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Mercaptoethylation. VI. Preparation and Some Reactions of Ethyl 2-Mercaptoethylcarbonate

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Ethyl 2-hydroxyethylthiolcarbonate, in the presence of catalytic amounts of acetates of some of the rare-earth elements, is isomerized in practically quantitative yield to ethyl 2-mercaptoethylcarbonate. This compound is shown to be an excellent mercaptoethylating agent for primary and secondary amines. Several new 2-aminoethanethiols are reported.

In Part IV of this series,[1] a simple and convenient synthesis of ethyl 2-hydroxyethylthiolcarbonate (I) in 87–92% yield was described. This thiolcarbonate was shown to react with moderately to strongly basic primary and secondary amines in refluxing toluene to form 2-aminoethanethiols (II). The value of this synthesis was found to be limited owing to difficulties often encountered in separating the aminoethanethiol from an ethyl carbamate (III) produced in a side reaction. The reaction mechanism advanced to explain the formation of these products is illustrated in Chart I.

Thus, analogous to the base-catalyzed S → O acetyl migration which has been reported for 2-hydroxyethyl thiolacetate,[2] I in the presence of amine is thought to undergo an S → O carbethoxy rearrangement to yield the isomeric ethyl 2-mercaptoethylcarbonate (IV). Thiol IV is also unstable under basic conditions and decomposes *via* an intramolecular displacement to ethylene sulfide, carbon dioxide, and ethanol, ethylene sulfide subsequently reacting with amine to form the 2-aminoethanethiol (II). The side reaction resulting in the ethyl carbamate by-product arises from a more straightforward nucleophilic substitution following reaction path 2.

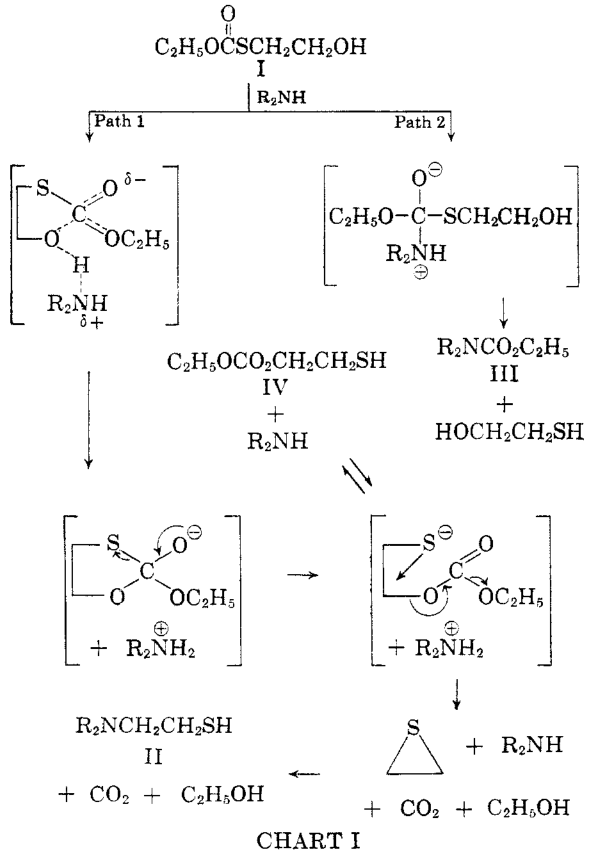

CHART I

From this mechanism it would follow that the formation of the contaminating carbamate III could be avoided, and a very convenient synthesis of 2-aminoethanethiols would be obtained if IV instead of I were employed as the precursor to the ethylene sulfide. A search of the literature revealed a reference to this compound by Culvenor and co-workers[3] who reported it as a component of a mixture containing primarily the isomeric I. Our first efforts to prepare pure IV in a satisfactory yield by standard procedures were unrewarding, 35% being the highest yield obtained by the reaction of ethyl chloroformate with 2-mercaptoethanol under acidic conditions.[1]

We now have found that IV can be obtained in practically quantitative yield by the isomerization of I with catalytic amounts of acetates of some of the rare-earth elements. Use of thiol IV as a mercaptoethylating agent for primary and secondary amines, in most cases, results in a more expedient synthesis and gives higher yields of 2-aminoethanethiols than other previously described procedures.

