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THE PHOTOCHEMISTRY OF SOME CHARGE-TRANSFER COMPLEXES OF CYCLOHEXENE

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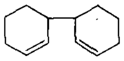
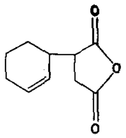
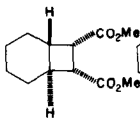
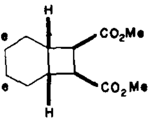
A solution of maleic anhydride in cyclohexene has an absorption band at 270 mμ shown by neither component and ascribable to the formation of charge-transfer complex. Such a solution, carefully deoxygenated and irradiated with filtered light (λ>285 mμ) so that 98% of the light absorbed was absorbed by the complex, gave rise to a mixture, the volatile portion of which was resolved into saturated and unsaturated fractions. The latter contained the diene (I), characterised as its tetrabromide, m.p. 157°, and the substitutive adduct (II) identified by conversion into cyclohexylsuccinic acid.


(I)


(II)


(III)


(IV)

The anhydrides of the saturated fraction were converted into the corresponding dimethyl esters and separated from unsaturated material by mercurating[1] the latter. Preparative gas-liquid chromatography then gave three components (III), (IV), and (V).

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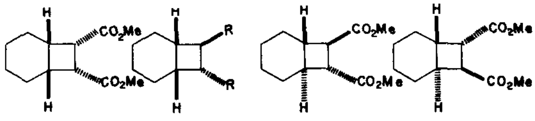
[1] **Kishimoto and Radin, *J. Lipid. Research* 1959, 1, 74.**

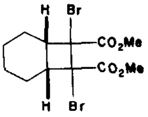


(V) (VI) a, $R = CO_2Me$ b, $R = CO_2H$ c, $R = CN$ (VII) (VIII)

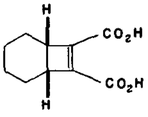
The cis-isomers (IV) and (V), individually equilibrated with sodium methoxide, gave the same mixture containing predominantly the trans-diester (VIa) (isolated by preparative gas-liquid chromatography) and a small quantity of the exo-isomer (IV). The acid (VIb) obtained by hydrolysis, had m.p. 200-201°.

The mixture obtained by equilibrating the diester (III) with sodium methoxide was shown by gas-liquid chromatography to be quite different from that obtained from the isomers (IV) and (V). Preparative gas-liquid chromatography allowed the isolation of the predominant component (VII). Models indicate that the alternative trans-diester (VIII) would have a much higher free energy because of considerable non-bonded interactions. It would therefore be expected not to be formed in significant amounts in an equilibration reaction.

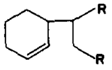
The presence of the cis-bicyclo(4,2,0)octane ring system in the diester (VIa), and hence in the isomers (IV) and (V), was established by bromination to the dibromides (IX), followed by debromination to the cyclobutene derivative (X) and oxidation to cis-cyclohexane-1,2-dicarboxylic acid.



(IX)



(X)



(XI)

The presence of the previously unknown trans-bicyclo(4,2,0)-octane nucleus in the two isomeric esters (III) and (VII) is inferred from the following evidence. Firstly, all five esters exhibit in their infrared spectra, under high resolution, two weak bands at $\sim$ 2995 and $\sim$ 3022 cm.$^{-1}$, which are presumably indicative of a common structural feature, and which occur in a region associated with the C-H stretching vibrations of small ring compounds. In general, *tert*. $>$C-H stretching vibrations are very weak, but since in certain cases adjacent oxygen substitution can lead to enhanced intensity[2], we ascribe the two bands to the group $>$CH-CO$_2$Me incorporated in a cyclobutane ring.

Secondly, the N.M.R. spectra of these isomeric diesters all exhibited a single peak at τ 6.35-6.47 (CO$_2$Me), except for isomer (III) which showed a doublet at τ 6.36 and 6.39. This is readily explained on the formulation given, for, in a *rigid trans*-fused bicyclooctane system, the ester groups of isomer (III) are in different environments whereas those of the isomer (VII) are held in virtually identical environments. It is difficult to reconcile the N.M.R. and I.R. data and the formation of only one new isomer on equilibrating the diester (III) with structures based on any ring system other than *trans*-bicyclo (4,2,0)octane.

Excitation of the charge-transfer absorption band of the fumaronitrile-cyclohexene system gave rise to the diene (I), the substitutive adduct (XI, R=CN) and the dinitrile (VIc), m.p. 80-81^{0}. The structure of this last compound follows from

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[2] Pozefsky and Coggeshall, *Analyt*. *Chem*. 1951, **23**, 1611.

its conversion into the diester (VIa) under conditions which induce no epimerisation.

Dimethyl maleate fails to form a charge-transfer complex with cyclohexene. Mixtures of the two components, irradiated with unfiltered light from a medium pressure mercury arc gave complex mixtures, shown to contain the diene (I), the substitutive adduct (XI, $R=CO_2Me$), and the five isomeric dimethyl esters (III), (IV), (V), (VIa) and (VII).

The theoretical implications of these results will be discussed elsewhere.

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