

Unexpected Staudinger Reaction of α -Azidophenylacetonitrile and Triphenylphosphine: Synthesis and Crystal Structure of Aminotriphenylphosphonium Salt of Phenylmalononitrile

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Staudinger reaction of α -azidophenylacetonitrile with triphenylphosphine in 1:2 molar ratio provides the triphenylphosphinazine derived from α -diazophenylacetonitrile, whereas in 2:1 molar ratio the final product is found to be the aminotriphenylphosphonium salt of phenylmalononitrile; X-ray structure analysis of this salt indicates that the anion and cation interact with one another *via* hydrogen bonding.

The reaction of a tertiary phosphine with an organic azide to produce an iminophosphorane after nitrogen evolution is known as the Staudinger reaction.¹ The primary imination products, phosphazides, are sometimes isolable and stable² or can be trapped *via* an intramolecular reaction,³ but as a rule they lose nitrogen at room or even lower temperatures to give the corresponding iminophosphorane compound in practically quantitative yields. An immense variety of azides have been employed in the Staudinger reaction, with the only limits apparently being the availability of the requisite azide and the thermal and shock stability of azides. Aromatic, aliphatic, heterocyclic, olefinic, carbonyl, alkoxy carbonyl, carbamido, tosyl, bisazides and metallic azides have been used.⁴ However, the Staudinger imination of trivalent phosphorus compounds with azides containing a CH-acidic group has not been investigated. It has only been briefly reported⁵ that the most acid azides reacted with tertiary phosphines to form phosphorus-substituted betaines.

The present investigation disclosed the unexpected behaviour of the reaction between α -azidophenylacetonitrile and triphenylphosphine. The intra- or inter-molecular protonation of the initially formed phosphazo-compound is of special interest since in this case the resulting betaine is capable of undergoing various conversions.

An earlier communication described the formation of the α -azidophenylacetonitrile **1** from 5-amino-4-phenyl-1,2,3-thiadiazole by diazotization, reaction with sodium azide and further

heating.⁶ In our hands, compound **1** was easily prepared by the two-step sequence: (a) reaction of phenylacetonitrile with *N*-bromosuccinimide in the presence of dibenzoyl peroxide (70%) and (b) bromine-azide exchange using a polymeric quaternary ammonium azide⁷ (84%).

When compound **1** was allowed to react with 2 equiv. of triphenylphosphine (TPP) in diethyl ether at room temperature for 2 h a precipitate **2** (82%) with mp 176–178 °C was formed and from the filtrate triphenylphosphinimine **3** was obtained. In order to identify unambiguously the structure of the reaction product X-ray structure determination of crystalline compound **2** was performed.

When the reaction between **1** and TPP was carried out in 2:1 molar ratio under the same conditions, nitrogen was evolved and the metal-free carbanion salt **4** (87%) was isolated as crystalline product, mp, 164–166 °C, and from the filtrate PhCN

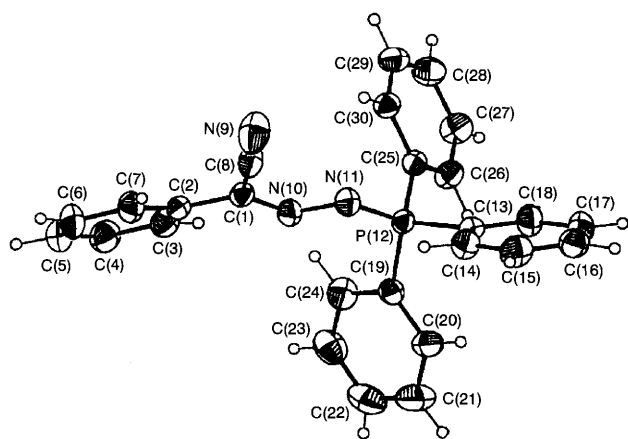


Fig. 1 Molecular structure of **2** showing 30% probability ellipsoids for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.468(3), C(1)–C(8) 1.428(3), C(1)–N(10) 1.301(3), C(8)–N(9) 1.143(4), N(10)–N(11) 1.356(2), N(11)–P(12) 1.637(2), P(12)–C(13) 1.792(2), P(12)–C(19) 1.801(3) and P(12)–C(25) 1.805(3). C(3)–C(2)–C(7) 118.7(2), C(1)–C(8)–N(9) 175.3(3), C(1)–N(10)–N(11) 115.4(2), C(8)–C(1)–N(10) 121.9(2), C(3)–C(2)–C(1)–N(10) –19.6(4), C(2)–C(1)–N(10)–N(11) –175.2, C(1)–N(10)–N(11)–P(12) –175.4(2), N(10)–N(11)–P(12)–C(13)/C(19)/C(25) –161.9(2)/–40.6(2)/79.7(2).

