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402. *Organic Photochemistry. Part I. The Irradiation of some Charge-transfer Complexes of Cyclohexene.**

By R. Robson, P. W. Grubb, and J. A. Barltrop.

Cyclohexene appears to form charge-transfer complexes with maleic anhydride and with maleic and fumaric nitriles. Irradiation by filtered light, which excites the complexes and not the components, gives rise to bicyclohex-2-enyl (I), the substitutive adducts (II) and (IIIb), and certain of the isomeric 7,8-disubstituted bicyclo[4,2,0]octanes (IV)—(XII). A theory is advanced to account for the stereoselectivity of the photo-addition reactions.

Irradiation of mixtures of cyclohexene and methyl maleate, which do not interact to form a charge-transfer complex, leads unselectively to the isomers (IVa)—(VIIIa) together with the bicyclohexenyl and cyclohex-2-enylsuccinic ester (IIIa).

Mixtures in solution of electron-donors and electron-acceptors rapidly and reversibly form loose 1 : 1 charge-transfer complexes which can be detected by the appearance of a broad and intense band in the visible or ultraviolet (u.v.) absorption spectrum at wavelengths longer than those for bands due to separate components. The properties and valence theory of charge-transfer complexes have been described in a number of reviews.[1,2]

Several photochemical reactions are known in which the first step is the excitation of a charge-transfer complex. Those resulting from irradiation of inorganic charge-transfer complexes have been reviewed by Uri [3] and by Orgel.[2] More recently, two reactions resulting from irradiation of organic charge-transfer complexes have been reported. Stevenson and Coppinger record [4] that irradiation of the charge-transfer complexes between tertiary aliphatic amines and halogenomethanes leads, *via* a radical process, to the hydrogen halide salt of the amine, and Bryce-Smith and Lodge [5] found that a 1 : 2-adduct was formed between benzene and maleic anhydride on irradiation with filtered light to which each component alone was transparent. The first step was formation of a bicyclo[4,2,0]-octadienedicarboxylic anhydride, which subsequently added to another molecule of maleic anhydride by a normal Diels–Alder reaction.

* Cf. Barltrop and Robson, *Tetrahedron Letters*, 1963, 597.

[1] Andrews, *Chem. Rev.*, 1954, **54**, 713; McGlynn, *ibid.*, 1958, **58**, 1113; Murrell, *Quart. Rev.*, 1961, **15**, 191.

[2] Orgel, *Quart. Rev.*, 1954, **8**, 422.

[3] Uri, *Chem. Rev.*, 1952, **50**, 411.

[4] Stevenson and Coppinger, *J. Amer. Chem. Soc.*, 1962, **84**, 149.

[5] Bryce-Smith and Lodge, *J.*, 1962, 2675.

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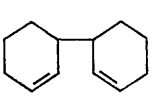
Photochemical dimerisation of olefins to give cyclobutane derivatives is a well-known reaction,[6] and in many cases[7] of intramolecular cyclobutane formation, the reacting olefinic groups have donor and acceptor properties. It seemed likely, therefore, that excitation of charge-transfer complexes between olefinic components would give rise to cyclobutane derivatives, and that the stereochemistry of the products might give information about the mechanism of the reaction. This paper records the result of an examination of this possibility. Cyclohexene was selected as the donor molecule and the acceptors chosen were maleic anhydride, fumaronitrile, and maleonitrile which form charge-transfer complexes with cyclohexene, and methyl maleate, which does not.

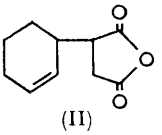
Results

Maleic Anhydride.—The u.v. absorption spectrum of maleic anhydride in cyclohexene shows a band due to charge-transfer absorption with $\lambda_{max.}$ 270 mμ, where there is only very weak absorption by a solution of maleic anhydride in chloroform. The use of saturated aqueous benzoic acid solution as a filter transmitting only light of wavelength greater than 285 mμ permitted irradiation of solutions of maleic anhydride in cyclohexene such that over 98% of the absorbed light was absorbed by the charge-transfer complex. The irradiation was conducted in the absence of oxygen.

Chromatography of the volatile products on alumina gave bicyclohex-2-enyl (I), characterised as the crystalline tetrabromide. Preparative gas chromatography (g.l.c.) isolated cyclohex-2-enylsuccinic anhydride (II), characterised by infrared (i.r.) spectrum and by hydrolysis and hydrogenation to cyclohexylsuccinic acid.



(I)



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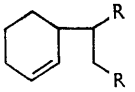

(III)

(*a*: R = CO_2Me)
(*b*: R = CN)

The volatile saturated products were separated from unsaturated material by treatment with mercuric acetate, after conversion into the dimethyl esters. Analytical g.l.c. indicated that the mixture of saturated esters contained three components (A, B, and C), in the proportions 19, 55, and 26%. The components, isolated by preparative g.l.c., were found to be isomers with the molecular formula $C_{12}H_{18}O_4$. It seemed likely that the substances were geometrical isomers of dimethyl bicyclo[4,2,0]octane-7,8-dicarboxylate, for they all exhibited in their high-resolution i.r. spectra weak bands at approximately 2995 and 3020 cm.$^{-1}$, which occur in a region associated with the C–H stretching vibrations of small-ring compounds. In general, tertiary ≥C–H stretching vibrations are very weak, but since adjacent oxygen substitution can lead to enhanced intensity,[8] we ascribe the two bands to the group >CH–CO_2Me incorporated in a cyclobutane ring.

Proof that these esters contain the bicyclo[4,2,0]octane system emerged subsequently and is discussed later. At this stage the problem is to determine the relative configurations of the components A, B, and C. There are six possible distinct isomers of 7,8-disubstituted bicyclo[4,2,0]octanes (neglecting optical isomers), three derived from a *cis*-fused and three derived from a *trans*-fused ring system. These are represented by (IV)—(IX), and are designated by the names shown (where the order of citation of prefixes is 1, ring junction; 2, inter-relation of R's; 3, relation of R's to ring junction):

[6] Mustapha, *Chem. Rev.*, 1952, **51**, 1.
[7] Cristol and Snell, *J. Amer. Chem. Soc.*, 1958, **80**, 1950; Büchi and Goldman, *J. Amer. Chem. Soc.*, 1957, **79**, 4741; Cookson and Crundwell, *Chem. and Ind.*, 1958, 1003; Büchi, Inman, and Lipinsky, *J. Amer. Chem. Soc.*, 1954, **76**, 4327.
[8] Pozefsky and Coggeshall, *Analyt. Chem.*, 1951, **23**, 1611.

