ACTA CHEMICA SCANDINAVICA 15 (1961) 1109–1123

Studies of Thioacids and Their Derivatives

V. *N*-Substituted Thiohydrazides

KAI ARNE JENSEN, HANS RUEDI BACCARO, OLE BUCHARDT,
GERT E. OLSEN, CHRISTIAN PEDERSEN and JENS TOFT

Chemical Laboratory of the University of Copenhagen, Copenhagen, Denmark

A large number of new thiohydrazides derived from mono-and dialkylhydrazines have been prepared. It is generally not possible to prepare thiohydrazides of the type $RCSNR'NH_2$ when the radical R′ is an aryl radical or a secondary or tertiary aliphatic radical; in these cases only thiohydrazides of the type RCS–NHNHR′ are formed. As a consequence of this rule, symmetric dialkyl hydrazines, R′NH–NHR′, do not react with carboxymethyl dithioates when the radical R′ is secondary or tertiary. Symmetric dialkylhydrazines with primary radicals react without difficulty, and asymmetric dialkylhydrazines, R'_2NNH_2, react in all cases with carboxymethyl dithioates. Monoalkylhydrazines with a primary alkyl group yield generally a mixture of the two isomeric thiohydrazides, but the N^2-alkylthiohydrazide, RCS–NHNHR′, is formed almost exclusively when R = *tert*-butyl.

With the exception of N^1- and N^2-methylthiobenzhydrazides, *N*-alkylthiohydrazides were hitherto unknown. They may in general be prepared in the same way as the unsubstituted thiohydrazides by reaction of carboxymethyl dithioates with the free hydrazine. Apart from certain symmetric dialkylhydrazines, the hydrazines are not less reactive than hydrazine itself.

Wuyts[1] prepared some *N*-arylthiohydrazides by heating a mixture of an arylhydrazine with a dithioacid, but in this reaction also hydrazones are formed, often as the only isolable products. Some thioformylarylhydrazines have been prepared by Baker *et al.*[2] and by Sato and Ohta[3]. In a few cases Wuyts[4] also tried the reaction of dithioacids with methylhydrazine and obtained the arylhydrazone of an N^1-methylthiohydrazide.

An *N*-methylthiobenzhydrazide was prepared by Jensen and Miquel[5], who considered their product to be N^2-methylthiobenzhydrazide because it forms an innercomplex nickel compound. It was, however, pointed out by Holmberg[6] and by Bähr and Schleitzer[7], that this thiohydrazide must be the N^1-methylthiohydrazide (I) because it has no acid character. This is very remarkable from a complex-chemical point of view, because from our experiences with thiosemicarbazides [8] only compounds with a potential HS-group would be expected to form innercomplex compounds. We even considered the possibility of an isomerisation of the methylthiobenzhydrazide during complex formation; but the methylthiobenzhydrazide isolated from nickel complex was shown to be identical with the starting material (m.p. 91—92°C, mixed m.p. 90—92°C).

Holmberg [9] prepared the isomeric N^2-methylthiobenzhydrazide (II) by hydrolysis of the reaction product of *l*-arabinose-thiobenzhydrazone with

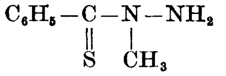
Table 1. Comparison of yields (%) of N^1- and N^2-alkyl (or aryl) thiohydrazides, $RCS-NR'NH_2$ and $RCS-NHNHR'$, formed in the reaction between dithioates and monoalkyl- or monoarylhydrazines. Numbers in parenthesis: The compounds were isolated in a crystalline state, but in such small amounts that no purification was attempted. In the cases where the yield is given as ~0, the ethereal solution became turbid with hydrogen chloride and a minute amount of an oil separated, but it is uncertain whether this contained the isomeric thiohydrazide or other by-products.

R R′		Methyl	*Iso*-propyl	*tert*-Butyl	Benzyl	β-Phenylethyl	Phenyl	*p*-Tolyl	2-Furyl
Methyl	N^1	65	53	~0	77		82	87	93
	N^2	0	35	42	14		10	(5)	~ 0
Ethyl	N^1						43		
	N^2						32		
Propyl	N^1						60		
	N^2						34		
*Iso*propyl	N^1				0		(2)		0
	N^2				87		90		76
Butyl	N^1	72			50	51	66	70	82
	N^2	~ 0			47	36	17	(12)	~ 0
*Iso*butyl	N^1						25		
	N^2						63		
sec-Butyl	N^1				0		0		0
	N^2						70		
tert-Butyl	N^1	~ 0					0		
	N^2	77					94		
Hexyl	N^1		(3)	(0.8)	(14)		44	16	
	N^2		37	59	59		48	56	
*Cyclo*hexyl	N^1	0			0		0		0
	N^2	82			73		85		78
Benzyl	N^1	69	(9)	8	(20)		22		52
	N^2	18	25	58	68		72		37
α-Phenylethyl	N^1			0			0		
	N^2			74			97		
β-Phenylethyl	N^1	43			17		41		
	N^2	18			52		34		
γ-Phenylpropyl	N^1						29		
	N^2						65		
Phenyl	N^1	0			0		0		0
	N^2	57			90		96		83

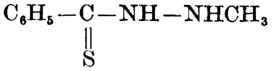
Table 2. N^1-Alkylthiohydrazides, $R-CSNR'NH_2$.

