Reactions of Cyclo-octatetraene and its Derivatives. Part V.[1] Addition of Bromotrichloromethane, Carbon Tetrachloride, and Thiophenol to Tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic Anhydride

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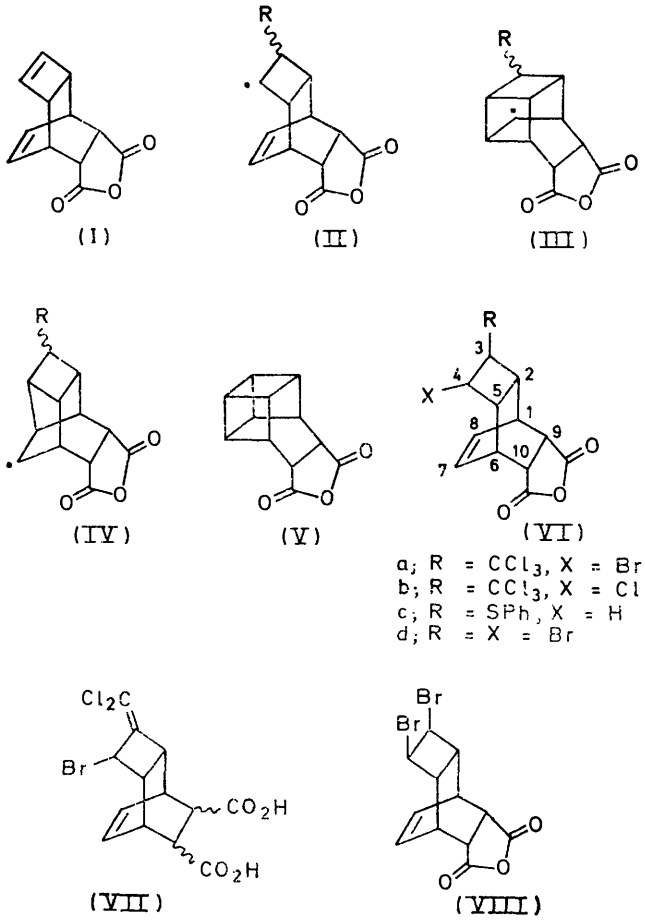
The free radical addition of bromotrichloromethane and carbon tetrachloride to tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride (I) results in *trans*-addition to the cyclobutene double bond. The structures (VIa) and (VIb) proposed for the products are based on n.m.r. studies of the adducts and various related compounds: by analogy structure (VIc) is suggested for the thiophenol adduct.

FOLLOWING the examination (at King's College) of free radical additions to norbornene,[2] bicyclo[2.2.2]octene,[3] and related systems, we have investigated similar reactions with the cyclo-octatetraene–maleic anhydride adduct tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride (I).[4]

Bromotrichloromethane, carbon tetrachloride, and thiophenol each formed a 1 : 1 adduct with compound (I), and the n.m.r. spectra of the adducts indicated that addition had taken place on the cyclobutene double bond (see below), which is also the site of attack in non-radical additions.[4-6] Initial attack of a free radical R· on compound (I) to give the intermediate (II) might have been expected to lead to products derived from a rearranged radical (III) or (IV), particularly in view of the ready photochemical conversion (I) ⟶ (V)[7] and the formation of ' half-cage ' products in the bromination of (I) and related compounds.[5,8] However, the adducts could be assigned structures (VIa), (VIb), and (VIc) severally, on the following evidence.

The n.m.r. spectrum (100 MHz) of the bromotrichloromethane adduct (VIa) showed a multiplet due to two vinylic protons at τ 3·2—3·7. In the region τ 5·0—5·35 there was a complex, asymmetrical multiplet (1H), which could be assigned to H-4, since in the products of 1,2-addition of bromotrichloromethane to olefins the proton adjacent to bromine invariably produces a signal at lower field than the >C*H*CCl$_3$ resonance.[9] Support for this assignment was provided by dehydrochlorination of the adduct (VIa) with methanolic potassium hydroxide to afford a product (VII),† the n.m.r. spectrum of which also showed an asymmetrical multiplet, at τ 5·0—5·35 (>C*H*Br). When the spectrum of the adduct (VIa) was recorded at 220 MHz, a great simplification of the multiplets due to H-4, H-7, and H-8 was observed. The vinylic protons now resonated as separate ' triplets,' *J* 7 Hz; this splitting is consistent with the proposed structure (VIa), but not with an isomer having the double bond in the four-membered ring.[10] The H-4 resonance also appeared as a ' triplet,' *J* 7·5 Hz, but unfortunately it was not possible to use this information to deduce the



