α-Azidopolynitroalkanes. Synthesis and vibrational spectra

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Methods for the preparation of α-azidopolynitroalkanes by reactions of polynitroalkanes or α-(difluoroamino)polynitroalkanes with NaN_3 were developed. In the case of tetranitromethane, one or two nitro groups can be substituted, depending on the reaction conditions. The reaction of 1,1,1-trinitroethane with NaN_3 affords nitro-1,2,3-triazole, together with 1-azido-1,1-dinitroethane. The IR spectra of α-azidopolynitroalkanes were studied.

Key words: substitution of nitro and difluoroamino groups by an azido group, tetranitromethane, fluorotrinitromethane, 1,1,1-trinitroethane, (difluoroamino)trinitromethane, (difluoroamino)fluorodinitromethane, 1-difluoroamino-1,1-dinitroethane, azidofluorodinitromethane, diazidodinitromethane, 1-azido-1,1-dinitroethane, nitro-1,2,3-triazole, carbamoyl azide, sodium azide; IR spectra.

In a continuation of studies of reactions of polynitro-compounds with nucleophiles,[1—3] we studied the interaction of polynitroalkanes with azide ion. Previously, a reaction of this type has been described for fluorotrinitromethane; this reaction gave azidofluorodinitromethane.[4] Nucleophilic substitution of a nitro group is believed to be peculiar only to fluorotrinitromethane.

The data that we have accumulated on the reactions of polynitro-compounds with nucleophiles[1—3] made it possible to suggest that replacement of nitro groups in polynitroalkanes by azido groups under the action of azide anion is a general reaction, at least, for polynitromethanes.

In fact, we found that the reaction of tetranitromethane with NaN_3 in a DMSO—CH_2Cl_2 mixture (at −20 to −15 °C) gives azidotrinitromethane (**1**) in a yield of 20—24%. When the reaction was carried out in pure DMSO or DMF, the yield of the product was only 10—14%. In aqueous acetone, this reaction gave a mixture of compound **1** and diazidodinitromethane (**2**) (identified by GLC) that was difficult to separate. Pure compound **2** can be obtained in 12% yield by the reaction of tetranitromethane with excess NaN_3 in aqueous ethanol at 5—10 °C. The formation of diazide **2** was also detected in the reaction of monoazide **1** with NaN_3 in aqueous ethanol (identified by GLC).

Fluorotrinitromethane reacts with NaN_3 in DMF at −20 to −15 °C to give azidofluorodinitromethane (**3**) in 30% yield.

The reactions of 1,1,1-trinitroethane with NaN_3 in DMF or DMSO or in their mixtures with ether (1 : 1) at 30—40 °C affords 1-azido-1,1-dinitroethane (**4**) in 2—3% yield* and nitro-1,2,3-triazole (**5**), which is apparently formed from 1,1,1-trinitroethane under the action of NaN_3 *via* intermediate 1,1-dinitroethene.

Thus, using 1,1,1-trinitroethane as an example, we showed that polynitro-compounds containing an H atom in the α-position with respect to the nitro group react with NaN_3 according to two routes: replacement of the nitro-group and elimination of HNO_2.

In our study of the reaction of α-(difluoroamino)polynitroalkanes with NaN_3, we found that the difluoroamino group is replaced by an azido group thus giving α-azidopolynitroalkanes as major products. This reaction is general; for example, (difluoroamino)trinitromethane is converted into azidotrinitromethane, (difluoroamino)fluorodinitromethane affords azidofluorodinitromethane, and 1-difluoroamino-1,1-dinitroethane gives rise to 1-azido-1,1-dinitroethane.

$$RC(NO_2)_2NF_2 \xrightarrow{N_3^-} RC(NO_2)_2N_3$$

$$R = NO_2,\ F,\ Me$$

Replacement of a difluoroamino group by an azido group occurs under milder conditions and, in some cases, gives higher yields of products than the above-

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* The yield can be increased by selecting appropriate reaction conditions, which will be demonstrated in a separate communication.

