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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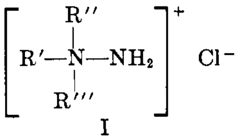
A very convenient method for preparing 1,1,1-trisubstituted hydrazinium chlorides[1] (I) by addition of chloramine to tertiary amines was reported by Omietanski and Sisler[2] several years ago. Preparation, properties, and reactions of hydrazinium compounds were presented a year later in a review article.[3] 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.



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

I

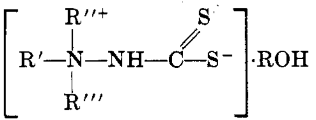
Since primary amines are well known to react with carbon disulfide to give the corresponding dithiocarbamates, it was interesting to see whether the hydrazinium amine group also would enter into such reactions. It was expected that the corresponding betaine-type dithiocarbamates, III, might be formed,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

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

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.

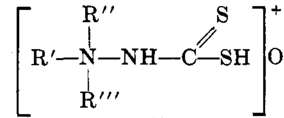
In most cases where R′, R″, or R‴ were either aromatic or araliphatic, unchanged hydrazinium chlorides were recovered, together with crystalline sulfur. Since no other products were isolated, those experiments will not be reported here. Those hydrazinium chlorides which had only aliphatic substituents, 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.



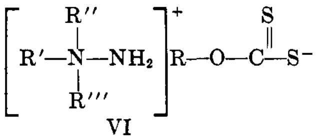
$$\left[R'-\overset{R''+}{\underset{R'''}{N}}-NH-\overset{S}{\overset{/\!/}{C}}-S^-\right]\cdot ROH$$

IV



$$\left[R'-\overset{R''}{\underset{R'''}{N}}-NH-\overset{S}{\overset{/\!/}{C}}-SH\right]^+ OR^-$$

V



$$\left[R'-\overset{R''}{\underset{R'''}{N}}-NH_2\right]^+ R-O-\overset{S}{\overset{\|}{C}}-S^-$$

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).

TABLE I

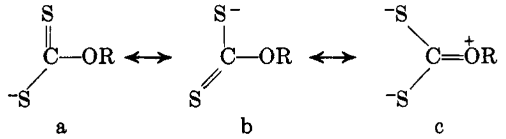
PREPARATION OF 1,1,1-TRISUBSTITUTED HYDRAZINIUM XANTHATES (VI)

R′	R″	R‴	R	Yield, %	M.p., °C.	% C		% H		% N		% S	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3	CH_3	CH_3	CH_3	88	48–49	32.94	32.70	7.74	7.74	15.37	15.14	35.18	35.20
C_2H_5	C_2H_5	C_2H_5	CH_3	91	65–66	42.82	42.75	8.98	8.88	12.49	12.48	28.58	28.61
$CH_2CH_2OCH_2CH_2$		$HOCH_2CH_2$	CH_3	47[a]	76–77 75–76	37.77	38.08 38.32	7.13	7.25 7.22	11.02	9.95 10.42	25.21	25.02 25.31
C_6H_5	C_2H_5	C_2H_5	CH_3	10[b]	54–55	50.73	50.73	7.74	7.74	10.76	10.77	24.63	24.63
CH_3	CH_3	CH_3	C_2H_5[c]	89	50–51	36.39	36.70	8.22	8.31	14.27	14.48	32.66	33.02
C_2H_5	C_2H_5	C_2H_5	C_2H_5	86	30–31	45.34	44.96	9.30	9.21	11.75	11.66	26.90	27.30

[a] Two fractions were obtained; less soluble, fine needles (5% yield) and more soluble columns (42% yield). They may have been different conformers resulting from two possible substitution directions of the quaternary morpholinium nitrogen. Their infrared spectra were nearly identical. [b] Crystalline sulfur, m.p. 114–115°, and unchanged starting hydrazinium chloride were first isolated in low yields. [c] The equivalent conductance of this compound at 25° was found to be 278.8 ohms^{-1} cm.^{2} (determined for a 0.0062 *N* solution in absolute ethanol).

of ethanol even in the presence of small amounts of acids or bases up to the temperature of 100° (no coalescence of iii with v and iv with vi).

Structure VI seems the most consistent with the experimental results.[4] The extreme low-field chemical shift observed for the methylene protons can perhaps be explained by the contribution of the resonance form VIIc, although this form has been reported[5] to contribute little to the structure of xanthate.



