REACTION OF α-POLYNITROALKYL SULFIDES WITH ELECTROPHILIC REAGENTS

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UDC 542.91:547.414:547.279.53

The reaction of polynitroalkane anions with sulfenyl chlorides leads to the formation of α-polynitroalkyl sulfides [1, 2]. While studying the properties of the α-trinitromethyl sulfides (I) it was found that the C–S bond is cleaved by hydroxyl-containing nucleophilic reagents (NR) [2]. The possibility of cleaving the C–S bond in α-polynitroalkyl sulfides by various types of electrophilic reagents (ER) was studied in the present paper.

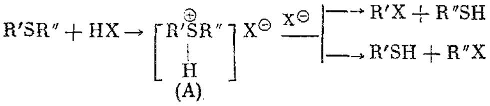
It is known [3, 4] that the C–S bond in organic sulfides is cleaved by ER. It proved that the trinitromethyl sulfides (I) are also not an exception. Thus, the C–S bond in (I) is cleaved by treatment with halogens or SO_2Cl_2 under mild conditions to give halotrinitromethanes and sulfenyl halides. Depending on the

$$\underset{\text{(Ia — e)}}{(NO_2)_3CSR'} \xrightarrow{X_2} (NO_2)_3CX + R'SX$$

$$R' = 2{,}4\text{-}(NO_2)_2Ph\,(a),\quad p\text{-}NO_2Ph\,(b),\quad Ph\,(c),\quad p\text{-}CH_3OPh\,(d),\quad CH_3\,(e);\quad X = Cl, Br$$

radical R' and the solvent, the yields of the reaction products vary from 40 to 90%.

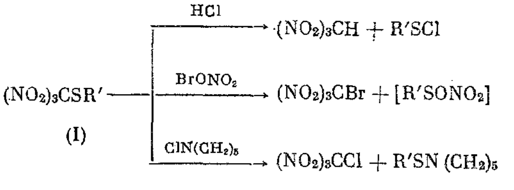
The reactions of sulfides with electrophilic reagents (hydrogen halides) are usually regarded as being electrophilic substitution at the sulfur atom: the initial formation of the sulfonium cation (A) and subsequent nucleophilic substitution at the α-carbon atom of the complex (A) [3, 4]*



$$R'SR'' + HX \rightarrow \underset{(A)}{\left[\begin{matrix} R'\overset{\oplus}{S}R'' \\ | \\ H \end{matrix}\right]} X^{\ominus} \xrightarrow{X^{\ominus}} \begin{cases} R'X + R''SH \\ R'SH + R''X \end{cases}$$

Taking this mechanism for the reaction of organic sulfides into account, it is possible to assume that the α-polynitroalkyl sulfides, due to the low electron density on the sulfur atom, will either not react at all with ER or else the reaction will proceed under drastic conditions. However, as was already mentioned, sulfides (I) react rapidly with ER under mild conditions.

While studying the reactions of (I) with unsymmetrically constructed electrophilic reagents ($BrONO_2$, HCl, N-chloropiperidine) it was found that the "electrophilic" portion of the reagent becomes attached to the carbon atom that bears the nitro group, while the "nucleophilic" portion becomes attached to the sulfur atom



$$\underset{(I)}{(NO_2)_3CSR'} \begin{cases} \xrightarrow{HCl} (NO_2)_3CH + R'SCl \\ \xrightarrow{BrONO_2} (NO_2)_3CBr + [R'SONO_2] \\ \xrightarrow{ClN(CH_2)_5} (NO_2)_3CCl + R'SN(CH_2)_5 \end{cases}$$

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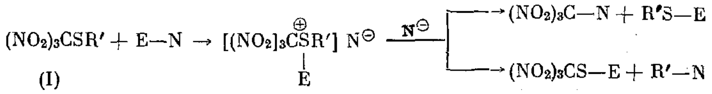
*The cleavage site of the C–S bond in complex (A) is determined by the relative stability of the intermediately formed carbonium ion ($R'^{\oplus}$ or $R''^{\oplus}$) [3].

Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1350-1355, June, 1974. Original article submitted November 28, 1973.

