Organic Selenium Compounds. XIII.* Insertion Reactions of Methylenediamines with Carbon Diselenide

K. A. JENSEN and L. HENRIKSEN

Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

The formation of dialkylaminomethyl dialkyl-diselenocarbamates (III) from tetraalkylmethylenediamines and carbon diselenide is described. Compounds III are very rapidly hydrolyzed to give formaldehyde and dialkylammonium diselenocarbamates (IV), and in the presence of oxygen the latter undergo oxidation. The oxidation products, previously referred to as bis(selenocarbamoyl) triselenides, are tentatively assigned the structure of tetracoordinate bis(diselenocarbamato)selenium(II) compounds.

In the ^{1}H NMR spectra of III the N-alkyl groups become magnetically equivalent at unusually low temperature. The simultaneous disappearance of the ^{77}Se satellites in the $Se-CH_2$ signal indicates that the interchange of N-alkyl groups between diastereotopic positions in the dialkyldiselenocarbamate portion of compounds III occurs through an ion pair rather than by rotation around the R_2N-CSe_2 bond.
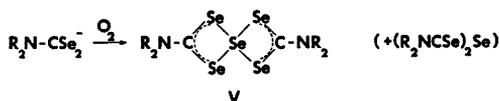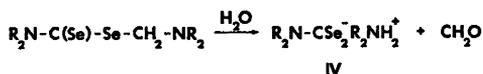
Kreutzkamp and Oei[1] have described the reaction of carbon disulfide with certain tetrasubstituted methylenediamines (I) which results in the formation of dialkylaminomethyl dialkyldithiocarbamates (II).

As a part of our studies of the reactivity of carbon diselenide we have investigated its reaction with some methylenediamines. We found that the reaction proceeded smoothly in dry hydrocarbon solvents, e.g. benzene or petroleum ether, to give dialkylaminomethyl dialkyldiselenocarbamates (III), the selenium analogues of II. However, under the reaction conditions used by Kreutzkamp and Oei

$R_2N-CH_2-NR_2+CY_2 \rightarrow$

I

$R_2N-CY-Y-CH_2-NR_2$

II: $Y=S$; III: $Y=Se$

a: $R=Me$
b: $R=Et$
c: $R,R=-(CH_2)_5-$
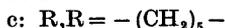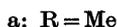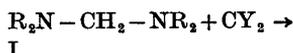
(ethanolic solution) we instead obtained dialkylammonium dialkyldiselenocarbamates (IV).

Chemical properties of compounds III. An investigation of the chemical properties of the compounds III showed that these are inert towards dry alcohols but, in contrast to their sulfur analogues, are easily hydrolyzed to give IV and formaldehyde. On addition of $NiCl_2.6H_2O$ to an ethanolic solution of an ester III a precipitate of the corresponding nickel(II) diselenocarbamate immediately separates. The hydrolysis is very rapid and may even be effected by the traces of water adsorbed on the walls of glass vessels or moisture from the air. When in contact with air, solutions of compounds IIIa−c smell of formaldehyde, and diselenocarbamate salts (IV) or compounds of type V eventually separate.

$$R_2N-C(Se)-Se-CH_2-NR_2 \xrightarrow{H_2O} R_2N-CSe_2^- R_2NH_2^+ + CH_2O$$

IV

$$R_2N-CSe_2^- \xrightarrow{O_2} R_2N-C \overset{Se}{\underset{Se}{<}} \overset{Se}{\underset{Se}{>}} C-NR_2 \quad (+(R_2NCSe)_2Se)$$

V

* Parts XII and XIV − XVII have been published: *Acta Chem. Scand.* 27 (1973) 3605; 24 (1970) 2055, 2061, 2065, 3213.

