Letters to the Editor

Intramolecular 1,3-C—C migration of fluorine in a σ complex formed by 2,4,6-trinitrofluorobenzene and the P-zwitterion

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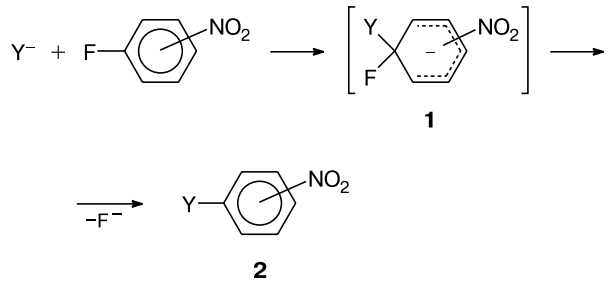
According to the kinetic data, isotope effects, and IR, UV, and NMR spectra, the nucleophilic aromatic displacement of the fluorine atom in nitrofluorobenzenes occurs, as a rule, by a two-step mechanism involving the formation of unstable intensely colored σ complexes **1** in the first step[1] (Scheme 1).

Scheme 1



All known transformations of σ complexes **1** involve elimination of the fluoride ion giving rise to new aromatic compounds **2**. As part of our ongoing studies of aromatic nucleophilic substitution, *i.e.*, displacement of the fluorine atom in nitrofluorobenzenes,[2,3] we performed the reaction of 2,4,6-trinitrofluorobenzene with P-zwitterion **3**.[4] At 3 °C, the reaction in CH_2Cl_2 affords the only (^{31}P and ^{19}F NMR spectroscopic data) crystalline dark-red phosphorus-containing compound in quantitative yield. Elemental analysis, (H, C, N, F, and P), IR, UV, and NMR (^1H, ^{13}C, ^{19}F, and ^{31}P) spectra, and X-ray diffraction data provided evidence that the resulting compound is zwitterion **5**, whose anionic moiety has the azaoctatetraene structure. Apparently, zwitterion **3** reacts with 2,4,6-trinitrofluorobenzene not as the C-nucleophile but as the mesomeric N-nucleophile. In the resulting σ complex **4**, the fluoride ion migrates to the electrophilic carbon atom of the ketene imine group giving rise to zwitterion **5**, in which the negative charge is delocalized in the [O—C—C—C—N—C—C—C—C—N—O]$^-$ bond system. The formation of the conjugated system is, apparently, the main driving force of this unusual transformation (Scheme 2).

The ^{31}P (162.02 MHz) and ^{19}F (282.4 MHz) NMR spectra show only doublets (δ_P 41.46, $^4J_{P,F}$ = 8.5 Hz, and δ_F −61.59 relative to $CFCl_3$, $^4J_{F,P}$ = 8.5 Hz). The ^{13}C NMR spectrum has a signal for the key carbon atom at δ_C 160.9 with the spin-spin coupling constants $^1J_{C,F}$ = 314.5 Hz and $^3J_{C,P}$ = 5.1 Hz (the spectrum was recorded on an AVANCE instrument operating at 100.68 and 150.925 MHz). The three-dimensional structure of product **5** was determined by X-ray diffraction and will be described in a special publication.

Therefore, we found the first transformation of σ complexes, which are formed by the nucleophilic aromatic

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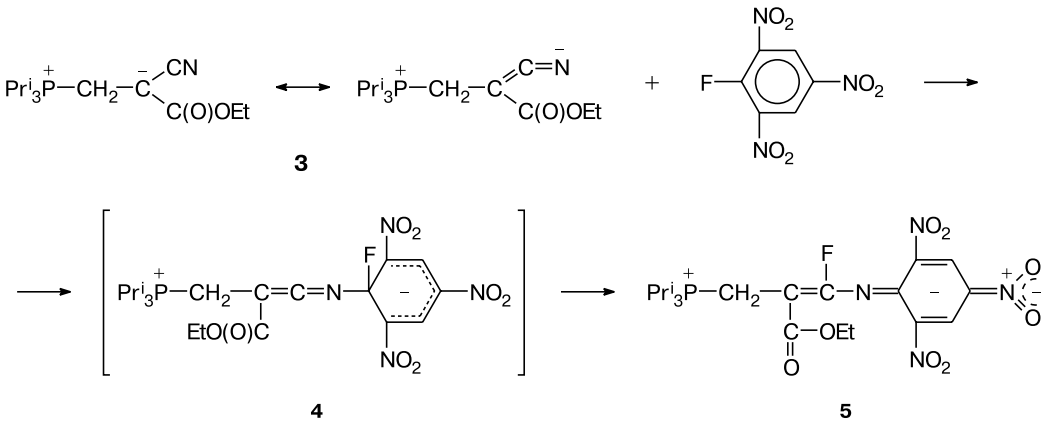
Scheme 2



displacement of the fluorine atom, where the fluorine atom is not eliminated as the fluoride anion but intramolecularly migrates to give highly conjugated negatively charged azaoctatetraene structure **5**.

