

## Organic Selenium Compounds

### XVII.\* Reactions of Carbon Diselenide with Active Methylene Compounds

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The reactions of carbon diselenide with active methylene compounds have been studied in order to compare the corresponding sulfur and selenium compounds. The primary products, the 1,1-diselenolates, have been transformed into *Se,Se'*-dialkyl derivatives (Table 1), diselenolans (Table 2), and diselenans (Table 3). A comparison of the infrared spectra of corresponding sulfur and selenium compounds allows an assignment of absorptions to which C-Se stretching vibrations contribute.

In 1963-64 we started an investigation of the reactions between carbon diselenide and active methylene compounds. The attempts to prepare defined selenium compounds met with success only in the case of malononitrile, and, after numerous unsuccessful attempts to prepare selenium derivatives from other active methylene compounds, we decided to study this type of reaction in more detail, using the more accessible carbon disulfide for the pilot experiments. This work has resulted in a rather extensive paper<sup>1</sup> on the reactions of carbon disulfide with active methylene compounds, and this should be consulted for a comparison with the results with carbon diselenide described in this paper.

On the basis of our experiences with the sulfur compounds we were, in most cases, able to prepare the analogous selenium compounds. Thus, CH-acidic compounds covering the *pK*-range 8-*ca.* 20, *viz.* malonic esters, ethyl cyanoacetate, malononitrile, ethyl acetoacetate, benzyl cyanide, acetophenone, 3-methyl-1-phenyl-5-pyrazolone, and fluorene could be transformed into 1,1-diselenolates which subsequently, by reactions with alkyl halides, were transformed into 1,1-bis(alkylseleno)methylene compounds or, with 1,2-dibromoethane and 1,3-dibromopropane, into 1,3-diselenolans and 1,3-diselenans, respectively. As in the case of the sulfur compounds, cyanamide

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closely resembled the CH-acidic compounds in its reactivity. The reaction with carbon diselenide gave rise to cyanimidodiselenocarbonates.

The conditions for carrying out reactions with carbon diselenide are more critical than for the analogous reactions with carbon disulfide, and the crucial point is the choice of both the solvent and the base. The following conclusions concerning solvent-base systems are based upon the observations that carbon diselenide is more reactive and correspondingly less selective towards bases than carbon disulfide. The 1,1-diselenolates and their *Se*-alkylated derivatives also show an increased sensitivity towards bases compared to their respective sulfur analogues.

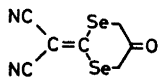
The use of hydroxylic solvents is limited to the preparations of the strongly stabilized 1,1-diselenolates. In these cases the methylene compound, *e.g.* malononitrile, is sufficiently acidic to ensure a very low concentration of the lyate ion. At the same time the diselenolate is almost non-basic. In aprotic solvents the nature of the base has a marked influence. The soluble base sodium 2-methyl-2-butanolate may be used in nonpolar solvents, *e.g.* ether or toluene, at low temperature only when the methylene compound is sufficiently acidic to ensure a virtually complete consumption of this base prior to the addition of carbon diselenide. Sodium hydride effectively converts even very weak CH-acids into carbanions and has, at the same time, a very low reactivity towards carbon diselenide. This base is therefore well suited for these reactions. However, the reaction of sodium hydride with CH-acids is, except when these are rather strong ( $pK < 12$ ), very slow in non-polar solvents. Addition of a cation solvating component, *e.g.* di(2-methoxyethyl) ether (diglyme), gives satisfactory reaction rates, and such a system may be used for the reactions. However, in accordance with the results obtained with carbon disulfide, the best results were obtained in dipolar aprotic solvents. Of these we preferred dimethyl sulfoxide (DMSO) as the reaction medium. A few experiments, carried out in hexamethyl phosphoric triamide (HMP), gave results similar to those obtained in DMSO, indicating that this solvent might equally well be used. Dimethyl formamide (DMF) was discarded as a solvent for these reactions because it was found, in the investigation of the reactions with carbon disulfide, that DMF in the presence of sodium hydride reacted to give *N,N*-dimethyldithiocarbamates. However, DMF could often be used with advantage as a solvent for pre-prepared diselenolates. DMSO is not an ideal solvent either, because its melting point (18°C) precludes its use at low temperature.

In most cases the expected selenium compounds could be isolated, but the yields were generally lower than for the analogous sulfur compounds and in some cases extremely low (see Tables 1–3); part of the reason for this is that the reaction products are often difficult to purify. However, although the use of chromatographic separation methods gave definitely improved yields of the pure materials, these were still considerably lower than those of the sulfur analogues. Therefore, the main reason is that with the increased reactivity of carbon diselenide, as well as the 1,1-diselenolates and their *Se*-alkylated derivatives, side processes become more predominant in all stages of the reaction. It should be pointed out that apart from the higher reactivity towards

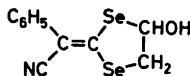


of oxygen. This, as well as the fact that the selenolates are stable in DMSO solution, indicates that these compounds are not easily oxidized. However, a nitrogen atmosphere is, in some cases, needed in order to exclude moisture.

In the sulfur series 1,3-dithiolanols, 1,3-dithiolanones, and 1,3-dithianones were obtained by reactions of 1,1-dithiolates with  $\alpha$ -haloaldehydes,  $\alpha$ -halocarboxylic acids, and  $\alpha$ -haloketones. With progargyl bromide either a 4-methylene-1,3-dithiolan or the isomeric 4-methyl-1,3-dithiole could be obtained. Dithiolanols could be transformed into dithioles, and dithiolanones into thiophene or thiazole derivatives (for details see Ref. 1). In the present investigation the main efforts were directed towards the determination of the reaction conditions giving optimal yields of the 1,1-diselenolates and their derivatives. Therefore, our attention was focused upon the standard derivatives listed in Tables 1–3. The preparations of a 1,3-diselenolan-4-ol (XXXVI) and a 1,3-diselenan-5-one (XXXV) in satisfactory yields serve, however, as examples to indicate that it is, in principle, possible to prepare such compounds. Therefore the experiments in this direction are being continued, especially with a view to the potential formation of selenophenes and selenazoles, and the study of *cis,trans*-isomeric forms.



XXXV



XXXVI

#### INFRARED SPECTRA

A comparison of the infrared spectra of the selenium compounds described here with those of the corresponding sulfur compounds<sup>1</sup> allows an identification of infrared absorption bands which are due, more or less, to vibrations of sulfur- and selenium containing groups.