Preparation of ethyl 2-mercaptoethylcarbonate (IV). The isolation of IV, which is formed by the isomerization of I with basic catalyst, is feasible because, at 9 mm. pressure, thiol IV boils 27° below the isomeric starting material. Thus, by effecting the isomerization of I with a suitable catalyst under distillation conditions, it is possible to distill IV away from the catalyst before decomposition can occur. Initial experiments with catalytic amounts of strong base, such as sodium methoxide, yielded

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(1) D. D. Reynolds, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5119 (1961), Part IV of this series.

(2) L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 817 (1952); J. S. Harding and L. N. Owen, *J. Chem. Soc.*, 1528 (1954); B. Sjöberg, *Ber.*, **74B**, 64 (1941).

(3) C. C. Culvenor, W. Davies, and W. E. Savige, *J. Chem. Soc.*, 4480 (1952).

only decomposition products. However, in investigating a weaker basic catalyst, 58–66% yields of IV were obtained by employing calcium and magnesium acetates at concentrations between 0.003% and 0.013% by weight of I. At lower catalyst concentrations, the isomerization occurred prohibitively slowly, whereas higher concentrations led to decreased yields due to more extensive decomposition.

Some of the salts of the rare-earth elements—such as uranyl, neodymium, thorium, cerous, and ceric acetates— were found to be even more effective (Tables I and II). The data of Table I also demonstrate rather strikingly the sensitivity of the preparation to catalyst concentration. Thus, although a 61% yield of IV was obtained when 750 g. of I was distilled in the presence of 200 mg. of uranyl acetate dihydrate, the yield was increased to 97 % by use of 12.5 mg. of catalyst.

TABLE I

ISOMERIZATION OF ETHYL 2-HYDROXYETHYLTHIOLCARBONATE WITH URANYL ACETATE

$$\underset{\text{I}}{C_2H_5OCOSCH_2CH_2OH} \xrightarrow{\text{catalyst}} \underset{\text{IV}}{C_2H_5OCO_2CH_2CH_2SH}$$

Wt. of $(AcO)_2UO_2 \cdot 2H_2O$,[a] Mg.	Wt. of I,[b] G.	Wt. of IV, G.	Yield, %	n_D^{25} of IV[c]
200	750	465	61	1.4534
100	750	560	74	1.4525
50	750	611	81	1.4522
25	750	660	88	1.4531
12.5	750	725	97	1.4532
0.00	750	0	0	

[a] Purchased from the General Chemical Co., New York, N. Y. [b] I had a b.p. 111°/9 mm., n_D^{25} 1.4782. [c] In all examples, IV had a b.p. 84°/9 mm. Pure IV has n_D^{25} 1.4522.

TABLE II

ISOMERIZATION OF ETHYL 2-HYDROXYETHYLTHIOLCARBONATE WITH ACETATE SALTS OF SOME OF THE RARE-EARTH ELEMENTS

Catalyst	Wt. of Catalyst, G.	Wt. of I, G.	Yield of IV, %	n_D^{25} of IV
Cerous acetate[a]	1.49	150	67	1.4528
	0.75	150	86	1.4522
	0.37	150	92	1.4521
	0.18	150	88	1.4532
Thorium acetate[a]	0.054	150	90	1.4536
Neodymium acetate[a]	0.068	150	89	1.4526
Basic ceric acetate[b]	1.51	150	90	1.4528

[a] Purchased from K and K Laboratories, Inc., Jamaica, N. Y. [b] Purchased from the A. D. Mackay, Inc., New York, N. Y. This same catalyst was re-used for six subsequent 150 g. (1.0 mole) runs with yields between 94 and 98% and n_D^{25} 1.4521 to 1.4528.

