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Studies of Thioacids and Their Derivatives

XII. Derivatives of Nitrodithioacetic Acid*

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The di-anion of nitrodithioacetic acid (I) is described as a resonance hybrid of formulae II–IV on the basis of infrared spectroscopic data and chemical data of the dipotassium salt and its derivatives, formed through the reaction with various alkyl halides. An unusual reaction is the elimination of the $=CH-NO_2$ group when the *S*-alkyl compounds are oxidized to sulfones. From nitroethane analogous compounds could only be isolated in very low yields by special methods. From nitromethane, carbon diselenide and potassium hyroxide an unstable compound is formed, which is tentatively formulated as 2-nitroethaneselenolate.

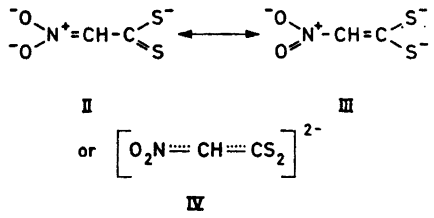
According to Freund[3] nitromethane, potassium hydroxide, and carbon disulfide react to form the dipotassium salt of *aci*-nitrodithioacetic acid (I). We became interested in this compound during our work on infrared spectra[4] and coordination compounds of dithioacids.

$$^{-}O_2N{=}CH{-}CS_2^{-},2K^{+}$$

I

The infrared spectrum of the dipotassium salt (I) shows a rather surprising feature: It has no absorption bands in the double bond region, whereas aliphatic nitro compounds normally exhibit strong absorption near 1550 cm^{-1} and the salts of *aci*-nitro compounds[5] have a strong band near 1600 cm^{-1}. This seems to be strong evidence for the formulation of the divalent anion as a resonance hybrid:

* In No. I of this series[1] the results of papers Nos. II–XI were summarized. The editing of papers Nos. IX–XI has been delayed. In the meantime, further material on the chemistry of thioacids has accumulated in this laboratory and will be published as No. XII, etc., of this series. The recent paper by Gompper and Schaefer[2] prompts us to deviate from the planned sequence.



II III

or $\left[O_2N{=}CH{=}CS_2\right]^{2-}$

IV

The chemical reactions of I are in accordance with formula III, *i.e.* it reacts as the divalent anion of 2-nitroethylene-1,1-dithiol. The infrared spectrum shows, however, that formula II has some weight.

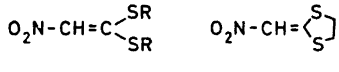
The infrared spectrum of the dipotassium salt of *aci*-nitroacetic acid, $KO_2N{=}CH{-}CO_2K$, shows the same main feature as the infrared spectrum of the dithio compound, while the chemical properties of dipotassium *aci*-nitroacetate are mainly in accordance with a structure corresponding to formula II.

CHEMICAL PROPERTIES OF THE DI-ANION OF NITRODITHIOACETIC ACID

Nitrodithioacetic acid could neither be isolated as the free acid nor as a salt of the monovalent anion. By addition of one equivalent of hydrochloric acid to the dipotassium salt, a clear solution was formed. On evaporation *in vacuo* decomposition took place with formation of a brown resin. On addition of an excess of hydrochloric acid, a yellow residue, probably polymeric, was formed.[3]

It can, however, be concluded that the anion corresponds to a rather strong divalent acid ($pK_1 < 2$) since an aqueous solution of the dipotassium salt is almost neutral (pH of 0.01 N aqueous solution $\simeq 8$). Potentiometric titration of the dipotassium salt with hydrochloric acid indicates that $pK_2 \simeq 5.2$. In this respect the dithio compound differs from the dipotassium salt of nitroacetic acid, which in aqueous solution has a strongly basic reaction because of hydrolysis to the monovalent anion (according to Pedersen [6] nitroacetic acid has $pK_1 \simeq 1.7$ and $pK_2 = 9$).

