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Stereochemistry in CF_3PCl_3F: Trifluoromethyltrichlorofluorophosphorane.

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The new molecule CF_3PCl_3F is formed in the reaction of CF_3PCl_2 with ClF and exists in a trigonal bipyramidal framework. The fluorine atom and the trifluoromethyl group assume axial positions as indicated by ^{19}F nuclear magnetic resonance measurements. New descriptive data on chlorine monofluoride are also given.

Introduction

Attention has been focused on the spatial arrangement of atoms and groups bonded to pentavalent phosphorus and the results have indicated that the most electronegative units assume axial positions in a trigonal bipyramidal structure.[1] When one or more CF_3 groups are bonded halophosphoranes, however, some ambiguity exists. The ^{19}F n.m.r. spectrum of CF_3PF_4 has been interpreted in terms of a molecule with an axial CF_3 group contrary to the general conclusion reached above.[1] Alternatively one could also conclude that the molecule existed with an equatorial CF_3 in a trigonal bipyramid or with an axial CF_3 in a tetragonal pyramid depending on the underlying assumptions one is willing to propose. On the other hand, the $(CF_3)_nPCl_{5-n}$ molecules have structures[2,3] which are totally consistent with the earlier stereochemical generalization. It is clear, therefore, that much more data on the fluorocarbonhalophosphoranes is needed with particular emphasis on experiments designed to give stereochemically significant results. The present work makes use of the ^{19}F nuclear magnetic resonance method to obtain further information along these lines.

It was of interest to synthesize the new molecule, CF_3PCl_3F, in which the electronegativity of the CF_3 group is only marginally greater than that of the chlorine atoms. These units might then be expected to compete for one of the axial sites with the fluorocarbon group having a small advantage. These conclusions were based upon the electronegativity values of Cl = 3.0, CF_3 = 3.4 and F = 4.0, and it was expected further that the relatively large masses of the chlorine atoms and the CF_3 group would preclude rapid intramolecular exchange processes. The n.m.r. experiments confirmed these expectations.

(1) E. L. Muetterties, W. Mahler and R. Schmutzler, *Inorg. Chem.*, *2*, 613 (1963).
(2) J. E. Griffiths, *J. Chem. Phys.*, *44*, 3510 (1964).
(3) J. E. Griffiths and A. L. Beach, *ibid.*, *44*, 2686 (1966).

Trifluoromethyltrichlorofluorophosphorane was formed in the low temperature (—160° to —83°C during 3 hours) reaction of liquid CF_3PCl_2 (3.46 mmole; v.p. at 17.3°, 330.4 mm, lit.[4] 329.1 mm) with gaseous chlorine monofluoride[5] (3.46 mmole).[7] The new phosphorane was separated from everything else except CF_3PCl_4 by passing the mixture formed in the reaction through traps held at —45, —64 and —196°C. The fraction held at —64° which contained CF_3PCl_3F and a small amount of CF_3PCl_4 impurity (0.0944 gm sample yielded 0.0457 Cl; calc'd. 0.0447 gm Cl for CF_3PCl_3F) was transferred in vacuum to a 5 mm O.D. glass tube and its F^{19} n.m.r. spectrum at —50°C was measured at 56.4 MHz. The results are listed in the Table along with those for CF_3PCl_4 and $(CF_3)_2PCl_3$ which have not appeared before.

Table I. F^{19} Nuclear Magnetic Resonance Spectra*

Compound	δ(P-F)	δ(C-F)	$J_{P\text{-}F}$	$J_{P\text{-}F(C)}$	$J_{F(P)\text{-}F(C)}$
CF_3PCl_3F	—206	—0.1	1000	149	8.4
CF_3PCl_4	—	1.1	—	154	—
$(CF_3)_2PCl_3$	—	—0.1	—	193	—

* Chemical shifts relative to CF_3COOH are in ppm and spin spin coupling constants are in cycles/second.

The chemical shift δ(P-F) relative to CF_3COOH has a value characteristic of an apical fluorine atom not undergoing positional exchange (cf. —211 ppm for PCl_4F)[8] and a comparison of the chemical shift δ(C-F)

(4) L. K. Petersen and A. B. Burg, *J. Am. Chem. Soc.*, *86*, 2587 (1964).
(5) Commercial chlorine monofluoride contains several impurities which may be removed by passing the gas through vacuum traps maintained at —150° and —196° several times until the sample held at —196° is tensimetrically pure. Vapor pressures in the range —138 to —112°C determine the equation $\log_{10} p(mm) = 8.1593 - 0.0163T + 1.75 \log_{10}T - 1099.8/T$ from which the normal b.p. = — 100.7°C, ΔH_v = 3.41 kcal mole^{-1} and the T. C. = 19.8 e.u. were calculated. The melting point was observed at — 152.3 ± 0.2°C (lit.[6] - 155°C). Useful check points for vapor pressure measurements at — 111.86 and — 126.9°C are 372.3 and 109.9 mm respectively, and the corresponding calculated values are 372.22 and 109.84 mm. Published data[6] differ considerably from the present values and give an abnormally low Trouton constant of 13.2 e.u. The Trouton constant from the new data is more consistent with the accepted values of 18.6 and 18.5 e.u. for fluorine and chlorine respectively.
(6) O. Ruff and F. Laass, *Z. Anorg. Allgm. Chem.*, *183*, 216 (1929).
(7) Chlorine monofluoride had been used earlier by the present author for the preparation of $PClF_4$ from PF_3. Low temperatures are important to moderate these reactions and also to reduce the tendency for $PClF_4$, for example, to undergo disproportionation into PF_5 and PCl_2F_3.
(8) R. R. Holmes, R. P. Carter, J., and G. E. Petersen, *Inorg. Chem.*, 3, 1748 (1964).

in CF_3PCl_3F with those in CF_3PCl_4 and $(CF_3)_2PCl_3$, where the CF_3 groups are known to be in apical positions,[2,3] indicates an apical CF_3 group. If the fluorine atom were undergoing rapid intramolecular exchange a smaller downfield chemical shift would be expected resulting from the averaging of the equatorial and axial shifts.

From these results and those presented earlier, one must conclude that the generalization of Muetterties, Mahler, and Schmutzler[1] concerning the relation between electronegativity and stereochemistry in trigonal bipyramidal molecules appears to be valid over a wide range of substituents. The case of CF_3PF_4, however, is still open to question since additional evidence based upon vibrational spectroscopy[9] favors an equatorial CF_3 contrary to the conclusions based upon ^{19}F n.m.r. results. In addition, the influence of the steric requirements of large atoms and groups, particularly in the fluorocarbonhalophosphoranes, has still to be properly evaluated.

(9) J. E. Griffiths, Molecular Spectroscopy Symposium, Ohio State University, Columbus, Ohio, 1966, Paper M2.

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