

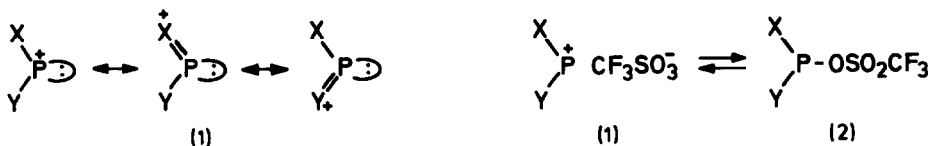
REACTIONS OF AMINOPHOSPHINES WITH TRIFLUORMETHANESULFONIC ACID:
 PHOSPHENIUM ION (TWO-COORDINATE PHOSPHORUS ION) OR TRICOVALENT
 PHOSPHORUS PRODUCTS?

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Abstract. The title reaction is shown to give phosphonium ion products (1), mixtures of (1) and tricovalent substitution products (2), or other products, depending on the nature of the substituents on phosphorus.

Two-coordinate phosphorus compounds have been known since 1964 and are now well characterized.¹ Phosphenium ions (1) are members of this class and have been known for a decade, but only about ten are characterized, mainly by their very low-field ³¹P NMR



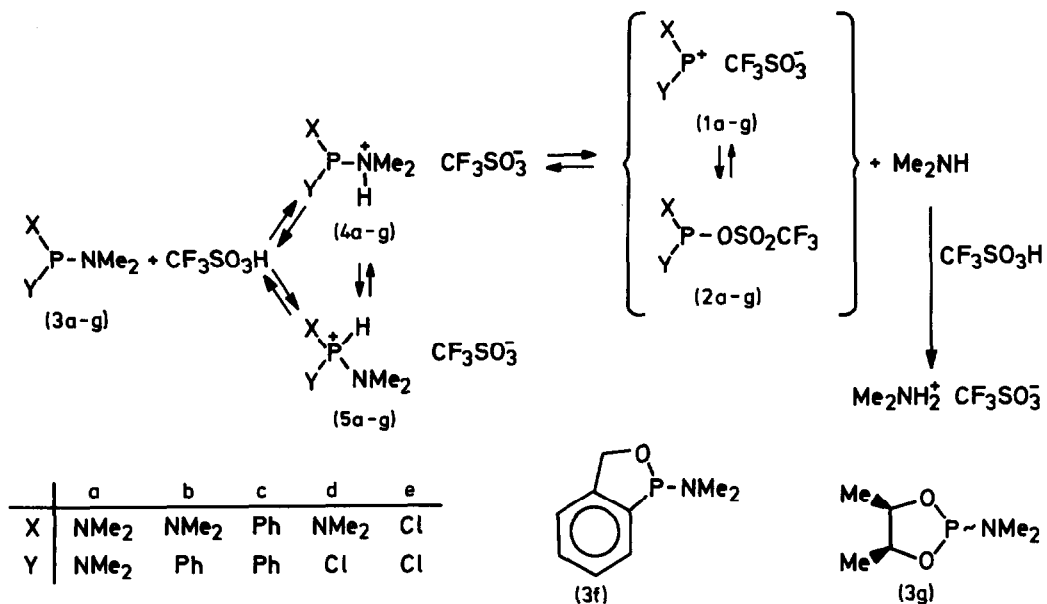
chemical shifts.² The positive charge is stabilized by delocalisation, and all but one of the phosphonium ions hitherto prepared have Y = NR₂ (the exception being (ferrocenyl)₂P⁺³). They have all been obtained from XYPCl or XYPF and AlCl₃, PF₅ or other strong Lewis acids.

This paper evaluates another potential route to phosphonium ions, viz. elimination of NMe₂ groups from tricovalent phosphorus by means of protonation. It is shown that a phosphonium ion (1), X = Y = NMe₂, is formed from (Me₂N)₃P and CF₃SO₃H, and that several other aminophosphines give rise to equilibrium mixtures of phosphonium ions (1) and tricovalent substitution products (2).

Trifluoromethanesulfonic acid was selected as the proton donor because of the low nucleophilicity of its anion. Acids with more nucleophilic anions as e.g. HCl are known to give tricovalent substitution products.⁴ Seven aminophosphines (3a-g) (Scheme) have been included in this study.

In a typical experiment trifluoromethanesulfonic acid (10 mmol) was added dropwise to the aminophosphine (5 mmol) in dry CDCl₃ (5 ml) at 0° under nitrogen. A sample (0.5 ml) was withdrawn for NMR analysis and the remaining mixture stirred at 25° for 2-24 h. A crystalline precipitate, shown to be Me₂NH₂⁺CF₃SO₃⁻ (IR, m.p.), started to form within few minutes and was subsequently isolated in a nearly quantitative yield in most cases.

From the formation of Me₂NH₂⁺CF₃SO₃⁻ and the NMR data, as discussed in the following, a general reaction scheme is proposed (Scheme).



Scheme

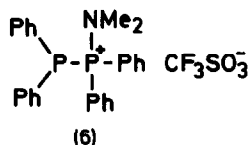
The ^{31}P NMR spectra of the reaction mixture from (3a) showed after a few minutes the most prominent signal at δ_{P} 43.4 (d, $^1J_{\text{PH}}$ 630 Hz). This is assigned to (5a) because of the high-field shift and the large $^1J_{\text{PH}}$ coupling constant. A small signal at δ_{P} 269.4 (s) increased with time as the other signal decreased, and was the only prominent signal after 24 h (> 90% from the ^{31}P integral). The corresponding low-field ^1H NMR signal (δ_{H} 3.28, d, $^3J_{\text{PH}}$ 9.8 Hz) and the low-field ^{31}P signal are indicative of a phosphonium ion (1a) and agree well with published values for $(\text{Me}_2\text{N})_2\text{P}^+ \text{AlCl}_4^-$ (δ_{P} 264, δ_{H} 3.22, d, J 9.6 Hz in CH_2Cl_2 ⁵). A very weak ^{31}P signal at δ_{P} 153.0 observed during the reaction may be due to (4a).

