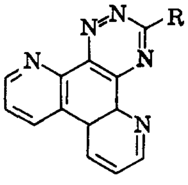
Table IV

as-Triazino[5,6-*f*][4,7]Phenanthrolines



R	Yield, %	M.p., °C.	Crystn. solvent	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2-Pyridyl	50.0	325	Dimethylformamide	$C_{18}H_{10}N_6$	69.68	3.25	69.58	3.43
4-Methyl-2-pyridyl	61.7	321–322	Dimethylformamide	$C_{19}H_{12}N_6$	70.36	3.63	70.15	3.68
4-Phenyl-2-pyridyl	65.9	358–359	Dimethylformamide	$C_{24}H_{14}N_6$	74.55	3.63	74.24	3.78
2-Thiazolyl	62.5	348–349	Dimethylformamide	$C_{16}H_8N_6S \cdot H_2O$	57.49	2.99	57.65	3.19[a]

[a] *Anal.* Calcd.: N, 25.15. Found: N, 25.33.

test tube at 260° for 5 hr. After cooling, the resulting solid was finely powdered and suspended in 30 ml. of a saturated solution of potassium cyanide. After standing overnight the solid was removed by filtration, dried, and extracted repeatedly with hot benzene. Removal of the benzene and crystallization of the residue from methanol yielded 1.0 g. of material melting at 234° (41.8%). An analytical sample melted at 235–236°.

Anal. Calcd. for $C_{13}H_7N_3$: C, 76.10; H, 3.41. Found: C, 75.85; H, 3.66.

5-Cyano-1,10-phenanthroline.—The procedure was the same as for 2-cyano-1,10-phenanthroline except that the starting product was 5-bromo-1,10-phenanthroline. From 3 g. of the latter compound and 1.5 g. of cuprous cyanide there was obtained 1.2 g. (50.6%) of 5-cyano-1,10-phenanthroline, melting at 212–213° after crystallization from benzene. The analytical sample was dried to constant weight at 100°.

Anal. Calcd. for $C_{13}H_7N_3$: C, 76.10; H, 3.41. Found: C, 76.27; H, 3.64.

Acknowledgment.—The author acknowledges the contribution of Mr. Ben Klodell to the earlier stages of this work.

Alkylation of Organic Disulfides[1]

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The reaction of disulfides with alkyl halides has been demonstrated to proceed with the ultimate formation of trialkylsulfonium salts.[3] The process is slow at room temperature but may be accelerated by the addition of mercuric iodide as catalyst.[4] The process proposed for the formation of the sulfonium salt involves initial alkylation on sulfur followed by decomposition of the resulting salt to the sulfonium halide (eq. 1).[5,6] Evidence for this is found in the isolation of the mercuric iodide double salt of diethylethylthiosulfonium iodide from the reaction of ethyl iodide and diethyl disulfide in the presence of mercuric iodide.[5] Prolonged treatment of the reactants resulted in the corresponding sulfonium salt. It has also been observed that the reactivity of alkyl halides toward sulfides is greater than toward disulfides[7] and that the reaction is first order in disulfide.[8]

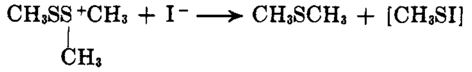
$$\mathrm{RSSR + R'X \longrightarrow RR'S^+SR\ X^- \longrightarrow R'_2RS^+X^-} \qquad (1)$$

We have recently reported the formation of a stable alkylated disulfide, dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate (**1**) from the reaction of methyl disulfide with trimethyloxonium 2,4,6-trinitrobenzenesulfonate.[9] We now wish to establish the extent of the applicability of this rapid and facile means of alkylating disulfides.