Dipotassium nitrodithioacetate was found to react with methyl or ethyl bromide to form thioacetals of nitroketene (Va and Vb). Similar reactions took place with other organic compounds with reactive halogen atoms. The



V VI

V a: $R=CH_3$, V b: $R=C_2H_5$; V c: $R=CH_2CO_2H$

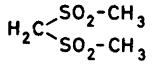
V d: $R=CH_2C_6H_5$; V e: $R=CH_2COC_6H_5$

reactions with sodium bromoacetate, benzyl chloride, phenacyl bromide, and ethylene bromide took place with the formation of compounds Vc—e and VI.*

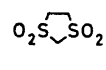
Attempts to prepare derivatives of nitrodithioacetic acids were, however, not in all cases successful. When the reaction was too slow, side reactions took place with the formation of sulfur and dark oils which resisted attempts at purification. Thus, compound Vc could only be prepared from bromoacetic acid and not from chloroacetic acid, and no well-defined compounds were obtained from the reactions of I with 1,3-dibromopropane, 1,3-dichloroacetone, methyl chloroformate, benzylidene chloride, benzoyl chloride, α,β-dibromosuccinic acid, or 2,4-dinitrochlorobenzene. However, the problem was not pursued very extensively, and it is possible that by varying the reaction conditions or methods of purification, better results could be obtained.

On attempts to reduce I with sodium borohydride, the starting material (I) was recovered unchanged.

By oxidation of the dithioacetals V and VI with hydrogen peroxide in acetic acid a remarkable reaction took place with elimination of the $=CH-NO_2$ grouping and oxidation of the sulfide to a sulfone. Thus, Va formed bis(methylsulfonyl)methane [7,8] (VII), and VI formed 1,3-dithiolan-1,1,3,3-tetraoxide [9] (VIII), both known compounds, which were identified on the basis of their melting points and infrared spectra.



VII



VIII

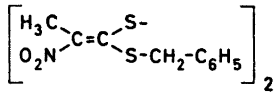
With nickel salts (I) gives an extremely intense red colour which turns blue-black on exposure to air, or more rapidly on addition of hydrogen peroxide. A study of this reaction and similar reactions with other dithio acids will be published in a forthcoming paper. A planned, more extensive investigation of coordination compounds of transition metals with 1,1-dithiols has, however, been made redundant by the recent investigations of this type of compound by Fackler *et al.*[10]

HOMOLOGUES OF NITRODITHIOACETIC ACID

Numerous attempts with different solvents and bases were carried out to prepare analogues of (I) from nitroethane, 1- and 2-nitropropane, 1,4-dinitrobutane, or phenylnitromethane, but with very little success. In alcoholic solutions xanthates were formed. The potassium salts of *aci*-nitroethane and *aci*-1-nitropropane reacted with carbon disulfide in dioxan solution but the reaction products decomposed almost immediately in the presence of air, and quickly in the presence of water. The potassium salts of *aci*-2-nitropropane or *aci*-phenylnitromethane apparently did not react with carbon disulfide under these conditions.

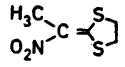
* Compounds Va and VI have also been prepared by Gompper and Schaefer.[2]

Attempts to prepare analogues of compounds V—VI directly from the crude products prepared in dioxan yielded a well-defined compound in only one case. The product prepared from the potassium salt of *aci*-nitroethane and carbon disulfide reacted with benzyl chloride to form the disulfide IX. This, at least, indicates that some of the corresponding dithiolate was present in the crude product.



IX

However, the experiences from the preparation of other 1,1-dithiolates, reported in a following paper,[11] have shown that a remarkable improvement of the yields may often be achieved by using dimethylformamide or dimethylsulfoxide as solvents. The reaction of nitroethane with sodium hydride, carbon disulfide and ethylene bromide in dimethylsulfoxide afforded 2-(1′-nitroethylidene)-1,3-dithiolan (X) in a 7 % yield. From 1,3-dibromopropane the corresponding dithian was formed.

