THE FISSION OF THE CYCLOPROPANE RING OF α-THUJENE.

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The outstanding feature of the structure of the terpenes of the thujane group is the presence of a cyclopropane ring. The comparative instability of this ring is responsible for the characteristic reactions of these terpenes, such as the addition of water or hydrogen chloride to form alcohols and hydrochlorides derivable from α-terpinene (I).

Examples of the fission of the cyclopropane ring in these compounds forming monocyclic terpenes are firstly the isomerisation of sabinene (II) to α-terpinene by means of dilute acid (Wallach, Annalen, 1906, 350, 165), and secondly the hydrogenation of α-thujene (III) and sabinene to 1:2-dimethyl 3-isopropyl cyclopentane (IV) (Kasansky, Berichte, 1929, 62, 2206; Richter, Wolff and Presting, ibid., 1931, 64, 871).

The fission of the cyclopropane ring of α-thujene by dilute acid with formation of α-terpinene takes place as readily as with sabinene. In this connection the well crystallised adducts of α-terpinene with maleic anhydride and p-benzoquinone provide a convenient means of identifying this terpene, and also of eliminating it from the reaction mixture, since it reacts quantitatively with maleic anhydride (Gascoigne, This Journal, 1940, 74, 355). By this means it is found that the product of the action of dilute acid on α-thujene contains, besides α-terpinene, another terpene which does not react in the cold with maleic anhydride. This terpene has been shown to be γ-terpinene (V) by the preparation of several characteristic crystalline derivatives and especially by the identity of its dihydrochloride with α-terpinene dihydrochloride (cf. Richter and Wolff, Berichte, 1927, 60, 477; Francesconi and Sernagiotto, Gazzetta, 1913, 43, i, 613).

Since γ-terpinene, like many other terpenes, is easily isomerised to α-terpinene by dilute acid, it is possible that
when the cyclopropane ring of a-thujene breaks, y-terpinene is first formed and is then partially isomerised to a-terpinene.

The rupture of the C4/C6 bond of a-thujene might be expected to lead to the formation, besides y-terpinene, of the alternative possibility, namely a-phellandrene (VI). This terpene is in fact formed in the reaction between a-thujene at its boiling point and maleic anhydride, and can be isolated as its maleic anhydride adduct. The main product of the reaction, besides p-cymene, is however the a-terpinene adduct. Since y-terpinene can be shown to react at its boiling point with maleic anhydride to give the a-terpinene adduct, any y-terpinene formed in this reaction must be immediately isomerised.

Since the a-thujene used is isolated from E. dives oil, in which it occurs associated with large amounts of a-phellandrene, it might seem that the appearance of a-phellandrene in the above reaction could be due to the presence of this terpene in the a-thujene. However, the a-phellandrene obtained from the ring fission of a-thujene is racemic, as is to be expected from stereochemical considerations, whilst the a-phellandrene of E. dives oil is dsevorotatory. Moreover the a-thujene used was freed from the last traces of a-phellandrene by leaving it to stand with an excess of maleic anhydride in the cold.

The opening of the cyclopropane ring of A3- or A4-carene (VII and VIII) and the cyclobutane ring of a-pinene (IX) by maleic anhydride with the formation, in each case, of both the a-terpinene and a-phellandrene adducts (Hultzsch, Berichte, 1939, 72, 1178) is analogous to the reaction with a-thujene. These are the only known examples of a "forced" diene synthesis, involving a double bond conjugated with a cyclopropane or cyclobutane ring.

Apparently a-phellandrene is not a product of the ring opening of a-thujene by dilute acid, firstly because no trace of its maleic anhydride adduct is to be found along with the a-terpinene product. Secondly, when the reaction is carried out in the presence of p-benzoquinone, only the a-terpinene adduct is formed; it is known that the a-phellandrene quinone adduct is formed more readily than the a-terpinene adduct (Gascoigne, loc. cit.). Finally, it seems improbable that the action of dilute acid or maleic anhydride on a-thujene can lead to the rupture of the C4/C5 bond with the formation of a cyclopentadiene homologue derived from IV. Such a compound...
when the cyclopropane ring of \( \alpha \)-thujene breaks, \( \gamma \)-terpinene is first formed and is then partially isomerised to \( \alpha \)-terpinene.

