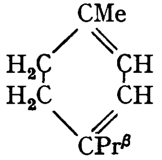
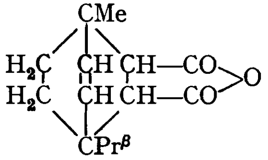
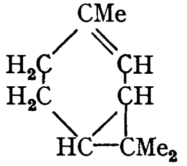
NOTE.

Observations on the Condensation Products from " α-Terpinene " and the Carenes with Maleic Anhydride. By N. F. GOODWAY and T. F. WEST.

DIELS, KOCH, and FROST (*Ber.*, 1938, **71**, 1163) condensed α-terpinene (I) and a compound formulated as (II) with maleic anhydride, expecting that both would yield the same product (III).


(I.)


(III.)


(II.)

The crude product obtained from (I) yielded a dicarboxylic acid, first obtained by Koch (Dissert., Kiel, 1932) as an uncrystallisable oil. This acid was described by Diels, Koch, and Frost (*loc. cit.*) as having m. p. 158°, and from it the anhydride (III), m. p. 66—67°, could be regenerated. Sfiras (*Recherches*, 1939, 115) prepared a similar product according to the method of Diels and his co-workers, but the acid obtained melted at 130—131° and the corresponding anhydride at 65—66°. This discrepancy has also been noticed by us, the highest melting point for the acid being 134° after repeated crystallisation from acetonitrile and methyl ethyl ketone, and the m. p. of the anhydride could not be raised above 62°.

The α-terpinene used by the above-mentioned and the present authors was prepared by the dehydration of terpineol with a solution of oxalic acid (Wallach, *Annalen*, 1893, **275**, 107). According to Dupont, Lévy, and Marot (*Bull. Soc. chim.*, 1933, **53**, 393) the product thus obtained consists of a mixture of α- and γ-terpinenes, 1 : 4-cineole, dipentene, and terpinolene, and since the last two can be made to condense with maleic anhydride (Hultzsch, *Angew. Chem.*, 1938, **51**, 921; *Ber.*, 1939, **72**, 1173) we concluded that the reason for the failure to reproduce the m. p. of 158° for the acid was to be found in the starting material. Neither Koch (*loc. cit.*) nor Diels, Koch, and Frost (*loc. cit.*) recorded the constants for the " α-terpinene " employed, but it is evident from the accounts that the samples represented the crude mixture of terpenes obtained from commercial α-terpineol. The terpene mixture which we obtained ($d_{15°}^{15°}$ 0·8583, $n_D^{20°}$ 1·4826, α_D + 0·35°) was therefore fractionally distilled (atm. press.) through an 8-bulb Young–Thomas column into five fractions. Each of these fractions was condensed separately with maleic anhydride; the first four gave acids of substantially the same m. p. :

					Acid (crude).	
Fraction.	B. p.	$d_{15°}^{15°}$.	$n_D^{20°}$.	α_D.	Yield, %.	M. p.
1	171—175°	0·8549	1·4780	+0·25°	17	128—129°
2	176—178	0·8557	1·4786	+0·25	13	—
3	178—179	0·8559	1·4793	+0·25	16	131
4	179—180	0·8567	1·4808	+0·3	2	124
5	Residue	—	—	—	Nil	—

From the compound formulated as (II) Diels, Koch, and Frost obtained an acid melting at 184° and concluded that the reaction did not yield the α-terpinene adduct as expected. Hultzsch (*Ber.*, *loc. cit.*) isolated an acid, m. p. 183°, $[\alpha]_D^{18°}$ − 8·7°, by condensing with maleic anhydride a fraction from German wood turpentine oil, which " wohl beide Carene enthielt ". With maleic acid as addendum, he claimed to have isolated the acid corresponding to the α-terpinene adduct, but the m. p. was not recorded throughout the paper in spite of the fact that he stated that this same acid was prepared from a number of other terpenes.

The evidence outlined above would appear to indicate that the addition of maleic anhydride to (II) does not yield the α-terpinene adduct. This evidence is open to two objections: (1) Although the constants of the terpene formulated as (II) were not recorded by Diels and his co-workers, the sample was presumably optically active (Simonsen, " The Terpenes," 1932, 2, 56, 64) and by analogy with the adducts from α- and β-phellandrenes (Goodway and West, J., 1938, 2028), the adduct (and derived acid) would be expected to display optical activity. The optically active products would presumably differ from those from the inactive α-terpinene even if structurally identical. We therefore attempted to resolve the acid obtained from the α-terpinene adduct by repeated crystallisation of the brucine salt, but the acid recovered showed no definite optical activity and its m. p. was invariably lower than that of the original acid. (2) The hydrocarbon formulated by Diels is Δ^4-carene, although it is referred to throughout the paper as Δ^3-carene * and in the absence of the constants and derivation of the sample of terpene there is no clue to its actual identity.

We hope to undertake a further study of the action of maleic anhydride on pure α-terpinene, Δ^3- and Δ^4-carene and 1 : 4-cineole which may throw light on these discrepancies, but in view of the work of Sfiras it has been throught desirable to record this account of preliminary experiments carried out before the war.

We are indebted to the Directors of Messrs. Stafford Allen and Sons Ltd. for the gift of the terpenes.—THE SIR JOHN CASS INSTITUTE, LONDON, E.C. 3. [*Received, February 27th*, 1940.]

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* Both the American and the British abstract of this paper (*Chem. Abstr.*, 1938, 7027; *Brit. Chem. Abstr.*, 1938, II, 331) erroneously refer to Δ^3-carene as containing a double bond conjugated with a *cyclo*propane ring. Sfiras (*loc. cit.*) has similarly confused Δ^3- and Δ^4-carene, since a hydrocarbon isolated from Kenya cypress oil was identified as Δ^3-carene and again formulated as Δ^4-carene.