32. *Application of the Diene Synthesis to Terpenoid Compounds. Part II. Observations on the Esters derived from some Maleic Anhydride Adducts.*

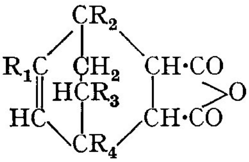
By T. F. West.

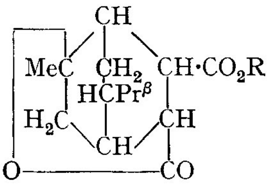
In Part I (J., 1940, 1162) it was found that the eucarvone–maleic anhydride adduct, like the caryophyllene adduct, gives dialkyl esters with alcoholic solutions of hydrogen chloride. It is now shown that the maleic anhydride adducts derived from $\Delta^{1:3}$-*cyclo*-

hexadiene, myrcene, and anthracene behave similarly, whereas the *cyclo*pentadiene adduct, like that from α-phellandrene, gives a monoalkyl lactonic ester. The reaction lends support to the suggestion of Goodway and West (J., **1940**, 702) that the α-terpinene–maleic anhydride adduct is derived from a mixture of terpenes. The colour reactions of a number of terpenoid compounds with a solution of tetranitromethane are described.

Goodway and West (J., 1939, 1853) have drawn attention to the fact that, although the maleic anhydride adducts from α-phellandrene and di*cyclo*hexenyl yield monoalkyl lactonic esters with alcoholic solutions of hydrogen chloride, the caryophyllene adduct, considered by Rydon (J., 1939, 537) to be derived from a conjugated *cyclo*heptadiene, gives dialkyl esters. On the other hand, West (J., 1940, 1162) has obtained dialkyl esters from the eucarvone–maleic anhydride adduct with both methyl- and ethyl-alcoholic hydrogen chloride.

It has now been found that similar treatment of the α-terpinene–maleic anhydride adduct with methyl-alcoholic hydrogen chloride leads to a mixed product, whereas the $\Delta^{1:3}$-*cyclo*hexadiene–maleic anhydride adduct gives a dialkyl ester exclusively and in good yield. The formulæ assigned by Diels and his co-workers being accepted, it is remarkable that these substituted *bicyclo*[2 : 2 : 2]octane systems derived from $\Delta^{1:3}$-*cyclo*hexadiene (I; R_1, R_2, R_3 and R_4 = H), α-phellandrene (I; R_1 = Me, R_3 = Pr^β, R_2 and R_4 = H), and α-terpinene (I; R_2 = Me, R_4 = Pr^β, R_1 and R_3 = H) behave differently. The result lends support to the inference of Goodway and West (J., 1940, 702) that the α-terpinene adduct may be an impure product derived from a mixture of terpenes in which α-terpinene predominates (cf. Booker, Evans, and Gillam, J., 1940, 1463). Furthermore, considered with the ease of addition of maleic anhydride to eucarvone (West, *loc. cit.*), it may be significant that Alder and Rickert (*Ber.*, 1937, **70**, 1364) obtained evidence, from an examination of the condensation products formed with acetylenedicarboxylic ester, for the presence of 1 : 5 : 5-trimethyl-$\Delta^{1:3}$-*cyclo*heptadiene in the α-terpinene prepared in the usual manner by the dehydration of α-terpineol. Hultzsch (*Ber.*, 1939, **72**, 1173) has reported that the α-phellandrene–maleic anhydride adduct cannot be reduced and that the corresponding dicarboxylic acid is unobtainable. The cause of the variation is not obvious from an examination of models and the reason for the formation of *dimethyl* esters from the maleic anhydride adducts derived from myrcene, isoprene, and anthracene and a *monomethyl lactonic* ester from the *cyclo*pentadiene adduct is equally obscure.


(I.)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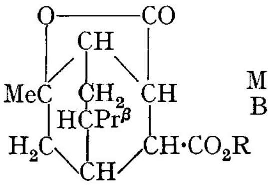
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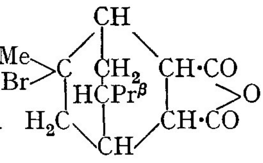
(IV.)

The conclusions of Linstead and Rydon (J., 1933, 580) and Adams and Gruber (*J. Amer. Chem. Soc.*, 1938, **60**, 2792) being applied, the formulæ (II) and (III) are the most probable for the lactonic esters * obtained from the α-phellandrene–maleic anhydride adduct. In an attempt to confirm this conclusion the methyl ester was treated with a solution of hydrogen bromide, followed by acetyl chloride. In analogy with the results of Koch (Dissert., Kiel, 1932) the formation of the bromo-anhydride (IV) was expected, but in practice the only product isolated was a monobasic *lactonic* acid identical with the acid (II) or (III) (R = H) obtained by saponifying the methyl ester.

