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Thermal Fragmentations

VI. The Preparation of Aryl *N*-Monoalkyldithiocarbamates and Their Behaviour upon Heating

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The reaction between aliphatic isothiocyanates and aromatic thiols forming *N*-monosubstituted dithiocarbamates, and the thermal stability of these compounds have been investigated. Most dithiocarbamates were easily accessible by mixing equimolar amounts of isothiocyanate and thiol without addition of solvent. The ^{1}H NMR spectra of the compounds were interpreted, and a case of hindered rotation about the CN bond is demonstrated and discussed. The thermal stability of some of the compounds were estimated from ^{1}H NMR spectra recorded at various temperatures. In one case $\Delta H°$ for the dissociation of the dithiocarbamate into isothiocyanate and thiol was calculated. Mass spectra have demonstrated that the first step in the main degradation route due to electron impact is identical to the thermal induced one.

The fragmentation of alkyl *N*,*N*-dialkyldithiocarbazates upon heating to give *N*-isothiocyanatoamines and thiols [1] led us to investigate the similar reaction with aryl *N*-monoalkyldithiocarbamates. As early as 1869 Hofmann [2] observed that on distillation of ethyl *N*-ethyldithiocarbamate at atmospheric pressure it fragmented into ethyl isothiocyanate and ethanethiol. Later, Delépine [3] and Braun [4] found that Hofmann's observation was characteristic of both alkyl *N*-alkyldithiocarbamates and the corresponding alkyl *N*-aryl compounds. In support Ottenbrite [5] reported the preparation of aryl isothiocyanates by thermal decomposition of methyl *N*-aryldithiocarbamates.

Since information about aryl *N*-monosubstituted dithiocarbamates is sparse in the literature, it was necessary to investigate not only the formation and fragmentation, but also the physical and chemical properties of these compounds.

The reaction between aliphatic isothiocyanates and aromatic thiols proceeds remarkably simply. Mixing equimolar amounts of the starting materials

without addition of solvent resulted usually in formation of analytically pure *N*-alkyl dithiocarbamates. The yields range from 30 to 100 % (see Table 1). The necessity of adding basic catalysts

$$R^1NCS + R^2SH \rightarrow R^1NHCSSR^2$$

to the reaction mixture, claimed by Roshdestwenski [6] and later by Cherbuliez *et al.*,[7] was not confirmed as illustrated by the reaction between methyl isothiocyanate and benzenethiol. One h after mixing the two components crystals began to separate. After 2 h the whole mixture had solidified and a quantitative yield of phenyl *N*-methyldithiocarbamate (Ia) was obtained. Nor was it found necessary to irradiate the mixture of the two compounds with an unfrosted incandescent lamp, as claimed in a Belgian patent [8] for the preparation of 4-chlorophenyl *N*-methyldithiocarbamate (Ii). Some of the compounds listed in Table 1 are mentioned in this patent, with melting points which in some cases are lower than the ones found by us. Also, the yields are improved by our method.

To obtain information about whether differences in reactivity, yields, and stability could be correlated with steric and electronic properties of the starting materials or the products, the reaction was performed with differently substituted aromatic thiols and various isothiocyanates. The identity of the products was confirmed by elemental analyses, IR [9] and ^{1}H NMR spectroscopy. In individual cases the mass spectrum also was recorded. Methods of preparation, yields, melting points, and elemental analyses are presented in Table 1.

The reactivity of alkyl isothiocyanates towards thiols is fairly high, but is exceeded by that of *N*-isothiocyanatodialkylamines, as pointed out by Anthoni, Larsen and Nielsen.[10] In most reactions the time necessary for complete solidification of the mixture was *ca.* 24 h, though great variations were found. For those mixtures which had solidified before the end of the investigation, the time varied from 2 h to 2 months. Thus formation of Ia was accomplished in 2 h, while the formation of 2,4,6-trimethylphenyl *N*-methyldithiocarbamate (If) lasted 2 months.

It was expected that the acidity of the thiol would have considerable effect on the time of reaction, assuming a mechanism consisting of a nucleophilic attack of the thiolate ion on the carbon atom of the NCS group. The results, however, seem to indicate that other factors are more important. Thus the time for solidification is approximately the same for the reactions between methyl isothiocyanate and benzenethiol, 4-methoxybenzenethiol, 4-methylbenzenethiol, and 4-fluorobenzenethiol though these thiols present pronounced differences in stability of the anions.