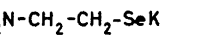


X

This result shows that, in principle, it is possible to prepare homologues of the compounds V—VI derived from higher nitroalkanes. Nevertheless, the difference in reactivity between nitromethane and the higher nitroalkanes is surprising. It can hardly be due to the difference in acidity but must be explained by some steric influence of the substituent in α-position to the nitro group. It seems that the effect of this is not only to impede the addition of CS_2 to the nitroalkane anion, but also to inhibit enethiolisation of the dithioic acids, when formed. As is well known, dithioic acids have a pronounced tendency to polymerise.

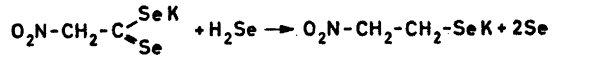
THE REACTION BETWEEN CARBON DISELENIDE AND NITROMETHANE

Carbon diselenide reacts readily with nitromethane and ethanolic potassium hydroxide and the infrared spectrum of the crude product indicates that a compound analogous to I has been formed. However, it has not been possible to isolate it in a pure state. On attempts to purify the crude product another compound was isolated which according to analyses is the potassium salt of 2-nitroethaneselenol (XI):



XI

This salt could be prepared in a fairly pure state but is very unstable and on heating decomposed explosively with an intense blue light. The formation of this compound can possibly be explained to have taken place by reduction of a diseleno compound corresponding to I with hydrogen selenide (formed by hydrolysis or alcoholysis of the diseleno compound):



NUCLEAR MAGNETIC RESONANCE SPECTRA

The nuclear magnetic resonance spectra of Va and VI (Table 1) show a simple pattern, corresponding well to the assigned structures. The spectra of compounds Vb and Vd show an interesting doubling of ethyl and benzyl

Table 1. NMR spectra.[a]

Compound	=CH—	$-CH_2-$	$-CH_3$	$-C_6H_5$
Va[b]	2.90, s, 1H	7.45, s, 6H		
Vb[c]	2.93, s, 1H	7.00, qui, $J = 8$, 4H[d]	8.6, m, 6H[e]	
Vd[b]	2.85, s, 1H	5.79, s, 2H 5.89, s, 2H		2.67, S 2.70, S } 10 H
VI[b]	2.42, s, 1H	6.45, s, 4H		

[a] Chemical shifts are in τ values, coupling constants in cps; s = singlet; qui = quintet; m = multiplet. Solvent: $CDCl_3$.
[b] 60 Mc/s with TMS as internal reference.
[c] 100 Mc/s with TMS as internal reference.
[d] By recording at 60 Mc/s this signal appeared as two overlapping quartets.
[e] The multiplet consisted of two overlapping triplets, $J = 8$. With spin decoupling at the quintet, the multiplet was changed to a doublet.

signals. This must be due to the magnetic anisotropy of the $=CHNO_2$ grouping, and it is interesting that the dimethyl thioacetal (Va) and the dithiolan (VI) do not give this doubling.

The absence of the doubling in the spectra of Va and VI can be explained on the basis of molecular models, which show that the methylene protons in VI are in fixed positions far from the anisotropic part of the molecule, and that the methyl groups in Va are more restricted in space than the methyl groups in Vb or the phenyl groups in Vd. This permits only the latter two groups to experience the magnetic anisotropy of the $=CHNO_2$ part of the molecules.

INFRARED SPECTRA

As mentioned, a characteristic feature of the infrared spectrum of I (Table 2) is the complete absence of the band near 1550 cm^{-1} found in the spectra of ordinary nitro compounds. The dithioacetals Va—e and VI all show a strong band near 1510 cm^{-1} which we assign to the anti-symmetric stretching frequency of the NO_2 group. The lower frequency is readily explained by the conjugation of the nitro group in these compounds and is in accordance with the values found for alkylnitroethylenes.[12] The symmetric frequency is found at 1250—1270 cm^{-1}, somewhat lower than for simple nitroethylenes.

In the infrared spectra of *aci*-nitro compounds two strong bands, assigned to C=N and N—O stretching,[5] are found at *ca.* 1600 cm^{-1} and *ca.* 1170 cm^{-1}. The infrared spectra of dipotassium nitroacetate and dipotassium nitrodithioacetate also show a strong band at *ca.* 1170 cm^{-1}, but the strong bands at 1480 cm^{-1} and 1380 cm^{-1}, respectively, are considered to correspond to the 1600 cm^{-1} band. The resonance structures II—III would explain these shifts to lower frequencies.