The very strong bands ascribed<sup>1</sup> mainly to the C=C or C=N double bond are found at essentially the same wavenumbers in the spectra of corresponding sulfur and selenium compounds, *i.e.* with a few exceptions between 1440 and 1530  $\text{cm}^{-1}$ . The derivatives of ethyl acetoacetate absorb at lower wavenumbers (*ca.* 1400  $\text{cm}^{-1}$ ) and for the ionic salts of 1,1-dithiols and 1,1-diselenols this band is found near 1300  $\text{cm}^{-1}$ . It often occurs at 5–10  $\text{cm}^{-1}$  lower wavenumbers for the selenium compounds than for the corresponding sulfur compounds; however, for the ionic diselenolates it is found at higher wavenumbers (*cf.* Table 4).

In the case of the selenium compounds the bands due to CN or CO groups are, if at all, usually only shifted a few  $\text{cm}^{-1}$  towards lower frequencies. How-

Table 1. *Se*, *Se'*-Dialkyl derivatives of 1,1-diselenols.

No.	R	Formula	Yield %	M.p. °C	Analyses
I	$(\text{CH}_3\text{Se})_2\text{C}=\text{C}(\text{CO}_2\text{CH}_3)_2$	$\text{C}_6\text{H}_{12}\text{O}_4\text{Se}_2$	43	78–79	Found: C 29.20; H 3.85; Se 47.38 Calc.: C 29.11; H 3.66; Se 47.84
II	$(\text{C}_6\text{H}_5\text{CH}_2\text{Se})_2\text{C}=\text{C}(\text{CO}_2\text{CH}_3)_2$	$\text{C}_{20}\text{H}_{20}\text{O}_4\text{Se}_2$	54	81–82	Found: C 49.91; H 4.33; Se 32.68 Calc.: C 49.81; H 4.18; Se 32.74
III	$(\text{CH}_3\text{Se})_2\text{C}=\text{C}(\text{CN})\text{CO}_2\text{C}_2\text{H}_5$	$\text{C}_8\text{H}_{11}\text{NO}_2\text{Se}_2$	16	72–74	Found: C 30.94; H 3.53; N 4.65; Se 50.75 Calc.: C 30.89; H 3.56; N 4.50; Se 50.76
IV	$(\text{C}_6\text{H}_5\text{CH}_2\text{Se})_2\text{C}=\text{C}(\text{CN})(\text{CO}_2\text{C}_2\text{H}_5)$	$\text{C}_{20}\text{H}_{19}\text{NO}_2\text{Se}_2$	28	109–110	Found: C 51.92; H 4.27; N 3.24; Se 34.50 Calc.: C 51.85; H 4.13; N 3.02; Se 34.08
V	$(\text{CH}_3\text{Se})_2\text{C}=\text{C}(\text{CN})_2$	$\text{C}_6\text{H}_6\text{N}_2\text{Se}_2$	57	61–62	Found: C 27.44; H 2.20; Se 59.40 Calc.: C 27.30; H 2.29; Se 59.80
VI	$(\text{C}_6\text{H}_5\text{CH}_2\text{Se})_2\text{C}=\text{C}(\text{CN})_2$	$\text{C}_{18}\text{H}_{14}\text{N}_2\text{Se}_2$	30	79–80	Found: C 52.00; H 3.47; N 6.67 Calc.: C 51.92; H 3.37; N 6.73
VII	$(\text{CH}_3\text{Se})_2\text{C}=\text{C}(\text{CN})\text{C}_6\text{H}_5$	$\text{C}_{11}\text{H}_{11}\text{NSe}_2$	37	29–32	Found: C 41.79; H 3.35; N 4.50 Calc.: C 41.93; H 3.52; N 4.45

Table 1. Continued.

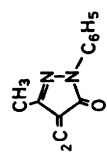
No.	R	Formula	Yield %	M.p. °C	Analyses
VIII	$(C_4H_5CH_2Se)_2C=C(CN)C_6H_5$	$C_{22}H_{19}NSe_2$	60	75-77	Found: C 59.25; H 4.32; N 3.16 Calc.: C 59.11; H 4.10; N 3.00
IX	$(C_6H_5CH_2Se)_2C=C(COCH_3)(CO_2C_2H_5)$	$C_{21}H_{22}O_2Se_2$	11	95-97	Found: C 52.35; H 4.66; Se 32.98 Calc.: C 52.50; H 4.58; Se 32.92
X	$(C_6H_5CH_2Se)_2C=CH(COC_6H_5)$	$C_{23}H_{20}OSe_2$	25	134-135	Found: C 58.77; H 4.50; Se 33.49 Calc.: C 58.73; H 4.29; Se 33.60
XI	$(CH_3Se)_2C=C_{13}H_9$ ( $C_{13}H_9$ : 9-fluorenylidene)	$C_{16}H_{14}Se_2$	13	95-96	Found: C 52.60; H 3.94; Se 43.05 Calc.: C 52.72; H 3.87; Se 43.36
XII	$(C_6H_5CH_2Se)_2C=C_{13}H_8$	$C_{23}H_{22}Se_2$	28	109-111	Found: C 64.90; H 4.53; Se 30.54 Calc.: C 65.13; H 4.29; Se 30.58
XIII	$(C_6H_5CH_2Se)_2C=C$ 	$C_{75}H_{22}N_2OSe_2$	38	134-135 (plates) 125-126 (needles)	Found: C 57.42; H 4.64; N 5.38; Se 30.38 Calc.: C 57.26; H 4.20; N 5.34; Se 30.15
XIV	$(CH_3Se)_2C=N-CN$	$C_4H_4N_2Se_2$	39	42-43	Found: C 19.94; H 2.55; N 11.66 Calc.: C 20.00; H 2.54; N 11.67
XV	$(C_6H_5CH_2Se)_2C=N-CN$	$C_{16}H_{14}N_2Se_2$	55	85-86	Found: C 48.93; H 3.69; N 7.23 Calc.: C 48.98; H 3.57; N 7.14

Table 2. 1,3-Diselenolans,  $\begin{matrix} \text{Se} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Se} \end{matrix} \text{R}$ , prepared from diselenolates and 1,2-dibromoethane.