stereochemistry of H-4. Studies of cyclobutane derivatives have shown no clear correlation between the coupling constants and the *cis* or *trans* relationship of vicinal protons,[11] and furthermore, long-range couplings

† Base-catalysed inversion of either of the carboxy-groups may have occurred.

[1] Part IV, G. I. Fray and R. G. Saxton, *Tetrahedron Letters*, 1973, 3579.
[2] D. I. Davies, L. T. Parfitt, C. K. Alden, and J. A. Claisse, *J. Chem. Soc.* (*C*), 1969, 1585.
[3] D. I. Davies and L. T. Parfitt, *J. Chem. Soc.* (*C*), 1969, 1401.
[4] G. Schröder, ' Cyclo-octatetraen,' Verlag Chemie, Weinheim, 1965, pp. 48, 49, and references therein.
[5] D. G. Farnum and J. P. Snyder, *Tetrahedron Letters*, 1965, 3861.
[6] I. A. Akhtar, Ph.D. Thesis, University of Bristol, 1969.
[7] S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Letters*, 1966, 1017.
[8] R. C. Cookson, J. Hudec, and J. Marsden, *Chem. and Ind.*, 1961, 21.
[9] D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*), 1969, 424.
[10] L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon Press, Oxford, 1969, p. 303.
[11] Ref. 10, p. 287.

such as 2,4-*exo* (or -*endo*) and 6,4-*exo* (or -*endo*) would be expected to be negligible since the four intervening σ-bonds are not coplanar; thus the presence or absence of such couplings cannot help in the determination of the configuration of H-4 (or H-3). However, the stereochemistry at C-3 and C-4 was deduced from chemical shift studies, as described below.

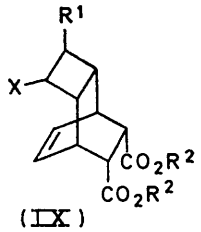
TABLE 1

Chemical shifts (τ) for H-3, H-4, H-7, and H-8 in the bromotrichloromethane adduct (VIa) and the *cis*- and *trans*-dibromides [(VIII) and (VId) [from 100 MHz spectra; solutions in $(CD_3)_2SO$]

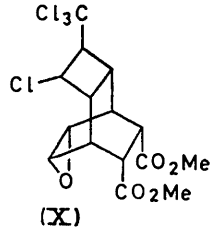
	Chemical shift			
Compound	H-7	H-8	H-4	H-3
(VIa)	3·35	3·55	5·2	6·6
(VId)	3·4	3·6	5·0	5·7
(VIII)	3·5	(2H)	5·6	(2H)

In Table 1, the chemical shift values for H-3, H-4, H-7, and H-8 in the bromotrichloromethane adduct (VIa) are compared with those in the *cis*- and *trans*-dibromides (VIII) and (VId).[5] It would be expected that, in the *trans*-dibromide (VId), the resonance of the *exo*-proton at C-4 would occur at lower field than that of the C-3 *endo*-proton (which is situated in the shielding zone of the double bond), and that H-7 would be deshielded by the *endo*-bromine atom at C-4. From Table 1 it could be concluded that the C-4 bromine atom in compound (VIa) has the *endo*-configuration, and it was reasonable to assume an *exo*-configuration for the trichloromethyl group, which would result from initial attack by the trichloromethyl radical on the less hindered *exo*-face of the cyclobutene double bond. Chain transfer from the intermediate radical (II; R = *exo*-CCl_3) evidently takes place from the *endo*-direction, leading to the *trans*-adduct (VIa), presumably because the alternative mode is greatly hindered by the bulk of the *exo*-trichloromethyl group. By analogy, the products of the addition of carbon tetrachloride and thiophenol were formulated as (VIb) and (VIc) respectively. Confirmation of these conclusions was obtained by the following series of structural transformations of the adducts (VIa) and (VIb).