The latter, the conspicuous so-called bis-(selenocarbamoyl)triselenides, are formed by an oxidation of IV, as has previously been reported.[2-4] It is remarkable that the diseleno-carbamates differ from their thio analogues in that they on oxidation disproportionate into a mixture of mono- and triselenides whereas the latter exclusively give disulfides. We suggest that this difference can be ascribed to an extra stabilization of the triselenides by coordination of the central selenium atom to 4 atoms of selenium so that these compounds are actually bis(diselenocarbamato)selenium(II) compounds (formula V) rather than open-chain triselenides. This assumption has recently received support from an X-ray analysis of the oxidation product from pyrrolidinium 1-pyr-rolidinecarbodiselenoate.[5]

It was attempted to introduce a second molecule of carbon diselenide into the esters III, which still possess a basic nitrogen atom. However, such a reaction did not take place. The expected products, methylene bis(seleno-carbamates) (VI), which were readily prepared from IV and methylene bromide, were not observed. Instead the main products were compounds V together with higher molecular-weight substances with a high selenium content. Similar results were obtained when the tetra-alkylmethylenediamines (I) were reacted with 2 mol of carbon diselenide.

$$2R_2N - CSe_2^- + CH_2Br_2 \rightarrow$$
$$\begin{array}{ccc} R_2N - C - Se - CH_2 - Se - C - NR_2 \\ \parallel \qquad\qquad\qquad\qquad \parallel \\ Se \qquad\qquad\qquad\qquad Se \\ \quad\; VI \end{array}$$
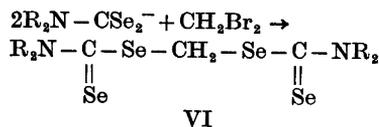
The formation of V in these reactions can be ascribed to hydrolysis of III to give diseleno-carbamate salts followed by air oxidation. The higher molecular-weight compounds formed have not been studied in detail, but they presumably correspond to the so-called CSe_2-polymers, the possible composition of which has been discussed previously.[6]

Structural considerations. Infrared and electronic spectra suggest that the products from I and carbon diselenide are normal, covalent diselenocarbamate esters in accordance with formula III. A comparison of the infrared spectra of the selenium compounds (III) and the corresponding sulfur compounds (II) showed

the expected shift in the 1000 cm^{-1} region towards lower wave numbers when sulfur was replaced by selenium.[7] The electronic spectra closely resemble those of other diselenocarba-mates.[8] The weak absorption band in the visible part of the spectrum, assigned to the $n - \pi^*$ transition,[8] manifests itself by a light yellow colour of the selenium compounds III, the sulfur compounds II being colourless.

However, the ^{1}H NMR spectra of the reaction products, recorded at room temperature, were not immediately consistent with structure III. Unexpectedly, the amide N-alkyl groups of IIIa $-$ c proved magnetically equivalent at room temperature, and the Se $-$ CH$_2$ signal showed no ^{77}Se satellites (neither could ^{77}Se
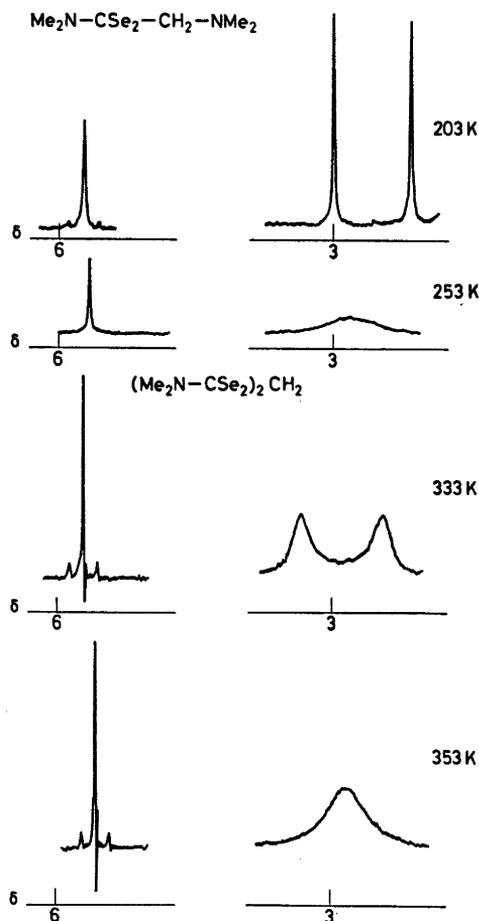

Fig. 1. Temperature dependent NMR spectra of compounds IIIa and VIa (solvent: toluene-d_8).

