SYNTHESIS AND REACTIONS OF AMIDE MERCAPTALS*

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During the six years which have passed since the discovery of amide mercaptals [1] two papers (apart from papers by the authors of the present communication) have appeared with descriptions of the preparation of only two compounds of this class, whereas about twenty papers have already appeared on their oxygen analogs—amide acetals—which were discovered at about the same time. In 1961 Böhme and Roer [2], who were probably not acquainted with our investigations, announced the preparation of the first formamide mercaptal by the reaction of chlorobismethylthiomethane with dimethylamine. Later, in 1962 Clemens and co-workers [3], starting from a formamidinium salt, obtained a 30% yield of N-(bismethylthiomethyl)-N-methylaniline or N-methylformanilide dimethyl mercaptal:

$$C_6H_5(CH_3)\overset{+}{N}=CH-N(CH_3)C_6H_5 \xrightarrow[CH_3S^{\ominus}]{CH_3SH} (CH_3S)_2CH-N(CH_3)C_6H_5$$

The inadequate attention devoted to this interesting class of compounds is probably to be explained by the absence of a convenient method for their synthesis. This paper describes a new preparative method for the synthesis of amide mercaptals, and also some of the reactions of the latter.

We have prepared amide mercaptals in good yields by the reaction of aliphatic thiols with complexes formed by disubstituted formamides with dimethyl sulfate in presence of an alkaline agent [4]. Complexes of substituted amides with dimethyl sulfate were first synthesized by Bredereck and co-workers [5-7]. In Table 1 we list the complexes used in the preparation of amide mercaptals. Some of them have not been prepared previously.

The complexes react with two molecular proportions of thiol in the following way:

$$[(CH_3)_2\overset{+}{N}=CH-OCH_3]\,CH_3SO_4^{\ominus} + RSH \xrightarrow{RS^{\ominus}} (CH_3)_2NCH(SR)_2 + CH_3SO_4^{\ominus} + CH_3OH$$

It is characteristic that the reaction goes only in presence of an alkaline agent, the action of which probably consists in the formation of an alkyl sulfide ion. The reaction is probably to be regarded as a nucleophilic substitution at a saturated carbon atom. As alkaline agent we used sodium alkyl sulfide, but we then went over to triethylamine, which facilitated the experimental procedure and raised the yield somewhat (to 70%) as a result of the occurrence of reaction in one stage. By this method we prepared a whole series of amide mercaptals [(IX)-(XXV)] with aliphatic substituents on the sulfur atom (Table 2). If the complex (I) is treated with one molecular proportion of sodium ethyl sulfide the N,N-dimethylformamide monothioacetal, 1-methoxy-1-(methylthio)trimethylamine (XXVI), which might have been expected is not formed, but the product is a mixture of the amide mercaptal (X) and N,N-dimethylformamide dimethyl acetal (XXVII):

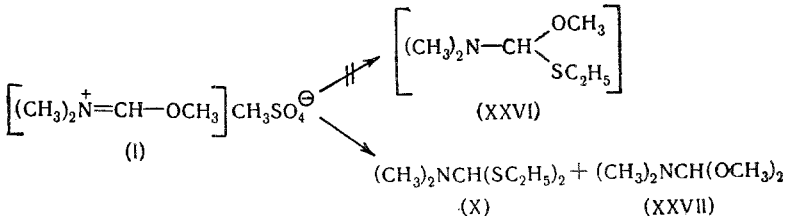

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TABLE 1

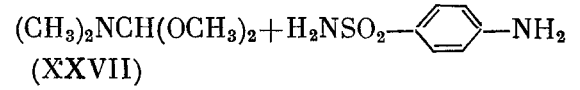
Complex with dimethyl sulfate	Original amide	T, °C	Time, h	n_D^{20} of complex	Yield, %	Lit. ref.
I	N,N-Dimethylformamide	60—80	2	1,4585	90	[6]
II	N,N-Dimethylacetamide	80	2	1,4629	60	[6]
III	4-Formylmorpholine	70—80	2	1,4840	Quant.	—*
IV	1-Formylpiperidine	70—80	3	1,4840	»	— †
V	N,N-Dimethylbenzamide	80	3	1,5162	60	[6]
VI	Tetramethylurea	80	3	1,4776	90	[8]
VII	1-Methyl-2-pyrrolidinone	80	3	1,4759	90	[7]
VIII	1,4-Diformylpiperazine	80	3	M. p. 80 (decomp.)	Quant.	— ‡

