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New Reaction of Pyridinium Ylide With 2,4,6-Trinitrofluorobenzene Leading to Stable Heptatrienide Moiety

Yuri G. Gololobov, Olesya A. Linchenko, Pavel V. Petrovskii,
Victor N. Khrustalev, and Irina A. Garbuzova

A.N. Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Science, 119991 M-334, Vavilov Str., 28, Moscow, Russia

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ABSTRACT: *A new reaction of pyridinium ylide (**4**) with 2,4,6-trinitrofluorobenzene leading to stable negatively charged heptatriene moiety (**6**) is described. This reaction proceeds via a new route of decomposition of intermediate σ-complex (**5**) occurring with the formation of ethylfluoroformate.*

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INTRODUCTION

In a previous publication [1], we have described an unusual aromatic nucleophilic substitution reaction. Phosphorus-containing zwitterion **1** bearing ethoxy and cyano groups at the carbanion center forms, upon reaction with 2,4-dinitrofluorobenzene (DNFB), the first example of *P*-zwitterions **3** with a negatively charged heptatriene moiety. This reaction proceeds via a new route of decomposition of the intermediate σ-complex **2** occurring with the formation of ethylfluoroformate (Scheme 1).

It would be very interesting to expand the scope of the reaction to other types of zwitterions and other electron-deficient fluoroarenes. In this work, we report on a new reaction for other type of carbanions, that is, pyridinium ylide derived from malonic ester **4** with 2,4,6-trinitrofluorobenzene (TNFB) leading to stable heptatrienide moiety **6**.

RESULTS AND DISCUSSION

Nucleophilicity of pyridinium ylide **4** is just below the nucleophilicity of zwitterion **2**. This follows from our observation that pyridinium ylide **4** reacts with DNFB very slowly. We will discuss in details the results of the latter reaction in the follow-up publication. Simultaneously, ylide **4** reacts with TNFB in $CDCl_3$ at room temperature very smoothly with the quantitative formation of an almost black powder. The formation of ethylfluoroformate was established by the ^{19}F NMR spectroscopy of the reaction mixture. Most likely, similar to Scheme 1, at the first stage of the reaction (Scheme 2), σ-complex **5** was formed. At the second stage, the rupture of the weak C—C bond between the α-C atom and the —C(O)OEt moiety took place because the presence of second —C(O)OEt group and positively charged nitrogen weakens the C—C(O)OEt bond in the σ-complex **5**. The latter yielded ethylfluoroformate and a new type of zwitterion (**6**).

Correspondence to: Yuri G. Gololobov; e-mail: Yugol@ineos.ac.ru.

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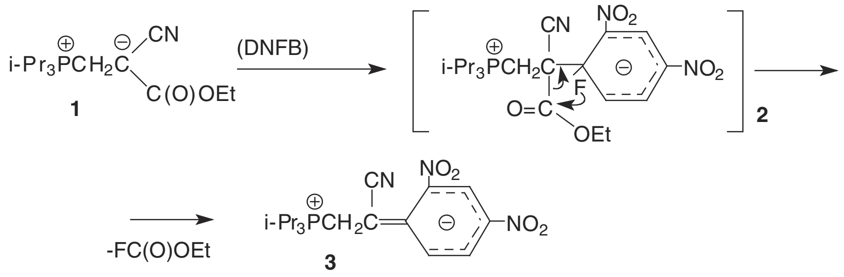
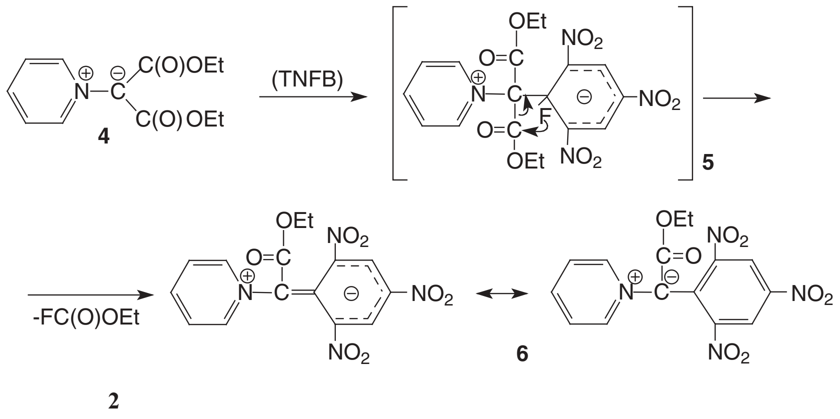


