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FREE-RADICAL THIYLATION OF DI-, TRI-, AND TETRACHLOROETHYLENES AND 1,1,2-TRICHLOROPROPENE WITH ORGANYL THIOLS AND DIARYL DISULFIDES

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UV-Irradiation and benzoyl peroxide initiated radical reactions of the title ethenes with aliphatic and aromatic thiols and diaryl disulfides are presented. From these reactions individual unsaturated sulfides RSCX=CYZ (X, Y, Z = H, Cl, CH_3) or mixtures of the above isomeric sulfides and saturated sulfides RSCXX'CX''X'''Y (X, X', X'', X''' = H, Cl; Y = H, Cl, CH_3) have been obtained. The reaction features in each given case and differences in the reaction course for thiols and disulfides are discussed. Reaction mechanisms explaining the differences in the process in each particular case are suggested.

KEY WORDS Free-radical thiylation, Arenethiols, Diaryl disulfides, Polychloroolefins.

I. INTRODUCTION

Before the present investigations the radical thiylation of chloroolefins such as vinyl chloride[1,2a,2b], vinylidene chloride,[4] *cis*- and *trans*-2-chloro-2-butene,[1,5a,5b] 1,1,3-trichloropropene,[6] and 1-chlorocyclohexene,[1,7a,7b] with hydrogen sulfide and thiols were known to lead to saturated sulfides:

$$RSH + R'CH{=}CR''Cl \longrightarrow RSCHR'CHR''Cl$$

R' = R'' = H, R = H[1], Me[2a], $HOCH_2CH_2$[3]; R' = H, R'' = Cl, R = CF_3[4]; R' = R'' = Me, R = H[1], Ac[5a,b]; R' = CH_2Cl, R'' = Cl, R= Bu, Ph[6]; RR'' = $(CH_2)_4$, R = H[1,7a], Ph[7a,b], Ac[7a], 4-ClC_6H_4, 4-$CH_3C_6H_4$[7b]

It has also been reported that in the presence of benzoyl peroxide the reaction of thiophenol and 4-methylbenzenethiol with trichloroethylene affords aryl β,β-dichlorovinyl sulfides:

$$ArSH + CHCl{=}CCl_2 \xrightarrow[-HCl]{Bz_2O_2} ArSCH{=}CCl_2$$

Ar = Ph[8a], 4-$CH_3C_6H_4$[8b]

However, neither the mechanism nor the extent of the reaction have been discussed.

The present research has allowed us to establish some regularities in the radical thiylation of polychloroethenes, CHX=CClY (X, Y = H, Cl) and CCl_2=CClR' (R' = Me, H, Cl) with organyl thiols RSH (R = Alk, Ar) and diaryl disulfides ArSSAr and to find some synthetically useful reactions among those studied.

II. REACTIONS WITH THIOLS

1. Dichloroethylenes, CHX=CClY (X, Y = H, Cl)

As early as 1959 Walling *et al.* attempted to carry out a radical reaction of 1-dodecanethiol with 1,2-dichloroethylene in the presence of azobisisobutyronitrile at 60 °C.[9] However, no products were obtained in this way. Trifluoromethanethiol with 1,1-dichloroethylene, when exposed to UV irradiation, gave 17% of $CF_3SCH_2CHCl_2$.[4]

We have found that the UV-initiated reaction of BuSH and PhSH with *trans*-CHCl=CHCl leads to the 2,2-dichloroethyl sulfides *1b,g,h*, the *trans-2b,g,h* and *cis*-β-chlorovinyl sulfides *3b,g,h*, the disulfides *4b,g,h* and the *cis-5b,g,h* and *trans*-bis(organylthio)ethenes *6b,g,h*[10] (Scheme 1).

$$\mathrm{RSH + CHCl{=}CHCl \longrightarrow \underset{1b,g,h}{RSCH_2CHCl_2} + \underset{2b,g,h,\ 3b,g,h}{\textit{trans-, cis-}RSCH{=}CHCl} + \underset{4b,g,h}{RSSR} + \underset{5b,g,h,\ 6b,g,h}{\textit{cis-, trans-}RSCH{=}CHSR}}$$

R = Ph (b), Bu (g), C_6H_{13} (h)

SCHEME 1

The above compounds were identified by IR and ^{1}H NMR spectroscopy (Table 1). When R = Ph, the sulfides *1*, *2*, and *3* (in a ratio of 42:43:15 in the starting mixture) were isolated separately by preparative chromatography.

When exposed to UV irradiation BuSH and CH_2=CCl_2 afforded $BuSCH_2CHCl_2$ (*1g*). This structure was confirmed by the presence of not only the (m/e 186) molecular ion, but also an intense peak of the fragment $BuSCH_2^+$ (m/e 103) in the mass spectrum of this sulfide. According to GLC and ^{1}H NMR parameters the latter was identical to *1g* obtained in the reaction with 1,2-dichloroethylene. This provides strong evidence for the fact that it is anomalous sulfides *1* that are formed in the above reaction. Refluxing of the sulfide *1g* leads to its dehydrochlorination to give the *trans*- and *cis*-β-chlorovinyl sulfides *2g* and *3g*.

