Highly Condensed Polycyclic Systems. Part IV.[1] Action of Concentrated Sulphuric Acid on 1,2,4,5-Tetrachloro-3,3-ethylenedioxytetracyclo-[3,2,0,0^{2,7},0^{4,6}]heptane: a Novel Rearrangement of a Quadricyclanone Acetal

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Treatment of 1,2,4,5-tetrachloro-3,3-ethylenedioxytetracyclo[3,2,0,0^{2,7},0^{4,6}]heptane (II; X = C·O·[CH$_2$]$_2$·O, R^1 = R^2 = Cl) with concentrated sulphuric acid results in a novel rearrangement to give 6,7-dichloro-3,4-ethylene-dioxybicyclo[3,2,0]hepta-3,6-dien-2-one (IV). Similar treatment of 1,2,3,4-tetrachloro-7,7-ethylenedioxybi-cyclo[2,2,1]hepta-2,5-diene (I; X = C·O·[CH$_2$]$_2$·O, R = H) yields 2-hydroxyethyl 2,3,4-trichlorobenzoate (X; X = OH).

Zinc in glacial acetic acid reacts with the 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene dimer (XII; X = C·O·[CH$_2$]$_2$·O, R = Cl), effecting selective replacement of two chlorine atoms by hydrogen, and affording 1,3,4,7,8,9-hexachloro-5,5:10,10-bis(ethylenedioxy)tricyclo[5,2,1,0^{2,6}]deca-3,8-diene (XII; X = C·O·[CH$_2$]$_2$·O R = H).

THE quadricyclane (tetracyclo[3,2,0,0^{2,7},0^{4,6}]heptane †) system is readily produced from bicyclo[2,2,1]hepta-dienes by the action of u.v. radiation,[3] and irradiation of the norbornadienone acetal (I; X = C·O·[CH$_2$]$_2$·O, R = H)[4] in dichloromethane gave the quadricyclanone acetal (II; X = C·O·[CH$_2$]$_2$·O, R^1 = R^2 = Cl) (cf. ref. 5).

When the acetal (II; X = C·O·[CH$_2$]$_2$·O, R^1 = R^2 = Cl) was treated with cold concentrated sulphuric acid, and the resulting solution was poured onto ice, a compound of molecular formula C$_9$H$_6$Cl$_2$O$_3$ was isolated. Its i.r. and u.v. spectra were suggestive of an αβ-unsaturated ketone, and the presence of a ketone function was confirmed by the formation of a 2,4-dinitrophenylhydrazone. The n.m.r. spectrum showed signals which could be assigned to the four protons of an ethylenedioxy-group, together with an AB quartet (J 3 Hz). Oxidative degradation of the product with hydrogen peroxide in aqueous methanolic sodium hydroxide[6] gave a dicarb-

oxylic acid, C$_6$H$_4$Cl$_2$O$_4$. This was identified as the cyclo-butenedicarboxylic acid (III) by its spectral characteristics, the cis-stereochemistry of the carboxy-groups being revealed by its conversion (with acetyl chloride) into a cyclic anhydride. The original unsaturated ketone could therefore be assigned structure (IV), containing a bicyclo[3,2,0]hepta-3,6-dien-2-one system.

If it is assumed that the formation of the product (IV) from the acetal (II; X = C·O·[CH$_2$]$_2$·O, R^1 = R^2 = Cl) is initiated by the protonation of the acetal group, rearrangement of the resulting cation (V) may be visualised in several different ways; the mode illustrated ‡ would give the stabilised ion (VI), which by subsequent cyclisation and hydrolysis could lead to the observed product (IV). It is interesting that this reaction, whatever its detailed mechanism, takes a course which is fundamentally different from the acid-catalysed rearrangements of the quadricyclanone acetals [II;

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† For notes on systematic nomenclature, see ref. 2.
‡ Orbital symmetry considerations[7] would forbid a concerted process, which would be the retro-[$_π2_s$ + $_π2_s$] cycloaddition of an olefinic bond to an allylic cation.

