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Iminodithiocarbonates. VI.[1] Reaction of Sulfur-substituted Carbonium Ion with Sodium Azide

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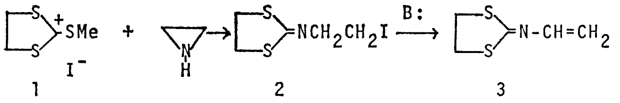
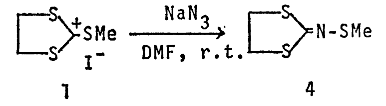
Synopsis. The reaction of 2-methylthio-1,3-dithiolan-2-ylium iodide **1** with sodium azide gave 2-methylthioimino-1,3-dithiolane **4**. Thiooxime **4** reacted with chloramine T and dimethyl sulfate to give sulfilimine **9** and sulfonium salt **10**, respectively.

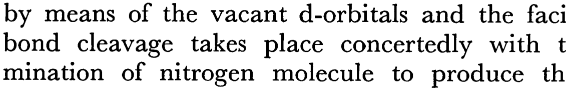
In a previous paper we reported on the reaction of 2-methylthio-1,3-dithiolan-2-ylium iodide **1** with ethyleneimine to produce 2-(β-iodoethylimino)-1,3-dithiolane **2**, which is easily converted into the conjugated *N*-vinyl monomer **3**.[2]



In this paper we wish to report on the reaction of the cation **1** with sodium azide as nitrogen-nucleophile. Cation **1** reacted with sodium azide in DMF at room temperature with evolution of nitrogen gas to give the thiooxime derivative **4** in 49% yield.

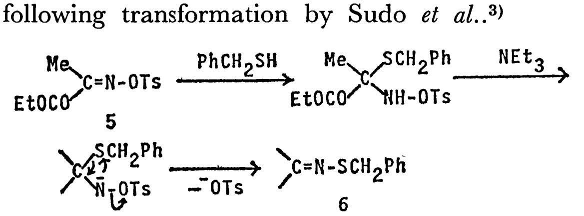


The structure of **4** was confirmed by elemental analysis and spectroscopic data. The NMR spectrum of **4** exhibited a singlet peak at δ 2.40 (SMe, 3H) and multiplet peaks centered at δ 3.4 (SCH_2CH_2S, 4H). The IR absorption band due to νC=N appeared at 1542 cm^{-1}. It is noteworthy that nitrogen gas evolution occurred even at room temperature, since ordinary organic azides do not decompose at such a low temperature. For the sake of explanation we postulate the sulfide participation which could accelerate the elimination of nitrogen gas: The methylthio group interacts with the negative charge on nitrogen atom by means of the vacant d-orbitals and the facile C–S bond cleavage takes place concertedly with the elimination of nitrogen molecule to produce the final product **4** as follows.



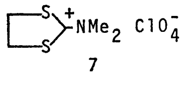
(1)

A similar explanation has been employed for the following transformation by Sudo *et al.*.[3]

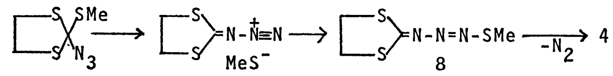


(2)

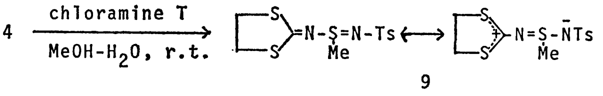
We see a similarity between the reactions (1) and (2). Thus the nitrogen gas in (1) corresponds to ⁻OTs in (2) as eliminating group. 2-Dimethylamino substituted cation **7**, which would not have effective participation toward azide, did not react with sodium azide and was recovered. Participation by a ring-sulfur atom would not be involved due to the steric requirement presumed to be unfavorable.



An alternative scheme for the formation of **4** may be one involving the triazene intermediate **8**.

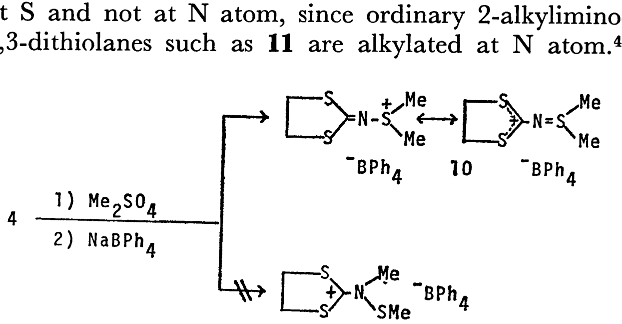


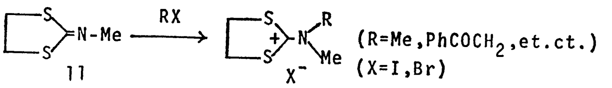
Reactions of thiooxime **4** newly obtained with chloramine T and dimethyl sulfate were undertaken, and **4** was found to react with chloramine T to give the sulfilimine **9** in 34% yield.



