

## PENTACHLOROTROPOLONE AND 3-HYDROXYPENTACHLOROTROPONE

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Pentachlorotropolone(3) was obtained by treatment of octachloro-cycloheptatriene(1) with concentrated sulfuric acid. Chlorination of 3 in liquid chlorine afforded a perchlorinated seven-membered reductone(12). Photolysis of 4-hydroxypentachlorobicyclo[3.2.0]-hepta-3,6-dien-2-one(18) gave 3-hydroxypentachlorotropone(19).

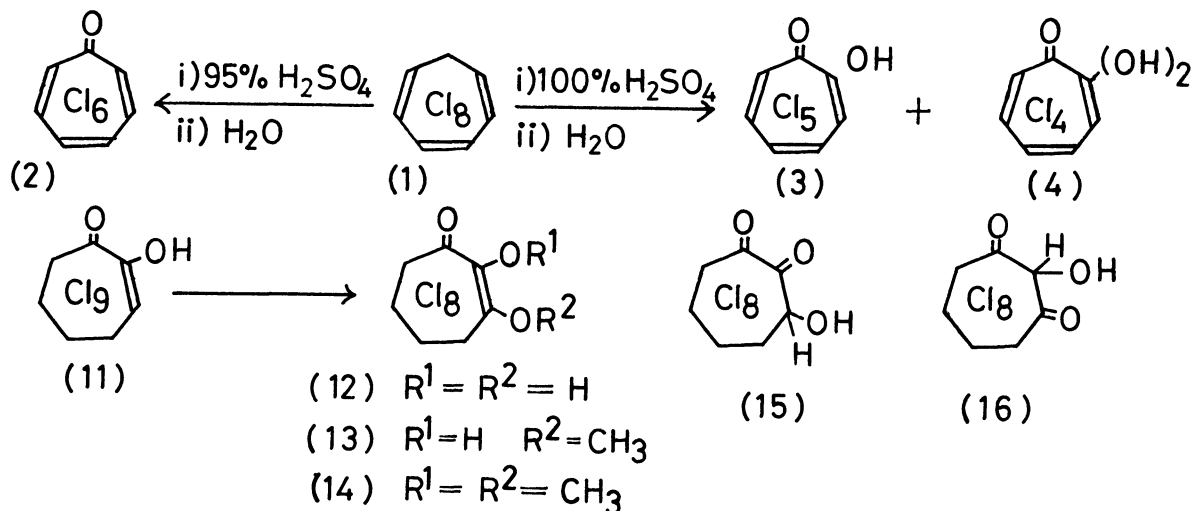
Chlorines on carbon may often be substituted by hydroxyl or carbonyl groups, and good examples are found in the syntheses of squaric acid<sup>1)</sup> and tropolone.<sup>2)</sup> In this communication, we present the chemistry of perchlorinated tropolone and some results investigated to find a precursor to a seven-membered ring oxocarbon.<sup>3)</sup>

When a mixture of octachlorocycloheptatriene(1) and 95% sulfuric acid was stirred at room temperature, hexachlorotropone(2) was the product,<sup>4)</sup> but with 100% sulfuric acid at 140°C 1 reacted to give pentachlorotropolone(3) in 96% yield. Under similar conditions, 2 gave 3. The reaction of 1 with 100% sulfuric acid at 220°C afforded a small amount of dihydroxytetrachlorotropone(4) in addition to 3. The structure of 3 was determined on the basis of the following facts: 1) Chlorination of 3 with refluxing thionyl chloride afforded 1 quantitatively; 2) treatment of 3 with methanol gave methyl pentachlorobenzoate(5); 3) <sup>13</sup>C NMR at room temperature showed four peaks indicating that there is a rapid equilibrium between two tautomers similarly to tropolone.<sup>5)</sup> The rapid tautomerism of 3 is interesting in relation to the boat-shaped structure of hexachlorotropone.<sup>6)</sup>