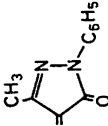
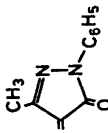
No.	R	Formula	Yield, %		M.p. °C	Analyses
			DMSO	DMF		
XVI	$=\text{C}(\text{CN})(\text{CO}_2\text{C}_2\text{H}_5)$	$\text{C}_6\text{H}_8\text{NO}_2\text{Se}_2$	21	36	111—113	Found: C 31.41; H 3.06; N 4.51 Calc.: C 31.09; H 2.94; N 4.53
XVII	$=\text{C}(\text{CO}_2\text{CH}_3)_2$	$\text{C}_8\text{H}_{10}\text{O}_4\text{Se}_2$	33		101—103	Found: C 29.61; H 3.28; Se 47.92 Calc.: C 29.29; H 3.02; Se 48.13
XVIII	$=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$	$\text{C}_{10}\text{H}_{14}\text{O}_4\text{Se}_2$		10	60—60.5	Found: C 34.03; H 3.95; Se 44.33 Calc.: C 33.72; H 3.93; Se 44.39
XIX	$=\text{C}(\text{CN})_2$	$\text{C}_6\text{H}_4\text{N}_2\text{Se}_2$	44		205—206	Found: C 27.75; H 1.61; Se 60.45 Calc.: C 27.53; H 1.54; Se 60.20
XX	$=\text{C}(\text{COCH}_3)(\text{CO}_2\text{C}_2\text{H}_5)$	$\text{C}_9\text{H}_{12}\text{O}_3\text{Se}_2$		12	70—72	Found: C 33.33; H 3.59; Se 48.50 Calc.: C 33.15; H 3.71; Se 48.42
XXI	$=\text{C}(\text{CN})(\text{C}_6\text{H}_5)$	$\text{C}_{11}\text{H}_9\text{NSe}_2$	30		71—73	Found: C 42.09; H 2.94; N 4.71; Se 50.17 Calc.: C 42.20; H 2.90; N 4.47; Se 50.43
XXII		$\text{C}_{13}\text{H}_{12}\text{N}_2\text{OSe}_2$	16		214—216	Found: C 42.59; H 3.70; N 7.82; Se 43.00 Calc.: C 42.18; H 3.27; N 7.57; Se 42.66
XXIII	9-Fluorenylidene	$\text{C}_{16}\text{H}_{12}\text{Se}_2$	11		123—124	Found: C 52.90; H 3.30; Se 43.53 Calc.: C 53.05; H 3.34; Se 43.60
XXIV	$=\text{N}-\text{CN}$	$\text{C}_4\text{H}_4\text{N}_2\text{Se}_2$	11	52	80—80.5	Found: C 20.58; H 1.78; N 11.84 Calc.: C 20.17; H 1.68; N 11.76

Table 3. 1,3-Diselenans,  $\begin{matrix} \text{Se} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Se} \end{matrix} \text{R}$ , prepared from diselenolates and 1,3-dibromopropane.

No.	R	Formula	Yield, %		M.p., °C	Analyses
			DMSO	DMF		
XXV	=C(CN) (CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> )	C <sub>9</sub> H <sub>11</sub> NO <sub>2</sub> Se <sub>2</sub>	15	40	107–108	Found: C 33.49; H 3.49; N 4.28 Calc.: C 33.46; H 3.44; N 4.33
XXVI	=C(CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	C <sub>9</sub> H <sub>11</sub> O <sub>4</sub> Se <sub>2</sub>		52	59–61	Found: C 31.76; H 3.57; Se 46.63 Calc.: C 31.58; H 3.51; Se 46.21
XXVII	=C(CN) <sub>2</sub>	C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> Se <sub>2</sub>		40	151–152	Found: C 30.63; H 2.41; Se 56.97 Calc.: C 30.45; H 2.19; Se 57.20
XXVIII	=C(COCH <sub>3</sub> ) (CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> )	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub> Se <sub>2</sub>		10	75–76	Found: C 35.47; H 3.94; Se 46.42 Calc.: C 35.31; H 4.15; Se 46.43
XXIX	=C(CN) (C <sub>6</sub> H <sub>5</sub> )	C <sub>13</sub> H <sub>11</sub> NSe <sub>2</sub>	45	18	110–111	Found: C 44.02; H 3.52; N 4.33 Calc.: C 44.05; H 3.39; N 4.28
XXX		C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> OSe <sub>2</sub>	38		185–187	Found: C 43.85; H 3.78; N 7.17 Calc.: C 43.75; H 3.65; N 7.29
XXXI	9-Fluorenylidene	C <sub>17</sub> H <sub>14</sub> Se <sub>2</sub>	5		148–149	Found: C 54.10; H 3.71; Se 42.13 Calc.: C 54.27; H 3.75; Se 41.98
XXXII	=N–CN	C <sub>5</sub> H <sub>6</sub> N <sub>3</sub> Se <sub>2</sub>	26	52	123–125	Found: C 23.80; H 2.49; N 11.02 Calc.: C 23.83; H 2.40; N 11.12



ever, the derivatives of ethyl acetoacetate form an exception: Compound XX has the C=O bands at  $1670\text{ cm}^{-1}$  (s) and  $1620\text{ cm}^{-1}$  (vs), whereas, for the corresponding sulfur compound,<sup>1</sup> they are at  $1704\text{ cm}^{-1}$  (vs) and  $1630\text{ cm}^{-1}$  (s). Any gross structural difference between XX and its thio analogue is precluded by the  $^1\text{H}$  NMR spectra of these two compounds. The following  $\tau$  values (in  $\text{CDCl}_3$ ) have been found for corresponding groups in these two compounds: 5.62, 5.63 (O-CH<sub>2</sub>); 6.57, 6.66 (X-CH<sub>2</sub>-CH<sub>2</sub>-X); 7.52, 7.57 (COCH<sub>3</sub>); 8.61, 8.63 (C-CH<sub>3</sub>).

In the  $1300\text{--}1000\text{ cm}^{-1}$  range there are somewhat greater differences between the spectra of corresponding sulfur and selenium compounds. However, the patterns of the spectra are not changed, *i.e.* the sequence of strong and weak bands, and shoulders are on the whole unchanged. That sulfur and selenium influence the symmetric deformation frequency of an attached CH<sub>3</sub> group is evident from a comparison of the spectra of the simpler CH<sub>3</sub>-S and CH<sub>3</sub>-Se compounds (*i.e.* those without ester groups or aromatic groups). As would be expected from both the influence of electronegativity<sup>3</sup> and the reported infrared spectra of dimethyl sulfide and selenide,<sup>4</sup> the CH<sub>3</sub> group attached to selenium absorbs at a somewhat lower frequency than when attached to sulfur. Similar differences are found for the CH<sub>2</sub> deformation frequencies of the five- and six-membered ring systems.

