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AN UNSYMMETRICAL PERCHLOROPENTACYCLODECANE FROM OCTACHLOROPENTACYCLO[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]DECANE-6,10-DIONE[1]

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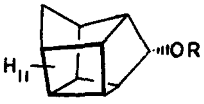
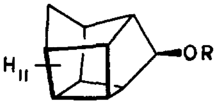
Dilling *et*. *al*. have suggested that solvolysis of the pentacyclodecanol tosylates 1 and 2 may proceed through bridged carbonium ions.[4] They found that acetolysis of *syn* tosylate 1 gives predominantly the unrearranged *syn* acetate 3, while acetolysis of *anti* tosylate 2 gives 15% of the unrearranged *anti* acetate 4 and 85% of the rearranged acetate 5. Perchlorodiketone 6 has also been reported to rearrange to give the symmetrical perchloropentacyclodecane 7 on reaction with phosphorus pentachloride, but the unrearranged product 8 was not found.[5]



1 R = Ts
3 R = Ac



2 R = Ts
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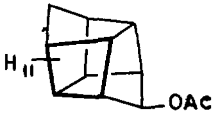
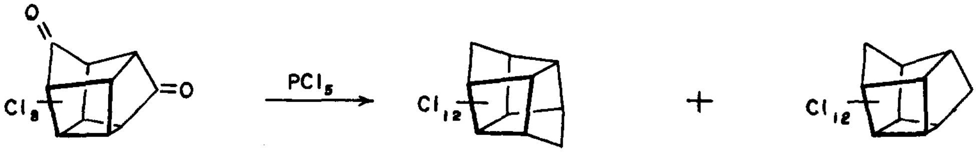


5

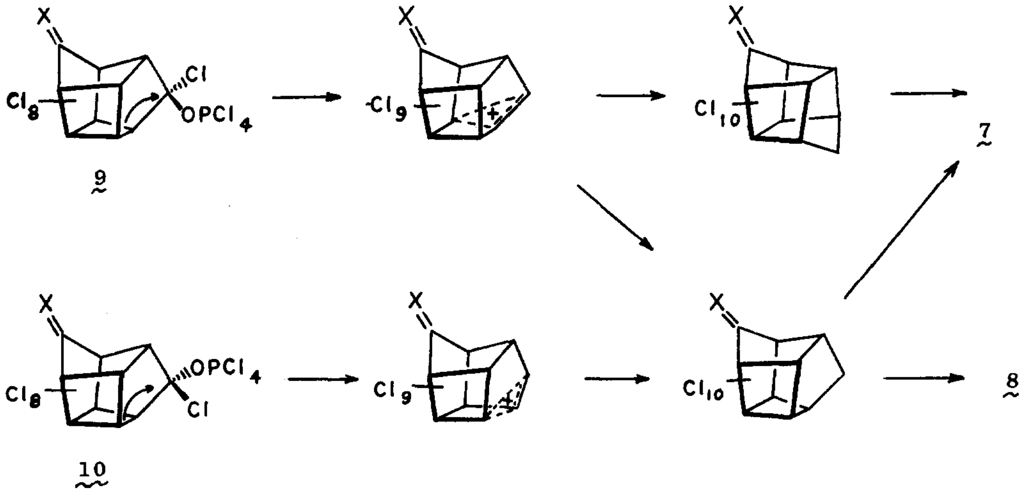


6 7 8

Complete rearrangement of 6 to 7 through a carbonium ion mechanism seemed unlikely on the basis of the behavior of tosylates 1 and 2. If rearrangement of the unsymmetrical chlorinated cage skeleton depends on the configuration of the leaving group as in tosylates 1 and 2, the unrearranged chlorocarbon 8 should also be formed from diketone 6. Due to their ball-like shape, closely related perchlorinated cage compounds may form solid solutions which cannot readily be separated by crystallization and which often have melting points resembling pure compounds.[6] This ball shape has also frustrated X-ray crystallographic attempts at structure determinations since the molecules may take up random orientations in the crystal.[7] Such properties of cage chlorocarbons may be responsible for compound 8 not being detected in the reaction products of diketone 6.

We find the reaction of diketone 6 with excess phosphorus pentachloride at 180° for 2 hours yields unrearranged product 8 and rearranged product 7 in 30 and 27% yields, respectively, according to glpc analysis.[8] The remaining unsaturated products were not characterized. Identification of the cage reaction products was achieved by comparison of infrared spectra of samples collected by gas chromatography with spectra of authentic 7 and 8. Chlorocarbon 7 is the known reaction product of hexachlorocyclopentadiene and aluminum chloride.[9] Independent synthesis of 8 is described on the following page.[10]

