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Unusual synthesis of phosphorus-containing 1,3-oxazine-2,4-dione of zwitter-ionic structure by the N-reaction of cyano-carbanion with 2,4,6-trinitrofluorobenzene

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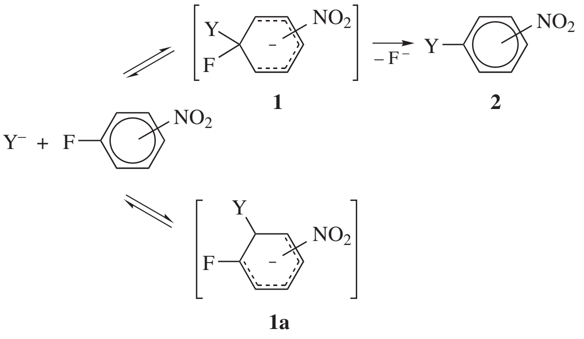
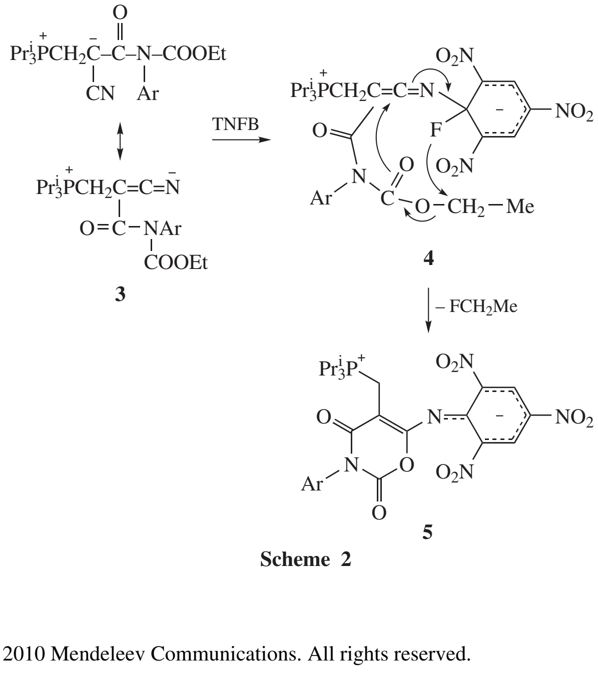
A phosphonium zwitterion containing a carbamate moiety is a cyano-carbanion, and it reacts with 2,4,6-trinitrofluorobenzene as an N-nucleophile to form substituted oxazine-2,4-dione and ethyl fluoride.

As a rule, the nucleophilic aromatic substitution of the fluorine atom in nitrofluorobenzenes occurs *via* the formation of σ-complexes **1a**, **1**[1] (Scheme 1).



Scheme 1

The transformations of σ^F-complexes **1** include elimination of the fluoride ion to give new aromatic compounds **2**. Previously,[2–6] we described unusual cases of the nucleophilic aromatic substitutions of fluorine atoms in polynitrofluorobenzenes. These investigations consider the 'nonconventional' chemistry of σ^F-complexes including reactions of nucleophilic aromatic substitution of fluorine in polynitrofluorobenzenes, which result in the polyconjugated structures rather than aromatic compounds.



Scheme 2

Here, we report a new unexpected example of cyano-carbanion N-reactivity concerning substitution of fluorine in 2,4,6-trinitrofluorobenzene. P-zwitterion containing a carbamate moiety **3** was used as a cyano-carbanion. The reaction of **3** with 2,4,6-trinitrofluorobenzene led to an unusual result. Substituted oxazine-2,4-dione **5** and ethyl fluoride were obtained. It is possible to assume that the transformation of intermediate **4** in oxazine **5** took place according to Scheme 2. However, the scheme of a cycle **5** formation seems to be more complex because the ^{19}F and ^{31}P NMR spectral monitoring of the reaction mass shows that, in the course of the reaction (for about two weeks), the signals appear and disappear periodically, which may be assigned to the intermediates that have not been identified yet. The IR, UV, ^{1}H and ^{13}C NMR spectra and X-ray diffraction analysis