Below  $1000\text{ cm}^{-1}$  there is a conspicuous change in the pattern of the infrared spectrum when sulfur is exchanged by selenium, because some bands are shifted considerably, while others remain in essentially the same place. The ionic salts exhibit two strong bands in the  $800\text{--}1000\text{ cm}^{-1}$  range; these bands can also often be recognized in the spectra of derivatives of the dithiolates and diselenolates. In the spectra of the methyl derivatives  $(\text{CH}_3\text{X})_2\text{C}=\text{C}(\text{CN})_2$  and  $(\text{CH}_3\text{X})_2\text{C}=\text{N}-\text{CN}$ , these bands occur with the same intensity as, and at similar wavenumbers to, the corresponding bands in the spectra of the ionic salts (*cf.* Table 4). Two additional, weaker bands in this region can easily be identified as rocking frequencies of the CH<sub>3</sub> group (*cf.* Ref. 4).

In our paper on 1,1-dithiolates,<sup>1</sup> we tentatively correlated the two above-mentioned bands with the =CS<sub>2</sub> group. This hypothesis has, however, to be modified in light of the results on the corresponding selenium compounds, only one of these bands showing a major shift when sulfur is substituted by selenium. For  $(\text{KS})_2\text{C}=\text{C}(\text{CN})_2$ , the  $960\text{ cm}^{-1}$  band is shifted *ca.*  $100\text{ cm}^{-1}$  towards lower frequencies and the assignment of it to the asymmetrical CSS stretching vibration is, therefore, undoubtedly correct. The  $870\text{ cm}^{-1}$  band, on the other hand, is subjected only to a minor shift by the substitution. On the basis of the following arguments, it seems very plausible that this band should be correlated with the =C(CN)<sub>2</sub> group and is, in fact, due to the symmetrical stretching vibration of the C-C-C grouping. This band has counterparts at approximately the same frequencies in the spectra of alkylidenemalononitriles (ethoxymethylenemalononitrile and isopropylidenemalononitrile) which do not possess sulfur- or selenium containing groups. It was found to be absent in the spectrum of 1,1-bis(methylthio)-ethylene,  $(\text{CH}_3\text{S})_2\text{C}=\text{CH}_2$ , having the ethylenedithiolate but not the C-C-C grouping.

The derivatives of both  $(\text{HS})_2\text{C}=\text{C}(\text{CN})_2$  and  $(\text{HSe})_2\text{C}=\text{C}(\text{CN})_2$  have two further, rather intense bands around  $1200\text{ cm}^{-1}$  and  $600\text{ cm}^{-1}$ . These bands

Table 4. Comparison of infrared spectra of alkali metal dithiolates and diselenolates, and their methyl derivatives.

Wavenumbers (cm <sup>-1</sup> )				Assignments	
(KS) <sub>2</sub> C=C(CN) <sub>2</sub> ·H <sub>2</sub> O	(KSe) <sub>2</sub> C=C(CN) <sub>2</sub>	(MeS) <sub>2</sub> C=C(CN) <sub>2</sub>	(MeSe) <sub>2</sub> C=C(CN) <sub>2</sub>		
2195 vs 2180 vs 1320 vs	2210 vs 2190 vs 1360 vs	2215 vs 2195 s 1450 vs 1420 s 1325 m 1318 m	2215 vs 2205 vs 1445 vs 1415 m 1282 m 1275 m	$\left. \begin{array}{l} \nu(\text{C}\equiv\text{N}) \\ \nu(\text{C}=\text{C}) \\ \delta_{\text{as}}(\text{CH}_3) \\ \delta_{\text{s}}(\text{CH}_3) \end{array} \right\}$ $\nu_{\text{as}}\left(=\text{C}\begin{array}{l} \text{C} \\ \text{C} \end{array}\right)^{\text{a}}$ $\left. \begin{array}{l} \rho(\text{CH}_3) \\ \nu_{\text{as}}\left(=\text{C}\begin{array}{l} \text{X} \\ \text{X} \end{array}\right) \\ \nu_{\text{s}}\left(=\text{C}\begin{array}{l} \text{C} \\ \text{C} \end{array}\right)^{\text{a}} \\ \nu(\text{X}-\text{C}) \end{array} \right\}$ $\omega\left(=\text{C}\begin{array}{l} \text{C} \\ \text{C} \end{array}\right)^{\text{a}}$ $\omega\left(\text{C}=\text{C}\begin{array}{l} \text{X} \\ \text{X} \end{array}\right)$	
1237 m	1211 m	1212 m	1196 m		
		982 m 960 m 930 m 921 m	930 w 920 m 910 s 817 m		
960 s	845 s	870 s	853 m		
870 m	830 m	707 vw	588 vw		
620 m	605 m	610 m	605 m		
507 m 490 m	466 m	476 m 457 m	448 vw 430 m		
(KS) <sub>2</sub> C=N-CN	(KSe) <sub>2</sub> C=N-CN	(MeS) <sub>2</sub> C=N-CN	(MeSe) <sub>2</sub> C=N-CN		
2150 vs 1315 vs	2155 vs 1360 vs	2185 vs 1480 vs 1420 m 1310 m	2180 vs 1480 vs 1420 m 1275 w 1265 m 1005 s		$\left. \begin{array}{l} \nu(\text{C}\equiv\text{N}) \\ \nu(\text{C}=\text{N}) \\ \delta_{\text{as}}(\text{CH}_3) \\ \delta_{\text{s}}(\text{CH}_3) \end{array} \right\}$ $\nu(\text{C}-\text{N})$ $\left. \begin{array}{l} \rho(\text{CH}_3) \\ \nu_{\text{as}}\left(=\text{C}\begin{array}{l} \text{X} \\ \text{X} \end{array}\right) \\ \nu(\text{X}-\text{C}) \end{array} \right\}$ $\omega(\text{C}-\text{N}=\text{C})$ $\omega\left(=\text{C}\begin{array}{l} \text{X} \\ \text{X} \end{array}\right)$
1035 s	1015 m 1000 m	1040 s	938 m 917 m		
980 s	870 vs	945 s	878 s		
595 w	572 w	715 w	615 vw		
560 w 520 w	505 w	562 m 505 w	550 m 468 w		