The content of bis-(butylthio)ethenes *5g* and *6g* in the reaction mixture was 25% (according to GLC) in a ratio of *5g*:*6g* = 53:47. To be certain about the formation of these products a fraction enriched with *5g* and *6g* to 40% was oxidized with H_2O_2. The resultant 1,2-(dibutylsulfonyl)ethylene *7g* (m.p. 145–146 °C) was isolated and identified by IR and ^{1}H NMR spectra (Table 1). The IR spectrum displays no double-bond absorption and this indicates that the compound under consideration is the *trans*-

TABLE 1

^{1}H NMR and IR Spectra of Compounds $RSCH_2CHCl_2$ (*1b,g*), $RSCH^1{=}CH^2Cl$ (*2b,g*, *3b,g*), $RSO_2CH{=}CHSO_2R$ (*7g*)

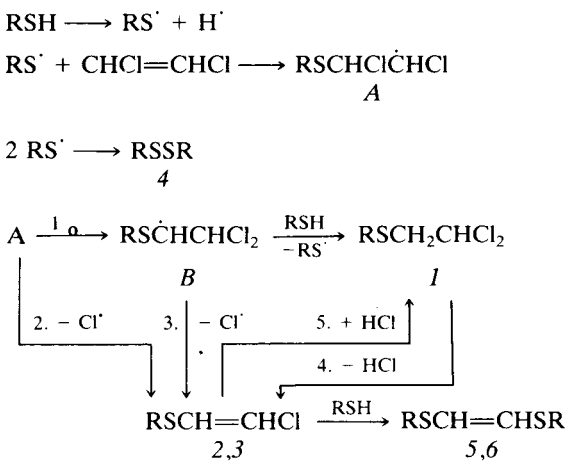
		^{1}H NMR, δ(ppm)					
	R	R	CH_2CHCl_2	H_1	H_2	(cps)	IR (cm^{-1})
1b	Ph	7.02–7.28 m (5H,Ph)	3.40 d (2H) 5.45 t (1H)				1582 (Ph) 2980 (CH)
1g	Bu	0.86 t (3H) 1.46 m (4H) 2.58 t (2H)	3.10 d (2H) 5.64 t (1H)				2960 (CH)
2b[a]	Ph	7.05–7.45 m (5H,Ph)		6.45 d (1H)	6.20 d (1H)	13.0	1585, 1540 (C=C)
3b[b]	Ph	6.98–7.57 m (5H,Ph)		6.43 d (1H)	6.02 d (1H)	6.0	1580, 1560 (C=C)
2g[c]	Bu	0.86 t (3H) 1.46 m (4H) 2.58 t (2H)		6.30 d (1H)	5.88 d (1H)	12.5	3085 (=CH) 1560 (C=C)
3g[d]	Bu	0.86 t (3H) 1.46 m (4H) 2.58 t (2H)		6.22 d (1H)	5.93 d (1H)	6.5	3085 (=CH) 1560 (C=C)
7g	Bu	0.88 t (3H) 1.52 m (4H) 3.04 t (2H)		7.32 s (2H)			3080 (=CH) 2985–2880 (CH) 1330, 1125 (SO_2)

Lit.: [a]δ(Ar) 7.15–7.40 m, δ(H^1) 6.47 d, δ(H^2) 6.20 d $J_{H^1H^2}$ 13.0[11]; [b]δ(Ar) 7.20–7.55 m, δ(H^1) 6.58 d, δ(H^2) 6.18 d, $J_{H^1H^2}$ 6.5[11]; [c]δ(H^1) 6.38 d, δ(H^2) 5.97 d, $J_{H^1H^2}$ 13.0[11]; [d]δ(H^1) 6.27 d, δ(H^2) 6.01 d, $J_{H^1H^2}$ 6.5[12].

isomer.[13] The absence of the *cis*-isomer is indicative of a possible cis-trans isomerization.

The most interesting result of this reaction is the formation of the 2,2-dichloroethyl sulfides *1* rather than 1,2-dichloroethyl sulfides as might be expected. This anomaly can most reasonably be explained in terms of the α,β-chlorotropic rearrangement of the primary radical *A* to the secondary radical *B* (Scheme 2).

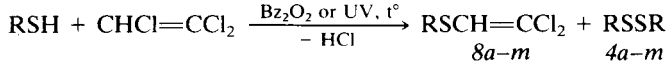
The formation of the sulfides *1* might be due to the addition of gaseous HCl to the β-chlorovinyl sulfides *2* and *3* (Scheme 2, pathway 5). This process is, however, unlikely since the sulfide *1* content of the reaction mixture should have increased with time which was not observed. On the other hand, the sulfides *2* and *3* may be formed either independently of the formation of the sulfides *1* (pathway 2), or from the radical *B* (pathway 3), or involving dehydrochlorination of the sulfides *1* (pathway 4). The contribution from pathway 4 appears to be negligible. First, the sulfides *2g* and *3g* are not formed in any noticeable amounts when the sulfide *1* is obtained from 1-butanethiol and 1,1-dichloroethylene, and, secondly, *1* undergoes dehydrochlorination only upon reflux with KOH in benzene.



SCHEME 2

2. *Tri- and Tetrachloroethylene*

Of all the reactions studied the radical one between organothiols and trichloroethylene is most interesting as a general convenient route to organyl β,β-dichlorovinyl sulfides *8*.[14] Neither variation of the substituent in the benzene ring of the arenethiols from electron-releasing (OMe) to electron-withdrawing (Cl), nor a change in the size and branching of the aliphatic group in the alkanethiols, nor use of functionally substituted aliphatic thiols have led to saturated trichloroethyl sulfides, $RSCHClCHCl_2$. The organyl β,β-dichlorovinyl sulfides *8a–m* and the diorganyl disulfides *4a-m* were the only reaction products (Scheme 3).