Table 1. Coalescence temperatures, T_C (K, ± 2).

Compound	Solvent Toluene-d_8			C_6D_5Br	$CDCl_3$
	$\Delta\nu$ (Hz)	T_C (K)	$\Delta G^{\ddagger}$ (kcal/mol)	T_C (K)	T_C (K)
IIa	30	303	15.1	283	243
IIIa	52	253	12.4	233	< 218[a]
VIIa	45	318	15.7		313
VIa	61	348	17.0		> 333[b]

[a] In CD_2Cl_2 coalescence was observed at ca. 193 K.   [b] The extent of exchange broadening suggests that coalescence will occur in the 343 – 348 K interval.

satellites be observed in the ^{13}C NMR spectrum of IIIa).

The latter fact implies that the CH_2 group cannot stay bonded to the same selenium atom all the time, and this observation prompted us to a closer investigation of the structure of compounds III.

The ^1H NMR spectra of IIIa and its thio analogue, IIa, were recorded as a function of temperature and solvent and compared to those of VIa and its thio analogue (VIIa), the latter two taken to represent the normal behaviour of diseleno- and dithiocarbamates.

Fig. 1 shows the temperature dependent spectra of IIIa and VIa (only amide – NCH_3 and $Se - CH_2$ signals shown) and demonstrates that the coalescence of the $N - CH_3$ signals of III is accompanied by the disappearance of the ^{77}Se satellites of the $Se - CH_2$ signal. In contrast to this behaviour these satellites in the spectrum of VIa are not affected by the interchange of the $N - CH_3$ groups.

The temperatures for coalescence of the amide – NCH_3 signals of IIa, IIIa, VIa, and VIIa in the solvents toluene-d_8, bromobenzene-d_5 and deuteriochloroform are recorded in Table 1.

An estimate of the barriers to exchange of methyl groups in toluene-d_8 was obtained by calculating $\Delta G^{\ddagger}$ at the coalescence temperature (T_C) using the relations $k_r = \pi/2^{\frac{1}{2}}\Delta\nu^{\circ}$ and $\Delta G^{\ddagger} = RT$ ln (kT_C/hk_r), where k_r is the reorientation rate constant.[9,10]

Similar calculations were not carried out for the solvents bromobenzene and chloroform since in many cases either T_C or the peak separation in the absence of exchange ($\Delta\nu^{\circ}$) could not be determined. However, it seems a safe estimate that the $\Delta G^{\ddagger}$ values for IIa

and IIIa both decrease by ca. 1 kcal/mol from toluene to bromobenzene and further by ca. 2 kcal/mol from bromobenzene to chloroform whereas VIa and VIIa show no significant difference between the barriers in toluene and chloroform.

The spectra of VIa and VIIa are consistent with the expected behaviour of normal diseleno- and dithiocarbamates, respectively. The ^{77}Se satellites in the spectrum of VIa are retained above the coalescence temperature in accordance with an exchange of N-methyl groups through rotation around the $C - N$ bond. The barrier for VIIa agrees very well with the value previously reported[11] for methyl N,N-dimethyldithiocarbamate (15.6 kcal/mol in o-dichlorobenzene). Likewise the lack of solvent sensitivity of both barriers is in accordance with previous reports on the rotational barriers for a number of thio- and selenoamide structures.[11-13]

Rotational barriers for diselenocarbamates have not previously been reported, but the value observed here for VIa suggests that this type of compound will normally conform to the general rule that a selenoamide structure displays a higher rotational barrier than its thio analogue.[13]

