Substitution of Dimethylamino-groups by Antimony Trifluoride

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Summary Dimethylamino-groups in both trimeric and tetrameric phosphonitriles can be substituted by antimony trifluoride *via* a stepwise non-geminal route.

THE fluorination of non-metal chlorides or bromides with antimony trifluoride is well established and the trifluoride will also cleave the P=N bond in phosphazo-derivatives: *e.g.* the conversion of $PhN{=}P(NEt_2)Cl_2$ into Et_2NPF_4 by Bermann and Van Wazer.[1] We have recently observed an alternative route for the reaction between antimony trifluoride and amino-substituted phosphorus compounds.

In experiments on the fluorination of dimethylaminochlorotetraphosphonitriles, in addition to the expected replacement of the chlorine atoms by fluorine, there was also a slower process in which dimethylamino-groups were also substituted. Thus in addition to three $P_4N_4F_4(NMe_2)_4$ isomers from $P_4N_4Cl_4(NMe_2)_4$, three isomeric pentafluorides, $P_4N_4F_5(NMe_2)_3$, also resulted. The reaction took place in refluxing tetrachloroethane and mass spectrometric evidence for intermediates of the type $P_4N_4ClF_4(NMe_2)_3$ and $P_4N_4Cl_2F_3(NMe_2)_3$ shows that the amine and chlorine replacement reactions are concurrent.

The substitution of amino-groups by antimony trifluoride has now been used as an alternative to the direct fluorination of amino-chlorides for the preparation of aminofluorophosphonitriles. *E.g.*, when the completely aminated tetramer $P_4N_4(NMe_2)_8$ was refluxed with an excess of antimony trifluoride in 1,2-dichloroethane, products containing the monofluoride and smaller amounts of both starting material and the difluorides were obtained. The former, $P_4N_4F(NMe_2)_7$, was separated by fractional crystallization and characterized by ^1H and ^{19}F n.m.r. spectroscopy. Further fluorination occurred in solvents of higher b.p. and two isomeric difluorides, $P_4N_4F_2(NMe_2)_6$, constituted 85% of the reaction product with 1,1,2-trichloroethane as solvent. In tetrachloroethane with 2 mol. equiv. of antimony trifluoride, three amino-groups were replaced and two of the three resulting isomers of $P_4N_4F_3(NMe_2)_5$ have been separated and characterized. With increasing amounts of the antimony compound and longer reflux times, it is possible to obtain tetra-, penta-, and hexa-fluoro-derivatives. Three of the tetrafluorides, $P_4N_4F_4(NMe_2)_4$, have been isolated and shown to be identical with those which result from fluorination of the non-geminal compound, $P_4N_4Cl_4(NMe_2)_4$. Three isomers with the stoicheiometry, $P_4N_4F_5(NMe_2)_3$, have also been isolated.

Analogous reactions with hexakisdimethylaminotriphosphonitrile, $P_3N_3(NMe_2)_6$, as expected, occur much less readily and prolonged reflux in tetrachloroethane is necessary to bring about amine replacement. After 7 h, the monofluoride, $P_3N_3F(NMe_2)_5$, can be isolated and this compound has been characterized. In contrast to the corresponding monochloride,[2,3] which is very hygroscopic, the fluoride is stable to atmospheric moisture. Further reaction for up to 7 days gives successively the di-, tri-, and small amounts of the tetra-fluoro-derivatives.

Preliminary evidence indicates that these amine replacement reactions follow a non-geminal path for both the trimer and tetramer, and the mechanism is expected to be similar to that postulated for the replacement of chlorine atoms in aminochlorophosphonitriles.[4,5] Indeed, as the aminated phosphonitriles are very strongly basic,[6] adduct formation with antimony trifluoride is expected to occur readily. The non-geminal reaction can then be rationalized since replacement of the second amine group at a $PF(NMe_2)$ group will occur less readily, owing to the reduced basicity of the adjacent ring nitrogen atoms, than one from a $P(NMe_2)_2$ group.

Extensions of the amine substitution reaction are being examined and preliminary results point to it being a valid method for preparing aminofluoroborazines.

(*Received, 24th January* 1972; *Com.* 098.)

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