[1] Part III, I. A. Akhtar and G. I. Fray, J. Chem. Soc. (C), 1971, 2802.

[2] J. Meinwald and J. K. Crandall, J. Amer. Chem. Soc., 1966, **88**, 1292.
[3] H. Prinzbach, Pure Appl. Chem., 1968, **16**, 17, and references quoted therein.
[4] K. Mackenzie, J. Chem. Soc., 1964, 5710.
[5] D. I. Davies and P. J. Rowley, J. Chem. Soc. (C), 1967, 2245.
[6] R. D. Temple, J. Org. Chem., 1970, **35**, 1275.
[7] R. B. Woodward and R. Hoffmann, Angew. Chem. Internat. Edn., 1969, **8**, 781.

$X = C(OMe)_2$, $R^1 = H$, $R^2 = H$ or Me][8] and of other reactions proceeding *via* 7-tetracycloheptyl cations,[9] in which cleavage of the four-membered ring [in the manner illustrated in (VII)] has been observed. The rearrangement of the cation (V) might be influenced by a number

(I)   (II)   (III)

(IV)   (V)

(VI)   (VII)

(VIII)   (IX)
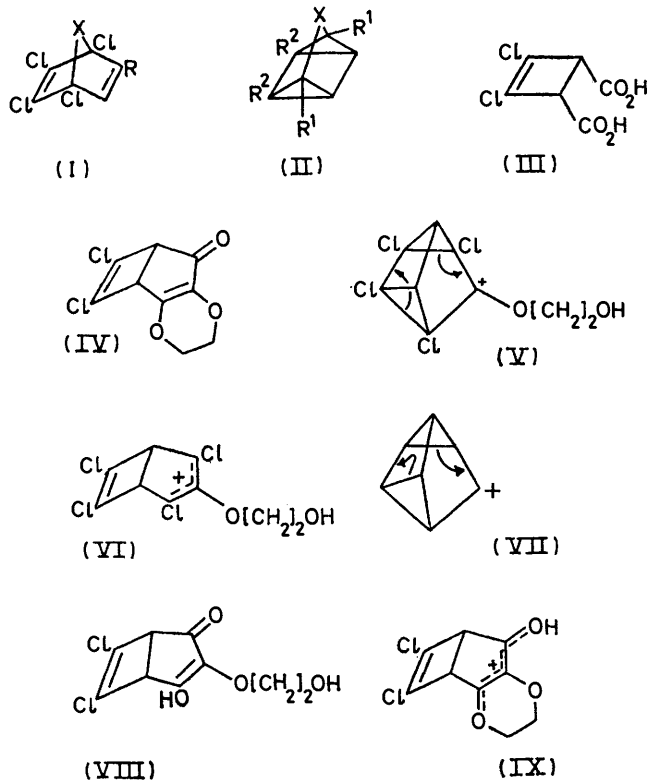
of factors, but it may be noted that the illustrated mode would follow from the assumption that $>C^+–Cl$ is more stable than $>C^+–H$.

Aqueous alkali converted the unsaturated ketone (IV) into a product $C_9H_8Cl_2O_4$. The n.m.r. spectrum revealed the presence of two hydroxy-groups (identified by deuterium exchange), two identical methine protons, and two pairs of methylene protons. The product was acidic, and with aqueous ethanolic iron(III) chloride solution a green-brown colouration was observed. The 2,4-dinitrophenylhydrazone was identical with that of the original ketone (IV), which was re-formed from the hydrolysis product when the latter was treated with sulphuric acid. The evidence is accommodated by the enolic β-diketone structure (VIII), which could result from attack by hydroxy-ion at the β-position of the αβ-unsaturated ketone (IV). The stability of the vinyl ether systems of the ketone (IV) in the presence of sulphuric acid presumably reflects a preferential protonation

at the carbonyl oxygen atom, which would lead to the highly stabilised cation (IX).