<sup>a</sup> These bands have counterparts in the spectra of ethoxymethylenemalononitrile (1226, 884, and 600 cm<sup>-1</sup>) and isopropylidenemalononitrile (1170, 890, and 625 cm<sup>-1</sup>).

also have counterparts in the reference substances ethoxymethylenemalononitrile and isopropylidenemalononitrile, and are therefore assigned to the  $=C(CN)_2$  group. This is also in agreement with the presence of similar bands in the spectra of tri- and tetracyanoethylene.<sup>5,6</sup>

For  $(KS)_2C=N-CN$  the  $980\text{ cm}^{-1}$  band is again shifted by *ca.*  $100\text{ cm}^{-1}$  towards lower frequencies on substituting sulfur by selenium, whereas the  $1035\text{ cm}^{-1}$  band is almost unchanged. It seems very plausible that the latter band should be assigned to the stretching vibration of the  $N-(CN)$  bond.

Both the sulfur and selenium compounds usually exhibit one or two weak bands in the  $400-550\text{ cm}^{-1}$  region; in the spectra of the selenium compounds they occur at wavenumbers *ca.*  $40\text{ cm}^{-1}$  lower than in the spectra of the corresponding sulfur compounds. It seems probable, therefore, that these bands should be assigned to vibrations of the  $=CX_2$  group.

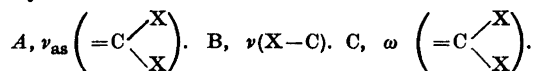
An interpretation of the absorptions below  $1400\text{ cm}^{-1}$  in terms of group frequencies seems to be a reasonable approximation only for the spectra of the simplest compounds, *i.e.* the salts and methyl derivatives of  $(HX)_2C=C(CN)_2$  and  $(HX)_2C=N-CN$ , where  $X=S$  or  $Se$ . Table 4 contains our tentative interpretations, derived using this concept, of the spectra of these compounds. A more detailed spectroscopic investigation of these compounds is in progress.

According to the concept of group frequencies, the  $=C(-X-C')_2$  group should give rise to four stretching vibrations, *viz.* the antisymmetric and symmetric combinations of the  $C-X$  and  $X-C'$  stretching vibrations, respectively. The latter pair may give rise to only one absorption because of very small coupling. In the case of the methyl derivatives given in Table 4, only two vibrations could be identified which were highly sensitive to exchange of sulfur by selenium. With increasing complexity of the molecules, the assignment of any single absorption to these vibrations become increasingly difficult. The asymmetric vibration of the  $CX_2$  group gives rise to absorptions in the same frequency region as the  $CH$  rocking vibrations, which also show a pronounced shift towards lower wavenumbers when sulfur is exchanged by selenium. Furthermore, it must be expected that various degrees of coupling between these two types of vibration occur in the spectra of most of the compounds. The  $X-C'$  stretching vibrations give rise to only weak absorptions, which are difficult to recognize except when the spectrum contains stronger neighbouring absorptions, *i.e.* in those cases when the degree of  $C-X$  character in each absorption is the most uncertain.

However, for many of the compounds a few absorptions which are conspicuously sensitive to the selenium-sulfur interchange can still be recognized. These absorptions are assumed to have substantial contributions from  $C-X$  vibrations. A list of such absorptions is presented in Table 5 and interpreted in accordance with the assignments given in Table 4.

In our paper on the corresponding sulfur compounds,<sup>1</sup> we assigned one or two bands, near  $740\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$ , respectively, to the  $S-C(\text{alkyl})$  vibration. The latter band, however, often remains almost unchanged when sulfur is substituted by selenium and therefore cannot be due to this vibration. The first band is shifted  $20-50\text{ cm}^{-1}$  towards lower frequencies by the exchange and therefore probably contains some contribution from an  $S-C$  vibration.

Table 5. Infrared bands ( $\text{cm}^{-1}$ ) of 1,1-diselenol derivatives and their sulfur analogues (designated by (S)), showing a major shift on substitution of sulfur with selenium. Tentative assignments:



Compound no.	A	B	C
XIV	878 vs	615 vw	468 w
XIV (S)	945 vs	715 w	505 m
XV	880 s	600 w	452 w
XV (S)	980 vs	715 m	509 w
XXIV	887 vs	595 vw	471 m
XXIV (S)	986 s	675 w	507 m, 514 w
XXXII	895 vs	570 vw	468 w
XXXII (S)	995 s	680 w	510 w, 500 w
V	817 m	588 vw	430 m
V (S)	921 m	707 vw	480 m
XIX	822 m	590 w	428 m
XIX (S)	950 s	675 m	498 m
XXVII	822 m	560 vw	428 m
XXVII (S)	965 s	690 w	498 m
I	830 w	600 w, 590 w	440 w
I (S)	890 m	710 w, 700 w	480 w
II	830 w	600 w	430 w
II (S)	890 m	660 m	470 w
III	835 m	560 vw	435 w
III (S)	910 m	685 vw	490 w
IV	800 w	615 m	445 w
IV (S)	905 m	737 s	495 w
XVI	810 w	562 w	445 w
XVI (S)	920 s	675 w	500 w
XXV	855 m		455 w
XXV (S)	915 m		495 w
XXIX	840 m		454 w, 434 w
XXIX (S)	930 m		485 w, 474 w
XX	895 m, 810 w, 790 w	565 w, sh	495 w
XX (S)	915 s, 870 w, 833 m, 857 m	688 w	520

A weak band near  $700 \text{ cm}^{-1}$  in the spectra of the sulfur compounds, which is shifted to *ca.*  $600 \text{ cm}^{-1}$  in the spectra of the selenium compounds, is probably due to the S-C' stretching vibration and not to the symmetric vibration of the  $\text{CS}_2$  group, since it is absent from the spectra of the ionic dithiolates and selenolates.

The absorptions which are due mainly to C-X stretching vibrations are usually shifted *ca.*  $100 \text{ cm}^{-1}$  towards lower wavenumbers when sulfur is exchanged by selenium. In some cases (see, for example, compound XX, Table 5) none of the bands exhibits a shift of this magnitude, but a great number of bands show a minor shift, *i.e.* extensive coupling of the C-X vibrations with a number of other vibrations occurs.