R	R′	Yield %	M.p., °C	Formula	Analyses					
					Carbon		Hydrogen		Nitrogen	
					Found	Calc.	Found	Calc.	Found	Calc.
Methyl	Methyl	65	79 – 80	$C_3H_8N_2S$	34.50	34.50	7.70	7.74	26.78	26.90
Methyl	Butyl	72	120 – 121	$C_6H_{14}N_2S.HCl$					15.17	15.32
Methyl	Benzyl	69	64 – 65	$C_9H_{12}N_2S$	60.00	59.98	6.89	6.71	15.70	15.55
Methyl	β-Phenylethyl	43	81 – 82	$C_{10}H_{14}N_2S$	61.90	61.83	7.32	7.27	14.34	14.42
Ethyl	Methyl	60	134 – 137	$C_4H_{10}N_2S.HCl$	30.90	31.05	7.13	7.18	18.15	18.13
*Iso*propyl	Methyl	53	170 – 172	$C_5H_{12}N_2S.HCl$	35.50	35.60	7.64	7.70		
tert-Butyl	Benzyl	8	108 – 110	$C_{12}H_{18}N_2S.HCl$	55.65	55.69	6.95	7.40		
Benzyl	Methyl	77	65 – 66	$C_9H_{12}N_2S$	60.10	60.00	6.50	6.72	15.48	15.53
Benzyl	Butyl	50	117 – 118	$C_{12}H_{18}N_2S.HCl$					10.63	10.82
Benzyl	β-Phenylethyl	17	65 – 67	$C_{16}H_{18}N_2S$	71.00	71.09	6.70	6.71	10.35	10.36
β-Phenylethyl	Butyl	51	138 – 140	$C_{13}H_{20}N_2S.HCl$					10.39	10.28
Phenyl	Methyl	82	91 – 92	$C_8H_{10}N_2S$					16.91	16.86
Phenyl	Ethyl	43	62.5 – 63	$C_9H_{12}N_2S$	60.05	59.98	6.76	6.71	15.32	15.55
Phenyl	Propyl	60	46 – 47	$C_{10}H_{14}N_2S$					14.57	14.42
Phenyl	Butyl	66	115 – 118	$C_{11}H_{16}N_2S.HCl$					11.28	11.43
Phenyl	*Iso*butyl	25	157 – 159	$C_{11}H_{16}N_2S.HCl$					11.58	11.43
			57 – 58	$C_{11}H_{16}N_2S$					13.57	13.45
Phenyl	Hexyl	44	137 – 140	$C_{13}H_{20}N_2S.HCl$					10.42	10.27
Phenyl	Benzyl	22	85.5 – 86	$C_{14}H_{14}N_2S$	69.40	69.40	6.00	5.83	11.57	11.56
Phenyl	β-Phenylethyl	41	66 – 67	$C_{15}H_{16}N_2S$	70.25	70.29	6.20	6.29	10.94	10.93
Phenyl	γ-Phenylpropyl	29	146 – 148	$C_{16}H_{18}N_2S.HCl$					9.24	9.13
p-Tolyl	Methyl	87	92 – 92.5	$C_9H_{12}N_2S$	59.90	59.98	6.72	6.71	15.52	15.55
p-Tolyl	Butyl	70	123 – 126	$C_{12}H_{18}N_2S.HCl$					10.89	10.82
p-Tolyl	Hexyl	16	57 – 57.5	$C_{14}H_{22}N_2S$	67.20	67.17	8.98	8.86	11.07	11.19
o-Hydroxyphenyl	Hexyl	83	123 – 124	$C_{13}H_{20}N_2OS$					11.10	11.10
p-Hydroxyphenyl	Methyl	70	116 – 117	$C_8H_{10}N_2OS$	52.90	52.74	5.55	5.53	15.50	15.38
p-Butoxyphenyl	Allyl	50	76 – 77	$C_{14}H_{20}N_2OS$					10.82	10.61
p-Butoxyphenyl	Propyl	70	57 – 58	$C_{14}H_{22}N_2OS$					10.51	10.53
p-Butoxyphenyl	Butyl	65	52 – 53	$C_{15}H_{24}N_2OS$					10.05	10.00
2-Furyl	Methyl	93	142 – 144	$C_6H_6N_2OS.HCl$	37.20	37.40	4.73	4.72	14.52	14.53
2-Furyl	Butyl	82	134 – 137	$C_9H_{14}N_2OS.HCl$					11.77	11.93
2-Furyl	Benzyl	52	80 – 81	$C_{12}H_{12}N_2OS$	62.20	62.06	5.31	5.21	12.02	12.06

formaldehyde. We have found that this isomer is formed in 5—10 % yield together with N^1-methylthiobenzhydrazide in the reaction between methylhydrazine and carboxymethyl dithiobenzoate or methyl dithiobenzoate.


$C_6H_5-C(=S)-N(CH_3)-NH_2$

I


$C_6H_5-C(=S)-NH-NHCH_3$

II

Methylhydrazine also reacts with most other carboxymethyl dithioates with predominant formation of N^1-methylthiohydrazides. In some cases, however, it was shown that the N^2-isomer is formed as a by-product, and methyl dithiopivaloate forms the N^2-isomer almost exclusively (Table 1).

All the N^1-methylthiohydrazides are obtained in crystalline form, but the reaction of carboxymethyl dithioates with higher monoalkylhydrazines in most cases results in the formation of oils. This is partly due to the fact that a mixture of the two isomeric hydrazides is formed, but it also seems that many of the N^2-alkylthiohydrazides with primary alkyl groups actually are liquids at room temperature. Even N^2-methylthiobenzhydrazide could not be induced to crystallise. In some cases these hydrazides crystallised by cooling below zero, but melted again beneath room temperature. Alkylthiobenzhydrazides with substituents in the *para*-position in the benzene nucleus are more liable to crystallise than the unsubstituted thiobenzhydrazides; this is the reason why some *p*-methyl- and *p*-butoxythiobenzhydrazides were prepared (Table 2). In most cases, however, crystalline primary alkylthiohydrazides could not be obtained directly from the reaction mixture; *N*-*iso*propyl-, and *N*-*tert*-butylthiohydrazides on the other hand crystallise readily.

The separation of the isomeric *N*-alkylthiobenzhydrazides was attained in the following way: The crude hydrazides were extracted with ether and the ether solution extracted with 1 N sodium hydroxide. From the alkaline solution the base-soluble hydrazides were set free with acetic acid and extracted with ether. The two ether solutions were dried and precipitated with dry hydrogen chloride. In most cases crystalline hydrochlorides of sufficient purity were obtained directly, so that a comparison of the yields of the two isomers could be obtained directly by weighing the crude hydrochlorides (Table 1). When crystalline thiohydrazides could be obtained from the hydrochlorides, the recrystallised thiohydrazides were analysed; in the cases where the thiohydrazide was an oil, the hydrochloride was recrystallised from ethanol or ethanol + ether.

A glance at Table 1 suffices to show that phenylhydrazine only forms N^2-substituted hydrazides. Also from *o*- and *p*-tolylhydrazine only one isomer was obtained, and Wuyts obtained from *p*-bromophenylhydrazine 71 % of N^2-*p*-bromophenylthiobenzhydrazide and 27 % of the corresponding hydrazone. It therefore seems safe to conclude that aromatic hydrazines never form N^1-arylthiohydrazides. It should be mentioned, by the way, that the formation of hydrazones by elimination of sulfur from thiohydrazides, which in many of Wuyts' experiments resulted in the predominant and often exclusive formation of hydrazones instead of hydrazides, has never been met with in our preparations of thiohydrazides from carboxymethyl dithioates.

Table 3. N^2-Alkylthiohydrazides, R—CSNHNHR′.