Apart from the disappearance of the ^{77}Se satellites simultaneosuly with the coalescence of the N-methyl signals in the spectrum of IIIa other anomalies are found in the spectra of IIa and IIIa. Firstly, IIIa displays a lower barrier to exchange of N-methyl groups than IIa, i.e. contrary to the usual trend. Secondly, both barriers are, contrary to those of VIa and VIIa, strongly solvent-dependent, the coalescence temperatures being lowered by an increase in solvent polarity. Thirdly, the

coalescence temperatures are lower than those of VIa and VIIa in all three solvents.

These results indicate that the energy barriers of compounds II and III are not barriers to rotation but rather barriers to transfer of the CH_2-NR_2 group from one Y atom (Y = S or Se) to the other. The solvent influence suggests an ion-pair mechanism for the exchange:
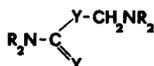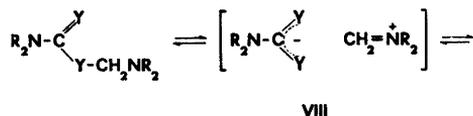
In the case of IIIa the disappearance of the [77]Se satellites furnishes direct evidence for the occurrence of a rearrangement reaction while for IIa such a process can only be inferred by analogy. However, we feel that in particular the fact that both exchange processes show the same solvent dependence, different from that found for VIa and VIIa, furnishes strong circumstantial evidence for an exchange by rearrangement also in the case of IIa. At least this appears to be the case in the more polar solvents, e.g. $CDCl_3$ ($\Delta T_{VIIa/IIa} = 70 °C$), whereas in toluene ($\Delta T = 15 °C$) the exchange might be effected by rotation as well.

In their tendency to undergo ionization II and III resemble the so-called N-(chloromethyl)-amines. N-(Chloromethyl)piperidine [14] is a solid, salt-like compound, insoluble in nonpolar solvents, and we found that its conductivity in acetonitrile or nitromethane solution amounts to ca. 20 % of that of a uni-univalent electrolyte. This would be in accordance with its formulation as N-methylenepiperidinium chloride, $C_5H_{10}N^+ = CH_2Cl^-$, the conductivity being diminished by strong ion-pair formation. It seemed possible that compounds II and III at higher temperatures might exist in a similar ionic structure, i.e. as methyleneiminium dithio- or diselenocarbamates, although they differ from the chloride in being readily soluble in non-polar solvents.

However, the conductivity of a freshly prepared solution of IIIc in acetonitrile was

almost zero. The conductivity of the solution increased somewhat with time, but this increase is due to hydrolysis by traces of water which it is almost impossible to exclude. The acetonitrile solution finally smelled of formaldehyde, and crystals of compound Vc separated.

The conductivity measurements show that compounds III are not ionic in the ground state. This conclusion is supported by the finding that they do not react with benzyl bromide to form benzyl diselenocarbamates. It must therefore be concluded that the structure VIII represents either an activated complex or a very unstable intermediate in the rearrangement reaction.

The fact that the barriers for the selenium compounds III are lower than for their thio analogues gives an explanation of their higher reactivity towards water. That the $Se-CH_2NR_2$ bond is more polar than the $S-CH_2NR_2$ bond is indicated by the CH_2 signal being found at lower field for the selenium compounds. For methylenepiperidinium chloride the CH_2 proton signal is as low as δ 8.4 (in CD_3NO_2).

For the sulfur compound IIa both methyl signals of the Me_2NCS group are shifted upfield when we shift from chloroform to chlorobenzene as the solvent, but the high field one is shifted most strongly (Table 2). For thioamides it has been found that substituents cis to C = S exhibit smaller shifts than trans substituents on dilution with benzene.[15,16] If this rule holds true also for the compounds discussed here the high field one of the nonequivalent N-methyl signals is due to the methyl group trans to C = S or C = Se.