The rupture of the \( C_4/C_6 \) bond of \( \alpha \)-thujene might be expected to lead to the formation, besides \( \gamma \)-terpinene, of the alternative possibility, namely \( \alpha \)-phellandrene (VI). This terpene is in fact formed in the reaction between \( \alpha \)-thujene at its boiling point and maleic anhydride, and can be isolated as its maleic anhydride adduct. The main product of the reaction, besides \( \pi \)-cymene, is however the \( \alpha \)-terpinene adduct. Since \( \gamma \)-terpinene can be shown to react at its boiling point with maleic anhydride to give the \( \alpha \)-terpinene adduct, any \( \gamma \)-terpinene formed in this reaction must be immediately isomerised.

Since the \( \alpha \)-thujene used is isolated from \( E. \ dives \) oil, in which it occurs associated with large amounts of \( \alpha \)-phellandrene, it might seem that the appearance of \( \alpha \)-phellandrene in the above reaction could be due to the presence of this terpene in the \( \alpha \)-thujene. However, the \( \alpha \)-phellandrene obtained from the ring fission of \( \alpha \)-thujene is racemic, as is to be expected from stereochemical considerations, whilst the \( \alpha \)-phellandrene of \( E. \ dives \) oil is levorotatory. Moreover the \( \alpha \)-thujene used was freed from the last traces of \( \alpha \)-phellandrene by leaving it to stand with an excess of maleic anhydride in the cold.

The opening of the cyclopropane ring of \( \Delta^3 \)- or \( \Delta^4 \)-carene (VII and VIII) and the cyclobutane ring of \( \alpha \)-pinene (IX) by maleic anhydride with the formation, in each case, of both the \( \alpha \)-terpinene and \( \alpha \)-phellandrene adducts (Hultzsch, Berichte, 1939, 72, 1178) is analogous to the reaction with \( \alpha \)-thujene. These are the only known examples of a "forced" diene synthesis, involving a double bond conjugated with a cyclopropane or cyclobutane ring.

Apparently \( \alpha \)-phellandrene is not a product of the ring opening of \( \alpha \)-thujene by dilute acid, firstly because no trace of its maleic anhydride adduct is to be found along with the \( \alpha \)-terpinene product. Secondly, when the reaction is carried out in the presence of \( p \)-benzoquinone, only the \( \alpha \)-terpinene adduct is formed; it is known that the \( \alpha \)-phellandrene quinone adduct is formed more readily than the \( \alpha \)-terpinene adduct (Gascoigne, loc. cit.).

Finally, it seems improbable that the action of dilute acid or maleic anhydride on \( \alpha \)-thujene can lead to the rupture of the \( C_4/C_5 \) bond with the formation of a cyclo-pentadiene homologue derived from IV. Such a compound
would almost certainly either possess a conjugated system of double bonds or else be readily isomerised in the experimental conditions to a conjugated diene and so would form characteristic adducts with maleic anhydride and benzoquinone.

Experimental.

Isolation of \(\alpha\)-Thujene.

The starting material was 13.6 Kg. of a low boiling fraction of \(E.\) *dives* oil kindly donated by W. K. Burnside Pty. Ltd. of Melbourne. This oil had \(\alpha_D -23^\circ\) and contained, besides \(\alpha\)-thujene, mainly 1-\(\alpha\)-phellandrene, p-cymene, piperitone, and aliphatic aldehydes and alcohols boiling below 150\(^\circ\). It was fractionated at atmospheric pressure between 145\(^\circ\) and 165\(^\circ\) using a five-bulb Gолодetz column, fractions being taken at each degree. After four fractionations the fractions 151\(^\circ\)/152\(^\circ\) to 154\(^\circ\)/155\(^\circ\) were combined (6.2 Kg. \(\alpha_D 7^\circ\)) and left with maleic anhydride (450 g.) in acetone (2 l) for an hour to remove the residual \(\alpha\)-phellandrene (cf. Birch, *This Journal*, 1937, 71, 332); from the rotation the \(\alpha\)-phellandrene content could be calculated to be roughly 8%; 1.25 equivalents of maleic anhydride were used). The product (5.8 Kg. \(\alpha_D 15^\circ\)) was then refluxed over sodium for five hours to free it from oxygenated impurities and finally refractionated. After two fractionations 4.5 Kg. of \(\alpha\)-thujene were obtained having the following properties: b.p. 152\(^\circ\)-153\(^\circ\)/760 mm. \([\alpha]_D^{21} 19^\circ\cdot61, D_4^{21} 0.8337, n_D^{21} 1.4497\). This product, as has been pointed out by Birch and Earl (*This Journal*, 1938, 72, 55), is a partially racemised \(\alpha\)-thujene, the optically pure substance having \([\alpha]_D\) approximately 37\(^\circ\).

Conversion of \(\alpha\)-Thujene to \(\alpha\)- and \(\gamma\)-Terpinene by Dilute Acid.