As a result, electrophilic substitution at the α-carbon atom, a new type of electrophilic substitution in the sulfide series, is observed.

If the electrophilic substitution was at the sulfur atom, then other products would be formed from (I). However, the formation



$$\underset{(I)}{(NO_2)_3CSR'} + E{-}N \rightarrow [(NO_2)_3C\overset{\oplus}{\underset{\underset{E}{|}}{S}}R']\,N^{\ominus} \xrightarrow{N^{\ominus}} \left\{\begin{array}{l} \rightarrow (NO_2)_3C{-}N + R'S{-}E \\ \rightarrow (NO_2)_3CS{-}E + R'{-}N \end{array}\right.$$

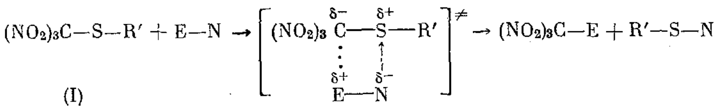
$E{-}N = H{-}Cl,\ Br{-}ONO_2,\ Cl{-}N(CH_2)_5$

of these compounds was not recorded in the reactions of (I) with the indicated electrophilic reagents.

It should be mentioned that the reaction of (I) with ER proceeds the same either in the light or in the dark and, as was shown on the example of the reaction with SO_2Cl_2, in the presence of acyl peroxides. These data testify to the nonradical character of the studied transformation.

Rules that indicate the important role of nucleophilic cooperation, shown by the "nucleophilic" portion of the reagent E–N, are detected when the reactions of sulfides (I) with ER are studied. This type of cooperation, where the "nucleophilic" portion (N) of the electrophilic reagent is coordinated with the heteroatom, thus facilitating reaction progress, is frequently manifested in the reactions of organoelement compounds [5].

Nucleophilic cooperation in the case of the α-polynitroalkyl sulfides is confirmed by the fact that the "softer" the nucleophilic portion of the ER the easier is the reaction of (I) with ER. For example, if the reaction of 2,4-$(NO_2)_2PhSC(NO_2)_3$ (Ia) with bromine goes to completion almost instantly (with the formation of ∼80% $(NO_2)_3CBr$ and 2,4-$(NO_2)_2PhSBr$), then only 20% of $(NO_2)_3CBr$ is formed in 1 h when (Ia) is reacted with $BrONO_2$, while most of (Ia) remains unreacted. In addition, HSO_3F in general does not react with (Ia), whereas HCl effects the complete cleavage of the C–S bond in this sulfide at 0-5°, and the reaction is ended in 0.5 h with the formation of $(NO_2)_3CH$ (77% yield) and 2,4-$(NO_2)_2PhSCl$ (86% yield). In the discussed examples the electrophilicity of $BrONO_2$ and HSO_3F is not lower than the electrophilicity of respectively Br_2 and HCl, nevertheless the "hard" groupings ONO_2 and OSO_2F impair the conditions for coordination of the sulfur atom in (Ia) and strongly hinder the reaction. It is probably for this reason that N-chloropiperidine reacts with (Ia) in 5 min (the yield of $(NO_2)_3CCl$ is 70%, and that of 2,4-$(NO_2)_2PhSN(CH_2)_5$ is 90%), whereas the reaction practically does not go with N-chlorosuccinimide. These data make it possible to assume that the reactions of (I) with ER proceed with nucleophilic cooperation, probably (by analogy with organometallic compounds [5]) via a cyclic 4-membered transition state*



$$\underset{(I)}{(NO_2)_3C{-}S{-}R'} + E{-}N \rightarrow \left[\begin{array}{ccccc} (NO_2)_3 & \overset{\delta-}{C} & — & \overset{\delta+}{S} & —R' \\ & \vdots & & \uparrow & \\ & \overset{\delta+}{E} & — & \overset{\delta-}{N} & \end{array}\right]^{\neq} \rightarrow (NO_2)_3C{-}E + R'{-}S{-}N$$