By maintaining a catalyst level of approximately 12.5 mg. of uranyl acetate dihydrate per 750 g. (5.0 moles) of I through periodic replacements of I, 4 kg. of I was isomerized to IV and isolated in greater than 98% yield.

TABLE III

MERCAPTOETHYLATION OF PRIMARY ALIPHATIC AMINES

$$RNH_2 + C_2H_5OCO_2CH_2CH_2SH \longrightarrow RNHCH_2CH_2SH + C_2H_5OH + CO_2$$

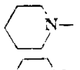
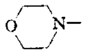
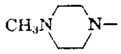
		% Yield by		%			Calcd., %			Found, %		
No.	R	A[b]	B[c]	Purity[d]	B.P./Mm.	n_D^{25}	C	H	N	C	H	N
1	C_2H_5—		69	99.2	75/63 52/21[e]	1.4751 1.4750[e]						
2	n-C_3H_7—		75	95.1	82/46 70/22[e]	1.4720 1.4710[e]						
3	i-C_3H_7—[a]	7	77	96.9	81/64[f]	—	50.4	10.9	11.8	50.7	10.8	11.5
4	n-C_4H_9—	32	66	97.2	81/18 84/19[e]	1.4694 1.4694[e]						
5	i-C_4H_9—[a]	37	72	97.2	76/23	1.4652	54.1	11.3	10.5	53.8	11.4	10.6
6	s-C_4H_9—[a]	42	68	95.3	83/33	1.4676	54.1	11.3	10.5	54.2	11.3	10.4
7	t-C_4H_9—[a]	15	64	99.2	71/28[g]	—	54.1	11.3	10.5	54.3	10.6	10.5
8	$CH_2{=}CHCH_2$—[a]	44	56	97.8	68/19	1.4936	51.3	9.4	12.0	50.9	9.3	11.6
9	n-C_6H_{13}—	66		99.0	97/7 102/9[h]	1.4680 1.4700[l]						
10	n-C_8H_{17}—[a]	64		98.5	83/0.3	1.4691	63.5	12.2	7.4	64.0	12.6	7.3
11	n-$C_{10}H_{21}$—[a]	68		97.8	120/0.6	1.4674	66.4	12.4	6.5	66.0	12.2	6.6
12	C_6H_{11}—[a]	65		98.0	99/7 153/4[i]	1.5040 1.5448[i]	60.4	10.7	8.8	60.3	10.7	8.6
13	$C_6H_5CH_2$—	72		100.0	84/0.1 109/2[j]	1.5585 1.5540[m]						
14	$HOCH_2CH_2$—[a]		17	94.9	74/0.02[k]	—	39.7	9.1	11.6	39.4	8.6	11.5

[a] New compound. [b] Reaction temperature was the atmospheric boiling point of the amine-toluene mixture. [c] Reaction conducted at 125–150° in an autoclave. [d] Purity determined by iodometric titration. [e] Ref. 5. [f] Crystallized as an inner salt with m.p. 34–35°. [g] Crystallized as an inner salt with m.p. 41–43°. [h] Ref. 7c. [i] The disagreement in physical constants with the literature value, ref. 4, precludes the possibility that these compounds have the same structure. [j] Ref. 9. [k] Crystallized with a m.p. 61–63°. [l] n_D^{20}, ref. 7c. [m] n_D^{20}, ref. 9.

TABLE IV

MERCAPTOETHYLATION OF SECONDARY AMINES

$$R_2NH + C_2H_5OCO_2CH_2CH_2SH \longrightarrow R_2NCH_2CH_2SH + CO_2 + C_2H_5OH$$

