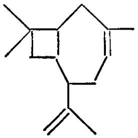
381. *Addition Reactions to Conjugated Systems. Part II. Caryophyllene and Maleic Anhydride.*

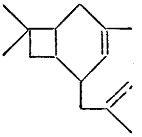
By Norman F. Goodway and Trustham F. West.

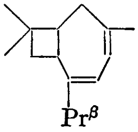
Contrary to the indication of the tests proposed by Sandermann and by Fieser the absorption spectrum of the mixture of sesquiterpenes known as caryophyllene shows the absence of any appreciable quantity of a conjugated isomeride.

The caryophyllene–maleic anhydride adduct fails to yield by the action of alcoholic hydrogen chloride a monoalkyl lactonic ester of the type derived from the normal adducts of α-phellandrene and di*cyclo*hexenyl. This result appears to throw doubt on the suggestion of Rydon that normal adduct formation takes place between caryophyllene and maleic anhydride and on the argument of diene addition to a *cis*-butadiene system which involves a seven-membered ring structure for the parent terpene.

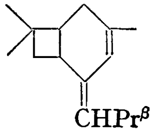
Rydon (*Chem. and Ind.*, 1938, **57**, 123) has suggested that the principal constituent of the mixture of hydrocarbons known as caryophyllene should be represented by structure (I) rather than by the older formulation (II) proposed by Ruzicka (*ibid.*, 1935, **54**, 509; cf. Ramage and Simonsen, *ibid.*, 1939, **58**, 447; Ruzicka *et al.*, *Helv. Chim. Acta*, 1939, **22**, 716).


(I.)


(II.)



(III.)

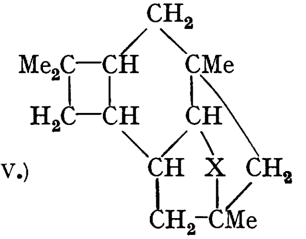


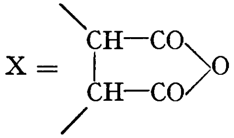
(IV.)

In support of his suggestion Rydon (this vol., p. 537) discussed the formation of the caryophyllene–maleic anhydride adduct obtained by Ruzicka and Zimmermann (*Helv. Chim. Acta*, 1935, **18**, 219). This adduct he considers to be " doubtless derived from the conjugated isomer (III) or (IV), both pre-existing in the sesquiterpene mixture and formed from the *iso*propylidene isomer by double bond migration during the reaction." The formation of a crystalline monomeric adduct he considered to indicate the presence of the *cis*-butadiene system in the conjugated isomeride (III), whereas (II) could lead only to the *trans*-butadienoid isomeride (IV).

Ruzicka and Zimmermann (*loc. cit.*) showed, however, that neither the caryophyllene–maleic anhydride adduct nor the corresponding dicarboxylic acid reacted with ozone, alkaline permanganate, perbenzoic acid or tetranitromethane. Ruzicka, Zimmermann, and Huber (*Helv. Chim. Acta*, 1936, **19**, 348) concluded that the product was not a normal diene adduct but the saturated compound (V) derived from the non-conjugated diene (II). This was supported by the molecular refraction of the esters of the adduct.

(V.)





If Rydon's theoretical formulation of the reaction is correct, however, the adduct must contain the double bond characteristic of the normal adduct and the lack of evidence of unsaturation must lie in the non-reactive nature of the double bond observed in many polyterpenoid compounds (cf. *Ann. Reports*, 1937, **34**, 328).

Sandermann (*Seifens.-Ztg.*, 1938, **65**, 553) has suggested that the yellow colour which always precedes the condensation of a diene and maleic anhydride might be utilised to indicate the presence of diene constituents in essential oils, but the results for a number of simpler terpenes (see experimental) show that the test is not applicable. Similarly the application of Fieser's colour reaction (*J. Amer. Chem. Soc.*, 1938, **60**, 159) of conjugated dienes with *p*-nitrobenzenediazonium chloride gives a positive reaction for Δ^3-carene and, contrary to the indication of these tests, the absorption spectrum of caryophyllene shows the absence of an appreciable quantity of the conjugated isomeride postulated by Rydon (*loc. cit.*).