Mechanism of the formation of compounds III. In the investigation of the chemical properties of III it was found that these compounds do not react with carbon diselenide to give VI although the dialkylaminomethyl nitrogen

Table 2. Solvent shift (δ values) of nonequivalent N-methyl signals at 233 K.

Compound	$CDCl_3$	C_6H_5Cl
IIa	3.64	3.19
	3.55	2.94
IIIa	3.69	3.22
		2.88

should be sufficiently basic to form a bond to carbon diselenide. On the basis of the result that a Se − Se′ rearrangement proceeds readily in III but not in VI we suggest that the formation of III from carbon diselenide and I proceeds by a primary addition to give the dipolar ion IX followed by rearrangement *via* a methyleneiminium intermediate (VIII):

$$R_2N - CH_2 - NR_2 + CSe_2 \rightarrow R_2N^+ - CH_2 - NR_2 \rightarrow$$
$$\underset{\overset{|}{CSe_2^-}}{}$$
$$IX$$

$$R_2NCSe_2^-CH_2 = NR_2^+ \rightarrow III$$
$$VIII$$

Even if the first step of the sequence could also take place from III and carbon diselenide, insertion of the latter would be blocked by the inability of the selenocarbamoylselenomethyl group to form a cation.

EXPERIMENTAL

Infrared spectra of KBr discs were recorded on a Perkin-Elmer model 337 grating spectrometer and visible spectra on a Unicam SP 800A instrument. The ^1H NMR spectra entered below were recorded at 40 °C on a Varian Model A-60A instrument with TMS as internal standard, and those used for the determination of coalescence temperatures (Table 1) on a Bruker WH-90 instrument.

Dimethylaminomethyl N,N-*dimethyldiselenocarbamate (IIIa)*. When a solution of carbon diselenide (0.85 g) in petroleum ether was added to a solution of N,N,N′,N′-tetramethylmethylene diamine (0.51 g) in petroleum ether a small amount of an oil separated after a few minutes. The solution was decanted from the oil and evaporated in vacuum. The residue was dissolved in 20 ml of pentane and the solution filtered and cooled at − 30 °C for 12 h. The compound separated as well-developed light yellow crystals. Yield 59 %. M.p. 48 − 49 °C. (Found: C 26.35; H 5.24; N 10.37. Calc. for $C_6H_{14}N_2Se_2$: C 26.44; H 5.20; N 10.36).

The corresponding sulfur compound (IIa) was prepared in a similar manner, using benzene as solvent and heating the solution at 40 °C for 15 min. The benzene was removed in vacuum and the residue dissolved in pentane. On cooling the compound separated as colourless crystals. Yield 56 %. M.p. 39 − 41 °C. (Found: C 40.44; H 7.92; N 15.72. Calc. for $C_6H_{14}N_2S_2$: C 40.68; H 7.80; N 16.07).

The main difference between the infrared spectra of II and IIa is found below 1000 cm⁻¹, where strong bands at 980 and 600 cm⁻¹ in

the spectrum of the sulfur compound are replaced by strong bands at 860, 530, and 495 cm⁻¹ in the spectrum of the selenium compound. However, there is also a characteristic difference in the 1200 cm⁻¹ region where a doublet at 1240 and 1260 cm⁻¹ in the spectrum of IIa is shifted to 1222 and 1196 cm⁻¹ in the spectrum of II. A pronounced difference in this region between corresponding sulfur and selenium compounds is only observed when the CS_2 and CSe_2 groups are bound to light groups, such as the methyl group in dithioacetates and diselenoacetates.[14]
^1H NMR spectra. IIIa $(CDCl_3)$: δ 2.36 (s, 6 H); 3.58 (s, 6 H); 5.58 (s, 2 H); (C_6D_6): 2.34; 2.27; 5.70. IIa $(CDCl_3)$: δ 2.34 (s, 6 H); 3.50 (s, 6 H); 5.15 (s, 2 H).