No.	R_2N—	Yield, %	Purity,[c] %	B.P./Mm.	n_D^{25}	Calcd., % C	H	N	Found, % C	H	N
1	$(C_2H_5)_2N$—	73	100.0	85/56 65/23[d]	1.4636 1.4680[k]						
2	$(n\text{-}C_3H_7)_2N$—	88	98.8	77/10 109/3[e]	1.4614 1.4502[l]	59.6	11.8	8.7	59.5	11.8	8.5
3	$(i\text{-}C_3H_7)_2N$—	10	99.0	73/13 125/16[e]	1.4686 1.4506[l]	59.6	11.8	8.7	59.3	11.8	8.7
4	$(n\text{-}C_4H_9)_2N$—	91	100.0	66/0.7 74/2[f]	1.4620 1.4635[m]						
5	$(i\text{-}C_4H_9)_2N$—	89	100.0	91/10 160–179[e]	1.4572 1.4678[l]	63.5	12.2	7.4	63.7	12.3	7.4
6[a]	$(sec\text{-}C_4H_9)_2N$—	20	98.6	93/8	1.4723	63.5	12.2	7.4	63.2	12.0	7.4
7	$(n\text{-}C_5H_{11})_2N$—	90	100.0	91/0.8 90/2.5[f]	1.4629 1.4643[m]						
8	$(i\text{-}C_5H_{11})_2N$—	92	99.6	85/1 105/5[g]	1.4600 1.4611[n]						
9	$(CH_2{=}CHCH_2)_2N$—	92	96.2	90/17 83/14[h]	1.4895 1.4970[n]	61.1	9.6	8.9	61.1	10.1	9.2
10		96	99.2	79/10 85/11[h]	1.4991 1.5015[h]						
11		92	98.9	92/10 101/15[h]	1.5021 1.5030[h]						
12		94	100.0	95/10 95/10[i]	1.5040 1.5045[i]						
13[a,b]		91	94.5	96/0.03[j]	—	46.6	8.8	13.6	46.4	8.9	13.6
14[a]	$HOCH_2CH_2\overset{CH_3}{N}$—	63	96.3	78/0.9	1.4977	44.4	9.6	10.4	44.7	9.6	10.2

[a] New compound. [b] Prepared from 2.2 moles of IV per mole of amine. [c] Determined by iodometric titration. [d] Ref. 7d. [e] Ref. 9. [f] Ref. 7a. [g] Ref. 7c. [h] Ref. 7e. [i] Ref. 10. [j] M.p. 46–47°. [k] n_D^{20}, ref. 7d. [l] n_D^{20}, ref. 9. [m] n_D^{20}, ref. 7a. [n] n_D^{20}, ref. 7c.

Mercaptoethylation with ethyl 2-mercaptoethylcarbonate (IV). With thiol IV readily available, an evaluation was made of its usefulness as a mercaptoethylating agent. The results obtained for the alkylation of examples of moderately to strongly basic primary and secondary amines, and of several aromatic primary amines, are summarized in Tables III, IV, and V, respectively.

TABLE V

MERCAPTOETHYLATION OF AROMATIC AMINES

$$RNH_2 + C_2H_5OCO_2CH_2CH_2SH \longrightarrow RNHCH_2CH_2SH + C_2H_5OH + CO_2$$

No.	R	Yield, %	B.P./Mm.	n_D^{25}
1	C_6H_5—	81	100/0.5 118/4[a]	1.6022 1.6030[c]
2	$p\text{-}CH_3C_6H_4$—	86	91/0.02 130/5[a]	1.5867 1.5862[c]
3	$p\text{-}CH_3OC_6H_4$—	78	120/0.02 151/4[a]	1.5914 1.5910[c]
4	$p\text{-}ClC_6H_4$—	67	112/0.02 130/0.5[b]	1.6127 1.6132[d]

[a] Ref. 9. [b] Ref. 11. [c] Ref. 9, n_D^{20}. [d] Ref. 11, n_D^{20}.

The procedure which was employed successfully with the secondary amines of Table IV and with most of the higher boiling primary amines (Nos. 9–13) of Table III entailed refluxing ethyl 2-mercaptoethylcarbonate with a two-fold molar excess of amine in toluene overnight under an efficient condenser.[4] The product was isolated by distillation.

