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Studies of Thioacids and Their Derivatives

XV. (Alkoxythiocarbonyl)hydrazines and [(Alkylthio)thiocarbonyl]hydrazines

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In connection with our studies of alkyl cyanates, thiosemicarbazides, tetrazines, and other compounds a great number of new (alkoxythiocarbonyl)hydrazines and [(alkylthio)thiocarbonyl]hydrazines have been prepared and the scope of the various methods have been investigated. [(Alkoxythiocarbonyl)thio]acetic acids react with monoalkylhydrazines with a secondary or tertiary alkyl group to form hydrazides of the type RO–CS–NH–NHR′. Monoalkylhydrazines with a primary alkyl group generally give a mixture of the two isomers, RO–CS–NH–NHR′ and RO–CS–NR′–NH_2 with exclusive or predominating formation of the latter when R′ is a small alkyl group. The product formed by the reaction of monoalkylhydrazines with carbon disulfide and potassium hydroxide, after alkylation gives dithiocarbazates of the type RS–CS–NR′–NH_2 even when R′ is a secondary alkyl group. However, *tert*-butylhydrazine gives only the isomer RO–CS–NH–$NHBu^t$.

Special methods were elaborated to prepare isomers which could not be prepared directly, such as RO–CS–NH–$NHCH_3$ and RS–CS–$N(C_6H_5)$–NH_2. Some compounds which could not be obtained by the above mentioned methods were prepared from acid chlorides of the types RO–CS–Cl and RS–CS–Cl or from *O,S*-dialkyl dithiocarbonates or dialkyl trithiocarbonates.

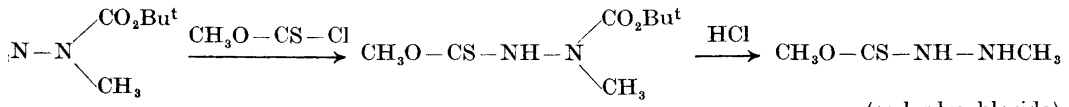
Only a few alkoxythiocarbonylhydrazines or "xanthogenhydrazides" have hitherto been known. Jensen [1] prepared "ethylxanthogenhydrazide" (ethoxythiocarbonylhydrazine), C_2H_5O–CS–NH–NH_2, and Wangel [2] prepared the corresponding benzyl derivative and several derivatives of ethoxy- and benzyloxythiocarbonylhydrazine. In connection with our studies of thiocarboxylic hydrazides [3,4] and thiosemicarbazides [5,6] a great number of new alkoxythiocarbonylhydrazines have been prepared. Some of these have also served as starting materials for the preparation of alkyl cyanates *via* 5-alkoxy-1,2,3,4-thiatriazoles.[7–10]

The alkoxythiocarbonylhydrazines were, in most cases, prepared from an [(alkoxythiocarbonyl)thio]acetic acid or "xanthogenacetic acid", RO—CS—SCH_2COOH, and hydrazine or an alkylhydrazine. In contrast to the thiocarbamates and dithiocarbamates these dithiocarbonates react rapidly with most hydrazines in the same way as carboxymethyl dithioates [4] and the steric influence is similar. Thus, methylhydrazine yielded 1-(alkoxythiocarbonyl)-1-methylhydrazines, RO—CS—$N(CH_3)$—NH_2, and alkylhydrazines with a larger primary alkyl group yielded a mixture of a 1-alkyl-1-alkoxy- and a 1-alkyl-2-alkoxythiocarbonylhydrazine, whereas alkylhydrazines with a secondary or tertiary alkyl group yielded exclusively a 1-alkyl-2-alkoxythiocarbonylhydrazine. The phenylhydrazide obtained from phenylhydrazine and *O*-ethyldithiocarbonates [2,11] has, as expected, the constitution C_2H_5O—CS—NH—NHC_6H_5. 1,2-Dimethylhydrazine and 1,1-dimethylhydrazine reacted without difficulty to give the corresponding alkoxythiocarbonylhydrazines, but no reaction occurred with 1,2-diisopropylhydrazine to give the anticipated hydrazide with a secondary alkyl group in the N^1 position.

Trimethylhydrazine and 1,1-diethylhydrazine reacted very slowly with [(alkoxythiocarbonyl)thio]acetic acids, but methoxythiocarbonyl derivatives of these hydrazines could be prepared from *O*-methyl chlorothioformate, CH_3O—CS—Cl. Similarly, phenoxythiocarbonylhydrazines could be prepared from *O*-phenyl chlorothioformate, C_6H_5O—CS—Cl. The route *via* an *S*-carboxymethyl ester could not be used in this case because all attempts to prepare [(phenoxythiocarbonyl)thio]acetic acid were unsuccessful. 1,2-Diisopropylhydrazine also reacted with CH_3O—CS—Cl to give the corresponding methoxythiocarbonylhydrazine, so this method can probably be used in all cases where the route *via* the *S*-carboxymethyl ester cannot be used.

O-Alkyl-*S*-methyl dithiocarbonates, RO—CS—SCH_3, react in the same way as the *S*-carboxymethyl esters and *tert*-butoxythiocarbonylhydrazine, Bu^tO—CS—NH—NH_2, was prepared in this way. The route *via* the *S*-carboxymethyl ester could not be used, because attempts to prepare Bu^tO—CS—SCH_2COOH were unsuccessful.

Whereas, as mentioned above, the alkyl- or aralkyl-2-alkoxythiocarbonylhydrazines can usually be prepared in one reaction from higher alkylhydrazines and aralkylhydrazines, lower alkylhydrazines and arylhydrazines give only one of the possible isomers, namely the 1,1- and 1,2-isomer, respectively. Special methods are therefore needed to prepare the other isomers. 1-Methoxythiocarbonyl-2-methylhydrazine was obtained in the following manner:



(as hydrochloride)

Attempts to prepare 1-methoxythiocarbonyl-1-phenylhydrazine were unsuccessful. Benzaldehyde phenylhydrazone reacted with *O*,*S*-dimethyl dithiocarbonate to give a product which had the anticipated composition. However, its infrared spectrum exhibited a strong C=O band so it must be concluded

Table 1. Alkoxythiocarbonylhydrazines (*O*-alkyl monothiocarbazates), $RO-CS-NR^1-NR^2R^3$ (or their hydrochlorides).

R	R^1	R^2	R^3	Yield, % *	Formula	M.p., °C		Analyses C	H	N	Cl	S
Me	H	H	H	40[a]	$C_2H_6N_2OS$	77–78	Found:	22.65	5.68	26.56		
							Calc.:	22.64	5.70	26.41		
Me	Me	H	H	74[b]	$C_3H_8N_2OS \cdot HCl$	143–145	Found:	23.00	5.58	18.14	22.64	
							Calc.:	23.01	5.80	17.89	22.64	
Me	H	H	Me	56[c]	$C_3H_8N_2OS \cdot HCl$	126–128	Found:	22.46	5.85	18.24		
							Calc.:	23.01	5.80	17.89		
Me	Me	H	Me	82[b]	$C_4H_{10}N_2OS \cdot HCl$	146–148	Found:	28.00	6.82		21.18	
							Calc.:	28.16	6.50		20.80	
Me	H	Me	Me	40[a]	$C_4H_{10}N_2OS$	105–106	Found:	36.05	7.40	21.00		
							Calc.:	35.81	7.51	20.89		
Me	Me	Me	Me	40[i]	$C_5H_{12}N_2OS$	47–49	Found:	36.45	7.29	17.05		
							Calc.:	36.59	7.32	17.07		
Me	H	Et	Et	20	$C_6H_{14}N_2OS \cdot HCl$	145–147	Found:	36.42	7.83	13.82		
							Calc.:	36.26	7.62	14.11		
Me	H	H	Pr^i	60[d]	$C_5H_{12}N_2OS \cdot HCl$	141–142	Found:	32.30	7.22	15.49	19.24	
							Calc.:	32.54	7.19	15.18	19.20	
Me	Pr^i	H	Pr^i	15[e]	$C_8H_{18}N_2OS \cdot HCl$	74–79	Found:				15.53	
							Calc.:				15.68	
Me	H	H	Bu^t	87[i]	$C_6H_{14}N_2OS$	60–61	Found:	44.25	8.96	17.38		
							Calc.:	44.40	8.70	17.27		
Me	$PhCH_2$	H	H	30[d]	$C_9H_{12}N_2OS \cdot HCl$	144–145	Found:	46.50	5.54		15.25	
							Calc.:	46.44	5.64		15.23	

Table 1. Continued.

