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Thermal Rearrangements of Allyl 2,2-Dichloro-, 1,2-Dichloro- and 1,2,2-Trichloro-substituted Vinyl Sulfides

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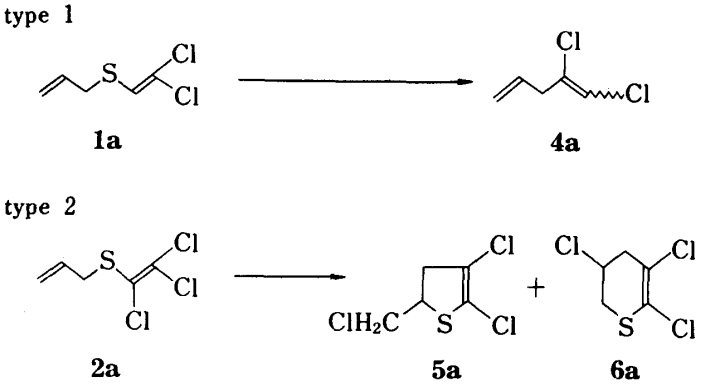
Thermal rearrangements of allyl perchlorovinyl sulfides, such as 2,2-dichloro-, 1,2-dichloro- and 1,2,2-trichloro-substituted vinyl sulfides, are shown to involve unique rearrangements of the carbon skeletons with migration of the chlorines.

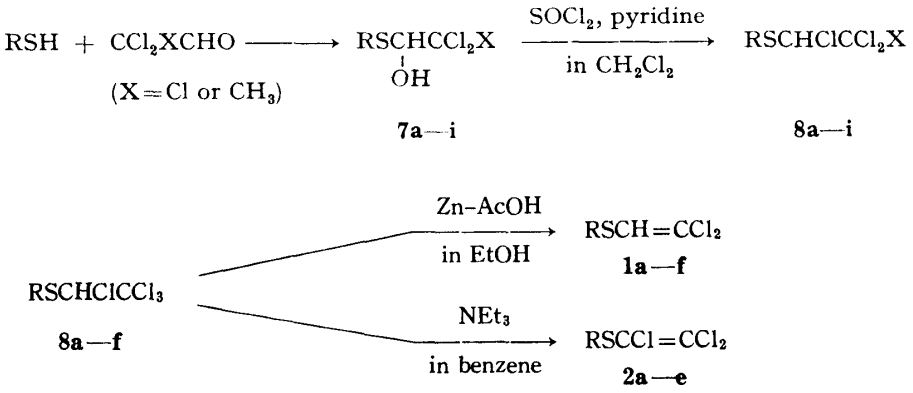
Keywords——2,2-dichlorovinyl sulfide; 1,2-dichlorovinyl sulfide; 1,2,2-trichlorovinyl sulfide; rearrangement; desulfurization; chlorine migration; 4,5-dihydrothiophenes; 3,4-dihydro-2*H*-thiopyrans; alkene sulfenyl chloride; [3,3]-sigmatropic rearrangement

Although many publications[1] have dealt with the thio-Claisen rearrangement, in our recent communication[2] 2,2-dichlorovinyl and 1,2,2-trichlorovinyl sulfides were reported to undergo unique thermal rearrangements along with migration of their chlorines, which are typified by the following two reactions.



We now wish to report details of our systematic investigation of these reactions together with full experimental data.

Substrates were 2-alkenyl sulfides linked to chlorinated 1-alkenyls, *i.e.*, $Cl_2C{=}CH-$ (**1a**—**f**), $Cl_2C{=}CCl-$ (**2a**—**e**) and $H_3C(Cl)C{=}CCl-$ (**3a**—**c**), which were prepared by the following routes.



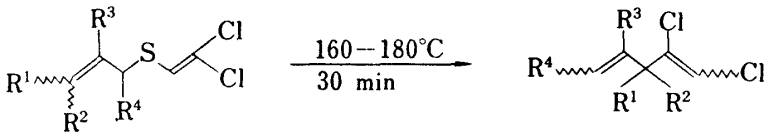
$$RSCHClCCl_2CH_3 \xrightarrow[\text{in THF}]{\textit{tert}\text{-BuOK}} RSCCl{=}CClCH_3$$

8g—i **3a—c**

R: $CH_2{=}CH{-}CH_2{-}$ (**1a**, **2a** and **3a**), $CH_2{=}C(CH_3){-}CH_2{-}$ (**1b**, **2b**, and **3b**),
$CH_3{-}CH{=}CH{-}CH_2{-}$ (*E*- and *Z*-configurations, **1c**, **2c** and **3c**),
$C_6H_5{-}CH{=}CH{-}CH_2{-}$ (*E*-configuration, **1d** and **2d**),
$(CH_3)_2C{=}CH{-}CH_2{-}$ (**1e** and **2e**) and 2-cyclohexen-1-yl (**1f**)

According to the previously reported method,[3] the sulfides (**8a—i**) were prepared by chlorination of the adducts (**7a—i**) obtained from the corresponding mercaptans and aldehydes. Among them, **8b—i** have not been reported previously. Dechlorination of **8a—f** in the zinc dust-acetic acid system, which had been reported for the preparation of **1a**,[3] gave the corresponding 2,2-dichlorovinyl sulfides, **1a—f**. The compounds **8a—e** were dehydrochlorinated quantitatively by treatment with triethylamine at room temperature, whereas **8g—i** were unreactive under the same conditions, but were dehydrochlorinated by treatment with potassium *tert*- butoxide at room temperature. Since the compounds **2a—d** and **3a—c** are thermally unstable, heating was avoided during the isolation procedures. The isolated **2a—d** and **3a—c** were nearly pure and were used for the subsequent reaction without distillation. Except for **1a**, the products (**1b—f**, **2a—e** and **3a—c**) have not been reported previously.

2-Alkenyl 2,2-dichlorovinyl sulfides, **1a—f**, underwent the type 1 rearrangement when heated at 160—180°C.