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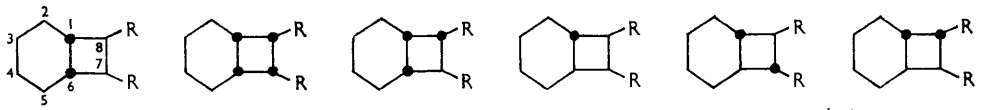
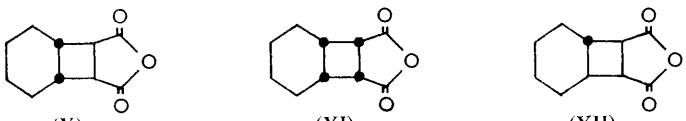


(IV) (V) (VI) (VII) (VIII) (IX)

(a: R = CO_2Me; b: R = CO_2H; c: R = CN)

Four-membered rings fused to five-membered rings in the *trans*-configuration would be extremely highly strained and so far as it known, there is no example of such a system. This being so, one can assume that the three tricyclic anhydrides which give rise to the esters A, B, and C have *cis*-fused anhydride rings (X), (XI), and (XII). This limits the possible structures of the esters to (IVa), (Va), and (VIIa). The final assignment of configuration depended on equilibration experiments.



(X) (XI) (XII)

The esters B and C, individually equilibrated with sodium methoxide, gave identical mixtures of approximately 5% of B and 95% of a new diester, D. Clearly, C is thermodynamically less stable than component B, which in turn is less stable than the isomer D. Since the *cis-cis-endo*-structure (V) experiences large non-bonded interactions between the ester groups and the cyclohexane ring, which are absent in the *cis-cis-exo*-structure (IV), we can assign the structures (IVa) and (Va) to isomers B and C, respectively. Hence isomer D must have the *cis-trans*-structure (VIa).

Equilibration of component A gave a mixture containing approximately 15% of A and 85% of a new substance E. Since A seems to have the structure (VIIa), E should be (VIIIa) or (IXa). From examination of models, (IXa) can be excluded as an equilibration product, for both ester groups are involved in large 1,3-non-bonded interactions with two hydrogen atoms. Thus the isomer E is probably the *trans-trans-anti*-system (VIIIa).

Confirmation of these assignments comes from an examination of the n.m.r. spectra of the dimethyl esters. These spectra were too complex to permit of certain identification of anything other than the protons of the methoxycarbonyl groups. It was found that only in component A were there two peaks corresponding to the protons on two distinguishable methoxycarbonyl groups. This confirms structure (VIIa) for A, since only in (VIIa) is the molecule rigid and asymmetrical. In the *cis*-fused structures (IVa)—(VIa) conformational inversions of the ring system average out the environments of the two ester groups and in both (VIIIa) and (IXa) the system is rigid but the ester groups are in virtually identical environments.

The pure diacids corresponding to the esters A, B, D, and E were prepared by mild alkaline hydrolysis. Hydrolysis of C under alkaline or acidic conditions induced complete epimerisation to the *cis-trans*-diacid (VIb). The diacid derived from C was obtained, contaminated with the diacid from D, by reaction with lithium iodide.

The structures of the saturated irradiation products were confirmed by degradation of the *cis-trans*-diacid to cyclohexane-*cis*-1,2-dicarboxylic acid (XVI). Bromination of the acid gave chiefly the *cis*-dibromide (XIII) instead of the expected *trans*-isomer (XIV), but the *cis*-dibromide could be debrominated by a method involving primary inversion to the *trans*-isomer by S_N2 replacement with bromide ion, followed by normal *trans*-debromination with iodide ion. The unsaturated acid (XV) gave cyclohexane-*cis*-1,2-dicarboxylic acid (XVI) on ozonolysis.

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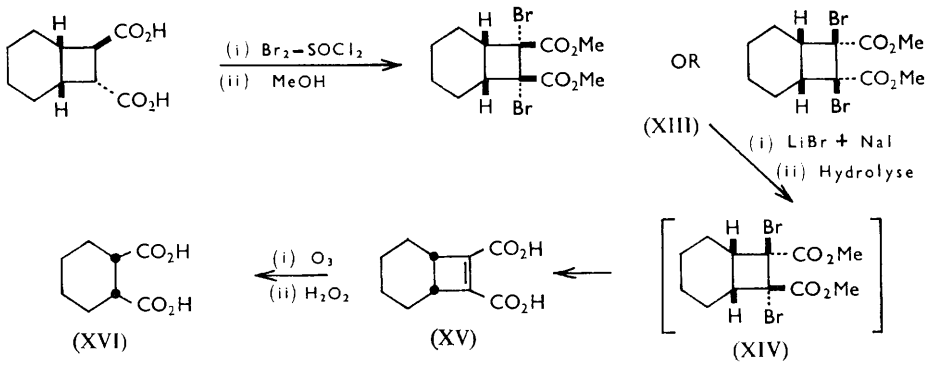
Confirmation that these irradiation products are derivatives of *cis*- and *trans*-bicyclo-[4,2,0]octane comes from the work of de Mayo and Yip.[9] These authors independently irradiated methyl maleate in cyclohexene (see below), obtaining dimethyl *cis*- and *trans*-bicyclo[4,2,0]octane-7,8-dicarboxylates and established structures by pyrolysis. The



cis-fused compounds gave cyclohexene and methyl fumarate and the *trans*-ring isomers gave unsaturated esters reduced to methyl sebacate.

Fumaronitrile.—Fumaronitrile dissolved in cyclohexene gives a charge-transfer complex $\lambda_{max.}$ 258 mμ, whereas fumaronitrile in chloroform has no absorption above 245 mμ. By the use of aqueous sodium sulphite as a filter transmitting only light of wavelength longer than 255 mμ, the charge-transfer complex can be excited with complete specificity. Irradiation of the complex under oxygen-free conditions gave a product the volatile portion of which was shown by analytical g.l.c. to contain only three components. The mixture was separated by chromatography on alumina, and the minor component was identified as bicyclohex-2-enyl (I). The other two components, one solid and the other liquid, were isomers of molecular formula $C_{10}H_{12}N_2$. The liquid was shown to be cyclohex-2-enylsuccinonitrile (IIIb) both spectroscopically and by hydrogenation and hydrolysis to cyclohexylsuccinic acid. The solid was treated with methanolic hydrogen chloride to convert nitrile groups into methoxycarbonyl groups *via* the imino-ether, and analytical g.l.c. showed that the product was a single component with retention time identical with that of dimethyl *cis*-bicyclo[4,2,0]octane-*trans*-7,8-dicarboxylate (VIa). The absence of any trace of the *cis-cis-exo*-isomer (IVa) showed that no epimerisation had occurred in the hydrolysis and methylation, and strongly suggested that the solid product was the *cis*-bicyclo[4,2,0]octane-*trans*-7,8-dinitrile (VIc). This was confirmed by hydrolysis to authentic *cis-trans*-diacid (VIb).