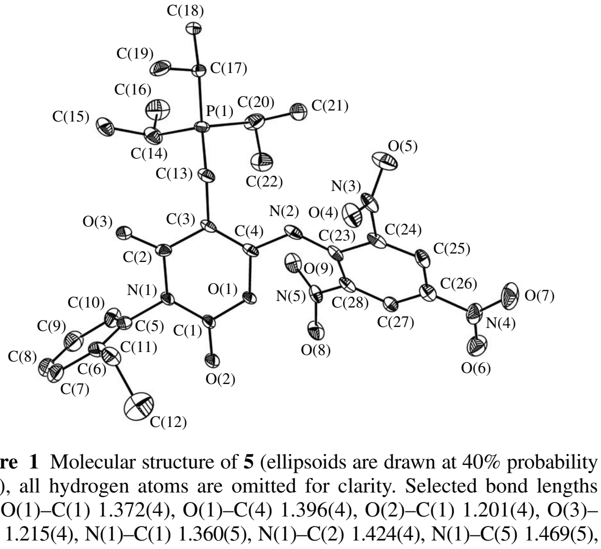


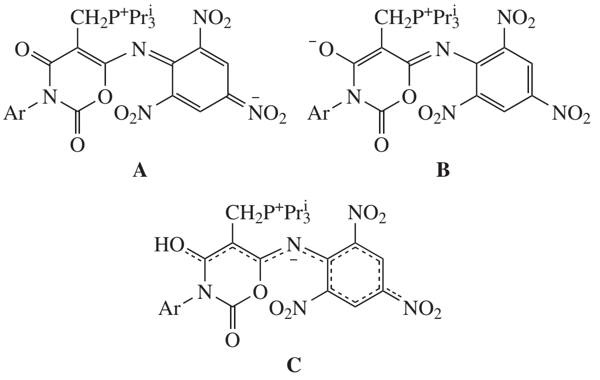
Figure 1 Molecular structure of **5** (ellipsoids are drawn at 40% probability level), all hydrogen atoms are omitted for clarity. Selected bond lengths (Å): O(1)–C(1) 1.372(4), O(1)–C(4) 1.396(4), O(2)–C(1) 1.201(4), O(3)–C(2) 1.215(4), N(1)–C(1) 1.360(5), N(1)–C(2) 1.424(4), N(1)–C(5) 1.469(5), N(2)–C(4) 1.321(4), N(2)–C(23) 1.343(5), N(3)–C(24) 1.474(4), N(4)–C(26) 1.443(5), N(5)–C(28) 1.467(4), C(2)–C(3) 1.432(4), C(3)–C(4) 1.365(5), C(3)–C(13) 1.506(4), C(23)–C(28) 1.424(4), C(23)–C(24) 1.428(4), C(24)–C(25) 1.353(5), C(25)–C(26) 1.389(5), C(26)–C(27) 1.387(5), C(27)–C(28) 1.377(5); selected bond angles (°): C(1)–O(1)–C(4) 123.3(3), C(1)–N(1)–C(2) 124.3(3), C(4)–N(2)–C(23) 125.6(3), N(1)–C(1)–O(1) 116.7(3), N(1)–C(2)–C(3) 115.6(3), C(4)–C(3)–C(2) 120.7(3), C(3)–C(4)–O(1) 119.2(3), C(28)–C(23)–C(24) 111.6(3), C(25)–C(24)–C(23) 126.5(3), C(24)–C(25)–C(26) 117.5(3), C(27)–C(26)–C(25) 121.3(3), C(28)–C(27)–C(26) 118.7(3), C(27)–C(28)–C(23) 124.2(3).

(Figure 1) confirm that the reaction gives a compound having a polyconjugated negatively charged moiety **5**.[†]

The molecular structure of **5** was unambiguously established by single-crystal X-ray diffraction analysis (Figure 1).[‡]

Compound **5** is a zwitterion, with the positively charged phosphonium $–CH_2–P^+Pr^i_3$ fragment and the negative charge localized over long chain of the conjugated bonds. (Structure **C**, Figure 2). It crystallizes in the monoclinic space group $P2_1/c$, with two crystallographically independent molecules in the unit cell. The two independent molecules are distinguished by only conformations of the ethyl groups, while their main skeleton remained practically unchanged. Therefore, only the average values of the geometric parameters of **5** are discussed below.

As it can be suggested from the X-ray data (Figure 1), compound **5** has two preferred resonance forms **A** and **B** presented in Figure 2. The presence of the resonance form **A** is also confirmed by the fact that the *para*-nitro group is almost coplanar to the C(23)–C(24)–C(25)–C(26)–C(27)–C(28) ring [the C(27)–C(26)–N(4)–O(6) torsion angle is –11.9(5)°], whereas the *ortho*-nitro groups [for value of the C(23)–C(24)–N(3)–O(4) torsion angle, see above, and the C(23)–C(28)–N(5)–O(9) torsion angle is 38.1(4)°] are substantially turned towards the same ring.



A **B**

C

Figure 2

The planar structure of the central heterocycle is determined by the extended system of conjugated bonds within the molecule of **5**. As a consequence, the N(1) atom adopts the trigonal-planar configuration [sum of the bond angles at N(1) is 360°]. The (*ortho*-ethyl)phenyl C(5)–C(6)–C(7)–C(8)–C(9)–C(10) and (2,4,6-trinitro)phenyl C(23)–C(24)–C(25)–C(26)–C(27)–C(28) rings are turned by 87.1(4) and 31.4(6)°, respectively, relative to the central ring due to the steric reasons.