When the compounds contain aromatic substituents, the spectra of corresponding sulfur and selenium compounds become so similar that the bands

to which C-S or C-Se vibrations contribute usually cannot be identified. This applies especially to the derivatives of fluorene and acetophenone. For the *S*- and *Se*-benzyl derivatives most of the bands due to the benzyl group could be eliminated by comparing the spectra with those of dibenzyl sulfide and selenide, so that a plausible assignment could also be made for some of these compounds (see compounds II, IV, and XV, Table 5).

### EXPERIMENTAL

Carbon diselenide was prepared from methylene chloride and selenium at elevated temperature, essentially as described by Ives *et al.*<sup>7</sup> and Treiber *et al.*<sup>8</sup> but, however, with some technical improvements which will be described in a forthcoming publication.

The analyses were carried out in the Microanalysis Department of this Laboratory (Chief Analyst Preben Hansen). The selenium determinations were performed by a modification of the combustion method<sup>9</sup> in which the selenium was collected as selenium dioxide and determined by iodometric titration.

Melting points were determined on a Kofler melting point microscope and are uncorrected.

The infrared spectra were recorded, using KBr discs, on a Perkin Elmer Model 337 grating spectrophotometer.

### Preparation of alkali metal diselenolates

Diselenolates were prepared from cyanamide, and the following active methylene compounds: ethyl cyanoacetate, dimethyl malonate, diethyl malonate, malononitrile, ethyl acetoacetate, acetophenone, benzyl cyanide, fluorene, and 3-methyl-1-phenyl-5-pyrazolone.

The diselenolates derived from malononitrile and cyanamide could be obtained as approximately pure solid salts, and were usually used as such, dissolved in dimethylformamide, for the preparation of derivatives. The other diselenolates were prepared as solutions in dimethyl sulfoxide (DMSO) or dimethylformamide (DMF).

*Potassium 2,2-dicyanoethylene-1,1-diselenolate*,  $(NC)_2C=C(SeK)_2$ . Carbon diselenide (1.70 g) was added with stirring at  $-10^\circ\text{C}$ , in an  $N_2$  atmosphere, to a solution of malononitrile (0.62 g) in 10 ml of 1 M potassium ethanolate in abs. ethanol. After 8 min another 10 ml of 1 M potassium ethanolate was added. After 8 min the red-brown reaction mixture was poured into 500 ml of dry ether. After standing for 1 h in a refrigerator the orange-coloured salt which had separated was filtered off under nitrogen, washed with ether and dried in a desiccator. Yield 2.98 g (96 %). (Found: C 15.01; H 0.0; Se 50.30. Calc. for  $C_4K_2N_2Se_2$ : C 15.39; Se 50.60.) The preparation has also been carried out with KOH in aqueous dioxan with a similar yield (95 %).

*Potassium cyanimidodiselenocarbonate*,  $NC-N=C(SeK)_2$ . Carbon diselenide (25 mmol in 10 ml of dioxan) was added with stirring and cooling at  $0^\circ\text{C}$  in a nitrogen atmosphere to a solution of cyanamide (25 mmol) in 10 ml of dioxan + 5 ml of ethanol, to which 25 mmol of potassium hydroxide dissolved in 2 ml of water had been added. After the addition of the  $CSe_2$ -solution an additional portion of 25 mmol KOH was added. On addition of ethanol (100 ml) a yellow solid separated. An additional crop was obtained by addition of ether; it was purified by dissolution in 2.5 ml of water and precipitation with ethanol. Total yield 60 %. (Found: C 8.41; N 9.33. Calc. for  $C_2K_2N_2Se_2$ : C 8.34; N 9.72.)

*DMSO-solutions of diselenolates*. Sodium hydride (16 mmol, freed from oil by extraction with pentane and then ether) was added to a solution of the active methylene compound (8 mmol) in DMSO (60 ml) at ca.  $15^\circ\text{C}$ . When the hydrogen evolution had stopped (ca. 10 min), carbon diselenide (8 mmol) was added dropwise over a period of 15 min. The solution was usually dark brown; however, in the case of malonic esters, it was green.

*DMF-solutions of diselenolates*. a) A solution of the active methylene compound (20 mmol) in DMF (50 ml) was cooled at  $-50^\circ\text{C}$ , and a solution of sodium 2-methyl-2-bu-

tanolate (20 mmol) in benzene (25 ml) was added. A solution of carbon diselenide (10 mmol) in benzene (10 ml) was added dropwise with stirring over a period of 30 min. Alternatively the methylene compound was added to a solution of sodium 2-methyl-2-butanolate in ether-benzene at  $-50^{\circ}\text{C}$ , carbon diselenide was added, and the solution was heated slowly to  $-20^{\circ}\text{C}$  and kept at this temperature for 1 h. Dimethylformamide was added to dissolve the red precipitate.

This method was used to prepare derivatives of dimethyl and diethyl malonate, but in other cases it gave much lower yields than the DMSO method.

Use of the weaker base sodium hydroxide gave positive results only with the more pronouncedly acid methylene compounds, such as ethyl acetoacetate and benzyl cyanide, and the yields of the derivatives were extremely low ( $\sim 1\%$ ).

b) The following procedure has been used to prepare derivatives of ethyl cyanoacetate in fair yields. A solution of ethyl cyanoacetate (20 mmol) in dioxan (30 ml) was stirred with pulverized KOH (20 mmol) for 15 min. Carbon diselenide (10 mmol) dissolved in dioxan (30 ml) was added at room temperature over a period of 10 min. The reaction mixture was diluted with ether (200 ml) and the brick-red precipitate was filtered off. This material was immediately dissolved in DMF for alkylation.

### Preparation of derivatives of the diselenolates

The general procedure is to add the equivalent amount of the halogen compound (methyl iodide, benzyl chloride or bromide, 1,2-dibromoethane, 1,3-dibromopropane) to the solution of the diselenolate in DMSO or DMF. The green colour of the DMSO-solutions of the diselenolates derived from dialkyl malonates turned red after addition of the halogen compounds. The solution was left at room temperature for several hours (1–24 h) and then poured into water and generally extracted with petroleum ether, ether or chloroform (in some cases the products crystallized from the aqueous solution). It was found to be advantageous to use the least polar solvent able to dissolve the desired product in order to minimize the amount of by-products in the extract. The dried solution was filtered through a short column of aluminium oxide and the solvent removed *in vacuo*. The crude products are usually brownish to orange-coloured and, although not very impure according to their melting points, required tedious recrystallizations in order to remove strongly coloured impurities. It was found convenient to use consecutive recrystallizations from alternating polar and non-polar solvents. The best suited solvents were the nonpolar solvents heptane (hexane for lower-melting compounds) or toluene, and the polar solvent methanol-water (or ethanol for the less soluble fluorene derivatives).