Me	H	H	$PhCH_2$	43 [d]	$C_9H_{12}N_2OS \cdot HCl$	150–151	Found:	46.70	6.04	12.12	15.40
							Calc.:	46.44	5.64	12.05	15.23
Me	H	H	Cyclohexyl	85 [d]	$C_8H_{16}N_2OS \cdot HCl$	141–142	Found:	42.75	7.66	12.32	15.94
							Calc.:	42.74	7.64	12.46	15.77
Me	H	$-CH_2(CH_2)_3CH_2-$		60 [i]	$C_7H_{14}N_2OS$	105–107	Found:	48.22	8.04	16.02	
							Calc.:	48.25	8.04	16.10	
Me	H	H	Ph	40 [c]	$C_8H_{10}N_2OS$	112–113	Found:	52.50	5.59	15.32	
							Calc.:	52.75	5.49	15.38	
Et [1,2]	H	H	H	80 [e]	$C_3H_8N_2OS \cdot HCl$	142–143	Found:	22.92	5.76		22.68
							Calc.:	23.01	5.80		22.64
Et	Me	H	H	64 [d]	$C_4H_{10}N_2OS \cdot HCl$	134–135	Found:	28.15	6.54	16.81	21.01
							Calc.:	28.16	6.50	16.41	20.80
Et	H	H	Me	20 [e]	$C_4H_{10}N_2OS \cdot HCl$	132–133	Found:	27.68	6.45	16.58	
							Calc.:	28.16	6.50	16.41	
Et	Me	H	Me	40 [b]	$C_5H_{12}N_2OS \cdot HCl$	134–135	Found:	32.35	6.90	15.28	
							Calc.:	32.54	7.09	15.18	
Et	H	Me	Me	55 [a]	$C_5H_{12}N_2OS$	82– 83	Found:	40.60	8.06	18.80	
							Calc.:	40.53	8.16	18.91	
Pr	H	H	H	90 [e]	$C_4H_{10}N_2OS \cdot HCl$	122–124	Found:	28.20	6.82		20.75
							Calc.:	28.16	6.50		20.80
Pr	Me	H	H	70 [d]	$C_5H_{12}N_2OS \cdot HCl$	95– 97	Found:	32.72	7.02		19.17
							Calc.:	32.54	7.09		19.20
Pr^i	H	H	H	87 [d]	$C_5H_{10}N_2OS \cdot HCl$	119–121	Found:	27.98	6.50		
							Calc.:	28.16	6.50		

Table 1. Continued.

Pr^i	Me	H	H	88 [d]	$C_5H_{12}N_2OS \cdot HCl$	111–113	Found:	32.70	6.95		19.00	
							Calc.:	32.54	7.09		19.20	
Bu	H	H	H	90 [d]	$C_5H_{12}N_2OS \cdot HCl$	120–122	Found:	32.30	7.10	15.50		
							Calc.:	32.54	7.09	15.18		
Bu	Me	H	H	71 [b]	$C_6H_{14}N_2OS \cdot HCl$	90– 91	Found:	36.30	7.84		18.04	
							Calc.:	36.26	7.62		17.84	
Bu^i	H	H	H	85 [c]	$C_5H_{12}N_2OS$	30– 31	Found:	40.30	7.92	19.06		
							Calc.:	40.53	8.16	18.91		
Bu^i	Me	H	H	66 [d]	$C_6H_{14}N_2OS \cdot HCl$	106–108	Found:	36.35	7.62		17.51	
							Calc.:	36.26	7.62		17.84	
Bu^s	H	H	H	85 [d]	$C_5H_{12}N_2OS \cdot HCl$	90– 92	Found:	32.60	6.82	15.37		
							Calc.:	32.54	7.09	15.18		
Bu^t	H	H	H	77 [i]	$C_5H_{12}N_2OS$	49– 50	Found:	40.83	8.23	18.75		21.60
							Calc.:	40.53	8.16	18.91		21.36
Pentyl	H	H	H	95 [f]	$C_6H_{14}N_2OS \cdot HCl$	115–116	Found:	35.99	7.65	13.82		
							Calc.:	36.26	7.61	14.10		
Neopentyl	H	H	H	84 [f]	$C_6H_{14}N_2OS \cdot HCl$	149–150	Found:	35.50	7.52			
							Calc.:	36.26	7.61			
Hexyl	H	H	H	83 [f]	$C_7H_{16}N_2OS \cdot HCl$	142–143	Found:	39.81	8.04	13.57		
							Calc.:	39.70	8.10	13.23		
1,2,2-Trimethylpropyl	Me	H	H	83 [d]	$C_8H_{18}N_2OS \cdot HCl$	161–162	Found:	41.70	8.49		15.17	
							Calc.:	42.36	8.46		15.63	
Heptyl	H	H	H	90 [f]	$C_8H_{18}N_2OS \cdot HCl$	133–134	Found:	42.25	8.31	12.57		13.90
							Calc.:	42.36	8.46	12.37		14.14

Table 1. Continued.

Cyclohexyl [a]	H	H	H	85	$C_7H_{14}N_2OS$	74 – 75	Found:	48.04	8.12	16.22		
							Calc.:	48.24	8.10	16.10		
Benzyl [a]	H	H	H	82 [c]	$C_8H_{10}N_2OS \cdot HCl$	60 – 61	Found:	52.75	5.32	15.52		
							Calc.:	52.72	5.53	15.39		
Benzyl	Me	H	H	78 [d]	$C_9H_{12}N_2OS \cdot HCl$	73 – 75	Found:	46.03	5.96		15.16	
							Calc.:	46.44	5.64		15.23	
o-Nitrobenzyl	Me	H	H	80 [h]	$C_9H_{11}N_3O_3S$	94 – 95	Found:	44.81	4.56	17.43		13.28
							Calc.:	44.30	4.68	17.05		13.28
α-Methylbenzyl	H	H	H	55 [i]	$C_9H_{12}N_2OS$	93 – 94	Found:	55.35	6.21	14.32		16.30
							Calc.:	55.09	6.17	14.28		16.30
Phenethyl	H	H	H	96 [i]	$C_9H_{12}N_2OS$	47 – 48	Found:	55.20	6.24	14.30		16.18
							Calc.:	55.09	6.17	14.28		16.30
Ph	H	H	H	30 [g]	$C_7H_8N_2OS$	121 – 122	Found:	50.45	4.62	16.44		
							Calc.:	50.00	4.80	16.66		
Ph	Me	H	H	76 [h]	$C_8H_{10}N_2OS \cdot HCl$	128 – 129	Found:	43.62	5.33		15.94	
							Calc.:	43.92	5.07		16.20	
Ph	H	Me	Me	75 [b]	$C_9H_{12}N_2OS$	109 – 110	Found:	54.70	6.16	14.18		
							Calc.:	55.09	6.17	14.28		
Ph	H	H	Ph	10 [h]	$C_{13}H_{12}N_2OS$	75 – 76	Found:	64.00	5.09	11.55		
							Calc.:	63.92	4.95	11.47		
Ph	Ph	H	Ph	66 [h]	$C_{19}H_{16}N_2OS$	158 – 159	Found:	71.30	5.02	8.75		
							Calc.:	71.24	5.03	8.75		

* The yields of the *N*-unsubstituted compounds are mean values from several preparations.