The effect of the character of the substituent attached to the sulfur atom (R') on the ease of reaction of (I) with ER increases in the order: $CH_3 < p\text{-}CH_3OPh < Ph < p\text{-}O_2NPh < 2,4\text{-}(NO_2)_2Ph$, i.e., with increase in the electron-acceptor properties of the radical R'. Thus, for example, SO_2Cl_2 in CH_3CN reacts almost instantly with 2,4-$(NO_2)_2PhSC(NO_2)_3$ (Ia) and p-$NO_2PhSC(NO_2)_3$ (Ib); with $PhSC(NO_2)_3$ (Ic) the reaction is ended in 0.5 h, with p-$CH_3OPhSC(NO_2)_3$ (Id) in a day, while SO_2Cl_2 practically does not react with $CH_3SC(NO_2)_3$ (Ie). A variable reactivity of (Ia) and (Ib) can be observed on the example of the reaction with bromine in CH_3CN, which is difficultly discernible in the reaction with SO_2Cl_2: if the first reacts instantly, then the second reacts only in a day. The discovered rule also testifies in support of nucleophilic cooperation, since the partial positive change on the sulfur atom increases with increase in the electron-acceptor properties of radical R' in (I), which, in turn, facilitates the approach of the nucleophilic portion of the electrophilic reagent E–N to it.

It is possible to assume that the ionization of (I) at the C–S bond occurs under the influence of the solvent, with the formation of the anion $C(NO_2)_3^{\ominus}$ and the sulfenium cation $R'{-}S^{\oplus}$, which on subsequent reaction with ER then given the obtained end products. However, it was shown by UV spectroscopy that such ionization fails to occur (absorption at λ 350 nm, characteristic for the $C(NO_2)_2^{\ominus}$ anion, is absent) in the

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*The open transition state is less probable, since it stipulates either preliminary ionization of the electrophile, which is hardly possible in the employed relatively low-polar media, or the ionization of (I) with the formation of $C(NO_2)_3^{\ominus}$, which is not observed (see below).

studied solvents (benzene, CH_2Cl_2, ether, dimethoxyethane (DME), CH_3CN). Nevertheless, the character of the solvent exerts an important effect on the reaction of (I) with ER. The following general rule is observed: the reaction is accelerated with increase in the polarity and basicity of the solvent, which probably testifies to an increase in the separation of the charges in the transition state [6], the solvation of which facilitates the entire process. For example, in either benzene or CH_2Cl_2 medium the reaction of (Ia) with bromine proceeds to the extent of 10% in 1 day, whereas the reaction is ended almost instantly in ether, DME or CH_3CN.

It is important to mention that if one of the NO_2 groups in (I) is replaced by either an alkyl moiety or a halogen atom, then the reactions with ER are hindered substantially. Thus, if (Ia) reacts rapidly with bromine and SO_2Cl_2 (CH_3CN), then α-dinitroalkyl sulfides $2,4\text{-}(NO_2)_2PhSC(NO_2)_2R$ (R = F, Cl, Br, CH_3) do not enter into these reactions. The indicated compounds also do not react with such strong electrophiles as N-chloropiperidine and chlorine. Apparently, the successful progress of the reactions with ER depends on the thermodynamic stability generated in the transition state of the polynitrocarbanion, $RC(NO_2)_2^{\ominus}$. The greater stability of the $C(NO_2)_3^{\ominus}$ anion when compared with the $RC(NO_2)_2^{\ominus}$ anions (where R = F, Cl, Br, CH_3) is confirmed by the different pK values (20°, H_2O) of the corresponding conjugated acids: 0.17 for $HC(NO_2)_3$ [7], 7.70 for $FCH(NO_2)_2$ [8], 3.53 for $ClCH(NO_2)_2$ [9], 3.6 for $BrCH(NO_2)_2$ [9], and 5.21 for $CH_3CH(NO_2)_2$ [7].