Diethylaminomethyl N,N-*diethyldiselenocarbamate (IIIb)*. When a solution of carbon diselenide (0.85 g) in pentane (5 ml) was added to a solution of N,N,N′,N′-tetraethylmethylenediamine (0.80 g) in pentane (5 ml) an exothermic reaction took place. On cooling a yellowish precipitate separated. This was identified as diethylammonium diethyldiselenocarbamate. The filtrate left on evaporation a yellow oil which decomposed on attempts at purification. However, the crude product gave acceptable analyses and spectra for the expected compound. (Found: C 37.55; H 7.02; N 8.37. Calc. for $C_{10}H_{22}N_2Se_2$: C 36.85; H 6.74; N 8.51). ^1H NMR spectrum $(CDCl_3)$: δ 1.12 (t, 6 H); 1.32 (t, 6 H); 2.67 (q, 4 H); 4.02 (q, 4 H); 5.55 (s, 2 H).

The compound is extremely sensitive to humidity. A pentane solution soon smells of formaldehyde and on standing deposits a reddish precipitate of the "triselenide" (Vb).

Se-Piperidinomethyl *piperidine-1-carbodiselenoate (IIIc)*. Carbon diselenide (0.85 g) dissolved in petroleum ether (5 ml) was added to a solution of 1,1′-methylenediperidine (0.79 g) in petroleum ether (5 ml). On standing light yellow crystals separated. Yield 1.42 g (88 %). M.p. 93 − 94 °C (recryst. from pentane). (Found: C 40.92; H 6.33; N 7.96; Se 44.70. Calc. for $C_{12}H_{22}N_2Se_2$: C 40.92; H 6.29; N 7.95; Se 44.83).

The corresponding sulfur compound (IIc), prepared in ethanolic solution, formed colourless crystals with m.p. 60 °C in accordance with Ref. 1.

In contrast to the selenium compound (IIIc) which in ethanolic solution rapidly forms the "triselenide" Vc, the sulfur compound is quite stable in this solvent. However, on standing of an ethanolic solution of IIc for 6 months crystals with m.p. 130 °C separated. These were identified as bis(pentamethylene)thiuram disulfide.

The main differences between the infrared spectra of IIIc and IIc is the replacement of strong bands at 975, 890, 640, and 575 cm⁻¹ in the spectrum of the sulfur compound by strong bands at 825, 782, 490, and 420 cm⁻¹ in the spectrum of the selenium compound.

Electronic spectra. λ_{max} nm (log ε): IIIc, 274 (4.24), 327 (4.00), 394 (2.59); IIc, 216 (3.88), 262 (3.72), 290 (3.66). ^{1}H NMR spectra (in CDCl$_3$). IIIc: broad, unresolved signals at δ 1.5 – 1.7 (12 H), 2.5 – 2.7 (4 H), and 4.2 – 4.3 (4 H), sharp singlet at δ 5.62 (2 H). IIc: similar signals at δ 1.5 – 1.7 (12 H), 2.5 – 2.7 (4 H), 4.1 – 4.3 (4 H), and 5.25 (s, 2 H).

Bis(1-piperidinecarbodiselenoato)selenium(II) (compound Vc). Carbon diselenide (1 mmol) in benzene (10 ml) was added dropwise to a stirred solution of 1,1'-methylenedipiperidine (0.5 mmol) in benzene (10 ml). The solution was first yellow but the colour changed to red when half of the carbon diselenide had been added. On standing in a refrigerator for 12 h a yellow precipitate had formed. This was filtered off, and pentane was added, which again gave a precipitate and a solution from which 45 % of pure IIIc could be isolated. Treatment of the precipitates with methylene chloride yielded a slight amount of insoluble, apparently high-polymeric material, some less soluble fractions with *ca.* 14 % C, and some more soluble fractions with *ca.* 24 % C. The latter had almost identical infrared spectra and were purified by dissolution in methylene chloride, filtration through Al$_2$O$_3$, and precipitation with hexane. The resulting reddish powder with m.p. 190 – 191 °C had the composition C$_{12}$H$_{20}$N$_2$Se$_5$. (Found: C 24.76; H 3.42; N 4.90. Calc.: C 24.55; H 3.43; N 4.77). The infrared spectrum of this product proved to be identical with that of a product prepared earlier by oxidation of piperidinium 1-piperidinecarbodiselenoate.