Solvents used for recrystallization: [a] diethyl ether; [b] diethyl ether-ethanol; [c] diethyl ether-petroleum ether; [d] ethyl acetate; [e] ethanol-ethyl acetate; [f] dichloromethane; [g] methanol-water; [h] ethanol-water; [i] pentane; [j] yield of crude product; a small portion was recrystallized from hexane (slightly soluble).

that the *O*-methyl derivative had been rearranged to the isomeric *S*-methyl derivative during the reaction.

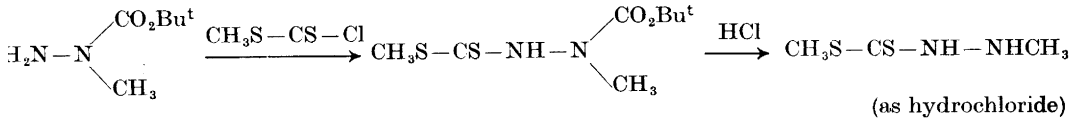
Most of the hydrazides prepared are liquid at room temperature and were isolated as hydrochlorides (see Table 1). They resemble the thiocarboxylic hydrazides [3,4] and differ from the thiosemicarbazides in having a definite basic character and being acids when they contain an NH group. Thus the compounds of the types RO—CS—NHNHR′ and RO—CS—NHNR′$_2$ are soluble in aqueous sodium hydroxide whereas compounds of the type RO—CS—NR′—NH$_2$ are insoluble.

Like the thiocarboxylic hydrazides the alkoxythiocarbonylhydrazines are rather unstable and easily form dihydrotetrazines, thiadiazoles, and other compounds. The free hydrazides usually attain a red colour in contact with air because of the formation of a small amount of a tetrazine.[12] The formation of 5-alkoxy-1,2,3,4-thiatriazoles from alkoxythiocarbonylhydrazines has been described recently,[7–10] other work on the chemistry of these compounds is in progress.

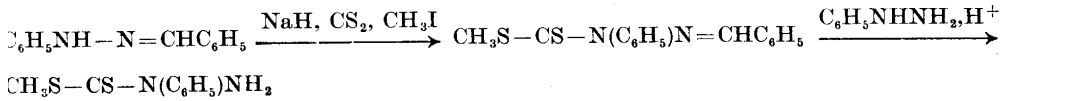
(Alkylthio)thiocarbonylhydrazines or alkyl dithiocarbazates, RS—CS—NH—NH$_2$ (and *N*-alkyl derivatives), cannot, as a rule, be prepared in a similar manner as the alkoxythiocarbonylhydrazines because {[(alkylthio)-thiocarbonyl]thio}acetic acids, RS—CS—SCH$_2$COOH, are more reactive than the alkoxy derivatives. Weakly basic hydrazines such as phenylhydrazine will attack mainly the —SCH$_2$COOH group but alkylhydrazines will usually split off also the RS group. However, Bu^{t}S—CS—SCH$_2$COOH reacted with hydrazines to give *tert*-butyl dithiocarbazates in slight yields. This is in so far of interest as these compounds could not be obtained by the reaction of alkali metal dithiocarbazates with *tert*-butyl bromide or iodide. Alkyl and aryl dithiocarbazates can conveniently be prepared from trithiocarbonates of the type (RS)$_2$CS and one mole of hydrazine or an alkyl hydrazine. Thus, methylhydrazine gives CH$_3$S—CS—N(CH$_3$)NH$_2$ and C$_2$H$_5$S—CS—N(NH$_3$)NH$_2$ with dimethyl trithiocarbonate and diethyl trithiocarbonate, respectively. From diphenyl trithiocarbonate and hydrazine El-Hewehi *et al.*[13] have obtained [(phenylthio)thiocarbonyl]hydrazine, C$_6$H$_5$S—CS—NHNH$_2$. In attempts to prepare this compound from phenyl chlorothioformate and hydrazine we instead obtained 2,5-di(phenylthio)-1,3,4-thiadiazole, formed by diacylation of the hydrazine.

Forsgren and Sandström [14] found that benzylhydrazine reacted with dimethyl trithiocarbonate to form the two isomeric benzyl[(methylthio)thiocarbonyl]hydrazines and from our experiences with the corresponding alkoxy compounds this can be expected to apply generally to higher alkyl hydrazines. In contrast hereto the reaction of a monoalkyl hydrazine with carbon disulfide followed by alkylation of the dithiocarbazate thus formed has been found to generally yield exclusively dithiocarbazates of the type RS—CS—NR′—NH$_2$. The only apparent exception was *tert*-butylhydrazine, which formed the 1,2-derivative, thus behaving as an arylhydrazine. By thin-layer chromatography it was ascertained that only one of the isomers is formed in these reactions. As alkylating reagent methyl iodide was used in most cases but both primary and secondary alkyl halides seem generally to react smoothly; *tert*-butyl halides, on the contrary, were unreactive (see above).

Since, by the above mentioned methods, methylhydrazine gives only the 1,1-derivative, and phenylhydrazine only the 1,2-derivative, special methods are required to prepare the isomers. They were obtained in the following manner:



and:



Attempts were made to prepare $CH_3S-CS-NH-NHCH_3$ by the reaction of the lithium salt of methylhydrazine (because this would be expected to contain the anion CH_3NH-NH^-) with carbon disulfide and methyl iodide, but one mole of methylhydrazine reacted under these conditions with two moles of carbon disulfide, eliminating hydrogen sulfide with the formation of 3-methyl-5-methylthio-1,3,4-thiadiazolin-2-thion, m.p. 88°C (prepared in another way by Busch and Ziegele [15]).

In contrast to the (alkoxythiocarbonyl)hydrazines the corresponding [(alkylthio)thiocarbonyl]hydrazines were, in all cases, crystalline at room temperature (see Table 2).

The reaction of alkylhydrazines with carbonyl sulfide or carbon diselenide will be described in subsequent papers.

EXPERIMENTAL

[(Alkoxythiocarbonyl)thio]acetic acids, RO–CS–SCH$_2$COOH

Although the xanthates of higher aliphatic alcohols are wellknown, the properties of their reaction products with chloroacetic acid have been described only in a few cases. The derivatives of propyl and butyl alcohols have been mentioned as plant growth substances [16] but no details of preparation and physical data were given, and also the *tert*-butyl derivative was mentioned. However, according to our experiences (see below) this compound cannot be prepared. The other isomers could be prepared without difficulties according to the detailed directions given for the preparation of the ethyl derivative.[17,18] The crude products were obtained in almost quantitative yields (calculated on the xanthates). However, it is not easy to obtain the acids in a pure state, and also for the well-known methyl and ethyl derivatives there are some discrepancies in the literature concerning their melting points. The compounds are best recrystallized from petroleum ether. Analytically pure samples were obtained by dissolving the acid in boiling hexane, cooling to *ca.* 10°C until 5–10 % of the dissolved acid had separated, usually as an oil (which contains the impurities), decanting the solution and cooling it for several hours at −30°C. Melting points and analyses are listed in Table 3. The *sec*-butyl derivative could not be obtained crystalline at room temperature, but the oil, purified in the same manner as the crystalline compounds, yielded after drying *in vacuo* correct analytical values. Also the 1,2,2-trimethylpropyl and the heptyl derivative were only obtained as oils; they were used without further purification for the preparation of the hydrazides.

Table 2. [(Alkylthio)thiocarbonyl]hydrazines (dithiocarbazates), $RS-CS-NR^1-NR^2R^3$.