1a—f **4a—f**

For example, on heating of **1a** at 160°C, the desulfurized product, 1,2-dichloro-1,4-pentadiene (**4a**), was obtained as a colorless liquid of bp 92—105°C, as a mixture of *E*-isomer and *Z*-isomer. A gas chromatogram of **4a** showed the two peaks corresponding to the geometrical isomers, and the ratio of *E*-isomer to *Z*-isomer was determined to be 42: 58. The two isomers were distinguished from each other by their vinyl proton signals in the proton magnetic resonance (PMR) spectrum of the mixture. The proton signal at lower field (6.11 ppm) can be assigned to the *E*-isomer and that at higher field (6.08 ppm) to the *Z*-isomer from the previously reported data.[4]

The same type of reaction proceeded in the runs with **1b—f**, and the results are summarized

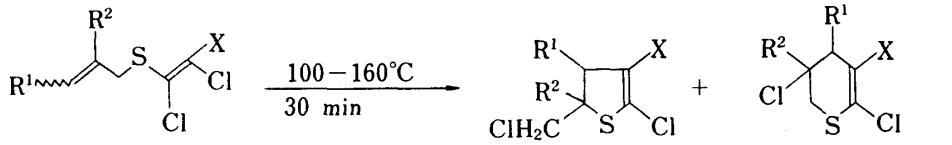
Table I. Thermal Rearrangement of 2-Alkenyl 2,2-Dichlorovinyl Sulfides (**1a—f**)[a]

Subst. No.	R^1	R^2	R^3	R^4	React. temp. (°C)	Product No.	Yield[b] (%)	*E*: *Z* Ratio[c] *E*	*Z*
1a	H	H	H	H	160	**4a**	53.5	42	58
1b	H	H	CH_3	H	160	**4b**	56.3	24	76
1c	CH_3	H	H	H	160	**4c**	56.9	36	64
1d	C_6H_5	H	H	H	180	**4d**	35.2	26	74
1e	CH_3	CH_3	H	H	180	**4e**	38.8	0	100
1f	2-Cyclohexen-1-yl				180	**4f**	39.5	36	64

a) General procedures are given in "Experimental."
b) Based on the product actually isolated.
c) Determined by GLC analysis.

in Table I. As can be seen, predominant formation of the *Z*-isomer was observed in every run, and in the case of **1e** the *Z*-isomer was obtained exclusively.

2-alkenyl 1,2,2-trichlorovinyl sulfides, **2a**—**d**, and 1,2-dichloro-1-propenyl sulfides, **3a**—**c**, underwent the type 2 rearrangement when heated at 100—160°C.



2a−**d** : X=Cl
3c−**c** : X=CH_3

5a−**d** : X=Cl
9a−**c** : X=CH_3

6a, **c** : X=Cl
10a−**c** : X=CH_3

For example, heating of **2a** at 120°C and distillation of the resulting oil gave a colorless liquid of bp 115—118°C (17 mmHg). By elemental analysis and GC–MS measurement, this material was confirmed to be composed of two substances, both of which have the same parent peak, *m/z* 202, and the molecular formula $C_5H_5Cl_3S$. The two substances were isolated by preparative gas chromatography and identified as 2,3-dichloro-4,5-dihydro-5-chloromethylthiophene (**5a**) and 3,5,6-trichloro-3,4-dihydro-2*H*-thiopyran (**6a**) on the bases of their PMR and carbon magnetic resonance (CMR) spectra and their chemical properties. The product **5a** was dehydrochlorinated by treatment with potassium *tert*-butoxide in tetrahydrofuran (THF) to yield 2,3-dichloro-5-methylthiophene (**11a**) whereas **6a** was resinified by the same procedure. Treatment of **6a** with benzenethiolate in ethanol gave 3-phenylthio-3,4-dihydro-5,6-dichloro-2*H*-thiopyran (**12a**). The PMR and CMR spectra of **11a**, and PMR spectrum of **12a** were consistent with the proposed structures.

The same type of rearrangement as seen on heating of **2a** was shown to proceed with not only 1,2,2-trichlorovinyl sulfides, **2b**—**d** but also 1,2-dichlorovinyl type sulfides, **3a**—**c**. It is noteworthy that 3-methyl-2-butenyl 1,2,2-trichlorovinyl sulfide (**2e**), a representative 3,3-disubstituted sulfide, was thermally stable and did not react even on being heated at 250°C. The results are summarized in Table II. The products, 4,5-dihydrothiophenes (**5a**, **b**, **9a**, **b** and **5c**, **d**, **9c** as diastereomeric mixtures) and 3,4-dihydro-2*H*-thiopyrans (**6a**, **10a**, **b**) were isolated by means of column chromatography and preparative gas chromatography. As can be seen in Table II, all runs produced higher yields of the former than of the latter. PMR, CMR and mass spectral data for these products (**5a**—**d**, **6a**, **9a**—**c**, **10a**, **b**) are listed in Table VIII. These data are consistent with the proposed structures. Identification of the products (**6c**, **10c**) which could not be isolated in a pure state was made on the basis of the spectral data for the material mixed with the 4,5-dihydrothiophene product, by analogy with the 3,4-dihydro-2*H*-thiopyrans obtained in the other runs.

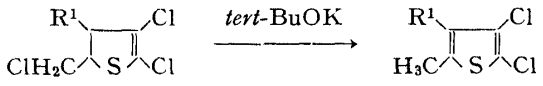
Table II. Thermal Rearrangement of 2-Alkenyl 1,2,2-Trichlorovinyl and 1,2-Dichloro-1-propenyl Sulfides (**2a**—**d** and **3a**—**c**)[a]

Subst. No.	X	R^1	R^2	React. temp. (°C)	Yield (%)[b] **5a**—**d**	(Product No.) **6a**—**d**
2a	Cl	H	H	120	33.2 (**5a**)	22.1 (**6a**)
2b	Cl	H	CH_3	100	26.1 (**5b**)	Trace
2c	Cl	CH_3	H	120	27.2 (**5c**)	16.3 (**6c**)
2d	Cl	C_6H_5	H	160	22.6 (**5d**)	Trace
3a	CH_3	H	H	100	33.2 (**9a**)	22.9 (**10a**)
3b	CH_3	H	CH_3	120	26.9 (**9b**)	13.2 (**10b**)
3c	CH_3	CH_3	H	120	22.2 (**9c**)	18.8 (**10c**)

a) General procedures are given in "Experimental."
b) Based on 4,5-dihydrothiophene/3,4-dihydro-2*H*-thiopyran ratio in the products as measured by GLC analysis.

A procedure similar to that used for **5a** resulted in dehydrochlorination of **5c, d** whereas **5b** did not react because of the lack of hydrogen at C_5. Nucleophilic substitution by benzenethiolate was carried out with **5b—d** and **6a—c**, as shown in Table IV.