The anhydride (VIb) was converted into the dimethyl ester (IXa), which on treatment with trifluoroperacetic acid in the presence of sodium carbonate[12] gave the epoxy-dimethyl ester (X); the oxiran ring could be assigned α-stereochemistry[13] by analogy with related compounds.[13,14] Hydrolysis of the epoxy-dimethyl ester (X) with 45% aqueous trifluoroacetic acid gave a hydroxy-lactone-carboxylic acid, formulated as (XIa) on the assumption that the hydroxy-group had been introduced at C-8 with β-stereochemistry; an α-configuration could result only from an abnormal hydrolytic opening of the oxiran ring in (X), and moreover would be expected to lead to a dilactone under the reaction conditions. The product (XIa) could also be obtained directly from the anhydride (VIb) by reaction with 85% aqueous hydrogen peroxide in trifluoroacetic acid, followed by dilution with water and heating under reflux. The

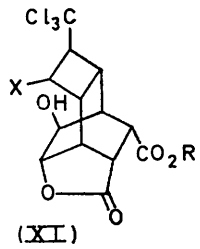


(IX)

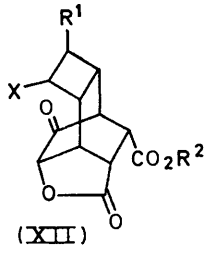


(X)

a; R^1 = CCl_3, X = Cl, R^2 = Me
b; R^1 = CO_2H, X = Cl, R^2 = H
c; R^1 = CCl_3, X = Br, R^2 = Me



(XI)



(XII)

a; X = Cl, R = H
b; X = Cl, R = Me
c; X = Br, R = Me

a; R^1 = CCl_3, X = Cl, R^2 = Me
b; R^1 = CO_2H, X = Cl, R^2 = H
c; R^1 = CCl_3, X = Br, R^2 = Me

hydroxy-lactone-carboxylic acid (XIa) was converted into the methyl ester (XIb), and oxidation with Jones reagent[15] then afforded the keto-lactone-methyl ester (XIIa). The anhydride (VIb), on reaction with concentrated sulphuric acid followed by treatment with water, gave the tricarboxylic acid (IXb); attempted oxidative degradation of this with concentrated nitric acid (*cf.* ref. 16) led to a product for which structure (XIIb) is suggested.

In another series of experiments the bromotrichloromethane adduct (VIa) was converted into the dimethyl ester (IXc), which on prolonged treatment with trifluoroperacetic acid (in the absence of sodium carbonate) gave the hydroxy-lactone-methyl ester (XIc) directly; this was then oxidised to the keto-lactone-methyl ester (XIIc).

The n.m.r. spectra of these transformation products of the adducts (VIa) and (VIb) confirmed the proposed stereochemistry at C-3 and C-4. The *endo*-configuration of H-3 results in shielding by the olefinic bond in the unsaturated dimethyl esters (IXa) and (IXc), and by the carbonyl group in the keto-lactone-methyl esters (XIIa) and (XIIc), as indicated by the chemical shift values given in Table 2. An *exo*-configuration for H-4 is consistent with the relatively small variations in its chemical shift for compounds in this series. As a corollary it

[12] W. D. Emmons and A. S. Pagano, *J. Amer. Chem. Soc.*, 1955, **77**, 89.
[13] G. I. Fray, R. J. Hilton, and J. M. Teire, *J. Chem. Soc.* (*C*), 1966, 592.
[14] D. Bryce-Smith, B. Vickery, and G. I. Fray, *J. Chem. Soc.* (*C*), 1967, 390.
[15] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 1953, 2548.
[16] L. Starr, *J. Chem. Soc.* (*C*), 1967, 1111.

should be noted that the observed shielding of H-3 in the keto-lactone-methyl esters (XIIa) and (XIIc) confirms the position of the keto-group with respect to this proton, and hence the position of the hydroxy-group in the hydroxy-lactone-methyl esters (XIb) and (XIc).