R: 4-$CH_3C_6H_4$ (*a*), Ph (*b*), 4-ClC_6H_4 (*c*), 4-$CH_3OC_6H_4$ (*d*), Et (*e*), Pr (*f*), Bu (*g*), C_6H_{13} (*h*), $CH_2C_6H_5$ (*i*), CH_2COOH (*j*), 3-$CH_3C_6H_4$ (*k*), *i*-Pr (*l*), *t*-Bu (*m*)

SCHEME 3

The structure of the sulfides *8a–m* obtained was supported by IR and ^1H NMR spectral data. Comparison of the physicochemical constants of the above compounds with those of the known β,β-dichlorovinyl sulfides obtained in other ways[15,16a,16b] and α,β-dichlorovinyl sulfides[17a–d] clearly supports the former structure. In order to finally solve the question of the structure of the sulfides *8* the latter were oxidized to the sulfones *9* (Scheme 4).[14]

In this case the formation of products which correspond completely, according to physical and chemical parameters, to the known β,β-dichloro-vinyl sulfones,[8a,8b,18,19]

$$RSCH{=}CCl_2 \xrightarrow[AcOH]{30\%\ H_2O_2} \underset{9a\text{–}j,n}{RSO_2CH{=}CCl_2} \quad (4)$$

R: 4-$CH_3C_6H_4$ (*a*), Ph (*b*), 4-$CH_3OC_6H_4$ (*d*), 4-ClC_6H_4 (*c*), Et (*e*), Pr (*f*), Bu (*g*), C_6H_{13} (*h*), $CH_2C_6H_5$ (*i*), CH_2COOH (*j*), 4-$O_2NC_6H_5$ (*n*)

SCHEME 4

and the ability of the two chlorine atoms in the sulfones obtained to be substituted by a nucleophile (an aromatic amine, for example[18-20]) indicate unambiguously their geminal arrangement in both the sulfone *9* and the starting sulfide *8*.

The reaction with arenethiols could be initiated by refluxing with organic peroxides, such as benzoyl peroxide. No sulfide $O_2NC_6H_4SCH{=}CCl_2$ was isolated in this case due to its spontaneous oxidation to the sulfone *9n* during the reaction. Similar high activity towards the oxidation of *p*-nitro substituted sulfur-containing compounds was observed by Kharasch who found that even organic peroxides were able to oxidize 2,4-dinitrobenzenesulfenyl chloride to the sulfonyl chloride.[21]

The reaction of alkanethiols with trichloroethylene could likewise be initiated with organic peroxides. The best results, however, are observed upon UV irradiation of refluxing mixtures of thiols and trichloroethylene,[14] the formation of disulfides being suppressed to a considerable degree.

Radical reactions of organylthiols with tetrachloroethylene are less specific. The reaction mixtures obtained from the reaction of tetrachloroethylene with propane- and butanethiol, respectively, contain three types of products: the trichlorovinyl sulfides *10f,g*, the dialkyl disulfides *4f,g*, and the geminal dichlorovinyl sulfides *8f,g* in a ratio of 53.9:36.4:9.7 for PrSH and 55.0:36.5:8.5 for BuSH (Scheme 5).[14]

Even more complicated is the reaction of tetrachloroethylene with aromatic thiols. Along with the aryl trichlorovinyl sulfides *10a–c*, the β,β-dichlorovinyl sulfides *8a–c* and the diaryl disulfides *4a–c*, the reaction mixtures contained the aryl α,β-dichlorovinyl sulfides *11a–c*, the 1,1,2,2-tetrachloroethyl sulfides *12a–c*, and the 1,2,2,2-tetrachloroethyl sulfides *13a–c* as well as the isomeric bis-(arylthio)dichloroethenes *14–16a–c*[22] (Scheme 5).

$$RSH + CCl_2{=}CCl_2 \xrightarrow{UV} \underset{10a\text{–}c,f,g}{RSCCl{=}CCl_2} + \underset{8a\text{–}c,f,g}{RSCH{=}CCl_2} + \underset{11a\text{–}c}{RSCCl{=}CHCl} +$$

$$+ \underset{4a\text{–}c,f,g}{RSSR} + \underset{12a\text{–}c}{RSCCl_2CHCl_2} + \underset{13a\text{–}c}{RSCHClCCl_3} + \underset{14a\text{–}c}{RSCCl{=}CClSR} \text{ } \underset{15a\text{–}c}{\textit{-cis, -trans}} +$$

$$+ \underset{16a\text{–}c}{(RS)_2C{=}CCl_2}$$

R = 4-$CH_3C_6H_4$ (*a*), Ph (*b*), 4-ClC_6H_4 (*c*), Pr (*f*), Bu (*g*)

SCHEME 5

The multicomponent mixtures obtained were analyzed by GLC using standard samples synthesized by known techniques, and by ^1H NMR spectroscopy and GLC-MS. Besides, treatment with dehydrochlorinating agents (triethylamine, Al_2O_3), which simplified the reaction mixtures, was employed.

TABLE 2

GLC–MS Data for the Reaction Mixtures Obtained in the Radical Reaction of ArSH with $CCl_2 = CCl_2$

