Organic Chemistry

Polynitro-substituted *N*-alkylalkaneimidoyl chlorides

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The reaction of α-fluorosubstituted polynitroalkylaldimines with HCl results in replacement of the fluorine atom by a chlorine atom. The hitherto unknown α-chlorosubstituted polynitroalkylaldimines have been obtained, and their X-ray structural investigation has been performed.

Key words: α-chlorosubstituted polynitroalkylaldimines; addition reaction; hydrogen chloride; conformation; lone electron pair.

Attempts to add fluorine, chlorine, or hydrogen chloride at the double bond of α-fluorosubstituted polynitroalkylaldimines (**1**) by passing the above gases through solutions of compounds **1** in acetic acid led to the conclusion[1] that only hydrogen chloride undergoes the reaction under these conditions.

$$\mathrm{X(NO_2)_2C(CH_2)_{\mathit{n}}N{=}CFC(NO_2)_2X} \xrightarrow{\mathrm{HCl}}$$

1a,b

$$\longrightarrow \mathrm{[X(NO_2)_2C(CH_2)_{\mathit{n}}NHC(F)ClC(NO_2)_2X]} \xrightarrow[\mathrm{-HF}]{}$$

$$\longrightarrow \mathrm{X(NO_2)_2C(CH_2)_{\mathit{n}}N{=}CClC(NO_2)_2X}$$

2a,b

a: $n = 1$; X = Me
b: $n = 2$; X = F

However, the reaction gave the products of the replacement of the fluorine atom with a chlorine atom, the hitherto unknown α-chlorosubstituted polynitroalkylaldimines (**2**), rather than the products of the addition of hydrogen chloride to compounds **1**. In our opinion, of the possible alternative ways for the formation of aldimine derivatives **2** (nucleophilic substitution of a fluorine atom by the chlorine atom or electrophilic addition of hydrogen chloride at the double bond followed by elimination of hydrogen fluoride), the second pathway takes place.

Hydrogen chloride dissolved in acetic acid is ionized to a considerable degree,[2] and the attack of a proton at the lone electron pair of the nitrogen atom or at the double bond initiating the second pathway seems preferable to the attack of a chloride ion at the carbon atom bonded to a fluorine atom substituent.

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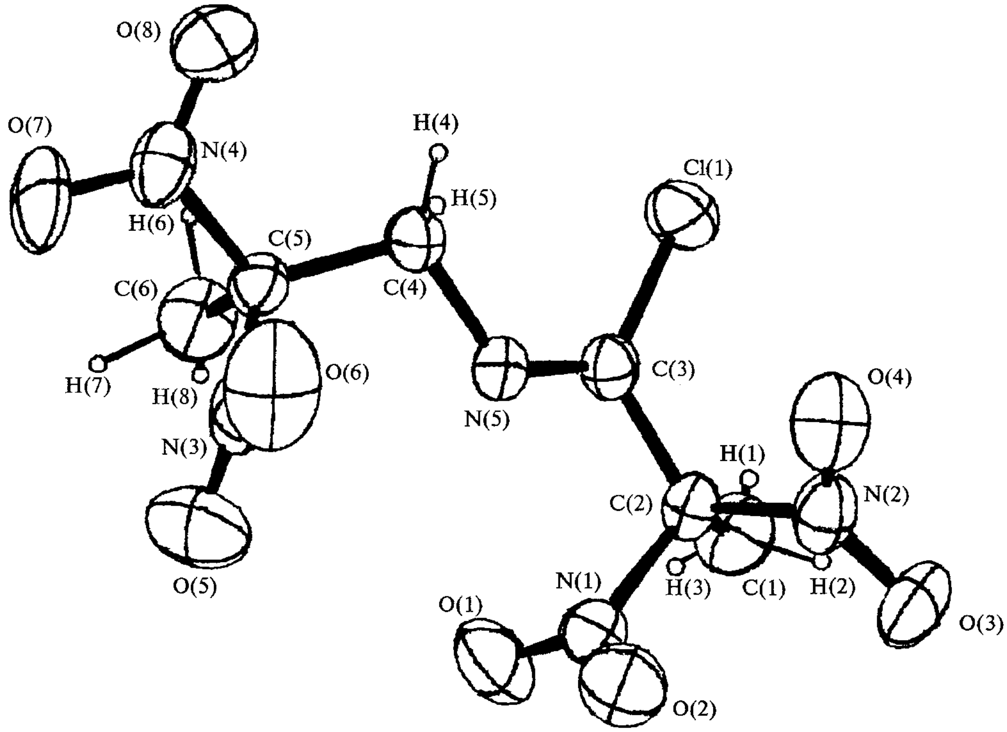

Fig. 1. Molecule of 3-chloro-2,2,6,6-tetranitro-4-aza-3-heptene **2a**.