TABLE 2

Chemical shifts (τ) for H-3 and H-4 in the dimethyl esters (IXa) and (IXc) and their transformation products (from 100 MHz spectra; solutions in $CDCl_3$)

Compound	Chemical shift H-4	Chemical shift H-3
(IXa)	5·4	6·65
(X)	5·25	*ca.* 6·3 [a]
(XIb)	*ca.* 5·25 [a]	6·25
(XIIa)	5·2	(6·6) [a,b]
(IXc)	5·3	6·65
(XIc)	5·2	6·1
(XIIc)	5·15	(6·6) [a,b]

[a] Overlapping resonances prevented a more precise determination. [b] Figures in parentheses are *minimum* τ values.

EXPERIMENTAL

Unless stated otherwise, n.m.r. spectra were measured in $CDCl_3$ at 100 MHz; i.r. spectra were recorded for Nujol mulls. The following compounds were prepared by the published method: tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride (I),[17] *cis-exo*-3,4-dibromotricyclo-[4.2.2.0^{2,5}]dec-7-ene-9,10-dicarboxylic anhydride (VIII),[5] and *trans*-3,4-dibromotricyclo[4.2.2.0^{2,5}]dec-7-ene-9,10-dicarboxylic anhydride (VId).[17]

Addition of Bromotrichloromethane to Tricyclo[4.2.2.0^{2,5}]-*deca-3,7-diene-9,10-dicarboxylic Anhydride* (I).—The anhydride (I) (3·6 g) in bromotrichloromethane (50 ml) was heated at 80° for 90 h in the presence of benzoyl peroxide (0·01 g). The solvent was evaporated off and the residue taken up in benzene (20 ml). The addition of light petroleum (b.p. 40—60°) precipitated white crystals, which were recrystallised from acetone–light petroleum to afford 4-endo-*bromo*-3-exo-*trichloromethyltricyclo*[4.2.2.0^{2,5}]*dec-7-ene*-9,10-*dicarboxylic anhydride* (VIa) (4·9 g), m.p. 194—195° (Found: C, 39·1; H, 2·4. $C_{13}H_{10}BrCl_3O_3$ requires C, 39·0; H, 2·5%), τ [$(CD_3)_2SO$] 3·2—3·7 (2H), 5·0—5·35 (1H), 6·4—7·1 (5H), and 7·4—7·6 (2H).

Addition of Carbon Tetrachloride to the Anhydride (I).—A solution of the anhydride (I) (5·0 g) and benzoyl peroxide (0·1 g) in carbon tetrachloride (350 ml) was boiled under reflux for 48 h. Evaporation of the solvent, followed by recrystallisation of the residue from chloroform–ether, yielded 4-endo-*chloro*-3-exo-*trichloromethyltricyclo*[4.2.2.0^{2,5}]-*dec-7-ene*-9,10-*dicarboxylic anhydride* (VIb) (6·2 g), m.p. 175—176° (Found: C, 43·7; H, 2·7; Cl, 39·3. $C_{13}H_{10}Cl_4O_3$ requires C, 43·85; H, 2·8; Cl, 39·8%), τ (60 MHz) 3·1—3·75 (2H), 5·15—5·5 (1H), 6·3—6·95 (5H), and 7·0—7·25 (2H).

Addition of Thiophenol to the Anhydride (I).—A mixture of the anhydride (I) (1·0 g), thiophenol (0·5 g), benzoyl peroxide (0·05 g), and benzene (15 ml) was boiled under reflux for 72 h. The resulting solution was washed with 10% sodium hydroxide solution (3 × 10 ml), then with water (3 × 25 ml), and was dried ($MgSO_4$). The solvent was removed by evaporation, and the residue recrystallised from benzene–light petroleum (b.p. 60—80°) to afford 3-exo-*phenylthiotricyclo*[4.2.2.0^{2,5}]*dec-7-ene*-9,10-*dicarboxylic anhydride* (VIc) (0·94 g), m.p. 174—176° (Found: C, 68·8; H, 5·5. $C_{18}H_{16}O_3S$ requires C, 69·2; H, 5·2%), τ (220 MHz) 2·6—3·0 (5H), 3·45—3·65 (2H), 6·6—6·8 (3H), 7·05 (2H, apparent s), 7·3—7·55 (2H), and 7·8—8·05 (2H).

