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STABLE CYCLOPENTADIENONE DERIVATIVES.
PERCHLORO-2H,5H-CYCLOPENTA[b]PYRAN-5-ONE AND -2,5-DIONE

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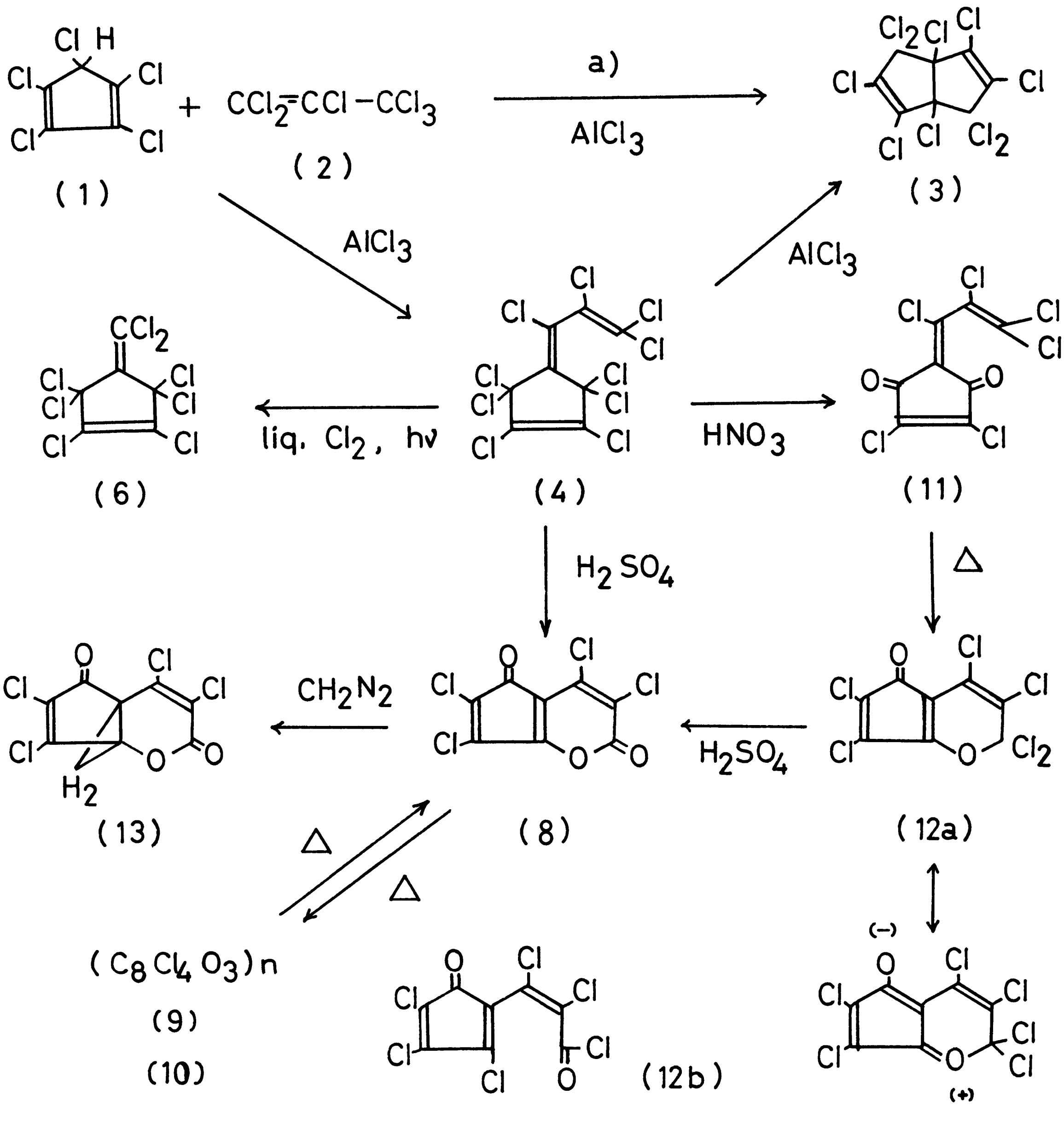
Perchloro-2H,5H-cyclopenta[b]pyran-5-one (12a) was obtained by thermal electrocyclic ring closure of diketone (11). Compound 12a was hydrolized to another stable cyclopentadienone derivative, perchloro-2H,5H-cyclopenta[b]pyrane-2,5-dione (8), which was prepared directly from (4) by treatment with sulfuric acid.