N-Substituted amides of 2,2-dinitrocarboxylic acids (**3**) are formed as by-products.

$CH_3(NO_2)_2CCH_2NHC(O)C(NO_2)_2CH_3$

3a

$F(NO_2)_2CCH_2CH_2NHC(O)C(NO_2)_2F$

3b

They can be separated from compounds **2** by recrystallization due to their lower solubility in organic solvents. Additional investigations are required to explain the pathway of their formation.

Diethyl ether and methanol turned out to be inappropriate as media for performing the reaction of compounds **1** with hydrogen chloride: the original compounds **1** were returned almost quantitatively after contact with hydrogen chloride.

The molecules of aldimines proved to be convenient objects for studying various types of intramolecular orbital interactions, including the orbitals of the nitro groups, halogen atoms, and the imine nitrogen atom.

The conformation of molecules **2a** and **2b** (Fig. 1, 2) is mainly governed by orbital interactions of the n(N)—π*(NO_2) type between the lone electron pair of the imine nitrogen atoms, *i.e.*, N(5) in compound **2a** and N(3) in **2b**, and the vacant molecular orbital of the nitro groups, *viz.*, the N(1)O(1)O(2) and N(3)O(5)O(6) groups in **2a** or the N(1)O(1)O(2) and N(4)O(5)O(6) groups in **2b**. The distances between N(5) and N(1) (2.613 Å), N(5) and N(3) (2.751 Å) in **2a** or N(3) and N(1) (2.679 Å), N(3) and N(4) (2.942 Å) in **2b**, as well as the torsion angles N(5)C(3)C(2)N(1) (11.0°), C(3)C(2)N(1)O(1) (77.8°), N(5)C(4)C(5)N(3) (54.0°), C(4)C(5)N(3)O(6) (117.6°) in molecule **2a** and N(1)C(1)C(2)N(3) (−13.7°), O(1)N(1)C(1)C(2) (−86.9°), N(4)C(5)C(3)N(3) (−11.3°), O(6)N(4)C(5)C(3) (−83.7°) in molecule **2b** provide evidence in favor of this interaction.

Thus, the n-type lone electron pair of the imine nitrogen atom is located in the plane of the aldimine fragment. Since the vacant π*-orbitals of both nitro groups of each molecule, localized at the respective nitrogen atoms, also lie in the same plane, the interaction is possible because the orbitals have similar symmetry.

A variety of conformations are admissible in the molecules studied, for example, the conformation due to the rotation of the 2,2-dinitropropyl fragment around the C(4)—N(5) bond in molecule **2a** or the rotation of the fluorodinitroethyl fragment around the C(3)—C(4) bond in molecule **2b**. Of these, only the strained conformations drawing the imine nitrogen atom together with the nitrogen atoms of the nitro groups are realized (see Figs. 1, 2).

The fluorodinitromethyl fragment in molecule **2b** has a typical structure (a similar structure has been found[1] for molecule **1a**): the fluorine atom is located almost

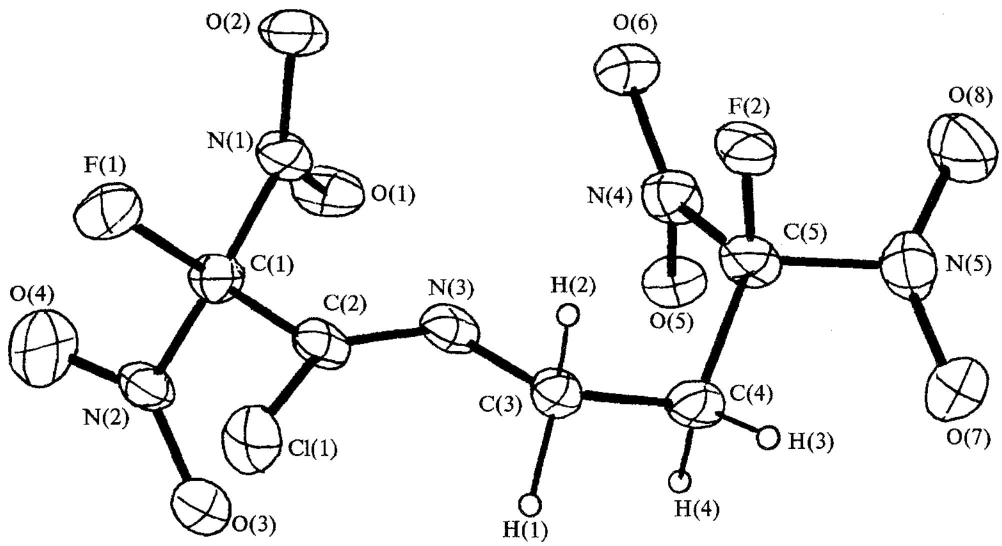

Fig. 2. Molecule of 2-chloro-1,6-difluoro-1,1,6,6-tetranitro-3-aza-2-hexene **2b**.

