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A REARRANGEMENT IN THE SYNTHESIS OF PERCHLORO-1,1-DIPHENYLETHYLENE FROM DDE, AND RELATED RESULTS

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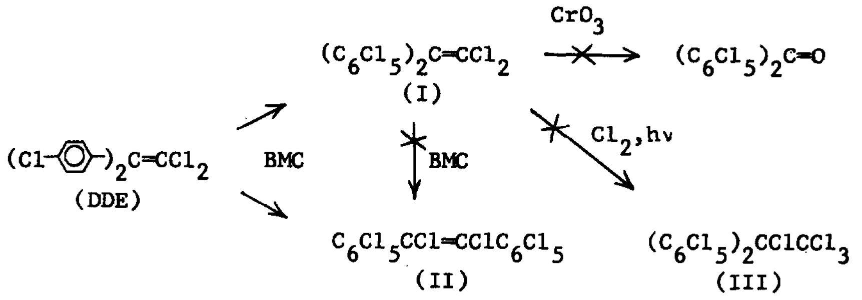
Alkaromatic chlorocarbons constituted exclusively of sp^2-hybridized carbon atoms possess extremely high thermal stability and chemical inertness.[1] Resistant polymeric chlorocarbons of such type have been reported.[2,3]

BMC (a mixture of SO_2Cl_2, $AlCl_3$ and S_2Cl_2) is a most powerful reagent for aromatic perchlorination of hydrocarbons and their chlorinated derivatives.[1,4,5] The authors report here the synthesis of a new chlorocarbon, the perchloro-1,1-diphenylethylene (I), from p,p'-dichloro-1,1-diphenyldichloroethylene (DDE)[6] by means of this reagent in 21.6% yield.

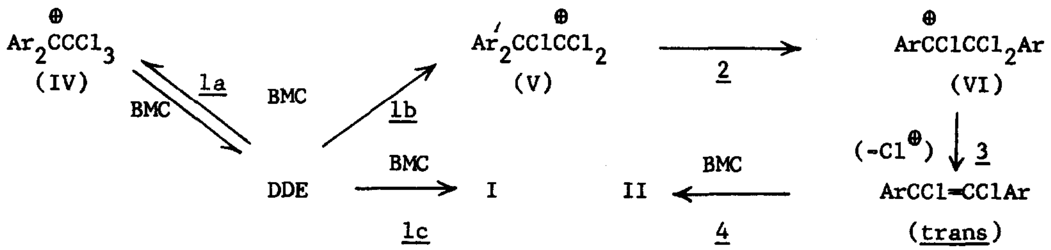
Anal. Calcd. for $C_{14}Cl_{12}$: C, 28.3; Cl, 71.7. Found: C, 28.5; Cl, 71.7. ir (KBr) ν 1563 (w) (C=C), 1520 (w) (1st arom.), 1370 (m) (2nd arom.), 1335 (s) (idem), 1304 (s) (idem), 1253 (m), 926 (s), 750 (s), 720 (m), 703 (m) cm^{-1}. uv (cyclohexane) λ (ε) 217 (61,000), 225 (50,000; sh), 270 (12,200; sh); 300 (2250; sh), 310 (1830) nm.

The major (78%) product is, nevertheless, trans-perchlorostilbene (II).[7] In fact, on account of the availability of DDE and the high yield of such rearrangement, this is possibly the best way to prepare II.

I is a colorless, crystalline compound melting at 203-5º. It does not rearrange with BMC. It is inert towards chromic acid in boiling acetic acid or even in concentrated sulfuric acid at 100º. Attempts to perform either solvolysis in 60% oleum at 100º or photochlorination in CCl_4 with chlorine and white light, have failed, the starting material being completely recovered.



The following mechanism is consistent with the results of the chlorination where Ar is not pentachlorophenyl.



Although the formation of carbonium ion IV is favoured over V on electronic (resonance with the aryl substituents) grounds, the latter is nevertheless expected to give immediate rearrangement to ion VI on account of the increased degree of resonance achieved, and also because of the release of compression between aryl groups. The failure of I to give II with BMC is doubtless due to the colossal steric strain of the perchlorinated counterpart of ion V caused by the repulsions among the alpha substituents and the four ortho chlorine atoms.[4] The resulting trans configuration arises from the steric repulsions between the two bulky aryl groups in VI (Step 3).[7,8]

Related rearrangements of 1,1-diphenylethanes have been reported in the following processes: a) the reduction of 1,1-diphenyl-2,2,2-trichloroethanes with zinc[9-11] or sodium;[12] b) the reduction of DDT with zinc and hydrochloric acid to p,p'-dichloro-1,1-diphenylethanes and p,p'-dichlorostilbene;[13] c) the reactions of DDD and p,p'-dichloro-1,1-diphenyltetrachloroethane with ferric chloride giving the corresponding p,p'-dichlorobibenzyls;[14,15] and d) the treatment of some 1,1-diphenylethanes with sulfuric acid.[16]

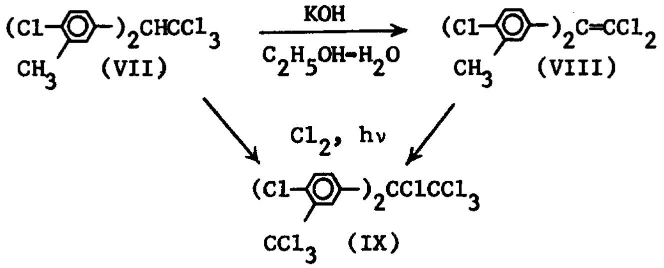
Because of the repulsions involving the four ortho chlorines, the benzene rings of I should be tilted with respect to the ethylene systems and, consequently, the π-electron interaction between these systems should be low.[17]

Accordingly the so-called K (conjugation) band in the ultraviolet shows considerable hypsochromic shift (shoulder at 270 nm) and consequently, the ^1L_b (secondary) band around 305 nm emerges clearly. The low (1563 cm^{-1}) C=C frequency indicates nevertheless that that interaction is significant in the ground state.

