Tetrahedron. Vol. 24, pp. 6485 to 6493. Pergamon Press 1968. Printed in Great Britain

HINDERED ROTATION IN DITHIOCARBAMOYL COMPOUNDS BY NMR MEASUREMENTS

ALKYLATION OF SULFUR COMPOUNDS BY TRIALKYLOXONIUM IONS*

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(*Received in USA* 27 *May* 1968; *Received in the UK for publication* 14 *June* 1968)

Abstract—The alkylation of methyl N,N-dialkyldithiocarbamates, of tetramethyl thiuram disulfide, and of bismethylthio-N-methylformimine has been shown to lead to the same symmetrical dithiocarbamidium salt resulting from alkylation on the thione sulfur atom. The NMR spectrum of the dithiocarbamidium ion showed approximately equal distribution of charge in the ion, resulting in a downfield shift of 0·20 to 0·50 ppm for the protons on carbon attached to nitrogen or sulfur. Its cyclic analog, 2-dimethylamino-1,3-dithiolenium ion, showed that its charge was about equally distributed, with downfield shifts of 0·40 to 0·60 ppm for the protons on carbon attached to nitrogen or sulfur when compared to 2-methylimino-1,3-dithiolane. Hindered rotation was observed around the C—N bond of methyl N,N-dialkyldithiocarbamates at ambient temperature (about 37°) by NMR, but none was observed in the corresponding thiuram disulfides at ambient temperature.

IN CONNECTION with studies on the thermal and photochemical transformations of some dithiocarbamate derivatives,[1,2] we have examined the action of trimethyloxonium salts and other alkylating agents on dithiocarbamates,[3] have established the structure of the products, and have determined the NMR spectra of representative thiuram disulfides and dithiocarbamates, which give information about hindered rotation.

The action of trimethyloxonium picrylsulfonate on tetramethyl thiuram disulfide (**1**) and on methyl N,N-dimethyldithiocarbamate (**2**) gave the same crystalline salt, m.p. 161–162°. From its elementary analysis, this salt could have one of the three structures: the symmetrical structure **3**, the sulfonium structure **4**, or the ammonium structure **5**. The same compound was obtained by alkylation† of the bismethylthio-N-methylformimine **6** with the oxonium picrylsulfonate.

The structure of the alkylation product was shown to be the symmetrical one **3**, rather than **4** or **5**, by the NMR spectrum, which in nitromethane showed two sharp singlets‡ at 3·78 and 2·89, integrating 1:1. This rules out structure **5**, but not necessarily **4**; the latter is eliminated by the transformation of the formimine **6** to **3**. Structure **5** is also ruled out by the hydrolysis of **3**, to a salt of dimethylamine.

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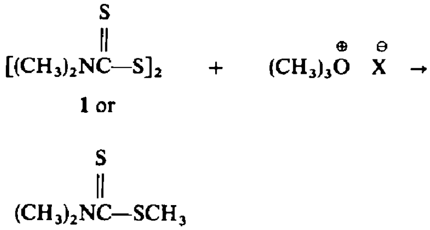
* Aided by Grant 2252-C from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is expressed to the donors of this grant.

† We are indebted to Dr. Lamar Field for suggesting this reaction.

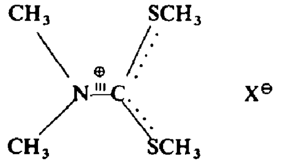
‡ NMR spectra are reported in delta units (ppm) relative to TMS unless otherwise indicated.

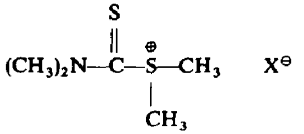

$[(CH_3)_2NC(=S)-S]_2 + (CH_3)_3O^{\oplus}\ X^{\ominus} \rightarrow$

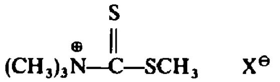
1 or

$(CH_3)_2NC(=S)-SCH_3$

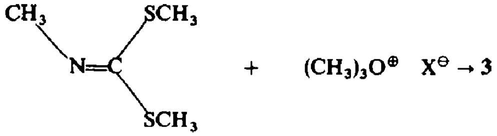
2

3


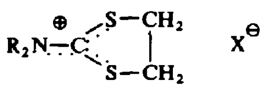
4

$(CH_3)_2N-C(=S)-\overset{\oplus}{S}(CH_3)-CH_3\ X^{\ominus}$

5

$(CH_3)_3\overset{\oplus}{N}-C(=S)-SCH_3\ X^{\ominus}$

$X^{\ominus} = 2,4,6,\text{-}(O_2N)_3C_6H_2SO_3^{\ominus}$

6


The symmetrical structures corresponding to 3 have been postulated by others for alkylation on dithiocarbamates in similar cases, including some dithiolenium