R	R^1	R^2	R^3	Formula	Method	Yield, %	M.p., °C	Analyses (C, H, N, S)			
Me	Me	H	H	$C_3H_8N_2S_2$	A [g]	70 [a]	93 – 94				
Me	Me	=C(Me)(Ph)		$C_{11}H_{14}N_2S_2$		53 [b]	76 – 77	Found:	55.35;	6.06;	11.91
								Calc.:	55.45;	5.92;	11.76
Me	H	H	Me	$C_3H_8N_2S_2 \cdot HCl$	C	31 [c]	140 – 141 [h]	Found:	21.13;	5.19;	16.10
								Calc.:	20.85;	5.22;	16.23
Me	H	Me	Me	$C_4H_{10}N_2S_2$	B [h]	70 [a]	96 – 97				
Me	Me	Me	Me	$C_5H_{12}N_2S_2$	A	40 [d]	48 – 49	Found:	36.45;	7.29;	17.05
								Calc.:	36.59;	7.32;	17.07
Me	Pr^i	H	H	$C_5H_{12}N_2S_2$	A	70 [e]	75 – 76	Found:	36.80;	7.42;	17.13
								Calc.:	36.59;	7.32;	17.07
Me	Pr^i	=CHPh		$C_{12}H_{16}N_2S_2$		90	71 – 72	Found:	57.13;	6.39	
								Calc.:	57.25;	6.59	
Me	H	H	Bu^t	$C_6H_{14}N_2S_2$	A	20 [e]	127 – 128	Found:	40.65;	7.69;	15.83
								Calc.:	40.44;	7.92;	15.72
Me	Cyclohexyl	H	H	$C_8H_{16}N_2S_2$	A	50 [e]	68 – 69	Found:	46.80;	7.64;	13.90
								Calc.:	47.05;	7.85;	13.72
Me	Cyclohexyl	=CHPh		$C_{15}H_{20}N_2S_2$		94	105 – 106	Found:	61.50;	6.90	
								Calc.:	61.63;	6.90	
Me	$PhCH_2$	H	H	$C_9H_{12}N_2S_2$	A [i]	90 [a]	91 – 92	Found:	50.80;	5.70;	13.07
								Calc.:	50.94;	5.70;	13.20
Me	$PhCH_2$	=CHPh		$C_{16}H_{16}N_2S_2$		95 [e]	132 – 133	Found:	63.90;	5.70	
								Calc.:	63.99;	5.37	
Me	$PhCH_2CH_2$	H	H	$C_{10}H_{14}N_2S_2$	A	90 [e]	84 – 84.5	Found:	53.30;	6.51;	12.08
								Calc.:	53.09;	6.24;	12.38

Table 2. Continued.

Me	$PhCH_2CH_2$	=CHPh		$C_{17}H_{18}N_2S_2$		90	115–116	Found:	64.70;	6.00		
								Calc.:	64.95;	5.77		
Me	Ph	H	H	$C_8H_{10}N_2S_2$	A	40 [f]	72– 74	Found:	48.52;	4.95;	14.24	
								Calc.:	48.48;	5.09;	14.14	
Me	Ph	=CHPh		$C_{15}H_{14}N_2S_2$	A	67 [b]	99–100	Found:	63.01;	5.18;	9.96	
								Calc.:	62.93;	4.93;	9.79	
Me	Me	H	Ph	$C_9H_{12}N_2S_2$	A	50 [f]	124–125	Found:	50.81;	5.76;	13.14	
								Calc.:	50.90;	5.70;	13.20	
Et	H	H	H	$C_3H_8N_2S_2$	B [j]	60 [f]	44– 45	Found:	26.29;	5.89;	20.52	
								Calc.:	26.47;	5.70;	20.58	
Et	Me	H	H	$C_4H_{10}N_2S_2$	B	55 [f]	42– 43	Found:	31.83;	6.78;	18.61	
								Calc.:	32.00;	6.71;	18.66	
Et	H	Me	Me	$C_5H_{12}N_2S_2$	B	40 [f]	62– 63	Found:	36.51;	7.19;	17.17	
								Calc.:	36.58;	7.37;	17.07	
Bu^t	Me	H	H	$C_6H_{14}N_2S_2$	B	14 [f]	55– 56	Found:	41.00;	8.04;	15.52;	35.30
								Calc.:	40.44;	7.92;	15.72;	35.92
Bu^t	H	Me	Me	$C_7H_{16}N_2S_2$	B	16 [f]	139–140	Found:	43.65;	8.44;	14.44;	33.20
								Calc.:	43.74;	8.39;	14.58;	33.30
Ph	Ph	H	Ph	$C_{19}H_{16}N_2S_2$	C	60 [b]	177–178	Found:	67.43;	4.95;	8.50	
								Calc.:	67.85;	4.80;	8.33	
$PhCH_2$	Me	H	H	$C_9H_{12}N_2S_2$	A	60 [e]	108–109	Found:	50.80;	5.75;	13.33	
								Calc.:	50.90;	5.70;	13.20;	30.20
p-$NO_2C_6H_4CH_2$	Me	H	H	$C_9H_{11}N_3O_2S_2$	A	80 [e]	149–150	Found:	42.24;	4.54		
								Calc.:	42.03;	4.31		

Solvents used for recrystallization: [a] benzene-petroleum ether; [b] ethanol; [c] ethanol-ethyl acetate; [d] pentane; [e] cyclohexane; [f] petroleum ether.

Melting points according to the literature: [g] 93–94 (method B [29]); [h] 97 (method A [38]); [i] 91–92 (method B,[14] together with the isomer); [j] 39–40;[28] [k] Melting point of the free base 42–43.

Table 3. [(Alkoxythiocarbonyl)thio]acetic acids, $RO-CS-SCH_2COOH$.

R	M.p., °C	Formula	Analyses (C, H, S)		
Methyl	47– 48 [a]	$C_4H_6O_3S_2$	Found: 28.92;	3.81	
			Calc.: 28.90;	3.64	
Ethyl	57– 58 [b]	$C_5H_8O_3S_2$	Found: 33.42;	4.57	
			Calc.: 33.30;	4.47	
Propyl	45– 46 [c]	$C_6H_{10}O_3S_2$	Found: 37.25;	5.20	
			Calc.: 37.10;	5.15	
Isopropyl	46– 47 [d]	$C_6H_{10}O_3S_2$	Found: 36.95;	5.10	
			Calc.: 37.10;	5.15	
Butyl	28– 30	$C_7H_{12}O_3S_2$	Found: 40.00;	5.58	
			Calc.: 40.30;	5.81	
Isobutyl	45– 46	$C_7H_{12}O_3S_2$	Found: 40.28;	5.95	
			Calc.: 40.30;	5.81	
sec-Butyl	liquid	$C_7H_{12}O_3S_2$	Found: 40.50;	5.82	
			Calc.: 40.30;	5.81	
Pentyl	46– 47	$C_8H_{14}O_3S_2$	Found: 43.00;	6.53	
			Calc.: 43.24;	6.35	
Neopentyl	60– 61 [e]	$C_8H_{14}O_3S_2$	Found: 42.70;	6.23	
			Calc.: 43.24;	6.35	
Hexyl	30– 31	$C_9H_{16}O_3S_2$	Found: 45.90;	6.83;	26.94
			Calc.: 45.70;	6.68;	27.10
Cyclohexyl	43– 45 [f]	$C_9H_{14}O_3S_2$	Found: 46.00;	6.12	
			Calc.: 46.10;	6.02	
Nonyl	21– 22	$C_{12}H_{22}O_3S_2$	Found: 52.25;	8.08	
			Calc.: 51.79;	7.97	
Undecyl	40.5–41	$C_{14}H_{26}O_3S_2$	Found: 55.06;	8.60	
			Calc.: 54.89;	8.55	
Benzyl	72– 73 [g]	$C_{10}H_{10}O_3S_2$	Found: 49.60;	4.37	
			Calc.: 49.59;	4.16	
o-Nitrobenzyl	114–115	$C_{10}H_9NO_5S_2$	Found: 41.75;	3.15	
			Calc.: 41.81;	3.14	
α-Methylbenzyl	98– 99	$C_{11}H_{12}O_3S_2$	Found: 51.55;	4.93;	25.03
			Calc.: 51.56;	4.72;	25.00
Phenethyl	56– 57	$C_{11}H_{12}O_3S_2$	Found: 51.25;	4.85;	24.93
			Calc.: 51.56;	4.72;	25.00

