217. *Application of the Diene Synthesis to Terpenoid Compounds. Eucarvone and Maleic Anhydride.*

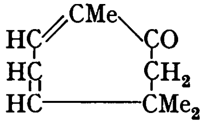
By T. F. West.

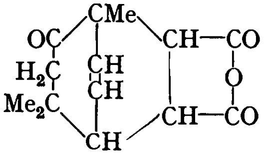
Eucarvone reacts with maleic anhydride in boiling benzene solution to give an *adduct*, $C_{14}H_{16}O_4$. This adduct yields *dimethyl* and *diethyl* esters on treatment with the corresponding alcoholic hydrogen chloride and therefore finds analogy with the behaviour of the caryophyllene–maleic anhydride adduct and invalidates one of the arguments used by Goodway and West to criticise Rydon's seven-membered ring structure for caryophyllene.

Goodway and West (J., 1938, 2028) have drawn attention to the fact that, whereas addition of maleic anhydride to the *cis*-butadienoid system in the α-phellandrene molecule takes place readily, in the case of the *trans*-butadienoid system in β-phellandrene the reaction is slow and incomplete (Goodway and West, *J. Soc. Chem. Ind.*, 1938, **57**, 37) and leads mainly to resinous material. It was therefore of interest to examine the effect on the course of diene addition when the *cis*-butadienoid system is situated in larger rings. Apart from the preliminary experiments of Koch (Dissert., Kiel, 1932) nothing appears to have been published concerning addition to cyclic compounds containing a conjugated system in rings larger than six-membered. Koch (*loc. cit.*) boiled a mixture of *cyclo*heptadiene with maleic anhydride in the absence of a solvent and reported the formation of a compound displaying the properties of a normal diene adduct. However, the amount of material involved was small and tests or constants to establish the identity of the *cyclo*heptadiene were omitted. Furthermore a number of authors have shown that, by boiling non-conjugated terpenes with maleic anhydride, compounds are obtained in which the proportion of maleic anhydride to terpene is 1 : 1 (*inter alia*, Diels, Koch, and Frost, *Ber.*, 1938, **71**, 1163; Hultzsch, *Angew. Chem.*, 1938, **51**, 921; *Ber.*, 1939, **72**, 1173).

It has now been found that eucarvone (I), reacting with maleic anhydride in boiling benzene solution, gives an *adduct* which, normal diene addition being assumed, can be formulated as (II).

(I.)





(II.)

In contradistinction to the behaviour of α-phellandrene, eucarvone does not react with a cold solution of maleic anhydride and the examination of models indicates that diene addition involves slight strain on the eucarvone molecule. The eucarvone was prepared by Baeyer's method from carvone, and its identity confirmed by the constants and preparation of the semicarbazone; the 2 : 4-*dinitrophenylhydrazone* was prepared.

Goodway and West (J., *loc. cit.*) have described the preparation of a series of monoalkyl lactonic esters by boiling the α-phellandrene–maleic anhydride adduct with alcoholic solutions of hydrogen chloride and have used (J., 1939, 1853) the formation of a dimethyl ester from the caryophyllene–maleic anhydride adduct as an argument against the suggestion of Rydon (J., 1939, 537) that in the case of caryophyllene normal diene addition takes place to the *cis*-butadienoid system in a seven-membered ring. It has now been established that, contrary to expectation in analogy with the behaviour of the α-phellandrene–maleic anhydride adduct, the eucarvone adduct gives dialkyl esters with both methyl- and ethyl-alcoholic hydrogen chloride when subjected to the treatment described by Goodway and West, whereas after prolonged boiling with *iso*propyl-alcoholic hydrogen chloride the adduct is recovered unchanged. This difference in behaviour towards methyl and ethyl alcohol as compared with *iso*propyl alcohol may depend on steric hindrance considerations, although this is not obvious from an examination of models. However, the formation of a dimethyl ester from the undoubted seven-membered ring diene, eucarvone, immediately invalidates one of the arguments used by Goodway and West in criticising Rydon's seven-membered ring structure for caryophyllene.