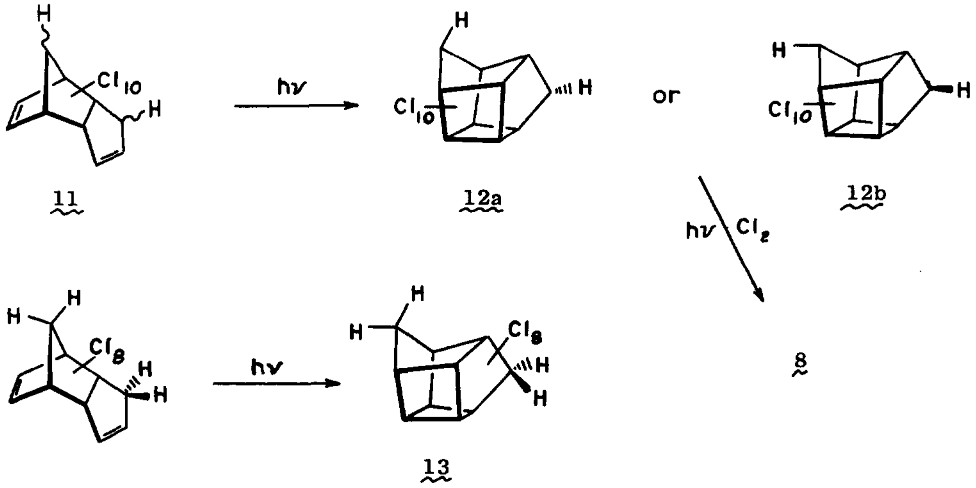
The proposed mechanism of chlorination of diketone 6 follows by analogy to the bridged ion mechanism proposed[4] for solvolysis of tosylates 1 and 2. Reaction of the cage carbonyl with phosphorus pentachloride may give both *anti* (9) and *syn* (10) intermediates. The *syn* would give unrearranged product while the *anti* would give predominantly rearranged product. Since the reaction occurs twice for each molecule, slightly more 10 must be formed to lead to the observed nearly 50-50 mixture of rearranged and unrearranged product.



X = O or Cl_2

On examination of molecular models of the unsymmetrical cage, the *syn* substituent at C-6 is found to be slightly more crowded by the chlorine atoms than is the *anti* substituent. Thus attack by PCl_6^- at a carbonyl coordinated with PCl_4^+ would be expected to occur on the less hindered *anti* side to give more intermediate 10 than intermediate 9, which is consistent with the proposed chlorination mechanism.

Two routes were initiated for synthesis of 8. The first proved simplest. Direct or preferably acetone-sensitized irradiation of the dimer 11 of 1,2,3,4,5-pentachlorocyclopentadiene yields cage compound 12a or 12b (88%; mp 382-4° after recrystallization from aqueous methanol; nmr: one line 5.39τ in $CDCl_3$). The single nmr line in 12 is consistent with either structure 12a or 12b. The hydrogens are equivalent within each isomer.[11]



11 12a 12b 8 13

Similar photoisomerization of the dimer of 1,2,3,4-tetrachlorocyclopentadiene was carried out at the same time, anticipating that the allylic chlorine of 11 might prove labile on irradiation. The cage product 13 (96%; mp 274-5° after recrystallization from hexane; nmr: an AB quartet centered at 7.31τ, $\Delta = 0.30$ ppm, $J = 12.2$ Hz) exhibits two distinct protons in its nmr spectrum which reflect the different chemical environments of its equivalent syn and equivalent anti hydrogens.[12] This difference verifies the proposition that an isomer of 12 bearing both a syn and an anti hydrogen would have two distinct nmr singlets.

Photochlorination of 12 proceeds rapidly in carbon tetrachloride to give chlorocarbon 8 (100%; mp 476-7° dec.; no ir bands 2.5 - 8μ). Its structure follows from its lack of infrared double bond or carbon-hydrogen bond absorptions, its mode of formation, and its non-identity with 7. Chlorination of 13 was not attempted.

The melting point of chlorocarbon 7 (Lit 485° dec)[9] and its infrared spectrum are very similar to the melting point and infrared spectrum of the new isomer 8. Major peaks in the spectrum of 8 overlap with major peaks in 7 with the exceptions of additional bands for 8 at 8.45 and 11.37 μ. Compounds 7 and 8 are readily separated by gas chromatography at 200 to 250° with 8 having the longer retention time.[8]

REFERENCES

1. Supported in part by grants from the U.S. Public Health Service, National Institute of General Medical Sciences (GM-12731), from a U.S. Public Health predoctoral fellowship (1-F1-GM-30, 339-01), and from the Petroleum Research Fund, administered by the American Chemical Society (PRF 2191-A1,4).
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8. At 200 to 250° on 5 ft. and 20 ft. columns packed with 5% SE-30 on 60/80 mesh acid washed Chromosorb W, DMCS treated.
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12. *Syn* and *anti* position follow convention in W. L. Dilling and C. E. Reineke, *Tetrahedron Letters*, 2547 (1967).