The IR absorption bands of **9** appeared at 1478 cm^{-1} (C=N) and at 955 cm^{-1} (S=N). The value due to νC=N highly shifted to a lower wave number indicating a strong conjugation between the C=N and S=N groups as formulated above. This was supported by the NMR of **9**. Thus the ring methylene protons shifted from δ 3.40 to 3.67 accompanied by the conversion of **4** into **9**.

Thiooxime **4** reacted with dimethyl sulfate at 40—50 °C to give *S*-methylated sulfonium salt **10** in 50% yield. It is surprising that the methylation occurred at S and not at N atom, since ordinary 2-alkylimino-1,3-dithiolanes such as **11** are alkylated at N atom.[4]





The NMR spectrum of **10** exhibited a singlet peak at δ 3.17 (SMe, 6H) and multiplet peaks centered at δ 3.66 (SCH_2CH_2S, 4H) and at δ 6.83(Ph, 20H). The presence of two equivalent methyl group supports *S*-methylation and excludes *N*-methylation. Sulfonium salt **10** is considered to be stabilized by delocalization of its positive charge into 1,3-dithiolane ring as formulated above.

Experimental

2-Methylthioimino-1,3-dithiolane ***4***. To a suspension of 11.2 g (0.04 mol) of 2-methylthio-1,3-dithiolan-2-ylium iodide⁵⁾ in 70 ml of DMF was added 2.6 g (0.04 mol) of sodium azide with stirring. Nitrogen gas was evolved and a brown suspension turned into a homogeneous solution. Sodium iodide was then precipitated as white needles. After being left to stand over-night, the solvent was removed under a reduced pressure under nitrogen atmosphere and the residue was poured into water and extracted with ether, dried over $MgSO_4$. Evaporation of ether and distillation gave 3.3 g (49%) of **4**; bp 111—113 °C (1 mmHg), IR: 1541 cm^{-1} (νC=N),, UV λ_{max}^{EtOH} 231, 295.5, 275(sh), and 448 nm, NMR (see text) Found⁶⁾: C, 28.61; H, 4.23; S, 57.72%. Calcd for $C_4H_7NS_3$: C, 29.10; H, 4.27; S, 58.14%.

Sulfilimine ***9***. 2.3 g (0.014 mol) of thiooxime **4** was added to a solution of 3.4 g (0.012 mol) of chloramine T in (30 ml)-MeOH (20 ml). Acetonitrile (20 ml) was added to the reaction mixture in order to crystallize the oily substance separated. Stirring was continued for 2 hr. Filtration followed by evaporation of the filtrates gave oily residues which were crystallized by washing with ether. **9** (1.24 g, 34%) was obtained as colourless prisms: mp 181—182 °C (recrystallized from ethanol), IR: 1478 cm^{-1} (νC=N), 1279, 1139 cm^{-1} (νSO_2), 955 cm^{-1} (νS=N), 1082 cm^{-1}. NMR (DMSO-d_6) δ: 2.30(Me, s, 3H), 2.45 (SMe, s, 3H), 3.67 (SCH_2CH_2S, m, 4H), 7.50 (Ar, m, 2H), and 7.97 (Ar, m, 2H).

Methylation of Thiooxime ***4***. 0.8 g (4.8 mmol) of **4** and 0.6 g (4.8 mmol) of dimethyl sulfate were heated at 40—50 °C for 1.5 hr. After the mixture was cooled, aq. solution of sodium tetraphenylborate (1.7 g in 50 ml H_2O) was added to give 1.2 g (50%) of **10**: mp, 199—201 °C (recrystallized from acetone-ether), IR; 710 and 740 cm^{-1}, NMR (DMSO-d_6) δ: 3.17 (SMe, s, 6H), 3.66 (SCH_2CH_2S, m, 4H), and 6.83 (Ph, m, 20H), Found: C, 70.09; H, 6.14; N, 2.76; S, 18.73%. Calcd. for $C_{29}H_{30}BNS_3$: C, 69.76; H, 6.06; N, 2.81; S, 19.23%.

References

1) Part V; Y. Ueno and M. Okawara, This Bulletin, **45**' 1797 (1972).

2) Y. Ueno and M. Okawara, *J. Polym. Sci. Part B*, **10**, 11 (1972).

3) R. Sudo, A. Kaneda, and N. Furuya, This Bulletin, **42**, 1380 (1969).

4) Y. Ueno, T. Nakai, and M. Okawara, *ibid.*, **44**, 1933 (1971).

5) R. Mayer and K. Schafer, *J. Prakt. Chem.*, [4] **26**, 270 (1964).

6) Contamination of a small amount of 1,3-dithiolan-2-one⁵⁾ after repeated distillation precluded the preparation of an analytically pure sample. Formation of 1,3-dithiolan-2-one might take place by the hydrolysis of cation **1** with water present in the solvent.⁵⁾