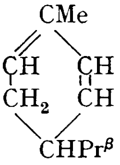
384. *Addition Reactions to Conjugated Systems. β-Phellandrene and Maleic Anhydride.*

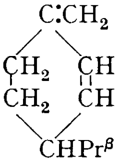
By Norman Frederick Goodway and Trustham F. West.

l-β-Phellandrene, free from the α-isomeride, gives with maleic anhydride a resinous product, from which a small quantity of adduct identical with that obtained from *l*-α-phellandrene has been isolated: the identity has been confirmed by the preparation of some esters. The relative reactivity of α- and β-phellandrene, in which the double bonds occur in the *cis*- and the *trans*-position respectively, is of value for the stereochemistry of more complex structures. The available evidence indicates that the *l*-α-phellandrene–maleic anhydride adduct is derived from β-phellandrene and maleic anhydride by thermal decomposition of the primary resinous product and not by prior conversion of the β- into the α-isomeride.

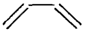
Although the condensation of maleic anhydride with α-phellandrene (I) has been widely studied (Diels and Alder, *Annalen*, 1928, **460**, 116; Littmann, *J. Amer. Chem. Soc.*, 1935, **57**, 586; 1936, **58**, 1316; private communication) and has been applied to the detection and the determination of this hydrocarbon, no serious attempt has been made to examine the condensation with β-phellandrene. In most examples of diene addition of maleic anhydride the double bonds constituting the conjugated system are either locked in the *cis*-position as in α-phellandrene, or else, as in aliphatic dienes, are free to assume such a " quasicyclic " position (A) (cf. Alder and Stein, *Angew. Chem.*, 1937, **50**, 510).



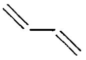
(I.)



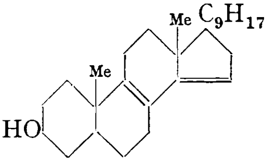
(II.)



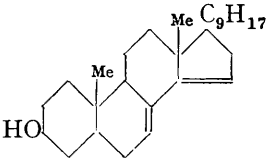
(A.)



(B.)



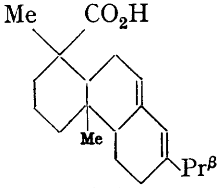
(III.)



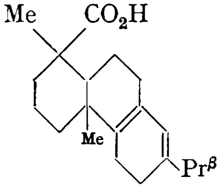
(IV.)

The double bonds in β-phellandrene (II) are locked in the *trans*-position (B) and examination of models of this type indicates that addition of maleic anhydride, or similar olefinic compound, to the ends of the conjugated system could take place only with considerable strain. In no analogous case does the reaction appear to have been studied with compounds of established constitution, but according to Callow (J., 1936, 462) ergosterol-D, which does not react with maleic anhydride at 135° (Windaus and Lüttringhaus, *Ber.*, 1931, **64**, 850), has a formula (III) which contains a conjugated system similarly locked in the *trans*-position. Fieser (" Natural Products related to Phenanthrene," 1937, p. 173) has stated that the formation of a characteristic addition product between ergosterol and maleic anhydride " shows for one thing that both of the double bonds must be located in the same ring," but this does not necessarily follow, since the double bonds of a conjugated system, although distributed between two rings, may yet possess a *cis*-configuration. Thus, both Laucht (*Z. physiol. Chem.*, 1935, **237**, 236) and Callow (*loc. cit.*) regard ergosterol-B_3 as having a structure in which the double bonds occupy the position shown in (IV), yet this sterol combines readily with maleic anhydride (Windaus, *Annalen*, 1931, **488**, 98), although the formulation of a normal adduct would be at variance with Bredt's rule.