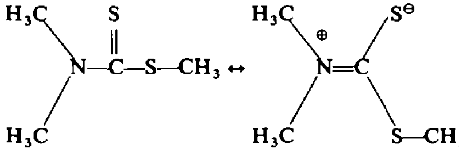
7

salts[4] 7. However, in some of these cases, structures have been based on UV absorption data, which does not conclusively rule out unsymmetrical structures analogous to 4.

Further NMR evidence confirming the symmetrical structure 3 was obtained from the iodide (3, X = I). The NMR spectrum (using the chloroform peak at 7·33 ppm as a reference because of decomposition or insolubility when TMS was added) showed two sharp singlets at 3·68 and 2·82, integrating 1 : 1. In methylene chloride, the NMR spectrum showed that the alkylation product had partially reverted to reactants. Using the methylene chloride peak at 5·35 as a reference, singlets for the product were present at 3·70 and 2·84, as well as a broad singlet at 3·42 for the N-Me protons and a sharp singlet at 2·58 for the S-Me protons of methyl N,N-dimethyldithiocarbamate (**2**). A singlet for methyl iodide was present at 2·15.

Alkylation of methyl N,N-diethyldithiocarbamate with methyl iodide gave a yellow solid, m.p. 87–90° with decomposition, which was soluble in chloroform and methylene chloride. Its NMR spectrum (chloroform peak as a reference) showed a sharp, well resolved quartet centered at 4·26, a sharp singlet at 3·03 and a triplet at 1·48. These correspond to the N-methylene protons, the S-Me protons and the terminal Me protons on nitrogen, with correct integration. Reversion to reactants was evident from a broad, unresolved signal centered at 3·90, a sharp singlet at 2·60, and a triplet at 1·20 for methyl N,N-diethyldithiocarbamate, and a singlet at 2·13 for methyl iodide. The NMR spectra are tabulated below.

Confirmatory evidence for the symmetrical structure **3** for the alkylation products was provided by a comparison of their NMR spectra with those of the corresponding methyl N,N-dialkyldithiocarbamate. The NMR spectrum of methyl N,N-dimethyldithiocarbamate (**2**) at ambient temperature showed a sharp singlet for the S-Me protons at 2·62 (line width at half-height, 1·5 c/s) and a broad singlet for the N-Me protons at 3·45 (line width at half-height, 7·0 c/s). The broadening of the N-Me signal is associated with two factors: hindered rotation around the C—N bond due to resonance structure **2a** and broadening caused by the quadruple moment of the N atom.[5] Hindered rotation around the C—N bond due to partial double bond character makes the two N-Me groups non-equivalent within the magnetic field



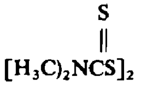
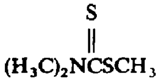
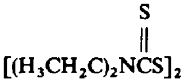
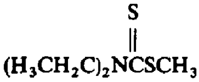
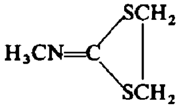
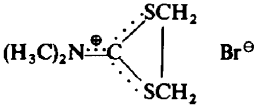
2 **2a**

because of the two non-equivalent S atoms. This results in a different chemical shift for the two N-Me groups. If the two S atoms are equivalent (as they are in the dithiocarbamidium structure **3**) there would be no line broadening of the N-Me signal, even with hindered rotation due to partial double bond character in the C—N bond.

The N-Me protons of the alkylation product **3** at ambient temperature appear as a sharp singlet in the NMR spectrum. The line width at half-height is 1·5 c/s, which is a decrease in line width of 5·5 c/s on alkylation. The alkylation product of methyl N,N-diethyldithiocarbamate shows the same phenomenon. The NMR spectrum of methyl N,N-diethyldithiocarbamate shows a broad signal for the N-methylene protons that is barely resolvable to a quartet at room temperature. The same protons in the alkylation product are well resolved into the expected quartet. These results are consistent with the symmetrical dithiocarbamidium structure **3**.