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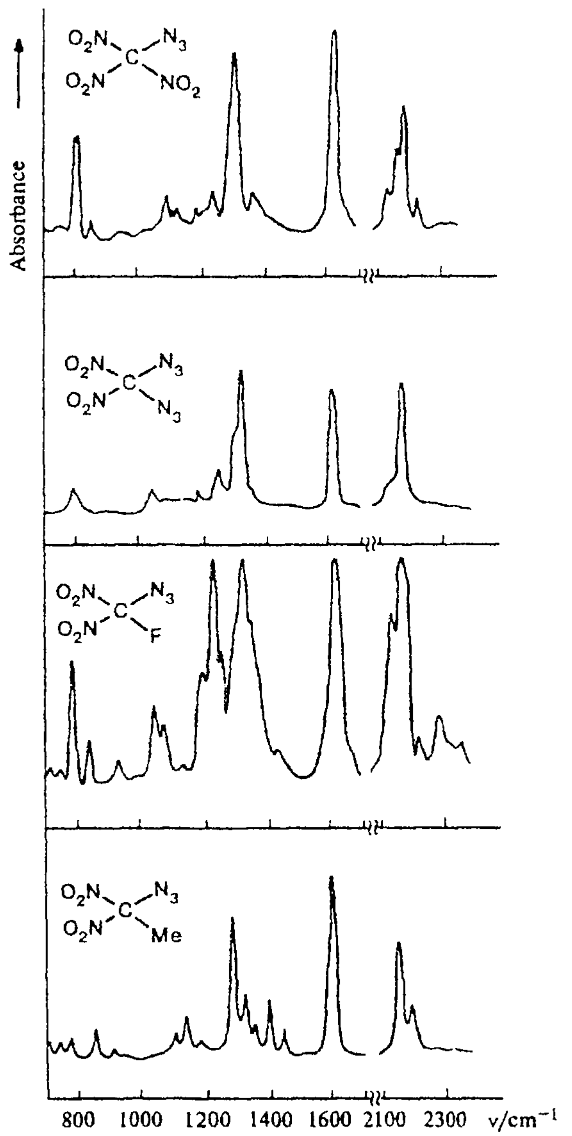

Fig. 1. IR spectra of α-azidopolynitroalkanes (in the gas phase).

described substitution of a nitro group. For example, the yield of 1-azido-1,1-dinitroethane from 1-difluoroamino-1,1-dinitroethane is 50%, while that from 1,1,1-trinitroethane is as low as 2—3%.

The α-azidopolynitroalkanes obtained are colorless liquids that can be distilled *in vacuo* without decomposition and are easily soluble in many organic solvents. The homogeneity of the products was proved by GLC, and their structures were confirmed by IR spectroscopy. Table 1 presents the frequencies of antisymmetrical stretching vibrations of nitro and azido groups and their peak (*E*) and integral (*A*) intensities.

Examination of the IR spectra indicates that the introduction of an azido group in the α-position with respect to the nitro group (see Fig. 1), like introduction of other electronegative substituents,[5] leads to displacement of bands corresponding to antisymmetrical and symmetrical vibrations of the NO_2 group to higher and lower frequencies, respectively. Additivity of the integral intensities of antisymmetrical vibrations of the NO_2 groups is observed, which is typical of ordinary polynitroalkanes.[6]

The spectra of the compounds studied exhibit a band in the 2185—2159 cm^{-1} range* (see Table 1), characteristic of ν_{as} of the azido group. In the spectra of the azidopolynitroalkanes under consideration, as in the spectra of most aliphatic azides, the ν_{as} band of the azido group is split into several components of different intensities. This splitting may be due to the Fermi resonance, which is not at variance with the degree of depolarization of two components in the Raman spectrum of compound **1** (ν 2185 cm^{-1}, w, ρ = 0.30; ν 2155 cm^{-1}, w, ρ = 0.53). Measurement of the integral intensities of the ν_{as} band corresponding to the N_3 group in the series of aliphatic azides indicates[7] that the intensity decreases when strong electronegative substituents are introduced in the α-position. In fact, in the series of compounds studied, the integral intensities ($A_{\nu_{as}}$) of the band for the N_3 group are approximately three times lower than the $A_{\nu_{as}}$ values for aliphatic azides, and remain constant (see the last column in Table 1). In the case of diazidodinitromethane, additivity of the integral and peak intensities of ν_{as} for the NO_2 group is observed.