The reaction between IIIc and carbon diselenide in benzene gave a similar result: along with unchanged IIIc the main product was compound Vc, a part of which separated from the benzene solution as well-developed red crystals.

Methylene bis(N,N-dimethyldiselenocarbamate (VIa). Dimethylammonium dimethylselenocarbamate was prepared by leading gaseous dimethylamine into a solution of carbon diselenide (0.85 g) in petroleum ether (50 ml). The crystalline precipitate (1.2 g) was suspended in methylene chloride (150 ml) and 1 g of methylene bromide was added. The mixture was heated to boiling for 5 min, cooled, washed with water and dried. The residue obtained by evaporation of the solution was dissolved in 10 ml of boiling toluene and the hot solution was filtered through Al$_2$O$_3$ (W-200 neutral). On addition of petroleum ether to the filtrate a reddish precipitate was obtained. This was dissolved in the minimum amount of hot toluene and the solution was freed from a red insoluble substance by centrifugation. On addition of pentane and cooling in ice yellow crystals separated (113 mg). M.p. 165 – 167 °C. (Found: C 19.05; H 3.31; N 6.20. Calc. for C$_7$H$_{14}$N$_2$Se$_4$: C 19.06; H 3.19; N 6.34). ^{1}H NMR (CDCl$_3$): δ 3.37 (s, 6 H); 3.68 (s, 6 H); 5.42

(s, 2 H; satellites 2 Se, J (^{77}Se – H) = 18 Hz).

Methylene bis-(1-piperidinecarbodiselenoate) (VIc). Carbon diselenide (10 mmol) in petroleum ether (50 ml) was added to piperidine (20 mmol) in the same solvent at room temperature. The resulting piperidinium 1-piperidinecarbodiselenoate (3.4 g) was dissolved in methylene chloride and methylene bromide (2 g) was added. The mixture was heated until it just boiled and left at room temperature for 1 h. Then hexane (30 ml) was added and the precipitated product was filtered off, washed thoroughly with water to remove piperidinium bromide, dried, and recrystallized from toluene. Yield 2.08 g (80 %). M.p. 200 – 201 °C. (Found: C 29.78; H 4.16; N 5.29. Calc. for C$_{13}$H$_{22}$N$_2$Se$_4$: C 29.89; H 4.21; N 5.36).

^{1}H NMR spectrum (CDCl$_3$): broad, unresolved signals at δ 1.75 (12 H); 3.80 (4 H); and 4.44 (4 H); sharp singlet at 5.51 (2 H; satellites 2 Se; J (^{77}Se – H) = 19 Hz).

Methylene bis(N,N-dimethyldithiocarbamate) (VIIa). Dimethylammonium dimethyldithiocarbamate was prepared from dimethylamine (50 mmol) dissolved in petroleum ether (200 ml) and carbon disulfide (25 mmol). The precipitate was filtered off and immediately dissolved in methylene chloride (40 ml). Methylene iodide (25 mmol) was added and the solution was left at room temperature for 4 h. The reaction mixture was washed with water and evaporated to dryness. The residue was recrystallized from toluene-petroleum ether to give 2.7 g (68 %) of VIIa. (Found: C 33.25; H 5.75; N 11.07. Calc. for C$_7$H$_{14}$N$_2$S$_4$: C 33.07; H 5.51; N 11.02).