* Found: C 34.37; 34.42; H 6.18; 6.29; S 13.48; 13.64%. $C_7H_{15}NO_6S$. Calculated: C 34.84; H 6.25; S 13.30%.

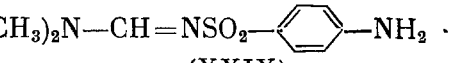
† Found: C 39.79; 39.98; H 7.29; 7.37; S 13.58; 13.69%. $C_8H_{17}NO_5S$. Calculated: C 40.10; H 7.17; S 13.39%.

‡ Found: C 29.73; H 5.93; S 17.11%. $C_{10}H_{22}N_2O_{10}S_2$. Calculated: C 30.44; H 5.62; S 16.25%. The hygroscopicity of the complex made it difficult to obtain good analysis.

To identify the amide acetal (XXVII) isolated we brought it into reaction with p-aminobenzenesulfonamide with the object of obtaining the bisformamidine (XXVIII) [9]. However, unexpectedly the reaction went only at the amide grouping, and as a result we obtained N'-(p-aminophenylsulfonyl)-N,N-dimethylformamidine (XXIX). The isomeric N,N-dimethyl-N'-p-sulfamoylphenylformamidine (XXX) differs from (XXIX) in properties and melting point [10].

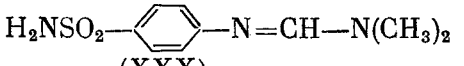


(XXVII)



(XXIX)

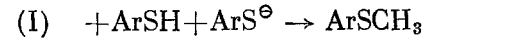
(XXVIII)



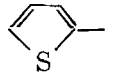
(XXX)

The presence of a free amino group in (XXIX) was proved by the azo-coupling reaction with 2-naphthol.

We made an attempt to extend the reaction of the dimethyl sulfate complexes with two molecular proportions of thiol. With aromatic thiols the reaction led to the formation of the corresponding aryl methyl sulfides and not the expected amide mercaptals:



(I)

(XXXI) Ar = C_6H_5; (XXXII) Ar = 

In this case it is evident that the thiols are S-methylated by the complex. The aryl methyl sulfides were identified by oxidation to the corresponding sulfones.

Attempts to prepare mercaptals of amides of acids other than formic, starting from the complexes (II), (V), (VI), and (VII), were not successful. In the reactions of these complexes with thiols in some cases only the original amide could be isolated.

The infrared spectra of the amide mercaptals contain a band at about 1670 cm^{-1}, which can be assigned to the stretching vibrations of the C=N bond, as in the case of amide acetals and "amide chlorides" [11]. In view of