The obtained data, in combination with the effect of the R' radical on the progress of the reactions of (I) with ER (see above), make it possible to assume that nucleophilic coordination at the sulfur atom can be even somewhat ahead of electrophilic attack at the α-carbon atom of (I) (which is also observed in the reactions of other organoelement compounds with ER [5]).*

In contrast to the strong effect exerted by the stability of the generated anion ($RC(NO_2)_2^{\ominus}$) on the reaction of ER with α-polynitroalkyl sulfides ($R'SC(NO_2)_2R$), the stability of the sulfenium cation ($R'S^{\oplus}$) apparently does not play a major role, since, as was mentioned above, $p\text{-}CH_3OPhSC(NO_2)_3$ (Id) reacts with ER much more slowly than $PhSC(NO_2)_3$ (Ic). This indicates the absence of prior attack of the electrophile at the carbon atom of the trinitromethyl group with a freeing of the sulfenium cation, $p\text{-}CH_3OPhS^{\oplus}$, since the opposite picture would be observed in the opposite case because of the better stabilization of the positive charge of this cation due to the +M effect of the $p\text{-}CH_3OPh$ radical. All of this again confirms nucleophilic cooperation when α-polynitroalkyl sulfides are reacted with ER.

A different possible scheme for explaining the obtained results, namely the one-electron oxidation of (I) with the intermediate formation of the cation-radical $(NO_2)_3C-\dot{\overset{+}{S}}-R'$ and the anion-radical $[E-N]^{\dot{-}}$, is not real, since in harmony with this scheme the process should slow up with increase in the electron-acceptor properties of the R' radical in (I); actually the opposite rule is observed. Another, somewhat improbable scheme, also drops out: the oxidation of the ER via the transfer of one electron to the nitro group of (I), since in this case, for example, the Br_2 molecule would be oxidized more easily than Cl_2, whereas actually the reaction with Br_2 proceeds much more slowly. Thus, $PhSC(NO_2)_3$ (Ic) reacts with Cl_2 in 2 h to give $(NO_2)_3CCl$ in 86% yield, whereas only traces of $(NO_2)_3CBr$ are formed with Br_2 in one day, and 92% of the starting (Ic) is recovered unchanged. We will also mention that the formation of products, testifying to the cleavage of the R'–S bond in the $R'-S-C(NO_2)_3$ molecule, was not observed in a single experiment.

On the whole, it is possible to conclude from the obtained data that in α-polynitroalkyl sulfides, under the influence of the electron-acceptor action of several nitro groups at the α-carbon atom, the sulfur changes its character strongly when compared with ordinary organic sulfides, and becomes electrophilic to a substantial degree.

EXPERIMENTAL METHOD

Absolute solvents were used in the work. See [2] for the synthesis of the starting polynitroalkane salts and known α-polynitroalkyl sulfides. The completeness of reaction was checked by TLC.

Trinitromethyl-(2,4-dinitrophenyl)sulfide (Ia).† To a solution of 11.7 g of $2,4\text{-}(NO_2)_2PhSCl$ in 40 ml of freshly purified dichloroethane at 30° was added 11 g of the K salt of trinitromethane (TNM). The mixture was stirred at 30° for 8 h, and the precipitate was separated. The filtrate was evaporated in vacuo

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*In the studied process the assumption of purely nucleophilic substitution at the sulfur atom in (I) seems highly doubtful, especially for such reagents as Cl_2 or Br_2. In addition, as was found by us, the (I) compounds do not react with such NR as $Br^{\ominus}$ (for example, (Ic), which reacts easily with Cl_2, Br_2 and other ER, and does not react under the same conditions with a large excess of $(C_2H_5)_4NBr$).

†This method is more convenient than that described in [2].

(not above 20°), and the residue was washed with hexane until it became solid, and then it was recrystallized from a 1:2 $CHCl_3$–hexane mixture. We obtained 11 g (63%) of (Ia), mp 68-69°; see [2].

Trinitromethyl-(p-nitrophenyl)sulfide (Ib). In the same manner as the preceding, from 2.5 g of p-NO_2PhSCl [10] in 15 ml of dichloroethane and 2.5 g of the K salt of TNM (with stirring for 1 h at 0-3°) we obtained 3.48 g (87%) of (Ib) with mp 125-127° (decompn.) (from CCl_4). Found: C 27.78; H 1.40; N 18.07; S 10.70%. $C_7H_4O_8N_4S$. Calculated: C 27.64; H 1.33; N 18.42; S 10.52%. Infrared spectrum (ν, cm^{-1}): 1300, 1605 ($C(NO_2)_3$), 1345, 1530 (NO_2 in the ring).

