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SYNTHESIS AND ISOLATION OF A PERCHLOROTRIPHENYLCARBONIUM SALT

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THE synthesis of a number of carbon free radicals possessing extraordinarily high inertness has been announced recently,[1] a most remarkable example being the perchlorotriphenylmethyl (PTM) radical (I).

Such unusual behavior is ascribed to essentially complete steric shielding of the normally reactive tricovalent central carbon by two triads of *ortho* chlorines and the three benzene rings.

The authors wish to report now the synthesis and isolation of a stable salt of the corresponding chlorocarbon cation: the *perchlorotriphenylcarbonium hexachloroantimoniate* (II). This salt can be obtained in an almost quantitative yield either from I, or from perchloro-3-diphenylmethylenecyclohexa-1,4-diene (III),[2] by reaction with antimonium pentachloride in sulfuryl chloride. It consists of dark-green crystals with a reddish reflectance.

Anal. Calcd. for $C_{19}Cl_{21}Sb$: C, 20.8; Cl, 68.0. Found: C, 20.6; Cl, 68.0.

The infrared spectrum of this compound shows the strong characteristic band for $(SbCl_6)^-$.[3]

ir (KCl pellet)

ν 1498 (s) (C_6Cl_5), 1363 (s) (C_6Cl_5), 1332 (m), 1242 (s), 1120 (s), 595 (s), 340 (s) ($SbCl_6^-$) cm^{-1}.

uv-vis (H_2SO_4)

λ (ε) 229 (58,500) (max), 255 (44,000) (sh), 320 (13,500) (max), 690 (30,000) (max) nm.

These crystals can be kept under water for some days without significant decomposition. However, when disolved in wet methylene chloride this salt hydrolyses rapidly to give perchloro-α,α-diphenylquinomethane (IV).

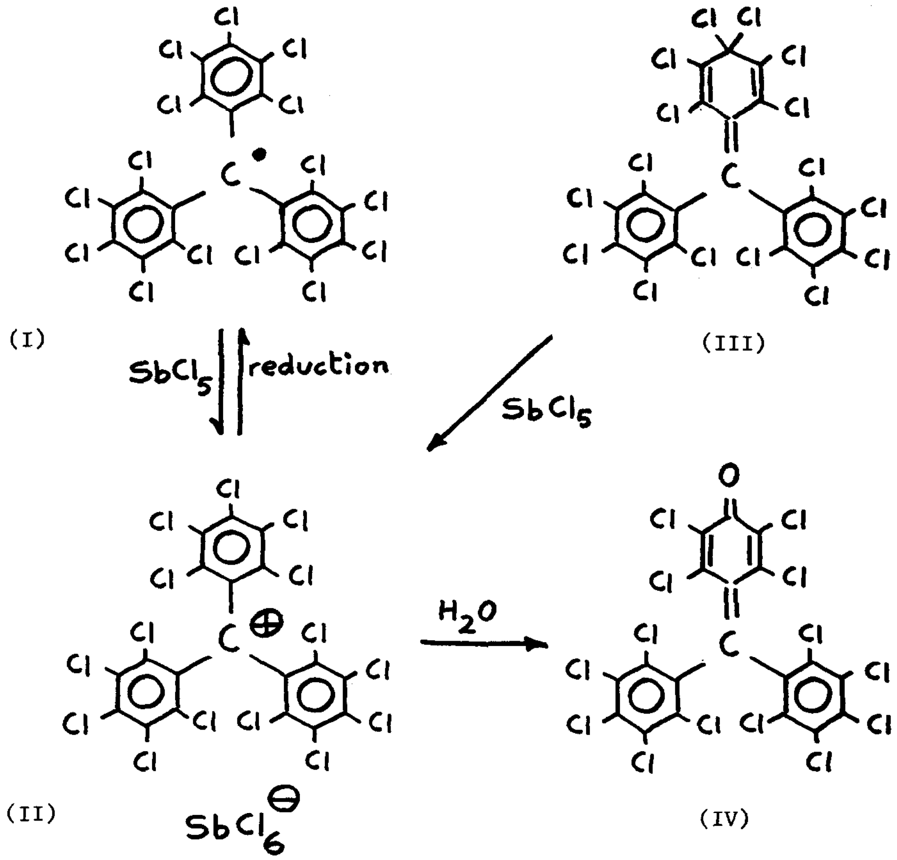
Anal. Calcd. for $C_{19}OCl_{14}$: C, 30.8; Cl, 67.0. Found: C, 30.8; Cl, 67.1.

ir (KBr pellet)

ν 1660 (s) (C=O), 1565 (w) (C=C) cm^{-1}.

II reacts with solid potassium bromide giving I.

It is believed that electronic effects do not play any decisive role in stabilizing the perchlorotriphenylcarbonium ion since it is known that the perchlorophenyl groups are overall electron-attracting substituents.[4] Consequently, its stability is regarded as due to steric shielding although, in spite of the high ring dihedral angle relative to the bonding plane of the trivalent central carbon atom, some charge delocalization on the ring might be present.



The steric shielding of the central carbon should be comparable to that of I. Accordingly, hydrolysis does not give the normal product (perchlorotriphenylcarbinol) but perchloroketone IV.

As far as its reduction to I is concerned, since this is an electron-transfer process steric hindrance appears not to be applicable.

The authors are presently engaged in developing the interesting and promising chemistry of this and other related perchlorocarbonium ions, particularly their remarkable reaction with cycloheptatriene.

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