Melting points according to literature: [a] 38;[17] [b] 53–54;[17] 57.5–58;[18] [c] 39–42;[34] [d] 40–43;[34] [e] 60–61;[35] [f] 42.5–45 [36] (like the other compounds in this series, this compound is almost colourless, not pale yellow-red, as described in Ref. 36); [g] 71–72.[37]

tert-Butoxythiocarbonylhydrazine and phenoxythiocarbonylhydrazine could not be prepared by the above-mentioned standard method. However, *tert*-butoxythiocarbonylhydrazine was obtained from hydrazine and *O*-*tert*-butyl-*S*-methyldithiocarbonate, $Bu^tO-CS-SMe$, whilst phenoxythiocarbonylhydrazines could be prepared from phenoxythiocarbonyl chloride, PhO−CS−Cl. (PhO−CS−SMe, on the other hand, yielded *S*-methyldithiocarbazate, $MeS-CS-NHNH_2$, in addition to thiocarbonohydrazide, *i.e.* the *O*-phenyl group proved to be more reactive than the *S*-methyl group).

For the preparation of the xanthates the following methods were used:

a) From the alcohol, potassium hydroxide, and carbon disulfide. Except for those cases where the alcohol was a solid at room temperature, or some higher secondary alcohols, this general method could be used. The higher primary alcohols reacted well but a larger excess of alcohol and addition of a small amount of water had to be used.

b) The alcoholate was prepared from metallic potassium and the alcohol in boiling xylene. This method was used to prepare the xanthate derived from 3,3-dimethyl-2-butanol (pinacolyl alcohol).

c) The sodium xanthate was prepared from the alcohol dissolved in diethyl ether, with sodium hydride and carbon disulfide. This method was used to prepare the xanthates derived from neopentyl alcohol, α-methylbenzyl alcohol and phenethyl alcohol. It was also found more convenient and economical for the preparation of pentyl-, hexyl-, heptyl-, cyclohexyl-, nonyl-, undecyl-, and benzyl-xanthates than the potassium hydroxide method which was first used.

d) The xanthate was prepared from the alcohol and potassium hydroxide in dioxan solution. This method was used for the preparation of potassium *o*-nitrobenzylxanthate.

The procedures used in the various cases are illustrated by the following examples:

[(*Pentyloxythiocarbonyl*)*thio*]*acetic acid.* 28 g of potassium hydroxide (0.5 mol) and 1 g of water were dissolved in 150 g of pentanol (1.7 mol) by gentle heating, and after cooling 40 g of carbon disulfide (0.53 mol) was added. The precipitate of the xanthate which separated on standing of the solution for 2 h in a refrigerator was filtered and washed with ether. Yield 67 g (67 %).

The xanthate (0.33 mol) was dissolved in 100 ml of water and the solution added with stirring and cooling to a neutralized solution of chloroacetic acid (32 g) in 100 ml of water. After standing for 24 h the solution was extracted with ether, made strongly acid by addition of 35 ml of conc. hydrochloric acid and again extracted with ether. The latter ether solution was washed with water, dried with sodium sulfate and the ether removed *in vacuo*. The remaining oil crystallized on cooling in dry ice-acetone and was recrystallized from ether-petroleum ether. Yield 83 %.

[(*Neopentyloxythiocarbonyl*)*thio*]*acetic acid.* To a solution of neopentyl alcohol (13.2 g) in ether (50 ml) was added 3.6 g of sodium hydride and stirred for 24 h. Then 8.8 g of carbon disulfide was added and the stirring continued for 1 h. The crude xanthate was filtered, dissolved in water, and converted to the carboxymethyl ester as described above. Yield 70 %.

[(*1,2,2-Trimethylpropyloxythiocarbonyl*)*thio*]*acetic acid.* Potassium *tert*-butoxide was prepared by refluxing a mixture of potassium (4.3 g) *tert*-butyl alcohol (8.4 g) and xylene (150 ml) for 5 h; 10.2 g of 3,3-dimethyl-2-butanol (pinacolyl alcohol) was added to the hot mixture and after cooling to room temperature 8.4 g of carbon disulfide was added in small portions with stirring. The stirring was continued for 30 min and 50 ml of water was added to dissolve the xanthate; after separation from the xylene layer the aqueous solution of the xanthate was added to a neutralized solution of 9.5 g of chloroacetic acid and the carboxymethyl derivative isolated as described above. Yield 15 g (64 %) of an oil which did not crystallize; it was used without further purification for the preparation of the corresponding hydrazide.

[(o-*Nitrobenzyloxythiocarbonyl*)*thio*]*acetic acid.* *o*-Nitrobenzyl alcohol (10 g) was dissolved in dioxan (40 ml) and carbon disulfide (8 ml) and a solution of potassium hydroxide (5.6 g) in water (4 ml) were added. The mixture was kept for 2 h in a refrigerator and the potassium *o*-nitrobenzyl xanthate was filtered and washed with dioxan. Yield 24 g (97 %), m.p. 120°C (decomp.). When chloroacetic acid was used for the subsequent reaction yields were low but satisfactory yields were obtained with bromoacetic acid: To a solution of the potassium xanthate (10 g) in water (50 ml) a solution of bromoacetic acid (5.6 g) in 2 N sodium hydroxide (20 ml) was added. After 7 h the solution was extracted with ether, cooled with ice, and [(*o*-nitrobenzyloxythiocarbonyl)thio]acetic

acid was precipitated upon addition of conc. hydrochloric acid. It was filtred, washed with water and dried over H_2SO_4. Yield 6.3 g (59 %).

Attempts to prepare [(*tert*-butoxythiocarbonyl)thio]acetic acid were unsuccessful. When potassium *tert*-butylxanthate (prepared from potassium *tert*-butoxide and carbon disulfide in xylene) was added to an aqueous solution of sodium chloroacetate at 0°C there was an instantaneous evolution of a gas which was shown by gas chromatography to be a mixture of isobutene and carbonyl sulfide. From the acidified solution mercaptoacetic acid was isolated (identified by its infrared spectrum). However, the solution also contained other, unidentified substances and the ratio between the amounts of isobutene and carbonyl sulfide was less than 1:1. Nevertheless, this experiment indicates that this carboxymethyl ester will be unstable and will decompose according to the equation: $(CH_3)_3CO-CS-SCH_2COOH \rightarrow (CH_3)_2C=CH_2+COS+HSCH_2COOH$. However, the methyl ester, $(CH_3)_3CO-CS-SCH_3$, was prepared and could be transformed into the corresponding hydrazide (*q.v.*).

Attempts to prepare [(phenoxythiocarbonyl)thio]acetic acid, $PhO-CS-SCH_2COOH$, were equally unsuccessful and even the preparation of potassium phenyl xanthate, $PhO-CS-SK$, proved difficult. Its preparation has been claimed twice in the literature but we were unable to confirm these statements. According to an old paper [19] potassium phenyl xanthate is obtained by heating potassium phenolate with carbon disulfide in a sealed tube. When repeating this experiment we have only obtained *O,O'*-diphenyl monothiocarbonate, $(PhO)_2CS$, and potassium trithiocarbonate (identified by m.p. and infrared spectrum of the carboxymethyl ester) together with unreacted potassium phenolate and carbon disulfide. In an Italian patent [20] it has further been claimed that potassium phenyl xanthate can be prepared from potassium phenolate and carbon disulfide in ethanolic solution. As it would be expected only potassium ethylxanthate is obtained in this way. However, potassium phenylxanthate is formed from potassium phenolate and carbon disulfide in dimethylformamide solution as shown by the fact that on addition of methyl iodide *O*-phenyl *S*-methyl dithiocarbonate, $PhO-CS-SMe$, can be isolated from this solution.[21] However, the solid which could be precipitated by addition of ether to the dimethylformamide solution yielded on dissolution in water and addition of sodium chloroacetate only bis(carboxymethyl)trithiocarbonate.