To explore if steric crowding affects the reaction, 2,4,6-trimethylbenzenethiol was treated with methyl, ethyl, and isopropyl isothiocyanates. The times of reaction were 2 months, 1 day, and 1 week, respectively. When methyl isothiocyanate was treated with benzenethiol, 2-methylbenzenethiol, and 2,4,6-trimethylbenzenethiol, the times were 2 h, 2 days, and 2 months, respectively. Mixing the same three thiols with isopropyl isothiocyanate gave respective times of 1 day, 2 days and 1 week.

Even if the preceding information reveals no simple relationship between steric effects and reactivity, the fact that *t*-butyl isothiocyanate did not react

Table 1. *N*-Monoalkyldithiocarbamates $R^1NHCSSR^2$

Compound	R^1	R^2	Method	Yield	M.p. °C	Formula	Analyses (C, H, N, S)
Ia	Me	C_6H_5	A[8]	100	131 – 132	$C_8H_9NS_2$	Found: 52.48; 5.02; 7.66; 34.72 Calc.: 52.42; 4.95; 7.64; 34.99
Ib	Me	2-MeC_6H_4	A[8]	100	92 – 93	$C_9H_{11}NS_2$	Found: 54.60; 5.57; 7.01; – Calc.: 54.78; 5.62; 7.10; –
Ic	Me	3-MeC_6H_4	A	100	83 – 84	$C_9H_{11}NS_2$	Found: 54.80; 5.70; 7.07; 32.31 Calc.: 54.78; 5.62; 7.10; 32.50
Id	Me	4-MeC_6H_4	A[8]	100	90 – 91	$C_9H_{11}NS_2$	Found: 54.60; 5.53; 7.05; 32.36 Calc.: 54.78; 5.62; 7.10; 32.50
Ie	Me	4-$Bu^tC_6H_4$	A[8]	50	161 – 162	$C_{12}H_{17}NS_2$	Found: 60.01; 7.20; 5.86; 26.61 Calc.: 60.21; 7.14; 5.85; 26.79
If	Me	2,4,6-$Me_3C_6H_2$	A	70	106 – 107	$C_{11}H_{15}NS_2$	Found: 58.45; 6.83; 6.20; – Calc.: 58.65; 6.71; 6.22; –
Ig	Me	4-$MeOC_6H_4$	A	100	129 – 130	$C_9H_{11}NOS_2$	Found: 50.45; 5.23; 6.53; 29.87 Calc.: 50.67; 5.20; 6.57; 30.06
Ih	Me	4-FC_6H_4	A	100	132 – 133	$C_8H_8NS_2F$	Found: 47.50; 4.04; 6.91; – Calc.: 47.74; 4.01; 6.96; –
Ii	Me	4-ClC_6H_4	B[8]	100	111 – 112	$C_8H_8NS_2Cl$	Found: 44.10; 3.75; 6.49; 29.93 Calc.: 44.13; 3.70; 6.43; 29.45
Ij	Me	4-BrC_6H_4	B	80	136 – 137	$C_8H_8NS_2Br$	Found: 36.61; 3.09; 5.36; 24.28 Calc.: 36.65; 3.08; 5.34; 24.46
Ik	Me	2-$NH_2C_6H_4$	C[12]	80	91 – 92	$C_8H_{10}N_2S_2$	Found: 48.25; 5.16; 14.14; – Calc.: 48.45; 5.08; 14.12; –
Il	Me	4-$NH_2C_6H_4$	C[12]	77	103 – 104	$C_8H_{10}N_2S_2$	Found: 48.05; 5.05; 13.94; 32.18 Calc.: 48.45; 5.08; 14.12; 32.34
Im	Me	4-$NHCOCH_2C_6H_4$	D	84	167 – 169	$C_{10}H_{12}N_2OS_2$	Found: 49.80; 5.00; 11.63; 26.80 Calc.: 49.97; 5.03; 11.66; 26.68

Table 1. Continued.