		Ar	
	Compound	**C_6H_5[a]**	**4-$CH_3C_6H_4$**
4	ArSSAr	218 $[M]^+$	246 $[M]^+$
8	$ArSCH{=}CCl_2$	204 $[M]^+$, 169 $[M—Cl]^+$, 134 $[M—2Cl]^+$, 109 $[PhS]^+$	218 $[M]^+$, 183 $[M—Cl]^+$, 148 $[M—2Cl]^+$, 168 $[M—Cl—CH_3]^+$, 123 $[TolS]^+$
10	$ArSCCl{=}CCl_2$	238 $[M]^+$, 203 $[M—Cl]^+$, 168 $[M—2Cl]^+$, 133 $[M—3Cl]^+$, 156 $[M—CCl_2]^+$, 109 $[PhS]^+$	252 $[M]^+$, 217 $[M—Cl]^+$, 182 $[M—2Cl]^+$, 147 $[M—3Cl]^+$, 170 $[M—CCl_2]^+$, 202 $[M—Cl—CH_3]^+$, 123 $[TolS]^+$
11	$ArSSCl{=}CHCl$	204 $[M]^+$, 169 $[M—Cl]^+$, 134 $[M—2Cl]^+$, 156 $[M—CHCl]^+$, 109 $[PhS]^+$	218 $[M]^+$, 183 $[M—Cl]^+$, 148 $[M—2Cl]^+$, 168 $[M—Cl—CH_3]^+$, 123 $[TolS]^+$
12	$ArSCCl_2CHCl_2$		288 $[M]^+$, 253 $[M—Cl]^+$, 218 $[M—2Cl]^+$, 183 $[M—3Cl]^+$, 148 $[M—4Cl]^+$, 205 $[M—CHCl_2]^+$, 123 $[TolS]^+$
13	$ArSCHClCCl_3$	274 $[M]^+$, 239 $[M—Cl]^+$, 204 $[M—2Cl]^+$, 169 $[M—3Cl]^+$, 134 $[M—4Cl]^+$, 157 $[M—CCl_3]^+$, 109 $[Phs]^+$	288 $[M]^+$, 253 $[M—Cl]^+$, 218 $[M—2Cl]^+$, 183 $[M—3Cl]^+$, 148 $[M—4Cl]^+$, 171 $[M—CCl_3]^+$, 123 $[TolS]^+$
14-16	$ArSCCl{=}CClSAr$ and $(ArS)_2C{=}CCl_2$	312 $[M]^+$, 277 $[M—Cl]^+$, 242 $[M—2Cl]^+$, 203 $[M—PhS]^+$, 168 $[M—PhS—Cl]^+$, 109 $[PhS]^+$	340 $[M]^+$, 305 $[M—Cl]^+$, 270 $[M—2Cl]^+$, 217 $[M—TolS]^+$, 182 $[M—TolS—Cl]^+$, 123 $[TolS]^+$

[a] After purification on aluminium oxide.
[b] After purification on silica gel.

The formation of the aryltetrachloroethyl sulfides *12* and *13* was proven by GLC-MS of the resultant reaction mixtures (Table 2).

In spite of its complexity the present reaction can be used with arenethiols for preparing aryl trichlorovinyl sulfides, since tetrachloroethyl sulfides are readily dehydrochlorinated with triethylamine and the aryl dichlorovinyl sulfide content of the reaction mixture does not exceed 1–2%. The trichlorovinyl sulfide *10c*, for example, was prepared in this manner after treatment with triethylamine.[22]

As with trichloroethylene, the best initiation procedure involves UV irradiation of a refluxing mixture of arenethiol and tetrachloroethylene (Table 3).

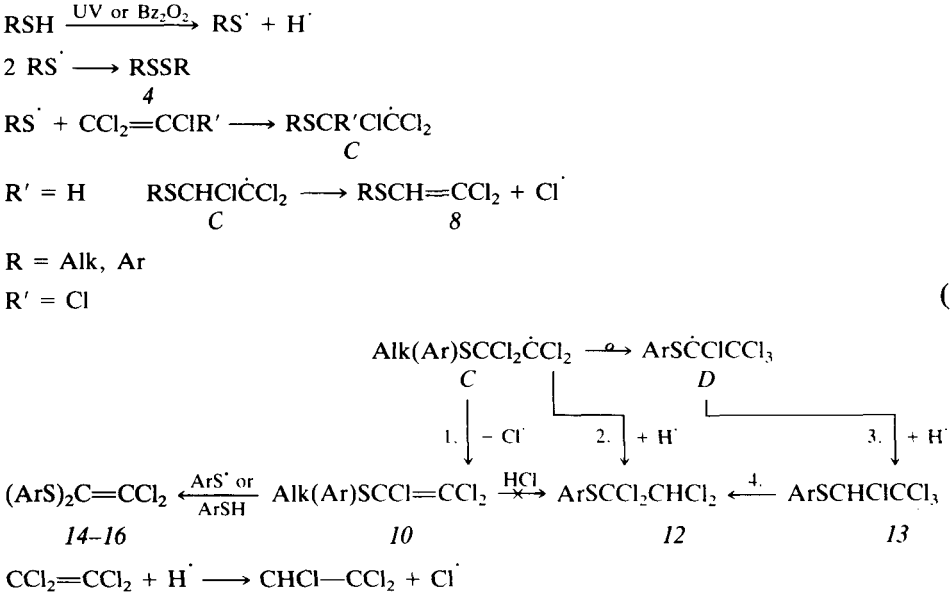
As to the mechanism of the radical interaction of organyl thiols with tri- and tetrachloethylene it should be noted that if the saturated sulfides are formed, as in the case of tetrachloroethylene, they should not be regarded as intermediates, since their content increases with time instead of decreasing (Table 3). Therefore the reaction

TABLE 3

The Reaction Product Distribution (% of Total Content by GLC) vs. Reaction Time and the Method of Initiation for the Reaction of TolSH with CCl_2=CCl_2

Initiation	Reaction time, h	TolSH	*4a*	*8a + 11a*	*10a*	*12a*	*13a*	*13a/12a*	*10a/(12a + 13a)*
Benzoyl peroxide, reflux	2.5	95.7	0.4	–	3.5	–	0.4	–	8.8
	9.2	82.6	2.8	0.4	11.3	0.1	2.8	28.0	3.9
	16.5	65.3	6.6	0.6	20.9	0.8	5.8	7.3	3.2
UV irradiation, reflux	10.0	16.3	10.8	1.1	52.6	5.5	13.5	2.4	2.7

mechanism involving the formation of intermediate radical *C* must be considered as the most reasonable one (Scheme 6).