It is proposed, when circumstances permit, to investigate the eucarvone adduct closely and to compare its properties with those of the caryophyllene–maleic anhydride adduct described by Ruzicka and Zimmermann (*Helv. Chim. Acta*, 1935, **18**, 219) and also the application of the diene reaction to large ring compounds containing the butadienoid system. It has, however, been thought advisable to record this account of experiments initiated before the outbreak of war.

EXPERIMENTAL.

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

The eucarvone was prepared from carvone (obtained by fractional distillation under reduced pressure from caraway oil and having a ketone content of 96% when determined by the hydroxylamine hydrochloride method) in the manner described by Baeyer (*Ber.*, 1894, **27**, 810) and had b. p. 70—75°/2 mm., $d_{15^\circ}^{25^\circ}$ 0·9459, $n_{\mathrm{D}}^{22^\circ}$ 1·5080. Confirmation of its identity with the product described by Baeyer was obtained by the preparation of the semicarbazone, m. p. 183—185° (Found : N, 20·4. Calc. for $C_{11}H_{17}ON_3$: N, 20·3%). *Eucarvone* 2 : 4-*dinitrophenylhydrazone*, prepared by the standard method, had m. p. 152—153° (decomp.) after two crystallisations from ethyl alcohol (Found : N, 16·9. $C_{16}H_{18}N_4O_4$ requires N, 17·0%).

Preparation of the Adduct with Maleic Anhydride.—Eucarvone (15 g.) was added to maleic anhydride (10 g.) dissolved in benzene (15 ml.); a yellow colour developed immediately. No reaction occurred in the cold (cf. α-phellandrene; Diels and Alder, *Annalen*, 1928, **460**, 116) and the mixture was heated under reflux for 6 hours on a hot plate. After standing overnight, the crystals which separated were roughly dried between filter-papers (11·2 g.) and recrystallised from methyl alcohol; the *eucarvone–maleic anhydride* adduct (8·9 g.) had m. p. 165—167° (Found : C, 67·5; H, 6·65. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·45%).

Treatment of the Eucarvone–Maleic Anhydride Adduct with Solutions of Hydrogen Chloride in Various Alcohols.—(a) *Methyl-alcoholic hydrogen chloride.* The eucarvone–maleic anhydride adduct (3 g.) was boiled for 8 hours with 40 ml. of methyl alcohol saturated in the cold with dry hydrogen chloride. The bulk of the alcohol was removed by distillation under reduced pressure and the crystals which separated were filtered off, dried on filter-paper, and recrystallised from benzene–light petroleum. The white crystalline *dimethyl* ester (1·7 g.) had m. p. 102—103° (Found : C, 65·2; H, 7·6. A monomethyl lactonic ester, $C_{15}H_{20}O_5$, requires C, 64·3; H, 7·1%. A dimethyl ester, $C_{16}H_{22}O_5$, requires C, 65·3; H, 7·5%).

(b) *Ethyl-alcoholic hydrogen chloride.* The eucarvone–maleic anhydride adduct (4 g.) was added to 65 ml. of absolute ethyl alcohol saturated with hydrogen chloride and, after standing overnight, the mixture was refluxed for 9 hours. On standing overnight and scratching, crystals (3·6 g.) separated, m. p. 93—95°, unchanged by recrystallisation from light petroleum–benzene (Found : C, 66·95; H, 7·85. A monoethyl lactonic ester, $C_{16}H_{22}O_5$, requires C, 65·3; H, 7·5%. A *diethyl* ester, $C_{18}H_{26}O_5$, requires C, 67·1; H, 8·1%). The ethyl-alcoholic mother-liquor on concentration under reduced pressure gave a further 0·7 g. of the diethyl ester. No evidence was obtained of the presence of a monoethyl ester.

(c) iso*Propyl-alcoholic hydrogen chloride.* The eucarvone–maleic anhydride adduct (3 g.) was mixed with 40 ml. of *iso*propyl alcohol saturated with hydrogen chloride and, after standing overnight, boiled for 9 hours. The bulk of the alcohol was removed under reduced pressure and the precipitate which then separated was drained on a porous tile and crystallised from light petroleum–benzene. The white crystals obtained (1·1 g.) had m. p. 165—166°, unchanged by admixture with an equal weight of the eucarvone–maleic anhydride adduct.

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