\(\alpha\)-Thujene (50 ml., 41.7 g.) and 5% alcoholic hydrochloric acid (100 ml.) were initially immiscible, but on standing for about five minutes the mixture gradually became warm, with resulting miscibility. The mixture was refluxed for fifteen minutes, cooled, poured into water and the oil washed with water and left for an hour with maleic anhydride (40 g.) in acetone (60 ml.). After removal of the acetone the residue was heated on the water bath for fifteen minutes with 20% sodium hydroxide (150 ml.) and steam distilled. The precipitated sodium salt was
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converted by the usual method to $\alpha$-terpinene maleic anhydride adduct. Yield, 14 g., 20%.; m.p. 60°/61° not depressed by admixture with the authentic substance.

The oil recovered from the steam distillation (32 ml.) on fractionation at 24 mm. gave two fractions: 

(a) 80°-82°, 
(b) 100°-115°. (b) contained chlorine, and was probably a mixture of $\alpha$-terpinene mono- and dihydrochlorides; it was not further examined. (a) was $\gamma$-terpinene. Yield, 18·5 g., 45%.

Nitrosochloride: m.p. 109° from light petroleum.
Nitrolpiperide: m.p. 146° from ethyl acetate.
Nitrosate: m.p. 112° from light petroleum.

(Cf. Richter and Wolff, Berichte, 1930, 63, 1714; Murayama, Chem. Abstracts, 1922, 16, 1568.)

Dihydrochloride, m.p. 51° from methyl alcohol, mixed melting point with $\alpha$-terpinene dihydrochloride 51°.

Addition of Maleic Anhydride to $\alpha$-Thujene.

$\alpha$-Thujene (136 g.) was heated with maleic anhydride (100 g.) as described for $\alpha$-terpinene (Gascoigne, loc. cit.); the reaction was considerably more vigorous. The p-cymene and unchaged maleic anhydride were distilled off up to 130° at 20 mm. and the remainder distilled up to 200° at 2 mm. The viscous oil so obtained was mixed with a little light petroleum, filtered from fumaric acid, and redistilled at 2 mm., b.p. 150°-173°.

The distillate was mixed with an equal volume of light petroleum and left in a freezing mixture. After three hours the crystallised dl-$\alpha$-phellandrene maleic anhydride adduct was filtered off. Yield, 7·6 g., 3%; plates from aqueous alcohol, m.p. 91° not depressed by admixture with the authentic substance prepared by recrystallising together equal weights of the dextro and laevor adducts from better fennel and E. dives oil respectively.

The filtrate from the $\alpha$-phellandrene adduct could not be further crystallised and was converted through the insoluble sodium salt to $\alpha$-terpinene maleic anhydride adduct. Yield, 38 g., 16%; fine needles from light petroleum, m.p. 60°/61°.

Formation of p-Cymene.

$\alpha$-Thujene (27 g.) was heated with maleic anhydride (20 g.) as described and the mixture then steam distilled, yielding a light yellow oil (11 g., 41%), b.p. 173°-178°. This would not react with maleic anhydride, and would
not give a solid nitrosochloride, nitrosite or hydrochloride. It was not oxidised by cold aqueous chromic acid, but on boiling for three hours terephthalic acid was precipitated; dimethyl ester, plates from methyl alcohol, m.p. 140°, not depressed by admixture with the authentic substance.

**Addition of Maleic Anhydride to γ-Terpinene at its Boiling Point.**

γ-Terpinene (5.5 g.) was heated with maleic anhydride (4 g.) in the usual way. Yield of α-terpinene adduct, 0.82 g., 9%. M.p. 60°/61° not depressed by admixture with the authentic substance.

**Conversion of α-Thujene to α-Terpinene p-Benzquinone Adduct.**

α-Thujene (14 ml., 1 mol.) was added to a suspension of quinone (18.5 g., 2 mol.) in 0.05 N. alcoholic hydrochloric acid (60 ml.). On warming, a deep red colour appeared, due to the formation of quinhydrone. The mixture was refluxed for two hours and then steam distilled. The α-terpinene quinone adduct was recovered from the residue as already described (Gascoigne, loc. cit.). Yield, 1.5 g., 7%; recrystallised twice from methyl alcohol with charcoal m.p. 87°/88°, not depressed by admixture with the authentic adduct prepared from α-terpinene.

The quinone adduct of dl-α-phellandrene, prepared by recrystallising together equal weights of the dextro and laevo adducts (cf. Diels and Alder, Berichte, 1929, 62, 2365), melts at 91°, mixed melting point with the above product from α-thujene, 61°/65°.

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