Low temperature studies of the NMR spectra of methyl N,N-dimethyldithiocarbamate, its methyl iodide alkylation product, and methyl N,N-diethyldithiocarbamate, confirmed the presence of hindered rotation in the dithiocarbamates and the equivalence of the N-Me groups in the alkylation product **3**. At 0° the two N-Me groups of methyl N,N-dimethyldithiocarbamate were a well resolved doublet with the peaks at 3·59 and 3·41. At −40° two separate singlets were present at 3·64 and 3·45.

NMR SPECTRA AT AMBIENT TEMPERATURE[a]

Compound	Solvent	Reference	α-N protons	β-N protons	α-S protons
 $[(H_3C)_2NC(=S)S]_2$	$CDCl_3$	TMS	3·65	—	—
 $(H_3C)_2NC(=S)SCH_3$	$CDCl_3$	TMS	3·45 (broad)	—	2·62
$H_3CN{=}C(SCH_3)_2$	$CDCl_3$	TMS	3·25	—	2·53, 2·35
$(H_3C)_2N\overset{\oplus}{\cdots}C(SCH_3)_2\ X^{\ominus}$[b]	CH_3NO_2	CH_3NO_2	3·78	—	2·89
$(H_3C)_2N\overset{\oplus}{\cdots}C(SCH_3)_2\ I^{\ominus}$	$CHCl_3$	$CHCl_3$	3·68	—	2·82
	CH_2Cl_2	CH_2Cl_2	3·70	—	2·84
$(H_3C)_2N\overset{\oplus}{\cdots}C(SCH_3)_2\ X^{\ominus}$[c]	CH_3NO_2	CH_3NO_2	3·85	—	2·91
 $[(H_3CH_2C)_2NC(=S)S]_2$	$CDCl_3$	TMS	4·03 q	1·38 t (broad)	—
 $(H_3CH_2C)_2NC(=S)SCH_3$	$CDCl_3$	TMS	3·89 q (broad)	1·27 t	2·62
$(H_3CH_2C)_2N\overset{\oplus}{\cdots}C(SCH_3)_2\ I^{\ominus}$	$CHCl_3$	$CHCl_3$	4·26 q	1·48 t	3·03
$(H_3CH_2C)_2N\overset{\oplus}{\cdots}C(SCH_3)_2\ X^{\ominus}$[c]	C_6H_6	C_6H_6	4·05 q	1·25 t	2·77
	$CDCl_3$	TMS	3·13	—	3·48 m
	CH_3CN	CH_3CN	3·53	—	4·04

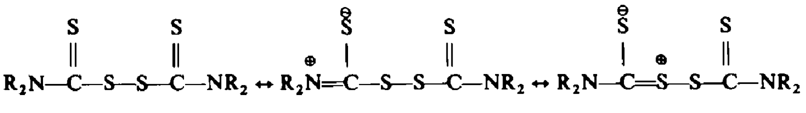
[a] All values are in delta units and sharp unless indicated otherwise. All absorptions are singlets or the center of a triplet (t), quartet (q), or multiplet (m) as indicated.

[b] $X^{\ominus}$ = picrylsulfonate.

[c] $X^{\ominus}$ = *p*-nitrobenzenesulfonate.

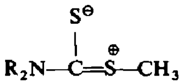
These two singlets and the singlet for the S-Me protons at 2·65 were of equal height at −40° and all had a line width at half-height of 1·5 c/s. At 0° the N-methylene protons of methyl N,N-diethyldithiocarbamate were separated into two well resolved quartets centered at 4·06 and 3·78. The S-Me singlet was at 2·64 and the terminal Me groups were a triplet at 1·29. There was no change in the spectrum at −40°. The two sharp singlets present at ambient temperature for the alkylation product remained at 0° and −40°; the line width at half-height for both singlets was 1·5 c/s over the temperature range studied.

