, 2459; Alexander and Mudrak, *J. Amer. Chem. Soc.*, 1950, 72, 1810, 3194; 1951, 73, 59; Arnold, Smith, and Dodson, *J. Org. Chem.*, 1950, 15, 1256). While *cis*-elimination predominates, *trans*-elimination can also occur, as shown by Alexander and Mudrak (*loc. cit.*) in their study of the thermal decomposition of *cis*-2-phenylcyclohexyl acetate. Now, in the case of (–)-menthyl acetate (I) there is the possibility of *cis*-elimination between carbon atoms 2 and 3, as well as between C₍₃₎ and C₍₄₎, besides the possibility of *trans*-elimination between C₍₂₎ and C₍₃₎. Since elimination towards the tertiary carbon atom would be expected to predominate (Barton, *loc. cit.*), the product of pyrolysis of (–)-menthyl acetate should be mainly (+)-*p*-menth-3-ene together with some (+)-*trans-p*-menth-2-ene.



In the present investigation the (+)-*p*-menthene obtained by pyrolysis of (–)-menthyl acetate (Van Pelt, jun., and Wibaut, *loc. cit.*) was analysed quantitatively for (+)-*p*-menth-3-ene and (+)-*trans-p*-menth-2-ene by the method of Hückel and Tappe (*Annalen*, 1939, 537, 113). This method is based on the observation that (+)-*p*-menth-3-ene is completely racemised in refluxing alcoholic toluene-*p*-sulphonic acid while (+)-*p*-menth-2-ene is unaffected. It was found that the optical rotation of the (+)-*p*-menthene dropped from $\alpha_D^{18} + 94.5^\circ$ ($l = 1$ dm.; homogeneous) to a constant value of $\alpha_D^{18} + 36.9^\circ$ ($l = 1$ dm.; homogeneous) after being heated under reflux with alcoholic toluene-*p*-sulphonic acid for 4 hours. Assuming that the optical activity of the mixture is a direct function of its composition and knowing the optical rotations of the pure components, we calculate the composition of the (+)-*p*-menthene to have been (+)-*p*-menth-3-ene 65.5%, (+)-*trans-p*-menth-2-ene 34%, racemised *p*-menthene 0.5%.

It has thus been shown that a considerable proportion of (+)-*trans-p*-menth-2-ene is present in the product of pyrolysis of (–)-menthyl acetate. This is formed by *cis*- and/or *trans*-elimination between C₍₂₎ and C₍₃₎; but *cis*-elimination between C₍₃₎ and C₍₄₎ towards the tertiary carbon atom, giving (+)-*p*-menth-3-ene, is the predominating process. This result is in line with that obtained in the pyrolysis of methyl (–)-menthylxanthate which was shown to form a (+)-*p*-menthene having $[\alpha]_D + 114.8^\circ$ (homogeneous) (Tschugaev, *Ber.*, 1899, 32, 3332). Hückel and Tappe (*loc. cit.*) showed by their racemisation procedure that this menthene contained 70% (+)-*p*-menth-3-ene and 30% (+)-*trans-p*-menth-2-ene. These two components were also proved to be present by Jachard (*Bull. Inst. pin.*, 1933, 42, 67, 79, 97) using Raman-spectra measurements. A mechanism similar to that postulated for the pyrolysis of acetates has been proposed by several workers (Barton, *loc. cit.*; Hückel, Tappe, and Legutke, *Annalen*, 1940, 543, 191; Stevens and Richmond, *J. Amer. Chem. Soc.*, 1941, 63, 3132; Alexander and Mudrak, *loc. cit.*).

EXPERIMENTAL

Pyrolysis of (–)-Menthyl Acetate.—(–)-Menthyl acetate (63 g.), $\alpha_D^{17} - 71.13^\circ$ ($l = 1$ dm.; homogeneous), was decomposed at 450° by the method of Van Pelt, jun., and Wibaut (*loc. cit.*). The menthene (32.5 g., 74%) was separated from unchanged menthyl acetate by fractional distillation at 17 mm. through a 15-cm. column packed with glass helices. After being heated over sodium on a steam-bath for 2 hours the (+)-*p*-menthene was redistilled at 11 mm. The distillate had $\alpha_D^{16} + 93.18^\circ$ rising to $\alpha_D^{18} + 94.47^\circ$ after being kept over sodium for 7 days and to $\alpha_D^{18} + 94.84^\circ$ ($l = 1$ dm.; homogeneous) after a further 2 months over sodium. This product had $[\alpha]_D^{16} + 116.9^\circ$ (homogeneous), $d_4^{20} 0.8108$, $n_D^{20} 1.4509$, and $[R_L]_D 45.86$ (Calc. : 45.71).

Analysis of (+)-p-Menthene.—The composition of the (+)-*p*-menthene obtained as above was estimated by the procedure of Hückel and Tappe (*loc. cit.*). 1.0-ml. portions of the (+)-*p*-menthene, $\alpha_D^{18} + 94.47^\circ$ ($l = 1$ dm.; homogeneous), were heated under reflux with 1.4-ml. portions of toluene-*p*-sulphonic acid solution (29.4 g. of *p*-Me·C₆H₄·SO₃H, 4H₂O per 100 ml. of ethyl alcohol solution) for varying periods. The menthene was recovered by adding water,

washing the oil with sodium carbonate solution, and drying (Na_2SO_4). The following values for α_D^{18} ($l = 1$ dm.; homogeneous) were obtained after 0, 0.25, 0.5, 1, 2, 4 hours respectively: $+94.97^\circ$, $+51.62^\circ$, $+43.50^\circ$, $+39.99^\circ$, $+37.50^\circ$, $+36.94^\circ$. The residual constant optical activity must be due to (+)-*trans-p*-menth-2-ene. The values of α_D for optically pure (+)-*p*-menth-3-ene and (+)-*trans-p*-menth-2-ene being taken as $+88.0$ and $+108.0^\circ$ respectively (Hückel, Tappe, and Legutke, *loc. cit.*; McNiven and Read, *J.*, 1952, 153), the composition of the (+)-*p*-menthene, $\alpha_D^{18} +94.47^\circ$ ($l = 1$ dm.; homogeneous), can be calculated to be as stated above.

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