The side reactions depicted in Equations 1 and 2

$$\underset{\text{II}}{R_1R_2NCH_2CH_2SH} + n\text{IV} \longrightarrow \underset{\text{V}}{R_1R_2N(CH_2CH_2S)_{n+1}H} + nC_2H_5OH + nCO_2 \quad (1)$$

$$\underset{\text{II}}{R_1NHCH_2CH_2SH} + \text{IV} \longrightarrow \underset{\text{VI}}{R_1N(CH_2CH_2SH)_2} + C_2H_5OH + CO_2 \quad (2)$$

account for the rest of the yields of products, the reaction of Equation 2, of course, pertaining only to the mercaptoethylation of primary amines. Both of these side reactions are more prevalent at lower reaction temperatures. This is particularly true with the low-boiling primary amines (Nos. 1–8, Table III), owing to decreased reaction rates which allow greater selectivity of the alkylating agent for the various nucleophiles present. In the monomercaptoethylation of primary amines, for example, enhancement of such selectivity favors further mercaptoethylation of II to VI (Equation 2)

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(4) Piperazine, No. 13, is an exception. See Footnote *b*.

rather than the alkylation of the starting amine, since II would be a stronger base and probably more nucleophilic than the starting amine.

This effect, which is reflected in the poor yields (7–44%) of 2-aminoethanethiols obtained by the procedure described for amines 1–8, Table III, is overcome by conducting the reaction in a rocking-type autoclave, a positive displacement pump being used to meter IV into the amine-solvent mixture at a preset elevated temperature. This allows the mercaptoethylating reaction to be initiated and completed at a temperature well above the atmospheric boiling point of the amine. As an example of the benefits derived from such a modification, the 7% yield of 2-isopropylaminoethanethiol obtained at a reaction temperature of about 50°—*i.e.*, the boiling point of isopropylamine—was increased to 77% yield by conducting the reaction at 140° for 15 min. in an autoclave. Similar increases in yields were obtained for a number of other low-molecular-weight amines, as summarized in Table III under Method B. Woodburn and Pautler[5] have previously prepared ethyl-, *n*-propyl-, and *n*-butylaminoethanethiols in 38, 52 and 57% yields, respectively, by heating ethylene sulfide and a one-fold molar excess of amine at 150–200° in an autoclave for six hours. Bergmann and Kaluszyner,[6] however, preferred to prepare 2-ethylaminoethanethiol in 16% yield from the corresponding aziridine rather than synthesize the sensitive ethylene sulfide precursor. The yields of 2-aminoethanethiols reported in Tables III and IV represent a substantial improvement over those obtained by direct reaction of amine with ethylene sulfide,[5–7] and the elimination of the isolation and handling of ethylene sulfide allows these procedures to readily be adapted to large-scale use.

Although we believe the procedures just described constitute the best syntheses thus far described for 2-aminoethanethiols derived from the moderately to strongly basic primary and secondary amines, they are not applicable to the mercaptoethylation of aromatic amines. When thiol IV was heated with aniline for fifteen hours at 175°, little or no reaction occurred. As aniilne will react with ethylene sulfide at room temperature,[7c] it was apparent that a base stronger than aniline was required to catalyze the decomposition of IV to ethylene sulfide. A catalytic amount of sodium methoxide has now been found suitable for this purpose, and with it the four 2-arylaminoethanethiols of Table V were readily prepared.

A typical synthesis involves the charging of an autoclave with three moles of arylamine, one mole of I, benzene, and 1 g. of sodium methoxide. The mixture is heated for one hour at 150°, cooled, and the product isolated by distillation. The utility of this method of synthesis is emphasized by the fact that Bergmann *et al.*[6] chose what they considered to be the simpler route to 2-phenylaminoethanethiol in 33% yield from the corresponding isothiuronium salt rather than employ a procedure involving ethylene sulfide and aniline which is known to give 75% yields of product. Their choice was probably motivated by a desire to avoid the tedious preparation of sizable quantities of ethylene sulfide.