TABLE III. Dehydrochlorination of **5a—d** with *tert*-BuOK[a]

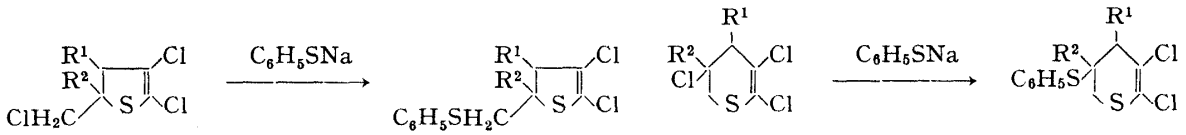


5a—d **11a—d**

Substrate No.	React. time (h)	Product No.	R^1	Yield[b] (%)
5a	2	**11a**	H	39.8
5c	3	**11c**	CH_3	57.3
5d	3	**11d**	C_6H_5	61.7

a) The general procedure is given in "Experimental." Molar ratio: **5a—d**: *tert*-BuOK=1: 1.5.
b) Based on the product actually isolated.

TABLE IV. Substitution of **5b—d** and **6a—c** with Benzenethiolate[a]



5b—d **13b—d** **6a, c** **12a, c**

Substrate No.	React. time (h)	Product No. (R^1, R^2)	Yield[b] (%)
5b	3	**13b** (H, CH_3)	56.0
5c	3	**13c**[c] (CH_3, H)	36.4
5d	3	**13d** (C_6H_5, H)	58.5
6a	2	**12a** (H, H)	50.5
6c	3	**12c**[c] (CH_3, H)	23.2

a) The general procedure is given in "Experimental." Molar ratio; **5b—d** or **6a, c**: C_6H_5SNa=1: 1.5.
b) Based on the product actually isolated.
c) Obtained by starting from the mixture of **5c** and **6c**.

The mechanism for the reactions of types 1 and 2 may be depicted as illustrated in Chart 1. Both reactions are initiated by a [3, 3]-sigmatropic rearrangement to form a chlorinated thiocarbonyl compound II, which is unstable and susceptible to release of β-chlorine as an anion, giving a thiiranium ion. The reactions of types 1 and 2 are distinguished by the subsequent recombination of the chlorine anion and the thiiranium ion; in the former, the chlorine anion attacks at C_3, whereas in the latter it attacks at the sulfur.

Where X=H and Y=Cl, desulfurization from the thiiran with chlorine migration proceeds to give III (type 1). Susceptibility of thiiran to desulfurization has been reported in several papers.[5] The predominant formation of *Z*-isomer in this reaction presumably arises because the attack of the chlorine anion at the three-membered ring carbonium ion may be inhibited on the side of the bulky 2-alkenyl group (see Chart 2).

On the other hand, where X=Cl and Y=Cl or CH_3, sulfenyl chloride formation by attack of the chlorine anion on the sulfur proceeds to give IV, and intramolecular addition leads to

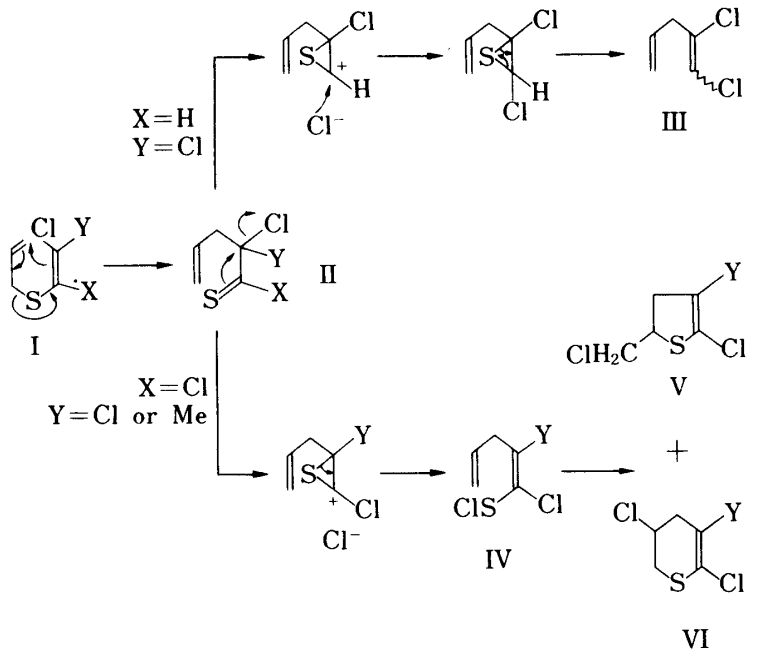


Chart 1

the formation of 4,5-dihydrothiophene, V, and 3,4-dihydro-2*H*-thiopyran, VI. The higher yield of V than of VI may arise because the attack of the chlorine anion is more favored at the A carbon than at the B carbon, which is sterically hindered by the R^1 and R^2 substituent in the intermediary episulfonium ion[6] involved in the sulfenyl chloride addition (see Chart 3).

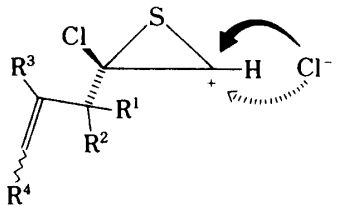


Chart 2

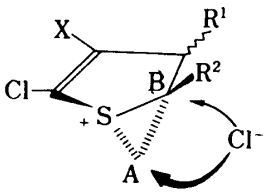
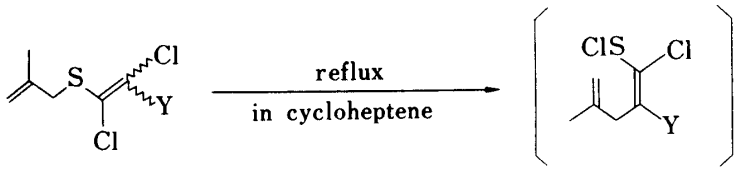
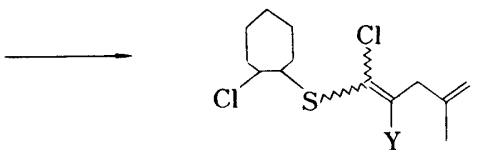


Chart 3

The intermediacy of the sulfenyl chloride IV was confirmed by trapping it as an adduct of cycloheptene. When **2b** was heated in cycloheptene under reflux, 2-chlorocycloheptanyl 1,2-dichloro-4-methyl-1,4-pentadienyl sulfide (**14a**) was obtained as a colorless liquid, yield;



2b : Y=Cl
3b : Y=CH_3



14a : Y=Cl
14b : Y=CH_3

42.3%. In the case of **3b**, 2-chlorocycloheptanyl 1-chloro-2,4-dimethyl-1,4-pentadienyl sulfide (**14b**) was obtained by a similar procedure. These results provide strong evidence supporting the above mechanism.