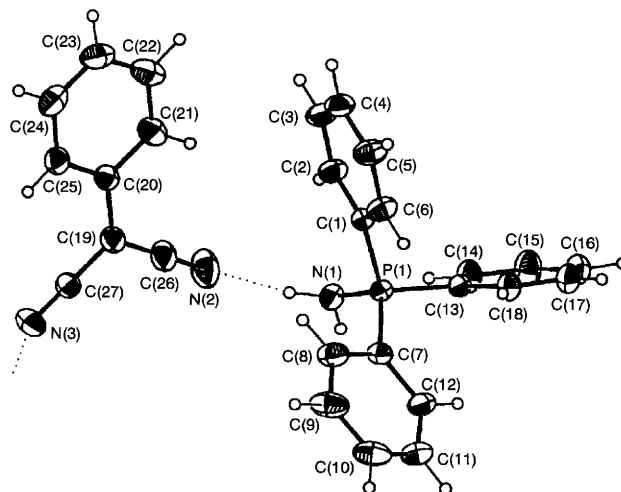
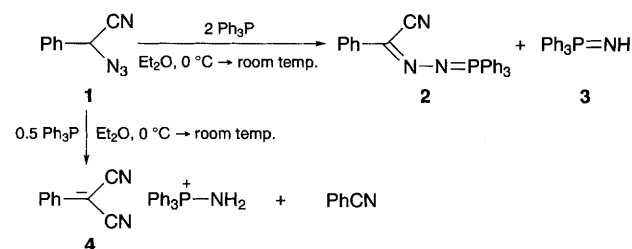
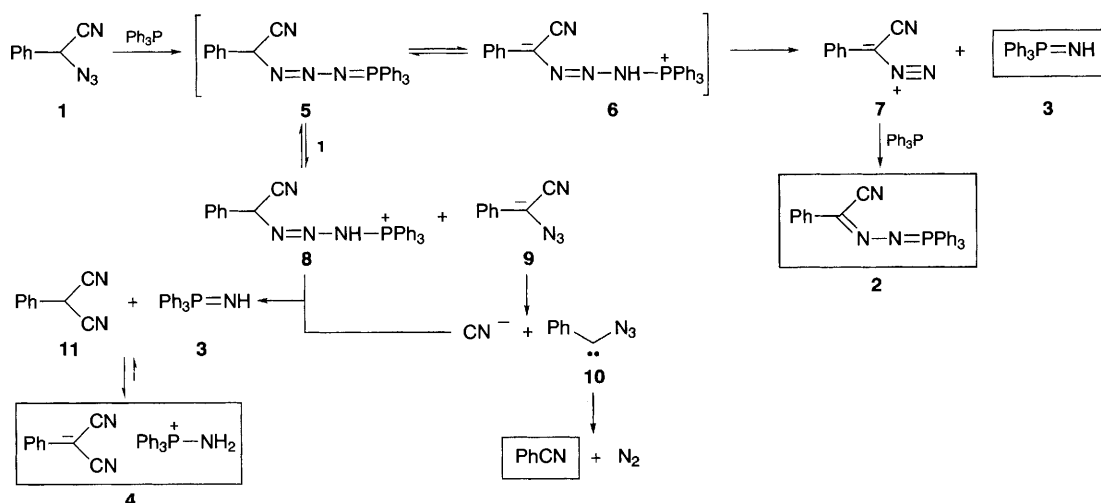


Fig. 2 Molecular structure of compound **4** (ellipsoids at 30% probability level). Selected bond and angles (°): P(1)–N(1) 1.622(2), C(19)–C(20) 1.456(3), C(19)–C(26) 1.392(4), C(19)–C(27) 1.393(4), C(26)–N(2) 1.158(4) and C(27)–N(3) 1.155(4). C(26)–C(19)–C(27) 116.9(2), C(21)–C(20)–C(25) 117.4(2), C(19)–C(26)–N(2) 178.9(3), C(19)–C(27)–N(3) 178.6(3), C(13)–P(1)–N(1)–H(111) –169(2) and C(13)–P(1)–N(1)–H(112) 52(2).