However, even by the use of alternating polar and nonpolar solvents it is difficult to obtain a satisfactory purification without great loss of material. In more recent preparations we have found the use of short aluminium oxide columns well suited for the purification of the products. An amount of adsorbent which will just retain the desired product is sufficient to effect a satisfactory separation. Thin layer chromatography was found less suited.

The procedure is illustrated by the following example. The reaction mixture from sodium hydride (10 mmol), benzyl cyanide (5 mmol), carbon diselenide (5 mmol), and benzyl bromide (10 mmol) in DMSO-ether was diluted with water and extracted with ether. The residue (2.15 g) from the dried ether extract was extracted with boiling hexane ( $3 \times 30$  ml). The hot hexane extracts were filtered through a glass filter funnel on which was placed a 5 mm layer of basic aluminium oxide (5 g) (Woelm, activity grade 1) covered with a layer of sand and a filter paper disc. The funnel was subsequently washed with hot hexane (20 ml), and the filtered solution was cooled to room temperature (in some experiments an almost pure, crystalline substance separated at this stage). The cooled solution was run through two successive columns each filled with 5 g of the above mentioned material in a 15 mm layer. The columns were eluted at a rate of 5–10 ml/min with petroleum ether (*ca.* 40 ml) followed by petroleum ether with 10% ether. The hexane and petroleum ether fractions contained only unreacted benzyl bromide and small amounts of dibenzyl triselenocarbonate and dibenzyl diselenide. The 2-[bis(benzylseleno)-methylene]-2-phenylacetonitrile was contained in the first 120 ml of the petroleum ether-ether eluate. (In some experiments overload of the column caused this substance to start appearing, mixed with the triselenocarbonate, in the petroleum ether fraction.)

Cooling of this eluate to  $-15^{\circ}\text{C}$  yielded very pure VIII (760 mg, m.p.  $76-77^{\circ}\text{C}$ ). Evaporation of the mother liquor and recrystallization from hexane gave an additional 160 mg with m.p.  $71-75^{\circ}\text{C}$ .

In most cases the final products were colourless and, according to thin layer chromatography, they were pure substances. However, the derivatives of 3-methyl-1-phenyl-5-pyrazolone were definitely orange, and the derivatives of fluorene bright yellow. The dibenzyl derivatives also seem to have a genuine yellow colour in cases where the other derivatives are colourless.

The compounds prepared have been listed in Tables 1-3. The yields are based upon added carbon diselenide because it was often found advantageous to use an excess of the active methylene compound to ensure a low concentration in the solution of bases other than its carbanion. Most of the preparations were carried out both in DMF and DMSO solution, but the yields in the first case were generally much lower. They have only been indicated in the tables when higher yields were obtained in DMF, or if the preparation was only carried out in this solvent.

The following examples illustrate the procedures used (for analyses, etc., see Tables 1-3).

*1,3-Diselenolan-2-ylidenecyanamide (XXIV)*. Potassium cyanimidodiselenocarbonate (2 mmol) was dissolved in 10 ml of DMF (containing 10-20 % of water) at  $0^{\circ}\text{C}$  and 1,2-dibromoethane (2 mmol) was added. After standing for 5 h at room temperature the solution was diluted with water to 60 ml, heated to boiling, treated with active carbon and filtered. On cooling 70 mg of a colourless solid separated. Extraction of the mother liquor yielded another 30 mg. Total yield 52 %. Colourless crystals were obtained after recrystallization twice from benzene-heptane (3:1; 4 ml). M.p.  $80-80.5^{\circ}\text{C}$ .

*[Bis(methylseleno)methylene]malononitrile (V)*. Potassium 2,2-dicyanoethylene-1,1-diselenolate (1 mmol) was dissolved in DMF (6 ml). Methyl iodide (2 mmol) was added at  $-20^{\circ}\text{C}$ , and the temperature was allowed to rise to room temperature over a period of 4 h. A precipitate was removed from the solution by centrifugation and the solution diluted with 30 ml of water. On cooling a dark orange solid separated (yield of crude product 57 %). On recrystallization from ether the compound formed long colourless needles with m.p.  $61-62^{\circ}\text{C}$  (yield 34 %).

*[Bis(benzylseleno)methylene]acetophenone (X)*. Benzyl chloride (6 mmol) was added to a DMSO solution of the diselenolate (3 mmol), prepared from acetophenone. After standing for 18 h at room temperature the solution was diluted with water and extracted with ether. The residue, after evaporation of the ether, was washed with ether and yielded 261 mg of light yellow crystals; another 29 mg was obtained by chromatographing the ether solution on  $\text{Al}_2\text{O}_3$ . Total yield 25 %. M.p.  $134-135^{\circ}\text{C}$  after recrystallization from ethanol.

*2-Phenyl-2-(1',3'-diselenan-2'-ylidene)acetonitrile (XXIX)*. 1,3-Dibromopropane (3 mmol) was added to a DMSO solution (25 ml) of the diselenolate (3 mmol), prepared from phenylacetonitrile, and the solution was kept for 18 h at room temperature. The intensely red solution was diluted with 50 ml of water and 20 ml of a saturated NaCl solution and extracted twice with 50 ml portions of ether. The residue from the evaporation of the ether yielded on recrystallization from pentane-methylene chloride 314 mg; another 51 mg was obtained from the mother liquor on recrystallization from methanol. Total yield 45 %. M.p.  $110-111^{\circ}\text{C}$  after recrystallization from pentane-ether-methylene chloride.