SCHEME 1

Physico-chemical methods confirmed the composition of compound **6**. The structure of zwitterion **6** was established by X-ray diffraction. UV/Vis spectroscopy in acetone showed $\lambda_{max} = 419$ nm ($\varepsilon = 18{,}300$) and 535 nm ($\varepsilon = 24{,}300$). The IR spectrum showed an intense band at 1643 cm^{-1} (COOEt). This suggests a high degree of interaction between the −C(O)OEt group and the negative charge. The IR spectrum also contained intense bands at 1264 cm^{-1} (*para*-NO_2) and 1322 cm^{-1} (*ortho*-NO_2), which could be the result of the formation of a system of conjugated bonds. In the ^1H NMR spectra, the ring protons of zwitterion **6** were shifted upfield in comparison to the aromatic protons of TNFB (8.67 and 9.18 ppm, correspondingly) due to the negatively charged heptatriene fragment. The X-ray diffraction study of **6** has also confirmed its zwitterionic nature (Fig. 1, Table 1).

The molecule consists of a central carbon atom bonded to three planar substituents. The substituents are oriented in a "propeller-like" fashion. The C1—C10 bond length (1.415(2) Å) has an intermediate value between the C_{sp2}—C_{ar} (1.470 Å) and C_{sp2}=C_{sp2} (1.350 Å) bond lengths. Moreover, the distances within the C11—C12—C13—C14—C15 moiety (1.369(3)–1.384(3) Å) are significantly shorter than the C10—C11 (1.433(3) Å) and C10—C15 (1.437(3) Å) linkages, and the C1—C7 bond length (1.441(3) Å) is substantially shorter than the corresponding C_{sp2}—C_{sp2} (1.488 Å) bond length. Furthermore, the *ortho*-NO_2 groups in the 2,4,6-trinitrophenyl substituent turn away from the phenyl ring plane (the dihedral angles between the planes of the *ortho*-NO_2 groups and phenyl ring are 35.2° and 44.1°), while the *para*-NO_2 group is almost coplanar to this plane (the corresponding dihedral angle is 2.6°). The N3—C13 distances (1.452(2) Å) are shorter than the N2—C11 (1.469(2) Å) and N4—C15 (1.477(2) Å) linkages. The bond length distribution within the 2,4,6-trinitrophenyl fragment clearly indicates a considerable contribution of the quinoid resonance form.

Thus, the data obtained unequivocally point out to a bipolar character of molecule **6**; the negative charge is delocalized over the fragment that includes the C(1)—C(10) bond, the C11—C12—C13—C14—C15 moiety, and *para*-NO_2 group, whereas the positive charge is localized on the N1 nitrogen atom.



SCHEME 2

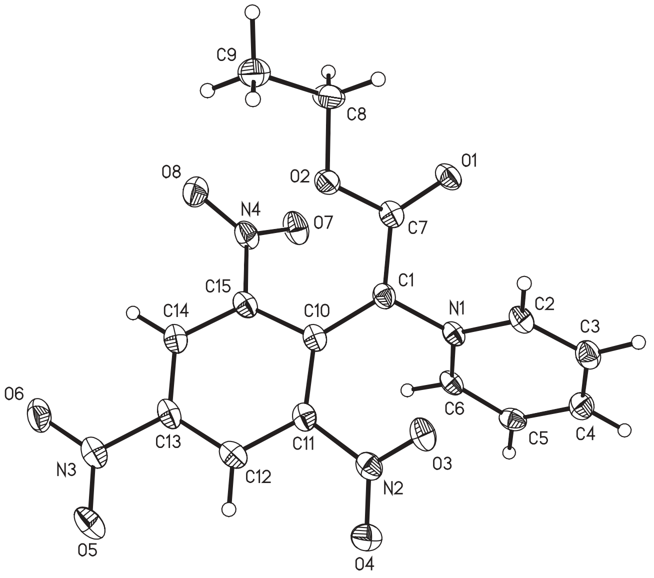


FIGURE 1 Molecular structure of **6** along with the atom labeling scheme.