When methyl disulfide was treated with trimethyloxonium 2,4,6-trinitrobenzenesulfonate, alkylation occurred on sulfur without subsequent cleavage of the sulfur–sulfur bond (eq. 2). When alkylated disulfide **1** (where R = R′ = CH_3) was dissolved in a solvent containing iodide ion, immediate formation of iodine, methyl sulfide, and methyl disulfide took place (eq. 3 and 4).[9] This suggests that it is the presence of iodide as the counter ion in previous preparations reported in the literature[3] that initiates the decomposition of the alkylated disulfides, probably through a displacement reaction involving attack of iodide ion on sulfur.

$$\mathrm{RSSR + R'_3O^+X^- \longrightarrow \underset{\mathbf{1}}{RR'S^+SR\ X^-} \longrightarrow \underset{\mathbf{2}}{RR'_2S^+X^-}} \qquad (2)$$

X = 2,4,6-trinitrobenzenesulfonate



$$\mathrm{\underset{\displaystyle CH_3}{CH_3SS^+}CH_3 + I^- \longrightarrow CH_3SCH_3 + [CH_3SI]} \qquad (3)$$

$$\mathrm{2CH_3SI \longrightarrow CH_3SSCH_3 + I_2} \qquad (4)$$

The methylation reaction has been applied to ethyl, *n*-propyl, *sec*-butyl, *n*-butyl, phenyl, *p*-tolyl, and *p*-anisyl disulfides (Table I).

Ethyl disulfide was found to react in the same manner as its methyl analog, yielding only the ethylmethylethylthiosulfonium salt. With higher homologs, or with aryl disulfides, the only pure compound isolated in the alkylation reaction was the sulfonium salt **2**, in

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[1] Supported in part by Grant GM 8185 from the National Institutes of Health, U. S. Public Health Service.

[2] Abstracted in part from the Ph.D. Thesis of D. J. Pettitt.

[3] J. Goerdeler in "Methoden der Organischen Chemie" (Houben-Weyl), E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1955, p. 182.

[4] Hilditch and Smiles[5] report that in the reaction of ethyl iodide with ethyl disulfide no visible change occurs for 2 or 3 months. At the end of 3 years the only product isolated was the triethylsulfonium salt. This compares with a reaction time of 3 days in the presence of mercuric iodide.

[5] T. P. Hilditch and S. Smiles, *J. Chem. Soc.*, **91**, 1394 (1907).

[6] O. Hass and G. Daugherty, *J. Am. Chem. Soc.*, **62**, 1004 (1940).

[7] M. L. Selker and A. R. Kemp, *Ind. Eng. Chem.*, **36**, 16 (1944).

[8] W. Scheele and W. Triebel, *Kautschuk Gummi*, **11**, WT 127 (1958).

[9] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963); **29**, 2702 (1964).

TABLE I

ALKYLATION PRODUCTS OF ORGANIC DISULFIDES[a]

$RSSR \longrightarrow RR'S^+SR\ TNBS^-$

R	R′	Product obtained	M.p., °C.	Yield, %	Calcd. % C	Calcd. % H	Calcd. % N	Found[b] % C	Found[b] % H	Found[b] % N
Methyl	Methyl	**1**[c]	164–165	90	26.92	2.76	10.46	27.20	2.73	10.61
Methyl	Ethyl	**1**	126–128	67	28.91	3.15	10.12	28.60	3.46	10.34
Ethyl	Methyl	**1**	128–129	83	30.76	3.53	9.78	30.86	3.48	9.61
Ethyl	Ethyl	**1**	118–119	....	32.50	3.86	9.48	32.32	4.04	9.65
n-Propyl	Methyl	**2**[d]	163.5–164	...	33.24	3.80	10.58	32.92	4.06	10.47
n-Butyl	Methyl	**2**[e]	193-193.5	68[f]	35.03	4.16	10.21	35.22	4.38	10.52
sec-Butyl	Methyl	**2**[e]	135–136	73[f]	35.03	4.16	10.21	35.32	4.20	10.50[g]
Phenyl	Methyl	**2**	228–229.5	...	38.98	3.04	9.74	39.19	3.07	9.69
p-Tolyl	Methyl	**2**	250.5–251.5[h]	...	40.44	3.39	9.43	40.79	3.47	9.71
p-Anisyl	Methyl	**2**	209.5–210	39	39.04	3.28	9.11	38.71	3.63	9.02