(6)

SCHEME 6

A similar mechanism has been suggested for the formation of triethyl-(β,β-dichlorovinyl)silane by the γ-initiated reaction of triethylsilane with trichloroethylene.[23]

It is possible to explain the formation of the sulfides *8* and *10* in terms of an alternative Scheme 7 involving $RS^{\cdot}$ and $\dot{C}H{=}CCl_2$ and $\dot{C}Cl{=}CCl_2$ radical recombination.

$$CR'Cl{=}CCl_2 \xrightarrow{UV} \dot{C}R'{=}CCl_2 + Cl^{\cdot} \text{ or}$$
$$RS^{\cdot} + CR'Cl{=}CCl_2 \longrightarrow RSCl + \dot{C}R'{=}CCl_2$$
$$RS^{\cdot} + \dot{C}R'{=}CCl_2 \longrightarrow RSCR'{=}CCl_2$$
$$R' = H, Cl$$

SCHEME 7

It has been reported,[23] however, that the geminal chlorine atoms in trichloroethylene are 30 times more reactive than an individual chlorine atom. Therefore, according to Scheme 7, it is more reasonable to expect the sulfide $RSCCl{=}CHCl$ to appear:

$$CHCl{=}CCl_2 \xrightarrow{UV} CHCl{=}\dot{C}Cl + Cl^{\cdot}$$
$$CHCl{=}\dot{C}Cl + RS^{\cdot} \longrightarrow RSCCl{=}CHCl$$

Furthermore, comparison of the C—H and C—Cl bond energies (E_{C-H} and E_{C-Cl} = 104 and 138 kcal/mole, respectively) allows one to draw the conclusion that the formation of a $\dot{C}Cl{=}CCl_2$ radical which, in the case of trichloroethylene, would give trichlorovinyl sulfides $RSCCl{=}CCl_2$, is more likely. On the other hand, the above alternative mechanism fails to explain the appearance of the aryl tetrachloroethyl sulfides *12* and *13* in the case of tetrachloroethylene. Special experiments have shown that the trichlorovinyl sulfides *10* do not add gaseous HCl under the reaction conditions.[22] The appearance of the sulfides *12* and *13* can only be explained by stabilization of the intermediate radical $ArSCCl_2\dot{C}Cl_2$ and the rearranged radical $ArS\dot{C}ClCCl_3$ via the addition of $H^{\cdot}$ (Scheme 6). The sulfide *12* → *13* isomerization is unlikely, since the reverse process, an increase in the relative content of *12*, occurs in the reaction course (Table 3). This fact can reasonably be attributed to either *13* → *12* isomerization or a gradual predominance of reaction pathway 2 over *C* → D radical rearrangement (Scheme 6).

The unexpected appearance of the β,β-dichlorovinyl sulfides *8* in the reaction with tetrachloroethylene seems to be due to the tetrachloroethylene → trichloroethylene conversion under the reaction conditions (Scheme 6). A calculation using the heats of formation of the radicals $H^{\cdot}$ and $Cl^{\cdot}$ (52.10 and 28.95 kcal/mole, respectively) and those of tetra- and trichloroethylene gives $\Delta H = -28 \div -31$ kcal/mole which indicates this process to be thermodynamically possible. An alternative mechanism (Scheme 8) was rejected on the basis of direct experiments with UV irradiation of propyl trichlorovinyl sulfide *10f* and 1-hexanethiol in tetrachloroethylene which had revealed the presence of trichloroethylene and hexyl β,β-dichlorovinyl sulfide *8h* and no propyl β,β-di-chlorovinyl sulfide *8f* in the reaction mixture.[14]

$$RSCCl{=}CCl_2 + H^{\cdot} \longrightarrow RSCHCl\dot{C}Cl_2 \longrightarrow RSCH{=}CCl_2 + Cl^{\cdot}$$

SCHEME 8

III. DIARYL DISULFIDES AND POLYCHLOROETHYLENES CCl_2=CClR (R = H, Cl)

In general, diaryl disulfides are more convenient to handle than the corresponding thiols and, at the same time, equally capable to generate thiyl radicals. The energy of the S—S bond homolytic dissociation is known to be of the same order as that of the S—H bond.

It has been shown,[24,25] however, that the absence of the reducing H· radical in the reaction mixture strongly affects the reaction course.

The radical reaction of diaryl disulfides with trichloroethylene is completely devoid of the selectivity common in the reactions with thiols. The reaction products are the aryl β,β-dichlorovinyl sulfides *8a–c*, the aryl α,β-dichlorovinyl sulfides *11a–c*, the aryl trichlorovinyl sulfides *10a–c* as well as the trichloroethylene dimer, 1,1,3,3,4,4-hexachloro-1-butene,[24,25] (Scheme 9) which is not generated in the case of thiols.[15]

$$ArSSAr + CHCl{=}CCl_2 \longrightarrow \underset{8a-c}{ArSCH{=}CCl_2} + \underset{11a-c}{ArSCCl{=}CHCl} +$$

$$\underset{10a-c}{ArSCCl{=}CCl_2} + \underset{13a-c}{ArSCHClCCl_3} + CCl_2{=}CHCCl_2CHCl_2$$

Ar = 4-$CH_3C_6H_4$ (*a*), Ph (*b*), 4-ClC_6H_4 (*c*)

The formation of the above compounds was proven by GLC using standard mixtures of known composition[22] and by ^{1}H NMR spectra displaying signals of the =CH groups of the aryl β,β- and aryl α,β-dichlorovinyl sulfides *8* and *11*. The presence of proton signals, δ (ppm): 5.44 s (Ar = 4-$CH_3C_6H_4$) and 5.38 s (Ar = 4-ClC_6H_4), characteristic of the sulfides *13*[22] leads to the conclusion that these compounds are likely to be formed in the above reaction.

The structure of the trichloroethylene dimer was ascertained by IR, ^{1}H NMR, and mass spectra. In particular, the mass spectrum exhibits, along with the (m/e 260) molecular ion, an intense peak of the $[M\text{-}CHCl_2]^+$ molecular fragment (m/e 177) and a peak of the $(CHCl)^+$ ion (m/e 83); singlet signals of two protons (6.59 and 6.06) occur in the ^{1}H NMR spectrum.