It is not possible to estimate the activation energy necessary for rotation around the C—N bond from the limited data obtained. One interesting observation is that tetramethyl thiuram disulfide shows a sharp singlet (line width at half-height of 1·5 c/s) at ambient temperature, even though the atomic environment around the C—N bond is identical with methyl N,N-dimethyldithiocarbamate. The N-methylene protons in tetraethyl thiuram disulfide also appear as a sharp well resolved quartet centered at 4·03 at ambient temperature, with a line width at half-height of 1·5 c/s for each peak. Apparently resonance structure **8b** is a more important contributor in the thiuram disulfides than resonance structure **2b** is in dithiocarbamate esters. Hindered rotation around the C—N bond of tetraalkyl thiuram disulfides was observed at lower temperatures, ca. −40°.



$$R_2N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-NR_2 \leftrightarrow R_2\overset{\oplus}{N}=\overset{S^{\ominus}}{\overset{|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-NR_2 \leftrightarrow R_2N-\overset{S^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{S}-S-\overset{S}{\overset{\|}{C}}-NR_2$$

8 **8a** **8b**

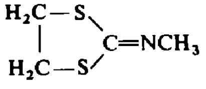


$$R_2N-\overset{S^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{S}-CH_3$$

2b

The downfield shifts observed in the alkylation product 3 compared to the analogous protons in the dithiocarbamates also support the charge-delocalized dithiocarbamidium structure 3. Alkylation of methyl N,N-dimethyldithiocarbamate resulted in a downfield shift of about 0·25 for both the N-Me and S-Me protons. With methyl N,N-diethyldithiocarbamate, downfield shifts of about 0·40 for the N-methylene protons, 0·48 for the S-Me protons and 0·25 for the terminal Me protons were observed on alkylation. These data indicate that the alkyl groups attached to nitrogen and sulfur are deshielded to approximately the same extent.

To compare the extent of downfield shift occurring in the open dithiocarbamidium salts with the cyclic dithiolenium salts 7, 2-methylimino-1,3-dithiolane 9 was synthesized from sodium N-methyldithiocarbamate and 1,2-dichloroethane. The NMR spectrum showed a singlet at 3·15 for the N-Me group, with the S-methylene protons further downfield at 3·47 (center of multiplet). Using the reported NMR data for the 2-dimethylamino-1,3-dithiolenium ion,[4e] this corresponds to a downfield shift of 0·61 for the ring protons and 0·47 for the N-Me protons on alkylation. These data indicate approximately equal distribution of charge on nitrogen and sulfur in the cyclic ion. These downfield shifts are small compared to the shifts observed in 2-alkyl-1,3-dioxolenium cations,[6] where, compared to 2-alkyl-1,3-dioxolanes, the ring protons were shifted downfield by 1·5 to 1·7 units.



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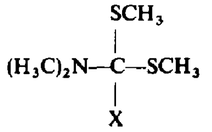
To verify the reported chemical shifts for protons in the 2-dimethylamino-1,3-

dithiolenium ions (7), compared to the parent uncharged structure 9, the methyl iodide alkylation product (7, X = I) was prepared, m.p. 180–183° with decomposition. Its lack of solubility prevented the determination of its NMR spectrum; the elemental analyses supported the 2-dimethylamino-1,3-dithiolenium iodide structure 7. Alkylation with methyl bromide gave a 29% yield of the corresponding bromide, m.p. 171–172°. The NMR spectrum showed two sharp singlets at 4·04 and 3·53, integrating 4:6 respectively (based on the acetonitrile peak at 1·96). The product from the reaction of sodium N,N-dimethyldithiocarbamate and 1,2-dibromoethane had a reported melting point of 174°.[4c]

A very limited look at the chemical reactivity of the dithiocarbamidium ion was made with the hope of obtaining nucleophilic attack at the central C atom to form tetrahetero carbon species **10**.



$$(H_3C)_2N\text{—}\overset{\displaystyle SCH_3}{\underset{\displaystyle X}{C}}\text{—}SCH_3$$

$X = OCH_3, N(C_2H_5)_2, NC_4H_4, SCH_3$

10

A nitromethane solution of N,N-dimethyl-S,S′-dimethyldithiocarbamidium picrylsulfonate was treated with methanol and an equivalent amount of triethylamine. The only product isolated was methyl N,N-dimethyldithiocarbamate. Reaction of N,N-dimethyl-S,S′-dimethyldithiocarbamidium iodide with sodium methoxide in methylene chloride or chloroform gave no identifiable products.