In	Me	$C_6H_5CH_2$	A[3,11]	37	47 – 48	$C_9H_{11}NS_2$	Found:	54.99;	5.70;	7.24;	–
							Calc.:	54.78;	5.62;	7.10;	–
Io	Me	$4\text{-}ClC_6H_4CH_2$	A	45	75 – 76	$C_9H_{10}NS_2Cl$	Found:	46.80;	4.45;	5.89;	27.52
							Calc.:	46.64;	4.35;	6.04;	27.67
Ip	Me	$2,3,4,5,6\text{-}F_5C_6$	A	100	131 – 132	$C_9H_4NS_2F_5$	Found:	35.04;	1.49;	5.09;	23.40
							Calc.:	35.16;	1.48;	5.13;	23.47
Iq	Me	$2\text{-}COOHC_6H_4$	–	50	149 – 150	$C_9H_9NO_2S_2$	Found:	47.39;	4.04;	6.05;	–
							Calc.:	47.55;	3.99;	6.16;	–
IIa	Et	C_6H_5	E	30	33 – 34	$C_9H_{11}NS_2$	Found:	54.96;	5.65;	7.16;	–
							Calc.:	54.78;	5.62;	7.10;	–
IIb	Et	$2\text{-}MeC_6H_4$	A	37	35 – 36	$C_{10}H_{13}NS_2$	Found:	57.04;	6.34;	6.66;	–
							Calc.:	56.83;	6.20;	6.63;	–
IIc	Et	$3\text{-}MeC_6H_4$	A	70	56 – 57	$C_{10}H_{13}NS_2$	Found:	56.80;	6.28;	6.60;	–
							Calc.:	56.83;	6.20;	6.63;	–
IId	Et	$4\text{-}MeC_6H_4$	A	62	61 – 62	$C_{10}H_{13}NS_2$	Found:	56.60;	6.26;	6.55;	30.07
							Calc.:	56.83;	6.20;	6.63;	30.34
IIe	Et	$2,4,6\text{-}Me_3C_6H_2$	A	100	51 – 52	$C_{12}H_{17}NS_2$	Found:	60.35;	7.16;	5.76;	26.64
							Calc.:	60.20;	7.16;	5.85;	26.79
IIf	Et	$4\text{-}MeOC_6H_4$	A	100	99 – 100	$C_{10}H_{13}NOS_2$	Found:	52.88;	5.88;	6.18;	28.09
							Calc.:	52.83;	5.76;	6.16;	28.21
IIIa	Pr^i	C_6H_5	A	47	77 – 78	$C_{10}H_{13}NS_2$	Found:	57.20;	6.37;	6.68;	–
							Calc.:	56.83;	6.20;	6.63;	–
IIIb	Pr^i	$2\text{-}MeC_6H_4$	A	76	53 – 54	$C_{11}H_{15}NS_2$	Found:	58.85;	6.75;	6.21;	28.59
							Calc.:	58.64;	6.71;	6.22;	28.46
IIIc	Pr^i	$3\text{-}MeC_6H_4$	A	75	50 – 51	$C_{11}H_{15}NS_2$	Found:	58.52;	6.70;	6.10;	–
							Calc.:	58.64;	6.71;	6.22;	–

Table 1. Continued.

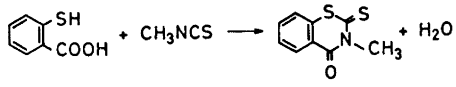
IIId	Pr^i	4-MeC_6H_4	A	55	54 – 55	$C_{11}H_{15}NS_2$	Found:	58.84;	6.71;	6.15;	–
							Calc.:	58.64;	6.71;	6.22;	–
IIIe	Pr^i	2,4,6-$Me_3C_6H_2$	A	36	65 – 66	$C_{13}H_{19}NS_2$	Found:	61.60;	7.62;	5.54;	–
							Calc.:	61.61;	7.56;	5.53;	–
IIIf	Pr^i	$C_6H_5CH_2$	A[11]	71	35 – 36	$C_{11}H_{15}NS_2$	Found:	58.55;	6.78;	6.21;	–
							Calc.:	58.64;	6.71;	6.22;	–
IVa	Bu^s	4-MeC_6H_4	A	63	34 – 35	$C_{12}H_{17}NS_2$	Found:	59.96;	7.21;	5.83;	–
							Calc.:	60.20;	7.16;	5.85;	–
Va	cyclohexyl	C_6H_5	A	100	87 – 88	$C_{13}H_{17}NS_2$	Found:	62.02;	6.88;	5.60;	25.59
							Calc.:	62.10;	6.82;	5.57;	25.51
Vb	cyclohexyl	3-MeC_6H_4	A	100	68 – 69	$C_{14}H_{19}NS_2$	Found:	63.50;	7.22;	5.25;	23.94
							Calc.:	63.35;	7.22;	5.28;	24.16
Vc	cyclohexyl	4-MeC_6H_4	A	50	50 – 60	$C_{14}H_{19}NS_2$	Found:	63.32;	7.30;	5.28;	–
							Calc.:	63.35;	7.22;	5.28;	–
VIa	Ph	C_6H_5	A	100	133 – 134	$C_{13}H_{11}NS_2$	Found:	63.30;	4.51;	5.61;	–
							Calc.:	63.64;	4.52;	5.71;	–
VIb	Ph	4-MeC_6H_4	A	60	151 – 152	$C_{14}H_{13}NS_2$	Found:	64.88;	5.17;	5.33;	–
							Calc.:	64.82;	5.05;	5.40;	–
VIc	Ph	4-ClC_6H_4	A	40	145 – 146	$C_{13}H_{10}NS_2Cl$	Found:	55.85;	3.67;	4.93;	–
							Calc.:	55.80;	3.60;	5.01;	–
VId	Ph	4-BrC_6H_4	A	100	137 – 138	$C_{13}H_{10}NS_2Br$	Found:	48.02;	3.20;	4.22;	–
							Calc.:	48.15;	3.11;	4.32;	–