When the norbornadienone acetal (I; $X = C\cdot O\cdot[CH_2]_2\cdot O$, R = H) was treated with concentrated sulphuric acid, the product was the aromatic hydroxy-ester (X; X = OH). Compare this with the thermal rearrangement of the acetal (I; $X = C\cdot O\cdot[CH_2]_2\cdot O$, R = H), which affords the corresponding chloro-ester (X; X = Cl) (together with 1,2,3,4-tetrachlorobenzene).[4] The reaction of the ethylene acetal (I; $X = C\cdot O\cdot[CH_2]_2\cdot O$, R = H) with sulphuric acid is, however, unlike those of related dimethyl acetals; for example, the compound [I; $X = C(OMe)_2$, R = Ph] yields 2,3,4,5-tetrachlorobiphenyl by hydrolysis of the acetal group followed by extrusion of carbon monoxide.[10] This difference of behaviour probably results from the generally slower hydrolysis rates of norbornadienone ethylene acetals (*cf.* ref. 11). The rearrangement of

(X)

compound (I; $X = C\cdot O\cdot[CH_2]_2\cdot O$, R = H) might be initiated by *C*-protonation (see Scheme);* rearrange-

(XI)   (XII)   (XIII)

(I; $X = C\cdot O\cdot[CH_2]_2\cdot O$, R = H) ⟶

(X; X = OH)

SCHEME

ment to a dioxolenium cation could then be followed by hydrolysis and loss of hydrogen chloride.

* The mechanism suggested in the Scheme involves protonation of the chlorinated double bond of the norbornadienone acetal, but an equivalent mechanism may be written for initial protonation of the other olefinic bond.
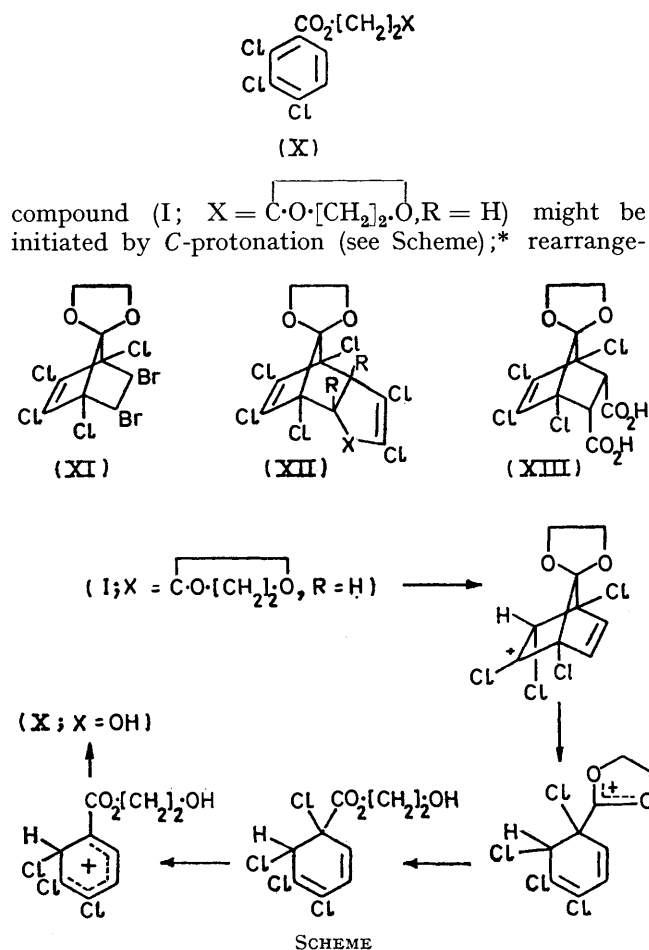
[8] P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Amer. Chem. Soc.*, 1968, **90**, 7271; P. G. Gassman and D. S. Patton, *ibid.*, p. 7276.

[9] M. Brookhart, R. K. Lustgarten, D. L. Harris, and S. Winstein, *Tetrahedron Letters*, 1971, 943, and references cited therein.

[10] D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Amer. Chem. Soc.*, 1966, **88**, 582.

