

## THE REACTION OF ALDRIN, PHOTOALDRIN AND ISODRIN WITH PHTHALOYL PEROXIDE

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(Received in UK 13 July 1979)

**Abstract**—The reactions of aldrin and photoaldrin with phthaloyl peroxide in carbon tetrachloride provided the respective carbon tetrachloride adducts, epoxides and cyclic phthalates of the corresponding *cis*-diols.

Under the same conditions isodrin yielded the half-cage ketone (14), the cyclic phthalate (17) and the novel half-cage adduct (15).

The *syn*-hydroxy derivatives (1 and 2) are important mammalian metabolites of the insecticides dieldrin<sup>1</sup> and endrin<sup>2</sup> respectively. While these compounds have been synthesised<sup>3</sup> in admixture from hexachlorocyclopentadiene and 7-benzoyloxynorbormadiene, a more selective route would be of interest. An alternative approach was suggested by the reported<sup>4</sup> reaction of norbornene with phthaloyl peroxide in carbon tetrachloride which provided the cyclic phthalates (3 and 4) in addition to a norbornene-carbon tetrachloride adduct.

Treatment of aldrin (5) with an equimolar quantity of phthaloyl peroxide in refluxing carbon tetrachloride yielded the known<sup>5</sup> adduct (6) and small amounts of dieldrin (7) and the cyclic phthalate (8). The formulation of the latter compound as 8 rather than 9 followed from the <sup>1</sup>H NMR spectrum. This showed, *inter alia*, singlets at  $\delta$  2.49 and 2.82 for H<sub>3</sub>, H<sub>4</sub> and H<sub>2</sub>, H<sub>7</sub> respectively as well as two doublets,  $J = 13.5$  Hz, at  $\delta$  2.06 for H<sub>12a</sub> and 1.6 for H<sub>12b</sub>, with the latter clearly involved in W-type coupling,  $J = 1.8$  Hz with H<sub>4</sub>, H<sub>5</sub> at  $\delta$  4.01. Analogously, phthaloyl peroxide in carbon tetrachloride converted photoaldrin (10) into photodieldrin (11), an inseparable mixture of carbon tetrachloride adducts and the cyclic phthalate (12). The structure of 12 follows from the observance of H<sub>3</sub> and H<sub>4</sub> as doublets,  $J = 5.6$  Hz, at  $\delta$  4.67 and 4.9 in the <sup>1</sup>H NMR spectrum.

Three products, identified as 14, 15 and 17, were isolated from the reaction of isodrin (13) with phthaloyl peroxide in carbon tetrachloride or bromotrichloromethane. The half-cage ketone (14) presumably resulted from rearrangement of endrin (16), which is known<sup>6,7</sup> to proceed with facility. In addition to the characteristic IR band at 1600 cm<sup>-1</sup> for the 1,2-dichloroethylene moiety the phthalate (17) displayed two CO bands at 1740 and 1760 cm<sup>-1</sup>. This was reminiscent of the behaviour of the rearranged phthalate (4), which showed<sup>4</sup> two bands at 1737 and 1712 cm<sup>-1</sup>, whereas the phthalates (3, 8 and 9) exhibited a single band *ca* 1730 cm<sup>-1</sup>. However, analysis of the <sup>1</sup>H NMR spectrum of 17 aided by spin-decoupling fully confirmed the assigned structure. In particular H<sub>4</sub>, H<sub>5</sub> were observed as a doublet at  $\delta$  4.19 W-coupled,  $J = 2$  Hz, to H<sub>12a</sub> which was also coupled,  $J = 11.4$  Hz to the geminal H<sub>12b</sub>. The remaining compound 15 was also obtained if isodrin was reacted with carbon tetrachloride in the presence of an equimolar quantity of dibenzoyl peroxide. The IR spectrum showed a band at 1650 cm<sup>-1</sup> characteristic<sup>8</sup> of a 1,1-dichloroethylene group, and the <sup>13</sup>C NMR spectrum revealed the presence of thirteen different C atoms of which six did not bear hydrogens and the two of these at

$\delta$  113.6 and 142.4 could be assigned as olefinic carbons. The <sup>1</sup>H NMR spectrum was not amenable to detailed analysis but doublets for two geminal protons at  $\delta$  1.58 and 1.77,  $J = 11.4$  Hz, could be discerned along with a singlet at  $\delta$  5.29 in the region characteristic of  $\text{>CHCl}$ .