We believe that, in the preparation of distillable 2-arylaminoethanethiols, both the standard isothiuronium synthesis and the method involving preformed ethylene sulfide are superseded by the procedure recommended here. This is, of course, subject to the condition that the parent amine be inert to the base catalyst under the experimental conditions described.

It was expected that correlations between the steric requirements of the amine and its ease of reaction with ethylene sulfide would become apparent in studying the mercaptoethylation of the primary and secondary aliphatic amines of Tables III and IV. The good yields of 2-aminoethanethiols obtained from the primary amines of Table III by the autoclave procedure, and the lack of a definite trend in yields indicate there is no pronounced steric effect, even with the comparatively hindered *tert*-butylamine. Evidently serious steric interactions are encountered only with amines possessing higher degrees of branching near the site of reaction (on the carbon *alpha* to the nitrogen), such as are observed with di-isopropyl- and di-*sec*-butylamines (Nos. 3 and 6, Table IV). This fact is reflected in the low yields obtained both by the overnight refluxing procedure (10 and 20%, respectively) and by the autoclave method, which gave only 28 and 23% yields, respectively. Interestingly enough, similar branching on the beta-carbon, as in di-isobutylamine (No. 5, Table IV), had no apparent adverse effect on the obtainable yield (90%) of 2-di-isobutylaminoethanethiol.

In general, when stored under an atmosphere of nitrogen, the 2-aminoethanethiols of Tables III, IV, and V were found to be indefinitely stable at room temperature. 2-Diallylaminoethanethiol (No. 9, Table IV), however, is an exception. After this material had stood at room temperature over a period of a month, its refractive index had increased from n_D^{25} 1.4895 to n_D^{25} 1.5080, and the —SH absorption (3.93 μ) in the infrared region of the spectrum had decreased to a negligible value.

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(5) H. M. Woodburn and B. G. Pautler, *J. Org. Chem.*, **19**, 863 (1954).

(6) E. D. Bergmann and A. Kaluszyner, *Rec. trav. chim.*, **78**, 289 (1959).

(7) (a) H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, **69**, 2672 (1947). (b) W. Reppe and F. Nicolai, United States Patent **2,105,845** (1938). (c) G. I. Braz, *Zhur. Obshcheĭ Khim. S.S.S.R.*, **21**, 688 (1951). (d) N. F. Albertson and R. O. Clinton, *J. Am. Chem. Soc.*, **67**, 1222 (1945). (e) R. O. Clinton, V. J. Salvador, S. C. Laskowski, and C. M. Suter, *J. Am. Chem. Soc.*, **70**, 950 (1948).

Attempted redistillation of the material that originally had a boiling point of 90°/17 mm., gave no constant boiling fraction and more than 40% of the material remained as pot residue, boiling above 175°/0.008 mm., and with a refractive index of n_D^{25} 1.5293. The elemental analyses of the fractions collected during the attempted redistillation as well as the pot residue were all correct for $C_8H_{10}NS$, the empirical formula for 2-diallylaminoethanethiol. Except for the disappearance of the —SH band, the infrared spectra of all fractions and of the pot residue were quite similar to the spectra of the freshly prepared 2-diallylaminoethanethiol. The possibility that the thiol had inadvertently undergone oxidation to the disulfide was precluded by the preparation of an authentic sample of disulfide which had a boiling point of 135°/0.02 mm. and n_D^{25} 1.5180. These observations would therefore suggest that a polymerization was involved in which the thiol was adding to the double bond to give a polymeric aminosulfide.[8] Interestingly enough, 2-allylaminoethanethiol, (No. 8, Table III) which might be expected to behave in a similar manner, remained stable and unchanged under the same storage conditions.

EXPERIMENTAL

Materials. Ethyl 2-hydroxyethylthiolcarbonate, b.p. 111°/9 mm., n_D^{25} 1.4782, was prepared by a previously described procedure.[1] The amines were freshly distilled over calcium hydride.