Scheme 1



Scheme 2

was isolated. Staudinger reaction between **1** and TPP in 1:1 molar ratio provided **2** as minor product and **4** as major product (Scheme 1). This compound is stable at room temperature for months and can also be handled without problem. Its IR spectrum showed two bands in the region of the cyano group and ³¹P NMR spectrum displayed a signal at δ 35.8. The ¹³C NMR spectrum showed a signal at δ 27.2 due to a quaternary carbon atom. Slow recrystallization from dichloromethane/diethyl ether afforded crystals suitable for an X-ray structural analysis.† As far as the CSD is concerned it is the first time that the structure of the anion is reported. As in **2**, the *ipso* angle in the anion is affected by the cyano groups [Δα = -2.6(2)°]. This anion displays a different pattern of bond distances than that of the TCNQ molecules. The π electrons are delocalized over the C(19) and the cyano groups which is evident from the shortening and elongation of the Csp²-Csp and Csp-N bonds and the loss of the double bond character of the Car-Csp² bond and hence the quinoid character of the phenyl ring [average values for the Csp²-Csp, Csp-N and Cphenyl-Csp² bond lengths and Csp-Csp²-Csp angles in 217 structures: 1.425(16), 1.144(17) and 1.391(21) Å, and 116(2)°, respectively].

In the cation, the P=N⁺ bond agrees quite well with the averaged value given above and also with the value of 1.615 Å reported for the aminotriphenylphosphonium bromide and chloride compounds.¹⁰ The hybridization of the N(1) atom is sp³ and both hydrogen atoms are involved in hydrogen bonds with the anion producing chains along the *b* axis. The whole crystal is built up of centrosymmetrically related chains connected by C-H...electronic π cloud of phenyl rings.

A rational mechanism for the formation of the unexpected phosphinazide **2** and the metal-free carbanionic salt **4** is depicted in Scheme 2 and involves the formation of the phosphazide **5** in the first step of the reaction. This intermediate may undergo either intramolecular or intermolecular protonation on the nitrogen atom adjacent to the phosphorus.¹¹ The intramolecular protonation leads to the betaine **6** which by elimination of triphenylphosphinimine **3** provided the diazo compound **7**. Further reaction of **7** with a second equivalent of TPP yields the phosphinazide **2**. The reaction between diazodiarylmethanes and TPP to give phosphinazides has been recently reported.¹² The intramolecular protonation of the initially formed phosphazide **5** by the action of the CH-acidic group of **1** affords the aminophosphonium ion **8** and the carbanion **9**. The latter undergoes loss of the cyanide anion to give the azidocarbene **10** which is then transformed into benzonitrile after extrusion of nitrogen.¹³

Finally, nucleophilic attack of the cyano anion on the aminophosphonium cation **8** with concomitant elimination of nitrogen and triphenylphosphinimine **3** provides the phenyl-

malononitrile **11**, which undergoes proton abstraction by the action of the strong base **3** to give the salt **4**.

Recent examples on the preparation of related metal-free carbanion salts, namely tetraalkylammonium of malonic dialkyl esters,¹⁴ carbazole and dibenzoazepine¹⁵ and their application as initiators for the quantitative anionic polymerization of α-activated olefins at room temperature have been described. In all cases this type of salt has been prepared under strong basic conditions.

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Footnote

† Crystal data for **2**: C₂₆H₂₀N₃P, monoclinic, *P*₂/*c*, *a* = 13.4391(5), *b* = 10.1473(3), *c* = 17.2610(9) Å, β = 112.434(3)°, *V* = 2175.8(2) Å³, *D_c* = 1.238 g cm⁻³, *Z* = 4, μ = 12.27 cm⁻¹, crystal dimensions 0.17 × 0.50 × 0.33 mm, 3705 independent reflections, *R*(*R_w*) = 0.044(0.058) for 3098 [*I* > 2σ(*I*)] observed reflections. Max. final Δ*F* peak 0.28 e Å⁻³.