[a] TNBS = 2,4,6-trinitrobenzenesulfonate. [b] Microanalyses by C. F. Geiger, Ontario, Calif. [c] Compound **1** is the alkylated disulfide. [d] Compound **2** is the sulfonium salt, $RR_2'S^+TNBS^-$. [e] Compound **2** appeared to form from **1** during recrystallization. [f] Yield reported for compound **1**. [g] Analytical data obtained on the sulfonium salt formed by methylation of 2-butanethiol [h] With decomposition.

which two of the substituent groups originated from the alkylating agent. In the case of *p*-tolyl disulfide the structure of the sulfonium salt was verified by its independent synthesis from trimethyloxonium trinitrobenzenesulfonate and *p*-toluenethiol.

In the reaction of *n*-butyl disulfide with trimethyloxonium trinitrobenzenesulfonate, the material initially precipitated from solution had a melting point of 94–96°. A solution of this salt in nitromethane liberated iodine when treated with aqueous potassium iodide at room temperature, indicating the strong possibility of the presence of a sulfur–sulfur bond. The material obtained after recrystallization from nitromethane–ether or acetonitrile–ether melted a hundred degrees higher, however, and did not liberate iodine under identical conditions. Furthermore, the n.m.r. spectrum of the compound prior to recrystallization gave a 2:3 ratio of aromatic protons to protons attached to the methyl group on sulfur, while the compound after recrystallization gave a 2:6 ratio. Again, in the reaction of *sec*-butyl disulfide, the material initially precipitated liberated iodine and melted considerably lower than the analytical sample. In the case of aryl disulfides, the only product isolated was the sulfonium salt **2**.

The stability of alkylated disulfides appears to be a function of features of the molecule other than the presence of the sulfur–sulfur bond. Dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate (**1**) can be recovered from nitromethane (Spectroquality, dried over Molecular Sieve) after 6 hr. with no change in melting point, infrared spectrum, and behavior towards iodide ion.[10] In contrast, recrystallization of butylmethylbutylthiosulfonium 2,4,6-trinitrobenzenesulfonate from the same solvent yields the corresponding sulfonium salt.

The reactions of **1** with iodide ion and with water indicate that the sulfur–sulfur bond in the alkylated disulfide is particularly susceptible to nucleophilic attack. Although nucleophiles, *per se*, are not present during reaction, the possibility of the solvent or contaminants in the solvent acting as a nucleophile has not been eliminated. For example, the reaction of **1** with water would form a sulfenic acid **3** (eq. 5) which by disproportionation could lead to additional disulfide as described by Kharasch, *et al.*[11] The net result would be formation of more than 1 mole of sulfonium salt per mole of alkylated disulfide. When *p*-tolyl disulfide was treated with a 4.5 *M* excess of oxonium salt, a yield of greater than 100% of sulfonium salt was observed, based on 1:1 stoichiometry.

$$R_2S^+SR + HOH \longrightarrow R_2S + \underset{\textbf{3}}{RSOH} + H^+ \qquad (5)$$

The sulfur–sulfur bond cleavage can be represented as bimolecular, with the nucleophile participating in bond breakage, or as a unimolecular heterolysis to give a sulfenium ion which then reacts with nucleophile. If the sulfenium ion were present as a discrete entity, it is in exceedingly low concentration since sulfenium ions have been observed to be a highly colored species,[12,13] and marked color changes were not observed during the course of the reaction.

Experimental

Alkylation of Disulfides.—As an example of a procedure leading to the formation of an alkylated disulfide, 1.4 g. (0.015 mole) of redistilled methyl disulfide was dissolved in 15 ml. of nitromethane, and 3.50 g. (0.0100 mole) of trimethyloxonium 2,4,6-trinitrobenzenesulfonate was added in one portion. The mixture was stoppered and swirled until the oxonium salt dissolved (about 10 min.). After 30 min., 30 ml. of absolute ether was added to the yellow solution to precipitate the product. The solid was isolated by filtration, washed quickly with 20 ml. of ether and 20 ml. of pentane, and air dried for about 1 min. Drying was completed at reduced pressure. The yield of cream-colored solid, m.p. 160–162°, was 3.60 g., 90%. After one recrystallization from nitromethane–ether and two from acetonitrile–ether, 2.4 g. (60%) of nearly white product was obtained, m.p. 164–165°.