The carboxylate group of the nitroacetate anion gives rise to strong bands at 1580 cm^{-1} and 1320 cm^{-1}, assigned to the anti-symmetric and symmetric stretching vibrations of the $-CO_2^-$ group. The infrared spectrum of I shows a band at 1220 cm^{-1} which corresponds to bands near 1300 cm^{-1} in the spectra of other ethylene-1,1-dithiolates.[11] A band at 545 cm^{-1} in the spectrum of I seems also to be due to the CS_2 group.

The infrared spectrum of I shows an intense band at 1410 cm^{-1} and similar bands are found in the spectra of dipotassium nitroacetate and the dithioacetals Va—e and VI. These bands are sensitive to deuteration and they disappear together with the bands assigned to the nitro group when the compounds Va and VI are oxidized to the sulfones VII and VIII. We assign these bands to the partly delocalized double bond of the groupings N—CH=C or N=CH—C. Another band due to this grouping is possibly found near 920 cm^{-1}. In aqueous solution I shows two very intense and broad infrared bands at 1375—1425 cm^{-1} (1380 and 1410 overlapping) and 1180—1230 cm^{-1} (1177 and 1220 overlapping). The infrared spectrum of an aqueous solution of dipotassium nitroacetate shows the same strong and broad band near 1400 cm^{-1} together with carboxylate bands at 1550 cm^{-1} and 1300 cm^{-1}. The 1220 cm^{-1} band, assigned to $-CS_2^-$, is missing and the NO_2 band is found at 1140 cm^{-1}.

The bands assigned to the structures NO_2, CO_2^-, and CS_2^- are only little affected by deuteration but most other bands are changed somewhat on deuteration, which indicates that most vibrations are coupled to some extent with CH vibrations.

A band in the 700—800 cm^{-1} range is affected only little by deuteration and it disappears when Va is oxidized to VII. It is therefore assigned to an N—O vibration.

The main feature of the infrared spectra of the dithioacetals (Va—e and VI) is the appearance of a very strong band near 1300 cm^{-1}. It is assigned to a deformation frequency of CH_3 or CH_2 bonded to sulfur. This band does not disappear when the compounds Va or VI are oxidized to the sulfones VII and VIII. The absorption bands of compound Va are listed in Table 2.

Table 2. Infrared absorption bands (cm^{-1}) of dipotassium nitroacetate, dipotassium nitrodithioacetate, and 1,1-bis(methylthio)-2-nitroethylene. [a]

$K_2(O_2NCHCO_2)$	$K_2(O_2NCHCS_2)$	$O_2N-CH=C(SCH_3)_2$	Correlation
3110 m		3140 m	CH
3100 m	3090 m	3000 w	CH
		2940 w	CH_3
1580 vs			CO_2^-
1505 m	1470 vw		
1480 s	1380 s	1510 s	NO_2
		1435 sh	CH_3
1420 s	1410 vs	1420 vs	N—CH=C
	1330 w		
1320 vs			CO_2^-
		1300 vs	SCH_3
1160 vs	1177 s	1260 vs	NO_2
	1220 s		CS_2^{-2}
1045 s	1000 s	1035 m	CH
		965 w	
		950 w	
940 s	920 vs	922 s	N—CH=C
810 s	782 m		CH
768 } s	735 s	785 s	NO_2
760 }			
		732 m	
		720 m	
695 w	698 m	675 s	CH
	545 m		CS_2^{-2}

[a] Spectra recorded from KBr discs. The spectra recorded from nujol mulls showed approximately the same absorption maxima. For the spectra recorded from aqueous solutions, see the text.

The infrared spectra of the other thioacetals (Vb—e and VI) are more complicated but they all show the strong bands assigned to the NO_2 group (1510—1540 cm^{-1}, 1250—1270 cm^{-1}, and 760—790 cm^{-1}), the N—CH=C group (1405—1430 cm^{-1} and 920—960 cm^{-1}) and the SR group (1290—1310 cm^{-1}).