Catalyzed isomerization of ethyl 2-hydroxyethylthiolcarbonate (I) *to ethyl 2-mercaptoethylcarbonate* (IV). *General procedure.* Ethyl 2-hydroxyethylthiolcarbonate and catalyst in the amounts given in the text and listed in Tables I and II were placed in the stillpot of a distillation apparatus equipped with an 18-in., glass-helices-packed column and attached to a variable reflux-rate stillhead. The system was evacuated with a water aspirator and the product distilled at a rate to maintain a stillhead temperature of 84°/9 mm. Particularly in the experiments employing calcium and magnesium acetates, some loss of vacuum occurred during the distillation, owing to the formation of low-boiling decomposition byproducts—*i.e.*, ethylene sulfide, carbon dioxide, and ethanol. In such cases, the boiling point of the product ranged from 84°/9 mm. to 90°/16 mm. Distillation was continued until the stillhead temperature began to rise above this range.

General mercaptoethylation procedure for secondary amines and higher-boiling primary amines. With the exception of piperazine, a mixture of the amine (3.0 moles) and anhydrous toluene (500 ml.) was brought to reflux under an efficient condenser topped by an acetone-Dry Ice trap. Ethyl 2-mercaptoethylcarbonate (150 g., 1.0 mole) was then added dropwise to the reaction mixture over a 1-hr. period. After refluxing overnight, the 2-aminoethanethiol was isolated by distillation through a 14-in., glass-helices-packed column equipped with a variable take-off head.

Bis-2-mercaptoethylpiperazine (No. 13, Table III) was prepared in a similar manner from 2.2 moles of ethyl 2-mercaptoethylcarbonate and 1 mole of piperazine. The product in this case was isolated by distillation through an 8-in. Vigreux column.

General mercaptoethylation procedure for low-boiling primary amines. A charge consisting of amine (3.0 moles) and benzene (150 ml.) was loaded into a stainless-steel autoclave. The autoclave was sealed, placed in a rocking heater-stand, and heated to 125–150°. Agitation was started at this point and ethyl 2-mercaptoethylcarbonate (150 g., 1.0 mole) was metered into the autoclave by means of a Lapp Pulsafeeder metering pump. This addition required approximately 15 min., and was followed by addition of 50 ml. of benzene. Agitation was continued for 5–10 min. at the operating temperature, the final pressure reaching 500–1500 p.s.i., depending on the vapor pressure of the amine used.

The autoclave was removed from the heater stand, cooled to room temperature, vented in a hood, and the product isolated by distillation through a 14-in., glass-helices-packed column equipped with a variable take-off head. In some instances, the mixture from the autoclave contained a considerable amount of solid carbamate salt ($R_2NCO_2^{\ominus}$ $R_2\overset{\oplus}{N}H_2$). This material, however, was usually unstable to heat and it decomposed into its components (amine and carbon dioxide) before the distillation of the desired product commenced.

General mercaptoethylation procedure for aromatic amines. A mixture consisting of the aromatic amine (3.0 moles), ethyl 2-mercaptoethylcarbonate (150 g., 1.0 mole), benzene (150 ml.), and sodium methoxide (1.0 g.) was introduced into a stainless-steel autoclave. The autoclave was sealed and and heated with agitation for 1–3 hr. at 125–150°. After cooling, the mixture was removed from the autoclave and the product was isolated by distillation through a 14-in. Vigreux column equipped with a variable take-off head.

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ROCHESTER, N. Y.

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(8) See E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Vol. 2, Chemical Publishing Co., Inc., New York, 1960, p. 29, for leading references concerning the addition of mercaptans to unsaturates.

(9) F. I. Rachinskii, N. M. Slavachevskaia, and D. V. Ioffe, *Zhur. Obshcheĭ Khim. S.S.S.R.*, **28**, 2998 (1958).

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(11) Y. K. Yuryev, S. V. Dyatlovitskaya, and L. G. Bulavin, *Zhur. Obshcheĭ Khim. S.S.S.R.*, **27**, 3271 (1957).