Table 1. Antisymmetrical vibrations of the nitro and azido groups in azidopolynitroalkanes and their peak (E/cm^{-1} mol^{-1} L) and integral (A/cm^{-2} mol^{-1} L) intensities

Compound	ν_{as}/cm^{-1} (CH_2Cl_2)		E		$A \cdot 10^{-3}$		$A \cdot 10^{-3}$, per 1 group	
	NO_2	N_3	NO_2	N_3	NO_2	N_3	NO_2	N_3
$(O_2N)_3CN_3$	1614	2184	1015	474	27.4	10.5	9.10	10.5
$(O_2N)_2C(N_3)_2$	1601	2174	883	882	17.5	23.4	8.90	11.7
$(O_2N)_2CF(N_3)$	1613	2180	792	448	16.5	11.6	8.25	11.6
$MeC(NO_2)_2N_3$	1585	2151	832	379	18.5	11.2	9.25	11.2

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* Previously,[4] in addition to the band at 2200 cm^{-1}, a band at 1700 cm^{-1} was observed in the IR spectrum of compound **3**; this band was assigned to impurities. According to our data, the band at 1700 cm^{-1} is due to traces of DMF, *i.e.*, the solvent used for the reaction. This band disappears when the sample is thoroughly purified.

Experimental[*]

IR spectra were recorded on a UR-10 instrument in thin films between germanium glasses for liquids; the spectra in the gas phase were recorded in a standard (10 cm) cell with NaCl windows. The spectra for solutions of substances in CH_2Cl_2 were recorded in a cell of constant thickness with NaCl windows. The thickness of the cell was monitored using the interference pattern. Integral intensities were calculated by a standard procedure, the areas below the curves being measured with a planimeter. Raman spectra were obtained using a DFS-12 spectrophotometer with a He—Ne-laser for liquids. Spectral studies were carried out for chromatographically pure samples. GLC analysis was carried out on a LKhM-8 chromatograph equipped with a katharometer, the length of the column was 30 cm, and fluorosilicone QF-1 (10%) on Chromosorb P (0.15—0.25 mesh) was used as the stationary phase. Helium was used as the carrier gas; the temperature was 70 °C.

Reaction of polynitroalkanes with sodium azide

Azidotrinitromethane (1). Sodium azide[**] (4.4 g, 68 mmol) was added with intense stirring and cooling (−20 to −15 °C) over a period of 10—15 min to a solution of tetranitromethane (11.75 g, 60 mmol) in a mixture of anhydrous DMSO (30 mL) and anhydrous CH_2Cl_2 (30 mL) cooled to −20 °C. The mixture was stirred for an additional 2 h at the same temperature. During this period NaN_3 gradually dissolved and evolution of a gas occurred. The reaction mixture was poured into a mixture of CH_2Cl_2 (30 mL) and ice water (150 mL) (this was accompanied by intense gas evolution), the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×30 mL). The combined organic solutions were washed with a cold 0.5% solution of Na_2CO_3 (2×30 mL) and water (2×50 mL) and dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the residue was distilled to give 2.7 g (23.5%) of azidotrinitromethane (1), b.p. 70—72 °C (35 Torr). Repeated distillation afforded chromatographically pure product **1**, b.p. 71—72 °C (35 Torr), $n_D^{19.5}$ 1.4673, d_4^{20} 1.6128. Found (%): N, 43.45. CN_6O_6. Calculated (%): N, 43.75. Mol. weight: found, 191 (cryoscopy in benzene); calculated, 192.

Diazidodinitromethane (2) and carbamoyl azide (6). At −10 to −5 °C, a solution of NaN_3 (8 g, 123 mmol) in 18 mL of water was added with stirring over a period of 20 min to a solution of tetranitromethane (9.8 g, 50 mmol) in 60 mL of EtOH. The mixture was stirred for 2—2.5 h at 5—10 °C until a homogeneous solution formed and poured into a mixture of CH_2Cl_2 (30 mL) and ice water (150 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×30 mL). The combined organic solutions were washed with a cold 0.5% solution of Na_2CO_3 (2×30 mL) and water (2×30 mL) and dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the residue was distilled to give 1.8 g of unreacted tetranitromethane, b.p. 30—45 °C (10 Torr), and 1.14 g (12%) of diazidodinitromethane **2**, b.p. 60—62 °C (10 Torr). After repeated distillation, b.p. 61—62 °C (10 Torr), n_D^{20} 1.4880. According to GLC, the product was 98% pure. Elemental analysis for compound **2** could not be carried out, since the sample decomposed with explosion. Mol. weight: found, 184 (cryoscopy in nitrobenzene). CN_8O_4. Calculated, 188.