Attempts to prepare carboxymethyl phenylxanthate from *O*-phenyl chlorothioformate, $PhO-CS-Cl$, and the disodium salt of mercaptoacetic acid yielded *O,O*-diphenyl monothiocarbonate.

Since carboxymethyl phenylxanthate could not be prepared, phenoxythiocarbonylhydrazines had to be prepared by another route. They were obtained from the reaction of hydrazines with *O*-phenyl chlorothioformate (see below).

Alkoxythiocarbonylhydrazines. (*O*-Alkyl monothiocarbazates)

Method A: From [(alkoxythiocarbonyl)thio]acetic acids. 1-Methyl-1-[(*o*-nitrobenzyloxy)-thiocarbonyl]hydrazine was precipitated in almost quantitative yield and practically pure (m.p. 92—95°C) by addition of methylhydrazine to a cooled neutralized solution of [(*o*-nitrobenzyloxythiocarbonyl)thio]acetic acid. Yield after recrystallization from ethanol containing a little water: 70—80 %. In all other cases where the carboxymethyl xanthate was used as starting material the following procedure was followed.

To a solution of the [(alkoxythiocarbonyl)thio]acetic acid (0.1 mol) in 50 ml of 2 N sodium hydroxide, hydrazine, or the alkyl hydrazine (0.1 mol) was added. After 1 h the pH of the solution was brought to pH = 5—6 and it was extracted with ether. When an alkylhydrazine had been used the ether solution was extracted three times with 0.1 N sodium hydroxide and will then only contain a hydrazide of the type $RO-CS-NR'NH_2$. The alkaline solutions were acidified with acetic acid and extracted with ether; this ether solution will contain a hydrazide of the type $RO-CS-NH-NHR'$. The ethereal solutions were dried with sodium sulfate and the hydrochlorides were precipitated by bubbling hydrogen chloride through the cooled solution. In the few cases where the hydrazide was crystalline it was liberated by addition of dilute aqueous ammonia to the

hydrochloride. Otherwise the hydrochloride was recrystallized from ethyl acetate, ethanol-ether or methylene chloride.

The (alkoxythiocarbonyl)hydrazines prepared have been listed in Table 1.

Methylhydrazine yielded only a hydrazide of the first type, whereas *tert*-butylhydrazine and monoalkylhydrazines with a secondary alkyl group (isopropyl, cyclohexyl, α-methylbenzyl) yielded only hydrazides of the second type (soluble in sodium hydroxide). Benzylhydrazine yielded both types (the same was shown qualitatively to be the case with butyl- and hexylhydrazine).

Method B: From O,S-*dialkyl dithiocarbonates. O,S*-Dimethyl dithiocarbonate reacts with hydrazine hydrate to give methoxythiocarbonylhydrazine. Hydrazine hydrate (5 ml) was added slowly with stirring to an ice-cooled solution of *O,S*-dimethyl dithiocarbonate (13.2 g) in ethanol (15 ml). On standing of the solution in a refrigerator methoxythiocarbonylhydrazine separated as colourless crystals (yield 60 %; m.p. 72–74°C), identical with the substance prepared by method A.

This method was used to prepare *tert*-butoxythiocarbonylhydrazine *via* the hitherto unknown dithiocarbonate:

O-tert-*Butyl*-S-*methyl dithiocarbonate*, $(CH_3)_3CO-CS-SCH_3$. Potassium *tert*-butylxanthate (1 mol) was suspended in 1 l of dry ether and methyl iodide (1 mol) was added. The mixture was stirred for 48 h at room temperature, the solid was filtered and the ether removed *in vacuo*. The residue (yield 61 %) was a yellowish oil which could only be distilled with great loss at 28–31°C and 0.05 mm Hg. The infrared spectrum of the distillate was identical with that of the crude product, so that distillation is not necessary, when the substance has to be used for the following preparation. The ester begins to decompose visibly at about 55°C, and at 65°C rapid decomposition takes place with the formation of isobutene, carbonyl sulfide, and methanethiol. The elemental analysis of the distilled product was slightly high in hydrogen and low in sulfur, probably because of some content of isobutene. The NMR spectrum shows two peaks at 8.35 τ and 7.51 τ. The integrated curves correspond to the ratio 1:3, the signal from the *S*-methyl protons being found at lower field. This confirms the structure and shows that no isomerisation to *S-tert*-butyl ester has taken place. This is also evident from the absence of a CO band in the infrared spectrum.

tert-*Butoxythiocarbonylhydrazine*, $(CH_3)_3CO-CS-NH-NH_2$. Anhydrous hydrazine (14.4 g; 0.45 mol) was added to a solution of the foregoing compound (49.2 g; 0.30 mol) in 1000 ml of anhydrous diethyl ether and the mixture was stirred for 18 h. The solution was decanted from a precipitate and the ether was removed by evaporation, leaving a yellowish oil which crystallized by addition of pentane. The crystals were filtered and recrystallized from pentane. Yield 25.2 g (57 %). M.p. 49–50°C. The ether-insoluble solid (3.1 g) was identified by m.p. (172–173°C) and infrared spectrum as thiocarbonohydrazide. The preparation has been carried out with equimolecular amounts of hydrazine and the ester without perceptible formation of thiocarbonohydrazide but the yield was approximately the same.

tert-Butoxythiocarbonylhydrazine forms colourless crystals which are rather soluble in water. It is decomposed rapidly with gas evolution (COS and CO_2) on addition of 1 N hydrochloric acid. Its infrared spectrum is almost identical with that of *sec*-butoxythiocarbonylhydrazine between 4000 cm^{-1} and 1500 cm^{-1} but shows the characteristic *tert*-butyl bands at 1360 cm^{-1} and 1380 cm^{-1}.

The reaction between *O*-phenyl *S*-methyl dithiocarbonate and hydrazine in ether was found to proceed in a different manner: From 0.92 g of the ester and 0.16 g of anhydrous hydrazine in 20 ml of ether were obtained 0.15 g of thiocarbonohydrazide (56 %, relative to hydrazine) and 0.25 g of methyl dithiocarbazate (40 %), corresponding to a 96 % conversion of the hydrazine. The reaction products were identified by their melting points and infrared spectra.

O,S-Dimethyl dithiocarbonate reacted with phenylhydrazine (a benzene solution was refluxed for 24 h) to give $CH_3O-CS-NH-NHC_6H_5$ (also prepared by method A) without formation of the isomer (or a dithiocarbazate).

S-*Methyl 3-benzylidene-2-phenylmonothiocarbazate*, $CH_3S-CO-N(C_6H_5)-N=CHC_6H_5$ *O,S*-Dimethyl dithiocarbonate also reacted with benzaldehyde phenylhydrazone when a solution of the two components in triethylamine was refluxed for 24 h. When the solution was concentrated and cooled yellowish crystals separated. On recrystallization from ethanol the compound was obtained as colourless crystals (yield 70 %) with m.p. 104–

105°C and the expected composition. (Found: C 66.90; H 5.29; N 10.34; S 11.98. Calc. for $C_{15}H_{14}N_2OS$: C 66.67; H 5.18; N 10.37; S 11.84). However, its infrared spectrum showed a strong band at 1680 cm^{-1}, thus it must be concluded that rearrangement of the *O*-methyl derivative had occurred during the reaction. The compound was a pure substance according to thin-layer chromatography. The *O,S*-dimethyl dithiocarbonate used in this preparation showed no C=O infrared band and according to gas chromatography was free from the *S,S*-isomer.