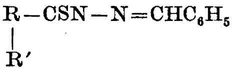
R	R′	Yield %	M.p., °C	Formula	Analyses					
					Carbon		Hydrogen		Nitrogen	
					Found	Calc.	Found	Calc.	Found	Calc.
Methyl	*tert*-Butyl	77	166—171	$C_6H_{14}N_2S.HCl$					15.37	15.34
			85— 86	$C_6H_{14}N_2S$					19.23	19.17
Methyl	*Cyclo*hexyl	82	90— 91	$C_8H_{16}N_2S$	55.75	55.70	9.40	9.36	16.19	16.25
Methyl	Benzyl	18	165—166	$C_9H_{12}N_2S.HCl$					12.72	12.92
Methyl	*β*-Phenylethyl	18	116—117	$C_{10}H_{14}N_2S.HCl$					11.76	11.63
Methyl	Phenyl	57	95—96 [a]	$C_8H_{10}N_2S$					16.80	16.86
			80—81 [a]						16.93	16.86
*Iso*propyl	Methyl	35	177—178	$C_5H_{12}N_2S.HCl$	35.70	35.60	7.65	7.70		
*Iso*propyl	Hexyl	37	120—121	$C_{10}H_{22}N_2S.HCl$					11.76	11.73
*Iso*propyl	Benzyl	25	155—156	$C_{11}H_{16}N_2S.HCl$					11.30	11.45
tert-Butyl	Methyl	42	118—120	$C_6H_{14}N_2S$	49.45	49.27	9.56	9.66	19.22	19.17
			158—160	$C_6H_{14}N_2S.HCl$					15.49	15.34
tert-Butyl	Hexyl	59	100—101	$C_{11}H_{24}N_2S.HCl$	52.25	52.25	9.90	10.01	11.19	11.08
tert-Butyl	Benzyl	58	60— 61	$C_{12}H_{18}N_2S$	64.70	64.72	8.09	8.16	12.60	12.60
tert-Butyl	*α*-Phenylethyl	74	190—191	$C_{13}H_{20}N_2S.HCl$	57.05	57.22	7.92	7.76	10.53	10.37
Benzyl	Methyl	14	121—122	$C_9H_{12}N_2S.HCl$					12.81	12.93
Benzyl	*Iso*propyl	87	46— 47	$C_{11}H_{16}N_2S$					13.52	13.45
Benzyl	Butyl	47	166—168	$C_{12}H_{18}N_2S.HCl$					10.66	10.82
Benzyl	Hexyl	59	140—143	$C_{14}H_{22}N_2S.HCl$					9.96	9.77
Benzyl	*Cyclo*hexyl	73	70—70.5	$C_{14}H_{20}N_2S$					11.32	11.28
Benzyl	Benzyl	68	81— 82	$C_{15}H_{16}N_2S$	70.30	70.29	6.31	6.29	10.90	10.93
Benzyl	*β*-Phenylethyl	52	102—103	$C_{16}H_{18}N_2S$	71.10	71.09	6.69	6.71	10.29	10.36
Benzyl	Phenyl	90	91.5—92 [b]	$C_{14}H_{14}N_2S$					11.51	11.56
β-Phenylethyl	Butyl	36	117—120	$C_{13}H_{20}N_2S.HCl$					10.37	10.28
Phenyl	Methyl	10	169—170	$C_8H_{10}N_2S.HCl$	47.50	47.45	5.41	5.48	14.05	13.83
Phenyl	Ethyl	32	50— 52	$C_9H_{12}N_2S$	60.00	59.98	6.63	6.71	15.36	15.55
Phenyl	Propyl	34	144—147	$C_{10}H_{14}N_2S.HCl$					12.30	12.16
Phenyl	*Iso*propyl	90	112—112.5	$C_{10}H_{14}N_2S$					14.55	14.42
Phenyl	Butyl	17	44— 45	$C_{11}H_{16}N_2S$					13.32	13.45
Phenyl	*Iso*butyl	63	79— 80	$C_{11}H_{16}N_2S$					13.60	13.45
Phenyl	*sec*-Butyl	70	66.5—67.5	$C_{11}H_{16}N_2S$					13.51	13.45
Phenyl	*tert*-Butyl	94	119—120	$C_{11}H_{16}N_2S$					13.58	13.45

Table 3. Continued.

R	R'	Yield %	M.p., °C	Formula	Analyses					
					Carbon		Hydrogen		Nitrogen	
					Found	Calc.	Found	Calc.	Found	Calc.
Phenyl	Hexyl	48	109–113	$C_{13}H_{20}N_2S.HCl$					10.39	10.27
Phenyl	*Cyclo*hexyl	85	106–107	$C_{13}H_{18}N_2S$	66.75	66.74	7.75	7.74	11.87	11.96
Phenyl	Benzyl	72	147–148	$C_{14}H_{14}N_2S$	69.52	69.75	5.93	5.68	11.57	11.56
Phenyl	α-Phenylethyl	97	103–104	$C_{15}H_{16}N_2S$					11.01	10.93
Phenyl	β-Phenylethyl	34	90– 91	$C_{15}H_{16}N_2S$	70.15	70.29	6 18	6.29	10.89	10.93
Phenyl	γ-Phenylpropyl	65	76–77.5	$C_{16}H_{18}N_2S$	71.00	71.09	6.70	6.71	10.28	10.36
			152–154	$C_{16}H_{18}N_2S.HCl$					9.02	9.13
Phenyl	Phenyl	96	69.5– 70 c	$C_{13}H_{12}N_2S$					12.38	12.27
			90– 91 c						12.35	12.27
Phenyl	*o*-Tolyl	83	125–127	$C_{14}H_{14}N_2S$	69.35	69.40	5,81	5.83	11.60	11.56
Phenyl	*p*-Tolyl	60	98–99 d	$C_{14}H_{14}N_2S$	69.35	69.40	5.81	5.83	11.59	11.56
m-Nitrophenyl	Phenyl	75	122–123	$C_{13}H_{11}N_3O_2S$	57.30	57.14	3.91	4.06	15.50	15.38
p-Tolyl	Hexyl	56	54.5– 55	$C_{14}H_{22}N_2S$	67.10	67.15	8.82	8.90	11.26	11.19
2-Furyl	*Iso*propyl	76	84– 85	$C_8H_{12}N_2OS$					15.12	15.21
2-Furyl	*Cyclo*hexyl	78	176–179	$C_{11}H_{16}N_2OS.HCl$					10.70	10.74
2-Furyl	Benzyl	37	85– 86	$C_{12}H_{12}N_2OS$	62.30	62.06	5.12	5.21	11.97	12.02
2-Furyl	Phenyl	83	107–108	$C_{11}H_{10}N_2OS$					12.70	12.84

a) Dimorphous; m.p. in lit.[1] 82°C. b) Lit.[1] 89°C. c) Dimorphous; the low-melting form is transformed into the high-melting by seeding. M.p. in lit. 88[1], 87–88[5], and 89–90[20]°C. d) Lit.[1] 96°C.