Similarly to tropolone itself, 3 forms various kinds of metal salts easily. For example, shaking a mixture of an ethereal solution of 3 and sodium hydrogen-carbonate solution precipitated yellow crystals of sodium pentachlorotropolonate(6) immediately. Treatment of 3 with antimony(V) chloride gave stable tetrachloro(pentachlorotropolonato)antimony(V)(7) in 57% yield, the structure of which was confirmed on the basis of elemental analysis, IR and UV spectra.<sup>7)</sup>

Reaction of 6 with alkaline hydrogen peroxide gave pentachlorobenzoic acid(8) without ring opening, in contrast to the behavior of tropolones which afforded carboxylic acid derivatives by ring opening.<sup>8)</sup> Rearrangement to a benzenoid compound is also brought about by ethereal diazomethane, thereby giving a 1:1 mixture of 2-methoxypentachlorotropone(9) and 5. These facts indicate that 3 is stable under acidic conditions whereas it easily rearranges to a benzenoid compound with

radical reagents or basic conditions.<sup>9)</sup> 2-Acetoxyoctachlorotropone(10) was obtained by the reaction of 6 with acetyl chloride in 30% yield.



Chlorination of 3 with liquid chlorine in a sealed tube without irradiation afforded oily material(11) quantitatively, which was unstable toward moisture and gave white crystals of 2,3-dihydroxyoctachlorocyclohept-2-en-1-one(12), a perchlorinated reductone,<sup>10)</sup> quantitatively on standing in air. The hydrolysis as well as the reaction of methanol toward 11 indicate the presence of an active chlorine in 11 and accord with the proposed structure. Methylation of 12 with ethereal diazomethane gave 2-hydroxy-3-methoxyoctachlorocyclohept-2-en-1-one(13) and 2,3-dimethoxyoctachlorocyclohept-2-en-1-one(14) successively. Treatment of 11 with methanol gave 13 in 93% yield. The structures of 12, 13 and 14 were proved by a combination of elemental analyses, IR and UV spectra. The <sup>13</sup>C NMR spectra of 13 and 14 are consistent with the assigned structures. The UV spectrum of 12 in dichloromethane consisted of only one peak at 235 nm, but in ethanol, it showed a different spectrum containing a shoulder at 250 nm and a peak at 365 nm. The intensity of the 365 nm peak increased rapidly within three min after dissolution, then slowly decreased, and both peaks disappeared upon standing over night. Like the seven-membered reductone, which isomerized quickly in a solution and exists as an equilibrium mixture between endiol and two keto forms,<sup>10)</sup> 12 seemed to isomerize in ethanol giving a mixture of 12, 1,2-diketone(15) and 1,3-diketone(16). The UV maximum at 365 nm might be due to 15, but we have no evidence for the existence of 16. The reaction product was identified as pentachlorophenol(17). Compound 12 decomposes to 17 not only in ethanol but also in acetone, ethyl acetate or acetonitrile on standing over night at room temperature. The mechanism of the rearrangement has not been clarified. Treatment of 12 with acetyl chloride gave a crystalline mixture of at least four kinds of products.

Attempts to obtain a polyhydroxypolyhalotropone by hydrolyzing a chlorine of 2 with sodium acetate in acetic acid resulted in the isolation of pentachlorobenzene.

Photolysis of 4-hydroxypentachlorobicyclo[3.2.0]hepta-3,6-dien-2-one(18) in dichloromethane using a low-pressure mercury lamp afforded 3-hydroxypentachloro-