Crystal data for **4**: C₁₈H₁₇NP⁺C₉H₅N₂⁻, monoclinic, *P*₂/*c*, *a* = 11.0129(4), *b* = 13.8928(5), *c* = 15.5746(7) Å, β = 106.463(3)°, *V* = 2285.2(2) Å³, *D_c* = 1.219 g cm⁻³, *Z* = 4, μ = 11.83 cm⁻¹, crystal dimensions 0.33 × 0.27 × 0.17 mm, 3895 independent reflections, *R*(*R_w*) = 0.040(0.046) for 3034 [*I* > 2σ(*I*)] observed reflections. Max. final Δ*F* peak 0.24 e Å⁻³. Philips PW1100, four circle diffractometer, Cu-Kα radiation, graphite monochromator, ω/2θ scan, θ_{max} = 65°. Semi-empirical ψ-scan absorption correction was applied. Refinement on *F_o* with full-matrix anisotropic thermal model for the non-hydrogen atoms while H atoms, obtained unambiguously from difference Fourier synthesis were refined isotropically. Most of the calculations were performed using the XTAL System⁸ on a VAX6410 computer. The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*, vol. IV.⁹ The weighting schemes were established as to give no trends in ⟨ωΔ*F*⟩ vs ⟨*F_o*⟩ and ⟨sinθ/λ⟩. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635; Y. G. Gololobov, I. N. Zhmurova and L. F. Kasukhin, *Tetrahedron*, 1981, **37**, 437; Y. G. Gololobov, and L. F. Kasukhin, *Tetrahedron*, 1992, **48**, 1406.
- H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 1921, **4**, 861; L. Horner and A. Gross, *Liebigs Ann. Chem.*, 1955, **591**, 117; G. Wittig and K. Schwarzenbach, *Liebigs Ann. Chem.*, 1961, **650**, 1; J. E. Leffler, U. Housberg, T. Tsuno and I. Forsblad, *J. Org. Chem.*, 1961, **26**, 4810;

- J. A. Van Allan and C. A. Reynolds, *J. Heterocyclic Chem.*, 1968, **5**, 471.
- 3 P. Molina, A. Arques and M. V. Vinader, *J. Org. Chem.*, 1990, **55**, 4724.
- 4 A. W. Johnson, W. C. Kaska, K. A. Ostojca-Starzewski and D. A. Dixon, in *Ylides and Imines of Phosphorus*, ed. A. W. Johnson, Wiley, New York, 1993, ch. 12, p. 385.
- 5 Y. G. Gololobov, N. I. Gusar and M. P. Chaus, *Tetrahedron*, 1985, **41**, 793.
- 6 G. L'abbé, M. Deketele, E. Vanderstede and S. Topper, *Bull. Soc. Chim. Belg.*, 1988, **97**, 163.
- 7 A. Hassner and M. Stern, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 478.
- 8 S. R. Hall, H. D. Flack and J. M. Stewart, 'Xtal3.2', ed. University of Western Australia, Lamb: Pert, 1994.
- 9 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. IV.
- 10 M. B. Hursthouse, N. P. C. Walker, C. P. Warrens and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1985, 1043.
- 11 V. P. Prokopenko, N. V. Proklina and P. P. Onys'ko, *Zh. Obshch. Khim.*, 1984, **54**, 812 [*J. Cren. Chem. USSR (Engl. Transl.)*, 1984, **54**, 721].
- 12 D. Bethell, R. Bourne and M. Kasran, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2081.
- 13 D. P. Cox, R. A. Moss and J. Terpinski, *J. Am. Chem. Soc.*, 1983, **105**, 6513.
- 14 M. T. Reetz, S. Hütte and R. Goddard, *J. Am. Chem. Soc.*, 1993, **115**, 9339.
- 15 M. T. Reetz, S. Hütte, R. Goddard and U. Minet, *J. Chem. Soc., Chem. Commun.*, 1995, 275.