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Making a study of the dual reactivity of the anions of polynitroalkanes, in the present paper we studied the reaction of these anions with sulferyl chlorides. According to [1, 2], in this reaction the anions of mononitro compounds form α -mononitroalkyl sulfides, i.e., the attack is at the C atom of the anion, while in [3] the assumption was made that the reaction proceeds in a different direction, namely the oxygen atom of the nitro group is attacked. As regards the reaction of polynitro compounds, then only one American patent is known, in which it is reported that trinitromethyl 2.4-dinitrophenyl sulfide is obtained from the Ag salt of trinitromethane (TNM) and the appropriate sulfenyl chloride in ether [4].

We made a detailed study of the reaction of sulfenyl chlorides with the salts of TNM and of the gemdinitroalkanes, dinitromethane (DNM) and 1.1-dinitroethane (DNE), and it was shown that this reaction can serve as a general method for the synthesis of α -polynitroalkyl sulfides (I)-(III)

$$\begin{array}{c} \operatorname{RC(NO_2)_2} \circ \operatorname{M} \oplus + \operatorname{R'SCI} \to \operatorname{RC(NO_2)_2SR'} + \operatorname{MCI}_{(I) - (III)} \end{array}$$

The yields and some of the properties of the obtained compounds are given in Table 1.

All of the studied reactions proceed under mild conditions $(0-5^{\circ})$ in 0.5-1 h, in either 1.2-dimethoxyethane or ether (as a suspension in the latter case).* The K salts of the polynitroalkanes were used, except for the preparation of the two DNM derivatives (IIIa-b), where it is more convenient to use the piperidine salt of DNM, which is soluble in dimethoxyethane, in which connection the best results were obtained using a salt sulferry chloride ratio equal to 2:1. This is due to the fact that the α -dinitromethyl sulfides (IIIa-b), which are formed as a reaction product, are stronger CH acids than DNM, and displace the latter from its salts†

$$HC(NO_2)_2 {}^{\odot}H_2 \overset{\oplus}{N} \xrightarrow{(III a - b)} HC(NO_2)_2 SR' \xrightarrow{+ HC(NO_2)_2 {}^{\odot}H_2 \overset{\oplus}{N}} R'SC(NO_2)_2 {}^{\odot}H_2 \overset{\oplus}{N} \xrightarrow{(III a - b)} + CH_2(NO_2)_2 SR' \xrightarrow{(III a - b)} R'SC(NO_2)_2 \overset{\oplus}{N} \xrightarrow{(III a - b)}$$

Acids (IIIa-b) were isolated from the piperidine salts by treatment with dry HCl in ether.

The purity of the obtained compounds was confirmed by the TLC method (KSK silica gel, eluant either a 1:1 or 1:2 mixture of benzene and hexane). The synthesized compounds have the structure of α -(IV), which was polynitroalkyl sulfides, and not of the isomeric O-sulfenylation products C = N

O,N proved by the IR and UV spectroscopy data: in the IR spectra of (I)-(III) are present bands that are characteristic for either the $C(NO_2)_3$ or the $C(NO_2)_2$ group, and a band is absent at 1630-1640 cm⁻¹, which band is characteristic for the C=N bond in the O-derivatives of acipolynitroalkanes, in which compounds it is exceedingly intense [5]; a maximum in the 280-330 nm region is absent in the UV spectra, which maximum is characteristic for the O-derivatives of polynitroalkanes [5].

*The quantitative formation of chloride ion was always observed under these conditions. †Dinitromethyl 2.4-dinitrophenyl sulfide (IIIa) in its acidity even exceeds TNM, and displaces it from its salts, while (IIIc) does not exceed the acidity of DNM.

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Com- pound	R	R'	Yield, %	Bp, °C(p, mm of Hg)	Mp, °C	n_{D}^{20}
Ia Ib Ic	NO ₂ NO ₂ NO ₂	2,4-(O ₂ N) ₂ Ph Ph CH ₃	50 * 93 93	40(1)	68 12—13 —	1,5592 1,4950
IIa IIb IIc	CH ₃ CH ₃ CH ₃	2,4-(O ₂ N) ₂ Ph Ph CH ₃	91 94 92	 45(3)	68,5-69,5 17-18	1,5605 1,4900
IIIa	н	$2,4-(O_2N)_2Ph$	81	· - ·	75-77	_
IIIb IIIc	H H	Ph CH ₃	70 87	50-51(1)	(decompn.) 29-29,5	1,4966

TABLE 1. α -Polynitroalkyl Sulfides RC(NO₂)₂SR'

* The yield of (Ia) was 65% when we used the Ag salt of TNM in CH₃CN.