The reaction of tetranitromethane with NaN_3 in aqueous ethanol or aqueous acetone was carried out according to the same procedure. In this case, the solution of reaction products in CH_2Cl_2 was poured in a Petri dish. After evaporation of the solvent and azidopolynitromethanes, the carbamoyl azide (**6**) was left as slightly yellowish crystals, m.p. 96—97 °C (*cf.* Ref. 11). Found (%): C, 13.54; H, 2.00; N, 64.50. CH_2N_4O. Calculated (%): C, 13.54; H, 1.96; N, 64.20. IR (solid), ν/cm^{-1}: 1692, 1712 (C=O); 2150, 2190 (N_3).

Compound **6** was also obtained from diazidodinitromethane **2**. A mixture of diazidodinitromethane **2** (1 g) in 20 mL of CH_2Cl_2 and water (0.5 mL) containing traces of H_2SO_4 was stirred for 2 h at 20 °C. The organic layer was separated, dried with anhydrous $MgSO_4$, and poured in a Petri dish. After evaporation of CH_2Cl_2, 0.1 g of crystalline product **6** was left, m.p. 96—97 °C. The melting point of its mixture with an authentic sample obtained from tetranitromethane was undepressed.

Azidofluorodinitromethane (3). At to −25 to −15 °C, NaN_3 (5 g, 74 mmol) was added with stirring over a period of 10—20 min to a solution of fluorotrinitromethane (8.45 g, 50 mmol) in 30 mL of anhydrous DMF. The mixture was stirred for 3 h at −25 to −15 °C and poured in a mixture of CH_2Cl_2 (30 mL) and ice water (150 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×30 mL). The combined organic solutions were washed with a cold 0.5% solution of Na_2CO_3 (2×30 mL) and water (2×50 mL) and dried with anhydrous $MgSO_4$. CH_2Cl_2 was removed under atmospheric pressure using a 25-cm-long dephlegmator, and the residue was distilled *in vacuo* to give two fractions: 1.3 g with a boiling point of 30—44 °C (70 Torr) and 2.4 g with a boiling point of 45—52 °C (70 Torr). The former fraction was a mixture of fluorotrinitromethane with azidofluorodinitromethane (identified by GLC). The latter fraction was azidofluorodinitromethane containing some fluorotrinitromethane. Repeated distillation gave chromatographically pure azidofluorodinitromethane **3**, b.p. 51—52 °C (20 Torr) (*cf.* Ref. 4), n_D^{20} 1.4321, d_4^{20} 1.5404. Found (%): N, 42.3. CFN_5O_4. Calculated (%): N, 42.4. Mol. weight: found, 162 (cryoscopy in nitrobenzene); calculated, 165.

1-Azido-1,1-dinitroethane (4) and nitro-1,2,3-triazole (5). At 30—40 °C, NaN_3 (6.5 g, 100 mmol) was added with stirring over a period of 10 min to a solution of 1,1,1-trinitroethane (12 g, 7.28 mmol) in dry DMSO (40 mL) and anhydrous ether (40 mL). The mixture was stirred for 3 h at 30—40 °C. During this period, NaN_3 gradually dissolved, which was accompanied by gas evolution and by separation of the reaction mixture into layers. The mixture was cooled to −10 °C and poured into 150 mL of ice water. The ethereal layer was separated, and the aqueous layer was extracted with ether (3×30 mL). The combined organic solutions were washed with water and dried with anhydrous $MgSO_4$. The ether was removed *in vacuo* using a 25-cm-long dephlegmator, and the residue was diluted with 40 mL of *n*-pentane and cooled to −50 °C. The precipitate was filtered off on a cooled filter and washed with 20 mL of chilled *n*-pentane to give 3 g of a precipitate. The mother liquor was concentrated *in vacuo* using a 20-cm dephlegmator and cooled to −50 °C. The precipitate that formed was filtered on a cooled filter and washed with

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[*] This study has been presented as a Ph. D. Thesis;[8] later, a patent appeared describing the replacement of nitro groups by azido groups under the action of LiN_3.[9] The properties of α-azidopolynitroalkanes studied by us were partly reported in a previous paper.[10]

[**] From here on, dry NaN_3 was used, which was purified by precipitation with acetone from an aqueous solution.