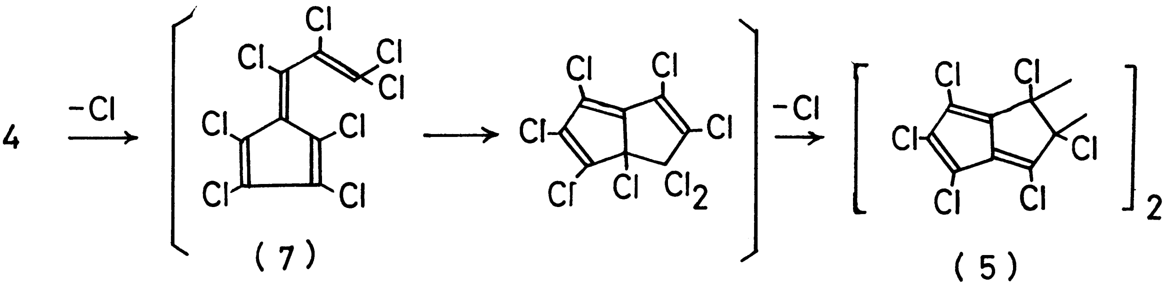
Although the preparations of polychlorinated cyclopentadienone were investigated by several groups of workers, its synthesis has not been successful[1,2] and only a report dealing with the preparation of perchlorocyclopentadienoneiron tricarbonyl complex has been published.[3,4] Work in our laboratories on the electrocyclic reactions of polychlorinated conjugated dienones[5] led us to investigate the synthesis of stable cyclopentadienone derivatives.

When 1,2,3,4,5-pentachlorocyclopentadiene (1)[6] was allowed to react with hexachloropropene (2)[7] in the presence of anhydrous aluminum chloride at refluxing temperature of carbon tetrachloride, the product was perchlorobicyclo[3.3.0]-octa-2,6-diene (3).[8] However, when the reaction was carried out in dichloromethane, the product was perchloro-3-(3-cyclopentenylidene)propene (4), mp 108°C,[9] ir (cm^{-1}) 1648, 1620, 1565; uv λmax (nm, logε) 221(4.41), 285sh(3.09); cmr (δ TMS, ppm) ($CDCl_3$) 139.8, 137.8, 135.5, 135.3, 128.1, 122.1, 82.0, 80.9; nqr (MHz) (77°K) 37.220, 37.607, 37.618, 38.026, 38.100, 38.262, 38.520, 38.733, 38.854, 38.975. The cmr spectrum revealed the presence of two doubly allylic dichloromethylene carbons,[10] both of which are under the similar circumstances in the molecule. The before mentioned spectral data and limited chemical transformations clearly support the proposed structure (4).

Compound 4 gave 3 in quantitative yield upon treatment with catalytic amount of anhydrous aluminum chloride in refluxing carbon tetrachloride. Therefore, 4 must be an intermediate of the reaction a) (Scheme 1). Dechlorination of 4 with copper powder in petroleum benzine (bp 68-70°C) gave brownish red crystals, a dimer of hexachloropentalene (5).[11] This transformation is well interpreted by assuming the intermediary formation of perchlorovinylfulvene (7), which, under the reaction conditions, gives the dihydropentalene derivative, followed by the dechlorination to the dimer of perchloropentalene (Scheme 2).



Scheme 1



Scheme 2

Compound 4 was not chlorinated in liquid chlorine without irradiation, but it suffered chlorinolysis to give perchloro-4-methylenecyclopentene (6) on irradiation with sun light.