within 6 months with benzenethiol, 4-methoxybenzenethiol, or phenylmethanethiol indicates that steric effects do have importance. One might object that the reason for these results was that the corresponding dithiocarbamates might be unstable at room temperature and fragment into thiol and isothiocyanate (see later), but as Wakamori *et al.*[11] have prepared benzyl *N-tert*-butyldithiocarbamate from the corresponding sodium salt and benzyl chloride and purified it by distillation (b.p. 130 – 133°C/0.04 mmHg), this possibility seems very unlikely.

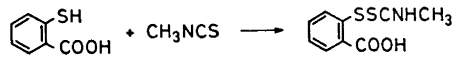
A part of the explanation may be the absence of solvent. This means that the surroundings of the reactants were different in the various experiments. As different reactants will differ in ability to solvate one another, the degree of freedom with which the molecules can "move around" differs far more in these experiments than in comparable series where both reactants are solvated with the same solvent. The rate at which crystallization occurs might in some cases be of importance to the time of reaction found, but infrared spectroscopy showed that in the reaction between methyl isothiocyanate and 2,4,6-trimethylbenzenethiol it was impossible to detect any trace of If after the mixture had been left for 1 month at room temperature. This suggests that the reaction does not just proceed slowly, but that other factors play a dominant role.

Some experiments were carried out with added solvent (ethanol), but in all cases the time of reaction was prolonged; *e.g.* the formation of Ia from methyl isothiocyanate and benzenethiol was not accomplished in 5 h when the reaction was performed in ethanol, compared to a reaction time of 2 h without the use of solvent.

The reaction between methyl isothiocyanate and 2- and 4-aminobenzenethiols was shown by Anthoni *et al.*[12] to give dithiocarbamates. It was concluded that the reactivity of the aromatic groups concerned towards the isothiocyanate function appears to decrease in the order $SH > NH_2 > OH$. As an extension of this investigation we examined the reaction of methyl isothiocyanate and 2-mercaptobenzoic acid. After prolonged standing of an ethanolic solution of the two compounds at room temperature, 3-methyl-2-thioxo-3,4-dihydro-2H-benzo[e]-1,3-thiazin-4-one was obtained.

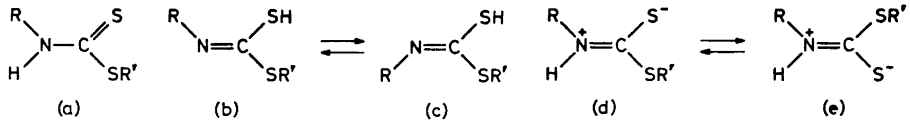


This product was earlier prepared from the same compounds + "cation exchange resin KU-2" [13] by reflux in toluene for 2 h. However, reducing the time of reaction to 1 week resulted in the formation of the expected 2-carboxyphenyl *N*-methyldithiocarbamate (Iq). The reactivity of the aromatic SH group towards isothiocyanates thus seems to exceed that of the COOH group.



Iq

In the ^{1}H-NMR spectrum of phenyl *N*-methyldithiocarbamate (Ia) (Table 2) the phenyl protons occurred as a singlet (5H) at $\tau = 2.43$ ppm, the NH proton gave a broad signal (1H) at $\tau = 2.5 - 3.3$ ppm and the methyl signal (3H) consisted of a doublet centered at $\tau = 6.87$ ppm ($J = 4.9$ Hz). After shaking the solution of Ia with deuterium oxide it produced a spectrum consisting of a singlet at $\tau = 2.43$ ppm and a singlet at $\tau = 6.87$ ppm (intensities 5:3). This shows that the doublet at $\tau = 6.87$ ppm arises from coupling with a labile hydrogen atom, so a structure like (a) seems most likely.



Accordingly nonequivalence of the methyl protons due to hindered rotation about a double bond as in the structures (b) and (c) is of no importance. This was also seen from the IR spectrum of the compound, which showed no absorption in the SH-stretching region but did show a NH-stretching absorption. Cooling the $CDCl_3$ solution of Ia to -40°C caused no change in the ^{1}H-NMR spectrum. Consequently hindered rotation about the CN bond caused by structures like (d) and (e) does not contribute in the temperature interval investigated. A similar investigation on IIIa, in which a greater tendency to hindered rotation could be expected, gave the same result.