The main feature of the infrared spectra of the sulfones (VII and VIII) is the absence of all bands assigned to the nitro group and the N—CH=C group, and the appearance of strong SO_2 bands near 1100 cm^{-1} and 850 cm^{-1}.

ULTRAVIOLET SPECTRA

Whereas dipotassium nitroacetate exhibits an absorption band at approximately the same wavelength as the sodium salt of nitromethane (but less intense), all the derivatives of nitrodithioacetic acid show a considerable bathochromic shift (Table 3). This effect is even greater than for the anions of nitroalkenes.[13] As expected, the bathochromic shift is especially large for the nitrodithioacetate anion (I) and points to an extensive delocalization of the π-electrons, in accord with formulae II—IV.

Table 3. Ultraviolet spectra.

Compound	λ_{max}, mμ	log ε	Solvent ($C \sim 10^{-4}$ mole/l)
$K_2[O_2NCHCO_2]$	277	3.22	water
I	403	4.06	water
Va	357	4.17	ethanol (96 %)
	297	3.79	
Vb	359	4.17	»
	302 sh	3.77	
Vd	359	4.14	»
	299 sh	3.80	
Ve	357	3.74	»
	247	4.27	
VI	354	4.19	»
	220	3.51	

EXPERIMENTAL

Spectra. The infrared spectra were recorded on a Perkin Elmer Model 21 B double beam spectrophotometer and ultraviolet spectra on a Perkin Elmer Model 137 UV spectrophotometer.

Nuclear magnetic resonance spectra were recorded on a Varian Model A 60 or HA 100 apparatus.

Dipotassium nitrodithioacetate (I). This was prepared as described by Freund.[3] The conditions are critical, and the directions should be followed carefully. To purify the crude product, 5 g was dissolved in 15 ml of water and precipitated by addition of 30 ml of ethanol; this process was repeated four times. (Found: N 6.59. Calc. for $C_2HK_2NO_2S_2$: N 6.58). From potentiometric titration of a 0.005 M solution with hydrochloric acid the equivalent weight 213 (calc. 213) and $pK_2 = 5.2$ were found.

Dipotassium nitroacetate. This was prepared according to the literature.[14] Yield 36 g (67 %) from 50 g of nitromethane. The salt was pure after washing with methanol.

1,1-Bis(methylthio)-2-nitroethylene (Va). 2.1 g of (I) and 2.9 g of methyl iodide were dissolved in 40 ml of 50 % aqueous methanol and stirred for 2 h. The yellow crystals (1.61 g; 98 %) were recrystallized from ethanol. M.p. 125—126°C. (Found: C 29.20; H 4.42; N 8.41; S 38.70. Calc. for $C_4H_7NO_2S_2$: C 29.10; H 4.27; N 8.48; S 38.76).

In a similar manner were prepared:

1,1-Bis(ethylthio)-2-nitroethylene (Vb). Yield 1.28 g (66 %) from 2.1 g of I and 2.2 g of ethyl bromide. M.p. 64—66°C. (Found: C 37.35; H 5.98; N 7.38; S 33.10. Calc. for $C_6H_{11}NO_2S_2$: C 37.31; H 5.74; N 7.25; S 33.14).

1,1-Bis(benzylthio)-2-nitroethylene (Vd). Yield 2.9 g (93 %) from 2.1 g of I and 2.6 g of benzyl chloride. M.p. 121—122°C. (Found: C 60.80; H 4.99; N 4.16; S 19.96. Calc. for $C_{16}H_{15}NO_2S_2$: C 60.56; H 4.77; N 4.41; S 20.16).

1,1-Bis(phenacylthio)-2-nitroethylene (Ve). Yield 3.51 g (94 %) from 2.1 g of I and 4.0 g of phenacyl bromide. Recrystallization of the brownish product from acetone afforded light yellow crystals, m.p. 173—174°C. (Found: C 57.75; H 3.93; N 3.68; S 17.05. Calc. for $C_{18}H_{15}NO_4S_2$: C 57.89; H 4.05; N 3.76; S 17.17).