Table 4. Benzalhydrazones of *N*¹-Alkylthiohydrazides,



$$\underset{\displaystyle R'}{R-CS\overset{}{N}}-N=CHC_6H_5$$

R	R′	Yield, %	M.p., °C	Formula	Analyses					
					C		H		N	
					Found	Calc.	Found	Calc.	Found	Calc.
H	CH_3	80	82−82.5	$C_9H_{10}N_2S$	60.55	60.70	5.65	5.66	15.80	15.69
CH_3	CH_3	65	115−116	$C_{10}H_{12}N_2S$	62.35	62.50	6.36	6.29	14.42	14.56
C_2H_5	CH_3	65	37− 38	$C_{11}H_{14}N_2S$	64.15	64.20	6.95	6.85	13.55	13.58
C_6H_5	CH_3	82	127−128	$C_{15}H_{14}N_2S_4$	71.10	70.90	5.46	5.56	10.94	11.07

The different behaviour of phenylhydrazine and methylhydrazine might be ascribed to the electrophilic character of the phenyl radical. A glance at Table 1 shows, however, that the difference is rather due to a steric influence; *tert*-butylhydrazine, like phenylhydrazine, gives exclusively the *N*²-isomer. Also, alkylhydrazines with a secondary alkyl group, like *cyclo*hexylhydrazine, α-phenylethylhydrazine, and *sec*-butylhydrazine, give exclusively, or almost exclusively, the *N*²-isomer (Table 3). An *N*¹-isomer could only be isolated in the case of *iso*propylhydrazine, and only in minute amount. In contrast, alkylhydrazines with primary alkyl groups generally form both isomers. As mentioned above, methylhydrazine only forms a small amount of the base-soluble isomer. With the higher alkylhydrazines the two isomers were formed in amounts of the same order of magnitude. A larger primary alkyl group favours the formation of a larger amount of the *N*²-isomer, but even with rather bulky alkyl groups the *N*¹-isomer is formed in appreciable amount (*cf.* Table 1). When R of the acid radical RCS- is a secondary or tertiary alkyl group, however, the *N*²-isomer is formed almost exclusively.

Table 5. *NN*′Dialkylthiohydrazides, R−CSNR′NHR′.

R	R′	Yield, %	M.p., °C	Formula	Analyses					
					C		H		N	
					Found	Calc.	Found	Calc.	Found	Calc.
C_6H_5	CH_3	81	135−145	$C_9H_{12}N_2S.HCl$	50.15	49.90	6.06	6.06	12.66	12.92
$C_6H_5CH_2$	CH_3	57	46− 47	$C_{10}H_{14}N_2S$	62.05	61.80	7.30	7.26	14.45	14.41
C_6H_5	$C_6H_5CH_2$	40	113−114	$C_{21}H_{20}N_2S$					8.50	8.43

It is a striking consequence of the difference between primary and secondary alkylhydrazines that symmetric di-secondary-alkylhydrazines, like di-*iso*propylhydrazine and di*cyclo*hexylhydrazine, are quite unreactive towards carboxymethyl dithioates. After 24 h the dithioates could be recovered unchanged. In contrast, *NN'*-dipropylhydrazine and *NN'*-dibenzylhydrazine react in the same way as the monoalkylhydrazines.

NN'-Diphenylhydrazine (hydrazobenzene) does not react, whereas *NN*-diphenylhydrazine reacts in the normal way. *NN'*-Di-*tert*-butylhydrazine is at present unknown, but would undoubtedly be unreactive.

The effect of the acid radical on the relative amounts of the two isomers is not so clear as the effect of the alkyl group (Table 1). It should be pointed out that the numbers represent yields in actual preparations and not the results of physico-chemical measurements. Considerable variation in the yields may therefore be expected in different preparations, although duplication of the preparations in several cases showed that the yields were quite reproducible. The reaction proceeds rapidly already during adjustment of the pH of the solution or during the mixing of the solutions of the dithioate and the hydrazine, so no constancy of pH or temperature during reaction can be claimed. It is, however, evident that carboxymethyl dithioacetate is more liable to give the N^1-isomer than dithioates of higher molecular weight whereas methyl dithiopivaloate and methyl dithio*iso*butyrate show the opposite behaviour. It also seems that carboxymethyl dithiophenylacetate and β-phenyldithiopropionate give higher yields of the N^2-isomers than do aromatic and heterocyclic dithioates. This difference may not be real, but it would be quite understandable from steric reasons.

The asymmetric *NN*-dialkylhydrazines react easily with carboxymethyl dithioates in the normal way, irrespective of the nature of the alkyl groups. A large number of such hydrazides were prepared (Table 6) since we observed that *NN*-dimethyldithiobenzhydrazide had a much higher bacteriostatic effect than the unsubstituted thiohydrazides.

NN'-Dimethylhydrazine reacts with carboxymethyl dithioates in the normal way giving N^1N^2-dimethylthiohydrazides (Table 5). The behaviour of some higher symmetric dialkylhydrazines was discussed above.

Most of the alkylthiohydrazides are colourless (white). The phenylthioacethydrazides are easily obtained as dazzling white, crystalline powders, but the thiobenzhydrazides are often more difficult to purify. N^1-Methylthiobenzhydrazide has been described in the literature [5,6] as yellowish or chamois but is actually colourless. Some thiohydrazides of benzoic and furoic acid have a genuine yellow colour: the phenylthiohydrazides are sulfur-yellow, *o*- and *p*-tolylthiobenzhydrazide, and *N*-(thiobenzoyl)-aminomorpholin have a slightly more intensive colour. Alkylhydrazides are generally colourless; some of them were at first obtained with a slight yellow colour, but in most cases they became colourless on repeated recrystallisation with addition of Darco G 60. The hydrochlorides are more often yellow; thus all the hydrochlorides of alkyl-2-furanthiocarboxyhydrazides have an intensive yellow colour. The hydrochloride of N^2-γ-phenylpropylthiobenzhydrazide is yellow, whereas the hydrochloride of the isomer is white; both the free thiohydrazides are, however, colourless.

Table 6. N^2-Dialkylthiohydrazides, R—CSNHNR′R″.