The trichloroethylene dimer is formed independently of the formation of the sulfides *8*, *10*, and *13*. The same product is also obtained by the reaction of an individual trichloroethylene with acetyl peroxide.[26]

The radical reaction of tetrachloroethylene with diaryl disulfides is, on the contrary, more selective than that with the corresponding thiols. In this case, the aryl trichlorovinyl sulfides *10a–c*, characterized by GLC and direct isolation, and hexachloro-1,3-butadiene are the reaction products[25] (Scheme 10).

$$ArSSAr + CCl_2{=}CCl_2 \xrightarrow{UV,\ t^\circ} \underset{10a-c}{ArSCCl{=}CCl_2} + CCl_2{=}CClCCl{=}CCl_2$$

Ar = 4-$CH_3C_6H_4$ (*a*), Ph (*b*), 4-ClC_6H_4 (*c*)

SCHEME 10

In general, due to the double bond deactivation by four chlorine atoms the UV irradiated reaction proceeds rather reluctantly and requires refluxing. But even in this case the conversion of the diaryl disulfides does not exceed 40% for 25 hr.

Unlike the reaction with thiols, the formation of the trichloroethylene dimer and hexachloro-1,3-butadiene in that with diaryl disulfides indicates that tri- and tetrachloroethylene occur in the reaction mixture as active species. Therefore, the mechanism involving the vinyl radicals *E*, *F*, and *G* (Scheme 11) and rejected for the

$$CCl_2{=}\dot{C}Cl + \dot{R}' \xleftarrow{UV} CCl_2{=}CClR' \xrightarrow{UV} CClR'{=}\dot{C}Cl + Cl^{\cdot}$$
$$\quad E \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad G$$
$$\qquad\qquad\qquad\qquad\quad \downarrow UV$$
$$\qquad\qquad\qquad\qquad CCl_2{=}\dot{C}R' + Cl^{\cdot}$$
$$\qquad\qquad\qquad\qquad\quad F$$

$$ArSSAr \overset{UV}{\rightleftharpoons} 2\ ArS^{\cdot}$$

a. $ArS^{\cdot}\ (ArSSAr) + CCl_2{=}\dot{C}Cl \longrightarrow ArSCCl{=}CCl_2 + (Ar\dot{S})\ R' = Cl$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad 10$

$$2\ CCl_2{=}\dot{C}Cl \longrightarrow CCl_2{=}CClCCl{=}CCl_2$$

b. R′ = H

$$ArSCCl{=}CCl_2 + (ArS^{\cdot}) \xleftarrow{E} ArS^{\cdot}\ (ArSSAr) \xrightarrow{G} ArSCCl{=}CHCl + (ArS^{\cdot})$$
$$\quad 10 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad 11$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow F$$
$$\qquad\qquad\qquad\qquad\qquad ArSCH{=}CCl_2 + (ArS^{\cdot})$$
$$\qquad\qquad\qquad\qquad\qquad\quad 8$$

$$ArSCH{=}CCl_2 + Cl_2 \longrightarrow ArSCHClCCl_3$$
$$\quad 8 \qquad\qquad\qquad\qquad\quad 13$$

$$CHCl{=}CCl_2 + CCl_2{=}\dot{C}H + Cl^{\cdot} \longrightarrow CCl_2{=}CHCCl_2CHCl_2$$

SCHEME 11

$$ArS^{\cdot} + CCl_2{=}CClR' \longrightarrow ArSCClR'\dot{C}Cl_2 + ArSCCl_2\dot{C}ClR'$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C \qquad\qquad\qquad\quad H$$

a. R′ = Cl $\qquad$ C = H

$$ArSCCl_2\dot{C}Cl_2 \longrightarrow ArSCCl{=}CCl_2 + Cl^{\cdot}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad 10$$

b. R′ = H

$$ArSCCl{=}CCl_2 \xleftarrow{-H^{\cdot}} ArSCHClCCl_2 \xrightarrow{-Cl^{\cdot}} ArSCH{=}CCl_2$$
$$\quad 10 \qquad\qquad\qquad\quad C \qquad\qquad\qquad\quad 8$$
$$\qquad\qquad\qquad\qquad\quad ArSCCl_2\dot{C}HCl \xrightarrow{-Cl^{\cdot}} ArSCCl{=}CHCl$$
$$\qquad\qquad\qquad\qquad\qquad\quad H \qquad\qquad\qquad\quad 11$$

SCHEME 12

reaction with thiols should be regarded as more preferable in this case. This is the most appropriate mechanism to account for the formation of the α,β-dichlorovinyl sulfides *11* and trichlorovinyl sulfides *10* from trichloroethylene and the predominant formation of the trichlorovinyl sulfides *10* from tetrachloroethylene, on the one hand, and for the difference in the reaction course with diaryl disulfides and thiols, on the other hand. The alternative Scheme 12 involving the intermediate radicals *C* and *H* cannot explain the latter.

IV. Reactions of arenethiols and diaryl disulfides with 1,1,2-trichloropropene

1,1,2-Trichloropropene, a representative of the polychloroethenes $CCl_2{=}CClR$ with R = Me was selected by us to study the possibility of the preparation of the sulfides *17* $ArSC(CH_3){=}CCl_2$ under radical conditions. Previously these sulfides had been prepared by nucleophilic substitution of chlorine in 1,1,2-trichloropropene by the arenethiolate ion:[27]