Experimental

Infrared (IR) spectra were taken on a Hitachi EPI-G2 spectrophotometer. PMR spectra were recorded on a Hitachi R-24B spectrometer and CMR spectra were recorded on a JEOL JNM-FX90Q spectrometer; all chemical shifts are given in ppm downfield from tetramethylsilane (TMS). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet, br d = broad doublet and br t = broad triplet. GC–MS spectra were measured with a JEOL JMS-D100 machine.

2-Alkenyl 1,2,2,2-Tetrachloroethyl Sulfides and 2-Alkenyl 1,2,2-Trichloropropyl Sulfides (8a—i)——2-Alkenyl 1,2,2,2-tetrachloroethyl sulfides, **8a**—**f**, were prepared according to the previously reported method,[3)]

TABLE V. $R^1R^2C{=}C(R^3){-}CH(R^4){-}S{-}CHClCCl_2X$ **8b—i**

Compd. No.	X	R^1	R^2	R^3	R^4	bp (°C/mmHg)	IR $\nu_{max}^{liq.}$ cm^{-1} (>C=C<)	PMR δ (ppm in $CDCl_3$, J = Hz)	Formula (M.W.)	Analysis Calcd (Found) C	H
8b	Cl	H	H	CH_3	H	84—86/6	1645	5.32 (1H, s, –CHCl–) 5.01 (3H, br s, =CH_2) 3.41 (2H, ABq, J = 14 and 16, –CH_2–) 1.85 (3H, br s, –CH_3)	$C_6H_8Cl_4S$ (254.00)	28.37 (28.82	3.17 3.25)
8c	Cl	CH_3	H	H	H	99—100/2	1665	5.31 (1H, s, –CHCl–) 5.25—5.90 (2H, m, (–CH=)$_2$) 3.40 (2H, br d, J = 6, –CH_2–) 1.72 (3H, d, J = 6, –CH_3)	$C_6H_8Cl_4S$ (254.00)	28.37 (28.76	3.17 3.23)
8d	Cl	C_6H_5	H	H	H	——[a)]	1600 1580	7.10—7.45 (5H, m, aromatic protons) 6.58 (1H, d, J = 15, C_6H_5–C<u>H</u>=) 6.10 (1H, sextet, J = 15 and 6, =C<u>H</u>–CH_2–) 5.37 (1H, s, –CHCl–) 3.60 (2H, br d, J = 6, –CH_2–)	$C_{11}H_{10}Cl_4S$ (316.07)	41.80 (42.18	3.19 3.30)
8e	Cl	CH_3	CH_3	H	H	99—102/0.2	1655	5.30 (1H, s, –CHCl–) 5.00—5.35 (1H, m, =CH–) 3.47 (2H, br d, J = 7, –CH_2–) 1.72 (6H, br s, (–CH_3)$_2$)	$C_7H_{10}Cl_4S$ (268.03)		
8f	Cl	2-Cyclohexen-1-yl				119—121/0.2	1650	5.65—6.00 (2H, m, (=CH–)$_2$) 5.44 (1H, s, –CHCl–) 3.65—3.95 (1H, m, >CH–S) 1.40—2.30 (6H, m, (–CH_2–)$_3$)	$C_8H_{10}Cl_4S$ (280.04)	34.31 (34.75	3.60 3.79)
8g	CH_3	H	H	H	H	105—108/10	1630	5.45—6.15 (1H, m, =CH–) 5.16 (1H, s, –CHCl–) 5.00—5.45 (2H, m, =CH_2) 3.41 (2H, br d, J = 7, –CH_2–) 2.30 (3H, s, –CH_3)	$C_6H_9Cl_3S$ (219.49)	32.83 (32.77	4.13 4.15)

Compd. No.	X	R^1	R^2	R^3	R^4	bp (°C/mmHg)	IR $\nu_{max}^{liq.}$ cm^{-1} (>C=C<)	PMR δ (ppm in $CDCl_3$, J=Hz)	Formula (M.W.)	Analysis Calcd (Found) C	H
8h	CH_3	H	H	CH_3	H	107—109/11	1650	5.13 (1H, s, –CHCl–) 4.80—5.05 (2H, m, $=CH_2$) 3.35—3.55 (2H, m, $-CH_2-$) 2.39 (3H, s, $-CCl_2CH_3$) 1.78 (3H, br s, $-CH_3$)	$C_7H_{11}Cl_3S$ (233.58)	35.99 (35.58	4.15 4.13)
8i	CH_3	CH_3	H	H	H	108—109/7	1665	5.35—6.10 (2H, m, $(=CH-)_2$) 5.18 (1H, s, –CHCl–) 3.41 (2H, br d, J=6, $-CH_2-$) 2.29 (3H, s, $-CCl_2CH_3$) 1.74 (3H, s, $-CH_3$)	$C_7H_{11}Cl_3S$ (233.58)	35.99 (35.66	4.15 4.25)

a) Not distillable and purified by silica gel column chromatography using *n*-hexane as an eluent.

