

Base-promoted Rearrangement of 2,3,5,6-Tetrachloropentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,8,11-trione

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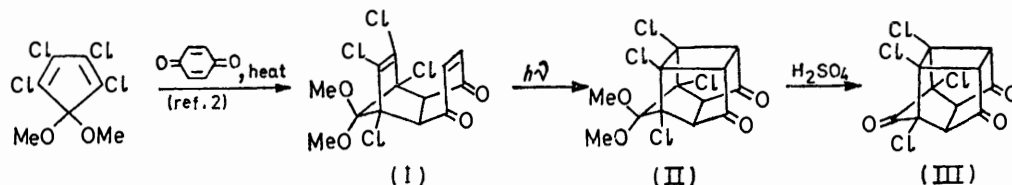
Reaction of the title compound (III) with an excess of sodium hydroxide in refluxing toluene results in a novel rearrangement, affording 6-chloro-*cis*-1,2-dihydrobenzocyclobutene-1,2,3-tricarboxylic acid (IVa).

SEMIBENZYLIC ACID rearrangement of $\alpha\alpha'$ -dichloro-ketones has been commonly utilized for the synthesis of strained ring systems.¹ This paper reports the isolation and characterization of an unexpected product arising from the semibenzylic acid rearrangement of 2,3,5,6-tetrachloropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,8,11-trione (III).

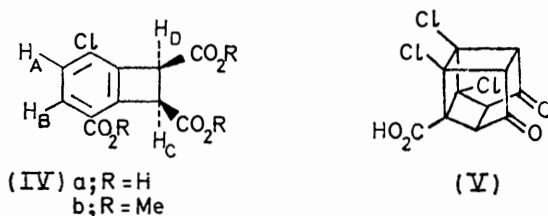
Compound (III) was prepared *via* the illustrated reaction sequence. The Diels–Alder adduct (I) from

¹ (a) P. E. Eaton and T. W. Cole, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 962, 3157; (b) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, jun., *ibid.*, 1968, **90**, 1014; (c) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Org. Chem.*, 1968, **33**, 1454; (d), R. J. Stedman, L. S. Miller, L. D. Davis, and J. R. E. Hoover, *ibid.*, 1970, **35**, 4169.

tetrachlorocyclopentadienone dimethyl acetal and *p*-benzoquinone² was irradiated in acetone solution under nitrogen,³ affording the cyclized product (II) (93%).



Hydrolysis of (II) in concentrated sulphuric acid⁴ afforded the hygroscopic triketone (III) (80%).⁴

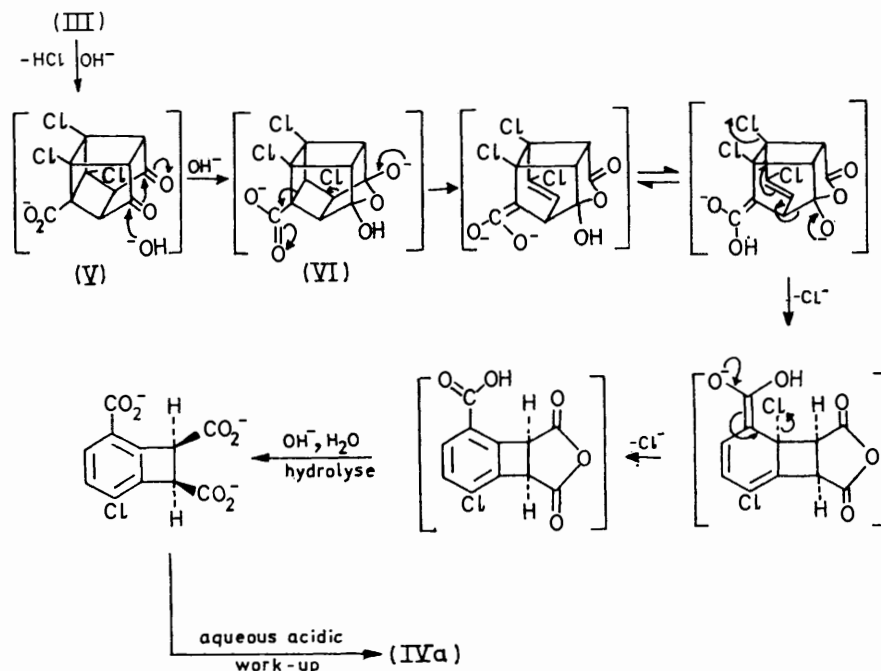


When a solution of the ketone (III) in toluene was refluxed over an excess of sodium hydroxide, a brown oil was obtained. After work-up, this oil was chromatographed on silica gel, affording a small quantity of

The i.r. spectrum of (IVa) (KBr) displayed bands at 3000vbr and at 1700 and 1730 cm^{-1} , suggesting the presence of both conjugated and nonconjugated carboxy-

groups. The presence of a 1,2,3,4-tetrachloro substituted benzene ring was suggested by the n.m.r. spectrum, which displayed an AB pattern (2H) centered at δ [(CD₃)₂CO] 7.63 ($\Delta\delta$ 25 Hz, J_{AB} 8 Hz). A sharp singlet (2H) at δ 4.78 corresponded to the protons (H_C and H_D) on the cyclobutane ring. The adventitious equivalence of H_C and H_D could be removed by adding a few drops of [²H₆]benzene to the solution;⁵ an AB pattern (J_{CD} ca. 6 Hz) resulted.