TABLE 2

No.	Formula	B. p., °C (p, mm)	n_D^{20}	d_4^{20}	Yield, %, by the method		Found, %			Calculated, %		
					a	b	C	H	S	C	H	S
IX	$(CH_3)_2NCH\begin{matrix}SCH_2\\ \vert \\ SCH_2\end{matrix}$	102,5—104 (15)	1,5660	1,161	—	58	—	—	—	—	—	—
X	$(CH_3)_2NCH(SC_2H_5)_2$	90(7)	1,5103	0,990	56	70	—	—	—	—	—	—
XI	$(CH_3)_2NCH(SC_3H_7)_2$	115—116 (12)	1,5045	0,964	—	69	52,10; 52,36	10,08; 9,96	30,69; 30,79	52,10	10,19	30,88
XII	$(CH_3)_2NCH(SC_3H_7-i)_2$	92—96 (8)	1,4968	0,947	—	66	52,51; 52,27	10,19; 10,08	30,90; 30,92	52,10	10,19	30,88
XIII	$(CH_3)_2NCH(SC_4H_9)_2$	135—138 (6)	1,4978	0,949	48	—	—	—	—	—	—	—
XIV	$(CH_3)_2NCH(SC_4H_9-t)_2$	93—93,5 (6)	1,4954	0,934	3	55	—	—	—	—	—	—
XV	$(CH_3)_2NCH(SC_6H_{13})_2$	116—120 (0,01)	1,4919	0,927	—	72	61,69; 61,79	11,69; 11,60	22,08; 22,40	61,78	11,41	22,01
XVI	$(CH_3)_2NCH(SC_6H_{13}-t)_2$	136—137 (3)	1,5011	—	60*	—	61,35; 61,32	11,26; 11,34	22,26; 22,37	61,78	11,41	22,01
XVII	$(CH_3)_2NCH(SC_7H_{15})_2$	141—142 (0,01)	1,4903	0,915	—	46	63,66; 63,74	11,64; 11,84	19,91; 19,99	63,99	11,68	20,03
XVIII	$(CH_3)_2NCH(SC_9H_{19})_2$	174—180 (0,02)	1,4848	0,907	—	52	67,15; 67,00	11,84; 11,77	17,18; 17,32	67,20	12,08	17,10
XIX	$(CH_3)_2NCH(SC_{10}H_{21})_2$		1,4830	0,901	—	64	68,60; 68,48	12,21; 12,14	16,07; 16,06	68,60	12,21	15,90
XX	$(CH_3)_2NCH(SCH_2C_6H_5)_2$	154—155 (0,015) M. p. 23°	1,6013	—	64	—	67,25; 67,04	6,74; 6,83	21,12; 21,21	67,29	6,98	21,14
XXI	$(CH_3)_2NCH(SCH_2CH=CH_2)_2$	74(0,8)	1,5302	1,001	—	43	53,48; 53,26	8,51; 8,59	31,47; 31,23	53,13	8,44	31,52
XXII	$(CH_2)_5NCH(SC_2H_5)_2$	101—103 (1)	1,5285	1,023	—	60	55,08; 55,16	9,74; 9,83	29,23; 29,24	54,90	9,56	29,00
XXIII	$O(CH_2CH_2)_2NCH(SC_2H_5)_2$	121—123 (1,6)	1,5299	1,086	—	62	48,79; 48,82	8,53; 8,72	28,59; 28,58	48,82	8,66	28,96
XXIV	$O(CH_2CH_2)_2NCH(SC_3H_7)_2$	134—135,5 (0,6)	1,5202	1,051	—	59	52,68; 52,84	9,16; 9,09	25,52; 25,68	52,90	9,30	25,71
XXV	$(SC_2H_5)_2CHN(CH_2CH_2)_2 \cdot NCH(SC_2H_5)_2$	M. p. 82,5—83,5°	—	—	—	60	47,40; 47,32	8,61; 8,41	35,77; 35,94	47,35	8,54	36,15

*(XVI) was prepared from (X) by transmercaptalization.

this the reactivity of amide mercaptals, like that of amide acetals [12], may be explained by ionization with formation of an (alkylthio)(dialkylamino)carbonium ion.

$$R_2NCH(SR')_2 \rightleftarrows [R_2\overset{+}{N} = CHSR']SR'^{\ominus}$$

The reactions of amide mercaptals were studied in the main for the case of N,N-dimethylformamide diethyl mercaptal (X). We investigated the reactions of amide mercaptals with thiols, alcohols, amines, amides, and compounds with an active methylene group. In amide mercaptals both alkylthio groups are fairly readily replaced when they are heated with higher alkanethiols with formation of new amide mercaptals in good yield. This provides yet another way for the preparation of amide mercaptals:

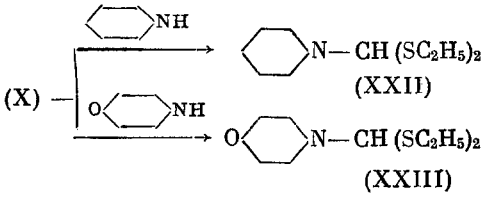
$$(CH_3)_2NCH(SC_2H_5)_2 \xrightarrow{2RSH} (CH_3)_2NCH(SR)_2 + 2C_2H_5SH$$

(X)

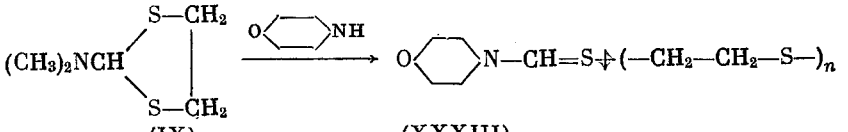
(XV) R=C_6H_{13}-*n*; (XVI) R=C_6H_{13}-*t*;
(XVII) R=C_7H_{15}-*n*

The reaction starts at 100-110° and continues with vigorous liberation of the thiol for 30-40 min. With aromatic thiols reaction takes a more complicated course and is being studied at present.

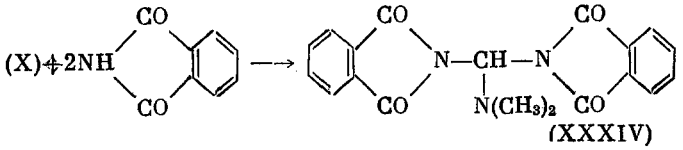
As reported previously [9], compounds containing a primary amino group (amines, amides, sulfonamides, ureas) react with amide mercaptals with elimination of two molecules of thiol and formation of substituted formamidines. When amide mercaptals are heated with secondary amines, such as piperidine or morpholine, it is not the alkylthio groups which are replaced, but the substituted amino group (transamination) with formation of a new amide mercaptal:



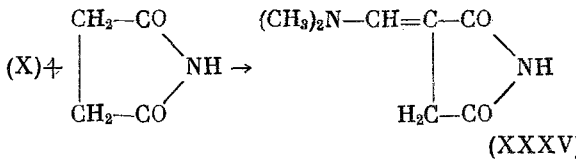
It must be mentioned, however, that the transamination does not go altogether smoothly. It is evident that at high temperatures amide mercaptals undergo cleavage to some extent with formation of a dialkyl sulfide and a thio amide. In the reaction of the amide mercaptal (X) with morpholine it was shown by gas-liquid chromatography that the transamination product contains 4-(thioformyl)morpholine. It is interesting that in an attempt to prepare 4-(1,3-dithiolan-2-yl)morpholine by transamination we were unable to isolate this substance, but obtained only 4-(thioformyl)morpholine (XXXIII):



Tertiary amines do not react with amide mercaptals. Unlike secondary amines, compounds containing a secondary amide (imide) group react with amide mercaptals with elimination, not of a secondary amine, but a thiol. Thus, reaction with phthalimide leads to the separation of two molecules of thiol and the formation of N,N'-[(dimethylamino)methylene]diphthalimide (XXXIV) [13]:



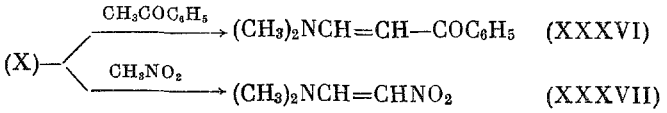
With succinimide reaction goes at the methylene group with formation of the 2-[(dimethylamino)methylene] derivative (XXXV):



(XXXV)

The structure of the latter was confirmed by the infrared spectrum, which contains a diffuse band at about 3150 cm^{-1} characteristic for the stretching vibrations of an associated NH group and also an intense band in the region 1600-1620 cm^{-1} characteristic for a double bond conjugated with a hetero atom and a C=O group, and also for the deformation vibrations of an NH group.