Maleonitrile.—Maleonitrile was prepared by photochemical isomerisation of fumaronitrile in solution in acetonitrile.[10] A solution of maleonitrile in cyclohexene shows a charge-transfer band at $\lambda_{max.}$ 255 mμ, whereas a solution of maleonitrile in hexane has no absorption above 245 mμ. Consequently the use of saturated aqueous sodium sulphite as filter permitted specific excitation of the charge-transfer complex. This irradiation was carried out under oxygen-free conditions. The volatile part of the product was resolved into bicyclohex-2-enyl and material which was separated into two main peaks by preparative g.l.c. The fraction with longer retention time, esterified with methanolic hydrogen chloride, gave the *cis-cis-exo*- (IVa), *cis-cis-endo*- (Va), and *cis-trans*-diesters (VIa), together with unesterified dinitrile.

This last was shown to be the *cis-cis-endo*-dinitrile (Vc), for on further esterification it gave a mixture of the *cis-trans*-diester (VIa) and the *cis-cis-endo*-diester (Va). Since the

[9] de Mayo and Yip, *Proc. Chem. Soc.*, 1963, 54.
[10] Barltrop and Grubb, unpublished work.

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dinitrile had a retention time quite different from that of authentic *cis-trans*-dinitrile (VIc) it follows that the formation of *cis-trans*-diester must have been due to epimerisation of the *cis-cis-endo*-dinitrile. An identical epimerisation during the hydrolysis of the *cis-cis-endo*-diester has already been described. Furthermore, the steric hindrance associated with the cyanide groups in the *cis-cis-endo*-structure accounts for the slow rate of esterification noted above.

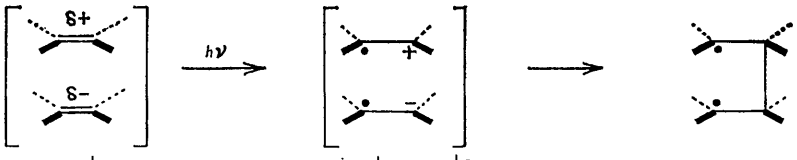
The second fraction, of shorter retention time, when esterified, gave rise to the *cis-trans*-diester (VIa) and dimethyl cyclohex-2-enylsuccinate (IIIa).

Dimethyl Maleate.—Finding no evidence for a charge-transfer complex in the system, we irradiated with unfiltered u.v. light solutions of dimethyl maleate in cyclohexene. The volatile fraction of the reaction products gave mainly bicyclohex-2-enyl and dimethyl cyclohexenylsuccinate (IIIa), together with saturated material which was separated by preparative g.l.c. into four fractions, identified as the *cis-trans*-diester (VIa) (19%), the *trans-trans-anti*-diester (VIIIa) (2·7%), the *cis-cis-exo*-diester (IVa) (2·4%), and the *cis-cis-endo*-diester (Va) (<1%) by comparison of i.r. spectra and g.l.c. retention times with those of authentic samples.

Since the *trans-cis*-diester (VIIa) had a retention time very close to that of the *cis-trans*-diester (VIa), it was thought that small quantities of the former could possibly be present in the isolated sample of the latter, unrevealed by i.r. spectra or g.l.c. This was shown to be the case, for g.l.c. of the sample, after equilibration, showed a small peak corresponding to the *trans-trans-anti*-isomer (VIIIa), produced by equilibration of (VIIa). This was isolated by preparative g.l.c. and identified by comparison of its i.r. spectrum with that of an authentic sample.

Discussion

The observed distribution of products from the three charge-transfer systems can be rationalised by conformational analysis of the ring-fusion process assisted by a few very reasonable hypotheses. For charge-transfer absorption to occur, there must be appreciable π-orbital overlap between the two olefinic groups, and the most favoured arrangement is that with the two double bonds parallel and one vertically above the other (XVII). The excited state of the charge-transfer complex approximates to the state produced by transfer of one electron from the donor to the acceptor,[11] and may be represented as (XVIII). The subsequent bond formation is postulated to take place in two stages. In a non-polar solvent such as cyclohexene, the first step would probably be bonding between the ion centres, leaving a diradical such as (XIX), but it is immaterial to the argument whether the ion or the radical centres combine first.



complex (XVII) — excited complex (XVIII) — (XIX)

In the following discussion the radical centres are taken to be planar, with the odd electrons in *p*-orbitals at right angles to the plane, but because of rapid inversion it would make no difference if they were in fact pyramidal, as some evidence [12] suggests. Where cyclohexene is the donor molecule, it is reasonable to suppose that the primary bond is formed axially to the six-membered ring. All reactions of known mechanism involving addition to double bonds in six-membered rings proceed by primary axial bond formation,[13]

[11] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.
[12] Walling, "Free Radicals in Solution," Wiley and Sons Inc., New York, 1957, p. 502.
[13] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.

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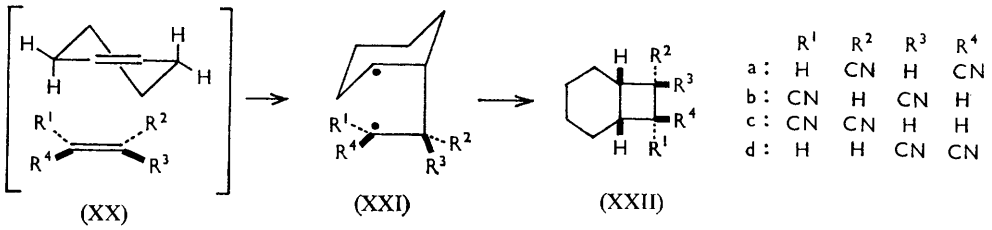
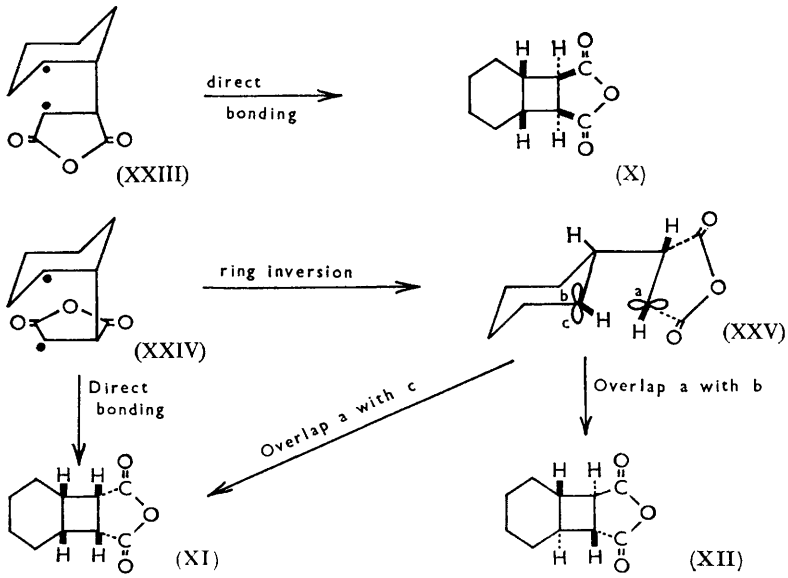
and in the charge-transfer complex, the double bond of the acceptor molecule will be axially disposed with respect to the cyclohexene ring.