Attempted sublimation of (IVa) afforded a mixture of (IVa) and the corresponding carboxylic anhydride, as evidenced by the presence of additional i.r. absorption (KBr) at 1788 and 1862 cm^{-1} ; this doublet is characteristic of strained, cyclic acid anhydrides.⁶ The n.m.r.



SCHEME

colourless crystals. On the basis of spectroscopic evidence the structure (IVa) was assigned to this product; no trace of the expected product (V) of semibenzyl acid rearrangement of (III) was detected.

² E. T. McBee, W. R. Dively, and J. E. Burch, *J. Amer. Chem. Soc.*, 1955, **77**, 385.

³ R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 1964, 3062.

spectrum of the mixture in [²H₆]acetone exhibits two sets of signals, the upfield set being identical to those

⁴ K. V. Scherer, jun., *Tetrahedron Letters*, 1966, 5685.

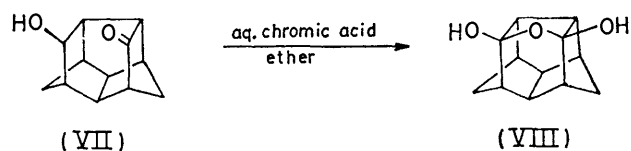
⁵ (a) P. Laszlo, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 231; (b) A. P. Marchand, W. R. Weimar, jun., A. L. Segre, and A. M. Ihrig, *J. Magnetic Resonance*, 1972, **6**, 316.

⁶ W. G. Dauben and W. W. Epstein, *J. Org. Chem.*, 1959, **24**, 1595.

of (IVa). The set appearing at lower field corresponds to the acid anhydride [δ 5.05br (2H, s) and 7.70 (AB system)]. The peaks corresponding to the acid anhydride disappear completely from the spectrum after the solution is treated with D₂O for several days; the only peaks remaining correspond to H_A—H_D of (IVa). Primarily on the basis of these observations, we assign the *cis* stereochemistry to the vicinal carboxylic acid groups in (IVa).

Compound (IVa) was further characterized as its trimethyl ester (IVb). Structural information was gained from the mass spectra of compounds (IVa and b). That of (IVa) showed the molecular ion at m/e 270/272, possessing the intensity profile characteristic of the Cl multiplet,⁷ and peaks at m/e 252, 208, and 180 (base peak) which arise *via* dehydration (to form the corresponding acid anhydride) followed by elimination of CO₂ and cycloelimination of CO₂ + CO; such fragmentation behaviour is common for *cis*-1,2-dicarboxylic acids and their corresponding anhydrides.⁸ The mass spectrum of (IVb) displayed the molecular ion at m/e 312/314, with a similar intensity profile to (IVa), and major peaks at m/e 281 ($M^+ - \text{OMe}$), 253 ($M^+ - \text{CO}_2\text{Me}$, base peak), and 194 ($M^+ - 2\text{CO}_2\text{Me}$); this fragmentation behaviour is common for vicinal diesters.⁹

A reasonable mechanism for the formation of (IVa) *via* base-promoted rearrangement of (III) might invoke the intermediacy of the normal product (V) of semi-benzylic acid rearrangement of (III)¹ (Scheme). We suggest that (V) thus formed is not stable to the reaction conditions and thus cannot be isolated. Instead, it continues to react with base to afford (IVa); this process is facilitated by the presence of two additional carbonyl groups in (V), and the process of aromatization provides the driving force for the rearrangement. The intermediate (VI) (Scheme) is suggested by analogy with the



previously observed formation of the dihydroxy-ether (VIII) *via* aqueous chromic acid oxidation of the keto-alcohol (VII).¹⁰

EXPERIMENTAL

I.r. spectra were obtained for dispersions in KBr. N.m.r. spectra were obtained at 60 MHz for solutions in [2H₆]-acetone (Me₄Si internal standard). Mass spectra were obtained with a Hitachi RMU-6E spectrometer.

1,2,3,4-Tetrachloro-1,4,4a,8a-tetrahydro-9,9-dimethoxy-endo-1,4-methanonaphthalene-5,8-dione (I).—A mixture of tetrachlorocyclopentadienone dimethyl acetal¹¹ (52.8 g,

0.2 mol) and *p*-benzoquinone (21.6 g, 0.2 mol) was dissolved in dry toluene (100 ml) and refluxed for 24 h. The mixture was then evaporated and the residue was recrystallized from benzene-hexane to give pale yellow crystals (I) (54 g, 73%), m.p. 160.5—163° (lit.,² 162—164°).