Alkylation of Disulfides Leading to Sulfonium Salts.—The reaction and purification procedures were identical with those described above. In a typical application, 2.5 g. (0.01 mole) of *p*-anisyl disulfide and 3.5 g. (0.01 mole) of oxonium salt yielded *p*-tolyldimethylsulfonium trinitrobenzenesulfonate, m.p. 250.5–251° dec.

In an independent synthetic route for the sulfonium salt, a small amount of *p*-toluenethiol was added to a mixture of excess trimethyloxonium trinitrobenzenesulfonate in a few milliliters of nitromethane. After stirring the mixture for several minutes, ether was added and the precipitate was isolated by filtration. Recrystallization yielded a product with m.p. 253.5–254.5°

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(10) Although there was no tendency for **1** to form **2** under the reaction conditions, **2** was the sole product isolated from aqueous nitromethane.

(11) N. Kharasch, W. King, and T. C. Bruice, *J. Am. Chem. Soc.*, **77**, 931 (1955).

(12) N. Kharasch, C. M. Buess, and W. King, *ibid.*, **75**, 6035 (1953).

(13) It has been observed in our laboratory that the reaction of silver 2,4,6-trinitrobenzenesulfonate with aromatic sulfenyl halides yields highly colored solutions.[2] The colors are a function of substituents on the aromatic ring and are believed attributable to sulfenium ion formation.

dec.; the mixture melting point with the product from the disulfide was 252–253.5° dec.

Reaction of Dimethylmethylthiosulfonium Trinitrobenzenesulfonate with Iodide Ion.—A solution of 1.5 g. (0.010 mole) of sodium iodide in 5 ml. of acetone was added to 2.0 g. (0.0050 mole) of the alkylated disulfide in 5 ml. of acetone. The color of iodine formed immediately. After 5 min. the mixture was titrated with 0.10 *N* sodium thiosulfate; 21 ml. (0.0021 equiv., 84%) were required. Analysis of a pentane extract of the solution by gas chromatography showed a 2:1 ratio of methyl sulfide to methyl disulfide.

Preparation of Hydrazinium Xanthates

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Contribution No. 74 from Washington Research Center,
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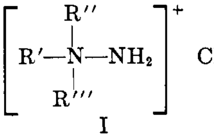
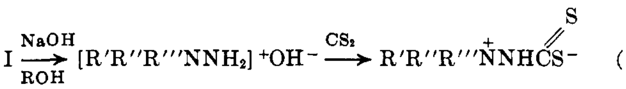
A very convenient method for preparing 1,1,1-trisubstituted hydrazinium chlorides[1] (I) by addition of chloramine to tertiary amines was reported by Omietanski and Sisler[2] several years ago. Preparation, properties, and reactions of hydrazinium compounds were presented a year later in a review article.[3] It was pointed out there that the primary amine nitrogen of the hydrazinium salts is nonbasic. For this reason hydrazinium salts do not add another molecule of acid to form double salts $R'R''R'''NNH_3X_2$. The hydrazinium amine group generally resists alkylation but sometimes may be acylated. Hydrazinium salts are thus formally closer to quaternary ammonium salts than to primary amines.



$$\left[\mathrm{R'}-\overset{\mathrm{R''}}{\underset{\mathrm{R'''}}{\mathrm{N}}}-\mathrm{NH_2}\right]^+ \mathrm{Cl}^-$$

I

Since primary amines are well known to react with carbon disulfide to give the corresponding dithiocarbamates, it was interesting to see whether the hydrazinium amine group also would enter into such reactions. It was expected that the corresponding betaine-type dithiocarbamates, III, might be formed, as follows. We found that the reaction did not obey eq. 1. Our results are the subject of this paper.