The crystal packing of molecules in **5** is stacking along the *a* axis. In the crystal, the molecules are bound by weak intermolecular C–H···O hydrogen bonds.

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[†] A solution of 2,4,6-trinitrofluorobenzene (TNFB) (0.116 g, 0.52 mmol) in CH_2Cl_2 (15 ml) was added dropwise with stirring to a solution of a zwitter-ion **3**[7] (0.210 g, 0.52 mmol) in CH_2Cl_2 (15 ml). The solution immediately turned red; the colour intensity increased with time. A solution left in the closed vessel for 13 days; then, reaction mass was analyzed for P,F-containing compounds by ^{19}F and ^{31}P NMR spectroscopy. In the ^{19}F NMR spectrum, a signal at –211 ppm was found. In the ^{31}P NMR spectrum, the main signal was at 42.2 ppm. A volatile matter was removed from the reaction mass at 30 °C and normal pressure and collected in a cooled up to –40 °C CCl_4 solution. In the solution obtained, ^{19}F NMR fixed a signal of C_2H_5F at –211 ppm. After removal of CH_2Cl_2, brown powder was cristallized from acetone (60% yield). The subsequent crystallization from ethyl acetate gave red crystals of compound **5**, mp 245 °C. ^{1}H NMR ([$^2H_6$]DMSO, 600.220 MHz) (for numeration of atoms hereinafter, see Figure 1) δ: 7.277 [m, H-C(9)], 7.120 [d, H-C(10)], 3.360 [d, H-C(13), $^2J_{HP}$ 11.8 Hz], 2.859 [ds, H-C(14), H-C(17), H-C(20), $^3J_{HH}$ 7.2 Hz, $^2J_{HP}$ 12.9 Hz], 1.355 and 1.359 [2dd, H-C(15), H-C(16), H-C(18), H-C(19), H-C(21), H-C(23), $2\times{}^3J_{HH}$ 7.2 Hz, $2\times{}^3J_{HP}$ 15.64 Hz], 8.806 [H-C(25), H-C(27)], 2.370 [q, AB-system, H-C(11), $^2J_{HH}$ 14.5 Hz, $^3J_{HH}$ 7.6 Hz], 1.085 [t, H-C(12), $^3J_{HH}$ 7.6 Hz]. ^{13}C NMR ([$^2H_6$]DMSO, 150.925 MHz): 146.85 [C(1)], 163.34 [C(2)], 79.83 [d, C(3), ^2J 5.8 Hz], 157.48 [d, C(4), ^3J 3.6 Hz], 141.54 [C(5)], 134.8 [C(6)], 129.40, 129.42 [C(7), C(8)], 129.47 [C(9)], 127.17 [C(10)], 23.79 [C(11)], 14.59 [C(12)], 14.25 [d, C(13), ^1J 21.8 Hz], 21.21 [d, C(14), C(17), C(20), ^1J 39.3 Hz], 16.86 [d, C(15), C(16), C(18), C(19), C(21), C(22), ^2J 2.9 Hz], 135.11 [C(23)], 143.68 [C(24), C(28)], 123.87 [C(25), C(27)], 141.67 [C(26)], 23.79 [C(12)], 14.59 [C(27)]. IR (KBr, pellets, ν/cm^{-1}): 1752 ($\nu_{C(O)O}$), 1667 ($\nu_{C(O)N}$), 1560 (conjugate bond system), 1309 ($\nu_{as\ NO_2}$). UV (acetone, λ_{max}/nm): 444.5 (ε 10000). Found (%): C, 54.29; H, 5.55; N, 11.27; P, 4.96. Calc. for $C_{28}H_{34}N_5O_9P$ (%): C, 54.63; H, 5.53; N, 11.38; P, 5.04.

[‡] *Crystallographic data*. The crystal of **5** ($C_{28}H_{34}N_5O_9P$, $M = 615.57$) is monoclinic, space group $P2_1/c$, at $T = 100$ K: $a = 15.8691(15)$, $b = 19.1186(17)$ and $c = 20.2680(18)$ Å, $\beta = 109.873(1)°$, $V = 5783.0(9)$ Å^3, $Z = 8$, $d_{calc} = 1.414$ g cm^{-3}, $F(000) = 2592$, $\mu = 0.158$ mm^{-1}. Data were collected on a Bruker SMART APEX II CCD diffractometer [λ(MoKα)-radiation, graphite monochromator, ω and φ scan mode] and corrected for absorption using the SADABS program.[8] The structure was solved by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [$U_{iso}(H) = 1.5U_{eq}(C)$ for the Me groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for the other groups]. The final divergence factors were $R_1 = 0.097$ for 7750 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.233$ for all 11147 independent reflections, $S = 1.016$. All calculations were carried out using the SHELXTL program.[9]

CCDC 741943 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, 2010.