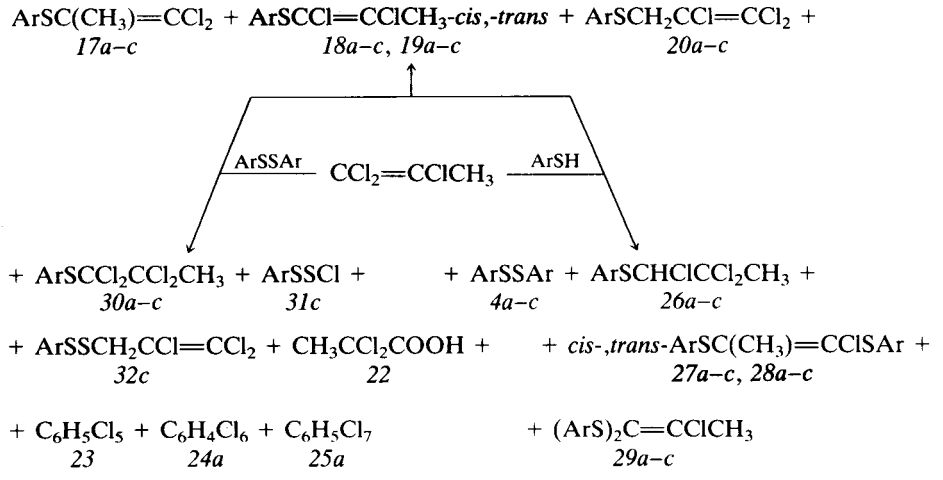
$$PhSH + CCl_2{=}CClCH_3 \xrightarrow{NaOH,\ DMF} \underset{17}{PhSC(CH_3){=}CCl_2}$$

However, already the photochemical oligomerization of 1,1,2-trichloropropene has shown that in radical reactions the behavior of the latter should be markedly different from that of tri- and tetrachloroethylene. Unlike these ethenes, 1,1,2-trichloropropene affords the allyl radicals $CCl_2{=}CCl\dot{C}H_2$ and $CH_2{=}CCl\dot{C}Cl_2$ rather than the vinyl radicals $CCl_2{=}\dot{C}CH_3$ and $\dot{C}Cl{=}CClCH_3$[28]. As a result, UV irradiation leads to a multicomponent mixture of products $C_6H_5Cl_5$ *23*, $C_6H_4Cl_6$ *24*, and $C_6H_5Cl_7$ *25* among which the compounds with the tentative structure of 1,1,2,4,5,6-hexachloro-1,4-hexadiene *24a* and 1,1,2,4,4,5,5-heptachloro-1-hexene *25a* are present in the largest amounts.

In fact, the UV-initiated reaction of both arenethiols[29] and diaryl disulfides[30] proceeds non-regioselectively and non-stereospecifically, the main reaction course in the two cases being the formation of all the possible isomers of the dichloropropenyl sulfides *17a–c*, *18a–c*, *19a–c* and the trichloroallyl sulfides *20a–c* (Scheme 13).

The difference between the reactions of 1,1,2-trichloropropene with arenethiols and diaryl disulfides is that the former, along with the diaryl disulfides *4a–c*, affords the 1,2,2-trichloropropyl sulfides *26a–c* and the diaryltrichloropropenes *27a–c*, *28a–c*, and *29a–c*, absent in the reaction with diaryl disulfides. The reaction with diaryl disulfides, besides the products *17a–c*, *18a–c*, *19a–c*, and *20a–c*, common to both reactions, yields the 1,1,2,2-tetrachloropropyl sulfides *30a–c* as well as 2,2-dichloropropanoic acid *22* and the products of oligomerization of trichloropropene *23*, *24a*, and *25a*. Only traces of trichloropropene oligomers were found in the reaction with arenethiols whereas in that with diaryl disulfides the oligomerization is so efficient that it is not possible to separate the products *23–25* from the sulfides *17–20* and *30–32* by conventional techniques.

And, at last, in the case of di-(*p*-chlorophenyl) disulfide the disulfides *31c* and *32c*, formed by homolytic cleavage of the C—S bond in the former, have been found.



SCHEME 13

The products in the multicomponent mixtures formed were identified by chemical, physicochemical, and spectral methods (elemental analysis, GLC, ^{1}H NMR, and GC-MS (Table 4). In particular, in the ^{1}H NMR spectra, all the three isomeric dichloropropenyl sulfides poorly separated by GLC, even on capillary columns, give well-defined proton signals of three methyl groups, δ, ppm 1.79–1.89 s, 20.30–2.34 s, 2.45–2.48 s for *17*, *18*, and *19*, respectively, and additionally 2.27–2.30 s for $CH_3C_6H_4$ with Ar = 4-$CH_3C_6H_4$. The signals 2.30–2.34 s and 2.45–2.48 s ppm were tentatively assigned to the *cis*- and *trans*-isomers of *18* and *19* based on the fact that the *cis*-position in sulfides RSCCl=CHCl is more shielded.

Taking into account the composition of the reaction mixtures and the absence of trichloropropene oligomers formed by vinyl radicals it may be concluded that the reaction with both arenethiols and diaryl disulfides follows the same mechanism involving the formation of intermediate *I* and *J* radicals and an allyl radical $CCl_2{=}CClC^{\cdot}H_2$ (Scheme 14).