In contrast to this behaviour, cooling of benzyl *N*-methyldithiocarbamate (In) produced a splitting of the doublet from the methyl signal into two doublets. Following the temperature dependence of the change in the methyl doublet showed that at 40°C there was one broad doublet, which on cooling showed a minor change in chemical shift ($\tau = 6.81$ to $\tau = 6.77$ ppm, $J = 4.8$ Hz) and at the same time became sharper and of lower intensity, while a new doublet appeared at $\tau = 6.95$ ppm, ($J = 5.3$ Hz). Simultaneously the singlet from the CH_2-group split up into two singlets. In the interval -15 to -40°C the integrals of the two doublets had a ratio of 2:1. A similar investigation of 4-chlorobenzyl *N*-methyldithiocarbamate (Io) yielded one doublet at 45°C and a ratio of 18:7 between the two doublets formed by cooling to -40°C. In IIIf it was not possible to detect any splitting of the methine signal on cooling, but at temperatures below 30°C there was a clear splitting of the methylene singlet, showing that a new singlet arises at *ca.* 4 Hz lower field. Simultaneously a faint change in the methyl signal could be detected (a new doublet appeared at a slightly higher field).

We therefore conclude that there definitely is hindered rotation about the CN bond in the benzyl compounds investigated, when the solutions are cooled. This hindrance may arise from structures like (d) and (e) which Holloway and Gitlitz found of importance for methyl *N*,*N*-dimethyldithiocarbamate.[14]

The absence of splitting in the low temperature spectra of the *S*-phenyl dithiocarbamates might result from (1) coincidence of chemical shift in the two forms (2) predominance of one form, *e.g.* (a) or (a′), to a high degree, or (3) a low barrier to rotation.

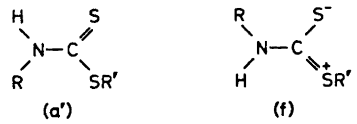
For some *N*,*N*-disubstituted carbamates [15] and for some thioamide derivatives [16] differences in barrier to internal rotation has been explained as arising from cross conjugation. In the present case the difference between the low

Table 2. Chemical shift[a] (τ, ppm) and coupling constants (J, Hz) of some aliphatic protons of *N*-monoalkyldithiocarbamates in $CDCl_3$ (5 % solution, 40°C). Multiplicity given in parentheses.