Amide mercaptals readily react with other compounds containing an active methylene group, e. g., acetophenone and nitromethane:



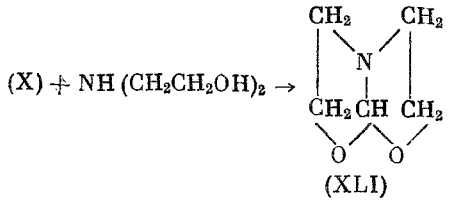
(XXXVI) (XXXVII)

The alkylthio groups in amide mercaptals can also be replaced by alkoxy groups by heating the mercaptals with higher alcohols, and as a result amide acetals are formed:

$$(X) + 2ROH \rightarrow (CH_3)_2NCH(OR)_2$$

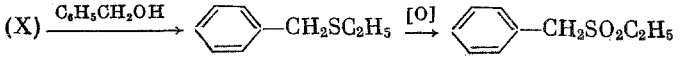
(XXXVIII) R=C_6H_{13}; (XXXIX) R=C_7H_{15}; (XL) R=C_8H_{17}

With 2,2'-iminodiethanol simultaneously two thiol molecules and one molecule of dimethylamine are eliminated with formation of the recently described [14] tetrahydrooxazolo[2,3-b]oxazole (XLI):



(XLI)

However, not in all cases does reaction go in accordance with this scheme. When N,N-dimethylformamide diethyl mercaptal (X) was heated with benzyl alcohol not the amide acetal, but benzyl ethyl sulfide was isolated; it was identified by oxidation to the corresponding sulfone. As yet, this unexpected reaction is difficult to explain.



EXPERIMENTAL

Preparation of Complexes from Disubstituted Amides and Dimethyl Sulfate. A mixture of equimolecular amounts of the amide and dimethyl sulfate was heated at 70-80° for 2-3 h. The complex formed was washed with dry benzene and then dry ether. Residual solvent was removed in a vacuum. The yields and constants of the complexes obtained are listed in Table 1. The complexes (III), (IV), and (VIII) have not been described previously.

General Method for the Preparation of the Formamide Mercaptals (IX)-(XXV). a) 0.1 mole of the complex formed by the substituted formamide with dimethyl sulfate was added with stirring and cooling to −10° to 0.1 mole of dry sodium alkyl sulfide in 100 ml of hexane. The reaction mixture was stirred at this temperature for 2 h, then 0.1 mole of the thiol was added, and the mixture was stirred for 2 h and then left overnight. The hexane layer was decanted from the precipitate, solvent was removed, and the residue was distilled.

b) 1 mole of triethylamine was added with stirring to a mixture of 1 mole of the complex and 2 moles of the thiol cooled to −10°. The mixture was stirred for 2 h at this temperature and then left overnight. The upper layer was separated and distilled. The constants, yields, and analyses of the amide mercaptals are given in Table 2.

Reaction of the Complex (I) with One Molecular Proportion of Thiol. A solution of sodium ethyl sulfide prepared from 15.6 g of ethanethiol and 5.7 g of sodium in absolute methanol was added to a mixture of 49.8 g of the

complex (I) and 100 ml of hexane with stirring and cooling to −10°. After 3 h the hexane layer was separated, and after removal of solvent the residue was vacuum-distilled. After several distillations we isolated 5.3 g (24%) of the amide mercaptal (X) and 4 g (27%) of N,N-dimethylformamide dimethyl acetal (XXVII), b. p. 101.5-103.5°; n_D^{20} 1.3993. The literature [15] gives: b. p. 101-102°; n_D^{25} 1.3957.

1 g of the acetal (XXVII) was heated with 0.7 g of p-aminobenzenesulfonamide to 110° with simultaneous removal of the methano liberated by distillation. By crystallization of the residue from alcohol we obtained 0.4 g (30%) of N'-(p-aminophenylsulfonyl)-N,N-dimethylformamidine (XXIX), m. p. 168.5-170°. Found: C 47.45; 47.65; H 5.46; 5.43; S 14.28; 14.28%. $C_9H_{13}N_3O_2S$. Calculated: C 47.70; H 5.78; S 14.10%.