^{1}H NMR spectrum (CDCl$_3$; 33 °C): singlet at δ = 5.35 (2 H), broad signal with two peaks at δ 3.39 and 3.50 (12 H). Coalescence temperature 40 °C, see Table 1.

N-*Methylenepiperidinium chloride* was prepared from 1,1'-methylenedipiperidine and acetyl chloride.[14]

^{1}H NMR spectrum (CD$_3$NO$_2$): broad signals at δ 1.92 (6 H) and δ 4.18 (4 H), singlet at δ 8.40 (*ca.* 2 H).

Molar conductivity (25 °C; *c* 0.1 – 0.01 mol/l): 13.8 S cm^2 mol^{-1} in nitromethane and 34 S cm^2 mol^{-1} in acetonitrile. According to the values found for the conductivity of uni-univalent electrolytes in nitromethane[18] and acetonitrile,[19] the chloro compound is 15 – 20 % dissociated under these conditions. Its physical properties and the presence of only one CH$_2$ signal in the NMR spectrum suggest that the undissociated molecules are ion pairs rather than molecules with covalently bound chlorine.

Diethylmethyleneiminium chloride was prepared from N,N,N',N'-tetraethylmethylenediamine and benzoyl chloride.[14]

^{1}H NMR spectrum (CDCl$_3$): δ 1.49 (t, 6 H), 3.95 (q, 4 H), and 8.55 (s, 2 H), unchanged after 24 h.

Molar conductivity in acetonitrile (25 °C; *c* 0.008 mol/l): 41.2 S cm^2 mol^{-1}. The conductivity diminished with time and after 24 h

reached the value 14.9 S cm² mol⁻¹, corresponding to complete hydrolysis to diethylammonium chloride, which was found to have this conductivity under the same conditions.

REFERENCES

1. Kreutzkamp, N. and Oei, H. Y. *Arch. Pharm. 299* (1966) 906. ℤ
2. Barnard, D. and Woodbridge, D. T. *J. Chem. Soc.* (1961) 2922.
3. Rosenbaum, A., Kirchberg, H. and Leibnitz, E. *J. Prakt. Chem. [4] 19* (1963) 1.
4. Rosenbaum, A. *J. Prakt. Chem. [4] 37* (1968) 200.
5. Husebye, S. *Personal communication.*
6. Henriksen, L. *Int. J. Sulfur Chem. 8* (1973) 389.
7. Jensen, K. A., Henriksen, L. and Nielsen, P. H. In Klayman, D. L. and Günther, W. H. H., Eds., *Organic Selenium Compounds*, Wiley-Interscience, New York 1973, pp. 846 – 848.
8. Shankaranarayana, M. L. *Acta Chem. Scand. 24* (1970) 2065.
9. Gutowsky, H. S. and Holm, C. H. *J. Chem. Phys. 25* (1956) 1228.
10. Frost, A. A. and Pearson, R. G. *Kinetics and Mechanism*, 2nd. Ed., Wiley, New York 1961, p. 98.
11. Sandström, J. *J. Phys. Chem. 71* (1967) 2318.
12. Lidén, A. and Sandström, J. *Acta Chem. Scand. 27* (1973) 2567.
13. Jensen, K. A. and Sandström, J. *Acta Chem. Scand. 23* (1969) 1911.
14. Böhme, H. and Hartke, K. *Chem. Ber. 93* (1960) 1305.
15. Walter, W., Schaumann, E. and Paulsen, H. *Justus Liebigs Ann. Chem. 727* (1969) 61.
16. Sandström, J. and Uppström, B. *Acta Chem. Scand. 21* (1967) 2254.
17. Jensen, K. A. *Ann. N.Y. Acad. Sci. 192* (1972) 115.
18. Gill, N. S. and Nyholm, R. S. *J. Chem. Soc.* (1959) 3997.
19. Popov, A. I. and Skelly, N. E. *J. Amer. Chem. Soc. 76* (1954) 5309.