We shall consider first the most simple case, that of the fumaronitrile–cyclohexene system. There are two almost identical configurations of the charge-transfer complex, which may be represented by (XXa) and (XXb). Primary bond formation will then give rise to the diradicals (XXIa) and (XXIb), respectively.



Secondary bond formation will in each case give the *cis-trans* isomer (XXIIa ≡ XXIIb ≡ VIc) which is the only observed product.

With the maleonitrile–cyclohexene system, the diradicals produced by excitation and primary bond formation from the two possible configurations of the charge-transfer complex will be (XXIc) and (XXId). Here, immediate secondary bond formation will give rise to the *cis-cis-endo*-isomer (XXIIc ≡ Vc) from the *endo*-diradical (XXIc) and the *cis-cis-exo*-isomer (XXIId ≡ IVc) from the *exo*-diradical (XXId). However, in both diradicals, there is a tendency to minimise dipole-dipole repulsion by rotation about what was the maleonitrile double bond, giving the diradicals (XXIa) from (XXIc) and (XXIb) from (XXId). As in the fumaronitrile system, secondary bonding then gives the *cis-trans*-isomer (VIc) in each case. Models show that there is no significant barrier to free rotation about this bond due to hydrogen atoms on the cyclohexane ring. The fact that a large



quantity of the *cis-trans*-isomer is produced is proof that formation of the cyclobutane ring is a two-step process, the time between steps being of the same order as the time required for rotation about the single bond.

The maleic anhydride-cyclohexene system is analogous to the maleonitrile system in

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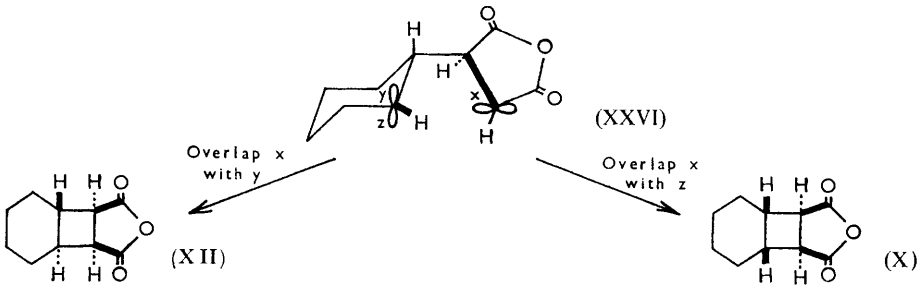
that there are *exo*- and *endo*-configurations of the charge-transfer complex, giving *exo*- (XXIII) and *endo*- (XXIV) diradicals on excitation and primary bond formation, and that direct secondary bond formation will give rise to the *cis-cis-exo*- and *cis-cis-endo*-products (X) and (XI), respectively. In the *endo*-diradical (XXIV), there are large non-bonded interactions between the anhydride ring and hydrogen atoms attached to the cyclohexane ring, and there will be a strong tendency for the axially-substituted diradical to go over to the equatorially-substituted configuration (XXV) by ring inversion. The lobe (a) of the *p*-orbital of the radical centre on the anhydride ring may then overlap with either lobe (b) or lobe (c) of the other radical centre. Overlap with (b) gives the *trans-cis*-anhydride (XII), and overlap with (c) gives rise to the *cis-cis-endo*-isomer (XI).

Ring inversion of (XXIII), which has very small non-bonded interactions, is not expected. If it did occur, the diradical (XXVI) would result. Here the second bond may be formed by overlap of the *p*-orbital lobe (x) with either (y) or (z), to give the *trans-cis*-isomer (XII) or the *cis-cis-exo*-isomer (X), respectively.



It is difficult to see how the *trans-cis*-isomer (XII) could arise other than by ring inversion between the stages of a two-step mechanism. Ring inversion may be excluded in both the nitrile systems, however, as among the expected products would be isomers which were not in fact observed in these systems.

Little is known about the processes involved in the indiscrimate irradiation of dimethyl maleate in cyclohexene, and a rational interpretation of the distribution of products is not feasible at this stage. The reaction is seen to be much less stereospecific than in the case of the charge-transfer system, as all five known isomers are produced.

de Mayo and Yip have reported [9] the irradiation of methyl maleate in cyclohexene. They obtained five isomeric 7,8-disubstituted bicyclo[4,2,0]octanes in the form of the dicarboxylic acids, one of which was present in amounts too small for investigation. The remaining four were deduced to be the *cis-trans*-isomer, one of the two *cis-cis*-isomers, and both of the possible *trans-trans*-isomers. The last two were converted into the *trans-cis*-diacid by treatment with acetic anhydride followed by hydrolysis.

Melting points were given for these five acids, and we compared these with the melting points of the diacids obtained from the maleic anhydride–cyclohexene system as described above. The melting points of our *cis-trans*- and *trans-cis*-acids agreed with those given by de Mayo; the melting point of our *cis-cis-exo*-acid agreed with that of de Mayo's unspecified *cis-cis*-isomer; and that of our *trans-trans-anti*-acid corresponded with that of one of de Mayo's claimed *trans-trans*-isomers. The melting point of our *cis-cis-endo*-acid did not correspond to the fifth melting point given by de Mayo.

The discrepancy between these sets of results cannot be discussed profitably at this stage.

Experimental

Materials.—" Deactivated alumina " refers to Spence's Grade H alumina containing 5% (v/w) of 10% aqueous acetic acid. " Petroleum " refers to the fraction of b. p. 40—60°. Cyclohexene used in irradiations was percolated through Spence Grade H alumina, refluxed over

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sodium wire under nitrogen for 12 hr., and fractionally distilled under nitrogen. Dry, oxygen-free, nitrogen was obtained by passing " white spot " nitrogen through alkaline pyrogallol and concentrated sulphuric acid, then over anhydrous calcium chloride.

Irradiation Apparatus.—All irradiations were conducted in a Hanovia photochemical reactor of 250-ml. capacity, fitted with a 500 w. Hanovia medium-pressure mercury lamp. The filter solution, which also acted as coolant, was circulated through a quartz inner jacket. All solutions were deoxygenated before irradiation by refluxing them in a stream of nitrogen, which then displaced air from the reactor.