TABLE 1 Crystal Data and Structure Refinement for **6**

Molecular formula	$C_{15}H_{12}N_4O_8$
Molecular weight	376.29
Temperature	100.0(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 24.360(2)$ Å $b = 7.4337(7)$ Å $c = 17.9945(17)$ Å $\beta = 106.088(5)°$
Volume	3130.9(5) Å^3
Z	8
Density (calculated)	1.597 mg/m^3
Absorption coefficient	0.132 mm^{-1}
F(0 0 0)	1552
Crystal size	$0.30 \times 0.24 \times 0.04$ mm^3
θ range for data collection	1.74° to 26.08°
Index ranges	$-30 \leq h \leq 30$, $-9 \leq k \leq 9$, $-22 \leq l \leq 22$
Reflections collected	13,875
Independent reflections	3055 [R(int) = 0.0426]
Completeness to $\theta = 26.08°$	98.4%
Absorption correction	Semiempirical from equivalents
Maximum and minimum transmission	0.996 and 0.965
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3055/0/244
Goodness-of-fit on F^2	1.011
Final R indices [for 2369 reflections with $I > 2\sigma(I)$]	$R_1 = 0.0396$, $wR_2 = 0.0888$
R indices (all data)	$R_1 = 0.0571$, $wR_2 = 0.0980$
Largest difference peak and hole	0.262 and −0.261 eÅ^{-3}

In our article [1], we reported the first example of nucleophilic aromatic substitution reactions of fluorine atom in a highly electron-deficient arene by 1,3-zwitterion **1**, giving stable heptatriene moiety **3** with conjugated anion. In this article, we describe the second example of this type that gives the similar heptatriene moiety **6**. This allows us to suggest that we have actually discovered a new type of transformation for σ-complexes that leads to the heptatrienic systems. This expands our knowledge of the properties of σ-complexes and enables us to synthesize new perspective synthones.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker spectrometers Avance AMX-400 (^{1}H 400.1 MHz) and Avance AMX-600 (^{13}C 150.9 MHz), δ (ppm), multiplicity, number of protons, reference of protons, J/Hz. The IR spectra were recorded on a Nicolet IR-Fourier-spectrometer Magna-IR-750 (ν/cm^{-1}). UV/Vis spectra were recorded on a Carl Zeiss spectrometer Specord M-40 (nm) (acetone). The reactions were carried out under dry N_2.

1-(Ethoxycarbonylpyridiniomethylidene)-2,4,6-trinitrocyclohexadienide **6**

To the mixture of TNFB (92 mg, 0.4 mmol) and **4** (95 mg, 0.4 mmol), $CDCl_3$ (0.5 mL) was added. The reaction mixture was left for a week. The ^{19}F NMR spectra contained one signal at −16.47 ppm (FC(O)OEt) [1]. Ether was added, and the resulting crystalline black powder was filtered off. Yield: 148 mg (99.3%); mp: 112–115°C. The ^{1}H NMR spectra matched that of compound **6** (see below). The crude product was crystallized twice (CH_3CN and ether mixture); mp 127–128°C. Calcd. for $C_{15}H_{12}N_4O_8$: C, 47.87; H, 3.19; N, 14.89. Found: C, 47.85; H, 3.11; N, 14.89. ^{1}H NMR ($CDCl_3$): 1.22 (t, 3H, $C\mathit{H_3}CH_2O$, $^3J_{\mathrm{HH}} = 7.2$); 4.11 (q, 2H, $CH_3C\mathit{H_2}O$, $^3J_{\mathrm{HH}} = 7.2$); 7.70 (m, 2 H, H_m); 8.04 (t, 1H, H_p, $^3J_{\mathrm{H}p\mathrm{H}m} = 7.2$); 8.27 (d, 2H, H_o, $^3J_{\mathrm{H}o\mathrm{H}m} = 7.2$), 8.67 (s, 2H, CH-C($NO_2$)). ^{13}C NMR ($CDCl_3$): 14.2 ($\mathit{C}H_3CH_2O$); 60.3 ($CH_3\mathit{C}H_2O$); 98.2 ($C_{1\mathrm{Ar}}$); 125.5, 127.0, 130.4 ($CH_{\mathrm{Py}}$); 137.5 ($C_{\mathrm{P}}$-$NO_2$); 140.0 ($CH_m$); 144.6 ($C_o$-$NO_2$); 146.1($\mathit{C}$=$C_{1\mathrm{Ar}}$), 163.1 (CO). IR (KBr): 1264 cm^{-1} (*para*-NO_2), 1322 (*ortho*-NO_2), 1643 (C(O)OMe).

