Novel nucleophilic aromatic substitution of the fluorine atom yielding a stable heptatrienide structure

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C-Nucleophilic aromatic displacement of the halogen atom from 1-halo-2,4-dinitrobenzenes gives a novel aromatic system due to decomposition of an intermediate σ-complex.[1]

However, betaine derivative **1** [2] containing a carbanion and a phosphonium fragment reacts with 1-fluoro-2,4-dinitrobenzene (Scheme 1) to give a zwitter-ion **3** containing a highly conjugated and negatively charged heptatrienide fragment as the major product rather than an aromatic compound.

A "normal" arylation product of zwitter-ion **1** was also isolated from the reaction mixture in low yield.

Presumably, zwitter-ion **3** is formed as the result of decomposition of σ-complex **2** involving an intra- or intermolecular interaction of the F atom with the carbonyl C atom of the ester group, which results in cleavage of the weakened C—C bond (*cf.* Ref. 3) to give ethyl fluoroformate identified by ^{1}H and ^{19}F NMR and IR spectroscopy. The structure of compound **3** was proved by elemental analysis, IR, UV, and NMR spectroscopy, X-ray diffraction analysis, and chemical transformations. According to these data, the negative charge in zwitter-ion **3** is delocalized over the system of bonds $[N—C—C—C—C—C—C—N—O]^-$. Apparently, the formation of such a highly conjugated system is a driving force of the formation of zwitter-ion **3**.

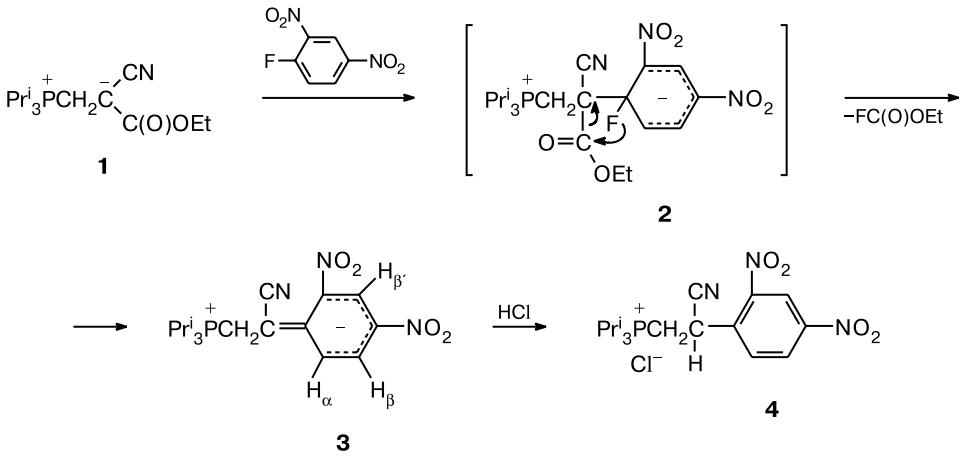
Protonation of a dark cherry solution of zwitter-ion **3** in CH_2Cl_2 with an ethereal solution of HCl instantaneously gave colorless phosphonium salt **4**. The structure of salt **4** was unambiguously proved by ^{1}H and ^{31}P NMR and IR spectroscopy.

The described example of the formation of the highly conjugated system **3** is probably a special case of a novel general reaction involving both various electrophilic fluoroaromatic compounds and zwitter-ions of the type **1** in which a functional group in the α-position is loosely bound to the carbon atom.

NMR spectra were recorded on a Bruker AMX-400 instrument (400.1 (^{1}H), 282.4 (^{19}F), and 162.0 MHz (^{31}P)). IR spectra were recorded on a Magna-IR-750 FTIR spectrometer (Nicolet).