A solution of tetranitromethane produces a yellow colour with the dimethyl esters

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* (Joint note with Dr. N. F. Goodway.) In the paper of Goodway and West (J., 1938, 2028), page 2031, line 20 *et seq.* should read "0·1378 G. of the methyl ester, dissolved in neutral alcohol by heating to 50°, required 0·3 ml. of 0·05N-sodium hydroxide ($C_{14}H_{21}O_2$·CO_2H requires 10·4 ml.). 0·115 G. of the ethyl ester under the same conditions required 0·5 ml. ($C_{15}H_{23}O_2$·CO_2H requires 8·2 ml.)."

obtained from the myrcene–, isoprene–, anthracene– and $\Delta^{1:3}$-*cyclo*hexadiene–maleic anhydride adducts and the product derived from the α-terpinene adduct. The monomethyl lactonic esters from the α-phellandrene and *cyclo*pentadiene adducts display no evidence of unsaturation. The eucarvone–maleic anhydride adduct finds another analogy with the caryophyllene adduct in not giving a reaction with tetranitromethane (cf. Ruzicka and Zimmermann, *Helv. Chim. Acta*, 1935, **18**, 219). On the contrary the dialkyl esters prepared from both these adducts (Goodway and West, J., 1939, *loc. cit.*; West, *loc. cit.*) show a yellow colour with the reagent. The presence of a double bond in the caryophyllene adduct remains uncertain (Ruzicka and Zimmermann, *loc. cit.*; Rydon, *loc. cit.*; Goodway and West, *loc. cit.*), but in the case of the eucarvone adduct the lack of evidence of unsaturation must reside in the non-reactive nature of the double bond observed in some polyterpenoid compounds (*Ann. Reports*, 1937, **34**, 328).

It is fortunate that the thoroughly investigated maleic anhydride adducts from *cyclo*pentadiene and $\Delta^{1:3}$-*cyclo*hexadiene provide, respectively, saturated mono- and unsaturated di-alkyl esters similar to those reported, in the present and previous papers, as derivable from terpenoid compounds. When circumstances permit, it is proposed to investigate further the constitution of the esters obtained from these typical adducts.

EXPERIMENTAL.

(Carbon and hydrogen determinations are by Drs. Weiler and Strauss, Oxford.)

Preparation of the Esters.—(*a*) The anthracene–maleic anhydride adduct (Clar, *Ber.*, 1931, **64**, 2198) (3 g.), m. p. 62°, was refluxed for 8 hours with 10 vols. of methyl alcohol saturated in the cold with dry hydrogen chloride. The crystals (2·9 g.) which separated on standing were recrystallised from methyl alcohol. The white *dimethyl* ester had m. p. 151° (Found: C, 74·4; H, 5·4; OMe, 18·85. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6; OMe, 19·25%). (*b*) Myrcene–maleic anhydride adduct (Diels and Alder, *Annalen*, 1928, **460**, 81) (10 g.), m. p. 34°, gave, on similar treatment and after removal of the alcohol, an oil which was kept for a few days over paraffin wax and solid caustic potash in a vacuum desiccator before purification by fractional distillation. The *dimethyl* ester (7·8 g.) had b. p. 176—178°/3 mm., $n_D^{20°}$ 1·4922 (Found: C, 68·5; H, 8·6; OMe, 21·9. $C_{16}H_{24}O_4$ requires C, 68·6; H, 8·6; OMe, 22·1%). (*c*) The isoprene–maleic anhydride adduct (Diels and Alder, *Annalen*, 1929, **470**, 101) (3·9 g.), m. p. 62—64°, treated as described in (*b*), gave a dimethyl ester which was not fully purified. It had b. p. 128—130°/3 mm. (Found: C, 60·3; H, 7·9; OMe, 23·1. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5; OMe, 29·2%). (*d*) The $\Delta^{1:3}$-*cyclo*hexadiene adduct (Diels and Alder, *Annalen*, 1928, **460**, 115) (5 g.), m. p. 147—148°, treated as described above, gave, after removal of the bulk of the methyl alcohol, white crystals (4·4 g., m. p. 64—67°); after recrystallisation from light petroleum the *dimethyl* ester (3·2 g.) had m. p. 69—71° (Found: C, 64·5; H, 7·1; OMe, 28·2. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1; OMe, 27·7%). (*e*) The *cyclo*pentadiene adduct (Diels and Alder, *Annalen*, 1928, **460**, 111) (7 g.), m. p. 164°, treated as described above, gave a product (6·5 g.) (m. p. 170° indefinite, sintering at 80°), which was separated into two components by repeated extraction with warm light petroleum. After recrystallisation from light petroleum the *monomethyl lactonic* ester (2·4 g.) had m. p. 83—84° (Found: C, 61·2; H, 6·0; OMe, 15·4. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1; OMe, 15·8%). The monobasic *lactonic* acid, insoluble in light petroleum, crystallised from xylene in small blunt prisms (1·3 g.), m. p. 203—204° (Found: C, 59·5; H, 5·5; OMe, 0; equiv., 183. $C_9H_{10}O_4$ requires C, 59·3; H, 5·5%; equiv., 182). (*f*) In a typical experiment the α-terpinene–maleic anhydride adduct (Diels, Koch, and Frost, *Ber.*, 1938, **71**, 1163; cf. Goodway and West, J., 1940, 702) (7 g.), m. p. 62°, was refluxed for 8 hours with methyl-alcoholic hydrogen chloride (70 ml.), the bulk of the alcohol removed under reduced pressure, and the concentrated solution poured into water. The oil was extracted with ether, and the ethereal solution washed successively with 2N-sodium carbonate and water and then dried over sodium sulphate. After recovery of the solvent, the oil obtained (6 g.) solidified, on prolonged standing, to a waxy, crystalline mass which was soluble in cold methyl alcohol and light petroleum. After two fractional distillations under reduced pressure the main fraction (4 g.) had b. p. 150—152°/2 mm., m. p. 50—53°, acid value 55·4 (the alkali was gradually absorbed to give this figure), ester value 196·7 (Found: C, 68·8; H, 8·4; OMe, 15·7. A monomethyl lactonic ester, $C_{15}H_{22}O_4$, requires C, 67·5; H, 8·3; OMe, 11·7%. A dimethyl ester, $C_{16}H_{24}O_4$, requires C, 68·6; H, 8·6; OMe, 22·1%).