During an early preparation of the acetal (II; X = C·O·[CH₂]₂·O, R¹ = R² = Cl) from the norbornadienone acetal (I; X = C·O·[CH₂]₂·O, R = H) [obtained by addition of 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene to 1,2-dibromoethylene followed by debromination of the product (XI) with zinc in glacial acetic acid[4]], a compound $C_{14}H_{10}Cl_6O_4$ was isolated in minute yield. It was shown that this product resulted from selective dechlorination (zinc in acetic acid) of the ethylenedioxycyclopentadiene dimer (XII; X = C·O·[CH₂]·O, R = Cl),[4] which could have been present as an impurity in the dibromide (XI). Structure (XII; X = C·O·[CH₂]₂·O, R = H) was proved for the hexachloro-compound as follows. With concentrated sulphuric acid, specific hydrolysis of the cyclopentenone acetal group occurred to yield the keto-acetal (XII; X = CO, R = H) (cf. refs. 11 and 12), and subsequent oxidation with potassium permanganate in acetone gave the dicarboxylic acid (XIII), identical with an authentic specimen prepared from 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene and maleic anhydride.

EXPERIMENTAL

Unless stated otherwise, light petroleum refers to the fraction of b.p. 60—80°. N.m.r. spectra were measured at 100 MHz; i.r. spectra were determined for Nujol mulls, and u.v. spectra for ethanolic solutions.

1,2,4,5-Tetrachloro-3,3-ethylenedioxytetracyclo[3,2,0,0²,⁷,-0⁴,⁶]*heptane* (II; X = C·O·[CH₂]₂·O, R¹ = R² = Cl].—A solution of the norbornadienone acetal (I; X = C·O·[CH₂]₂·O, R = H) [4] (4·0 g) in dichloromethane (900 ml) was irradiated with u.v. light at room temperature under nitrogen for 48 h, using a Hanovia Photoreactor equipped with a 125 W medium-pressure mercury-arc surrounded by a quartz water-jacket. The solvent was removed under reduced pressure, and the residue was chromatographed on silica. Elution with benzene–light petroleum (1 : 1) gave the *acetal* (2·3 g, 57%), m.p. 74—75° (from light petroleum) (Found: C, 37·8; H, 2·1; Cl, 49·6. $C_9H_6Cl_4O_2$ requires C, 37·5; H, 2·1; Cl, 49·2%), τ (CCl₄) 5·77 (s, 4H) and 7·41 (s, 2H).

6,7-Dichloro-3,4-ethylenedioxybicyclo[3,2,0]*hepta-3,6-dien-2-one* (IV).—The finely powdered acetal (II; X = C·O·[CH₂]₂·O, R¹ = R² = Cl) (5·0 g) was added in small portions, with stirring, to ice-cold concentrated sulphuric acid (100 ml). Stirring was continued for 1 h, and then the yellow mixture was poured onto ice. The resulting gummy solid was collected in ether, and the ethereal solution was dried (MgSO₄) and evaporated. Light petroleum (b.p. 80—100°) was distilled from the residue (to remove water), and crystallisation from methanol finally afforded the unsaturated *ketone* (2·7 g, 67%), m.p. 125—125·5° [Found: C, 46·2; H, 2·6; Cl, 30·4%; *M* (mass spectrum), 232. $C_9H_6Cl_2O_3$ requires C, 46·5; H, 2·6; Cl, 30·6%; *M* (³⁵Cl),

232], $\nu_{max.}$ 1698 and 1630 cm⁻¹, $\lambda_{max.}$ 286 (ε 7350), τ (CDCl₃) 5·6—5·8 (2H), 5·8—6·0 (2H), 6·11 (d, 1H, *J* 3 Hz), and 6·35 (d, 1H, *J* 3 Hz).

The *2,4-dinitrophenylhydrazone* (prepared in ethanolic sulphuric acid) formed orange needles, m.p. 287—288° (from dichloromethane–ethanol) (Found: C, 43·2; H, 2·6; Cl, 17·2; N, 13·8. $C_{15}H_{10}Cl_2N_4O_6$ requires C, 43·6; H, 2·4; Cl, 17·2; N, 13·6%).

