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REACTIONS OF CYCLO-OCTATETRAENE AND ITS DERIVATIVES. PART II.[1]

2:1- AND 2:2-ADDUCTS OF CYCLO-OCTATETRAENE AND CITRACONIC ANHYDRIDE.

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Reaction of maleic anhydride with cyclo-octatetraene affords a 1:1-adduct of structure (I; R=H).[2] An attempt to obtain the corresponding adduct (I; R=Me) of citraconic anhydride, by heating an equimolar mixture of the two reagents for 2 hr. at *ca*. 180°, unexpectedly led to a 2:2-adduct, $C_{26}H_{24}O_6$,† m.p. 324-328° (from acetone-ether). Furthermore, when the reaction was carried out in refluxing mesitylene or o-dichlorobenzene, using 2 mol. of cyclo-octatetraene, a 2:1-adduct, $C_{21}H_{20}O_3$,† m.p. 188-189° (from ether-benzene), was isolated. It was shown (by t.l.c.) that each of these products was accompanied by the other; however, the 2:1-adduct could not be converted into the 2:2-adduct by heating with citraconic anhydride. The structures of the adducts were elucidated as follows.

The i.r. spectrum of the 2:1-adduct (hexachlorobutadiene mull) showed absorption characteristic of C=O in a five-membered anhydride ring at $\nu_{max.}$ 1840 and 1765 cm.$^{-1}$, and C=C absorption at 1640 cm.$^{-1}$. In the 100 MHz n.m.r. spectrum ($CDCl_3$ solution; room-temperature), signals appeared at τ 3.35 - 3.8 (2H), 3.9 - 4.45 (2H), 5.8 - 6.2 (2H), 6.2 - 6.65 (2H), 6.75 - 7.0 (1H), 7.0 - 7.25 (1H), 7.3 - 8.4 (7H), and 8.64 (s, 3H). When heated, cyclo-

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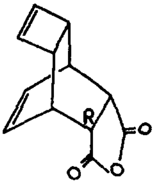
†Elemental analysis and molecular weight (mass spectrometer).

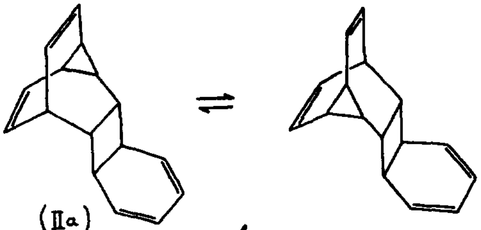
octatetraene forms four dimers, one of which has the structure (IIa $\rightleftharpoons$ IIb), in which rapidly reversible valence isomerism of the homotropilidene system gives rise to a temperature-dependent n.m.r. spectrum.[3] Re-examination of the n.m.r. spectrum of the 2:1-adduct at -80^{o} [$(CD_3)_2CO$ solution] revealed a marked temperature effect, the total number of vinylic protons apparently increasing from four to six, with a corresponding decrease in the number of methine protons. Accordingly, the compound $C_{21}H_{20}O_3$ could be formulated as the adduct of citraconic anhydride and the cyclo-octatetraene dimer (II), and indeed reaction of these components was shown to afford an identical product (mixed m.p. and comparison of the i.r. spectra). By analogy with the maleic anhydride adducts of other bicyclo|4,2,0|octa-2,4-dienes,[4] the 2:1-adduct may be represented as the Diels-Alder product (IIIa $\rightleftharpoons$ IIIb).

During the course of this work, Daub and Trautz[5] isolated an analogous 2:1-adduct after reaction of cyclo-octatetraene and vinylene carbonate at 180^{o}.

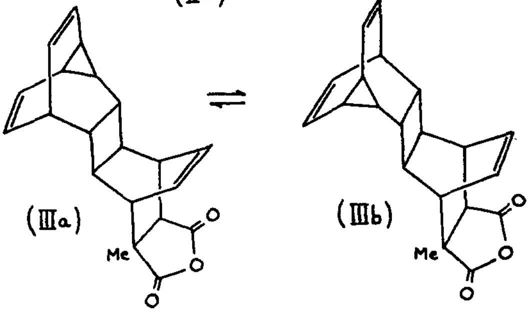
The 2:2-adduct, $\nu_{max.}$ (hexachlorobutadiene mull) 1835, 1770, and 1630 $cm.^{-1}$, gave a 100 MHz n.m.r. spectrum which showed signals at τ ($CDCl_3$) 3.35 - 3.8 (4H), 4.65 - 5.0 (4H), 6.75 - 7.05 (4H), 7.05 - 7.35 (6H), and 8.43 (s, 6H). Since dimerisation of cyclo-octatetraene could be assumed to have preceded the formation of the 2:1-adduct, it was likely that the dimer (IV), which is known to react with two molecules of dimethyl acetylenedicarboxylate to give a product depicted as (V),[6] was the progenitor of the 2:2-adduct. This was confirmed by the demonstration that an identical 2:2-adduct could be produced from the dimer (IV) and citraconic anhydride. Such an adduct would be expected to be a mixture of isomers having structures (VI; R=Me, R'=H) and (VI; R=H, R'=Me), the illustrated stereochemistry being based on the assumptions (a) that addition takes place in a manner analogous to that observed with cyclo-octa-1,3,5-triene, and (b) that no isomerisation of the resulting tricyclo $[4,2,0,0^{2,5}]$octane system occurs. Unfortunately, attempts to achieve a separation of isomers (by g.l.c. of the esterified adduct) failed.



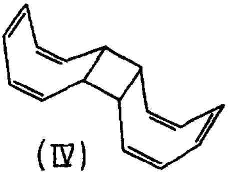
(I)



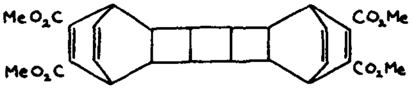
(IIa) (IIb)



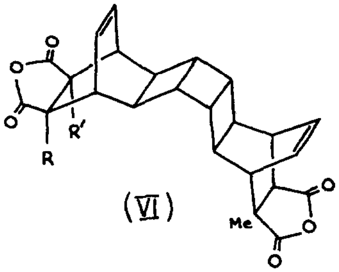
(IIIa) (IIIb)



(IV)



(V)



(VI)

The dienophilic reactivity of the double bond in citraconic anhydride is reduced, relative to that in maleic anhydride, by both steric and electronic effects of the methyl group;[7] moreover, the equilibrium concentration of bicyclo[4,2,0]octa-2,4,7-triene in cyclo-octatetraene is very low (ca. 0.01% at 100°[8]). It is perhaps understandable, therefore, that the dimerisation of cyclo-octatetraene should take place at a much faster rate than its reaction with citraconic anhydride.

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