

Dual reactivity of the phosphonium zwitterion formed by the reaction of triisopropylphosphine with ethyl 2-cyanoacrylate toward 2,4-dinitro- and 2,4,6-trinitrofluorobenzenes

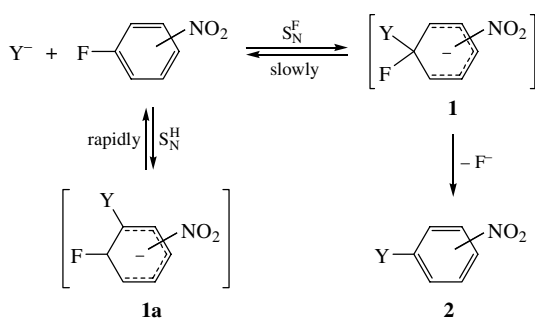
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A phosphonium zwitterion formed by the reaction of triisopropylphosphine with ethyl 2-cyanoacrylate possesses a dual reactivity: while this ion reacts with 2,4-dinitrofluorobenzene as a C-nucleophile, it reacts with 2,4,6-trinitrofluorobenzene as an N-nucleophile.

The nucleophilic aromatic substitution of the fluorine atom in nitrofluorobenzenes occurs, as a rule, *via* the formation of σ complexes **1** (Scheme 1).¹ With fluorine in a ring, *ipso*-replacement is always preceded by rapid and reversible formation of σ^H adducts **1a** as kinetically controlled products.



Scheme 1

The transformations of σ complexes **1** involve elimination of the fluoride ion giving new aromatic compounds **2**. Previously,^{2–4} we described unusual nucleophilic aromatic substitutions of fluorine atoms in polynitrofluorobenzenes without elimination of the fluoride anion. In this work, zwitterion **3** obtained *via* a reaction of triisopropylphosphine with ethyl 2-cyanoacrylate suggest the delocalization of the anionic charge in zwitterion **3**.⁵ Therefore, zwitterion **3** would be expected to possess a dual reactivity toward electrophiles resulting in the formation of either C- or N-derivatives depending on the electrophile structure. However, there is no information on transformations of the cyanacetic ester carbanions that would involve an electrophilic attack at the N-anionic centre of these carbanions. This study reports the dual reactivity of phosphonium zwitterion **3**. Depending on the structure of the electrophile, this zwitterion behaves as an either C- or N-nucleophile (structures **3a** and **3b**, respectively).

The attack of 2,4-dinitrofluorobenzene (DNFB) by the C-anionic centre of zwitterion **3a** led to the polyconjugated heptatrienide **5** and ethyl fluoroformate. The structure of compound **5** was established by IR and NMR (¹H, ¹³C, ³¹P)² spectroscopy and X-ray diffraction.⁶ The formation of phosphonio heptatrienide zwitterion **5**⁺ seems to include an intramolecular attack of the C(O)OEt group by the fluorine atom.

Most likely, this is the CN group that weakens the C–C(O)OEt bond in σ complex **4**. This effect of the CN group leads to the rupture of the weakened C–C bond between the α -C atom and the C(O)OEt moiety. The formation of ethyl fluoroformate in this reaction was established by IR and NMR (¹H, ¹⁹F) spectroscopy.² The lengthening of the conjugation chain due to the attachment of the CN group to the carbon atom bearing a double bond is, most likely, the driving force of the process. However, contrary to the reaction between zwitterion **3** and DNFB, zwitterion **3** reacts with 2,4,6-trinitrofluorobenzene (TNFB) with the formation of N-derivative **7**⁺ (Scheme 2).

At 3 °C, according to ³¹P and ¹⁹F NMR spectroscopic data, the reaction between zwitterion **3** and TNFB in CH₂Cl₂ quantitatively affords the only product, *i.e.*, a crystalline dark red phosphorus-containing compound. Elemental analysis (H, C, N, F and P) and IR, UV and NMR (¹H, ¹³C, ¹⁹F and ³¹P) spectra provided evidence that the resulting compound is zwitterion **7** with a conjugated azaoctatetraene anionic moiety.

