

SYNTHESIS AND ISOLATION OF A PERCHLOROTRIPHENYLCARBANION SALT

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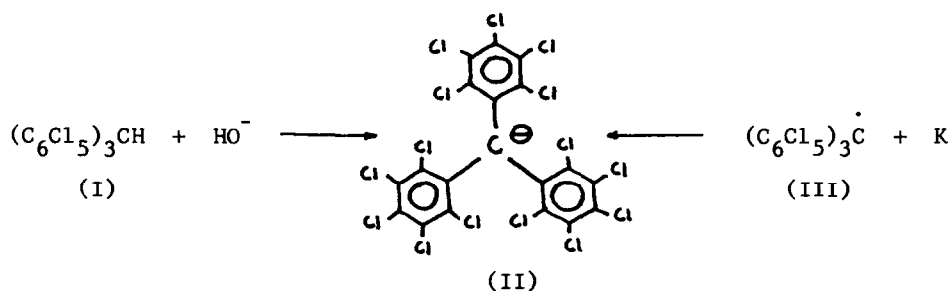
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THE synthesis of the first "inert carbon free radicals" which possess an exceptional chemical passivity, even towards highly reactive species, has been announced.¹ These are alkaromatic chlorocarbon radicals, perchlorotriphenylmethyl, or PTM (III), being one of this type. They can be obtained by two alternative ways, with oxidation of the corresponding perchlorocarbanions being one method.²

The perchlorotriphenylcarbanions are remarkably stable red-wine colored species. In fact, their solutions can be prepared with base from α H-quasiperchlorotriphenylmethanes in DMSO-containing solvents. They can also be formed in ethyl ether in high yields by attack of alkali metals on the radicals.



The authors report now the isolation of the first stable salt of this kind: the tetraethylammonium perchlorotriphenylmethide which has been obtained in a high yield as a garnet-colored, crystalline powder from a solution of the potassium salt and tetraethylammonium bromide in THF. It shows the characteristic infrared and nmr spectra of tetraethylammonium ion.

Anal. Calcd. for $C_{27}H_{20}Cl_{15}N$: C, 36.4; H, 2.3; Cl, 59.7; N, 1.6. Found: C, 36.7; H, 2.1; Cl, 59.7; N, 1.5. ir (KBr pellet) ν 1498 (m), 1480 (m) ($(C_2H_5)_4N^+$), 1360 (s), 1330 (m) (aromatic) cm^{-1} . nmr (pyridine) τ 6.60 (q, 2, $J = 6.84$ Hz, $CH_3CH_2N^+$), 8.76 (t, 3, $J = 6.84$ Hz, $CH_3CH_2N^+$). vis (C_2H_5OH) λ (ϵ) 510 (28,500) (max) nm.

In solution, this salt is very stable towards water or ethanol but reacts with diluted hydrochloric acid to give I. As the non-isolable alkali-metal salts,² it is oxidized to III with iodine.

The stability of this salt is comparable to that of perchlorotriphenylcarbonium hexachloroantimoniate which has also been reported recently.³ It is concluded, therefore, as in the radical and the carbonium ion, that it must be caused by steric shielding since the high dihedral angle of the phenyl rings with respect the bonding plane of the central trigonal carbon of II clusters the bulky ortho chlorines around such a carbon. Furthermore, any alternative electronic effect that would assist the carbanion would destabilize the carbonium ion, or vice versa.

The higher stability of the ammonium salt as compared to the alkali-metal salts might be traced to inability of the quaternary ammonium ion to act as an acceptor in the electron-transfer process.

As in the case of the perchlorotriphenylcarbonium ions, the factor keeping the perchlorotriphenylcarbanions from being as inert as the corresponding radicals may be the inherent chemical affinity arising from the existence of the electric charge.

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References

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