Trinitromethyl-(p-methoxyphenyl)sulfide (Id). With stirring, 1.35 g (0.8 ml) of SO_2Cl_2 was added to a solution of 2.78 g of $(p\text{-}CH_3OPh)_2S_2$ [11] in 10 ml of CH_2Cl_2 at 20°. After 0.5 h the solution was cooled to 0° and 3.8 g of the K salt of TNM was added. The mixture was stirred at 0-3° for 0.5 h, and the KCl precipitate (1.40 g; 94%) was separated. The filtrate was evaporated in vacuo (≤20°), and the residue was recrystallized from pentane with supercooling. We obtained 4.1 g (70%) of (Id), mp 36-38. Found: C 33.50; H 2.65; N 14.56; S 11.16%. $C_8H_7O_7N_3S$. Calculated: C 33.23; H 2.44; N 14.53; S 11.07%. Infrared spectrum (ν, cm^{-1}): 1300, 1595, 1605 ($C(NO_2)_3$), 1263 ($H_3C-O-Ph$).

Fluorodinitromethyl-(2,4-dinitrophenyl)sulfide (II). a) K Salt of Dinitromethyl-(2,4-dinitrophenyl)-sulfide* (III). With stirring, 5.65 g of 2,4-$(NO_2)_2PhSCl$ in 20 ml of DME was added at 0-3° to a suspension of 6.95 g of the K salt of dinitromethane in 20 ml of DME. The mixture was stirred at 0-3° for 1.5 h, and the precipitate was separated and washed in succession with chilled water (2 × 40 ml), alcohol and ether. We obtained 6.71 g (82%) of (III), mp 275° (decompn.).

b) Reaction of (III) with $FClO_3$. With stirring, into a suspension of 6.71 g of (III) in 70 ml of CH_3CN at 20° was slowly passed a stream of $FClO_3$ (for 6-7 h until the suspension was decolorized), and the $KClO_3$ precipitate (2.32 g; 96%) was separated. The filtrate was evaporated in vacuo (≤20°), and the residue was purified by freezing from hexane. We obtained 5 g (79%) of (II) as a pale yellow thick oil; n_D^{20} 1.5945. Found: C 26.40; H 1.02; N 17.52; S 9.80; F 5.85%. $C_7H_3O_8N_4SF$. Calculated: C 26.09; H 0.94; N 17.39; S 9.95; F 5.90%. F^{19} NMR spectrum: 1.05 ppm (CF_3COOH). Infrared spectrum (ν, cm^{-1}): 1305, 1600 ($C(NO_2)_3$), 1347, 1550 (NO_2 in the ring).

Reaction of Trinitromethyl Sulfides (I) with Electrophilic Reagents. a) Reaction with Chlorine. With stirring, dry Cl_2 was passed for 40 min into a solution of 1.65 g of (Ia) in 5 ml of DME at 0-3°, after which the mixture was diluted with pentane, and the 2,4-$(NO_2)_2PhSCl$ precipitate (0.87 g; 80%) was separated (mp 97-98°; see [12]). The filtrate was washed with water and then dried over $MgSO_4$. The solvent was distilled off, and the residue was vacuum-distilled. We obtained 0.65 g (75%) of $(NO_2)_3CCl$ with bp 56° (40 mm); see [13].

The reaction was run in a similar manner with (Ic) (0-3°, 2 h; yield of $(NO_2)_3CCl$ = 86%) and with (Ie) (0-3°, 5 h; yield of $(NO_2)_3CCl$ = 63%).

b) Reaction with SO_2Cl_2. To a solution of 1.75 g of (Ia) in 5 ml of CH_3CN at 20° was added 2 ml of SO_2Cl_2, and after 5 min the mixture was poured into water and extracted with ether. The extract was washed with water, dried over $MgSO_4$, evaporated, and the residue was vacuum-distilled. We obtained 0.77 g (80%) of $(NO_2)_3CCl$.