Consideration of this data in the light of possible modes of formation (*vide infra*) suggested structure 15 for this compound. Attempts to provide a chemical confirmation for this deduction by oxidising 15-14 using methods employed<sup>8</sup> in a less sterically encumbered situation were unsuccessful.

Clearly the initial step in the formation of 15 is addition of a trichloromethyl radical to isodrin forming the radical 18. Transannular bond formation, as noted<sup>9</sup> in the addition of *p*-chlorobenzenethiol to isodrin, followed by intramolecular hydrogen abstraction would generate the radical 19, which by chlorine atom ejection or abstraction could provide 15. Alternatively, chlorine abstraction or expulsion from 18 could lead to the cyclopropane derivative 20, a process which has some precedent.<sup>10</sup> The subsequent rearrangement of 20-15 would presumably follow the same pathway as the analogous rearrangements of the corresponding epoxide<sup>6,7</sup> and aziridines.<sup>11</sup> So far efforts to distinguish between these alternative pathways have been impeded by our inability to effect an independent synthesis of 20 from 13.

### EXPERIMENTAL

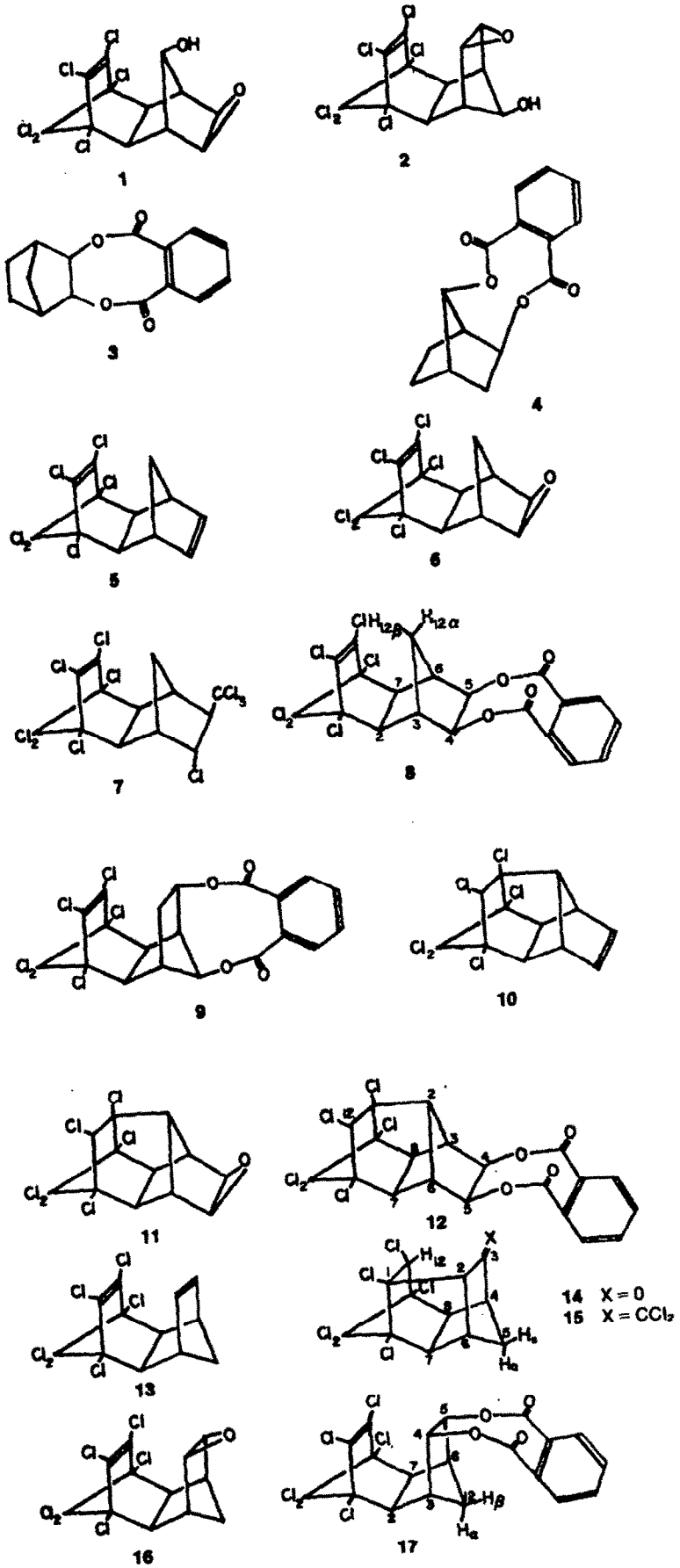
IR spectra were recorded for Nujol mulls on a Unicam SP 200 spectrophotometer. <sup>1</sup>H NMR spectra were recorded at 90 MHz by the U.L.I.R.S., and the <sup>13</sup>C NMR spectrum at 15.08 MHz on a Bruker WP 60 spectrometer. In both cases spectra were recorded for CDCl<sub>3</sub> solutions with internal TMS.