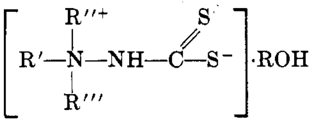


$$\mathrm{I} \xrightarrow[\mathrm{ROH}]{\mathrm{NaOH}} \underset{\mathrm{II}}{[\mathrm{R'R''R'''NNH_2}]^+\mathrm{OH}^-} \xrightarrow{\mathrm{CS_2}} \underset{\mathrm{III}}{\mathrm{R'R''R'''}\overset{+}{\mathrm{N}}\mathrm{NH}\overset{\mathrm{S}}{\mathrm{C}}\mathrm{S}^-} \qquad (1)$$

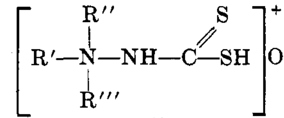
The first step of was readily accomplished by treating I with either methanolic or ethanolic sodium hydroxide. The second step was carried out without isolating the intermediate II.

In most cases where R′, R″, or R‴ were either aromatic or araliphatic, unchanged hydrazinium chlorides were recovered, together with crystalline sulfur. Since no other products were isolated, those experiments will not be reported here. Those hydrazinium chlorides which had only aliphatic substituents, $R' = R'' = R''' = CH_3$ or C_2H_5, gave high yields of yellow, crystalline, low-melting, hygroscopic products. Elemental analysis showed that these materials were associated with one molecule of alcohol. Similar products were obtained in low to moderate yields from one aromatic and one heterocyclic hydrazinium. The presence of alcohol in the molecule was confirmed by gas chromatography.

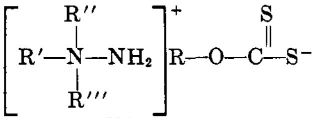
Three possible structures, IV, V, and VI, were envisaged for the reaction products. On treatment of aqueous solutions of these materials with salts of heavy metals, such as copper, lead, nickel, cobalt, and mercury, colored metal derivatives precipitated. Although they could not be sufficiently well purified to provide meaningful analytical data, these derivatives were nitrogen-free. It thus appeared that the products of the reaction of hydrazinium hydroxides II with carbon disulfide in alcoholic solutions were not dithiocarbamates, IV or V, but xanthates VI.



IV



V



VI

This conclusion was in agreement with n.m.r. results. A rather stable compound VI ($R' = R'' = R''' = CH_3$; $R = C_2H_5$) was particularly well studied. The n.m.r. spectrum of this compound in pyridine-d_5 consisted of the following: (i) a singlet (relative intensity 9) centered at τ 6.06; (ii) a singlet (relative intensity 2) centered at 2.47 (when D_2O was added to the sample, this absorption disappeared); (iii) a triplet (relative intensity 3) centered at 8.64; and (iv) a quartet (relative intensity 2) centered at 5.13. The n.m.r. spectrum of the sample, after adding 1 equiv. of dry ethanol, showed all of the original absorption bands. In addition, there appeared a second triplet centered at τ 8.69 (v) and a broad multiplet centered near 6.12 (vi).

The n.m.r. spectra were observed at several temperatures between 25 and 100° with no appreciable change in their appearance. Similar results were obtained when D_2O and dimethyl sulfoxide-d_6 were used as solvents for the n.m.r. experiments.

The above data suggest the following structure for the compound: (1) three methyl groups attached to positive nitrogen (absorption i); (2) two mobile protons of the type NH, OH, or SH (absorption ii); and (3) one ethyl group (absorptions iii and iv) attached to an electron-deficient atom, probably oxygen. The chemical shift of the methylene quartet (iv) is to the lower field than any $R-CH_2-O-$ methylene chemical shift we have observed in model compounds. The ethoxy group does not exchange with the ethoxy group

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[1] Although *Chemical Abstracts* uses the name hydrazonium, rather than hydrazinium, we prefer the more common nomenclature proposed in ref. 3.

[2] G. M. Omietanski and H. H. Sisler, *J. Am. Chem. Soc.*, **78**, 1211 (1956).

[3] H. H. Sisler, G. M. Omietanski, and B. Rudner, *Chem. Rev.*, **57**, 1021 (1957).