Dehydrochlorination of the Bromotrichloromethane Adduct (VIa).—The adduct (VIa) (0·50 g) was heated with a solution of potassium hydroxide (0·23 g) in methanol (5 ml) under reflux overnight. The product was poured into water (20 ml), acidified with hydrochloric acid, and extracted with ether. The extract was washed with water, dried, and the solvent evaporated to afford 4-endo-*bromo*-3-*dichloromethyl-enetricyclo*[4.2.2.0^{2,5}]*dec-7-ene*-9,10-*dicarboxylic acid* (VII) (410 mg), m.p. 106—110° (from ether) (Found: C, 40·8; H, 3·0. $C_{13}H_{11}BrCl_2O_4$ requires C, 40·5; H, 2·8%), τ [$(CD_3)_2SO$] 3·2—3·8 (2H), 5·0—5·35 (1H), 6·5—7·3 (5H), and 7·4—7·6 (1H).

Dimethyl 4-endo-*Chloro*-3-exo-*trichloromethyltricyclo*-[4.2.2.0^{2,5}]*dec-7-ene*-9-endo,10-endo-*dicarboxylate* (IXa).—Treatment of the carbon tetrachloride adduct (VIb) with methanolic sulphuric acid under reflux gave the *dimethyl ester* (IXa), m.p. 135—136° (from methanol) (Found: C, 44·7; H, 4·1; Cl, 35·2. $C_{15}H_{16}Cl_4O_4$ requires C, 44·8; H, 4·0; Cl, 35·3%), $\nu_{max.}$ 1732 cm^{-1}, τ 3·3—3·7 (2H), 5·25—5·55 (1H), 6·39 (6H, s), 6·5—6·7 (1H), 6·7—6·95 (2H), 6·95—7·15 (2H), and 7·15—7·4 (2H).

Dimethyl 4-endo-*Chloro*-7α,8α-*epoxy*-3-exo-*trichloro-methyltricyclo*[4.2.2.0^{2,5}]*decane*-9-endo,10-endo-*dicarboxylate* (X).—Trifluoroperacetic acid [from hydrogen peroxide (0·7 ml; 85%) and trifluoroacetic anhydride (7 ml)] in dichloromethane (10 ml) was added in portions to an ice-cold solution of the unsaturated dimethyl ester (IXa) (0·50 g) in the same solvent (15 ml) containing anhydrous sodium hydrogen carbonate (1·5 g). The mixture was kept in the refrigerator overnight and then maintained at room temperature for 24 h. The mixture was filtered, and the filtrate evaporated under reduced pressure to afford a residue which was crystallised from methanol to give the *epoxy-dimethyl ester* (X) (0·36 g), m.p. 190·5—191·5° (Found: C, 42·8; H, 4·0; Cl, 33·9. $C_{15}H_{16}Cl_4O_5$ requires C, 43·1; H, 3·9; Cl, 33·9%), $\nu_{max.}$ 1747 and 1735 cm^{-1}, τ 5·15—5·4 (1H), 6·05—6·45 (9H), 6·65—6·85 (1H), and 7·0—7·6 (5H).

4-endo-*Chloro*-7α,8β-*dihydroxy*-3-exo-*trichloromethyltri-cyclo*[4.2.2.0^{2,5}]*decane*-9-endo,10-endo-*dicarboxylic Acid* 10,7-*Lactone* (XIa).—Hydrogen peroxide (1 ml; 85%) was added to a solution of the carbon tetrachloride adduct (VIb) (1·5 g) in trifluoroacetic acid (15 ml), and the mixture kept at room temperature for 24 h. Water (10 ml) was then added and the mixture heated under reflux overnight. The resulting crystalline solid was filtered off, washed with methanol, and recrystallised from tetrahydrofuran to give the *hydroxy-lactone-carboxylic acid* (XIa) (0·62 g), m.p. 279—280° (decomp.) (Found: C, 40·25; H, 3·1; Cl, 36·1. $C_{13}H_{12}Cl_4O_5$ requires C, 40·0; H, 3·1; Cl, 36·3%), $\nu_{max.}$ 3240, 1800, and 1697 cm^{-1}.