exactly in the plane of one nitro group and is simultaneously located approximately in the plane of the second nitro group. Two lone electron pairs of the halogen atom simultaneously interact with the highest levels of the π-type MO of both nitro groups in two mutually perpendicular planes. The antibonding combination of the lone electron pairs interacts with a vacant antibonding MO of the polar C—N bond. The p—π-type interaction should draw the O and Hal atoms together, shorten the N—O and C—Hal chemical bonds, and elongate the C—N bonds, which completely agrees with the calculations[3] and with the results of this study.

Experimental

3-Chloro-2,2,6,6-tetranitro-4-aza-3-heptene (2a) and 2,2,6,6-tetranitro-3-oxo-4-azaheptane (3a). Excess HCl gas was slowly passed at 20—25 °C through a stirred solution of compound **1a** (5.94 g) in glacial AcOH (50 mL). The solution was kept for 2 h without stirring and poured into ice water (250 mL). The precipitate was filtered off, washed with water, dried in the air, and recrystallized from CCl_4 to give 3.8 g (61 %) of **2a**, m.p. 62—63 °C. Found (%): C, 22.9; H, 2.5; Cl, 10.9; N, 22.2. $C_6H_8ClN_5O_8$. Calculated (%): C, 22.98; H, 2.57; Cl, 11.30; N, 22.33. ^1H NMR (CD_3CN, TMS), δ: 4.6 (s, 2 H, CH_2); 2.5 (s, 3 H, CH_3); 2.2 (s, 3 H, CH_3). The precipitate of **3a** that remained undissolved after recrystallization was filtered off and recrystallized from $CHCl_3$—CCl_4 to give 0.45 g (7.5 %) of **3a**, m.p. 90—91 °C. Found (%): C, 23.6; H, 3.3; N, 23.7. $C_6H_9N_5O_9$. Calculated (%): C, 24.42; H, 3.07; N, 23.27. ^1H NMR (CD_2Cl_2, TMS), δ: 7.4 (br.s, 1 H, NH); 4.4 (d, 2 H, CH_2, J = 6.0 Hz); 2.4 (s, 3 H, CH_3); 2.2 (s, 3 H, CH_3).

2-Chloro-1,6-difluoro-1,1,6,6-tetranitro-3-aza-2-hexene (2b) and 1,6-difluoro-1,1,6,6-tetranitro-2-oxo-3-azahexane (3b). The above procedure starting from compound **1b** (6.38 g) afforded 3.98 g (59 %) of **2b** and 0.38 g (5 %) of **3b**. **2b**: m.p. 58—59 °C. Found (%): C, 17.3; H, 1.3; Cl, 10.4; F, 11.6; N, 20.4. $C_5H_4ClF_2N_5O_8$. Calculated (%): C, 17.90; H, 1.03; Cl, 10.57; F, 11.32; N, 20.87. **3b**: m.p. 85—86 °C. Found (%): C, 19.3; H, 1.8; F, 12.0; N, 21.7. $C_5H_5F_2N_5O_9$. Calculated (%): C, 18.94; H, 1.59; F, 11.98; N, 22.08. ^1H NMR (CD_2Cl_2, TMS), δ: 7.3 (br.s, 1 H, NH); 3.8 (m, 2 H, CH_2, J = 6.5 Hz and 6.0 Hz); 3.2 (dt, 2 H, CH_2, J = 6.5 Hz and 17.7 Hz).

Table 1. Atomic coordinates (×10^5) in the structure of crystalline 3-chloro-2,2,6,6-tetranitro-4-aza-3-heptene **2a**

Atom	*x*	*y*	*z*
Cl(1)	45906(2)	29496(4)	−1870(5)
O(1)	50293(4)	49673(4)	−63263(7)
O(2)	46832(5)	66734(5)	−47068(6)
O(3)	33207(5)	59177(6)	−29928(7)
O(4)	40457(4)	59353(5)	−3371(6)
O(5)	67836(5)	56867(6)	−45962(6)
O(6)	68270(5)	64322(6)	−13524(7)
O(7)	78824(6)	43709(7)	−10037(7)
O(8)	72216(5)	36279(6)	14859(6)
N(1)	47154(6)	55389(7)	−49616(8)
N(2)	38502(7)	56081(7)	−21076(8)
N(3)	67821(6)	55976(6)	−26337(7)
N(4)	73264(7)	40872(6)	−2585(8)
N(5)	54728(7)	46626(7)	−18208(7)
C(1)	39013(8)	37117(8)	−44800(9)
C(2)	43296(7)	46817(8)	−33296(8)
C(3)	48803(8)	41987(9)	−17966(9)
C(4)	60264(7)	42134(9)	−4324(8)
C(5)	66918(7)	42509(8)	−17176(9)
C(6)	67380(8)	32346(8)	−34095(9)
H(1)	38434(35)	31922(45)	−39889(65)
H(2)	34242(45)	36046(55)	−46987(65)
H(3)	40639(45)	33970(65)	−55179(75)
H(4)	59290(35)	33747(65)	3109(65)
H(5)	60718(50)	46928(75)	6234(75)
H(6)	67867(45)	22599(65)	−26128(75)
H(7)	71539(45)	34152(65)	−43166(65)
H(8)	63311(35)	30862(75)	−41052(85)