Since the yields of the C-sulfenylation products, namely the α -polynitroalkyl sulfides (I)-(III), are quite high (see Table 1^{*}) and the reaction mixtures do not contain other substances, which means also the possible decomposition products of the O-sulfenyl derivatives (IV), it may be assumed that the reaction proceeds only in one direction, namely at the C atom of the polynitro carbanion.

Compounds (I)-(III) gradually decompose at room temperature, but they can be stored at low temperature (the aliphatic α -polynitroalkyl sulfides for several days, while the aromatic derivatives are more stable). In contrast to the α -mononitroalkyl [3] and α -dinitroalkyl (II) derivatives, in the α -trinitromethyl sulfides (I) the C-S bond is quite labile toward the action of hydroxyl-containing solvents (H₂O, alcohols), resembling in this respect the Hal-S bond in sulfenyl halides. Thus, the reaction of (Ia, b) with CH₃OH gives the esters of the corresponding sulfenic acids and TNM. The reaction of (Ia) with CH₃OH at 20° is completely

$$(NO_2)_3C - SR' + CH_3OH \rightarrow (NO_2)_3CH + R'S - OCH_3$$

ended in 2 h, the methanolysis of (Ib) proceeds to the extent of only 10% in 4 h, while (Ic) fails to react with CH₃OH in a day (concentration of (Ia-c) in CH₃OH ~ $1.2 \cdot 10^{-2}$ mole/liter). As a result, an increase in the electronegativity of the R substituent in (I) makes the C-S bond more sensitive to the action of nucleophilic reagents. For comparison we will mention that the reverse picture holds for the sulfenyl halides, and here CH₃SC1 reacts instantaneously with CH₃OH at -20° [6], while refluxing is necessary for the reaction of 2,4-(NO₂)₂Ph·SC1 with CH₃OH [7].

In contrast to the free C-H acids, namely dinitromethyl sulfides (IIIa-c), their salts are stable at room temperature. For example, the Ag salt of (IIIa) remains unchanged for a month at 20°. This salt, and also the K salts of compound (IIIa-c), can be obtained by exchange reaction from the corresponding piperidine or ammonium salts. The anions of the indicated dinitromethyl sulfides (III) have a distinct absorption maximum in the UV spectrum, which is shifted toward longer wavelengths when going from the 2,4-dinitrophenyl sulfide derivatives (IIIa) to the methyl sulfide derivative (IIIc) (Table 2).

The piperidine and K salts of (IIIa) do not react with $CH_{3}I$ and 2,4-dinitrobenzenesulfenyl chloride in aprotic dipolar solvents, which apparently is due to the low nucleophilicity of the anion of acid (IIIa). The reaction of the Ag salt of (IIIa) with $CH_{3}I$ in $CH_{3}CN$ (20°, 3 days) gives a complex mixture, in which connection one of the products is (IIa)

$$2,4-(\mathrm{NO}_2)_2\mathrm{PhSC}(\mathrm{NO}_2)_2^{\,\ominus}\mathrm{Ag}^{\oplus}+\mathrm{CH}_3\,\mathrm{I}\xrightarrow[-\mathrm{Ag}\,\mathrm{I}]{2,4-(\mathrm{NO}_2)_2\mathrm{PhSC}(\mathrm{NO}_2)_2\mathrm{CH}_3}_{(\mathrm{IIa})}$$

The salts of the dinitromethyl sulfides (III) are easily chlorinated and give the corresponding α -chlorodinitromethyl sulfides (V) in 70-95% yields

$$\begin{split} \mathrm{R'SC(\mathrm{NO}_2)_2}^{\oplus}\mathrm{M}^{\oplus} + \mathrm{Cl}_2 &\to \mathrm{R'SC(\mathrm{NO}_2)_2}\mathrm{Cl} + \mathrm{MCl} \\ \mathrm{(V)} \\ \mathrm{R'} &= 2,4\text{-}(\mathrm{NO}_2)_2\mathrm{Ph} \text{ (a); } \mathrm{CH}_3 \text{ (b); } \mathrm{M}^{\oplus} = \mathrm{K}^{\oplus}, \underbrace{\qquad}_{N}^{\oplus}\mathrm{H}_2 \end{split}$$