Reaction of the Complex (I) with Benzenethiol. From 13 g of the complex (I) and 7.2 g of benzenethiol by method (b) we obtained 3.6 g (45%) of methyl phenyl sulfide (XXXI), b. p. 88-91° (60 mm). The sulfide (XXXI) was oxidized with 30% hydrogen peroxide in glacial acetic acid to methyl phenyl sulfone, m. p. 86-88° (from CCl_4). A mixture with a known sample [16] melted at the same temperature.

Reaction of the Complex (I) with 2-Thiophenethiol. By the same method from 18.4 g of the complex (I) and 20 g of 2-thiophenethiol we obtained 5 g (45%) of methyl 2-thienyl sulfide (XXXII). The melting point of the methyl 2-thienyl sulfone prepared by the oxidation of (XXXII) was 45-46.5°. A mixture with a known sample [17] had m.p. 46-47°.

N,N-Dimethylformamide Dihexyl Mercaptal (XV). A mixture of 7.2 g of (X) and 9.4 g of 1-hexanethiol was heated above 110°, and the ethane thiol formed in the reaction was distilled off. By vacuum distillation of the residue we obtained 9.0 g (78%) of the amide mercaptal (XV).

N,N-Dimethylformamide Di-t-hexyl Mercaptal (XVI). From 7.2 g of (X) and 9.4 g of t-hexyl mercaptan we obtained 6.7 g (60%) of (XVI).

N,N-Dimethylformamide Diheptyl Mercaptal (XVII). In an analogous way, from 7.2 g of (X) and 10.6 g of 1-heptanethiol we obtained 10.0 g (78%) of the amide mercaptal (XVII).

1-Formylpiperidine Diethyl Mercaptal (XXII). 7.2 g of the mercaptal (X) was refluxed with 3.4 g of piperidine for 2 h. On distillation we obtained 4.5 g (51%) of 1-formylpiperidine diethyl mercaptal (XXII).

4-Formylmorpholine Diethyl Mercaptal (XXIII).* This was prepared analogously in 40% yield from 7.2 g of (X) and 3.5 g of morpholine.

4-(Thioformyl)morpholine (XXXIII). 6.0 g of N,N-dimethyl-1,3-dithiolan-2-amine (IX) was heated with 8.7 g of morpholine for 3 h at 150-160°. In the distillation of the mixture we isolated a fraction of b. p. 106-110° (0.4 mm), which crystallized when cooled; yield 50%; m. p. 67.5-69° (from petroleum ether). The literature [18] gives m. p. 68.5°. Found: C 45.54; 45.37; H 6.62; 6.67; S 24.21; 24.41%. C_5H_9NOS. Calculated: C 45.72; H 6.93; S 24.41%.

N,N'-[(Dimethylamino)methylene]diphthalimide (XXXIV). Heating of a mixture of 3.6 g of (X) and 5.9 g of phthalimide to 170° with simultaneous removal of ethanethiol by distillation gave 4 g (57%) of (XXXIV), m. p. 201-203.5° (in a sealed capillary; from N,N-dimethylformamide). The literature [13] gives m. p. 197°. Found: C 64.87; 65.02; H 4.31; 4.44; N 12.24; 12.18%; M (ebullioscopically) 346.7. $C_{19}H_{15}N_3O_4$. Calculated: C 65.30; H 4.30; N 12.31%; M 349.6.

2-[(Dimethylamino)methylene]succinimide (XXXV). By the method described above, from 1.8 g of (X) and 1.0 g of succinimide we obtained 0.8 g (50%) of (XXXV), m. p. 229-231° (from alcohol). Found: C 54.53; 54.32; H 6.60; 6.45; N 18.26; 18.12%. $C_7H_{10}N_2O_2$. Calculated: C 54.60; H 6.54; N 18.20%.