TABLE VI. $R^1R^2C{=}C(R^3)-CH(R^4)-S-CH{=}CCl_2$ **1b—f**

Compd. No.	R^1	R^2	R^3	R^4	bp (°C/mmHg)	IR $\nu_{max}^{liq.}$ cm^{-1} (>C=C<)	PMR δ (ppm in $CDCl_3$, J=Hz)	Formula (M.W.)	Analysis Calcd (Found) C	H
1b	H	H	CH_3	H	75—76/6	1645 1565	6.19 (1H, s, $-SCH{=}CCl_2$) 4.87 (2H, br s, $CH_2=$) 3.27 (2H, br s, $-CH_2-$) 1.80 (3H, br s, $-CH_3$)	$C_6H_8Cl_2S$ (183.10)	39.37 (39.58	4.41 4.41)
1c	CH_3	H	H	H	65—67/0.5	1665 1570	6.22 (1H, $-SCH{=}CCl_2$) 5.30—5.65 (2H, m, $(=CH-)_2$) 3.25 (2H, br d, J=6, $-CH_2-$) 1.70 (3H, d, J=5, $-CH_3$)	$C_6H_8Cl_2S$ (183.10)	39.37 (39.42	4.41 4.88)
1d	C_6H_5	H	H	H	——[a]	1600	7.00—7.40 (5H, m, aromatic protons) 6.18 (1H, s, $-SCH{=}CCl_2$) 5.70—6.45 (2H, m, $(=CH-)_2$) 3.26 (2H, br d, J=6, $-CH_2-$)	$C_{11}H_{10}Cl_2S$ (245.17)	53.89 (53.97	4.11 4.20)
1e	CH_3	CH_3	H	H	79—81/0.3	1665 1570	6.20 (1H, s, $-SCH{=}CCl_2$) 5.20 (1H, br t, J=7, =CH–) 3.33 (2H, br d, J=7, $-CH_2-$) 1.73, 1.67 (6H, br s, $(-CH_3)_2$)	$C_7H_{10}Cl_2S$ (197.12)	42.64 (42.93	5.11 5.11)
1f	2-Cyclohexen-1-yl				92—93/0.15	1645 1565	6.35 (1H, s, $-SCH{=}CCl_2$) 5.40—6.05 (2H, m, $(=CH-)_2$) 3.45—3.75 (1H, m, >CH–S) 1.40—2.20 (6H, m, $(-CH_2-)_3$)	$C_8H_{10}Cl_2S$ (209.13)	45.95 (46.14	4.82 4.88)

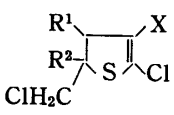
a) Not distillable and purified by silica gel column chromatography using *n*-hexane as an eluent.

TABLE VII. $R^4 \sim\!\!\sim CH=C(R^3)-C(R^1)(R^2)-CCl=CHCl$ **4a–f**

Compd. No.	R^1	R^2	R^3	R^4	bp (°C/mmHg)	IR $\nu_{max}^{liq.}$ cm^{-1} (>C=C<)	PMR δ (ppm in $CDCl_3$, J=Hz)	MS m/z (M^+)	Formula (M.W.)	Analysis Calcd (Found) C	H
4a	H	H	H	H	92—105/760	1645 1620	6.11 (s, *E*-form), 6.08 (s, *Z*-form) (1H, =CHCl) 5.40—6.00 (1H, m, =CH–) 4.90—5.35 (2H, m, $=CH_2$) 2.95—3.35 (2H, m, $-CH_2-$)	136	$C_5H_6Cl_2$ (137.01)	43.83 (43.35	4.41 4.34)
4b	H	H	CH_3	H	110—123/760	1655 1610	6.17 (t, J=1, *E*-form), 6.12 (t, J=0.8, *Z*-form) (1H, =CHCl) 4.81 (2H, br s, $=CH_2$) 3.19 (br s, *Z*-form), 3.03 (br s, *E*-form) (2H, $-CH_2-$) 1.72 (3H, br s, $-CH_3$)	150	$C_6H_8Cl_2$ (151.04)	47.71 (47.82	5.34 5.38)
4c	CH_3	H	H	H	110—118/760	1645 1610	6.11 (s, *E*-form), 6.02 (*s*, *Z*-form)(1H, =CHCl) 5.45—5.90 (1H, m, =CH–) 4.80—5.20 (2H, m, $=CH_2$) 3.83 (br q[a], J=6, *Z*-form), 3.24 (br q[a], J=6, *E*-form) (1H, –CH–) 1.25 (d, J=6, *E*-form), 1.19 (d, J=6, *Z*-form) (3H, $-CH_3$)	150	$C_6H_8Cl_2$ (151.04)	47.71 (47.31	5.34 5.17)
4d	C_6H_5	H	H	H	105—120/3	1640 1605	6.90—7.40 (5H, m, aromatic protons) 6.15 (s, *E*-form), 6.13 (s, *Z*-form)(1H, =CHCl) 5.70—6.35 (1H, m, =CH–) 4.80—5.35 (2H, m, $=CH_2$) 4.34 (br d, J=7, *Z*-form), 3.44 (br d, J=7, *E*-form) (1H, –CH–)	212	$C_{11}H_{10}Cl_2$ (213.11)	62.00 (61.89	4.73 4.56)
4e	CH_3	CH_3	H	H	71—72/27	1640 1600	6.16 (1H, s, =CHCl) 5.85—6.05 (1H, m, =CH–) 4.85—5.25 (2H, m, $=CH_2$) 1.27 (6H, s, $(-CH_3)_2$)	164	$C_7H_{10}Cl_2$ (165.06)	50.94 (50.99	6.11 6.14)
4f	2-Cyclohexen-1-yl				93—106/20	1645 1605	6.09 (d, J=1, *E*-form), 6.06 (d, J=0.3, *Z*-form) (1H, =CHCl) 5.15—6.00 (2H, m, –CH=CH–) 3.60—3.90 (m, *Z*-form), 2.90—3.30 (m, *E*-form)(1H, >CH–) 1.35—2.20 (6H, m, $(-CH_2-)_3$)	176	$C_8H_{10}Cl_2$ (177.01)	54.26 (54.03	5.69 5.51)

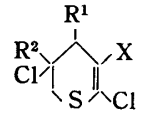
a) br q=broad quintet.

TABLE VIII.