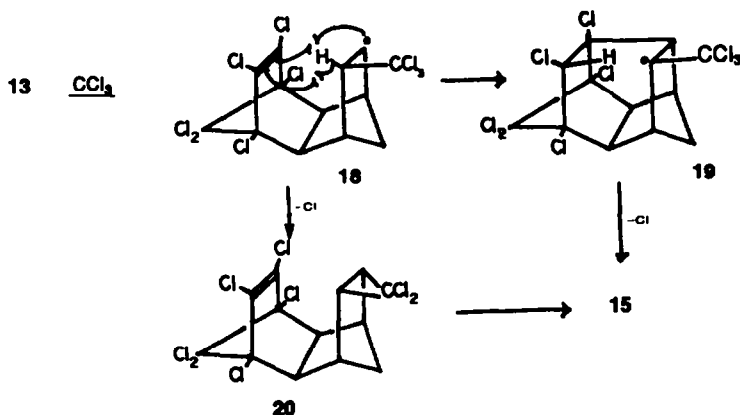
#### Reaction of aldrin with phthaloyl peroxide

Aldrin (2.3 g) and phthaloyl peroxide<sup>12</sup> (1 g) in CCl<sub>4</sub> (100 ml) were heated under reflux for 40 hr. The cooled soln was chromatographed on silica gel. Elution with CCl<sub>4</sub> gave successively the known adduct<sup>5</sup> 7, (1.5 g) from MeOH identical with an authentic sample, and 6 (0.12 g) from MeOH. Subsequent elution with benzene provided 8 (0.15 g), m.p. 319-323° (dec) from CHCl<sub>3</sub>-MeOH. (Found: C, 45.1; H, 2.25. Calc. for C<sub>20</sub>H<sub>12</sub>Cl<sub>6</sub>O<sub>2</sub>: C, 45.4; H, 2.27%); IR (Nujol) 1725, 1600 cm<sup>-1</sup>; NMR  $\delta$  1.6 (br. d, H<sub>12a</sub>,  $J_{12a,12b} = 13.5$  Hz), 2.06 (d, H<sub>12b</sub>), 2.49 (s, H<sub>3</sub> and H<sub>4</sub>), 2.82 (s, H<sub>2</sub> and H<sub>7</sub>), 4.01 (d, H<sub>4</sub> and H<sub>5</sub>,  $J_{4,5,12a} = 1.8$  Hz) 7.65 (s, 4 H, ArH).