With diethylamine an unidentifiable liquid was isolated as well as a trace amount of methyl N,N-dimethyldithiocarbamate. With pyrrole the only products isolated were pyrrole and a small amount of methyl N,N-dimethyldithiocarbamate. The reaction with pyrrole was done in methylene chloride so that the dithiocarbamate might have resulted from decomposition of the dithiocarbamidium iodide in the solvent rather than from a reaction with pyrrole.

The reaction of N,N-dimethyl-S,S′-dimethyldithiocarbamidium iodide with dimethyl sulfide gave trimethylsulfonium iodide in 79% yield and a quantitative yield of methyl N,N-dimethyldithiocarbamate. The solvent was methylene chloride so it is not certain if the dithiocarbamidium ion acts as an alkylating agent toward dimethyl sulfide or whether the products came from decomposition to the dithiocarbamate and methyl iodide followed by alkylation by the methyl iodide.

The reactivity of the cyclic analog, 2-dimethylamino-1,3-dithiolenium ion, toward nucleophiles has previously been studied.[7]

EXPERIMENTAL

All m.p. are corrected and all b.p. are uncorrected. All solvents used were analytical reagent grade and dried with 4 Å molecular sieves (Fisher) unless noted otherwise. Infrared spectra were recorded with a Perkin–Elmer Model 421 unless indicated otherwise. A Cary Model 14 was used for UV spectra. The NMR spectra were recorded using a Varian A-60 spectrometer equipped with a V-6057 variable temp probe. TMS was used as an internal standard unless indicated otherwise and all chemical shifts are in delta units (ppm). Micro-analyses were performed by Galbraith Laboratories, Inc. and by Micro-Tech Laboratories.

Anhydrous picrylsulfonic acid was prepared in 92% yield by the method of Pettitt and Helmkamp[3c] with the following modifications. The acetone soln containing crude picrylsulfonic acid dihydrate was evaporated under vacuum until a solid resulted. At room temp, enough acetone was added to obtain soln, an equivalent amount of chloroform added, and the soln was cooled in an acetone–dry ice bath to promote crystallization. The tan solid was collected from the cold slurry, washed with chloroform and dried at 78° (0·25 mm) for 2 hr. The off-white solid melted with decomposition at 192–195°, lit. m.p. 193–195°.[3c] The IR spectrum in KBr had the following absorptions (cm^{-1}): 3600–2500-broad s, 3100 w, 1652 w, 1610 m, 1550 (broad) s, 1405, vw, 1358 s, 1272 s, 1252 (center of doublet) vw, 1240 s, 1190 vw, 1128 m, 1075 m, 1040 m, 930 m, 905 m, 830 w, 755 s, 740 m, 728 s, 720 (shoulder) w, 665 (shoulder) w, 640 s.

Trimethyloxonium picrylsulfonate[8] was prepared in 59% yield, m.p. with decomposition 181–183°, reported (above ref.) 181–183°. Our sample showed no effervescence in the range 125–135°, even with rapid heating;[3c] the identity of our product as the desired oxonium salt was confirmed by satisfactory elemental analyses for C, H, N and S. The IR spectrum of the oxonium salt in KBr was characterized by the following bands (cm^{-1}): 3600–3250 (broad) m, 3085 m, 1650 vw, 1610 m, 1570–1500 (broad) m, 1358 s, 1272 s, 1255 vw, 1240 s, 1125 m, 1075 m, 1040 m, 930 m, 905 w, 830 vw, 755 s, 740 m, 730 s, 720 (shoulder), 640 s.

Alkylation of tetramethyl thiuram disulfide (**1**). To a stirred soln of tetramethyl thiuram disulfide[9] in 15 ml nitromethane was added gradually 0·355 g of trimethyloxonium picrylsulfonate at room temp. A white solid precipitated immediately, and the reaction mixture was stirred an additional 30 min. Anhydrous ether (25 ml) was added to the suspension, and the solid was filtered and washed with 20 ml anhyd ether to give 0·280 g ivory crystals. The ppt was insoluble in benzene, chloroform, acetone, carbon disulfide, ethyl acetate, acetonitrile, and only sparingly soluble in hot nitromethane. Repeated treatment with hot nitromethane dissolved a portion of the solid, and to the resulting solution was added anhydrous ether, causing 0·097 g (28%) of ivory prisms to separate, m.p. 243–246° (dec). The IR spectrum in KBr was characterized by the following absorption (cm^{-1}): 3220–3120 (broad) w, 3100 (sharp) w, 1600 m, 1540–1530 s, 1462 m, 1455 (shoulder) w, 1351 s, 1271 s, 1221 s, 1120 m, 1070 m, 1035 m, 1010 w, 910 m, 900 m, 840 w, 823 w, 750 s, 734 m, 721 s, 638 s. The analysis corresponds to the hemihydrated dimethylamine salt of picrylsulfonic acid. The total yield of this product, including the portion which did not dissolve, was 0·230 g (66%). (Found: C, 27·82; H, 2·86; N, 16·61; S, 9·24. Calc. for $C_8H_{10}N_4O_9S\cdot\frac{1}{2}H_2O$. C, 27·67; H, 3·19; N, 16·14; S, 9·23%).