The solutions, when cold, were transferred to the reactor by nitrogen pressure, and a slow stream of nitrogen was passed over their surface during the irradiation

Gas Chromatography.—For analytical work, the Pye Argon Chromatogram was used (column dimensions 4 ft. × $\frac{3}{16}$ in.). Comparison chromatograms were always conducted one immediately after the other. Where retention times (r_t) are quoted, the conditions used are denoted as A and B. A refers to a column of 29% of Apiezon " L " plus 3·7% of sodium hexonate on B.D.H. Embacel, operated at 160°, 10 lb./sq. in. B refers to the same column at 180°, 8 lb./sq. in. Conditions other than A and B are given in full in the text.

For preparative g.l.c., the column was 30% of Apiezon " L " on Embacel (300 cm. × 0·375 in.), operated at 200° and 10 lb./sq. in., unless otherwise stated. The machine incorporated a bypass to a flame ionisation detector; an electrostatic precipitator and cold trap were used to collect the material coming off the column. All substances recovered from preparative g.l.c. were freed from Apiezon " L " by chromatography on silica gel. Petroleum eluted any Apiezon " L " and ether eluted the separated material which was then distilled.

Irradiation of the Maleic Anhydride–Cyclohexene Charge-transfer System.—(*A*) Commercial maleic anhydride was purified by recrystallisation from chloroform followed by sublimation. In a typical irradiation, maleic anhydride (*ca.* 1 g.) dissolved in cyclohexene (245 ml.) was irradiated under oxygen-free conditions for 1·5 hr., a saturated aqueous solution of benzoic acid being used as a filter.

The solution, on evaporation, yielded a viscous yellow oil (1·72 g. per 1 g. of maleic anhydride) which was roughly fractionated by distillation. Two fractions were collected from 6·74 g. of liquid product: (1) (0·065 g.), b. p. 35—110°/0·1 mm., (2) (3·54 g.), b. p. 110—190°/0·2—0·5 mm.

Fraction (1) (65 mg.) was chromatographed on deactivated alumina. Petroleum (250 ml.) eluted a clear oil (28 mg.) whose i.r. spectrum was identical with that of authentic bicyclohex-2-enyl [14] (I) [tetrabromide prisms (from acetic acid), m. p. and mixed m. p. 157° (lit.,[15] m. p. 158°)].

Fraction (2) (0·80 g.) was separated into three fractions by preparative g.l.c. (30% of Apiezon " L," 210°, 15 lbs./sq. in. 465 × 2·5 cm.). The fraction of shortest retention time (50 mg.) had an i.r. spectrum identical with that of authentic cyclohex-2-enylsuccinic anhydride.[16] The oil (39 mg.) was heated with potassium carbonate (0·5 g.) in water (5 ml.) at 100° for 45 min., acidified, and extracted with ether. The gummy solid (31 mg.) obtained by evaporation of the ether extract was dissolved in ethanol (50 ml.) and shaken with Adams catalyst (16 mg.) under hydrogen at atmospheric pressure for 2 hr. The product was a solid (30 mg.) which, after 4 crystallisations from water, was shown to be identical with authentic cyclohexylsuccinic acid [16] by m. p. and mixed m. p. (145—146°) and by comparison of i.r. spectra.

(*B*) Seven repeated irradiations yielded 5·42 g. of product boiling over the range of 116—163°/0·1—0·3 mm., which was heated with potassium carbonate (13 g.) in water (40 ml.) for 0·5 hr. The mixture was diluted with water, washed with ether, and acidified. A gummy acid (5·61 g.) was isolated with ether and methylated with excess of diazomethane in dry ether at room temperature for 18 hr. Evaporation of the solution gave a mixture (5·89 g.) of saturated and unsaturated methyl esters, from which the unsaturated material was removed by mercuration.[17]

The mixed esters (5·89 g.) in methanol (150 ml.) were heated under reflux with mercuric acetate (50 g.) for 3·5 hr. The resulting solution was diluted with ether (500 ml.) and washed with (3%) aqueous acetic acid, water, aqueous potassium carbonate, and water (200 ml.). The

[14] Hofman and Damm, *Chem. Zentr.*, 1926, *I*, 2342.
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residue, obtained by evaporating the dried ethereal solution, was chromatographed on deactivated alumina (150 g.). Elution with benzene containing 15% ether by volume (500 ml.) gave, on evaporation, a mixture of saturated methyl esters (1·81 g.), which distilled as an oil, b. p. 100—110° (bath)/0·05 mm. (Found: C, 64·5; H, 8·2. Calc. for $C_{12}H_{18}O_4$: C, 63·7; H, 8·0%).

The mixed saturated esters (1·51 g.) were separated into three components by preparative g.l.c. in twelve batches of *ca.* 0·12 g. Examination of the collected components by g.l.c. indicated that each was contaminated with considerably less than 1% of the others.

The first fraction [r_t(A), 23·6 min.] (163 mg.) gave *dimethyl* trans-*bicyclo*[4,2,0]*octane*-cis-7,8-*dicarboxylate* (VIIa), b. p. 99—101° (bath)/0·05 mm. (Found: C, 63·6; H, 7·9. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%); $\nu_{max.}$ 2995w, 3022w, 1735s, 1078w, 1039m, 977w, and 839w. The n.m.r. spectrum (CCl_4 solution) showed a doublet at τ 6·36 and 6·39.

The second fraction [r_t(A), 28·2 min.] (531 mg.) gave *dimethyl* cis-*bicyclo*[4,2,0]*octane*-exo-cis-7,8-*dicarboxylate* (IVa), b. p. 102—104° (bath)/0·5 mm. (Found: C, 63·5; H, (7·9%); ν 2995w, 3021w, 1735s, 1060m, and 1030m. The n.m.r. spectrum showed a singlet at τ 6·37.

The third fraction [r_t(A), 32·2 min.] (28·7 mg.) gave *dimethyl* cis-*bicyclo*[4,2,0]*octane*-endo-cis-7,8-*dicarboxylate* (Va), b. p. 101—104° (bath)/0·05 mm. (Found: C, 63·5; H, 8·1%); ν 2993w, 3021w, 1735s, 1073m, 1028m, 1000w, 949w, and 834w. The n.m.r. spectrum (CCl_4 solution) showed a singlet at τ 6·35.

Equilibration of the cis-*Esters*.—The ester was heated with approximately half its weight of sodium methoxide in about ten times its weight of dry methanol in a sealed tube at 65° overnight. Dilute hydrochloric acid was added and the aqueous solution was extracted with several small quantities of ether. The ethereal extract was washed with saturated brine and kept with excess of diazomethane for *ca.* 0·5 hr. Evaporation of the resulting solution afforded the equilibrated esters.