Treatment of 4 with 98% sulfuric acid at 120°C gave a deep red crystalline Compound, $C_8Cl_4O_3$ (8), ir 1750sh, 1730, 1625, 1570, 1510, 1390, 1340, 1160, 1130, 980, 910, 875, 835, 760, 740; uv λmax 228(4.16), 332(3.93), 240sh(4.04), 488 (2.72), and two kinds of white crystals, (9) and (10). Compound 8 polymerizes at approximately 180°C without melting to a 1:1 mixture of 9 and 10. At room temperature, 8 gradually changes to intractable polymeric materials. On the basis of these spectral data and on the argument presented below, we propose the structure (8), perchloro-2H,5H-cyclopenta[b]pyrane-2,5-dione, for the red compound.

By means of Soxhlet apparatus technique using carbon tetrachloride as a solvent, 9 was separated from 10, which is less soluble in the solvent. Both of the crystals gave 8 upon heating at approximately 300°C under reduced pressure. Ir of 9: 1788, 1735, 1612, 1535, 1380, 1312, 1195; ir of 10: 1790, 1750, 1617, 1532, 1380, 1310, 1195. Not only are the carbonyl and carbon-carbon double regions in the infrared spectra of these crystals virtually similar, but there is a gross similarity of the entire spectra.

On the other hand, nitric acid reacted with 4 exothermally to give a clear reaction mixture, from which a slightly yellow oily product was precipitated by dilution with ice-water. Extraction of the product with carbon tetrachloride and evaporation of the solvent under vacuum left the oily materials, which crystallized on trituration in aqueous methanol. Recrystallization from methanol gave an analytical sample, $C_8Cl_6O_2$ (11), mp 92°C; ir 1710, 1630, 1590; uv λmax 230sh (4.16), 248(4.32), 255-256(4.32), 267sh(4.21), 277sh(4.16), 288sh(4.05), 300sh (3.84), 330sh(3.33); cmr (CD_3COCD_3) 180.2, 179.3, 153.7, 151.4, 140.7, 128.2, 127.3, 124.6. The structure (11) is compatible with the spectral data, and the reaction of 4 with nitric acid is analogous to that of 6, giving perchloro-2-methylenecyclopent-4-ene-1,3-dione.

Compound 11 is unstable in the air and decomposes gradually with the liberation of hydrochloric acid to give an unidentified mixture. However, 11 isomerizes to a deep red compound (12) in high yield in refluxing carbon tetrachloride under anhydrous conditions, $C_8Cl_6O_2$ (12), mp 100°C; ir 1745, 1620, 1575, 1510, 1250; uv λmax 254(4.11), 302(3.76), 445(2.97); cmr ($CDCl_3$) 180.3, 163.4, 149.3, 143.8, 131.6, 130.8, 122.6, 121.7. Two structures, (12a) and (12b), are conceivable for the red product. Although it is not possible to make definitive structural assignment for the compound on the basis of ir, uv, and cmr spectroscopy, 12a seemed preferable, because 1) 12 shows only one carbonyl band in the infrared region, 2) 12 gives 8 on treatment with 90% sulfuric acid at room temperature, and 3) the structure 12a gives a good explanation of the reactivity of the compound stabilized by cyanine-like mesomerism,[14) whereas the substance having the structure 12b should give easily a dimer.

Compound 8 reacted with diazomethane in diethyl ether with vigorous evolution of nitrogen gas and gave slightly yellow crystals, $C_9H_2Cl_4O_3$ (13), mp 157.5°C; ir 3085, 1760, 1730, 1610w, 1590, 1360, 1310, 1270, 1225, 1165, 1100, 1030, 965, 945, 895, 880, 860, 795; uv 257(4.08); cmr (CH_3COCH_3) 185.0, 155.3, 144.4, 129.6, 123.7, 70.0, 43.9, 34.4; pmr (δTMS, ppm) (CD_3COCD_3) 3.15(d), 2.80(d), $|J_{AB}|$ 6.1cps. On the basis of elemental analysis, high resolution mass spectroscopy, and the spectral data described above, the structure 13 was assigned to the product.15)

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