The mother liquors were evaporated, leaving 0·173 g yellow solid. Recrystallization from nitromethane–ether–petroleum ether afforded 0·046 g (21%, based on 2 moles starting material giving 1 mole product) of colorless needles, m.p. 158–159°. An analytical sample had m.p. 160–160·5°. The salt melted without decomposition, and melted unchanged after melting and resolidification. The IR spectrum in KBr was quite similar to that of picrylsulfonic acid, with distinct changes in the fingerprint region, and was characterized by the following bands (cm^{-1}): 3100 w, 1609 w, 1540 s, 1448 w, 1425 (shoulder) w, 1403 w, 1352 s, 1311 w, 1250 (center of doublet) s, 1226 m, 1115 m, 1070 m, 1053 m, 1032 m, 970 (broad) w, 940 (broad) w, 922 w, 900 (center of doublet) m, 750 s, 732 s, 724 s, 635 s. The analysis corresponds to structure **3**, **4**, or **5**. (Found: C, 29·91; H, 3·24; N, 12·84; S, 22·41. Calc. for $C_{11}H_{14}N_4O_9S_3$: C, 29·86; H, 3·19; N, 12·66; S, 21·74%).

The above experiment was repeated many times; an improved procedure for isolating the product consisted in filtering the initial precipitate from the nitromethane solvent in which the salt **3** was dissolved, and treating this soln in the manner described to obtain 0·089 g (25%) of **3**, m.p. 159–160°. The initial solid was washed repeatedly with nitromethane, giving 0·393 g (72%) of the amine salt hemihydrate.

Alkylation of methyl N,N-*dimethyldithiocarbamate** **2**. Trimethyloxonium picrylsulfonate (2·60 g) was added to a stirred soln of 0·989 g of **2** in 75 ml nitromethane at room temp, and stirring was continued for 75 min; the mixture was protected from atmospheric moisture. The solvent was removed under vacuum, the residue was washed with acetone and anhyd ether, and the product (2·76 g, 86%) melted at 161–162·5° without decomposition. A mixed m.p. with the alkylation product from the thiuram disulfide showed no depression. The IR spectrum in KBr corresponded also to that above. The Raman spectrum† showed the following bands (cm^{-1}): 2942 m, 2904 s, 2870 w, 1607 m, 1551 (broad) m, 1409 m, 1374 w, 1357 s, 1255 w, 1191 w, 1165 w, 1073 m, 1038 w, 944 w, 830 s, 772 w, 7·53 w, 702 w, 556 s, 493 w, 424 m, 360 m, 326 s, 234 m.

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* Prepared in 74% yield.[10] The NMR spectrum showed a broad singlet at 3·45 and a sharp singlet at 2·62, with relative areas 2:1.

† Determined on a solid sample, using a Cary Model 81 Recording Raman Spectrophotometer. We are indebted to Professor K. K. Innes and Dr. Marvin Kroll of Vanderbilt University for this spectrum.

Alkylation of methyl N,N-*dimethyldithiocarbamate* (2) *with methyl iodide.* The product, prepared following Hartke,[5d] decomposed at 93–94°, the temp varying with the rate of heating. The solid was soluble in $CHCl_3$ and CH_2Cl_2; the NMR spectrum showed partial decomposition to reactants in CH_2Cl_2 and the product was altered in both solvents when TMS was added. Using the $CHCl_3$ peak at 7·33 as a reference, the NMR spectrum showed two sharp singlets at 3·68 and 2·82 integrating 1:1. A $7{\cdot}28 \times 10^{-5}$ molar chloroform soln of the product showed one maximum in the UV spectrum with λ_{max} 277 mμ, $\varepsilon = 1{\cdot}10 \times 10^4$. The region below 260 mμ was blocked out by the solvent.