The hydroxy-lactone-carboxylic acid (XIa) was also obtained from the epoxy-dimethyl ester (X) by treatment with aqueous trifluoroacetic acid (45%) under reflux for 23 h.

Methylation of the hydroxy-lactone-carboxylic acid (XIa) with diazomethane in ether–tetrahydrofuran gave the *methyl ester* (XIb), m.p. 258—259° (decomp.) (from acetone–methanol) (Found: C, 41·75; H, 3·7; Cl, 35·2. $C_{14}H_{14}Cl_4O_5$ requires C, 41·6; H, 3·5; Cl, 35·1%), $\nu_{max.}$ 3380, 1794, and

[17] W. Reppe, O. Schlichting, W. Klager, and T. Toepel, *Annalen*, 1948, **560**, 1.

1710 cm^{-1}, τ 4·5—4·7 (1H), 5·0—5·55 (3H), 6·1—6·35 (4H), 6·75—7·4 (5H), and 7·4—7·6 (1H).

4-endo-*Chloro*-9-endo-*methoxycarbonyl*-8-*oxo*-3-exo-*trichloromethyltricyclo*[4.2.2.0^{2,5}]*decan*-10-endo,7α-*olactone* (XIIa).—The hydroxy-lactone-methyl ester (XIb) (170 mg) was dissolved in acetone (10 ml) and a solution of chromium(VI) oxide in aqueous sulphuric acid (Jones reagent [15]) was added dropwise, with stirring, until an excess was present. The resulting mixture was diluted with water and extracted with dichloromethane (3 × 20 ml). The solution was dried ($MgSO_4$), solvent removed by evaporation, and the residue recrystallised from methanol to afford the *keto-lactone-methyl ester* (XIIa) (140 mg), m.p. 232—234° (decomp.) (Found: C, 42·1; H, 3·3; Cl, 35·7. $C_{14}H_{12}Cl_4O_5$ requires C, 41·8; H, 3·0; Cl, 35·3%), $\nu_{max.}$ 1809, 1757, and 1713 cm^{-1}, τ 4·90 (1H, d, *J* 4·5 Hz), 5·05—5·35 (1H), 6·31 (3H, s), and 6·55—7·2 (7H).

4-endo-*Chlorotricyclo*[4.2.2.0^{2,5}]*dec*-7-*ene*-3-exo,9-endo,10-endo-*tricarboxylic Acid* (IXb).—The carbon tetrachloride adduct (VIb) (1·0 g) was dissolved in warm concentrated sulphuric acid (10 ml), the solution heated on a steam-bath for 1 h, and hydrogen chloride was evolved. The solution was poured into ice–water and the precipitated product filtered off, washed with water, and recrystallised from a large volume of water to afford the *chlorotricarboxylic acid* (IXb) (0·74 g), m.p. 230—231° (decomp.) * (Found: C, 52·0; H, 4·4; Cl, 12·0. $C_{13}H_{13}ClO_6$ requires C, 51·9; H, 4·4; Cl, 11·8%), $\nu_{max.}$ 1730 and 1687 cm^{-1}.

Nitric Acid Oxidation of the Chlorotricarboxylic Acid (IXb).—A mixture of the chlorotricarboxylic acid (IXb) (3·1 g) and concentrated nitric acid (15 ml) was heated on a steam-bath until the evolution of nitrous fumes had ceased (*ca.* 2 h). Water (20 ml) was then added and the solution evaporated to dryness. The residue was successively crystallised from aqueous acetone and acetone–benzene to afford 4-endo-*chloro*-7β-*hydroxy*-8-*oxotricyclo*[4.2.2.0^{2,5}]*decane*-3-exo,9-endo,10-endo-*tricarboxylic acid* 10,7-*lactone* (XIIb) (0·57 g), m.p. 297—298° (decomp.) (rapid heating) (Found: C, 49·6; H, 3·6; Cl, 11·1. $C_{13}H_{11}ClO_7$ requires C, 49·6; H, 3·5; Cl, 11·3%), $\nu_{max.}$ 1800, 1758, 1741, and 1710 cm^{-1}.