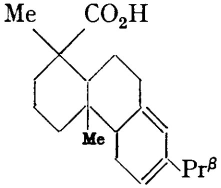
Abietic acid, for which structure (V) is now considered probable (Fieser and Campbell, *J. Amer. Chem. Soc.*, 1938, **60**, 159; Ruzicka and Sternbach, *Helv. Chim. Acta*, 1938, **21**, 565), reacts with maleic anhydride only above 100° to yield the same addition product as that obtained (Bacon and Ruzicka, *Chem. and Ind.*, 1936, 546) from lævo-pimaric acid, for which formulæ (VI*a*) (Fieser, *op. cit.*, p. 346) and (VI*b*) (Ruzicka and Sternbach, *loc. cit.*) are suggested. It is, therefore, inferred that the conversion of the more stable isomeride into the addition product proceeds through an isomerisation at the elevated temperature to lævo-pimaric acid. Sandermann (*Seifens. Ztg.*, 1937, **64**, 421) has noted that, although less reactive than α-phellandrene, which reacts rapidly with a solution of maleic anhydride at the ordinary temperature, β-phellandrene at 135° yields an amorphous or resinous polymeric product. A normal addition product was not expected, since its formulation (VII) would contravene Bredt's rule. The known tendency for an exocyclic double bond to migrate into the ring under the influence of acids suggests that the condensation takes place through an intramolecular rearrangement such as seems probable in the case of abietic acid.



(V.)

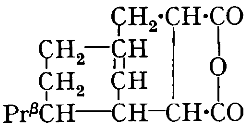


(VI*a*.)

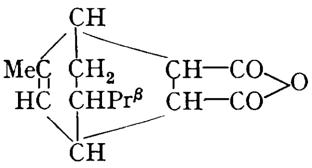


(VI*b*.)

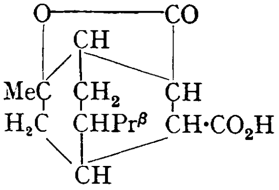
The resinous products of the reaction between maleic anhydride and *l*-β-phellandrene under various conditions yielded on vacuum distillation a small amount of material which appeared from its melting point, mixed melting point and optical rotation to consist mainly of the same compound as that obtained by the condensation of *l*-α-phellandrene and maleic anhydride (Goodway and West, *J. Soc. Chem. Ind.*, 1937, **56**, 472T; *Nature*, 1937, **140**, 934). In view of the difficulty of purifying the small quantity of material available from the β-isomeride, the identity of the two products was confirmed by the preparation and comparison of crystalline esters. Although the methyl, ethyl, and *iso*propyl esters corresponded in analysis to monoalkyl esters, they displayed no acid properties; they were insoluble in cold alkali and their alcoholic solutions could not be titrated. They probably correspond to the lactonic form (IX) of the adduct (VIII) (cf. the corresponding acid of Diels, Koch, and Frost, *Ber.*, 1938, **71**, 1163, from α-terpinene and maleic anhydride) and their constitution is being further investigated.



(VII.)



(VIII.)



(IX.)

The lævorotatory β-phellandrene used in these experiments was derived from the oil of *Abies balsamea*, Miller (Canada balsam oil), which yields the purest β-phellandrene obtainable (Macbeth, Smith, and West, this vol., p. 119). The absence of α-phellandrene can be concluded from the following: (a) no trace of α-phellandrene could be detected by the procedure of Goodway and West (*J. Soc. Chem. Ind.*, 1937, **56**, 472T) or of Birch (*J. Proc. Roy. Soc. New South Wales*, 1938, **71**, 54). (b) The maleic anhydride value of the β-phellandrene, determined by the method of Kaufmann, Baltes, and Josephs (*Ber.*, 1937, **70**, 908), increased in direct proportion to the period of heating during the reaction, the curve (Goodway and West, *J. Soc. Chem. Ind.*, 1938, **57**, 37) showing no point of inflexion such as would be anticipated from the very different rates of reaction of the two isomerides if both were present. (c) The maleic anhydride value (9·4) determined after two hours' heating at 100°, a period shown to be sufficient for complete reaction of any α-phellandrene present, corresponded to a "phellandrene" content of only 5%, the β-phellandrene being assumed to remain inactive during this period. (d) After a sample of the terpene had been treated with sufficient maleic anhydride to react with the amount of α-phellandrene corresponding to the adduct isolated, the unreacted β-phellandrene gave, on prolonged treatment with maleic anhydride solution and vacuum distillation of the resinous product, a yield of the *l*-α-phellandrene–maleic anhydride adduct corresponding to that obtained in the earlier experiments.