1,1-Bis(carboxymethylthio)-2-nitroethylene (Vc). A neutralized aqueous solution of bromoacetic acid (1.4 g) was added to a solution of 0.55 g of I in 10 ml of water. The mixture was stirred for one hour, after which the reaction mixture was acidified with hydrochloric acid and extracted with ether. The ether extract was dried with anhydrous magnesium sulfate, and the ether removed by evaporation. This yielded a colourless crystalline compound (0.42 g; 66 %), which after recrystallization from water (avoiding boiling of the solution) had a m.p. 156—157°C. (Found: C 28.58; H 2.93; N 5.24; S 24.68. Calc. for $C_6H_7NO_6S_2$: C 28.45; H 2.79; N 5.54; S 25.32). Equivalent weight by titration

as a divalent acid: 125.4. (Calc.: 126.5). From the titration curve it is estimated that $pK_1 = 2.5$ and $pK_2 = 3.2$.

With diazomethane in ether the acid yielded a dimethyl ester, $C_8H_{11}NO_6S_2$. Yield 55 %. M.p. 55.5–56°C after recrystallization from diethyl ether.

2-Nitromethylene-1,3-dithiolan (VI). 2.2 g of I and 2.0 g of ethylene bromide were dissolved in 100 ml of 50 % aqueous methanol and the solution was left for 3 days at room temperature. After this time a brown crystalline material had precipitated (1.52 g; 93 %). M.p. 108–110°C after recrystallization from water. (Found: C 29.20; H 3.10; N 8.50; S 39.52. Calc. for $C_4H_5NO_2S_2$: C 29.26; H 3.06; N 8.58; S 39.26).

Bis(methylsulfonyl)methane (VII). 1.6 g of Va was dissolved in acetic acid (45 ml) and 14 ml of 30 % hydrogen peroxide was added. The reaction mixture was left for 48 h. After this time, the initially yellow solution had become colourless. The solution was diluted to twice its volume with water, and concentrated to 10 ml *in vacuo*. The residue was twice treated with water (50 ml) with subsequent evaporations, the last time to dryness. The final product was a colourless oil which partly crystallized on treatment with ethanol. Several crystallizations from ethanol raised the melting point to 144°C (lit.[7]: 146–147°C); yield 258 mg (17 %). (Found: C 20.80; H 4.44; N 0.0; S 37.59. Calc. for $C_3H_8O_4S_2$: C 20.94; H 4.65; S 37.21).

1,3-Dithiolan-1,1,3,3-tetroxide (VIII). This was prepared in a similar manner as VII from 1.63 g of VI. Yield 0.61 g (36 %). M.p. 208–209°C after recrystallization from ethanol (lit.:[9] 210–211, 204–205). (Found: C 21.15; H 3.82; N 0.0; S 37.93. Calc. for $C_3H_6O_4S_2$: C 21.18; H 3.56; S 37.63).

Di(1-benzylthio-2-nitro-1-propenyl)disulfide (IX). A 1.3 M solution of potassium 2-propanolate in 2-propanol (50 ml) was added to a solution of nitroethane (5 g) in 2-propanol (10 ml). After a short time, the potassium salt of *aci*-nitroethane precipitated. A few minutes after precipitation had started, carbon disulfide (5.0 g) was added. This caused a fast reaction with darkening of the mixture and heat evolution. After 20–30 min precipitation of a brown amorphous solid started. As mentioned, it has not been possible to isolate a well-defined compound from this reaction product. On filtering it was transformed into a brown tar. However, a small amount of a benzyl derivative was formed when benzyl chloride (8.3 g) was added to the crude reaction mixture. After 24 h, addition of water caused a vigourous reaction to occur. The solution was evaporated to dryness *in vacuo*, the dry residue was extracted several times with acetone, and the acetone removed from combined acetone extracts by evaporation. The resulting red oil on treatment with ether-petroleum ether yielded red crystals (25 mg) which after several recrystallizations had the m.p. 148–164°C. By chromatography of the combined mother liquors a similar amount of the same compound was obtained. (Found: C 49.52; H 4.32. Calc. for $C_{20}H_{20}N_2O_4S_4$: C 49.88; H 4.20). The unsharp melting point, which could not be changed by changing solvents, *etc.*, indicates that the product is a mixture of the expected *cis-trans* isomers. Because of the small amount available, no attempts were made to separate the isomers.