Oxidative Degradation of the Unsaturated Ketone (IV).—A mixture of the unsaturated ketone (IV) (0·42 g), methanol (25 ml), 30% hydrogen peroxide solution (6 ml), and 1N-sodium hydroxide (15 ml) was stirred at 40° overnight, then acidified with sulphuric acid; the solution was saturated with sodium sulphate, and extracted with ether. The ethereal solution was washed with iron(II) sulphate solution, and then dried (MgSO₄). Evaporation, and treatment of the residue with carbon tetrachloride, afforded 3,4-*dichlorocyclobut-3-ene*-cis-1,2-*dicarboxylic acid* (III) (35 mg), m.p. 169·5—170·5° (decomp.) [from ether–light petroleum (b.p. 40—60°)] [Found: C, 34·3; H, 1·9; Cl, 33·5%; *M* (mass spectrum), 210. $C_6H_4Cl_2O_4$ requires C, 34·15; H, 1·9; Cl, 33·6%; *M* (³⁵Cl), 210], $\nu_{max.}$ 1735, 1720sh, 1682, and 1632 cm⁻¹, τ (Et₂O) −0·24 (s, 2H) and 6·06 (s, 2H).

The cyclic anhydride (prepared with acetyl chloride) crystallised from benzene–light petroleum; insufficient material was available for complete purification, but the product showed $\nu_{max.}$ 1865br, 1790, and 1625 cm⁻¹.

6,7-Dichloro-3-(2-hydroxyethoxy)-4-hydroxybicyclo[3,2,0]-*hepta-3,6-dien-2-one* (VIII).—The unsaturated ketone (IV) (2·3 g) in 10% methanolic potassium hydroxide (10 ml) was heated under reflux for 3 h. Most of the solvent was removed under reduced pressure, and then water was added and the solution was acidified with hydrochloric acid. The product was collected in ether in the usual way, and finally recrystallised from methanol to give the enolic β-*diketone* (1·5 g, 60%), m.p. 164—165° (Found: C, 43·2; H, 3·4; Cl, 28·0. $C_9H_8Cl_2O_4$ requires C, 43·05; H, 3·2; Cl, 28·2%), $\nu_{max.}$ 3022, 1685, 1665, and 1628 cm⁻¹, τ ([²H₆]acetone) 6·02 (t, 2H, *J* 4 Hz), 6·1—6·2 (2H), 6·26 (s, 2H), and 6·34 (t, 2H, *J* 4 Hz).

The product was acidic (hydrogen carbonate test), and with aqueous ethanolic iron(III) chloride solution gave a green-brown colour.

Reaction with 2,4-dinitrophenylhydrazine in ethanolic sulphuric acid gave a derivative identical with the 2,4-dinitrophenylhydrazone obtained from the unsaturated ketone (IV). On treatment with ethanolic sulphuric acid alone, the enolic compound recyclised to form the parent ketone (IV).

Reaction of 1,2,3,4-Tetrachloro-7,7-ethylenedioxybicyclo-[2,2,1]*hepta-2,5-diene* (I; X = C·O·[CH₂]₂·O, R = H) *with Concentrated Sulphuric Acid.*—A mixture of the finely-powdered norbornadienone acetal (I; X = C·O·[CH₂]₂·O, R = H) (0·8 g) and ice-cold concentrated sulphuric acid (15 ml) was warmed to room temperature overnight, and the resulting solution was poured onto ice. The solid product was collected by filtration, washed with water, dried, and finally recrystallised from ether–light petroleum to yield 2-*hydroxyethyl* 2,3,4-*trichlorobenzoate* (X; X = OH) (0·6 g, 83%), m.p. 62—63° (Found: C, 40·1; H, 2·6; Cl, 39·4. $C_9H_7Cl_3O_3$ requires C, 40·1; H, 2·6; Cl, 39·45%),

[11] K. Mackenzie and P. R. Young, *J. Chem. Soc.* (C), 1970, 1242.