5a—d: X=Cl
9a—c: X=CH$_3$

and



6a, c: X=Cl
10a—c: X=CH$_3$

Compound No.	X	R^1	R^2	bp (°C/mmHg)	IR $\nu_{max}^{liq.}$ cm^{-1} (⟩C=C⟨)	PMR δ (ppm in $CDCl_3$, J=Hz)	CMR δ (ppm in $CDCl_3$)	MS m/z (% rel. int.)	Formula (M.W.)	Analysis Calcd (Found) C	H
4,5-Dihydrothiophenes											
5a	Cl	H	H	115—118/17[a]	1610	3.70—4.25 (3H, m, H-5 and –CH_2Cl) 2.95—3.25 (2H, m, H-4)	121.90 (C-2, s), 115.53 (C-3,s), 46.22, 46.54 (C-4 and –CH_2Cl), 42.52 (C-5, s)	202 (M$^+$, 23) 167 (M – Cl, 6) 153 (M – CH_2Cl, 100) 140 (M – C_2H_2Cl, 22)	$C_5H_6Cl_2S$ (203.51)	29.51 (29.87	2.48 2.60)
5b	Cl	H	CH_3	90—91/5	1610	3.69 (2H, ABq, J=14 and 11, –CH_2Cl) 2.92(2H, ABq, J=21 and 15, H-4) 1.60 (3H, s, –CH_3)	122.14 (C-2, s), 115.02 (C-3, s), 56.67 (C-5, s), 52.18 (–CH_2Cl, t), 48.28 (C-4, t), 25.47 (CH_3, q)	216 (M$^+$, 29) 181 (M – Cl, 14) 166 (M – CH_2Cl, 100) 131 (M – CH_2Cl_2, 23)	$C_6H_7Cl_2S$ (217.54)	33.13 (33.56	3.24 3.34)
5c	Cl	CH_3	H	75—90/1[a]	1605	3.40—3.85 (3H, m, H-5 and –CH_2Cl) 2.95—3.35 (1H, m,H-4) 1.32 (3H, d, J=6, –CH_3)		216 (M$^+$, 52) 201 (M – CH_3, 71) 181 (M – Cl, 30) 166 (M – CH_2Cl, 100)	$C_6H_7Cl_2S$ (217.54)	33.13 (33.42	3.24 3.32)
5d	Cl	C_6H_5	H	—[b]	1610 1600	6.90—7.40 (5H, m, aromatic protons) 3.95—4.60 (2H, m, H-4 and H-5) 3.60—3.80 (2H, m, –CH_2Cl)		278 (M$^+$, 100) 243 (M – Cl, 68) 229 (M – CH_2Cl, 85) 194 (M – CH_2Cl_2, 79)	$C_{11}H_9Cl_2S$ (279.61)	47.25 (47.61	3.24 3.40)
9a	CH_3	H	H	99—102/15[a]	1630	3.50—4.00 (3H, m, H-5 and –CH_2Cl) 2.75—3.00 (2H, m, H-4) 1.76 (3H, s, –CH_3)	125.32 (C-3, s), 118.82 (C-2, s), 47.79, 47.19 (C-5 and –CH_2Cl), 42.48 (C-4, t), 14.74 (CH_3, q)	182 (M$^+$, 23) 147 (M – Cl, 9) 133 (M – CH_2Cl, 100) 120 (M – C_2H_2Cl, 4)	$C_6H_8Cl_2S$ (183.07)	39.36 (39.55	4.40 4.41)
9b	CH_3	H	CH_3	105—110/9[b]	1625	3.73 (2H, ABq, J=12 and 15, –CH_2Cl) 2.71 (2H, ABq, J=11 and 18, H-4) 1.75 (3H, s, C_3–CH_3) 1.59 (3H, s, C_5–CH_3)	125.75 (C–3, s), 118.96 (C–2, s), 57.70 (C–5, s), 52.77 (–CH_2Cl, t), 48.98 (C–4, t), 25.25 (C_5–CH_3, q), 14.95 (C_3–CH_3, q)	196 (M$^+$, 22) 161 (M – Cl, 19) 147 (M – CH_3Cl, 100) 125 (M – HCl_2, 58)	$C_7H_{10}Cl_2S$ (197.12)	42.65 (42.43	5.11 5.34)
9c	CH_3	CH_3	H	88—95/9[b]	1630	3.25—3.80 (3H, m, H-5 and –CH_2Cl) 2.95 (1H, br q, J=7, H-4) 1.73 (3H, s, C_3–CH_3) 1.17 (3H, d, J=7, C_4–CH_3)	129.71 (C-3, s), 118.28 (C-2, s), 55.54 (C-5, d), 48.65 (C-4, d), 46.81 (–CH_2Cl, t), 16.96 (C_4–CH_3, q), 13.38 (C_3–CH_3, q)	196 (M$^+$, 25) 181 (M – CH_3, 13) 161 (M – Cl, 13) 145 (M – CH_4Cl, 56) 125 (M – HCl_2, 15) 106 (M – C_4H_7Cl, 100)	$C_7H_{10}Cl_2S$ (197.12)	42.65 (43.03	5.11 5.42)
3,4-Dihydro-2*H*-thiopyrans											
6a	Cl	H	H	115—118/17[a]	1610	4.42 (1H, nonet, J=7 and 6, H-3) 2.80—3.35 (4H, m, H-2 and H-4)	120.37 (C-6, s), 118.13 (C-5, s), 52.27 (C-4, d), 42.57 (C-3, t), 36.77 (C-2, t)	202 (M$^+$, 36) 167 (M – Cl, 11) 153 (M – CH_2Cl, 40) 140 (M – C_2H_2Cl, 100)	$C_5H_6Cl_2S$ (203.51)	29.51 (29.87	2.48 2.60)
6c[c]	Cl	CH_3	H	75—90/1		3.90—4.40 (1H, m, H-3) 1.25 (3H, d, C_4–CH_3)		216 (M$^+$, 42) 201 (M – CH_3, 39) 181 (M – Cl, 26) 166 (M – CH_3Cl, 36) 154 (M – C_2H_3Cl, 80) 119 (M – $C_2H_3Cl_2$, 100)	$C_6H_7Cl_2S$ (217.54)	33.13 (33.42	3.24 3.32)
10a	CH_3	H	H	99—102/15[a]	1630	4.25—4.50 (1H, m, H-3) 3.10—3.45 (2H, m, H-2) 2.50—2.80 (2H, m, H-4)	124.34 (C-5, s), 116.76 (C-6, s), 53.42 (C-3, d), 41.39 (C-4, t), 37.06 (C-2, t), 21.08 (CH_3, q)	182 (M$^+$, 76) 147 (M – Cl, 60) 133 (M – CH_2Cl, 35) 120 (M – C_2H_3Cl, 100)	$C_6H_8Cl_2S$ (183.07)	39.36 (39.22	4.40 4.52)
10b	CH_3	H	CH_3	105—110/9[b]	1630	3.18 (2H, ABq, J=12 and 17, H-2) 2.61 (2H, ABq, J=7 and 14, H-4) 1.83 (3H, s, C_5–CH_3) 1.74 (3H, s, C_3–CH_3)	123.26 (C-5, s), 116.16 (C-6, s), 63.93 (C-3, s), 47.57 (C-4, t), 42.53 (C-2, t), 29.80 (C_3–CH_3, q), 21.18 (C_5–CH_3, q)	196 (M$^+$, 18) 161 (M – Cl, 21) 147 (M – CH_2Cl, 36) 125 (M – HCl_2, 100)	$C_7H_{10}Cl_2S$ (197.12)	42.65 (42.70	5.11 5.26)
10c[c]	CH_3	CH_3	H	88—95/9		3.80—4.40 (1H, m, H-3) 1.87 (3H, s, C_5–CH_3) 1.35 (3H, d, J=7, C_4–CH_3)		196 (M$^+$, 15) 146 (M – CH_2Cl, 24) 125 (M – HCl_2, 15) 105 (M – C_4H_7Cl, 78) 71 (HCl_2, 100)	$C_7H_{10}Cl_2S$ (197.12)	42.65 (43.03	5.11 5.42)

a) Purified by gas chromatography.
b) Purified by silica gel column chromatography using *n*-hexane as an eluent.
c) This product could not be isolated. Data consistent with the proposed structures of the products were obtained from unpurified mixture containing the 4,5-dihydrothiophene product.