EXPERIMENTAL METHOD

Absolute solvents were used in the study. See [8-10] for the synthesis of the starting K salts of the polynitroalkanes; the piperidine salt of DNM was obtained by the reaction of piperidine with a cooled ether

TABLE 2. Absorption Maxima and ε of Anions of α -Dinitromethyl Sulfides (IIIa-c) in Water*

Anion	λ _{max} , nm	8
2,4- $(NO_2)_2$ PhSC $(NO_2)_2^{\ominus}$	355	22 500
PhSC $(NO_2)_2^{\ominus}$	365	12 500
CH ₃ SC $(NO_2)_2^{\ominus}$	370	12 000

• The values of λ_{\max} and ϵ are the same for all of the studied (III) salts (K, Ag and piperidine salts).

solution of DNM, mp 67-68°. The preparation of the sulfenyl chlorides was described in [11, 12]. The purity of all of the obtained α -poly-nitroalkyl sulfides was confirmed by the TLC data.

<u>Trinitromethyl 2,4-Dinitrophenyl Sulfide (Ia)</u>. With stirring, to a solution of 2.35 g of the K salt of TNM in 12 ml of dimethoxyethane at 0-3° was added a solution of 2.35 g of 2,4-(NO₂)₂PhSCl in 8 ml of dimethoxyethane. The mixture was stirred at 0-3° for 1.5 h, and the KCl precipitate (0.67 g, 90%) was separated. The excess K salt of TNM was salted out with absolute ether. The filtrate was evaporated in vacuo (not exceeding 20°), and the residue was washed with hexane until it solidified, and then it was recrystallized from a 1:2 CHCl₃ -hexane mixture. We obtained 1.75 g (50%) of (Ia), mp 68-69°; see [4]. Found: C 24.13; H 0.93; N 20.37; S 9.36%; mol.wt. 356 (in benzene). C₇H₃O₁₀N₅S. Calculated: C 24.07; H 0.86; N 20.05; S 9.18%; mol.wt. 349. Infrared spectrum (ν , cm⁻¹): 1300, 1605 (C(NO₂)₃), 1355, 1540, 1555 (NO₂ in the ring).

The reaction of 1.84 g of 2,4-(NO₂)₂PhSCl in 25 ml of CH₃CN with 2 g of the Ag salt of TNM [13] in 30 ml of CH₃CN (1 h at 10°) gave 1.8 g (65%) of (Ia).

<u>Trinitromethyl Phenyl Sulfide (fb).</u> To a solution of 1.21 g of PhSCl in 10 ml of dimethoxyethane at 0-3° was added a solution of 1.9 g of the K salt of TNM in 10 ml of dimethoxyethane. The mixture was stirred at 0-3° for 1 h, the KCl precipitate (0.68 g, 94%) was separated, and the filtrate was worked up in the same manner as in the preceding experiment. We obtained 2.02 g (93%) of (fb), mp 12-13° (from pentane, with freezing); n_D^{20} 1.5592. Found: C 32.82; H 2.13; N 16.32; S 12.17%; mol.wt. 257 (in benzene). $C_7H_5O_6N_3S$. Calculated: C 32.44; H 1.94; N 16.22; S 12.35%; mol.wt.259. Infrared spectrum: 1295, 1600 cm⁻¹ (C(NO₂)₃).

<u>Trinitromethyl Methyl Sulfide (Ic)</u>. To a solution of 0.82 g of CH₃SCl in 30 ml of ether at 0-3° was added 1.9 g of the K salt of TNM. Then the cooling was removed and the mixture was stirred for 1 h, after which the KCl precipitate (0.75 g, 100%) was separated. The filtrate was evaporated in vacuo (not exceeding 20°), and the residue was distilled. We obtained 1.84 g (93%) of (Ic), bp 40° (1 mm); n_D^{20} 1.4950. Found: C 12.31; H 1.66; S 16.61%. C₂H₃O₆N₃S. Calculated: C 12.19; H 1.53; S 16.27%. Infrared spectrum: 1300, 1600 cm⁻¹ (C (NO₂)₃).