Attempts were also made to prepare this compound from benzaldehyde phenylhydrazone, sodium hydride, and *O*-methyl chlorothioformate in tetrahydrofuran (*cf.* the analogous reaction with dimethylthiocarbamoyl chloride [5]) but although the reaction proceeded as expected benzaldehyde phenylhydrazone was recovered almost quantitatively. This result can be explained by assuming that *S*-methyl monothiocarbazate is formed also in this case but is hydrolysed during the working up of the reaction mixture. The $-COSCH_3$ group is in fact very easily hydrolysed. This has also precluded elimination of the benzylidene group by the same method as was used for the corresponding dithiocarbazate (see p. 1932), the $-COSCH_3$ being removed instead of the benzylidene group in the acid medium.

Method C: From chlorothioformates. This method had to be used for the preparation of phenoxythiocarbonylhydrazines, derivatives of slightly reactive hydrazines, and some isomers which could not be prepared by Method A.

Phenoxythiocarbonylhydrazine. Hydrazine hydrate (5 g; 0.1 mol) was added slowly with stirring to a cooled solution of *O*-phenyl chlorothioformate (8.7 g; 0.05 mol) in ether (200 ml) and the stirring was continued for 1 h. The solution was decanted from the semisolid precipitate of hydrazinium chloride and the ether removed by evaporation. The crystalline residue was recrystallized from methanol-water (1:2). Yield 2.5 g (30 %). M.p. 118—119°C. The compound forms colourless crystals which are rather soluble in water.

The phenoxythiocarbonyl derivatives of methylhydrazine and dimethylhydrazine were prepared in a similar way. The first one did not crystallize and was isolated as the hydrochloride. When *O*-phenyl chlorothioformate was added to an aqueous solution of one mole of methylhydrazine and one mole of sodium hydroxide in water, instead of carrying the reaction out in ether solution with excess hydrazine, a solid compound was formed which according to analyses is *2-phenoxy-4-methylthiadiazolin-5-thione*, formed by reaction of the hydrazine with two moles of the chloride. M.p. 74—75°C after recrystallization from methanol. (Found: C 48.24; H 3.77; N 12.45. Calc. for $C_9H_8N_2OS_2$: C 48.22; H 3.60; N 12.50).

1-Phenoxythiocarbonyl-1,2-diphenylhydrazine. Hydrazobenzene (3 g) was dissolved in dioxan (50 ml) and to this solution was added with stirring a solution of 0.9 g of KOH in 3 ml of water and then a solution of *O*-phenyl chlorothioformate in 20 ml of dioxan. The mixture was stirred for 2 h at room temperature and filtered. On removal of the dioxan *in vacuo* a solid residue was obtained which on recrystallization from ethanol-water (1:1) yielded colourless crystals with m.p. 155—156°C.

The same procedure was used for the preparation of 1-phenoxythiocarbonyl-2-phenylhydrazine from phenylhydrazine. The crude product was highly coloured (dark green) and could only be purified to colourless crystals with great loss by recrystallization from ethanol-water (yield 15 %). This compound was also prepared in ether solution with triethylamine to bind HCl, but with no better yield.

1-Methoxythiocarbonyl-2-methylhydrazine. A solution of *O*-methyl chlorothioformate [22] (2.2 g) in ether (10 ml) was added dropwise to a stirred and cooled solution of 1-*tert*-butoxycarbonyl-1-methylhydrazine (6 g) in ether (20 ml). After standing for 1 h at room temperature the mixture was diluted with water and extracted with ether. The ether solution was dried with sodium sulfate and the ether removed *in vacuo*. The residue crystallized on addition of petroleum ether and yielded after recrystallization from petroleum ether 1-*tert*-butoxycarbonyl-1-methyl-2-methoxythiocarbonylhydrazine as colourless crystals with m.p. 101—102°C (yield 50 %). (Found: C 43.28; H 7.24; N 12.57. Calc. for $C_8H_{16}N_2O_3S$: C 43.63; H 7.32; N 12.72). This substance (2 g) was treated with 5 ml of cold conc. hydrochloric acid in which it dissolved with evolution of CO_2. The solution was rapidly evaporated to dryness *in vacuo* and the residue recrystallized from ethanol-ethyl acetate to yield the hydrochloride of 1-methoxythiocarbonyl-2-methylhydrazine as a colourless crystalline substance (Table 1).

Instead of the chlorothioformate ($CH_3O-CS-Cl$), di(methoxythiocarbonyl) disulfide $CH_3O-CS-S-S-CS-OCH_3$, could be used in this preparation. The hydrazine (1.46 g) and the disulfide (2.1 g) were dissolved in petroleum ether (20 ml). Crystalline sulfur separated slowly from the solution. After 24 h the solution was filtered and yielded on cooling directly 1.1 g of pure 1-*tert*-butoxycarbonyl-1-methyl-2-methoxythiocarbonylhydrazine.

The corresponding ethoxy derivative was obtained as an oil from di(ethoxythiocarbonyl) disulfide ("dixanthogen") and transformed without further purification into the hydrochloride of $C_2H_5O-CS-NH-NHCH_3$.

1-Methoxythiocarbonyl-2,2-diethylhydrazine. A solution of *O*-methyl chlorothioformate (0.33 g) in ether (10 ml) was added to a solution of 1,1-diethylhydrazine (0.30 g) in triethylamine (2 ml). After standing for 15 h the solution was filtered from triethylammonium chloride and extracted with 1 N hydrochloric acid. The aqueous solution was made alkaline and extracted with ether. The dried ether solution left on evaporation an oil (0.1 g). This was dissolved in dry ether and the hydrochloride precipitated by addition of an ether solution of hydrogen chloride. The methoxythiocarbonyl derivatives of trimethylhydrazine and 1,2-diisopropylhydrazine were prepared in a similar manner. Purification of the crude hydrochlorides was very difficult, therefore the yields of pure products were very small. (Table 1).

1-(Methoxythiocarbonylamino)piperidine. A solution of *O*-methyl chlorothioformate (1.1 g) in ether (10 ml) was added with cooling to a solution of 1-aminopiperidine (1 g) and triethylamine (1 g) in ether (10 ml). The solution was filtered from triethylammonium chloride and left on evaporation a crystalline residue which on recrystallization from pentane gave the hydrazide as colourless needles. This method was also used to prepare the crystalline 1-methoxythiocarbonyl-2,2-dimethylhydrazine (also obtained by Method A).

((Alkylthio)thiocarbonyl)hydrazines. (Alkyl dithiocarbazates)

Method A: From alkylhydrazines and carbon disulfide. Methyl dithiocarbazate, $CH_3S-CS-NHNH_2$, was prepared according to Busch [23] from potassium dithiocarbazate and methyl iodide (*cf.* also Ref. 24). In a similar way the derivatives of alkyl hydrazines were prepared, however, without isolating the potassium salt: To a solution of potassium hydroxide (0.1 mol) and the hydrazine (0.1 mol) in methanol (50 ml) carbon disulfide (0.1 mol) was added with cooling. After 1 h methyl iodide (0.1 mol) was added and after 2 h the solution was diluted with water and extracted with ether. The ether solutions were extracted with 1 N sodium hydroxide and the alkaline solutions acidified and extracted with ether. The ether solutions, which were extracted with sodium hydroxide, contain the hydrazides of the type $CH_3S-CS-NR-NH_2$; any isomers of the type $CH_3S-CS-NH-NHR$ will be found in the extracts from the acidified sodium hydroxide solutions. However, it was found that only one isomer is formed. This has the formula $CH_3S-CS-NR-NH_2$ when R is a primary or secondary alkyl group and the formula $CH_3S-CS-NH-NHR$ when R is *tert*-butyl or phenyl. This was substantiated by isolation of condensation products of all first mentioned compounds with benzaldehyde (or acetophenone). In contrast to the alkoxythiocarbonylhydrazines the ((alkylthio)thiocarbonyl)-hydrazines prepared were crystalline. They were obtained by evaporation of the dried ether solutions. Their properties are summarized in Table 2.