2-(1'-Nitroethylidene)-1,3-dithiolan (X). The sodium salt of nitroethane was prepared by addition of a solution of sodium 2-methyl-2-butanolate in benzene (*cf.* Ref. 11) to a solution of nitroethane in ether. The colourless precipitate was filtered, washed with ether and dried over phosphorus(V) oxide. The salt (40 mmoles) was suspended in dimethylsulfoxide (60 ml) and a solution of carbon disulfide (22 mmoles) in dimethylsulfoxide was added dropwise. After 1 h ethylene bromide (22 mmoles) was added and the solution was kept for 24 h at room temperature and then heated at 60°C for 30 min. The solution was diluted with water and extracted with ether. The residue after evaporation of the ether was dissolved in pentane-methylene chloride and the solution was filtered through Al_2O_3 and evaporated. Yield 2.1 g of an orange-coloured oil from which 142 mg of yellow crystals were obtained by addition of ether-pentane. Thin-layer chromatography of the mother liquor afforded 107 mg of the same substance, making the total yield 7 %. M.p. 123–125°C after recrystallization, first from methanol-water and then from ether-chloroform. (Found: C 34.09; H 4.13; N 7.94. Calc. for $C_5H_7NO_2S_2$: C 33.90; H 3.95; N 7.91). This compound was prepared by Gompper and Schaefer [8] in a different manner.

The preparation has been repeated several times but with no better yield. From an experiment with dimethylformamide as solvent 3 % of pure X was isolated.

Attempts were also made to prepare derivatives of nitrodithiopropionic acid by addition of nitroethane and carbon disulfide to a suspension of sodium hydride in dimethylsulfoxide and subsequent addition of methyl iodide, ethylene bromide, trimethylene bromide, or benzylchloride. Only in the last case could a well-defined substance be isolated (6 %). This was a colourless crystalline substance which according to analyses and infrared spectrum was *S*-benzyl acetothiohydroxamate, $CH_3-C(=NOH)-SCH_2C_6H_5$ (Found: C 59.40; H 6.42; N 7.71; S 17.16. Calc. for $C_9H_{11}NOS$: C 59.17; H 6.08; N 7.79; S 17.68). M.p. 145–148°C (toluene). This compound has formerly been obtained directly from the thiohydroxamic acid.[15] Its formation in our experiment shows that sodium hydride acts not only as a base but also as a reducing agent.

2-(1'-Nitroethylidene)-1,3-dithian. This was prepared from 1,3-dibromopropane in a similar manner as X. Yield 4 % of a yellow crystalline substance with m.p. 78–79°C after recrystallization from methanol. (Found: C 37.43; H 4.91; N 7.29; S 33.60. Calc. for $C_6H_9NO_2S_2$: C 37.70; H 4.71; N 7.33; S 33.51).

Potassium 2-nitroethaneselenolate (XI). A *ca.* 1 M ethanolic solution of potassium ethanolate, prepared by dissolving potassium in anhydrous ethanol, was dropped, with stirring, to a solution of carbon diselenide (1.70 g) and nitroethane (0.61 g) in anhydrous ethanol (10 ml), cooled at −80°C and kept under nitrogen. When 23 mmoles of C_2H_5OK had been added, the temperature was raised slowly to 0°C and the precipitate, which had separated, was filtered by suction and washed with ethanol and ether. (Found: C 11.89; H 2.05; N 7.62; Se 39.7. Calc. for $C_2H_4KNO_2Se$: C 12.50; H 2.10; N 7.30; Se 41.1). On slight heating or rubbing the compound explodes with emission of a very intense blue light.

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