The reaction was run in a similar manner with (Ib) (20°, 5 min; yield of $(NO_2)_3CCl$ = 50%), with (Ic) (20°, 0.5 h; yield of $(NO_2)_3CCl$ = 75%), and with (Id) (20°, one day; yield of $(NO_2)_3CCl$ = 76%). When (Ia) was reacted with SO_2Cl_2 in CH_2Cl_2 (20°, 3 days) the yield of $(NO_2)_3CCl$ was 50%.

c) Reaction with Bromine. To a solution of 1.3 g of (Ia) in 30 ml of ether at 20° was added 0.26 ml of Br_2. After 5 min the solvent was partially removed, the residue was diluted with pentane, and the 2,4-$(NO_2)_2PhSBr$ precipitate (0.88 g; 85%) was separated (mp 105-106°; see [14]). The solvent was removed, and the residue was vacuum-distilled. We obtained 0.66 g (78%) of $(NO_2)_3CBr$, bp 70° (25 mm); see [13].

The reaction was run in a similar manner with (Ib) (CH_3CN, 20°, one day; yield of $(NO_2)_3CBr$ = 40%; in addition, $(p\text{-}NO_2Ph)_2S_2$† was isolated, mp 180-183°; see [10]). When (Ia) was treated with Br_2 in CH_2Cl_2 (20°, one day) the yield of $(NO_2)_3CBr$ was 10%.

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*This method is more convenient than that described in [2].

†The disulfide was formed due to the instability of the intermediately formed p-NO_2PhSBr and its easy conversion to $(p\text{-}NO_2Ph)_2S_2$ (see, for example, [15]).

d) Reaction with HCl. With stirring, dry HCl was passed into a solution of 1.75 g of (Ia) in 5 ml of DME at 0-3°. After 0.5 h the mixture was diluted with pentane, and the 2,4-$(NO_2)_2PhSCl$ precipitate (1 g; 86%) was separated. The yield of TNM was 77% (determined by spectrophotometry).

e) Reaction with N-Chloropiperidine. To a solution of 1.75 g of (Ia) in 5 ml of CH_2Cl_2 at 20° was added 0.6 g of N-chloropiperidine [16]. After 5 min the mixture was diluted with pentane, and the 2,4-$(NO_2)_2PhSN(CH_2)_5$ precipitate (1.27 g; 90%) was separated; mp 151-153°. The compound was identified by comparison with an authentic specimen, which was obtained by reacting 2,4-$(NO_2)_2PhSCl$ with piperidine (ether, 20°, one h; 60% yield; mp 151-153° (from actone). Found: C 46.99, H 4.69, N 14.78; S 11.22%. $C_{11}H_{13}O_4N_3S$. Calculated: C 46.64; H 4.63; N 14.84; S 11.30%.

The solvent was removed, and the residue was vacuum-distilled. We obtained 0.67 g (69%) of $(NO_2)_3CCl$.

f) Reaction with $BrONO_2$. To a solution of 3.5 g of (Ia) in 10 ml of DME at 20° was added 34 ml of a 0.36 M solution of $BrONO_2$ in DME.* The mixture was kept at 20° for 1 h, diluted with ether, and washed with water. The ether layer was dried over $MgSO_4$, the ether was removed, and the residue was vacuum-distilled. We obtained 0.47 g (20%) of $(NO_2)_3CBr$.

CONCLUSIONS

1. Trinitromethyl sulfides ($R'-S-C(NO_2)_3$) when treated with electrophilic reagents (halogens, HCl, $BrONO_2$, N-chloramines) are cleaved at the C–S bond to give trinitromethane and sulfenic acid derivatives. Here the electrophilic portion of the reagent always attaches itself to the carbon atom of the polynitroalkyl group, which is a new type of electrophilic substitution in the sulfide series.

2. A theory was expressed regarding the role of internal nucleophilic cooperation due to coordination of the nucleophilic portion of the electrophilic reagent with the sulfur atom in polynitroalkyl sulfides.

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*The $BrONO_2$ solution was prepared by stirring (20°, 10 h) a mixture of 3.6 g of $AgNO_3$ and 1.1 ml of Br_2 in 50 ml of dimethoxyethane and subsequent separation of the AgBr precipitate (by analogy with [17]).