In the case of (3b) a prominent signal at δ_{P} 46.6 (d, $^1J_{\text{PH}}$ 580 Hz) and a smaller signal at δ_{P} 132.4 (s), assigned to (5b) and (4b), resp., decreased with time as a new signal, δ_{P} 183.4 (s), increased. After 2 h only a sharp singlet at δ_{P} 184.2 prevailed (> 95% from the ^{31}P integral). The ^1H NMR signals after 2 h consisted of a narrow phenyl multiplet (δ_{H} 7.49) and a broadened, unsymmetrical doublet (δ_{H} 2.86, J 11.4 Hz) in a 5:6 integral ratio. The doublet upon cooling was split into two equal intensity doublets (δ_{H} 3.18, $^3J_{\text{PH}}$ 16.7 Hz and δ_{H} 2.62, $^3J_{\text{PH}}$ 6.3 Hz at -50°), presumably due to hindered rotation about the P-N bond (ΔG^\ddagger ca. 12.5 kcal/mol). The phosphorus chemical shift of this product was very solvent dependent (hexane, δ_{P} 173.2; benzene, 182.1; CDCl_3 , 184.2; CH_2Cl_2 , 186.2; CD_3CN , 192.0 (decomp.)). These data strongly suggest that the product is an equilibrium mixture of a phosphonium ion (1b) and a tricovalent compound (2b), probably with the latter prevailing (cf. δ_{P} 154.4 for $\text{Ph}(\text{Me}_2\text{N})\text{POEt}$,⁶ δ_{P} > 260 for known phosphonium ions²).

The NMR data in case of (3f) were very similar to those of (3b). Intermediate ^{31}P NMR signals, a weak one at δ_{P} 65.8 (d, $^1\text{J}_{\text{PH}}$ 690 Hz) and a large at δ_{P} 168.3 (s) are assigned (5f) and (4f), resp. After 8 h these are largely replaced by a signal at δ_{P} 196.2 (> 90% from the ^{31}P integral). The ^1H NMR spectrum at this time showed that the signal from the CH_2 ring protons, which for (3f) is an ABX multiplet because of the asymmetric phosphorus center, now is a doublet (δ_{H} 5.17, $^3\text{J}_{\text{PH}}$ 11.5 Hz). Again, the low-field shift (cf. δ_{P} ca. 163 for tricovalent model compounds ⁷) and the equivalent CH_2 protons argue for the product being an equilibrium mixture of the phosphenium ion (1f) and the tricovalent compound (2f).

In the case of (3g) the starting material was a mixture of 90% of the trans isomer (δ_{P} 139.9), 7% of the cis isomer (δ_{P} 147.4), and 3% of the d,l compound derived from d,l-2,3-butanediol (δ_{P} 143.9). The reaction mixture showed no low-field ^{31}P NMR signals, although a nearly quantitative yield of $\text{Me}_2\text{NH}_2^+ \text{CF}_3\text{SO}_3^-$ was isolated after 2 h. An intermediate signal, δ_{P} 142.9 (s), assigned to (4g), was quickly replaced by a signal at δ_{P} 140.5 which after 1 h comprised 97% of the ^{31}P integral; the remaining 3%, δ_{P} 144.3, was due to the product from the d,l isomer. The fact that cis and trans (3g) gave only one product signal suggests again that the product is an equilibrium mixture, although the δ_{P} value shows the equilibrium to be strongly displaced towards the tricovalent form (2g) (cf. δ_{P} 135-150 for tricovalent model compounds ⁸).

The remaining aminophosphines (3c-e) did not give any evidence for products having phosphenium ion character. The reaction mixture from (3c) showed as the main signals in the ^{31}P NMR spectrum an AB system (δ_{P} 52.7 and -18.9, $^1\text{J}_{\text{PP}}$ 325 Hz), probably due to formation of (6). Similar "dimers" have been found by Cowley ⁹ on attempted generation of phosphenium ions from sufficiently nucleophilic phosphorus compounds. The ^{31}P NMR spectra



of the reaction mixtures from (3d) and (3e) showed that in each case at least five products had formed, and that several of these were common for (3d) and (3e) (δ_{P} 219.4 (PCl_3 ?), 168.2, 139.9). The spectra were void of signals due to the known $\text{Cl}(\text{Me}_2\text{N})\text{P}^+$ (δ_{P} 325 ⁵) or Cl_2P^+ (δ_{P} estimated around 360 ⁵). The many products may appear as a result of scrambling of NMe_2 , Cl, and OSO_2CF_3 groups on phosphorus.

From the above discussion it is concluded that phosphenium ions (1) are likely products from reactions of aminophosphines with strong acids, but that they react with nucleophiles even as weak as CF_3SO_3^- to give the covalent compounds (2), unless they are extensively stabilized by delocalisation over the substituents X and Y. For X = Y = NMe_2 , sufficient stabilisation occurs to allow (1) to be the prevailing component in solution,

whereas for X = Ph, Y = NMe₂ or OR, a mixture of (1) and (2) results, probably with (2) dominating. The implications of these results for the mechanism of substitution of NR₂ groups on tricovalent phosphorus, which is known to be acid catalyzed,¹⁰ are the subject of a forthcoming paper.

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