Dimethyl cis-*Bicyclo*[4,2,0]*octane*-trans-7,8-*dicarboxylate* (VIa).—Equilibration of the *cis-cis-endo*-isomer (24 mg.) gave a mixture (20 mg.) which was shown by g.l.c. to be identical with the mixture (19 mg.) obtained by similar treatment of the *cis-cis-exo*-isomer (23 mg.).

The above two equilibrated mixtures were combined with that obtained (0·143 g.) from a further equilibration of the *cis-cis-exo*-isomer (0·155 g.). The combined mixture (0·20 g.) was separated into two fractions by preparative g.l.c. The first fraction was shown to contain only one component by g.l.c. [r_t(A), 25·2 min.]. Distillation gave *dimethyl* cis-*bicyclo*[4,2,0]-*octane*-trans-7,8-*dicarboxylate*, b. p. 91—92° (bath)/0·05 mm. (Found: C, 64·0; H, 8·1%); ν 3021w, 2995w, 1735s, and 1023s. The n.m.r. spectrum (CCl_4 solution) showed a singlet at τ 6·47.

Dimethyl trans-*Bicyclo*[4,2,0]*octane*-anti-trans-7,8-*dicarboxylate* (VIIIa).—The mixture (0·132 g.) obtained by equilibration of the *trans-cis*-isomer (0·135 g.) was shown by g.l.c. to contain starting material [r_t(A), 23·6 min.] as a minor product. The major component, isolated by preparative g.l.c., gave, after purification, *dimethyl* trans-*bicyclo*[4,2,0]*octane*-anti-trans-7,8-*dicarboxylate* [r_t(A), 19·6 min.], b. p. 90—93° (bath)/0·05 mm. (Found: C, 63·9; H, 8·0%); ν 3023w, 2997w, 1730s, 1040m, 1010m, and 1093w. The n.m.r. spectrum (CCl_4 solution) showed a singlet at τ 6·41.

Bicyclo[4,2,0]*octane*-7,8-*dicarboxylic Acids*.—The diesters, dissolved in aqueous methanol containing 10% potassium hydroxide, were, unless otherwise stated, left at room temperature for 50 hr. and then acidified. The acids were isolated with ether. Any epimerisation occurring during hydrolysis was detected by treating small portions of the acids with diazomethane, and then analysing the esters by g.l.c.

The *cis-cis-exo*-diester (93 mg.) gave only the *cis-cis-exo*-isomer (76 mg.). Recrystallisation from acetone–benzene gave cis-*bicyclo*[4,2,0]*octane*-exo-cis-7,8-*dicarboxylic acid*, (IVb), m. p. 176—179° (Found: C, 60·2; H, 7·1. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%).

The *trans-cis*-diester (20 mg.) gave a product containing the *trans-cis*-isomer with a slight trace of the *trans-trans-anti*-isomer. Four recrystallisations from ether gave trans-*bicyclo*-[4,2,0]*octane*-cis-7,8-*dicarboxylic acid* (VIIb) (6 mg.), m. p. 151—155° (Found: C, 59·7; H, 7·1%).

The mixture of *cis-trans*- and *cis-cis-exo*-diesters obtained by equilibration of the *cis-cis-exo*-isomer (0·165 g.) was hydrolysed at the boiling point. The product (0·125 g.), on recrystallisation from acetone–benzene, gave cis-*bicyclo*[4,2,0]*octane*-trans-7,8-*dicarboxylic acid* (VIb) as

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thick prisms, m. p. 200—201° (Found: C, 60·4; H, 6·8%). This was shown to be identical with an analytically pure sample (m. p. 200—201°), obtained from *cis*-bicyclo[4,2,0]octane-*trans*-7,8-dinitrile (see below), by mixed melting point (200—201°) and i.r. spectra.

The *trans-trans-anti*-diester (20 mg.), obtained from the equilibration of the *trans-cis*-diester gave a product which, after three recrystallisations from acetone–benzene, afforded trans-*bicyclo*[4,2,0]*octane*-anti-trans-7,8-*dicarboxylic acid* (VIIIb) (5 mg.), m. p. 182—184° (Found: C, 61·5; H, 7·1%).

The *cis-cis-endo*-diester gave an acid consisting almost entirely of the *cis-trans*-isomer. The same result was obtained by hydrolysis with 50% sulphuric acid at 100° for 3 hr., although some *cis-cis-exo*-diacid was also formed. The *cis-cis-endo*-diester (44·5 mg.) was added to anhydrous lithium iodide (130 mg.) in lutidine (2 ml.), the mixture refluxed under nitrogen for 5½ hr., then diluted with water (20 ml.) and concentrated hydrochloric acid (4 ml.). A gummy acid (36 mg.) was isolated with ether. G.l.c. of the derived dimethyl ester showed that partial epimerisation had occurred, and measurement of peak areas indicated that the composition of the product was: *cis-cis-endo*-, 69%; *cis-cis-exo*-, 9%; *cis-trans*-diacid, 22%. Repeated recrystallisations from benzene gave products containing no *cis-cis-exo*-isomer, but between 30 and 48% of *cis-trans*. These products all showed rapid melting at 142—146° (Kofler) but some crystals persisted until *ca.* 200°. It seems likely that 142—146° represents the m. p. of the *cis-cis-endo*-diacid (Vb), but it is possible that it is the m. p. of a eutectic mixture of the *cis-cis-endo*- and *cis-trans*-acids.

Irradiation of the Fumaronitrile–Cyclohexene Charge-transfer Complex.—Cyclohexene (245 c.c.), saturated with fumaronitrile (*ca.* 0·45 g.), was deoxygenated and transferred to the reactor under oxygen-free conditions. A saturated aqueous solution of sodium sulphite was used as filter. Seven repeated irradiations (1·5 hr. each) yielded, after evaporation, a thick black gum which was distilled to give a viscous yellow liquid (4·91 g.), b. p. 140—180°/0·3 mm. The mixture (4·2 g.) was separated by chromatography on deactivated alumina (300 g.). Petroleum (600 ml.) eluted bicyclohex-2-enyl (144 mg.). Four fractions were obtained: (1) a brown solid (0·375 g.); (2) a solid (2·25 g.); (3) a liquid (0·767 g.), eluted by petroleum–benzene (3 : 1); and (4) a liquid (0·765 g.), eluted by ether.

G.l.c. indicated that fractions (2) and (4) were single components and that fraction (3) was a mixture of these two.

Fraction (2), on recrystallisation from carbon tetrachloride–petroleum gave cis-*bicyclo*-[4,2,0]*octane*-trans-7,8-*dinitrile* (VIc) (1·8 g.) as needles, m. p. 80—81° (Found: C, 75·1; H, 7·5; N, 17·3. $C_{10}H_{12}N_2$ requires C, 75·0; H, 7·5; N, 17·5%); ν (Nujol) 2230m.