Alkylation of bismethylthio-N-*methylformimine* (6) *by trimethyloxonium picrylsulfonate.* Bismethylthio-N-methylformimine* (6; 1·00 g) was treated with 2·62 g of the picrylsulfonate salt in 25 ml nitromethane for 1 hr. The product was isolated in 85% crude yield, and after purification by soln in acetone and addition of ether, melted at 161·5–162·6°; it gave no depression on mixed m.p. with 3 obtained by alkylation of methyl N,N-dimethyldithiocarbamate.

Methyl N,N-*diethyldithiocarbamate* was prepared from 52 ml Et_2NH, 100 ml EtOH, 15·3 ml CS_2 and 16 ml MeI; the yield was 32·5 g (79%), b.p. 72–73° (0·15 mm), (reported b.p. 256°).[11] The NMR spectrum showed a triplet at 1·27, a singlet at 2·62, and a broad, barely resolvable quartet at 3·89; the integration was 6:3:4 respectively.

Alkylation of methyl N,N-*diethyldithiocarbamate with methyl iodide*, carried out at room temp by Hartke's[4d] procedure, yielded 4·90 g (73%) of product melting with decomposition at temps depending on the rate of heating; the highest m.p. obtained was 87–90°. The product was soluble in $CHCl_3$ and CH_2Cl_2 but its NMR spectrum in both solvents showed some decomposition to reactants. Using $CHCl_3$ as a reference, the NMR spectrum of the product showed a sharp, resolved quartet at 4·26, a singlet at 3·03 and a triplet at 1·48 with the correct integrations. (Found: C, 27·43; H, 5·36; N, 4·45; S, 21·16. Calc. for $C_{17}H_{16}INS_2$: C, 27·54; H, 5·28; N, 4·59; S, 21·01%).

Alkylation of methyl N,N-*dimethyldithiocarbamate with methyl* p-*nitrobenzenesulfonate.* A soln of 2·54 g methyl *p*-nitrobenzenesulfonate and 1·58 g methyl N,N-dimethyldithiocarbamate in 70 ml nitromethane was refluxed for 90 min. The dark orange reaction was evaporated with a vacuum pump to yield 3·70 g of a red-orange oil. The NMR spectrum (based on the nitromethane peak) showed two singlets at 2·91 and 3·85, integrating 1:1, and a quartet centered at 8·10, as well as absorptions for the reactants. The relative yield of product was 80% based on the integration of the product and reactant signals. The oil solidified to a tan hygroscopic solid after 4 days of refrigeration. It was impure (m.p. 76–110°), and soluble in acetone and chloroform.

Heating a chloroform soln of the solid precipitated a solid no longer soluble in chloroform and non-hygroscopic. Recrystallization of this new solid in acetone gave a white solid, m.p. 152–153·5° with decomposition. Its NMR spectrum in a dilute acetone solution showed a singlet at 2·83 and a quartet at 8·10, integrating 6:4. The IR spectrum contained a band at 2430 cm^{-1} characteristic of alkylammonium salts and the solid had the correct composition for dimethylammonium *p*-nitrobenzenesulfonate. This apparently resulted from hydrolysis due to the presence of water in the chloroform. (Found: C, 38·82; H, 5·03; N, 11·10; S, 12·99. Calc. for $C_8H_{12}N_2O_5S$: C, 38·71; H, 4·87; N, 11·29; S, 12·91%).

Alkylation of methyl N,N-*diethyldithiocarbamate with methyl* p-*nitrobenzenesulfonate.* Methyl N,N-diethyldithiocarbamate (2·08 g) in 25 ml of a 20% dimethylformamide in benzene soln was alkylated with 2·75 g methyl *p*-nitrobenzenesulfonate. After refluxing for 90 min, 70 ml benzene were added to the reaction with two phases resulting. The NMR spectrum of the two phases showed the expected product in the phase composed of 3·043 g of yellow liquid. Both solvents were also present. The liquid was extracted with two 20 ml portions benzene to remove the dimethylformamide. The resulting liquid was evaporated under vacuum to remove the benzene. A yield of 1·182 g of yellow oil was obtained, which did not solidify after prolonged refrigeration. The NMR spectrum showed the expected product peaks as well as impurities. Using the benzene peak at 7·24 as a reference, the spectrum contained a sharp, resolved quartet at 4·05, a singlet at 2·77 and a triplet at 1·25, integrating 4:6:6.