1-(1-Cyano-2-triisopropylphosphonioethylidene)-2,4-dinitrocyclohexadienide (3). A solution of 1-fluoro-2,4-dinitrobenzene (3.25 g, 17.5 mmol) in CH_2Cl_2 or MeCN (25 mL) was added dropwise in an atmosphere of N_2 at 3—5 °C to a stirred solution of betaine **1** (5.0 g, 17.5 mmol) in the same solvent (75 mL). The reaction mixture turned dark cherry. After two days, light petroleum (100 mL) was added and the crystalline residue was filtered

Scheme 1



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off and washed with CCl_4. The resulting bright, nearly black crystals were repeatedly washed with cold acetone. The yield of compound **3** was 36%, m.p. 158—159 °C (from nitromethane). Found (%): C, 56.97; H, 6.98; N, 11.07. $C_{18}H_{26}N_3O_4P$. Calculated (%): C, 56.99; H, 6.86; N, 11.08. ^{1}H NMR (DMSO-d_6), δ: 1.38 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H}$ = 15.6 Hz, $^3J_{H,H}$ = 7.2 Hz); 2.88 (dsept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H}$ = 12.4 Hz, $^3J_{H,H}$ = 7.2 Hz); 3.72 (d, 2 H, CH_2P, $^2J_{P,H}$ = 11.6 Hz); 7.12 (d, 1 H, H_α, $^3J_{H,H}$ = 7.2 Hz); 7.54 (dd, 1 H, H_β, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 2.8 Hz); 8.32 (d, 1 H, $H_{\beta'}$, $^4J_{H,H}$ = 2.8 Hz). ^{31}P NMR (DMSO-d_6), δ: 44.44. IR (Nujol), ν/cm^{-1}: 2160 (CN); 1592 (conjugated hexadiene system); 1320, 1216 (NO_2). UV (acetone), λ_{max}/nm (ε): 478 (34 000).

In an analogous experiment, the solvent and volatile substances were removed from the reaction mixture and ethyl fluoroformate was identified by NMR and IR spectroscopy. ^{1}H NMR ($CDCl_3$), δ: 1.33 (dt, 3 H, $^3J_{H,H}$ = 9.2 Hz, $^5J_{H,F}$ = 1.2 Hz); 4.29 (dq, 2 H, CH_2O, $^3J_{H,H}$ = 9.2 Hz, $^4J_{H,F}$ = 0.8 Hz). ^{19}F NMR ($CDCl_3$, relative to $CFCl_3$), δ: −17.02 (br.s). IR (CH_2Cl_2), ν/cm^{-1}: 1824 (COOEt).

[2-Cyano-2-(2,4-dinitrophenyl)ethyl]triisopropylphosphonium chloride (4). A solution of hydrogen chloride in diethyl ether was added to a dark cherry solution of zwitter-ion **3** (0.05 g, 0.13 mmol) in CH_2Cl_2 (30 mL). The reaction mixture instantaneously became colorless. Then the solvent was removed and the residue was recrystallized from light petroleum—acetone (2 : 1). The powder obtained (0.04 g) was filtered off and washed with ether. The yield of salt **4** was 83%, m.p. 167—169 °C. ^{1}H NMR ($CDCl_3$), δ: 1.57 (ddd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H}$ = 16.3 Hz, $^3J_{H,H}$ = 7.0 Hz); 3.44 (dsept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H}$ = 13.4 Hz, $^3J_{H,H}$ = 7.0 Hz); 3.60 (m, 1 H, $C\underline{H}_AH_BP$); 3.87 (dd, 1 H, $CH_A\underline{H}_BP$, $^2J_{P,H}$ = 14.4 Hz, $^3J_{H,H}$ = 11.4 Hz); 5.67 (d, 1 H, $C\underline{H}CH_2P$, $^3J_{H,H}$ = 11.4 Hz); 8.57 (d, 1 H, H_α, $^3J_{H,H}$ = 7.2 Hz); 8.85 (d, 1 H, $H_{\beta'}$, $^4J_{H,H}$ = 1.7 Hz); 9.20 (d, 1 H, H_β, $^3J_{H,H}$ = 7.2 Hz). ^{31}P NMR ($CDCl_3$), δ: 43.74.

Crystallographic data for structure **3** have been deposited with the Cambridge Crystallographic Database with the additional number CCDC-270207 and can be made free available upon request to: CCDC, 12 Union Road, Cambridge CB2 1EZ UK; fax: +44 (122) 333 6033; e-mail: deposit@ccdc.cam.ac.uk.

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