A solution of the solid nitrile (109 mg.) in methanol (10 ml.) containing water (0·04 ml.) was saturated with dry hydrogen chloride and then heated under reflux for 3 hr. Water (15 ml.) was added to the residue obtained by evaporation, and the product was extracted with ether. The ethereal layer was washed with saturated brine and then treated with excess of diazomethane in ether. G.l.c. of the liquid product (124 mg.), revealed only one component and this had the same retention time as dimethyl *cis*-bicyclo[4,2,0]octane-*trans*-7,8-dicarboxylate.

A rapid stream of dry hydrogen chloride was bubbled through a solution of the solid dinitrile (0·445 g.) in methanol (20 ml.) for 2 hr. Evaporation gave a solid which was heated at 100° overnight with concentrated hydrochloric acid (10 ml.). Recrystallisation of the product (0·509 g.) from benzene–acetone gave *cis*-bicyclo[4,2,0]octane-*trans*-7,8-dicarboxylic acid (VIb) as thick prisms, m. p. 200—201° (Found: C, 60·6; H, 7·1. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%).

Fraction (4), eluted by ether, gave, on distillation, 2-(1,2-*dicyanoethyl*)*cyclohexene* (IIIb), b. p. 135—140° (bath)/0·05 mm. (Found: C, 74·9; H, 7·6; N, 17·0. $C_{10}H_{12}N_2$ requires C, 75·0; H, 7·5; N, 17·5%); ν 3010w, 2240m, 1650w, and 726s. The liquid nitrile (0·26 g.) in methanol (100 ml.) was shaken with 5% palladium on charcoal under hydrogen at atmospheric pressure, and the product was boiled with aqueous sulphuric acid (50% by wt.) for 3·5 hr. The organic material recovered with ether crystallised from benzene–acetone to give cyclohexylsuccinic acid, identified by m. p. and mixed m. p. (145—146°) with an authentic sample.

Bromination of cis-*Bicyclo*[4,2,0]*octane*-trans-7,8-*dicarboxylic Acid.*—The acid (0·78 g.) was heated under reflux with redistilled thionyl chloride (10 ml.) until it had dissolved (1 hr.). Bromine (10 ml.) was added and the mixture was heated under reflux for 5·5 days. After removal of the bromine in a stream of dry nitrogen, methanol (15 ml.) was added, and the resulting solution was heated under reflux for 1 hr. The methanol was distilled off, ether

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was added to the residue, and the ethereal solution was washed with water and then treated with excess of diazomethane in ether for 1 hr. Evaporation gave a viscous yellow liquid (1·40 g.) which was chromatographed on deactivated alumina (100 g.) [Woelm neutral alumina treated with water (5%)]. Petroleum containing benzene (5%) eluted two main fractions.

Recrystallisation of the first fraction (134 mg.) from petroleum gave *dimethyl* 7,8-*dibromo*-cis-*bicyclo*[4,2,0]*octane*-trans-7,8-*dicarboxylate* (XIV) as thick prisms, m. p. 76—78° (Found: C, 37·6; H, 4·0. $C_{12}H_{16}Br_2O_4$ requires C, 37·5; H, 4·2%). A small amount of the solid with sodium iodide in acetone solution rapidly liberated iodine when heated under reflux.

Recrystallisation of the second fraction (513 mg.) from carbon tetrachloride–petroleum and then from petroleum (b. p. 60—80°) gave *dimethyl* 7,8-*dibromo*-cis-*bicyclo*[4,2,0]*octane*-cis-7,8-*dicarboxylate* (XIII) as large crystals, m. p. 109—110° (Found: C, 37·3; H, 4·0%). A small amount of the solid with sodium iodide in acetone solution produced only a faint yellow colour when heated under reflux overnight. A mixture of a small amount of the solid, sodium iodide, and excess of lithium bromide in acetone rapidly liberated iodine at 100° in a sealed tube.

cis-*Bicyclo*[4,2,0]*oct*-7-*ene*-7,8-*dicarboxylic Acid* (XV).—A mixture of the above *cis*-dibromo-isomer (*ca.* 300 mg.) lithium bromide (2·1 g.), and sodium iodide (1·4 g.) in acetone (5 ml.) was heated in a sealed tube at 100° for 3 days, then diluted with water. The unsaturated esters was isolated with ether and hydrolysed with boiling aqueous methanolic potassium hydroxide. The recovered acidic material after five recrystallisations from benzene, gave cis-*bicyclo*[4,2,0]*oct*-7-*ene*-7,8-*dicarboxylic acid* (45 mg.) as plates, m. p. 160—161° (Found: C, 61·1; H, 5·7. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%); ν (Nujol) 1700s (CO_2H), 1653s and 1590vs (C=C); $\lambda_{max.}$ (in ethanol) 240 mμ, $\varepsilon_{max.}$ 8460.

Oxidation of cis-*Bicyclo*[4,2,0]*oct*-7-*ene*-7,8-*dicarboxylic Acid*.—A stream of ozonised oxygen was passed through a solution of the unsaturated acid (144 mg.) in ethyl acetate (20 c.c.) at −70° for 2 hr. The action of aqueous hydrogen peroxide on the product gave, after recrystallisation from ethanol–benzene, cyclohexane-*cis*-1,2-dicarboxylic acid (96 mg.) as large cubes, m. p. 191—192°, alone and when mixed with an authentic specimen.

Irradiation of the Maleonitrile–Cyclohexene Charge-transfer Complex.—Maleonitrile was prepared by photochemical isomerisation [10] of fumaronitrile as needles, m. p. 31—31·5° (lit.,[18] m. p. 30—31°). Saturated solutions of maleonitrile (*ca.* 0·65 g.) in cyclohexene (245 ml.) were deoxygenated and transferred to the reactor, then irradiated for 2 hr., saturated aqueous sodium sulphite solution being used as a filter. The product of eight irradiations was evaporated to a brown viscous liquid, which, on distillation, gave two volatile fractions and a brown solid residue. The first fraction, b. p. 65—90°/0·2 mm., was identified as bicyclohex-2-enyl.

The second fraction, a viscous yellow liquid (3·72 g.), b. p. 120—170°/0·15 mm., was chromatographed on deactivated alumina (50 g.). Petroleum (150 ml.) eluted a mixture (0·27 g.) shown by g.l.c. to contain bicyclohex-2-enyl together with other minor peaks. Benzene (200 ml.) followed by ether (200 ml.) eluted a yellow liquid (2·865 g.). Examination by g.l.c. revealed two main peaks at r_t(B) 11·7 and 22—23·5 min. the second comprising two peaks, incompletely resolved. The ratio of the areas of the main peaks was 3·5 : 1. Preparative g.l.c. separated the material into fractions corresponding to the peak of r_t 11·7 min. (1·29 g.) and that of r_t 22—23·5 min. (0·408 g.).