Attempts were made to isolate the *l*-α-phellandrene–maleic anhydride adduct from *l*-β-phellandrene by a process not involving distillation. Ether extraction of the resinous product obtained by evaporating the solvent at 80° was unsuccessful, but, after the resin had been heated for an hour at 180—200°, the extract yielded a small amount of material apparently identical with the above adduct but which could not be freed from the accompanying resinous material. It appears probable, therefore, that the *l*-α-phellandrene–maleic anhydride adduct isolated in these experiments is derived by the thermal decomposition of the primary resinous material obtained and not by prior conversion of the β-phellandrene into the α-isomeride. If abietic acid is correctly represented by formula (V), the mechanism of the condensation of maleic anhydride with β-phellandrene and with this acid would appear to be analogous, since in the latter case also, there is no evidence that lævo-pimaric acid is formed before the condensation occurs.

EXPERIMENTAL.

l-β-Phellandrene obtained from Canada balsam oil was separated from other constituents (mainly α- and β-pinene; Smith and West, *J. Soc. Chem. Ind.*, 1937, **56**, 300T) by systematic fractionation under reduced pressure. Batches having the following constants were used, all of which gave similar results: $d_{15}^{15^\circ}$ 0·8497—0·8505, $\alpha_D^{20^\circ}$ − 43·2° to − 50·25°, $n_D^{20^\circ}$ 1·4800—1·4805.

Condensation of β-Phellandrene and Maleic Anhydride.—(i) *l*-β-Phellandrene (10 g.), maleic anhydride (7 g.), and benzene (10 ml.) were heated on the water-bath under reflux for 3 hours, giving a yellowish-red opalescent liquid. Solvent and unchanged terpene, together with some maleic anhydride, were removed at 80°, and the residue distilled at 3 mm. The fraction collected at 100—175° solidified on standing and after recrystallisation from methyl alcohol had m. p. 107° (sintering at 87°); yield, 1·3 g. (7·6%). Repeated crystallisation raised the m. p. to 124—126° (not depressed by authentic *l*-α-phellandrene–maleic anhydride adduct) but reduced the yield to 0·2 g.

(ii) *l*-β-Phellandrene (10 g.), maleic anhydride (7 g.), and benzene (10 ml.) were heated on the water-bath under reflux for 12 hours. After the first hour the reaction mixture separated into a clear mobile upper layer, consisting mainly of the solvent, and a viscous opalescent lower layer, probably polymeric (if left at this stage, the lower layer changed in a few days into a solid brown resin). When this was worked up as before, a very small amount of material, m. p. 119° (sintering at 111°), was obtained which could not be purified.

These experiments are typical of many, carried out under comparable conditions, in which the course of the reaction appeared to depend on slight variations in procedure and the yield of the required product decreased in proportion to the amount of separation which occurred. Redistillation of the terpene and of the maleic anhydride immediately before use, alteration of the order of addition of the reactants, of the initial rate of heating and agitation did not indicate the cause of the variation and the variable nature of the course of the reaction under apparently identical experimental conditions may be of importance when the formation of a monomeric or polymeric maleic anhydride addition product is employed as a means of identifying diene hydrocarbons (cf. Bacon and Farmer, J., 1937, 1065). The use of acetone instead of benzene as solvent gave a similar variable yield, although layer formation was not observed owing to its solvent power for the resin.

(iii) The maximum yield of the *l*-α-phellandrene–maleic anhydride adduct was obtained as follows: *l*-β-phellandrene (10 g.), maleic anhydride (7 g.), and benzene (10 ml.) were heated on a hot plate under reflux for 18 hours. On distillation as before, the fraction, b. p. 160—180°/3 mm., gave by crystallisation from methyl alcohol 1·35 g. (7·8%) of a product, m. p. 118° (sintering at 106°). Repeated crystallisation raised the m. p. to 124·5—126° (not depressed by authentic *l*-α-phellandrene–maleic anhydride adduct), $[\alpha]_D^{22}$ − 8·73° (*c*, 5·04 in chloroform).