Higher homologues may be prepared by the same method by using the appropriate alkyl iodides or bromides, and benzyl derivatives by means of benzyl chloride; the *p*-nitrobenzyl derivative listed in Table 2 was prepared from *p*-nitrobenzyl bromide. Disubstituted hydrazines react in a similar way as the monosubstituted ones with carbon disulfide and potassium hydroxide. 1-Methyl-2-phenylhydrazine yielded, as expected, $CH_3S-CS-N(CH_3)-NHC_6H_5$ without a trace of the isomer; this is obvious from its NMR spectrum which shows no splitting (even at $-40°C$) of the $N-CH_3$ proton signal (6.41 τ). The $S-CH_3$ signal is found at 7.53 τ.

Only hydrazobenzene did not react under the usual conditions because of its very weakly basic character, but the dithiocarbazate was obtained in dimethylsulfoxide solution. This reaction has been described in another paper.[25]

This method was also used in the preparation of the dithiocarbazates derived from benzaldehyde phenylhydrazone and trimethylhydrazine.

1-(Methylthio)thiocarbonyl-1-phenylhydrazine, $CH_3S-CS-N(C_6H_5)NH_2$. Benzaldehyde phenylhydrazone (9.8 g) was dissolved in dimethyl sulfoxide (100 ml, dried over sodium hydride and freshly distilled), and sodium hydride (2.4 g; 50 % in oil) was added with stirring. When the hydrogen evolution had almost stopped, carbon disulfide (4 g), and, after stirring for ½ h, methyl iodide (7.1 g) were added and the stirring was continued for another ½ h. The reaction mixture was poured into ice-water and extracted twice with ether. The dried ($MgSO_4$) ether solution left on evaporation a yellow-red residue which was recrystallized to lemon-yellow needles from methanol. Yield 9.6 g (67 %) of methyl 3-benzylidene-2-phenyldithiocarbazate, m.p. 99–100°C.

The benzylidene group was removed by refluxing for 2 h a solution of the benzylidene derivative (2.86 g) and phenylhydrazine (1.08) in ethanol (20 ml) to which 5 drops of conc. hydrochloric acid had been added (*cf.* the method described by Cignarella [26]). The solution was diluted with water, filtered from benzaldehyde phenylhydrazone, neutralized, and the solvent removed *in vacuo*. The residue was recrystallized from petroleum ether and yielded colourless crystals with m.p. 72°C. No rearrangement to the isomer (m.p. 134–135 [27]) occurred on heating. With benzaldehyde the benzylidene derivative was reformed.

2-(Methylthio)thiocarbonyl-1,1,2-trimethylhydrazine was prepared from trimethylhydrazine in the same manner as the above mentioned benzylidene compound. On evaporation of the ether solution the dithiocarbazate crystallized in long needles, which on recrystallization from petroleum ether yielded colourless plates.

Method B: From trithiocarbonates. The reaction of hydrazine, methylhydrazine, 1,2-dimethylhydrazine or 1,1-dimethylhydrazine with symmetric trithiocarbonates (*cf.* Sandström [28,29]) has proved to be a convenient method for preparation of the corresponding dithiocarbazates, especially when it is desired to prepare larger amounts of them. The trithiocarbonate is diluted with the same volume of ethanol and the hydrazine is added with stirring. The reaction is exothermic and when hydrazine is used no heating is necessary. When an alkyl hydrazine is used the solution is heated with reflux until the evolution of the thiol has practically stopped. The dithiocarbazates separate in crystalline state by cooling and are recrystallized from petroleum ether.

Trimethylhydrazine and 1,1-diethylhydrazine reacted very slowly with dimethyl trithiocarbonate, so it is not practicable to prepare the derivatives of higher dialkylhydrazines or trialkylhydrazines in this manner.

Higher monoalkylhydrazines react well with trithiocarbonates but as shown by Forsgren and Sandström [14] a mixture of the two possible isomers is formed. The application of method B to the preparation of dithiocarbazates derived from higher monoalkylhydrazines is therefore only to be recommended when it is desired to prepare the isomer of the type RS–CS–NH–NHR′.

Trithiocarbonates of the type $RS-CS-SCH_2COOH$ [30] react with alkylhydrazines with the formation of the thiol in addition to mercaptoacetic acid, so usually no dithiocarbazates could be obtained. However, the *tert*-butyl derivative, $Bu^tS-CS-SCH_2COOH$, reacted with alkyl hydrazines to give *tert*-butyl dithiocarbazates. When it was dissolved in ice-cold 1 N NaOH and the equivalent amounts of methylhydrazine or 1,1-dimethylhydrazine were added, the dithiocarbazates $Bu^tS-CS-N(CH_3)-NH_2$ and $Bu^tS-CS-NH-N(CH_3)_2$ separated as colourless crystals in the course of 24–48 h, although in low yields (from the mother liquors a great amount of bis(carboxymethyl) trithiocarbonate was isolated). Further, the less reactive phenylhydrazine reacted generally with this type of trithiocarbonates (dissolved in 1 N NaOH) to form 1-(alkylthio)thiocarbonyl-2-phenylhydrazines, $RS-CS-NH-NHC_6H_5$. The methyl and propyl derivatives were obtained in 50 % yields after recrystallization from petroleum ether (m.p. 135°C and 125°C in accordance with the literature [31,32]).

Method C: From chlorodithioformates. The following compounds were prepared by this method.

1-Methyl-2-[(methylthio)thiocarbonyl]hydrazine (methyl 3-methyldithiocarbazate), $CH_3S-CS-NH-NHCH_3$. Methyl chlorodithioformate [33] (0.01 mol) was added dropwise with stirring to a solution of 1-*tert*-butoxycarbonyl-1-methylhydrazine [5] (0.02 mol) in anhydrous ether (20 ml). The ether solution was washed with water, the aqueous layer was extracted with ether and the combined ether extracts were dried and evaporated

in vacuo. The resulting oil crystallized on standing in a refrigerator. On recrystallization, first from methanol-water and then from petroleum ether, 1-*tert*-butoxycarbonyl-1-methyl-2-[(methylthio)thiocarbonyl]hydrazine, $CH_3S-CS-NH-N(CH_3)CO_2C(CH_3)_3$, was obtained as colourless crystals with m.p. 69–70°C. (Found: C 40.51; H 6.85; N 11.60. Calc. for $C_8H_{16}N_2O_2S_2$: C 40.75; H 6.78; N 11.87). This compound (1 g) was dissolved in conc. hydrochloric acid (5 ml) and the solution evaporated rapidly *in vacuo*. The residue was recrystallized from ethanol-ethyl acetate and yielded colourless crystals of the hydrochloride of 1-methyl-2-[(methylthio)thiocarbonyl]hydrazine. The free base separated as an oil which crystallized on cooling by neutralization of a concentrated aqueous solution of the hydrochloride.

2-[(Phenylthio)thiocarbonyl]-1,2-diphenylhydrazine was prepared from phenyl chlorodithioformate and hydrazobenzene by the same procedure as was described for the corresponding phenoxythiocarbonyl derivative, except that the temperature was kept at 70°C because the reaction was slower.

From the reaction of phenyl chlorodithioformate with excess anhydrous hydrazine in ether no hydrazide could be isolated. In addition to thiocarbonohydrazide and diphenyldisulfide a small amount (10 %) of a yellow crystalline substance was obtained, which according to analyses and mode of formation is 2,5-di(phenylthio)-1,3,4-thiadiazole. (Found: C 55.47; H 3.39; N 8.85. Calc. for $C_{14}H_{10}N_2S_3$: C 55.63; H 3.34; N 9.27). M.p. 100–101°C (recrystallized from ethanol-water).

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