Methylation of the dicarboxylic acid (XIIb) with diazomethane in ether–methanol afforded the *dimethyl ester*, m.p. 235—236° (from methanol) [Found: C, 52·3; H, 4·5; Cl, 10·4%; *M* (mass spectrum), 342. $C_{15}H_{15}ClO_7$ requires C, 52·55; H, 4·4; Cl, 10·35%; *M* (^{35}Cl) 342], $\nu_{max.}$ 1800, 1750, and 1720 cm^{-1}, τ [$(CD_3)_2SO$] 4·8—5·2 (2H), 6·38 (3H, s), 6·46 (3H, s), and 6·5—7·35 (7H).

Dimethyl 4-endo-*Bromo*-3-exo-*trichloromethyltricyclo*-[4.2.2.0^{2,5}]*dec*-7-*ene*-9-endo,10-endo-*dicarboxylate* (IXc).—The bromotrichloromethane adduct (VIa) on treatment with refluxing methanolic sulphuric acid overnight gave the *dimethyl ester* (IXc), m.p. 138—139° (from methanol) (Found: C, 40·1; H, 3·3. $C_{15}H_{16}BrCl_3O_4$ requires C, 40·3; H, 3·6%), $\nu_{max.}$ 1732 cm^{-1}, τ 3·15—3·6 (2H), 5·15—5·4 (1H), 6·40 (6H, s), 6·4—6·65 (1H), 6·65—6·85 (2H), 6·85—7·1 (2H), and 7·1—7·35 (2H).

4-endo-*Bromo*-8β-*hydroxy*-9-endo-*methoxycarbonyl*-3-exo-*trichloromethyltricyclo*[4.2.2.0^{2,5}]*decane*-10-endo,7α-*olactone* (XIc).—Trifluoroperacetic acid [from 85% hydrogen peroxide (0·5 ml) and trifluoroacetic anhydride (5 ml)] in dichloromethane (5 ml) was added to an ice-cold solution of the unsaturated dimethyl ester (IXc) (0·40 g) in the same solvent (15 ml). The mixture was kept overnight in the refrigerator and then at room temperature for 7 days. Evaporation of the solvent under reduced pressure followed by crystallisation of the residue from methanol yielded the *hydroxy-lactone-methyl ester* (XIc) (0·26 g), m.p. 244—245° (Found: C, 37·8; H, 3·3; halogen, 40·8. $C_{14}H_{14}BrCl_3O_5$ requires C, 37·5; H, 3·15; halogen, 41·5%), $\nu_{max.}$ 3380, 1794, and 1710 cm^{-1}, τ 4·35—4·55 (1H), 5·05—5·3 (2H), 5·3—5·55 (1H), 6·0—6·3 (4H), 6·7—7·35 (5H), and 7·4—7·55 (1H).

4-endo-*Bromo*-9-endo-*methoxycarbonyl*-8-*oxo*-3-exo-*trichloromethyltricyclo*[4.2.2.0^{2,5}]*decane*-10-endo,7α-*olactone* (XIIc).—Treatment of (IXc) with Jones reagent [15] as described for (IXb) gave the *keto-lactone-methyl ester* (XIIc), m.p. 225—226° (from methanol) (Found: C, 37·3; H, 2·5; halogen, 41·5. $C_{14}H_{12}BrCl_3O_5$ requires C, 37·65; H, 2·8; halogen, 41·7%), $\nu_{max.}$ 1800, 1746, and 1715sh cm^{-1}, τ 4·80 (1H, d, *J* 4·5 Hz), 5·05—5·3 (1H), 6·30 (3H, s), and 6·55—7·0 (7H).

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* The m.p. varied with the rate of heating. The value above was obtained when the sample was heated rapidly to 228°, and then at 1° min^{-1}.