

REACTIONS OF CYCLO-OCTATETRAENE AND ITS DERIVATIVES. PART IV.¹

THERMAL ISOMERISATION OF A TRICYCLO[4,2,0,0^{2,5}]OCTANE SYSTEM.

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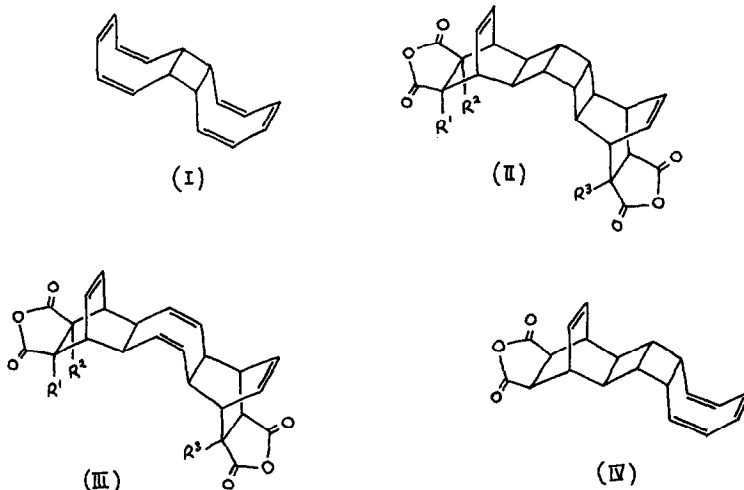
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Reaction of citraconic anhydride with the cyclo-octatetraene dimer (I) at ca. 180° was found to yield a product tentatively formulated as a mixture of the isomers (II; R¹=H, R²=Me, R³=Me) and (II; R¹=Me, R²=H, R³=Me).² However, the possibility of a tricyclo[4,2,0,0^{2,5}]octane → cyclo-octa-1,5-diene rearrangement in structure (II) was envisaged, since the n.m.r. spectrum showed, in addition to the resonance of four vinylic protons at τ 3.35 - 3.8, another low-field signal at τ 4.65 - 5.0(4H). Comparative experiments using maleic anhydride and dimer (I) have now indicated that the above product derived from citraconic anhydride should be assigned structure (III; R¹=H, R²=Me, R³=Me and/or R¹=Me, R²=H, R³=Me).

In refluxing benzene, maleic anhydride reacted with dimer (I) to give the previously reported³ 1:1 adduct; τ 3.60(2H, dd, J 4.5 and 3.5 Hz), 4.05(4H, br s), 4.22(2H, br s), 6.3 - 6.45(2H), 6.6 - 6.8(2H), 6.85 - 7.0(2H), 7.1 - 7.25(2H), and 7.6 - 7.8(2H). The expected stereochemistry of this adduct is shown in structure (IV). In refluxing toluene a 2:1 adduct (II; R¹=R²=R³=H) (decomp. without melting) was obtained. This was converted (methanol-sulphuric acid) into the more soluble tetramethyl ester, m.p. 175-176°, the n.m.r. spectrum of which clearly showed the presence of only four vinylic protons: τ 3.60(4H, dd, J 4 and 3.5 Hz), 6.42(12H, s), 6.95 - 7.25 (12H), and 7.68 (4H, s). When the 2:1 adduct (II; R¹=R²=R³=H) was heated in refluxing o-dichlorobenzene, and the product was subsequently esterified, an isomer of the above tetramethyl ester was isolated; m.p. 211-212°; τ 3.60(4H, dd, J 4 and 4 Hz), 4.83(4H, br s), 6.44(12H, s), 6.86(4H, s), and 7.0 - 7.25

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(8H). The rearrangement product of the 2:1 adduct (II; $R^1=R^2=R^3=H$) may therefore be assigned structure (III; $R^1=R^2=R^3=H$), the n.m.r. spectrum being consistent only with a highly symmetrical structure.



The thermolysis of syn-tricyclo[4,2,0,0^{2,5}]octane⁴ at 150° probably takes place, in part, by a symmetry-allowed retro-[$\pi 2_s + \pi 2_a$] process, since cis-trans-cyclo-octa-1,5-diene (isolated as the dimer⁵) is evidently formed. The rearrangement (II) \rightarrow (III) would perhaps be expected to take a non-concerted course, because the bicyclo[2,2,2]octene systems impose a constraint which would inhibit the generation of a trans-double bond in the eight-membered ring.

All new compounds gave correct analytical figures. N.m.r. data refer to 100 MHz spectra and $CDCl_3$ solutions.

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