2-[(Dimethylamino)methylene]acetophenone (XXXVI). By heating 3.5 g of (X) with 2.3 g of acetophenone for 2 h at 70-80° we obtained 2.2 g (72%) of (XXXVI), m. p. 90-90.5° (from ether). The literature [12] gives m.p. 90°.

N,N-Dimethyl-2-nitrovinylamine (XXXVII). In a similar way, from 7.0 g of (X) and 2.4 g of nitromethane we obtained 3.5 g (77%) of (XXXVII), m. p. 103-104° (from alcohol). The literature [12] gives m. p. 104°.

N,N-Dimethylformamide Dihexyl Acetal (XXXVIII). A mixture of 6.6 g of (X) and 10 g of hexyl alcohol was heated for 3 h at 110-115° with simultaneous distillation of ethanethiol. Excess of the alcohol was driven off, and

*(XXII) and (XXIII) prepared in this way contain some admixture of the corresponding thioformamides $C_5H_{10}NCHS$ and C_4H_8ONCHS which cannot be removed by distillation; this was shown by gas-liquid chromatography.

distillation of the mixture gave 5.7 g (60%) of (XXXVIII), b. p. 107.5-108° (1.5 mm); n_D^{20} 1.4308. Found: C 69.32; 69.05; H 12.71; 12.72%. $C_{15}H_{33}NO_2$. Calculated: C 69.42; H 12.80%.

N,N-Dimethylformamide Diheptyl Acetal (XXXIX). In a similar way, from 7.2 g of (X) and 9.4 g of heptyl alcohol we obtained 8 g (70%) of (XXXIX), b. p. 125° (0.6-0.8 mm); n_D^{20} 1.4348. Found: C 70.94; 71.11; H 12.68; 12.93%. $C_{17}H_{37}NO_2$. Calculated: C 71.06; H 12.99%.

N,N-Dimethylformamide Dicyclohexyl Acetal (XL). In a similar way, from 7.2 g of (X) and 8 g of cyclohexanol we obtained 3.4 g (33%) of (XL), b. p. 114-115° (1.5 mm); n_D^{20} 1.4685. The literature [14] gives: b. p. 76-77° (0.25 mm); n_D^{20} 1.4685. Found: C 69.82; 70.16; H 11.25; 11.46%. $C_{15}H_{29}NO_2$. Calculated: C 70.52; H 11.46%.

Tetrahydrooxazolo[2,3-b]oxazole (XLI). By refluxing 7.2 g of (X) with 4.2 g of 2,2'-iminodiethanol for 2 h we obtained 2.3 g (50%) of (XLI), b. p. 82-83° (21 mm); n_D^{20} 1.4670. The literature [14] gives: b.p. 65-66° (5 mm); n_D^{20} 1.4673. Found: C 52.01; 51.97; H 7.95; 8.04%. Calculated: C 52.16; H 7.88%.

Reaction of the Amide Mercaptal (X) with Benzyl Alcohol. By heating a mixture of 8.4 g of (X) with 13.4 g of benzyl alcohol for 1 h at 130-140° with simultaneous distillation of ethanethiol and then distilling the residue we obtained 6.0 g (85%) of benzyl ethyl sulfide, b. p. 89-90°(12 mm); n_D^{20} 1.5450. The literature [19] gives: b. p. 220-223°. Benzyl ethyl sulfide was identified by oxidation with hydrogen peroxide in glacial acetic acid into benzyl ethyl sulfone, m. p. 82.5-84° (from water). The literature [20] gives m. p. 84°. Found: C 58.58; 58.40; H 6.63; 6.54; S 17.29; 17.47%. $C_9H_{12}O_2S$. Calculated: C 58.68; H 6.57; S 17.40%.

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SUMMARY

1. A new method was developed for the synthesis of formamide mercaptals by the reaction of thiols with the dimethyl sulfate complexes of amides in presence of an alkaline agent.

2. A study was made of some reactions of amide mercaptals with thiols, alcohols, secondary amines, amides, and other compounds containing mobile hydrogen.

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