The structure of zwitterion **7** was established by a single-crystal X-ray diffraction analysis (Figure 1).[‡]

[‡] 1-(1-Cyano-2-triisopropylphosphonioethylidene)-2,4-dinitrocyclohexadienide **5** was obtained as described previously.²

2-Ethoxycarbonyl-3-fluoro-1-triisopropylphosphoniopropenylimino-(2,6-dinitro-4-acinitrocyclohexa-2,5-dienide) **7**. A solution of TNFB (0.4 g, 1.73 mmol) in CH₂Cl₂ (15 ml) was added dropwise with stirring to a solution of zwitterion **3** (0.49 g, 1.73 mmol) in CH₂Cl₂ (30 ml) under nitrogen at 3 °C. The solution immediately turned red, the colour intensity increased with time. The solvent was removed in a vacuum. Black powder product was obtained with a yield of 0.88 g (98.8%), mp 138–140 °C. After recrystallization from an acetonitrile–Et₂O–CCl₄ mixture, sparkling dark red crystals were obtained in 80–90% yield, mp 150–152 °C. ¹H NMR (CDCl₃, 400.13 MHz) δ : 1.26 (t, 3H, MeCH₂O, ³J_{HH} 7.1 Hz), 1.48 (ddd, 18H, Me₂CH, ³J_{PH} 14.5 Hz, ³J_{HH} 6.9 Hz), 2.84 (d, sept, 3H, Me₂CH, ²J_{PH} 14.5 Hz, ³J_{HH} 6.9 Hz), 3.46 (d, 2H, CH₂P⁺, ²J_{PH} 10.6 Hz), 4.17 (q, 2H, MeCH₂O, ³J_{HH} 7.1 Hz), 8.65 (s, 2H, H_{arom}). ¹³C NMR (CDCl₃, 100.68 MHz) δ : 14.6 (MeCH₂O), 17.2 (d, MeCHP, ²J_{CP} 3.7 Hz), 19.7 (d, CH₂P, ¹J_{CP} 45.5 Hz), 21.4 (d, CHP, ¹J_{CP} 39.6 Hz), 24.6 (d, N=C, ³J_{CF} 60.8 Hz), 60.1 (MeCH₂O), 123.5 (CHAr), 133.4 (*p*-O₂NC), 141.8 (CH₂C), 143.6 (*o*-O₂NC), 160.9 (dd, CF, ¹J_{CF} 314.5 Hz, ³J_{CP} 5.1 Hz), 168.9 (d, C=O, ³J_{CP} 7.3 Hz). ³¹P NMR (CDCl₃, 161.68 MHz) δ : 41.46 (P–C–C=C–F, ⁴J_{PF} 8.5 Hz). ¹⁹F NMR (CDCl₃, 282.4 MHz) δ : –61.59 (P–C–C=C–F, ⁴J_{FP} 8.5 Hz). IR (KBr pellets, ν /cm^{–1}): 1645 (ν_{COEt}), 1552 (conjugate bonds system), 1298 (ν_{asNO_2}). UV (acetone, λ_{max}/nm): 455.5 (ϵ 21500). Found (%): C, 48.69; H, 5.90; N, 10.94; P, 5.73; F, 3.44. Calc. for C₂₁H₃₀N₄O₈PF (%): C, 48.83; H, 5.81; N, 10.85; P, 6.01; F, 3.68.