Treatment of the dinitrile (r_t 22—23·5 min.) with methanolic hydrogen chloride (reflux, 3 hr.) gave a mixture (0·351 g.) containing three components shown by analytical g.l.c. under condition B to be the *cis-trans*-diester (r_t, 14 min.) (17%) the *cis-cis-exo*-diester (r_t, 15·5 min.) (42%) and the *cis-cis-endo*-diester (r_t, 18 min.) (11%), together with material (30%) having the same retention time as the unesterified dinitrile (r_t, 23·5 min.). Preparative g.l.c. permitted the isolation of these diesters and the establishment of their identity by comparison of their i.r. spectra with those of authentic samples. Hydrolysis under the usual conditions gave the *cis-trans*-diacid (19 mg.), m. p. 199—202°, from benzene–acetone, and the *cis-cis-exo*-diacid (35 mg.), m. p. 171—173° from benzene–acetone; which were shown by mixed m. p.s to be identical with authentic samples.

The recovered dinitrile, on recrystallisation from ether, gave cis-*bicyclo*[4,2,0]*octane*-endo-cis-7,8-*dinitrile* (Vc) (26 mg.), m. p. 90—91° (Found: C, 74·3; H, 7·3. $C_{10}H_{12}N_2$ requires C, 75·0; H, 7·55%); $\nu_{max.}$ 2240 cm.$^{-1}$ and no absorption in the carbonyl region. The dinitrile

[18] Linstead and Whalley, *J.*, 1952, 4839.

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(5 mg.) was esterified with methanolic hydrogen chloride (1 ml.) under reflux for 3 hr. Examination of the product by g.l.c. showed peaks corresponding to *cis-trans*-diester (3 parts), *cis-cis-endo*-diester (1 part), and unchanged dinitrile (trace).

The first fraction (r_t 11·7 min.), from the g.l.c. of the products of the irradiation, was purified by chromatography on silica gel (40 g.) followed by distillation at 135—155°/0·3—0·5 mm.

Esterification with methanolic hydrogen chloride (reflux, 3 hr.) of a portion of the material (0·248 g.) gave a product which, by g.l.c., appeared to contain dimethyl cyclohex-2-enylsuccinate (IIIa) (45%), and *cis-trans*-diester (55%).

The mixture of esters was treated with mercuric acetate (2 g.) in dry methanol (10 ml.) under reflux for 5 hr. The saturated fraction was obtained as described for the esters from the maleic anhydride system, and the unsaturated fraction was recovered by acidifying the aqueous washings with concentrated hydrochloric acid and extracting with ether. The saturated component (17 mg.) was identified as dimethyl *cis*-bicyclo[4,2,0]octane-*trans*-7,8-dicarboxylate by comparison of its i.r. spectrum with that of authentic diester, and by hydrolysis to the *cis-trans*-diacid, m. p. 200—202°. The unsaturated component (74 mg.) was identified as dimethyl cyclohex-2-enylsuccinate by comparison of i.r. spectra with authentic compound and by hydrogenation and hydrolysis to cyclohexylsuccinic acid, m. p. 144—145°.

Irradiation of Dimethyl Maleate in Cyclohexene.—A solution of dimethyl maleate (*ca.* 2·0 g.) in cyclohexene (245 c.c.) was deoxygenated and transferred to the reactor under oxygen-free conditions. Cold water was passed through the inner jacket of the reactor. Two irradiations (3 hr. each) with unfiltered light, yielded a viscous yellow liquid (6·97 g.) from which two fractions were collected by distillation: (1) (1·09 g.), b. p. 96—154°/14 mm.; (2) (2·51 g.), b. p. 92—168°/0·05 mm. Chromatography of fraction (1) on silica gel (25 g.) gave bicyclohex-2-enyl (231 mg.), dimethyl fumarate (100 mg.), and dimethyl cyclohex-2-enylsuccinate.

Fraction (2) (2·22 g.) was separated with mercuric acetate into saturated (1·217 g.) and unsaturated material (0·850 g.).

The unsaturated material was hydrogenated over 10% palladium on charcoal (100 mg.), esterified with diazomethane in ether, and distilled to give a liquid ester, b. p. 95—100° (bath)/0·05 mm., which was hydrolysed with aqueous methanolic potassium hydroxide. The recovered acidic material crystallised from acetone–benzene to give cyclohexylsuccinic acid, identified by m. p. and mixed m. p. (145—146°) with an authentic sample. Saturated material (1·22 g.) from the above mercuration was resolved by preparative g.l.c. into three fractions, A, B, and C. Examination of these fractions by analytical g.l.c. (A) indicated that fraction A (95 mg.) and fraction B (669 mg.) were very nearly single components with retention times equal to those of the *trans-trans-anti*-isomer (r_t, 20·4 min.) and the *cis-trans*-isomer (r_t 26·5 min.), respectively. Comparison of i.r. specta confirmed that fraction A (ν 1730s, 1040m, and 1010m) was dimethyl *trans*-bicyclo[4,2,0]octane-*anti-trans*-7,8-dicarboxylate. Although fraction B had an i.r. spectrum identical with that of dimethyl *cis*-bicyclo[4,2,0]octane-*trans*-7,8-dicarboxylate, it was shown to contain a small concentration of the *trans-cis*-isomer (see below).

Analytical g.l.c. (A) indicated that fraction C contained three components whose retention times corresponded to those of the *cis-trans*-isomer (r_t, 26·5 min.), the *cis-cis-exo*-isomer (r_t, 29·6 min.), and the *cis-cis-endo*-isomer (r_t, 33·9 min.). Fraction C (120 mg.) was separated into three fractions (D, E, and F) by preparative g.l.c. Fraction E (53 mg.) was shown to be a single component by analytical g.l.c. and was identified as dimethyl *cis*-bicyclo[4,2,0]octane-*exo-cis*-7,8-dicarboxylate by comparison of retention times and i.r. spectra. Fraction F appeared to consist mainly of dimethyl *cis*-bicyclo[4,2,0]octane-*endo-cis*-7,8-dicarboxylate by g.l.c. and i.r. spectral comparison with an authentic sample although traces of impurities were present.

Analytical g.l.c. (A) of the mixture obtained by equilibration of fraction B indicated that three components were present with retention times identical with those of the *trans-trans-anti*-isomer (r_t, 20·4 min.), the *cis-trans*-isomer (r, 26·5 min.), and the *cis-cis-exo*-isomer (r_t, 29·5 min.). The mixture (570 mg.) was separated into three fractions by preparative g.l.c. Dimethyl *trans*-bicyclo[4,2,0]octane-*anti-trans*-7,8-dicarboxylate (7·2 mg.) was identified by comparison of retention time and i.r. spectra with those of an authentic sample.

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