The Synthesis and Structure of a Dialkyl Cation of Hexakisdimethylaminocyclotriphosphazatriene

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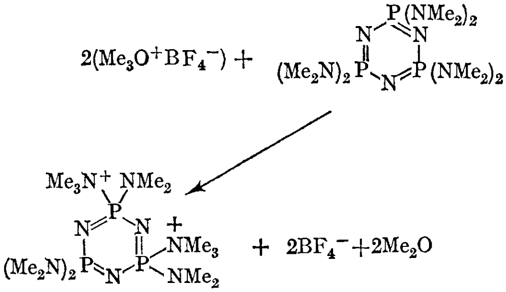
THE work of Shaw, *et. al.*, [1] on the basicity with respect to the proton of some partially and fully amino-substituted cyclotriphosphazatrienes presented arguments for protonation of the ring, rather than the exocyclic, nitrogen atom. The i.r. and n.m.r. data of Moeller and Kokalis[2] supported ring-nitrogen protonation, but further investigation of the question of the relative basicities of the ring, and exocyclic, nitrogen atoms seemed advisable.



(I)

Experiments in our laboratory, supported by analytical data, show that hexakisdimethylaminocyclotriphosphazatriene, $N_3P_3(NMe_2)_6$, reacts with trimethyloxonium tetrafluoroborate[3] in $MeNO_2$ solution to yield dimethylhexakisdimethylaminocyclotriphosphonitrilium difluoroborate (I) (60%) [m.p. 207—209° (decomp.), from MeOH] as a white solid, stable in air, soluble in polar organic solvents and insoluble in ether. The ionic nature of (I) is shown by the immediate precipitation of $NaBF_4$ upon addition of $NaBPh_4$ to a solution of (I) in CH_2Cl_2–MeCN and by the conductance data ($\Lambda = 54{\cdot}48$ cm.^{2}/ohm), which is in accord with literature data for a 1 : 2 electrolyte in 10^{-3}M nitrobenzene solution at 25°.[4]

The 60 Mc./sec. ^1H n.m.r. spectrum of (I) is too complex to allow unambiguous assignment of the structure. Information concerning the structure of (I) was obtained by hydrolysing a sample in 12M-HCl in a glass bomb (100°, 7 days), transferring the hydrolysed sample to a Kjeldahl nitrogen apparatus, distilling the amines into an HCl solution and evaporating the distillate to dryness. The residue was taken up in anhydrous trifluoroacetic acid, the insoluble NH_4Cl filtered off and the spectrum of the filtrate examined in a Varian A-60 n.m.r. spectrometer, following the work of Anderson and Silverstein.[5] The spectrum of the amine hydrochlorides obtained indicated the presence of Me_2NH_2Cl and Me_3NHCl, giving a five-line spectrum, analogous to the spectrum of a prepared mixture of Me_2NH_2Cl and Me_3NHCl. Integration of the signal, although complicated by overlap, gave a 2·3 : 1 ratio of Me_2NH_2Cl and Me_3NHCl in agreement with the expected 2 : 1 ratio.

The observation that alkylation occurs at the exocyclic nitrogen atoms is surprising because the ring nitrogen atoms are definitely the more sterically favourable positions. The isolation and characterization of (I) lends support to the idea that charge-transfer from exocyclic nitrogen to the ring is much smaller than originally presumed for hexa-aminocyclotriphosphazatrienes.[1]

At present we have analytical and conductance data for the following compounds: $\{N_3P_3(NMe_2)_6Me\}^+$ (BF_4^-), $\{N_3P_3(NMe_2)_6Et\}^+$ (BF_4^-), and $\{N_3P_3(NMe_2)_6Et_2\}^{2+}$ $(BF_4^-)_2$. Attempts to determine their structures are currently in progress along with further alkylation studies on other cyclotriphosphazatrienes and other inorganic ring systems.

One of us (J. N. R.) thanks NASA for financial support, in the form of a Traineeship.

(*Received, December 22nd*, 1967; *Com.* 1371.)

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