Hydrolysis of N,N-*dimethyl*-S,S′-*dimethyldithiocarbamidium picrylsulfonate* (3). A soln of 0·66 g of 3 in a mixture of 150 ml acetone and 15 ml water was refluxed for 1 hr; the acetone was evaporated *in vacuo* giving a yellow-orange soln that was neutral. Extraction with four 15 ml portions ether gave a yellow ether soln, and a solid appeared in the aqueous soln. The ether soln contained diacetone alcohol, as shown by the NMR and IR spectra.

The aqueous phase was cooled in ice, the solid collected, washed with 10 ml ether and air dried. There

* Prepared in 71% yield.[10] The NMR spectrum of the colorless liquid, bp 30° (0·50 mm), showed three equivalent singlets at 3·25, 2·53 and 2·35 ppm.

was obtained 0·19 g (27% yield) of an off-white solid which darkened at 230°. The IR spectrum showed a band at 2410 cm^{-1} characteristic of alkylammonium salts and the solid had the correct composition for dimethylammonion picrylsulfonate. (Found: C, 28·38; H, 3·02; N, 16·76; S, 9·70. Calc. for $C_8H_{10}N_4O_9S$: C, 28·41; H, 2·98; N, 16·56; S, 9·48%).

Reaction of N,N-*dimethyl*-S,S′-*dimethyldithiocarbamidium iodide* (3) *with dimethyl sulfide.* Me_2S (1·60 ml) was added to a yellow soln of 3·0 g of 3 in 25 ml CH_2Cl_2. After stirring at room temp for 16 hr, the light yellow reaction contained a white solid, which was collected, washed with CH_2Cl_2 and air dried, to yield 1·73 g (79%) trimethylsulfonium iodide, m.p. 208–211°, with decomposition.[12] Evaporation of the filtrate gave 1·45 g (100% yield) of methyl N,N-dimethyldithiocarbamate, m.p. 43–46°.

2-*Dimethylamino*-1,3-*dithiolenium iodide.* MeI (2·8 ml) was added to 1·50 g of 2-methylimino-1,3-dithiolane* with stirring at room temp. The excess MeI was evaporated after 10 min to yield an off white solid; this was triturated in 10 ml acetone, collected, washed with 15 ml acetone and was air dried. The yield was 2·1 g (66%), m.p. 180–183° with dec. (Found: C, 21·79; H, 3·83. Calc. for $C_5H_{10}INS_2$: C, 21·82; H, 3·66%).

2-*Dimethylamino*-1,3-*dithiolenium bromide.* MeBr (15 ml, previously cooled in a dry ice–acetone bath) was added to a soln of 3·70 g 2-methylimino-1,3-dithiolane in 50 ml abs EtOH (pre-distilled from Mg turnings) which was cooled in a dry ice–acetone bath. With a dry ice condenser in place, the reaction was stirred at 20° (heating was necessary) for 24 hr with the MeBr refluxing. A portion of MeBr bromide was allowed to escape and the reaction stirred at 40° for an additional 8 hr. The solvent and excess MeBr were evaporated under vacuum to give 5·70 g (90% crude yield) of solid; two recrystallizations from acetonitrile followed by drying at 78° (0·25 mm) over a mixture of P_2O_5 and paraffin shavings gave a 29% yield (2·54 g) of white solid, m.p. 171–172°, reported[4c] 174°. The NMR spectrum showed two sharp singlets at 4·04 and 3·53, integrating 4:6 respectively; the acetonitrile solvent peak at 1·96 was used as a reference.

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* Prepared in 35% yield by refluxing sodium N-methyldithiocarbamate and 1,2-dichloroethane in abs EtOH for 18 hr. The yellow product, b.p. 60° (0·10 mm), was isolated as described by R. W. Addor, J. Agr. Food Chem. 13, 207 (1965). Its NMR spectrum showed a singlet at 3·13 and a multiplet centered at 3·48 integrating 3:4 respectively.