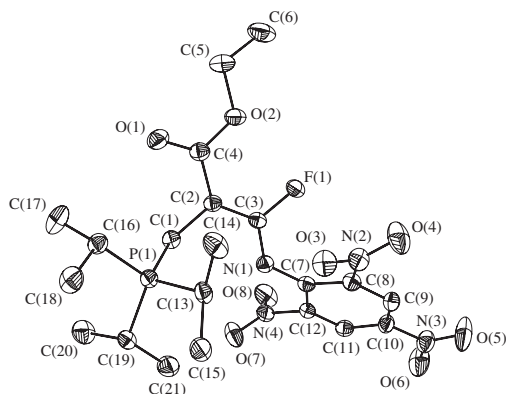


Figure 1 The crystal structure of **7** (50% ellipsoids); hydrogen atoms are omitted for clarity. Selected bond lengths (Å): F(1)–C(3) 1.358(3), O(1)–C(4) 1.216(3), N(1)–C(3) 1.317(3), N(1)–C(7) 1.342(3), N(2)–C(8) 1.468(3), N(3)–C(10) 1.456(3), N(4)–C(12) 1.476(3), C(2)–C(3) 1.366(3), C(2)–C(4) 1.445(3), C(7)–C(8) 1.421(3), C(7)–C(12) 1.430(3), C(8)–C(9) 1.380(3), C(9)–C(10) 1.373(4), C(10)–C(11) 1.387(3), C(11)–C(12) 1.355(3).

The molecule comprises of two planar moieties [O=C–C=C(F)–N and N=C(7)–C(12)] with a dihedral angle of 44.0°. A negative charge leads to the substantial redistribution of bond lengths in the trinitroaniline moiety: the C(11)–C(12) bond

in the trinitroaniline fragment is shorter than the C(8)–C(9), C(9)–C(10) and C(10)–C(11) bonds, and the C(12)–N(4) bond is longer than the other C_{ar}–NO₂ bonds, and the C(10)–N(3) bond is the shortest among them. Moreover, the *para*-nitro group is twisted from the aniline plane by only 6.8°, whereas while the *ortho*-nitro group at the C(8) atom is twisted by 34.1°, the *ortho*-nitro group at the C(12) atom is twisted by 62.1°. Apparently, because of a considerable contribution of the *para*-quinoid structure to the total molecular structure of **7**, the colour of this compound is deeper (almost black) than that of 2,4,6-trinitroaniline N-substituted derivatives (shades of red).

Zwitterion **3** seems to react with TNFB as mesomeric N-nucleophile **3b** but not as C-nucleophile **3a**. In the resulting σ complex **6**, the fluoride ion migrates to the electrophilic carbon atom of the ketene imine group giving zwitterion **7**, in which the negative charge is delocalised in the unsaturated bond system. Apparently, the formation of the conjugated system in zwitterion **7** is the main driving force of this unusual transformation (Scheme 2).

It is possible to explain this behaviour of zwitterion **3** with respect to TNFB as compared to DNFB by the steric effect of the second *ortho*-NO₂ group. Clearly, the approach of the C-anionic centre of zwitterion **3a** to the C–F bond should be sterically hindered. At the same time, the nitrogen atom of mesomeric zwitterion form **3b** should lack similar steric limitations. The steric effect of *ortho* substituents was also observed in the reaction of zwitterion **3** with substituted ArNCO.⁷

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[‡] Crystallographic data for zwitterion **7**. Crystals of C₂₁H₃₀N₄O₈FP (*M* = 516.46) are triclinic, space group *P* $\bar{1}$, at *T* = 270(2) K: *a* = 8.3595(10), *b* = 8.6016(11) and *c* = 17.474(2) Å, α = 89.486(5)°, β = 86.965(5)°, γ = 84.304(5)°, *V* = 1248.5(3) Å³, *Z* = 2, *F*(000) = 544, *d*_{calc} = 1.374 g cm^{−3}, μ = 0.170 mm^{−1}. The unit cell parameters and intensities of 12517 reflections were measured on an automated Bruker SMART 1000 CCD diffractometer [λ (MoK α) radiation, graphite monochromator, φ and ω -scanning techniques, θ_{\max} = 28°]. The absorption correction was applied using the SADABS program.⁸ The structure was solved by direct methods and refined by a full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and refined within the riding model with fixed isotropic displacement parameters. The final *R* factors were as follows: *R*₁ = 0.0568 for 3633 independent reflections with *I* > 2 σ (*I*) and *wR*₂ = 0.1515 for all 5917 independent reflections, GOF = 1.003. All calculations were carried out using the SHELXTL PLUS software (Version 5.10).⁹

CCDC 634446 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.

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