R	R′	R″	Yield, %	M.p., °C	Formula	Analyses					
						Carbon		Hydrogen		Nitrogen	
						Found	Calc.	Found	Calc.	Found	Calc.
H	Methyl	Methyl	61	84— 86	$C_3H_8N_2S$	34.80	34.60	7.73	7.74	26.56	26.90
Methyl	Methyl	Methyl	57	96— 97	$C_4H_{10}N_2S$	40.80	40.60	8.48	8.53	23.50	23.65
Phenyl	Methyl	Methyl	80	106—107	$C_9H_{12}N_2S$	59.85	60.00	6.83	6.72	15.45	15.52
Phenyl	Ethyl	Ethyl	20	64— 65	$C_{11}H_{16}N_2S$	63.20	63.42	7.68	7.74	13.29	13.45
Benzyl	Methyl	Methyl	56	99—100	$C_{10}H_{14}N_2S$	61.90	61.80	7.13	7.26	14.52	14.41
o-Hydroxyphenyl	Methyl	Methyl	74	165—166	$C_9H_{12}N_2OS$	55.25	55.09	6.25	6.17	14.13	14.28
o-Hydroxyphenyl	Methyl	Ethyl	70	145—146	$C_{10}H_{14}N_2OS$	57.25	57.13	6.60	6.71	13.54	13.33
o-Hydroxyphenyl	Ethyl	Ethyl	71	98— 99	$C_{11}H_{16}N_2OS$	58.80	58.91	7.01	7.19	12.69	12.49
o-Hydroxyphenyl	Butyl	Butyl	28	139—140	$C_{15}H_{24}N_2OS$	64.20	64.26	8.76	8.63	9.84	9.99
o-Hydroxyphenyl	*Iso*butyl	*Iso*butyl	93	105—106	$C_{15}H_{24}N_2OS$	64.10	64.26	8.54	8.63	9.76	9.99
o-Hydroxyphenyl	Methyl	Allyl	68	109—111	$C_{11}H_{14}N_2OS$	59.45	59.45	6.39	6.35	12.50	12.60
o-Hydroxyphenyl	Methyl	Propyl	71	107—108	$C_{11}H_{16}N_2OS$	58.85	59.91	7.02	7.19	12.46	12.49
o-Hydroxyphenyl	Methyl	Butyl	50	102—103	$C_{12}H_{18}N_2OS$	60.55	60.48	7.69	7.61	11.71	11.76
o-Hydroxyphenyl	Methyl	Benzyl	73	121—122	$C_{15}H_{16}N_2OS$	66.05	66.16	5.80	5.92	10.23	10.29
o-Hydroxyphenyl	Methyl	*Cyclo*hexyl	60	137—138	$C_{14}H_{20}N_2OS$	63.60	63.61	7.38	7.63	10.48	10.60
o-Methoxyphenyl	Methyl	Methyl	65	135—136	$C_{10}H_{14}N_2OS$	57.30	57.13	6.67	6.71	13.14	13.33
o-Propoxyphenyl	Methyl	Methyl	38	92— 93	$C_{12}H_{18}N_2OS$	60.60	60.47	7.57	7.60	11.28	11.76
o-*Iso*propoxyphenyl	Methyl	Methyl	30	92— 93	$C_{12}H_{18}N_2OS$	60.65	60.47	7.51	7.60	11.54	11.76
o-Butoxyphenyl	Methyl	Methyl	42	90— 91	$C_{13}H_{20}N_2OS$	62.00	61.88	8.00	7.99		
o-Hexyloxyphenyl	Methyl	Methyl	13	83— 84	$C_{15}H_{24}N_2OS$	63.70	64.24	8.38	8.63		
p-Hydroxyphenyl	Methyl	Methyl	53	157—158	$C_9H_{12}N_2OS$	54.95	55.09	6.21	6.17	14.12	14.28
p-Methoxyphenyl	Methyl	Methyl	77	125—126	$C_{10}H_{14}N_2OS$	57.15	57.13	6.66	6.71	13.22	13.33
p-Methoxyphenyl	Butyl	Butyl	24	68— 69	$C_{16}H_{26}N_2OS$	65.15	65.28	8.80	8.90	9.48	9.52
p-Butoxyphenyl	Methyl	Methyl	32	95— 97	$C_{13}H_{20}N_2OS$	62.00	61.88	7.97	7.99	11.00	11.10
p-Acetamidophenyl	Methyl	Methyl	90	167—168	$C_{11}H_{15}N_3OS$	55.60	55.67	6.26	6.36	17.76	17.72
m-Nitrophenyl	Methyl	Methyl	65	135—136	$C_9H_{11}N_3O_2S$	48.15	48.00	4.93	4.93	18.65	18.65
2-Furyl	Methyl	Methyl	60	81— 82	$C_7H_{10}N_2OS$	49.80	49.40	6.09	5.92	16.24	16.47
2-Thienyl	Methyl	Methyl	63	94— 95	$C_7H_{10}N_2S_2$	45.00	45.15	5.36	5.37	15.16	15.05
2-Thienyl(hydrochloride)	Ethyl	Ethyl	45	155—156	$C_9H_{14}N_2S_2.HCl$					11.08	11.17
										Cl 14.18	14.14

The higher *NN*-dialkylhydrazides are very photosensitive and rapidly turn yellow on exposure to daylight. The chemistry of this colour change has not been investigated.

The acid and base strengths of the thiohydrazides were determined by potentiometric titration of the hydrochlorides with 0.1 N NaOH in 50 % aqueous-alcoholic solution. In their pK_a values the monoalkylthiohydrazides, R—CSNHNHR′, do not differ significantly from the unsubstituted thiohydrazides, but the phenylthiohydrazides (R′ = C_6H_5) are somewhat stronger acids and weaker bases. The unsubstituted thiohydrazides have the following pK_a values: pK_{a1} = 5.0—6.0 (hydrazinium ion), and pK_{a2} = 10.2—11.2 (—CSNH— grouping). For the N^2-substituted thiohydrazides the following values were found:

R	R′	pK_{a1}	pK_{a2}
Alkyl or Aralkyl	Alkyl or Aralkyl	5.6—6.2	10.7—11.1
	Phenyl	4.4—4.7	9.3—10.1
Phenyl or 2-Furyl	Alkyl or Aralkyl	4.9—5.7	9.9—10.4
	Phenyl	4.2—4.3	9.2— 9.6

The N^2-dialkylthiohydrazides are somewhat stronger bases (pK_{a1} = 6.5—6.7) and weaker acids than the monoalkylthiohydrazides. Although they form salts with 1 N NaOH, the titration curves of the hydrochlorides with 0.1 N NaOH exhibit only one break. Naturally N^2-dialkylthiohydrazides containing phenolic hydroxyl groups, such as the *o*-hydroxy- and *p*-hydroxythiobenzhydrazides, form an exception. For these the values pK_{a1} = 4.9—5.7 and pK_{a2} = 10.6—11.2 were found.

The N^1-alkylthiohydrazides exhibit no acid function; they are somewhat stronger bases than the N^2-alkylthiohydrazides (pK_{a1} = 7.2—7.5).

EXPERIMENTAL

Monoalkylhydrazines

With the exception of methylhydrazine [10] and ethylhydrazine [11], all the monoalkylhydrazines were prepared by alkylation of hydrazine with the alkyl chloride or bromide [12,13]. Ethylhydrazine was also obtained, instead of the expected *NN′*-diethylhydrazine, by reduction of acetaldazine with sodium boron hydride. The following hydrazines were prepared: methylhydrazine, ethylhydrazine, allylhydrazine, propylhydrazine, *iso*propylhydrazine, butylhydrazine, *iso*butylhydrazine, *sec*-butylhydrazine, *tert*-butylhydrazine, hexylhydrazine, *cyclo*hexylhydrazine, benzylhydrazine, α-phenylethylhydrazine (b.p. 99—100°/2.2 mm), β-phenylethylhydrazine (b.p. 135°/12 mm), and γ-phenylpropylhydrazine (b.p. 265—267°/760 mm, and 142°/13 mm).