in which adducts obtained by admixture of the mercaptans[7] and chloral were chlorinated with thionyl chloride. By a similar procedure using α,α-dichloropropionaldehyde[8] in place of chloral, 2-alkenyl 1,2,2-trichloropropyl sulfides, **8g**—**i**, were prepared. Among them, **8b**—**i** which are new compounds, are listed in Table V with their IR and PMR spectral data.

2-Alkenyl 2,2-Dichlorovinyl Sulfides (1a—f)——Dechlorination of **8a** to **1a** by the use of zinc dust in acetic acid–ethanol has been reported,[3] and **1a**—**f** were prepared in a similar manner; IR and PMR spectral data are given in Table VI. The products, **1a**—**c**, **1e** and **1f**, could be purified by distillation under very low pressure at temperatures below those causing decomposition. The product **1d** was purified by silica gel column chromatography using *n*-hexane as an eluent.

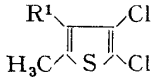
Thermal Rearrangement of 1a—f——Compounds **1a**—**f** underwent rearrangement on heating at 160—180°C. In the case of **1a**—**c**, the volatile products were collected by topping during the heating procedure. The reaction temperatures and yields of the products, 1,2-dichlorinated 1,4-pentadienes, are shown in Table I. Physical, spectral and analytical data are listed in Table VII. The *E*-/*Z*-isomer ratios were determined by GLC measurement (Shimadzu GC-7a; column, 5% FFAP on Chromosorb WAW-DMCS).

2-Alkenyl 1,2,2-Trichlorovinyl Sulfides (2a—e)——A solution of triethylamine (0.055 mol) in 10 ml of benzene was added in small portions to a stirred solution of **8a**—**e** (0.05 mol) in 50 ml of benzene at room temperature. Triethylamine hydrochloride deposited was filtered off. Evaporation of benzene from the filtrate under reduced pressure gave **2a**—**e**, in a nearly pure state. The methine protons of the starting **8a**—**e** were considerably quenched in the PMR spectra. Distillation for further purification was avoided, because of the thermal instability of the products. Exceptionally, **2e** was stable even at 250°C, and was purified as a liquid, bp 95—97°C/0.1 mmHg. IR ν_{max}^{liq} cm^{-1}: 1665 (>C=C<). PMR (ppm in $CDCl_3$, J=Hz) δ: 5.19 (1H, br t, J=7, -CH=), 3.51 (2H, br d, J=7, $-CH_2-$), 1.70 (6H, br s, $(-CH_3)_2$).

2-Alkenyl 1,2-Dichloro-1-propenyl Sulfides (3a—c)——A solution of potassium *tert*-butoxide (0.06 mol) in 30 ml of THF was added dropwise to a stirred solution of **8a**—**i** (0.05 mol) in 30 ml of THF with cooling. The stirring was continued for 1 h at room temperature. After addition of a small amount of water, CO_2 gas was bubbled through the mixture. The resulting mixture was concentrated under reduced pressure and extracted with diisopropyl ether (IPE). The IPE solution was dried over $MgSO_4$. Evaporation of IPE under reduced pressure gave almost pure **3a**—**c**. The methine protons of the starting **8g**—**i** were considerably quenched in the PMR spectra. Distillation for further purification was avoided, because of the thermal instability of the products.

Thermal Rearrangement of 2a—d and 3a—c——Compounds **2a**—**d** and **3a**—**c** (0.05 mol) were heated at the temperatures shown in Table II. Except for **2d**, distillation of the resulting oils under reduced pressure afforded a mixture of dihydrothiophenes, **5** or **9**, and dihydro-2*H*-thiopyrans, **6** or **10**. In the case of **2d**, **5d** was obtained by silica gel column chromatography using *n*-hexane as an eluent. The 4,5-dihydrothiophene/3,4-dihydro-2*H*-thiopyran ratios were determined by GLC measurement (Shimadzu GC-7a; column, 5% FFAP on Chromosorb WAW-DMCS). Compounds **5a**, **5c**, **6a**, **9a** and **10a** were isolated in a pure state by

TABLE IX.



11a—d

Compd. No.	R^1	bp (°C/mmHg)	IR ν_{max}^{liq} cm^{-1} (>C=C<)	PMR δ (ppm in $CDCl_3$, J=Hz)	CMR δ (ppm in $CDCl_3$)	MS m/z (M^+)	Formula (M.W.)	Analysis Calcd (Found) C	H
11a	H	95—97/24	1575 1565	6.42 (1H, q, J=1.1, H-4) 2.32 (3H, d, J=1.1, $-CH_3$)	136.95 (C-5, s), 124.86 (C-4, s) 122.71 (C-3, s), 120.72 (C-2, s) 15.70 ($-CH_3$, q)	166	$C_5H_4Cl_2S$ (167.05)	35.95 (36.08	2.41 2.62)
11c	CH_3	93—95/15	1570 1560	2.22 (3H, q, J=0.8, C_5-CH_3) 2.00 (3H, q, J=0.8, C_4-CH_3)	130.51 (C-5, s), 129.93 (C-4, s) 124.38 (C-3, s), 118.98 (C-2, s) 13.75, 12.78 (C_5-CH_3 and C_4-CHq)	180	$C_6H_6Cl_2S$ (181.08)	39.80 (40.12	3.34 3.51)
11d	C_6H_5	——[a]	1600 1580	7.10—7.50 (5H, m, aromatic protons) 2.27 (3H, s, $-CH_3$)		242	$C_{11}H_8Cl_2S$ (243.15)	54.34 (54.58	3.32 3.50)

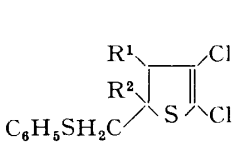
a) Purified by silica gel column chromatography using *n*-hexane as an eluent.

preparative GLC treatment (Hitachi 163T machine; column, 5% FFAP on Chromosorb WAW-DMCS for **5a**, **6a**, **9a** and **10a**; 20% SE-30 on Chromosorb WAW-DMCS for **5c**), and **9b**, **9c** and **10b** were isolated by silica gel column chromatography using *n*-hexane as an eluent. The products **6c** and **10c** could not be isolated in a pure state, presumably owing to the existence of diastereomers. Yields of the products are shown in Table II. The physical, spectral and analytical data are shown in Table VIII.