Compound	H^1	H^2	H^3	NH	J_{CH-NH}
$C_6H_5SCSNHCH_3^1$	6.87 (2)			2.5 – 3.3	4.9
o-$CH_3^2C_6H_4SCSNHCH_3^1$	6.87 (2)	7.53 (1)		3.1 – 3.8	5.0
m-$CH_3^2C_6H_4SCSNHCH_3^1$	6.86 (2)	7.58 (1)		2.8 – 3.5	5.0
p-$CH_3^2C_6H_4SCSNHCH_3^1$	6.87 (2)	7.57 (1)		3.0 – 4.0	5.0
p-$(CH_3^2)_3CC_6H_4SCSNHCH_3^1$	6.85 (2)	8.63 (1)		2.7 – 3.5	4.8
$2,^24,^36^2$-$(CH_3)_3C_6H_2SCSNHCH_3^{1c}$	6.89 (2)	7.60 (1)	7.67 (1)	3.1 – 3.6	4.8
p-$CH_3^2OC_6H_4SCSNHCH_3^1$	6.88 (2)	6.12 (1)		3.1 – 3.8	4.8
p-$FC_6H_4SCSNHCH_3^1$	6.82 (2)			3.0 – 4.0	4.9
p-$ClC_6H_4SCSNHCH_3^1$	6.83 (2)			2.7 – 3.9	5.0
p-$BrC_6H_4SCSNHCH_3^1$	6.84 (2)			2.8 – 3.8	5.0
o-$NH_2^2C_6H_4SCSNHCH_3^1$	6.88 (2)	5.5		3.0 – 3.5	4.9
p-$NH_2^2C_6H_4SCSNHCH_3^1$	6.90 (2)	5.9		3.0 – 3.5	4.8
p-$CH_3^2CONH^3C_6H_4SCSNHCH_3^{1b}$	7.01 (2)	7.92 (1)	– 0.13	0.8 – 1.2	4.8
$C_6H_5CH_2^2SCSNHCH_3^1$	6.78 (2)	5.44 (1)		2.7 – 4.3	4.5
p-$ClC_6H_4CH_2^2SCSNHCH_3^1$	6.77 (2)	5.47 (1)		2.7 – 2.8	4.5
$F_5C_6SCSNHCH_3^1$	6.75 (2)			2.5 – 3.0	4.8
o-$COOH^2C_6H_4SCSNHCH_3^{1b}$	6.99 (2)	0.3 – 0.8		2.0 – 2.6	4.5
$C_6H_5SCSNHCH_2^1CH_3^2$	6.33 (2 4)	9.80 (3)		3.0 – 4.0	5.2
o-$CH_3^3C_6H_4SCSNHCH_2^1CH_3^2$	6.32 (2 4)	8.90 (3)	7.55 (1)	3.1 – 4.1	5.2
m-$CH_3^3C_6H_4SCSNHCH_2^1CH_3^2$	6.32 (2 4)	8.87 (3)	7.57 (1)	3.0 – 4.0	5.3
p-$CH_3^3C_6H_4SCSNHCH_2^1CH_3^2$	6.32 (2 4)	8.90 (3)	7.58 (1)	2.9 – 3.9	5.2
$2^3,4,6^3$-$(CH_3)_3C_6H_2SCSNHCH_2^1CH_3^2$	6.37 (2 4)	8.92 (3)	7.60 (1)	3.0 – 3.6	5.2
p-$CH_3^3OC_6H_4SCSNHCH_2^1CH_3^2$	6.33 (2 4)	8.89 (3)	6.12 (1)	3.1 – 3.8	5.0
$C_6H_5SCSNHCH^1(CH_3^2)_2$	5.35 (2 7)	8.88 (2)		3.1 – 4.1	–
o-$CH_3^3C_6H_4SCSNHCH^1(CH_3^2)_2$	5.37 (2 7)	8.90 (2)	7.55 (1)	3.3 – 4.3	–
m-$CH_3^3C_6H_4SCSNHCH^1(CH_3^2)_2$	5.35 (2 7)	8.90 (2)	7.58 (1)	3.2 – 4.0	–
p-$CH_3^3C_6H_4SCSNHCH^1(CH_3^2)_2$	5.35 (2 7)	8.88 (2)	7.58 (1)	3.1 – 4.1	–
$2,4^3,6$-$(CH_3)_3C_6H_2SCSNHCH^1(CH_3^2)_2$	5.35 (2 7)	8.91 (2)	7.68 (1)	3.5 – 4.1	–
$C_6H_5CH_2^3SCSNHCH^1(CH_3^2)_2$	5.4 –	8.75 (2)	5.45 (1)	2.9 – 3.9	–
p-$CH_3^2C_6H_4SCSNHCH^1(CH_3)CH_2CH_3$	5.46 (2 6)	7.56 (1)		3.1 – 4.2	–
$C_6H_5SCSNHCH^1(CH_2)_5$	5.3 – 6.0			3.2 – 4.2	–
m-$CH_3^2C_6H_4SCSNHCH^1(CH_2)_5$	5.4 – 6.1	7.48 (1)		3.0 – 4.0	–
p-$CH_3^2C_6H_4SCSNHCH^1(CH_2)_5$	5.3 – 6.0	7.58 (1)		3.0 – 3.9	–
$C_6H_5SCSNHC_6H_5$				1.5 – 2.0	–
p-$CH_3^1C_6H_4SCSNHC_6H_5$	7.57 (1)			1.5 – 2.0	–
p-$ClC_6H_4SCSNHC_6H_5$				1.5 – 2.0	–

[a] The values given in the table are the centers of the multiplets.
[b] In $(CD_3)_2SO$ solution.
[c] Indices refer to the signals of the corresponding methyl groups.

temperature spectra of the *S*-benzyl and the *S*-phenyl compounds can be explained partly from cross conjugation. Thus it seems clear that a form like (f) will contribute more in the *S*-phenyl than in the *S*-benzyl compounds thus lowering the barrier to rotation about the CN bond in the former case.



In Table 2 the chemical shifts of the aromatic protons are omitted. They were all found in the region $\tau = 2.4$ to 2.7 ppm and showed the expected pattern. The chemical shift of the NH proton was significantly different in the *N*-alkyl and the *N*-aryl compounds ($\tau = 2.5$ to 2.0 and 2.0 to 1.5 ppm, respectively), a behaviour which can be explained from the difference in acidity of the NH proton in the two cases.