The following compounds are not mentioned in the literature: Benzylhydrazine, sulfate (m.p. 156—157°C; Found: N 12.76. Calc.: N 12.73). α-Phenylethylhydrazine (Found: C 71.10; H 8.83; N 22.37. Calc. C 70.45; H 8.88; N 20.57). β-Phenylethylhydrazine, sulfate (m.p. 166.5—167.5°C; Found: N 12.09. Calc. N 11.97). γ-Phenylpropylhydrazine, sulfate (m.p. 153—154°C; Found: N 11.32. Calc. N 11.29).

Dialkylhydrazines

The following *NN*-dialkylhydrazines were prepared by reduction of the corresponding nitrosamines with lithium aluminium hydride [14-16]: dimethylhydrazine, dipropylhydrazine, di*iso*propylhydrazine, dibutylhydrazine, di*iso*butylhydrazine, di-*sec*-butylhydrazine, dipentylhydrazine, methylethylhydrazine, methylpropylhydrazine, methyl*iso*propylhydrazine, methylbutylhydrazine, methylallylhydrazine, methyl*cyclo*hexylhydrazine, methylbenzylhydrazine, ethylpropylhydrazine, and ethylbutylhydrazine. For the *NN*-dialkylhydrazines with two different radicals, boiling points, yields and analyses are given below. Most of these hydrazines are new.

	Boiling point	Yield, %	Analyses, found	% N. calc.
NN-Methylethylhydrazine	83–84°/760 mm	50	38.10	37.80
NN-Methylpropylhydrazine	106–108°/760 mm	45	31.80	31.78
NN-Methyl*iso*propylhydrazine	104–106°/760 mm	45	31.87	31.78
NN-Methylbutylhydrazine [17]	130–132°/760 mm	55	28.15	27.42
NN-Methylallylhydrazine	110–112°/760 mm	40	32.46	32.53
NN-Methyl*cyclo*hexylhydrazine	68–69°/9 mm	65	21.58	21.85
NN-Methylbenzylhydrazine [18]	87–88°/6 mm	65	20.58	20.57
NN-Ethylpropylhydrazine	125–126°/760 mm	55	27.44	27.42
NN-Ethylbutylhydrazine	146–148°/760 mm	70	24.16	24.11

Most of the amines used for the preparation of the nitrosamines were prepared in the following way:

Benzylidine derivatives of primary amines were prepared by stirring the amine with benzaldehyde at room temperature. They were dried with $CaCl_2$ and distilled *in vacuo:* benzylideneethylamine (b.p. 93°/9 mm; 85 %), benzylidenepropylamine (b.p. 94°/8 mm; 83 %), benzylidene*iso*propylamine (b.p. 88–90°/10 mm; 81 %), benzylidenebutylamine (b.p. 113°/17 mm; 65 %), benzylidene*tert*butylamine (b.p. 91–93°/12 mm; 95 %), benzylideneallylamine (b.p. 96°/10 mm; 90%).

These benzylidene derivatives were alkylated with dimethyl or diethyl sulfate: A mixture of the benzylideneamine (1 mole), dimethyl or diethyl sulfate (1.05 mole) and benzene (50 ml) is heated carefully to 80°C, when a vigorous reaction sets in (it may be necessary to cool). The mixture is then refluxed for 15 min. or one hour, depending on whether dimethyl or diethyl sulfate was used for the reaction. After refluxing, the red or brown reaction mixture, which has separated into two layers, is extracted once with benzene (100 ml) and twice with light petroleum (100 ml). The residue is mixed with its own volume of ethanol and boiled with reflux for one hour. Then an equal volume of water is added, and the solution is evaporated *in vacuo.* A volume of 250 ml of 4 N hydrochloric acid is added, and the solution is again evaporated as far as possible *in vacuo.* The residue, a thick oil, is mixed with potassium hydroxide pellets, and the amine is distilled off, dried with potassium hydroxide and fractionated. In this way the following secondary amines were prepared: methylethylamine (58 %), methylpropylamine (40 %), methyl*iso*propylamine (55 %), methylallylamine (50 %), methylbutylamine (50 %), methyl-*tert*-butylamine (25 %), ethylpropylamine (65 %), ethyl*iso*propylamine (43 %), and ethylbutylamine (60 %). Methylbenzylamine was prepared from benzyl chlorid and methylamine. Methyl*cyclo*hexylamine was a commercial product.

The nitrosamines were prepared by the conventional method. The following nitrosamines are not mentioned in the literature: methyl-*tert*-butylnitrosamine, b.p. 70°/10 mm, m.p 22-24°C. (Found: N 24.10. Calc.: N 24.12). Ethylbutylnitrosamine, b. p. 98-100°/18 mm. (Found: N 21.20. Calc.: N 21.52).

NN'-Di*iso*propylhydrazine, and NN'-di*cyclo*hexylhydrazine, and NN'-dibenzylhydrazine, were prepared by hydrogenation of the corresponding azines. *NN'*-Dipropylhydrazine and *NN'*-dibutylhydrazine (b.p. 78–80°/12 mm) were obtained from the corresponding azines by reduction with lithium aluminium hydride [19].

Monoalkylthiohydrazides

The monoalkylthiohydrazides were in most cases obtained by the following general procedure: The carboxymethyl dithioate (0.01 mole) was dissolved in the equivalent amount of 1 N NaOH (10 ml), and to the cooled solution, a slight excess (10 %) of the free hydrazine (or in some cases a solution of a hydrazinium salt in the equivalent amount of sodium hydroxide) was added. The reaction proceeded almost instantaneously with slight heat evolution and separation of the hydrazide, generally as an oil. If necessary, a few drops of sodium hydroxide was added to bring the pH of the solution to 9—10. After standing for half an hour the solution was acidified with acetic acid and extracted three times with ether. The ether solution was extracted repeatedly with 1 N NaOH, until no turbidity appeared on acidification of the alkaline extract with acetic acid. The combined acidified alkaline extracts were extracted with ether. The two ether solutions, containing the two isomers of the monoalkylthiohydrazide, were dried with sodium sulfate. To each, an equal volume of light petroleum was added, and the hydrochloride of the thiohydrazide was precipitated with dry hydrogen chloride.

The alkylthiohydrazides of pivalic acid and the *N*-benzyl and *N*-hexylthiohydrazides of *iso*butyric acid were prepared from methyl dithiopivaloate and methyl dithio*iso*butyrate, respectively (the methylthiohydrazides of *iso*butyric acid were prepared in the usual way from the carboxymethyl ester). The reaction between hydrazines and methyl dithioates proceeds much slower than the reaction between carboxymethyl dithioates, and the yields are lower. The methyl ester and the hydrazine were dissolved in ethanol and kept for ca. 40 h; then the solvent was removed *in vacuo* and the residue was dissolved in ether and treated as above. The relative yields of the two isomers seem not to be greatly influenced by application of methyl dithioates instead of carboxymethyl dithioates. From methyl dithiobenzoate (17 g) and methylhydrazine we obtained 1.5 g of N^2-methylthiobenzhydrazide hydrochloride (7 %) and 11 g of N^1-methylthiobenzhydrazide (66 %).