[12] K. V. Scherer, R. S. Lunt, and G. A. Ungefug, *Tetrahedron Letters*, 1965, 1199.

$\nu_{max.}$ 3380 and 1706 cm^{-1}, τ (CCl$_4$) 2·4—2·75 (AB q, 2H, J 8·5 Hz), 5·6—5·8 (2H), 6·1—6·3 (2H), and 7·66 (s, 1H).

Hydrolysis of the ester (with aqueous trifluoroacetic acid) gave 2,3,4-trichlorobenzoic acid, identical with an authentic sample.

endo-1,3,4,7,8,9-Hexachloro-5,5:10,10-bis(ethylenedioxy)-tricyclo[5,2,1,0^{2,6}]*deca-3,8-diene* (XII; X = C·O·[CH$_2$]$_2$·O, R = H).—A mixture of the 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene dimer (XII; X = C·O·[CH$_2$]$_2$·O, R = Cl) [4] (2·0 g), glacial acetic acid (15 ml), and zinc dust (2·0 g) was stirred at room temperature for 2 h, and then poured onto ice. Extraction with dichloromethane, followed by evaporation of the extract, afforded the *hexachlorodiacetal* (1·5 g, 87%), m.p. 177—178° (from methanol) (Found: C, 37·3; H, 2·2; Cl, 46·95. C$_{14}$H$_{10}$Cl$_6$O$_4$ requires C, 36·95; H, 2·2; Cl, 46·7%), $\nu_{max.}$ 1630 and 1592 cm^{-1}, τ (CDCl$_3$) 5·7—6·1 (8H), (d, 1H, J 7·5 Hz), and 6·77 (d, 1H, J 7·5 Hz).

endo-1,4,5,7,8,9-Hexachloro-10,10-ethylenedioxytricyclo-[5,2,1,0^{2,6}]*deca-4,8-dien-3-one* (XII; X = CO, R = H).—A mixture of the hexachloro-diacetal (XII; X = C·O·[CH$_2$]$_2$·O, R = H) (1·0 g) and concentrated sulphuric acid (10 ml) was stirred at room temperature overnight, and then heated on the steam-bath for 1 h. The mixture was poured onto ice, and the solid product was filtered off, washed with water, and dried. Recrystallisation from ether furnished the *keto-acetal* (0·5 g, 55%), m.p. 152—153°

(Found: C, 35·2; H, 1·7; Cl, 51·4. C$_{12}$H$_6$Cl$_6$O$_3$ requires C, 35·0; H, 1·5; Cl, 51·8%), $\nu_{max.}$ 1720 and 1590 cm^{-1}, $\lambda_{max.}$ 252 (ε 6810).

Oxidation with Permanganate of the Keto-acetal (XII; X = CO, R = H).—Finely-powdered potassium permanganate (0·25 g) was added in portions during 2 h to a solution of the keto-acetal (XII; X = CO, R = H) (0·2 g) in dry acetone (25 ml) under reflux. The solvent was evaporated, water was added to the residue, and sulphur dioxide was passed into the mixture. The resulting solution was extracted continuously with ether for 24 h, and the extract was dried (MgSO$_4$) and evaporated. Recrystallisation of the residue from ether–light petroleum then gave 1,4,5,6-*tetrachloro-7,7-ethylenedioxybicyclo*[2,2,1]-*hept-5-ene-cis-endo-2,3-dicarboxylic acid* (62 mg), m.p. *ca.* 205° (decomp.) (Found: C, 34·75; H, 2·1; Cl, 37·6. C$_{11}$H$_8$Cl$_4$O$_6$ requires C, 34·9; H, 2·1; Cl, 37·5%), $\nu_{max.}$ 1725br and 1600 cm^{-1}.

The product was identical with a specimen prepared by heating 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene and maleic anhydride in xylene under reflux, followed by extraction of the product with sodium hydroxide, and subsequent acidification.