4,4-Dimethoxy-2,3,5,6-tetrachloropentacyclo[5.4.0.0.2⁶.0.3¹⁰.0.5⁹]undecane-8,11-dione (II).—Irradiation of compound (I) (15.0 g, 0.040 mol) in acetone (600 ml) under nitrogen with a 200 W Hanovia medium-pressure mercury lamp (Pyrex shield) for 8 h³ afforded a tan, microcrystalline solid. Recrystallization from benzene-hexane afforded colourless material (II) (13.75 g, 93%), m.p. 151.5—152.5°, ν_{max} 1770 and 1780 cm⁻¹ (CO); δ 3.56 (4H, s, methines) and 3.70(s) and 3.74(s) (6H, 2 × OMe); m/e 370/372/374/376/378 (M^+ , intensity profile characteristic of the Cl₄ multiplet⁷) (Found: C, 41.8; H, 2.6. C₁₃H₁₀Cl₄O₄ requires C, 42.0; H, 2.7%).

2,3,5,6-Tetrachloropentacyclo[5.4.0.0.2⁶.0.3¹⁰.0.5⁹]undecane-4,8,11-trione (III).—Treatment of compound (II) (1.0 g, 3 mmol) with concentrated sulphuric acid in methylene chloride at room temperature for 2 days⁴ gave the triketone (III) which when sublimed afforded a colourless microcrystalline solid (0.70 g, 80%), m.p. 211—212°, ν_{max} 1775, 1785, 1809, and 1824 cm⁻¹; δ 3.18br (s, methines); m/e 324/326/328/330/332 (M^+ , intensity profile characteristic of the Cl₄ multiplet⁷) (Found: C, 40.5; H, 1.25. C₁₁H₄Cl₄O₃ requires C, 40.1; H, 1.25%).

6-Chloro-*cis*-1,2-dihydrobenzocyclobutene-1,2,3-tricarboxylic Acid (IVa).—A suspension of the triketone (III) (6.00 g, 18.4 mmol) in dry toluene (150 ml) was concentrated by careful distillation to 100 ml. Crushed sodium hydroxide pellets (4 g, 0.1 mol) were added, and the mixture was refluxed for 45 min, then poured into ice-water (300 ml). The aqueous layer was separated and washed with diethyl ether (3 × 100 ml). The combined extracts yielded unchanged triketone (III) (0.15 g). The aqueous layer was acidified with hydrochloric acid and then extracted with diethyl ether (liquid-liquid extraction apparatus) for 3 days. The extract was washed with water (50 ml), dried (Na₂SO₄), filtered, and concentrated, affording a brown oil (3.8 g). Chromatography on silica gel (diethyl ether eluant) followed by recrystallization from acetone-hexane afforded a white crystalline solid (IVa) (750 mg, 13.1%), m.p. 264—265.5° (decomp.). A residual oil (*ca.* 2 g) resisted attempts at purification; however, its n.m.r. and i.r. spectra were essentially the same as those of (IVa). The n.m.r., i.r., and mass spectra of (IVa) are discussed in the text (Found: C, 48.8; H, 3.4. C₁₁H₇ClO₆ requires C, 48.8; H, 2.6%).

Ethereal diazomethane was added dropwise to a solution of the acid (IVa) (310 mg) in anhydrous diethyl ether (50 ml) until the yellow colour of the diazoalkane persisted. The mixture was set aside overnight; several drops of hydrochloric acid were then added to destroy unchanged diazomethane. The solution was washed with dilute sodium hydrogen carbonate solution, and the organic layer was dried (Na₂SO₂), filtered, and concentrated to afford crude trimethyl ester (IVb) (290 mg, 81%). Recrystallization

⁹ (a) R. Ryhage and E. Stenhagen, in 'Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York, 1963, pp. 444—451; (b) R. L. Cargill and M. R. Willcott, *tert. J. Org. Chem.*, 1966, **31**, 3938; (c) D. A. Bak and K. Conrow, *J. Org. Chem.*, 1966, **31**, 3608.

¹⁰ R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, 1964, **86**, 3162.

¹¹ P. G. Gassman and J. L. Marshall, *Org. Synth.*, 1968, **48**, 68

⁷ J. H. Beynon, 'Mass Spectrometry and its Applications to Organic Chemistry,' Elsevier, New York, 1960, pp. 298—299.

⁸ (a) J. H. Beynon, *ref. 7*, p. 375; (b) S. J. Weininger, V. T. Mai, and E. R. Thornton, *J. Amer. Chem. Soc.*, 1964, **86**, 3732.

from diethyl ether afforded colourless *crystals* (171 mg, 48%), m.p. 109.5—110.5°, ν_{\max} . 1605, 1728, 1750, and 3020 cm^{-1} , δ 7.65 ($\Delta\delta$ 23 Hz, J_{AB} 8 Hz, H_A and H_B), 4.83 ($\Delta\delta$ 7 Hz, J_{CD} 6 Hz, H_C and H_D), and 3.85, 3.72, and 3.70 (9H, $3 \times s$, $3 \times \text{CO}_2\text{Me}$); the mass spectrum is discussed in the text

(Found: C, 54.1; H, 4.15. $\text{C}_{14}\text{H}_{13}\text{ClO}_6$ requires C, 53.8; H, 4.2%).

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