The extents to which the two isomers were formed with different alkylhydrazines are seen from Table 1. The thiohydrazides were liberated by treatment of the hydrochlorides with dilute sodium hydroxide and neutralisation with acetic acid. When a thiohydrazide separated as an oil, the hydrochloride was used as such and recrystallised from ethanol + ethyl ether. The hydrochlorides can be isolated in a beautiful crystalline form, but they are somewhat unstable and soon begin to smell of hydrogen sulfide. On melting, the hydrochlorides split off some hydrogen chloride; melting points determined on a hot stage are therefore very ill-defined. The melting points of the hydrochlorides listed in Tables 2 and 3 were determined on substances contained in a sealed capillary tube; even then the melting points were not very sharp. The Kofler microscope hot-stage melting-point apparatus was used for melting point determination in all other cases.

The thiohydrazides were as a rule recrystallised from more or less dilute ethanol; the methylthiohydrazides could be recrystallised from water (N^2-*tert*-butylthioacethydrazide was easily soluble even in cold water), or water with a slight addition of ethanol; for the higher alkylhydrazides less dilute ethanol, and in a few cases ethanol without addition of water, was used. The phenylhydrazides were recrystallised from benzene + hexane, and this solvent was also used for recrystallisation in a few other cases. The thiohydrazides are generally very soluble in ethanol or benzene. Most of the thiohydrazides prepared were colourless, but some of the hydrazides of aromatic or heterocyclic thioacids had a distinct yellow colour. Properties and analyses of all the thiohydrazides prepared are listed in Tables 2 and 3. When one of the isomers is prevailing, or when both isomers are crystalline, the procedure may be somewhat simplified as shown in the following detailed descriptions:

N^1-*Methylthiophenylacethydrazide.* Carboxymethyl dithiophenylacetate (2.26 g) was dissolved in 1 N sodium hydroxide (10 ml); the yellow solution was cooled in ice, and a cold solution of methylhydrazinium sulfate (1.44 g) in 20 ml of 1 N sodium hydroxide was added together with a small excess quantity of sodium hydroxide solution to bring the pH to 9—10. Colourless crystals separated in a few minutes, and after standing for one hour the product was filtered off, washed with water and dried. The crude product (1.4 g) was recrystallised twice from benzene + light petroleum. Yield 1 g (55 %) of m.p. 65—66°C.

N^2-*Isopropylthiobenzhydrazide. Iso*propylhydrazine (0.85 g) was added with shaking and cooling to a solution of carboxymethyl dithiobenzoate (2.15 g) in 1 N NaOH (10 ml). After half an hour's standing at room temperature the pH of the solution was brought to 5 by addition of acetic acid. The crystalline precipitate was filtered off and dried. Yield 1.70 g (88 %). M.p. 112—112.5°C after recrystallisation from benzene + hexane.

N^2-*Benzylthiopivalic hydrazide.* A solution of methyl dithiopivaloate (3.00 g) and benzylhydrazine (2.44 g) in ethanol (5 ml) was kept for 40 h at room temperature. The ethanol was removed *in vacuo;* the residue was dissolved in ether (30 ml) and the solution was extracted with 1 N NaOH (10 + 5 × 5 ml). On acidification of the combined aqueous solutions with acetic acid the hydrazide separated in a crystalline state; it was filtered off and recrystallised from dilute (70 %) ethanol (15 ml). Yield 2.1 g (47 %); m.p. 60—61°C.

N^1-*Methylthioacethydrazide*. Carboxymethyl dithioacetate (1.5 g) was dissolved in 10 ml 1 N sodium hydroxide, and a solution of methylhydrazine sulfate (1.6 g) in 10 ml 2 N NaOH was added. After 2 h at room temperature, the solution was neutralised and the reaction product extracted with ether. The ether solution was dried (Na_2SO_4) and the ether evaporated *in vacuo*. A residue of colourless crystals was obtained; yield after crystallisation from benzene-light petroleum: 0.68 g (65 %) with m.p. 79—80°C. The compound is very soluble in water as opposed to the corresponding aromatic compounds.

N^1-*Methylthioformhydrazide* and N^1-*methylthiopropionic hydrazide* were prepared in a similar way from potassium dithioformate and carboxymethyl dithiopropionate, respectively. Both compounds are liquids at room temperature; the thiopropionyl derivative was isolated as the hydrochloride and the thioformyl derivative as the benzalhydrazone. This and other benzalhydrazones prepared from hydrochlorides of N^1-alkylthiohydrazides and benzaldehyde are listed in Table 4.

N^2-*Cyclohexylthiobenzhydrazide*. On addition of *cyclo*hexylhydrazine to a solution of carboxymethyl dithiobenzoate (1 g) in sodium hydroxide, an oil, which soon crystallised, separated. The solid product was stirred with 1 N NaOH (10 ml) and filtered. The undissolved residue (0.17 g; 15 %) had m.p. *ca.* 135°C, after recrystallisation from light petroleum 139—140°C. This product was not a hydrazide, but 2,5-diphenylthiadiazole (m.p. 139—141°C), formed from hydrazine which was contained as an impurity in the *cyclo*hexylhydrazine. (Found: C 71.25; H 4.20; N 11.86. Calc. for $C_{14}H_{10}N_2S$: C 70.58; H 4.23; N 11.76). The solution gave, on neutralisation, N^2-*cyclo*hexylthiobenzhydrazide as a precipitate (0.76 g; 69 %) with m.p. 105—106°C, after recrystallisation from light petroleum m.p. 106—107°.

NN′-Dialkylthiohydrazides

NN′-Dimethylhydrazine reacts easily with neutralised aqueous solutions of carboxymethyl dithioates. *NN′*-Dimethylthiobenzhydrazide separated as an oil and was extracted with ether and isolated as the hydrochloride. *NN′*-Dimethylthiophenylacethydrazide also separated as an oil, but was obtained crystalline on evaporation of the ethereal solution. *NN′*-Dipropylhydrazine, *NN′*-dibutylhydrazine, and *NN′*-dibenzylhydrazine react much slower (in the course of some hours); only *NN′*-dibenzylthiobenzhydrazide was isolated.

From *NN′*-di*iso*propylhydrazine, *NN′*-di*cyclo*hexylhydrazine and *NN′*-diphenylhydrazine (hydrazobenzene) no thioacylated derivatives could be obtained (a large number of carboxymethyl dithioates were tested).

Melting points and analyses of the compounds prepared are listed in Table 5.