The inertness of I towards strongly solvolyzing or oxidizing conditions results from the steric and electronic deactivating effects due to the accumulation of chlorines.[2,18] With regard to the inertness under photochlorination conditions it is pointed out that perchloro-1,1-diphenylethane (III) should have a prohibitive steric strain.[4,7,8,19]

In connection with the preceding reactions it has been found that photochlorination with chlorine and white light of either 1,1-di(3'-methyl-4'-chlorophenyl)-2,2,2-trichloroethane (VII)[20] or 1,1-di(3'-methyl-4'-chlorophenyl)dichloroethylene (VIII)[20] in carbon tetrachloride gives <u>1,1-bis(3'-trichloromethyl-4'-chlorophenyl)tetrachloroethane</u> (IX), m.p. 96-7º, in an 85% yield.[21]

<u>Anal</u>. Calcd. for $C_{16}H_6Cl_{12}$: C, 30.8; H, 1.1; Cl, 68.2. Found: C, 30.8; H, 1.2; Cl, 68.3. <u>ir</u> (KBr) ν 1595 (w), 1558 (w), 1404 (m), 1383 (m), 1055 (s), 860 (m), 800 (s), 770 (s), 745 (m), 687 (m) cm^{-1}. <u>uv</u> (cyclohexane) λ (ε) 220 (36,200), 240 (20,800), 269 (2440; sh), 279 (3295), 287 (3020) nm.



IX fails to perchlorinate with reagent BMC, two chlorines being introduced in the only product isolated in a state of purity, m.p. 254-5º.[21] (<u>Anal</u>. Calcd. for $C_{16}H_4Cl_{14}$: C, 27.7; H, 0.6. Found: C, 27.1; H, 1.1. <u>ir</u> (KBr) ν, 1531 (w), 1420 (s), 1387 (s), 1210 (m), 1060 (m), 985 (s), 900 (m), 815 (m), 785 (s), 770 (s), 740 (s), 690 (s), 675 (s) cm^{-1}). Such a failure is ascribed to strong deactivation of the ring by both steric shielding and the electronic effects of the substituents.

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References

1) M. Ballester, *Bull. Soc. Chim. Fr.*, **1966**, 7.
2) M. Ballester, J. Castañer and J. Riera, *J. Amer. Chem. Soc.*, **88**, 957 (1966).
3) M. Ballester, J. Castañer and J. Riera, Span. Pat. 300,179, May 23, 1964; U.S. Pat. 3,360,574, December 26, 1967; Can. Pat. 791,804, August 6, 1968.
4) M. Ballester, C. Molinet and J. Castañer, *J. Amer. Chem. Soc.*, **82**, 4254 (1960).
5) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley (1967), p 1131.
6) O. Grummitt, A. Buck and A. Jenkins, *J. Amer. Chem. Soc.*, **67**, 155 (1945).
7) M. Ballester, C. Molinet and J. Rosa, *Tetrahedron*, **6**, 109 (1959).
8) M. Ballester and J. Rosa, *Tetrahedron*, **9**, 156 (1960).
9) G. Goldschmiedt, *Chem. Ber.*, **6**, 985 (1873).
10) K. Elbs and H. Förster, *J. Prakt. Chem.*, **39**, 298 (1889).
11) K. Elbs, *J. Prakt. Chem.*, **47**, 44 (1893).
12) E. E. Harris and G. B. Frankforter, *J. Amer. Chem. Soc.*, **48**, 3144 (1926).
13) J. Forrest, O. Stephenson and W. A. Waters, *J. Chem. Soc.*, **1946**, 333.
14) E. E. Fleck, *J. Org. Chem.*, **12**, 708 (1947).
15) W. L. Walton, *J. Amer. Chem. Soc.*, **69**, 1544 (1947).
16) G. T. Barry and R. Boyer, *Can. J. Research*, **26B**, 518 (1948).
17) M. Ballester, J. Castañer, J. M. Codina and F. Lluch, *An. Real Soc. Espan. Fis. Quim.*, **56 B**, 197 (1960).
18) M. Ballester and J. Castañer, *An. Real Soc. Espan. Fis. Quim.*, **56 B**, 207 (1960).
19) M. Ballester and J. Castañer, *J. Amer. Chem. Soc.*, **82**, 4259 (1960).
20) R. Riemschneider, *J. Amer. Chem. Soc.*, **75**, 4853 (1953).
21) M. Ballester, J. Castañer and J. Riera, *U.S. Clearinghouse Fed. Sci. Tech. Inform.*, 1968, AD 672319.