As mentioned above, dithiocarbamates dissociate on heating forming isothiocyanates and thiols. The dissociation could conveniently be followed by heating the solutions used for the NMR measurements in the probe and observing not only the change in intensity and chemical shift of the alkyl signal, but also the growth of the SH signal. For Ia the dissociation temperature was estimated for solutions in bromobenzene, deuteriobromoform, and pentadeuterionitrobenzene, and it was found that the temperature of beginning dissociation was independant of the solvent used. Pentadeuterionitrobenzene

Table 3. The temperature dependence of the equilibrium $RNHCSSR' \rightleftharpoons RNCS + R'SH$. The dithiocarbamates were dissolved in pentadeuterionitrobenzene.

Compound	Temp. °C for beginning dissociation [a]	Temp. °C for 50 % dissociation [a]
Ia	60	120
Ib	> 160	–
Ic	110	> 160
Id	135	> 160
Ie	> 160	–
Ig	> 160	–
Ih	140	160
Ii	120	155
Ij	60	120
Ik	100	140
Im	145	> 160
In	140	> 160
Ip	120	140
IIa	120	160
IIIa	145	> 160
IIIb	> 160	–
VIb	90	140

[a] ±10°C.

was used as the solvent in the following experiments. The temperatures for beginning and 50 % dissociation are given in Table 3 for some dithiocarbamates. The highest temperature at which experiments could be performed was 160°C. An attempt to correlate the dissociation temperatures for the ringsubstituted *S*-phenyldithiocarbamates with Hammet σ-values showed no regularity.

A more detailed investigation of the temperature dependence of the dissociation equilibrium was carried out for Ia. The equilibrium concentrations were estimated from the integrals of the rising SH signal at $\tau = 6.47$ ppm, the total dithiocarbamate methyl signal centered at $\tau = 6.82$ ppm, and a growing singlet from methyl isothiocyanate at $\tau = 6.87$ ppm. A 0.577 M solution in pentadeuterionitrobenzene was used. The compositions estimated and the K_c's calculated are given in Table 4. From the graph of log K_c against T^{-1} (Fig. 1) $\Delta H°$ was calculated as 77.6 kJ/mol for the dissociation of Ia.

Table 4. Equilibrium constants at different temperatures for the process Ia $\rightleftharpoons$ $CH_3NCS + C_6H_5SH$ in pentadeuterionitrobenzene solution.

Temp. K	% (Ia)	K_c mol/l	$T^{-1} \times 10^3$ K^{-1}	log K_c
373	71.6	6.48	2.68	0.8116
383	63.7	11.92	2.62	1.0762
393	53.8	22.85	2.54	1.3589
403	46.4	35.80	2.48	1.5539
413	37.2	66.00	2.42	1.8195
423	27.0	113.8	2.36	2.0561

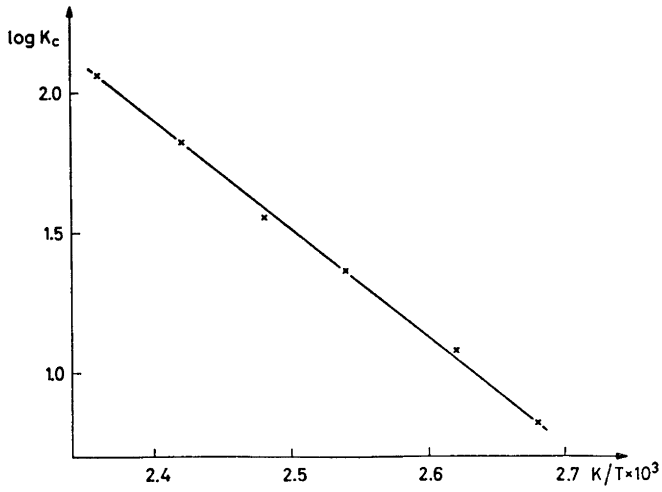


Fig. 1.

The mass spectra of Ia and methyl *N*-phenyldithiocarbamate have been studied in a paper by Thomson, Brown and Djerassi.[17] It was found that the spectra, apart from the molecular ions, could be interpreted as the spectra of the isothiocyanates superimposed on the spectra of the thiols. In the case of Ia a weak (0.2 % intensity relative to $\sum^{M}_{40}$) rearrangement peak corresponding to M – HNCS was observed. We have recorded the spectra of Ia, Ic, Id, Ie, Ii, In, and Va. With the exception of Ie and In the base peaks in the spectra corresponded to those of the thiols, and the spectra could be interpreted as mentioned above. The fragmentation pattern of Ie was analogous to previous findings, but the base peak was here found at *m/e* 151 ($C_9H_{11}S$), which corresponds to the loss of a methyl group from 4-*t*-butylbenzenethiol. In the spectrum of In $C_7H_7^+$ formed the base peak. An interesting deviation from the usual pattern is a peak corresponding to the loss of SH from the molecular ion (supported by a metastable ion at *m/e* 136.5).