VII

The infrared spectra of all our reaction products had strong absorption bands in the 1040–1055-, 1090–1115-, and 1170–1190-cm.$^{-1}$ ranges. The same infrared absorption pattern was observed for sodium ethyl xanthate and for tetraethylammonium ethyl xanthate.

Formation of xanthates from carbon disulfide and alcohols in the presence of strong bases is well known. When both alcohols and primary amines are present, a competition between these two groups can be expected. In the case of hydrazinium hydroxides II the primary amine group is not reactive enough to form a derivative with carbon disulfide. This is consistent with the general observations made earlier.[4] The hydrazinium hydroxides, strong bases themselves, catalyze instead the reaction of carbon disulfide with the alcohol. Hydrazinium xanthates VI are thus the main reaction products.

Experimental[6]

Materials.—Hydrazinium chlorides I were prepared in this laboratory by reaction of chloramine with the corresponding tertiary amines. The materials were recrystallized from methanol–ether to constant chloride values. Alcoholic sodium hydroxide was made by dissolving 98% Baker analyzed sodium hydroxide pellets in anhydrous methanol or ethanol. The concentration of sodium hydroxide was determined by titration. Baker analyzed reagent carbon disulfide, anhydrous commercial methanol and ethanol were used as received.

Preparation of 1,1,1-Trisubstituted Hydrazinium Xanthates.—The following general technique was employed. Between 0.01 and 0.1 mole of the hydrazinium chloride I was accurately weighed and dissolved in minimum amount of the anhydrous alcohol. The stoichiometric amount of sodium hydroxide solution in the same alcohol was then added. Although most sodium chloride precipitated immediately, it was not removed at this stage. A 20–30% excess of carbon disulfide was added, and the yellow mixture was left overnight at room temperature. Most of the alcohol was flash-evaporated at a reduced pressure, sodium chloride was filtered off, and the filtrate was diluted with acetone and cooled several hours at −20°. Additional sodium chloride, which precipitated out, was removed. The final filtrate, diluted with ether, was kept either at Dry Ice temperature for several hours or at −20° for several days. The yellow, crystalline precipitate was filtered, washed with ether, and vacuum dried. All products were recrystallized at least twice from alcohol–ether solutions. The results are summarized in Table I.

All these hydrazinium xanthates could be dried *in vacuo* at temperatures lower than their melting points without decomposition. Heated above their melting points, they degraded to a variety of products. Although some hydrazinium xanthates could be kept at room temperature for several months without apparent decomposition, others degraded readily on standing. Thus, VI (R′ = R″ = R‴ = R = C_2H_5) decomposed on standing for 1 week in a desiccator over calcium chloride.

N.m.r. Spectroscopy.—N.m.r. spectra were measured with a Varian Associates DP-60 n.m.r. spectrometer. Samples were prepared as 8% pyridine-d_5 solutions and were not degassed. Tetramethylsilane (TMS) was used as internal standard, and the spectra were calibrated by the side-band technique. Chemical shifts are reported in parts per million from TMS, with TMS assigned a value of 10.

Gas Chromatography.—Samples of VI (R′ = R″ = R‴ = CH_3 or C_2H_5; R = CH_3) were dissolved in water and analyzed on a 6-ft. column of Carbowax 1500 on an inert support at 75°. A Perkin-Elmer instrument was used. The composition of the solutions changed with time, but after acidification with hydrochloric acid no more change was detected. Methanol was identified as one of the components of the gaseous mixture. It was present in about the calculated amounts. The identity of methanol was confirmed by time-of-flight mass spectrometric analysis of the effluent stream.

Acknowledgment.—The authors are happy to acknowledge the cooperation of the following colleagues: Dr. R. W. McKinney and Mr. G. L. Kearns made the gas chromatographic and mass spectrometric determinations; Messrs. J. N. Lomonte and L. Peters determined the infrared spectra of hydrazinium xanthates; and Dr. A. Berlin assisted us with the interpretation of the n.m.r. data.

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[4] At the suggestion of the referee, VI (R′ = R″ = R‴ = CH_3; R = C_2H_5) was also prepared in 95% yield from the corresponding hydrazinium chloride and potassium xanthate. The resulting hydrazinium xanthate was identical with that made by the other technique.

[5] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature*, **177**, 1042 (1956).

[6] The melting points were determined on a Nalge–Axelrod melting point block and are uncorrected. Elemental analyses by Dr. C. Daessle, Montreal, Canada.