#### Reaction of photoaldrin with phthaloyl peroxide

Photoaldrin<sup>13</sup> (3.65 g) and phthaloyl peroxide (1.6 g) in CCl<sub>4</sub> (150 ml) were refluxed for 40 hr. Chromatography of the resulting soln on silica gel in CCl<sub>4</sub> gave an inseparable mixture of the





$\text{CCl}_4$ -adducts (2 g) m.p. 160–205° from  $\text{CHCl}_3$ -MeOH (Found: C, 29.9; H, 1.52. Calc. for  $\text{C}_{13}\text{H}_9\text{Cl}_{10}$ : C, 30.1; H, 1.55%). Elution with benzene gave successively 11<sup>13</sup> (0.9 g) and 12 (0.3 g) m.p. 288–290 (dec) from  $\text{CHCl}_3$ -MeOH. (Found: C, 45.7; H, 2.25. Calc. for  $\text{C}_{20}\text{H}_{12}\text{Cl}_4\text{O}_4$ : C, 45.4; H, 2.27%); IR (Nujol) 1730  $\text{cm}^{-1}$ ; NMR  $\delta$  2.53 (dd,  $\text{H}_7$ ,  $J_{7,8} = 6.2$  Hz,  $J_{2,7} = 2.6$  Hz), 2.91 (ddd,  $\text{H}_6$ ,  $J_{2,6} = 2.6$  Hz,  $J_{3,6} = 1.5$  Hz), 3.25 (br. s,  $\text{H}_4$ ), 3.34 (br. s,  $\text{H}_3$ ), 3.45 (t,  $\text{H}_2$ ), 4.67 (d,  $\text{H}_5$ ,  $J_{4,5} = 5.6$  Hz), 4.9 (d,  $\text{H}_4$ ), 4.88 (s,  $\text{H}_{12}$ ), 7.67 (s, 4 H, ArH).

#### Reaction of isodrin with phthaloyl peroxide

Isodrin (3.65 g) and phthaloyl peroxide (1.6 g) in  $\text{CCl}_4$  (150 ml) were heated under reflux for 40 hr. The resulting mixture was chromatographed on silica gel. Elution with  $\text{CCl}_4$  gave the half-cage adduct 15 (0.99 g), m.p. 174–175° from MeOH. (Found: C, 34.7; H, 1.71. Calc. for  $\text{C}_{13}\text{H}_9\text{Cl}_4$ : C, 34.8; H, 1.79%); IR (Nujol) 1650  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.58 (br. d.,  $\text{H}_{3a}$ ,  $J_{3a,5} = 11.4$  Hz), 1.77 (d,  $\text{H}_{5a}$ ), 3.0–3.13 (m, 3 H), 3.33–3.5 (m, 1 H), 3.6–3.75 (m, 1 H), 5.29 (s,  $\text{H}_{12}$ );  $^{13}\text{C}$  NMR  $\delta$  39.1; 42.9; 43.95; 53.7; 58.5, 61.6, 66.6, 73.1, 79.5, 85.0, 99.0, 113.6, 142.4. The half-cage ketone<sup>6</sup> 14 (0.4 g) was subsequently eluted with  $\text{CCl}_4$ -benzene (4:1), and finally benzene eluted 17 (0.6 g), m.p. 260–263° (dec). (Found: C, 45.1; H, 2.29. Calc. for  $\text{C}_{20}\text{H}_{12}\text{Cl}_4\text{O}_4$ : C, 45.4; H, 2.27%); IR 1760, 1740, 1600  $\text{cm}^{-1}$ ; NMR  $\delta$  1.67 (ddd,  $\text{H}_{12a}$ ),  $J_{12a,12\beta} = 11.4$  Hz,  $J_{4,5,12a} = 2$  Hz,  $J_{3,12a} \approx 1$  Hz), 2.52 (ddd,  $\text{H}_{12\beta}$ ,  $J_{3,12\beta} = 2$  Hz,  $J_{2,7,12\beta} \approx 1$  Hz), 2.90 (ddd,  $\text{H}_3$  and  $\text{H}_6$ ,  $J_{2,3} = 2$  Hz), 3.26 (dd,  $\text{H}_2$  and  $\text{H}_7$ ); 4.19 (d,  $\text{H}_4$  and  $\text{H}_5$ ), 7.4–7.8 (m, 4 H, ArH).

Repetition of the reaction on the same scale but using benzene in place of  $\text{CCl}_4$  led to the recovery of isodrin (2.9 g), half-cage ketone 14 (0.15 g), and 17 (0.15 g). Replacement of  $\text{CCl}_4$  by

bromotrichloromethane provided 15 (1.0 g), half-cage ketone 14 (0.45 g) and 17 (0.3 g).

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