15 mL of chilled *n*-pentane to give an additional 0.7 g of the precipitate.

The solvent from the mother liquor was removed *in vacuo* using a dephlegmator to give 0.9 g of an oil that contained, according to GLC, azidodinitroethane and trinitroethane in a ratio of 2 : 1. Preparative GLC of this oil gave 0.3 g (2.6%) of pure 1-azido-1,1-dinitroethane **4**, b.p. 78—80 °C (35 Torr), n_D^{18} 1.4570. Found (%): N, 44.0. $C_2H_3N_5O_4$. Calculated (%): N, 43.50. Mol. weight: found, 158 (cryoscopy in nitrobenzene); calculated, 161.

The combined precipitates (3.7 g, see above) were treated with 50 mL of boiling *n*-hexane, and the insoluble part was filtered off and washed on the filter with 40 mL of boiling *n*-hexane to give 0.24 g of nitro-1,2,3-triazole **5**, m.p. 159—162 °C.* After recrystallization from an ether—hexane mixture (1 : 3), m.p. 161—162 °C (*cf.* Ref. 12). Found (%): C, 21.31; H, 1.82; N, 50.32. $C_2H_2N_4O_2$. Calculated (%): C, 21.05; H, 1.75; N, 49.05. IR (pressed with KBr), ν/cm^{-1}: 1526 and 1329 (NO_2); 3165 (C—H); 3260 (N—H). ^{1}H NMR (CD_3COCD_3), δ: 6.68 (C—H); 9.18 (N—H). The ratio of integral intensities was 1 : 1. The signal at 9.18 ppm disappeared upon addition of D_2O.

Transformation of α-(difluoroamino)polynitroalkanes into α-azidopolynitroalkanes

Azidotrinitromethane (1). At −25 to −15 °C, a solution of (difluoroamino)trinitromethane (5 g, 24 mmol) in 20 mL of dry CH_2Cl_2 was added dropwise with intense stirring to a suspension of NaN_3 (2 g, 30 mmol) in 20 mL of dry DMF. The mixture was stirred for 40 min at −25 to −15 °C and poured in 150 mL of ice water. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×30 mL). The combined organic solutions were washed with water (2×30 mL) and dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the residue was distilled to give 0.8 g (17%) of chromatographically pure azidotrinitromethane, b.p. 65—66 °C (24 Torr). The product was identical to that obtained from tetranitromethane.

Azidofluorodinitromethane (3). This compound was obtained from (difluoroamino)fluorodinitromethane (5.25 g, 30 mmol) and NaN_3 (4 g, 60 mmol) in a mixture of DMF (20 mL) and CH_2Cl_2 (20 mL) by a similar procedure. Yield 1.83 g (37%), b.p. 51—52 °C (70 Torr). The product was identical to that obtained from fluorotrinitromethane.

1-Azido-1,1-dinitroethane (4). At 0—5 °C, NaN_3 (1.3 g, 20 mmol) was added with stirring in small portions over a period of 10 min to a solution of 1-difluoroamino-1,1-dinitroethane (1.71 g, 10 mmol) in 15 mL of anhydrous DMF. The mixture was stirred for 1.5 h at 0—5 °C. During this period, NaN_3 gradually dissolved and gases evolved. An additional 0.2 g of NaN_3 was added, and the mixture was stirred for an additional 0.5 h and poured into 50 mL of water. The oil thus obtained was extracted with ether (2×20 mL). The combined ethereal solutions were washed with water (3×20 mL) and dried with anhydrous $MgSO_4$. The ether was removed under atmospheric pressure using a 25-cm-long dephlegmator, and the residue was distilled *in vacuo* to give 0.82 g (50%) of 1-azido-1,1-dinitroethane identical to the product prepared from 1,1,1-trinitroethane, b.p. 78—80 °C (35 Torr), n_D^{20} 1.4560.

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* From the mother liquor, we isolated 3 g of the initial 1,1,1-trinitroethane.