X-Ray Crystal Structure Determination

Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1K CCD detector MoK_α radiation, graphite monochromator,

TABLE 2 Bond Lengths (Å) and Angles (°) for **6**

O(1)—C(7)	1.224(2)	N(4)—C(15)	1.477(2)
O(2)—C(7)	1.346(2)	C(1)—C(10)	1.415(2)
O(2)—C(8)	1.451(2)	C(1)—C(7)	1.441(3)
O(3)—N(2)	1.230(2)	C(2)—C(3)	1.375(3)
O(4)—N(2)	1.228(2)	C(3)—C(4)	1.386(3)
O(5)—N(3)	1.232(2)	C(4)—C(5)	1.385(3)
O(6)—N(3)	1.226(2)	C(5)—C(6)	1.369(3)
O(7)—N(4)	1.234(2)	C(8)—C(9)	1.497(3)
O(8)—N(4)	1.216(2)	C(10)—C(11)	1.433(3)
N(1)—C(2)	1.349(2)	C(10)—C(15)	1.437(3)
N(1)—C(6)	1.363(2)	C(11)—C(12)	1.378(3)
N(1)—C(1)	1.433(2)	C(12)—C(13)	1.375(3)
N(2)—C(11)	1.469(2)	C(13)—C(14)	1.384(3)
N(3)—C(13)	1.452(2)	C(14)—C(15)	1.369(3)
C(7)—O(2)—C(8)	116.71(14)	N(1)—C(6)—C(5)	120.86(17)
C(2)—N(1)—C(6)	119.85(15)	O(1)—C(7)—O(2)	122.48(17)
C(2)—N(1)—C(1)	121.43(16)	O(1)—C(7)—C(1)	125.49(17)
C(6)—N(1)—C(1)	118.72(15)	O(2)—C(7)—C(1)	111.96(15)
O(4)—N(2)—O(3)	123.84(17)	O(2)—C(8)—C(9)	106.91(15)
O(4)—N(2)—C(11)	117.44(16)	C(1)—C(10)—C(11)	126.31(17)
O(3)—N(2)—C(11)	118.65(15)	C(1)—C(10)—C(15)	121.92(17)
O(6)—N(3)—O(5)	123.66(16)	C(11)—C(10)—C(15)	111.76(16)
O(6)—N(3)—C(13)	118.41(16)	C(12)—C(11)—C(10)	124.08(18)
O(5)—N(3)—C(13)	117.93(16)	C(12)—C(11)—N(2)	113.27(16)
O(8)—N(4)—O(7)	124.47(17)	C(10)—C(11)—N(2)	122.33(16)
O(8)—N(4)—C(15)	117.61(16)	C(13)—C(12)—C(11)	119.25(18)
O(7)—N(4)—C(15)	117.81(16)	C(12)—C(13)—C(14)	121.30(17)
C(10)—C(1)—N(1)	119.98(16)	C(12)—C(13)—N(3)	119.03(18)
C(10)—C(1)—C(7)	125.52(16)	C(14)—C(13)—N(3)	119.67(17)
N(1)—C(1)—C(7)	114.47(15)	C(15)—C(14)—C(13)	118.21(18)
N(1)—C(2)—C(3)	121.01(18)	C(14)—C(15)—C(10)	125.22(18)
C(2)—C(3)—C(4)	119.41(18)	C(14)—C(15)—N(4)	113.52(17)
C(5)—C(4)—C(3)	119.21(18)	C(10)—C(15)—N(4)	120.80(16)
C(6)—C(5)—C(4)	119.51(18)		

ϕ and ω scan modes ($\theta_{\max} = 26^\circ$), and corrected for Lorentz and polarization effects and for absorption [3]. The structure was determined by direct methods and refined by a full-matrix least-squares technique on F^2 with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were placed in calculated positions and refined in riding mode with fixed thermal parameters. All calculations were carried out using the SHELXTL PLUS program (PC Version 5.10) [4]. Crystallographic data for **6** have been deposited with the Cambridge Crystallographic Data Center. CCDC No. 609224. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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REFERENCES

[1] Gololobov, Y. G.; Linchenko, O. A.; Petrovskii, P. V.; Starikova, Z. A.; Garbuzova I. A. 2007, 18(1), 108–115.

[2] Gololobov, Yu.; Linchenko, O. A.; Petrovskii, P. V.; Starikova, Z. A.; Garbuzova, I. A. Russ Chem Bull 2005, 54(10) 2471.

[3] Sheldrick, G. M. SADABS, V 2.01, Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS Inc.: Madison, WI, 1998.

[4] Sheldrick, G. M. SHELXTL, V 5.10, Bruker AXS Inc.: Madison, WI, 1998.