Action of Hydrogen Bromide on the Methyl Ester from the α-Phellendrene–Maleic Anhydride Adduct.—The methyl ester (Goodway and West, J., 1938, 2031) (4 g.), m. p. 103—104°, dissolved in a 15% solution of hydrogen bromide in glacial acetic acid (40 ml.), was heated in a sealed tube at 110—120° for 6½ hours. The acetic acid and hydrogen bromide were removed by distillation under reduced pressure and the red oily residue, which showed no tendency to crystallise, was boiled with acetyl chloride (5 ml.) for 2 hours. After standing for some weeks over solid caustic potash in a vacuum desiccator, the viscous product was triturated with a mixture of light petroleum (5 vols.) and benzene (1 vol.); the residue then crystallised. After repeated crystallisation from light petroleum–benzene (1 : 1), the white crystalline *acid* (0·3 g.) had m. p. 168—169° (Found: C, 66·5; H, 7·7; equiv., 266. A monobasic lactonic acid, $C_{14}H_{20}O_4$, requires C, 66·7; H, 7·9%; equiv., 252).

After the methyl ester had been saponified with methyl-alcoholic caustic potash, the *acid*, isolated in the usual manner and crystallised from light petroleum–benzene, had m. p. 167—169°, equiv. 273, and mixed m. p. with the above acid 168—169°.

Reaction with Tetranitromethane.—A solution of tetranitromethane (1 vol.) in AnalaR acetone (2 vols.) was added (0·2 ml.) to the compound (0·02 g.) dissolved in acetone (0·2 ml.); the colour of the solution recorded immediately remained unchanged after 30 minutes. All the observations were made on the same day with the same reagents.

Compound.	Colour with solution of tetranitromethane.
Monomethyl lactonic ester from α-phellandrene adduct	No change
Monomethyl lactonic ester from *cyclo*pentadiene adduct	,,
Lactonic acid from *cyclo*pentadiene adduct	,,
Dimethyl ester from anthracene adduct	Yellow
Dimethyl ester from myrcene adduct	Deep yellow
Dimethyl ester from isoprene adduct	,,
Dimethyl ester from $\Delta^{1:3}$-*cyclo*hexadiene adduct	Pale yellow
Mixed product from α-terpinene adduct	Yellow
Eucarvone adduct	No change
Dimethyl ester from eucarvone adduct	Pale yellow
Diethyl ester from eucarvone adduct	,,
Dimethyl ester from caryophyllene adduct	,,
Control	No change

The author thanks Dr. N. F. Goodway for his interest in this work and for kindly providing a sample of the product from the α-terpinene adduct, and is indebted to the Directors of Messrs Stafford Allen and Sons, Ltd., for the gift of the terpenes.

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