<u>1,1-Dinitroethyl 2,4-Dinitrophenyl Sulfide (IIa)</u>. To a solution of 2.35 g of 2,4-(NO₂)₂PhSCl in 15 ml of dimethoxyethane at 0-3° was added 2 g of the K salt of DNE. The mixture was stirred at 0-3° for 1 h, and the KCl precipitate (1.08 g, 93%) was separated. The filtrate was evaporated in vacuo (not exceeding 20°), and the residue was washed with 10 ml of hexane until it solidified, after which it was recrystallized from a 2:1 hexane -CHCl₃ mixture. We obtained 2.9 g (91%) of (IIa), mp 68.5-69.5°. Found: C 30.27; H 1.71; N 17.30; S 10.00%; mol.wt. 322 (in benzene). $C_8H_6O_8N_4S$. Calculated: C 30.01; H 1.89; N 17.50; S 10.01%; mol.wt. 320. Infrared spectrum (ν , cm⁻¹): 1310, 1570 (C(NO₂)₂), 1350, 1535 (NO₂ in the ring).

<u>1,1-Dinitroethyl Phenyl Sulfide (IIb)</u>. Similar to (IIa), from 1.2 g of PhSCl in 15 ml of dimethoxyethane and 1.58 g of the K salt of DNE was obtained 1.8 g (94%) of (IIb), mp 17-18° (from pentane); n_D^{20} 1.5605. Found: C 42.30; H 3.98; N 12.45; S 13.90%; mol.wt.227 (in benzene). $C_8H_8O_4N_2S$. Calculated: C 42.11; H 3.53; N 12.28; S 14.03%; mol.wt.228. Infrared spectrum: 1320, 1580 cm⁻¹ ((NO₂)₂C).

<u>1,1-Dinitroethyl Methyl Sulfide (IIc)</u>. Similar to (IIa), from 4.9 g of CH₃SCl in 30 ml of ether and 6.5 g of the K salt of DNE (3 h at 0-3°) was obtained 6.0 g (92%) of (IIc), bp 45° (3 mm); n_D^{20} 1.4900. Found: C 21.89; H 4.03; N 16.82; S 19.07%. C₃H₆O₄N₂S. Calculated: C 21.69; H 3.64; N 16.87; S 19.27%. Infrared spectrum: 1320, 1583 cm⁻¹ (C (NO₂)₂).

Dinitromethyl 2,4-Dinitrophenyl Sulfide (IIIa). To a solution of 8.5 g of the piperidine salt of DNM in 200 ml of dimethoxyethane at 0-3° was added a solution of 4.70 g of 2,4- $(NO_2)_2$ PhSCl in 30 ml of dimethoxyethane. The mixture was stirred at 0-3° for 1 h, and the precipitate of piperidine hydrochloride (2 g, 85%) was separated. The filtrate was evaporated in vacuo (not exceeding 20°) to 1/3 volume and diluted with 0.5 liter of ether. The obtained precipitate was separated and washed in succession with water (50 ml), alcohol (20 ml) and ether. We obtained 7.0 g (81%) of the piperidine salt of sulfide (IIIa), mp 150° (from CH₃OH).

Dry HCl was passed into a stirred suspension of 1.64 g of this salt in 100 ml of absolute ether at 0-3°. The KCl precipitate (0.5 g, 100%) was separated. The filtrate was evaporated in vacuo (not exceeding 20°),

and the residue was reprecipitated from dichloroethane solution with hexane. We obtained 1.2 g (94%) of (IIIa), mp 75-77° (decompn.). Found: C 27.59; H 1.49; N 18.20; S 10.54%. $C_7H_4O_8N_4S$. Calculated: C 27.64; H 1.32; N 18.42; S 10.54%.

<u>K Salt of Sulfide (IIIa)</u>. The piperidine salt of (IIIa) (2.2 g) was dissolved at 75° in 200 ml of water and then, with stirring, 5 g of KCl was added. The mixture was cooled to 0-3°, and the precipitate was washed in succession with alcohol and ether. We obtained 1.68 g (86.5%) of the K salt, mp 275° (decompn.). Found: K 11.2%. $C_7H_3O_8N_4SK$. Calculated: K 11.3%.

Ag Salt of Sulfide (IIIa). The piperidine salt of (IIIa) (3.02 g) was dissolved at 90° in 200 ml of water and then, with stirring, 3 g of AgNO₃ was added. The mixture was cooled to 0-3°, and the precipitate was separated and washed in succession with alcohol and ether. We obtained 3 g (95%) of the Ag salt, mp 162°.

<u>Chlorodinitromethyl 2,4-Dinitrophenyl Sulfide (Va)</u>. A stream of dry chlorine was passed through a stirred suspension of 2.29 g of the piperidine salt of sulfide (IIIa) in 100 ml of absolute ether at 0-3° until the suspension became colorless. The KCl precipitate (0.67 g, 94%) was separated. The filtrate was evaporated in vacuo (not exceeding 20°), and the residue was washed with hexane until it solidified, after which it was reprecipitated from dichloroethane solution with hexane. We obtained 1.3 g (65%) of (Va), mp 30-31°. Found: Cl 10.08%. $C_7H_3O_8N_4SCl$. Calculated: Cl 10.44%.