2-Ethoxycarbonyl-3-fluoro-1-triisopropylphosphonioprop-2-enylimino-(2,6-dinitro-4-*aci*-nitrocyclohexa-2,5-dienide) (5).* A solution of 2,4,6-trinitrofluorobenzene (0.4 g, 1.73 mmol) in CH_2Cl_2 (15 mL) was added dropwise with stirring to a solution of zwitterion **3** (0.49 g, 1.73 mmol) in CH_2Cl_2 (30 mL) under nitrogen at 3 °C. The solution immediately turned red, the intensity of the color increasing with time. The solvent was removed *in vacuo*, and a black powder was obtained in a yield of 0.88 g (98.8%), m.p. 138—140 °C. After recrystallization from an acetonitrile—diethyl ether—CCl_4 mixture, sparkling dark-red crystals were obtained in 80—90% yield, m.p. 150—152 °C. Found (%): C, 48.69; H, 5.90; N, 10.94; P, 5.73; F, 3.44. $C_{21}H_{30}N_4O_8PF$. Calculated (%): C, 48.83; H, 5.81; F, 3.68; N, 10.85; P, 6.01. IR (KBr pellets): ν(COOEt) 1645 cm^{-1}; $\nu_{as}(NO_2)$ 1298 cm^{-1}. UV (acetone), λ_{max} 455.5 nm (ε 21500). ^1H NMR ($CDCl_3$, 400.26 MHz), δ: 1.26 (t, 3 H, $C\underline{H}_3CH_2O$, $^3J_{H,H}$ = 7.1 Hz); 1.48 (ddd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H}$ = 14.5 Hz, $^3J_{H,H}$ = 6.9 Hz); 2.84 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H}$ = 14.5 Hz, $^3J_{H,H}$ = 6.9 Hz); 3.46 (d, 2 H, CH_2P^+, $^2J_{P,H}$ = 10.6 Hz); 4.17 (q, 2 H, $CH_3C\underline{H}_2O$, $^3J_{H,H}$ = 7.1 Hz); 8.65 (s, 2 H, H_{arom}). ^{13}C NMR ($CDCl_3$, 100.68 MHz), δ: 14.6 ($\underline{C}H_3CH_2O$); 17.2 (d, $\underline{C}H_3CHP$, $^2J_{C,P}$ = 3.7 Hz); 19.7 (d, CH_2P, $^1J_{C,P}$ = 45.5 Hz); 21.4 (d, CHP, $^1J_{C,P}$ = 39.6 Hz); 24.6 (d, N=C, $^3J_{C,F}$ = 60.8 Hz); 60.1 ($CH_3\underline{C}H_2O$); 123.5 (CH_{Ar}); 133.4 (C_p—NO_2); 141.8 ($CH_2\underline{C}$); 143.6 (C_O—NO_2); 160.9 (dd, CF, $^1J_{C,F}$ = 314.5 Hz, $^3J_{C,P}$ = 5.1 Hz); 168.9 (d, C(O), $^3J_{C,P}$ = 7.3 Hz).

X-ray diffraction study of compound 5. Crystals of zwitterion **5** ($C_{21}H_{30}N_4O_8FP$, M = 516.46) are triclinic, space group $P\bar{1}$, at T = 270 K a = 8.3595(10), b = 8.6016(11), c = 17.474(2) Å, α = 89.486(5), β = 86.965(5), γ = 84.304(5)°, V = 1248.5(3) $Å^3$, 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 (T = 120 K, λMo-Kα radiation, graphite monochromator, φ- and ω-scanning techniques, θ_{max} = 28°). The absorption correction was applied using the SADABS program.[5] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and refined isotropically with fixed positional (a riding model) and thermal parameters (U_{iso}(H) = 1.5U_{eq}(C) for CH_3 groups and U_{iso}(H) = 1.2U_{eq}(C) for all other groups). The final R factors were as follows: R_1 = 0.0568 for 3633 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.1515 for all 5917 independent reflections. All calculations were carried out with the use of the SHELXTL PLUS (Version 5.10) program package.[6] The tables of atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters for compound **5** were deposited with the Cambridge Structural Database.

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* The name of one of the mesomeric forms is given.