Dehydrochlorination of 5a—d with Potassium *tert*-Butoxide——A solution of potassium *tert*-butoxide (0.012 mol) in 10 ml of THF was added dropwise to a solution of 3,4-dihydro-5-chloromethylthiophenes, **5** (0.01 mol) in 10 ml of THF at 0—5°C with stirring, and stirring was continued for 1 h at room temperature. After addition of a small amount of water, CO_2 gas was bubbled through the mixture. The resulting mixture was concentrated under reduced pressure and extracted with IPE. The IPE solution was dried over $MgSO_4$. After removal of the IPE under reduced pressure, distillation of the resulting residue under reduced pressure gave 2,3-dichloro-5-methylthiophenes (**11**). Yields of the products are shown in Table III, and the spectral data are shown in Table IX.

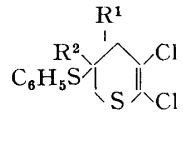
Substitution of 5a—d and 6a—c with Sodium Benzenethiolate——A solution of a dihydrothiophene, **5**, or a dihydro-2*H*-thiopyran, **6** (0.01 mol), in 10 ml of ethanol was added dropwise to 0.011 mol of sodium benzenethiolate in 30 ml of ethanol at room temperature. The reaction mixture was refluxed for 2 h. The precipitate of sodium chloride was filtered off, and the filtrate was concentrated under reduced pressure. The benzene solution of the resulting residue was washed with water and dried over $MgSO_4$. After removal of the benzene

TABLE X.



13b—d

and



12a, c

Compd. No.	R^1	R^2	bp (°C/mmHg)	IR $\nu_{max}^{liq.}$ cm^{-1} (>C=C<)	PMR δ (ppm in $CDCl_3$, J=Hz)	MS m/z (M^+)	Formula (M.W.)	Analysis Calcd (Found) C	H
13b	H	CH_3	140—145/0.3	1605 1585	7.05—7.50 (5H, m, aromatic protons) 3.31 (2H, s, $-SCH_2-$) 2.85 (2H, ABq, J=23 and 16, H-4) 1.57 (3H, s, $-CH_3$)	290	$C_{12}H_{12}Cl_2S_2$ (291.25)	49.49 (49.87	4.15 4.24)
13c	CH_3	H	——[a]	1600 1590	7.05—7.50 (5H, m, aromatic protons) 2.80—3.55 (4H, m, H-4, H-5 and $-SCH_2-$) 1.18 (3H, d, J=6, $-CH_3$)	290	$C_{12}H_{12}Cl_2S_2$ (291.25)	49.49 (49.95	4.15 4.27)
13d	C_6H_5	H	——[a]	1600 1585	6.85—7.40(10H, m, aromatic protons) 4.11 (1H, d, J=6, H-4)[b] 4.07 (1H, d, J=7, H-4)[c] 3.45—3.85 (1H, m, H-5) 3.22 (2H, d, J=6, $-SCH_2-$)[b] 3.21 (2H, d, J=7, $-SCH_2-$)[c]	352	$C_{17}H_{14}Cl_2S_2$ (353.33)	57.79 (57.65	3.99 4.03)
12a	H	H	105—107/0.1	1605 1585	7.05—7.60 (5H, m, aromatic protons) 4.36 (1H, nonet, J=7 and 6, H-3) 2.77—3.35 (4H, m, H-2 and H-4)	276	$C_{11}H_{10}Cl_2S_2$ (277.23)	47.66 (47.92	3.64 3.69)
12c	CH_3	H	——[a]	1600 1590	7.05—7.50 (5H, m, aromatic protons) 4.22 (1H, sextet, J=8 and 7, H-3) 2.85—3.25 (3H, m, H-2 and H-4) 1.16 (3H, d, J=7, $-CH_3$)	290	$C_{12}H_{12}Cl_2S_2$ (291.25)	49.49 (49.95	4.15 4.27)

a) Purified by silica gel column chromatography using *n*-hexane as an eluent.
b) C_4-Phenyl/C_5-phenylthiomethyl *trans*.
c) C_4-Phenyl/C_5-phenylthiomethyl *cis*.

under reduced pressure, distillation of the resulting residue under reduced pressure gave **12** or **13**. Yields of the products are shown in Table IV, and the spectral data are shown in Table X.

Trapping of the Intermediary Sulfenyl Chloride in the Thermal Reaction of 2b and 3b——A solution of 2-methyl-2-propenyl 1,2,2-trichlorovinyl sulfide, **2b**, or 2-methyl-2-propenyl 1,2-dichloro-1-propenyl sulfide, **3b** (0.05 mol), in 50 ml of cycloheptene was refluxed for 2 h. After removal of cycloheptene under reduced pressure, distillation of the resulting residue under reduced pressure gave **14a** or **14b**. **14a**: yield; 42.3% bp 133—135°C/0.3 mmHg. IR ν_{max}^{liq} cm^{-1}: 1645, 1565 (>C=C<): PMR (ppm in $CDCl_3$) δ: 4.65—5.05 (2H, m, $=CH_2$), 4.10—4.45 (1H, m, cycloheptanyl H-2), 3.60—3.95 (1H, m, cycloheptanyl H-1), 3.43, 3.32 (2H, br s, $-CH_2-$), 1.40—2.40 (13H, m, cycloheptanyl protons and $-CH_3$). MS *m/z*: 312 (M^+). **14b**: yield; 35.0%, bp 140—141°C/0.1 mmHg. IR ν_{max}^{liq} cm^{-1}: 1645 (>C=C<). PMR (ppm in $CDCl_3$) δ: 4.60—5.05 (2H, m, $=CH_2$), 4.10—4.50 (1H, m, cycloheptanyl H-2), 3.55—3.90 (1H, m, cycloheptanyl H-1), 3.12, 3.04 (2H, br s, $-CH_2-$), 1.95, 1.89 (3H, s, $-SCCl=CClCH_3$), 1.40—2.40 (13H, m, cycloheptanyl protons and $-CH_3$).

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References and Notes

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