In the paper by Thomson *et al.*[17] it was concluded that the absence of metastable ions for the fragmentation of the molecules into isothiocyanates and thiols indicated the possibility of a considerable amount of thermal dissociation taking place. We agree with this viewpoint when the temperature of the ion source is 200°C; however, since the results found by us are approximately identical using an ion source temp. of 70°C, this shows that the fragmentation routes due to electron impact are identical with the thermally induced ones, and that metastable ions for this fragmentation are not detected.

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of Chemical Laboratory II. Nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument with tetramethylsilane as internal reference. IR spectra were obtained on a Perkin Elmer model 137 grating spectrograph. The mass spectra were obtained using an AEI MS-902 mass spectrometer operating at 70 eV. The ion source temperature was kept at 70°C.

Methods of synthesis of the compounds listed in Table 1. The directions given below correspond to entries ("Method") in Table 1. *Method A.* Equimolar amounts of thiol and isothiocyanate were mixed without addition of solvent. After standing at room temperature (from 1 h to 2 months) colourless crystals were obtained. In most cases the compounds were analytically pure. Sometimes it was necessary to cool and scratch with a spatula to induce crystallization. When necessary the products were recrystallized by dissolving the compounds in benzene and precipitating them with pentane. *Method B.* Equimolar amounts (0.01 mol) of thiol and isothiocyanate were heated to form a homogenous melt. After standing for 1 – 2 weeks at room temperature, the crystallized material was recrystallized from benzene-pentane to give colourless crystals. *Method C.* Isothiocyanate (0.01 mol) and thiol (0.01 mol) were dissolved in ethanol (25 ml). The reaction mixture was allowed to stand for 24 h at room temperature and water was added dropwise to induce precipitation. By cooling and scratching crystallization was effected, and the product was finally recrystallized from a mixture of benzene and pentane. *Method D.* Methyl isothiocyanate (0.01 mol, 0.73 g) was added to a solution of 4-acetamidobenzenethiol (0.01 mol, 1.67 g) in ethanol (25 ml). After standing for 24 h crystals had separated from the solution. These were filtered off and washed with pentane. *Method E.* Ethyl isothiocyanate (0.01 mol, 0.87 g) was mixed with benzenethiol (0.01 mol, 1.10 g) without addition of solvent. After 24 h at room temperature the mixture was chilled, and scratching with a spatula afforded crystals which melted below room temperature. The oily product was dissolved in boiling ethanol and water and treated with active carbon. The hot solution was filtered and left overnight in a refrigerator. The yield was 30 % of colourless crystals with a m.p. of 33 – 34°C.

2,4,6-Trimethylbenzenethiol. This compound was prepared by the same method as described for the preparation of benzeneselenol.[18] The product obtained was a colourless liquid b.p. 58 – 62°C at 0.6 mmHg.[19] Yield 25 %.

3-Methyl-2-thioxo-3,4-dihydro-2H-benzo[e]-1,3-thiazin-4-one. Methyl isothiocyanate (0.01 mol, 0.73 g) and 2-mercaptobenzoic acid (0.01 mol, 1.54 g) were dissolved in ethanol (25 ml). After 1 month yellow crystals had separated. The crystals were filtered off and washed on the filter with acetone. On this treatment the crystals became colourless, and after washing with ether the material was analytically pure. M.p. 146 – 147°C.[13] The yield was 15 %. (Found: C 51.80; H 3.35; N 6.68. Calc. for $C_9H_7ONS_2$: C 51.65; H 3.37; N 6.69.) *IR-spectrum* (KBr, in cm^{-1}): 3062vw, 1790vs, 1595s, 1450s, 1418s, 1290vs, 1128m, 1098s, 1076s, 1005m, 948s, 790w, 745s, 685m, 572w, and 486w. *^1H NMR-spectrum* ($CDCl_3$): methyl signal at $\tau = 6.09$ ppm, a complex signal at $\tau = 1.7$ ppm (1 H) and a complex signal at $\tau = 2.34 - 2.90$ ppm (3 H).

2-Carboxyphenyl N-methyldithiocarbamate. Methyl isothiocyanate (0.01 mol, 0.73 g) and 2-mercaptobenzoic acid (0.01 mol, 1.54 g) were dissolved in ethanol. After 1 week at room temperature the solvent was evaporated *in vacuo* and the residue was recrystallized from ethanol. Yield 50 % of colourless crystals, mp. 149 – 150°C.

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