Methyl, Ethyl and iso*Propyl Esters from* l-*α-Phellandrene–Maleic Anhydride Adduct.*—The adduct (5—10 g.) obtained from *l*-α-phellandrene and maleic anhydride was boiled under reflux for 7—8 hours with a saturated solution of hydrogen chloride in the alcohol (10 ml. per g.). The bulk of the alcohol was then removed by evaporation under reduced pressure; the esters crystallised, on cooling, in 80—90% yield. They were recrystallised from light petroleum or light petroleum–benzene.

		Mono-alkyl ester requires:		Calc. for di-alkyl ester:		Found:	
Ester.	M. p.	C, %.	H, %.	C, %.	H, %.	C, %.	H, %.
Methyl	104°	67·7	8·3	68·6	8·6	67·7	8·2
Ethyl	98—99	68·6	8·6	70·1	9·1	68·5	8·6
iso*Propyl*	72	69·4	8·8	71·4	9·5	69·4	8·9

0·1378 G. of the methyl ester, dissolved in neutral alcohol by heating to 50°, required 10·3 ml. of 0·05N-sodium hydroxide ($C_{14}H_{21}O_2\cdot CO_2H$ requires 10·4 ml.). 0·115 G. of the ethyl ester under the same conditions required 8·5 ml. ($C_{15}H_{23}O_2\cdot CO_2H$ requires 8·2 ml.).

Methyl and Ethyl Esters from the Adduct obtained from β-Phellandrene.—The adduct (0·45 g.) was boiled for 8 hours with methyl-alcoholic hydrogen chloride (4·5 ml.). The excess of alcohol was evaporated at room temperature under reduced pressure; the crystals separating (0·35 g.) had m. p. 97°. After two recrystallisations from light petroleum–benzene the m. p. 103—104° was not depressed by the methyl ester obtained from the *l*-α-phellandrene–maleic anhydride adduct.

Similar treatment of the adduct (0·33 g.) with ethyl-alcoholic hydrogen chloride (3·5 ml.) gave a product (0·3 g.), which, after twice recrystallising from light petroleum–benzene, had m. p. 98°, not depressed by the ethyl ester from authentic *l*-α-phellandrene–maleic anhydride adduct.

Treatment of l-*β-Phellandrene free from* l-*α-Phellandrene.*—A mixture of *l*-β-phellandrene (13·6 g.), maleic anhydride (1·6 g.), and ether (16 ml.) was boiled under reflux for 30 minutes, poured into a beaker, and left overnight. The unchanged terpene was removed by steam-distillation and dried over sodium sulphate. It was not possible to isolate any of the *l*-α-phellandrene–maleic anhydride adduct from the resinous solid remaining in the distillation flask. The recovered terpene (6·5 g.), maleic anhydride (4·5 g.), and benzene (6·5 ml.) were heated on the water-bath for 3 hours, and the product distilled as in (i) above. The fraction obtained under the usual conditions, after recrystallising from methyl alcohol, had m. p. 116° (sintering at 111°); yield, 0·4 g. Further recrystallisation raised the m. p. to 123°, not depressed by authentic *l*-α-phellandrene–maleic anhydride adduct.

Attempts to isolate the Adduct from l-*β-Phellandrene and Maleic Anhydride without Distillation.*—A mixture of *l*-β-phellandrene (10 g.), maleic anhydride (7 g.), and benzene (10 ml.) was heated on the water-bath for 8 hours. Benzene and unchanged terpene were removed under reduced pressure at 80°, and the residue heated for an hour at 180—200° under reflux and then extracted repeatedly with ether; a white powdery resin remained. The extract was evaporated at room temperature, and the oily residue triturated with methyl alcohol. The small amount of solid remaining, after recrystallisation from methyl alcohol, had m. p. 113° (sintering at 101°) and admixture with authentic *l*-α-phellandrene–maleic anhydride adduct raised the m. p. to 123—125° (sintering at 119°), but the amount of material was insufficient for further purification. Repetition of this experiment, the period of heating at 180—200°, however, being omitted, yielded material which was completely soluble in cold methyl alcohol except for a small amount of resin.

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