Table 2. Atomic coordinates ($\times 10^4$) in the structure of crystalline 2-chloro-1,6-difluoro-1,1,6,6-tetranitro-3-aza-2-hexene **2b**

Atom	*x*	*y*	*z*
Cl(1)	1027(1)	1573(1)	3179(1)
F(1)	2429(1)	751(1)	1099(2)
F(2)	377(5)	3970(1)	868(2)
O(1)	6968(7)	1201(2)	200(3)
O(2)	3017(7)	1540(2)	−434(3)
O(3)	7563(7)	558(2)	2558(3)
O(4)	7474(8)	−182(2)	1330(4)
O(5)	7096(7)	2816(2)	794(3)
O(6)	3925(5)	2985(2)	−312(3)
O(7)	4522(8)	4453(2)	2033(4)
O(8)	3095(8)	4654(3)	359(6)
N(1)	4743(7)	1275(2)	254(3)
N(2)	6603(8)	409(2)	1789(4)
N(3)	2915(6)	2275(2)	1905(3)
N(4)	4784(7)	3114(2)	507(3)
N(5)	3531(9)	4342(2)	1226(4)
C(1)	4022(8)	1045(2)	1349(4)
C(2)	2759(8)	1700(2)	2115(4)
C(3)	1667(8)	2933(2)	2616(4)
C(4)	3004(9)	3424(2)	2468(4)
C(5)	2815(8)	3701(2)	1328(4)
H(1)	1927(79)	2785(20)	3476(38)
H(2)	−81(95)	3216(24)	2296(46)
H(3)	1948(81)	3889(20)	2901(38)
H(4)	4794(95)	3140(29)	2756(53)

The cell parameters for the crystals of compounds 2a and 2b were determined on a DRON-1 diffractometer with a monocrystal unit.

The crystals of $C_6H_8ClN_5O_8$ (**2a**) are rhombic, a = 19.236(3), b = 10.516(2), c = 6.250(1) Å, V = 1264.56 Å^3, d = 1.646 g cm^{-3}, λ = 0.711, space group $Pb2_1a$, Z = 4. Mol. mass 313.61.

The crystals of $C_5H_4ClF_2N_5O_8$ (**2b**) are monoclinic, a = 5.7295(5), b = 20.344(5), c = 12.096(3) Å, γ = 61.20(2)°; V = 1235.52 Å^3, d = 1.803 g cm^{-3}, λ = 1.5418, space group $P2_1/b$, Z = 4. Mol. mass 335.57.

In the case of compound **2a**, 1670 reflections were measured on a four-circle KM-4 diffractometer with κ-geometry (KUMA-DIFFRACTION) in the $0.02 < \sin\theta/\lambda < 0.645$ range. For compound **2b**, 1490 nonzero nonequivalent reflections ($I > 2.5(I)$) were measured on a DAR-UM diffractometer in the $0.056 < \sin\theta/\lambda < 0.656$ range. The structure of **2a** was solved by the direct method on a personal computer using the SHELX-86 program package. The structure of **2b** was solved by the direct method on a BESM-6 computer using the Rentgen-76 programs. The structures were refined in a full-matrix approximation to R = 0.056 (**2a**) and R = 0.065 (**2b**). The thermal parameters for the nonhydrogen atoms were refined in the anisotropic approximation, and those for the hydrogen atoms were refined in the isotropic approximation. The atomic coordinates in compounds **2a** and **2b** are given in Tables 1 and 2.

References

1. A. G. Korepin, P. V. Galkin, N. I. Golovina, L. O. Atovmyan, and L. T. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 742 [*Bull. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 582 (Engl. Transl.)].
2. V. Gutmann, *Coordination Chemistry in Non-aqueous Solutions*, Springer-Verlag, Wien, New York, 1968.
3. B. S. Fedorov, N. I. Golovina, L. S. Barinova, V. V. Arakcheeva, R. F. Trofimova, and L. O. Atovmyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2372 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2081 (Engl. Transl.)].

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