*Ethyl 1,3-diselenolan-2-ylidenecyanoacetate (XVI)*. a) A DMSO solution of the diselenolate prepared from ethyl cyanoacetate, to which the equivalent amount of 1,2-dibromoethane had been added, was kept for 20 h at room temperature, diluted with water and extracted with chloroform. The residue from the evaporation of the chloroform was dissolved in ether; the solution was then washed with water, dried and filtered through an  $\text{Al}_2\text{O}_3$  column. The residue from the ether solution yielded, on recrystallization from pentane-ether-methylene chloride, 133 mg (21 %) of XVI. It was further recrystallized from methanol to give a colourless product.

b) 1,2-Dibromoethane (5 mmol) was added to a solution of the potassium diselenolate (5 mmol), prepared from ethyl cyanoacetate (5 mmol) in 30 ml of DMF, and the solution was kept for 12 h at room temperature. The reaction mixture was filtered and the filtrate poured into 200 ml of water. On cooling to  $0^{\circ}\text{C}$  an orange-yellow solid separated. It was purified by filtering an ether solution through Florisil, followed by recrystallization from

methanol, ether, and again from methanol, to give, finally, colourless crystals with m.p. 111–113°C. Yield 36 %.

*Dimethyl 1,3-diselenolan-2-ylidenemalonate (XVII)*. a) The diselenolate was prepared from dimethyl malonate (4 mmol), sodium hydride (4 mmol) and carbon diselenide (2 mmol) in DMSO (25 ml). The solution was washed with pentane-ether (1:4), and 1,2-dibromoethane (2 mmol) was added. On standing of the solution at room temperature its colour changed from green to orange-red over a period of 2–3 h. The solution was poured into water, ether was added, and an insoluble material filtered off. The ether solution yielded 33 % of XVII after recrystallization from pentane-ether. A small residue from recrystallization was combined with the above-mentioned ether-insoluble material and recrystallized from 1,2-dichloroethane. It was identified as XXXIII (yield 3 %).

b) 1,2-Dibromoethane (1.5 mmol) was added at –40°C to a solution of the diselenolate prepared from dimethyl malonate (2 mmol), sodium 2-methyl-2-butanolate (2 mmol, in 15 ml of benzene) and carbon diselenide (1 mmol) in DMF (30 ml). The solution was kept at room temperature until its colour had changed from green *via* brown to pink, and was then poured into water and extracted twice with 100 ml portions of ether. A substance, insoluble both in water and ether, was filtered off. The ether solution yielded 24 % of XVII after recrystallization from ether-pentane. The mother liquor was chromatographed on Florisil and yielded 12 % of ethylene triselenocarbonate. The insoluble material yielded 15 % of the diselenetan (XXXIII) on recrystallization from chloroform.

*Tetramethyl 1,3-diselenetan-2,4-diylidenedimalonate (XXIII)*. A substance, insoluble in both water and ether, has repeatedly been isolated in several preparations of dimethyl 1,3-diselenolan-2-ylidenemalonate, both in DMSO and DMF, and under varied reaction conditions. In 10 preparations the yield of this substance has varied from 3 to 22 %, along with 18–33 % of dimethyl 1,3-diselenolan-2-ylidenemalonate and 1–12 % of ethylene triselenocarbonate. The analytical data are consistent with the formulation of this material as the diselenetan XXXIII, and its IR spectrum in the region above 1000  $\text{cm}^{-1}$  showed a one-to-one correspondence with the thio analogue prepared according to Ref. 10. After recrystallizations from chloroform it forms light yellow needles with m.p. 271–272°C. (Found: C 32.52; H 2.53; Se 36.12. Calc. for  $\text{C}_{12}\text{H}_{14}\text{O}_8\text{Se}_4$ ; C 32.59; H 2.74; Se 35.72.)

A similar substance has been isolated during preparations of the diselenolate derived from acetophenone. However, these products have yielded analytical values corresponding to more than two atoms of selenium (in one case practically three) and therefore are probably mixtures of a diselenetan and a triselenolan. Also this assignment was supported by the correspondence, above 1000  $\text{cm}^{-1}$ , of the IR spectrum of the product mixture with that of the thio analogue of the triselenolan.<sup>10</sup> Attempts to separate these compounds have so far been unsuccessful.

*5-Oxo-1,3-diselenan-2-ylidenemalononitrile (XXXV)*. 1,3-Dichloroacetone (2 mmol), dissolved in DMF, was added at –20°C to a solution of potassium 2,2-dicyanoethylene-1,1-diselenolate in DMF (6 ml). The temperature was raised to 20°C over a period of 5 h. A precipitate which had formed was removed by centrifugation and the solution was diluted with 30 ml of water. This caused a light brown solid to separate (0.42 g). On recrystallizations from ethyl acetate it yielded 0.15 g (26 %) of an orange-brown substance with m.p. 180–184°C. The compound has a distinct skin-irritating effect. (Found: C 28.92; H 1.53; Se 54.35. Calc. for  $\text{C}_7\text{H}_4\text{N}_2\text{OSe}_2$ ; C 28.95; H 1.39; Se 54.45.)

*2-Phenyl-2(4'-hydroxy-1',3'-deselenolan-2'-ylidene)acetonitrile (XXXVI)*. Phenylacetonitrile (2 mmol) was added to a benzene solution (40 ml) of sodium 2-methyl-2-butanolate (4 mmol). This was immediately followed by the slow addition of a solution of carbon diselenide (2 mmol) in benzene, while maintaining the temperature at 10°C. The resulting benzene solution was extracted with water. Chloroacetaldehyde (2 mmol), and  $\text{KH}_2\text{PO}_4$  (2 mmol) were then added to the aqueous layer; after a period of 5 min a further 2 mmol of  $\text{KH}_2\text{PO}_4$  was added. The solution was extracted three times with 60 ml portions of ether. The residue obtained by evaporation of the ether was recrystallized twice from toluene-heptane (1:1) and yielded colourless crystals with m.p. 118–124°C (decomp.). (Found: C 40.20; H 2.83; N 4.17. Calc. for  $\text{C}_{11}\text{H}_9\text{NOSe}_2$ ; C 40.12; H 2.74; N 4.26.)

Reference substances for the IR spectroscopic study: ethoxymethylenemalononitrile, m.p. 65–66°C, isopropylidenemalononitrile, prepared according to Ref. 11, and 1,1-bis(methylthio)ethylene. The latter was prepared from methyl dithioacetate by the



procedure described by Schuijl *et al.*<sup>12</sup> for the preparation of the higher homologues. Yield 57 %, b.p. 62–64°C, 18 mmHg. (Found: C 40.30; H 6.82; S 53.57. Calc. for C<sub>4</sub>H<sub>6</sub>S<sub>2</sub>: C 40.00; H 6.71; S 53.29.)

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