Now Goodway and West (J., 1938, 2028) have shown that esterification of the adduct of α-phellandrene and maleic anhydride with alcoholic hydrogen chloride leads to the formation of a monoalkyl lactonic ester and Adams and Gruber (*J. Amer. Chem. Soc.*, 1938, **60**, 2792) found that the adduct from di*cyclo*hexenyl behaved similarly. An attempt was made, therefore, to obtain a similar monoalkyl ester from the caryophyllene–maleic anhydride adduct. The liquid ester obtained by the action of methyl-alcoholic hydrogen chloride was different from the dimethyl ester melting at 156° prepared by Ruzicka and Zimmermann (*loc. cit.*) by the action of methyl iodide on the silver salt of the corresponding dicarboxylic acid, but the analytical figures for this liquid product also corresponded to the dimethyl ester which would be anticipated for a saturated adduct. These results appear to render doubtful the assumption of Rydon (*loc. cit.*) that normal adduct formation takes place and to invalidate the evidence which he adduces from the work of Goodway and West (*loc. cit.*). Furthermore Hultzsch (*Ber.*, 1939, **72**, 1173) showed that a number of terpenes of established constitution, lacking a conjugated system, reacted with maleic anhydride to give adducts of which the structure was not determined.

EXPERIMENTAL.

Colour Reactions.—The terpenes were obtained by the fractional distillation of suitable commercial essential oils and had the following constants :

Terpene.	$d_{15^\circ}^{15^\circ}$.	α_D.	$n_D^{20^\circ}$.	B. p.
Caryophyllene	—	− 8·7°	1·5005	105—108°/3 mm.
α-Phellandrene	0·8495	− 78·95	1·4766	72—74/30 mm.
β-Phellandrene	0·8501	− 47·25	1·4825	87/50 mm.
α-Pinene	0·8701	− 32·4	1·4730	76—78/60 mm.
Limonene	0·8472	+100·65	1·4736	93—95/65 mm.
Δ^3-Carene	0·8693	+ 4·9	1·4768	80—82/55 mm.

(a) *Maleic anhydride.* Each of the terpenes developed some yellow colour after the addition of a solution of maleic anhydride in benzene.

(b) p-*Nitrobenzenediazonium chloride.* The terpene (0·1 ml.), dissolved in glacial acetic acid (1 ml.), was added to 1 ml. of the *p*-nitrobenzenediazonium chloride solution prepared according to the method of Fieser and Campbell (*J. Amer. Chem. Soc.*, 1938, **60**, 168) :

Terpene.	Remarks.
Caryophyllene	Orange-red after 9 minutes (positive)
α-Phellandrene	,, ,, 3 ,, ,,
β-Phellandrene	,, ,, 5 ,, ,,
Δ^3-Carene	,, ,, 7 ,, ,,
Limonene	Yellow ,, 30 ,, (negative)
α-Pinene	,, ,, 30 ,, ,,
Control	Very pale yellow after 30 minutes

The fact that Δ^3-carene shows a positive reaction is of special interest, since this terpene does not contain a *cyclo*propane ring conjugated with a double bond as stated by Diels, Koch, and Frost (*Ber.*, 1938, **71**, 1163; cf. Hultzsch, *loc. cit.*).

Absorption Spectrum of Caryophyllene.—This measurement was kindly carried out by Dr. A. E. Gillam, who has reported as follows : " The absorption curve exhibits a maximum at 2640—2650 A., $\varepsilon_{\text{max.}} = 142$ (solvent, alcohol). From the low intensity of this absorption I consider it safe to infer that it is due to the presence of some unsaturated impurity (order 1—2% only). . . . Thus the data would be consistent with any unconjugated formulation but would be directly opposed to the presence of a compound having conjugated ethylene linkages, unless present only in traces."

Preparation of Dimethyl Ester from Caryophyllene–Maleic Anhydride Adduct.—The adduct (10 g.), m. p. 98°, prepared as described by Ruzicka and Zimmermann (*Helv. Chim. Acta*, 1935, **18**, 229), was boiled for 8 hours with 100 ml. of methyl alcohol saturated in the cold with hydrogen chloride. The alcohol was then removed by distillation under reduced pressure, and the liquid ester washed repeatedly with water and fractionally distilled under reduced pressure. This ester (4 g.) had b. p. 180—183°/3 mm., $n_D^{22^\circ}$ 1·4960, saponification value 299·8, acid value 5, and showed no tendency to crystallise (Found : C, 72·4; H, 9·3; OMe, 17·4. Calc. for a monomethyl lactonic ester $C_{20}H_{30}O_4$: C, 72·0; H, 9·0; OMe, 9·3%. Calc. for a dimethyl ester $C_{21}H_{32}O_4$: C, 72·4; H, 9·2; OMe, 17·8%).

We are indebted to Dr. A. E. Gillam for providing the absorption spectrum data and to Messrs. Stafford Allen and Sons Ltd. and Mr. G. E. Smith for the gift of the terpenes.

THE SIR JOHN CASS INSTITUTE, LONDON, E.C. 3.

[*Received, September 25th*, 1939.]