- 141.0(C-3,C-5), 131.0(C-2,C-6), 129.4(C-4). UV(CH<sub>3</sub>CN): 265(4.17), 348(3.39), 390sh(3.41), 400(3.43).
- (4) C<sub>7</sub>H<sub>2</sub>Cl<sub>4</sub>O<sub>3</sub>. mp 215°C. IR: 3200, 1550, 1535, 1510, 1400. UV(CH<sub>3</sub>CN): 330sh(3.60), 345(3.70), 382(3.76), 398(3.90). <sup>13</sup>C NMR(DMSO): 146.6, 143.7, 125.0, 122.0, 121.0, 120.5, 115.5.
- (6) C<sub>7</sub>Cl<sub>5</sub>O<sub>2</sub>Na·H<sub>2</sub>O. mp 238°C dec. IR: 3400, 1520, 1350.
- (7) C<sub>7</sub>Cl<sub>9</sub>O<sub>2</sub>Sb. mp 217°C dec. IR: 1480, 1440, 1375, 1280. UV(CH<sub>2</sub>Cl<sub>2</sub>): 245sh(4.80), 275(4.24), 288(4.24), 350(3.86).
- (10) C<sub>9</sub>H<sub>3</sub>Cl<sub>5</sub>O<sub>3</sub>. mp 116°C. IR: 1772, 1695, 1580, 1545, 1145. UV(C<sub>2</sub>H<sub>5</sub>OH): 267(4.25), 277(4.27), 330(3.41), 348(3.42), 390(3.41), 408(3.48).
- (12) C<sub>7</sub>H<sub>2</sub>Cl<sub>8</sub>O<sub>3</sub>·H<sub>2</sub>O. mp 115°C dec. IR: 3550-3400, 1720, 1580. UV(CH<sub>2</sub>Cl<sub>2</sub>): 235(3.99); (C<sub>2</sub>H<sub>5</sub>OH): 250sh(3.7), 365(3.5). \*These intensities are not reliable because of the instability of 12 in ethanol.
- (13) C<sub>8</sub>H<sub>4</sub>Cl<sub>8</sub>O<sub>3</sub>. mp 119°C. IR: 3400, 1735, 1580, 1440, 1280. UV(C<sub>2</sub>H<sub>5</sub>OH): 220(3.98), 235(3.93). <sup>13</sup>C NMR: 165.5, 134.4, 133.1, 90.9, 88.0, 86.0, 54.5.
- (14) C<sub>9</sub>H<sub>6</sub>Cl<sub>8</sub>O<sub>3</sub>. mp 94°C. IR: 1755, 1600, 1435, 1250. UV(C<sub>2</sub>H<sub>5</sub>OH): 235(3.98). <sup>13</sup>C NMR(CH<sub>3</sub>COCH<sub>3</sub>), 157.7, 129.8, 128.0, 87.7, 86.5(broad), 84.3, 56.0, 48.8.
- (19) C<sub>7</sub>HCl<sub>5</sub>O<sub>2</sub>. mp 177°C. IR: 1630, 1580. UV(CH<sub>3</sub>CN): 247sh(4.04), 277(4.26), 320-360(3.62). <sup>13</sup>C NMR(CH<sub>3</sub>COCH<sub>3</sub>): 164.2, 150.4, 135.7, 135.1, 134.8, 121.3, 118.1.
- (20) C<sub>8</sub>H<sub>4</sub>Cl<sub>4</sub>O<sub>3</sub>. mp 90-92°C. IR: 3240, 1700, 1550.
- (22) C<sub>8</sub>H<sub>3</sub>Cl<sub>5</sub>O<sub>2</sub>. bp 170-175°C/4mmHg. IR: 1735, 1665, 1550. UV(hexane): 273(4.09), 360(3.40). <sup>1</sup>H NMR(CCl<sub>4</sub>): 3.92.
- (23) C<sub>7</sub>Cl<sub>8</sub>O<sub>2</sub>. mp 70°C. IR: 1765, 1740, 1580. UV(hexane): 215(3.85), 277(3.73).
- (24) C<sub>7</sub>Cl<sub>10</sub>O<sub>2</sub>. mp 210°C. IR: 1770, 1750. <sup>13</sup>C NMR(CH<sub>3</sub>COCH<sub>3</sub>): 179.7, 100.6, 93.0, 82.4.

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