NN-Dialkylthiohydrazides

Each dialkylthiohydrazide was prepared from a neutralised aqueous solution of the carboxymethyl dithioate and a slight excess (10—20 %) of the hydrazine. The reaction proceeded almost instantaneously with slight heat evolution, separation of the hydrazide and disappearance of the colour of the solution. The higher alkylhydrazines are somewhat liable to give oily reaction products, but crystalline products could in most cases be obtained by addition of ethanol to the solution. In a few cases the oily hydrazide was extracted with ether and isolated as the hydrochloride.

The dialkylthiohydrazides were in most cases recrystallised from dilute ethanol (70 %) and then from benzene + hexane. N^2-Dimethylthioacethydrazide and the corresponding thioformyl compound are rather soluble in water. They were isolated by extraction of the neutralised reaction mixture with chloroform.

The dialkylthiohydrazides form colourless crystals. With the exception of the thioformyl derivatives they are quite stable in darkness, but they are more or less photosensitive. Especially the higher dialkylthiohydrazides are very sensitive to light and rapidly turn yellow on exposure to daylight.

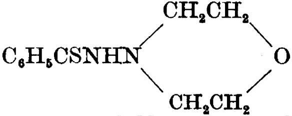
Melting points and analyses of the dialkylthiohydrazides prepared are listed in Table 6. In the following a few typical preparations are described:

N^2-*Dimethylthioformhydrazide.* To a solution of potassium dithioformate (1.16 g) in water (10 ml) a solution of dimethylhydrazinium chloride (0.96 g) was added, and the pH of the solution was brought to 8. After standing overnight the solution was extracted with chloroform. The chloroform layer was dried with sodium sulfate and evaporated *in vacuo*, and the colourless crystals were recrystallised from benzene + hexane. Yield 0.55 g (61 %). The compound is rather unstable; already after two days a lower melting point was found. The corresponding N^2-dimethylthioacethydrazide was prepared in the same way.

N^2-*Dimethylthiobenzhydrazide.* To a solution of carboxymethyl dithiobenzoate (2.1 g) in 1 N NaOH (10 ml) dimethylhydrazine (0.7 g) was added. After standing for one hour the solution was neutralised and the precipitate filtered. Yield 1.4 g (80 %) with m.p. 100–104°C; after recrystallisation from water or from benzene + hexane the m.p. was raised to 106–107°C. This compound was also prepared from methyl dithiobenzoate and dimethylhydrazine.

N^2-*Methylethyl-*o*-hydroxythiobenzhydrazide.* Carboxymethyl dithiosalicylate (5.7 g) was dissolved in the equivalent amount of 1 N NaOH, and methylethylhydrazine (2 g) was added. After cooling in ice, the crystalline thiohydrazide was filtered and recrystallised from dilute ethanol. Yield 3.7 g (70 %). M.p. 145–146°C.

N^2-*Diisobutyl-*o*-hydroxythiobenzhydrazide.* Carboxymethyl dithiosalicylate (1.14 g) was dissolved in 5 ml 1 N NaOH + 5 ml ethanol, and to the solution 0.9 g of *NN*-di*iso*butylhydrazine was added. Next day beautiful colourless crystal needles had formed. Yield 1.3 g (93 %). After recrystallisation from ethanol (70 %) and then from benzene + hexane, 0.80 g (57 %) with m.p. 105–105.5°C. The filtrate on addition of water and neutralisation gave only a small amount of an oily product.

N-*(Thiobenzoylamino)morpholin,*  $C_6H_5CSNHN\begin{smallmatrix}CH_2CH_2\\ \\ CH_2CH_2\end{smallmatrix}O$. Prepared in the general way from carboxymethyl dithiobenzoate and *N*-aminomorpholin. Yield 62 %. Recrystallisation from water. M.p. 147–148°C. (Found: C 59.55; H 6.42; N 12.65. Calc. for $C_{11}H_{14}N_2OS$: C 59.60; H 6.37; N 12.62).

N^2-*Dimethylthiopivalic hydrazide.* Methyl dithiopivaloate (3.00 g) and *NN*-dimethylhydrazine (1.20 g) were dissolved in ethanol (5 ml). After standing for four days the solution was evaporated to dryness and the residue was recrystallised from ethanol. Yield 0.10–0.12 g (3–4 %) of m.p. 119–120°C. (Found: N 17.49. Calc. for $C_7H_{16}N_2S$:N 17.48). According to these findings the reaction proceeds only to a very limited extent. No better yield was obtained by refluxing the solution.

REFERENCES

1. Wuyts, H. *Bull. soc. chim. Belges.* **38** (1929) 195; **39** (1930) 58; Wuyts, H. and Goldstein, M. *Bull. soc. chim. Belges.* **40** (1931) 497; Wuyts, H. and Lacourt, H. *Bull. soc. chim. Belges* **42** (1933) 1.
2. Baker, W., Ollis, W. D. and Poole, W. D. *J. Chem. Soc.* **1950** 3392.
3. Sato, T. and Okta, M. *Bull. Chem. Soc. Japan* **27** (1954) 624.
4. Wuyts, H. and Li Chia Kuang, *Bull. soc. chim. Belges.* **42** (1933) 153.
5. Jensen, K. A. and Miquel, J. F. *Acta Chem. Scand.* **6** (1952) 189.
6. Holmberg, B. *Arkiv Kemi* **9** (1955) 47.
7. Bähr, G. and Schleitzer, G. *Angew. Chem.* **68** (1956) 375.
8. Jensen, K. A. and Madsen, E. Rancke *Z. anorg. u. allgem. Chem.* **219** (1934) 243.
9. Holmberg, B. *Arkiv Kemi* **4** (1952) 105.
10. Hatt, H. H. *Organic Syntheses. Coll. Vol.* **2** (1959) 395.
11. Gever, G. and Hayes, K. *J. Org. Chem.* **14** (1949) 813.
12. Brit. Pat. 695,513 (1953).
13. Westphal, O. *Ber.* **74** (1941) 759.
14. Hanna, C. and Schueler, F. W. *J. Am. Chem. Soc.* **73** (1951) 4996; **74** (1952) 3693.

15. Zimmer, H., Andrieth, L. F., Zimmer, M. and Rowe, R. A. *J. Am. Chem. Soc.* **77** (1955) 790.
16. Vogel, A. I., Cresswell, W. T., Jeffery, G. H. and Leicester, J. *J. Chem. Soc.* **1952** 538.
17. Franchimont, A. P. N. and van Erp, H. *Rec. trav. chim.* **14** (1895) 318.
18. Hinman, R. L. *J. Am. Chem. Soc.* **78** (1956) 2463.
19. Renaud, R. and Leitch, L. C. *Can. J. Chem.* **32** (1954) 545.
20. Holmberg, B. *Arkiv Kemi* **7** (1954) 519.

Received January 23, 1961.