Dinitromethyl Phenyl Sulfide (IIIb). To 2.68 g of the piperidine salt of DNM in 60 ml of dimethoxyethane at 0-3° was added 1.25 g of PhSCl in 10 ml of dimethoxyethane. The mixture was stirred at 0-3° for 1 h, the precipitate of piperidine hydrochloride (0.95 g, 90%) was separated, and the filtrate was evaporated in vacuo (not exceeding 20°) in 1/3 volume and then diluted with 250 ml of ether. We obtained 1.58 g (70%) of the piperidine salt of sulfide (IIIb), mp 115-118° (decompn.) (from water).

To a stirred solution of 0.5 g of this salt in 25 ml of water was added 1 g of KCl. The mixture was cooled to 0-3°, and the precipitate was separated. We obtained 0.25 g (60%) of the K salt of sulfide (IIIb), mp 212° (decompn.). Found: K 15.3%. $C_7H_5O_4N_2SK$. Calculated: K 15.5%.

Dry HCl was passed into a stirred suspension of 1.53 g of the K salt of sulfide (IIIb) in ether at 0-3°. The KCl precipitate (0.45 g, 100%) was separated, the filtrate was evaporated in vacuo, and the residue was recrystallized from a CCl_4 -hexane mixture. We obtained 1.25 g (96%) of (IIIb), mp 29-29.5°. Found: C 39.23; H 2.94; N 13.01; S 14.94%. $C_7H_6N_2O_4S$. Calculated: C 39.26; H 2.82; N 13.08; S 14.94%. Infrared spectrum: 1323, 1587 cm⁻¹ (C(NO₂)₂).

<u>Dinitromethyl Methyl Sulfide (IIIc)</u>. To a solution of 3.4 g of CH₃SCl in 50 ml of ether at 0-3° was added 4.32 g of the K salt of DNM. The mixture was stirred at 0-3° for 1 h, the KCl precipitate (2.2 g, 98%) was separated, and NH₃ was passed into the stirred filtrate at 0-3°. The obtained precipitate was washed with ether. We obtained 4.43 g (87%) of the ammonium salt of sulfide (IIIc).

With stirring and heating (40°), to a solution of 5.56 g of this salt in 45 ml of water was added 8 g of KCl. The mixture was cooled to 0-3°, and the precipitate was separated. We obtained 4.88 g (64%) of the K salt of sulfide (IIIc), mp 180° (decompn.) (from 85% alcohol). Found: K 20.9%. $C_2H_3N_2O_4SK$. Calculated: K 20.5%.

Dry HCl was passed into a stirred suspension of 2.46 g of the K salt of sulfide (IIIc) in 50 ml of absolute ether at 0-3° until the suspension became colorless. The KCl precipitate (0.9 g, 93%) was separated, the filtrate was evaporated in vacuo (not exceeding 20°), and the residue was distilled. We obtained 1.15 g (59%) of (IIIc), bp 50-51° (1 mm); n_D^{20} 1.4966. The substance partially decomposes even during distillation, for which reason an analytically pure specimen could not be obtained. The compound was identified as the corresponding α -chloro derivative (Vb).

<u>Chlorodinitromethyl Methyl Sulfide (Vb)</u>. A stream of dry chlorine was passed into a stirred suspension of the K salt of sulfide (IIIc) in 50 ml of ether at 0-3° until the suspension became colorless. The KCl precipitate (1.4 g, 95%) was separated, the filtrate was evaporated in vacuo (not exceeding 20°), and the residue was distilled. We obtained 3.35 g (90%) of (Vb), bp 38-40° (1 mm); n_D^{20} 1.5044. Found: C 12.85; H 1.69; N 14.92; S 17.10; Cl 18.94%. C₂H₃N₂O₄SCl. Calculated: C 12.80; H 1.61; N 14.94; S 17.09; Cl 18.90%. Infrared spectrum: 1310, 1610 cm⁻¹ (C (NO₂)₂ in α -halodinitro compounds [14]).

CONCLUSIONS

The reaction of the salts of polynitroalkanes with sulfenyl chlorides proceeds by the C-sulfenylation scheme, with the formation of the corresponding α -polynitroalkyl sulfides.

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