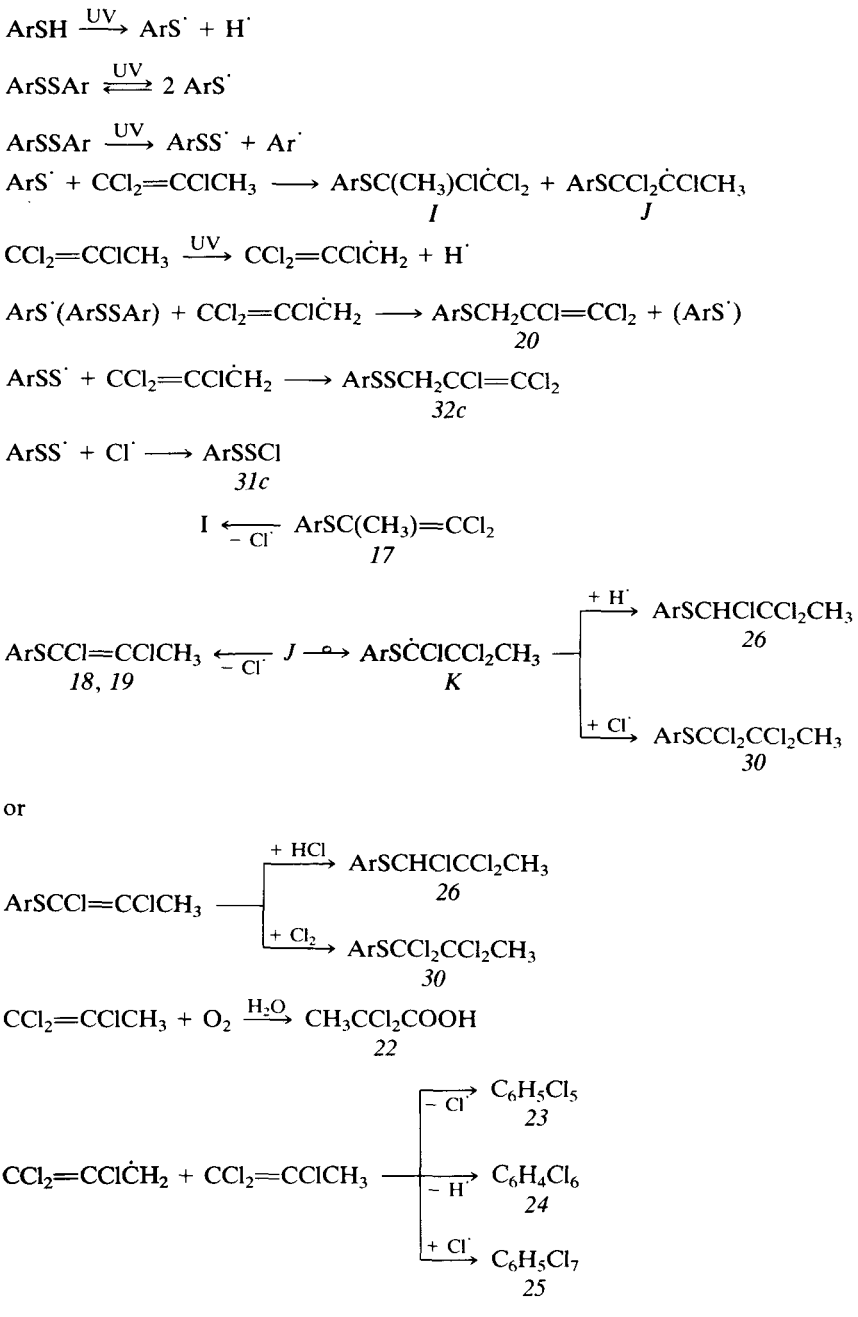
The stabilization of the radicals *I* and *J* by abstraction of Cl$^{\cdot}$ and the rearrangement of *J* to the secondary radical *K* followed by the addition of H$^{\cdot}$ in the case of thiols or Cl$^{\cdot}$ in the case of disulfides (or hydrochlorination of sulfides *18* and *19*, respectively) lead to the observed mixture of products. With diaryl disulfides a concomitant trichloropropene photooligomerization takes place. With thiols it is suppressed by their reducing ability. The lack of substitution of chlorine in the sulfides *17–19* by an ArS group in the case of disulfides suggests that the present process for ArSH seems to involve nucleophilic substitution of the chlorine atom in ArS-activated dichloropropenes by the arenethiol or the arenethiolate ion. A similar substitution of thiol for chlorine in NO_2 group-activated pentachloro-1,3-butadiene $CCl_2{=}CClC(NO_2){=}CCl_2$ was observed, for example, by Ol'dekop *et al.*[31]

The fact that the mechanism of the reaction of diaryl disulfides with trichloropropene is not the equivalent of that with tri- and tetrachloroethylene is likelv due to a

TABLE 4

GLC–MS Data for the Reaction Mixtures Obtained in the Reaction of ArSH and ArSSAr with $CCl_2{=}CClCH_3$

Compound	ArSH		ArSSAr	
	C_6H_5	4-ClC_6H_4	C_6H_5	4-ClC_6H_4
$ArSC{=}C(CH_3)(Cl_2)$ *17–19*	218 $[M]^{\ddagger}$ 109 $[ArS]^{+}$	252 $[M]^{\ddagger}$ 143 $[ArS]^{+}$ 108 $[C_6H_4S]^{\ddagger}$	218 $[M]^{\ddagger}$ 109 $[ArS]^{+}$	252 $[M]^{\ddagger}$ 143 $[ArS]^{+}$ 108 $[C_6H_4S]^{\ddagger}$
$ArSCH_2CCl{=}CCl_2$ *20*	252 $[M]^{\ddagger}$ 143 $[CH_2CCl{=}CCl_2]^{\cdot}$, 109 $[ArS]^{+}$	286 $[M]^{\ddagger}$ 143 $[ArS]^{+}$ + $[CH_2CCl{=}CCl_2]^{+}$ 108 $[C_6H_4S]^{\ddagger}$	252 $[M]^{\ddagger}$ 143 $[CH_2CCl{=}CCl_2]^{\cdot}$, 109 $[ArS]^{+}$	286 $[M]^{\ddagger}$ 143 $[ArS]^{+}$ + $[CH_2CCl{=}CCl_2]^{+}$ 108 $[C_6H_4S]^{\ddagger}$
$ArSCHClCCl_2CH_3$ *26*	254 $[M]^{\ddagger}$ 157 $[ArSCHCl]^{+}$ 109 $[ArS]^{+}$	288 $[M]^{\ddagger}$ 191 $[ArSCHCl]^{+}$ 143 $[ArS]^{+}$ 143 $[ArS]^{+}$ 108 $[C_6H_4S]^{\ddagger}$		
$ArSCCl_2CCl_2CH_3$ *30*			288 $[M]^{\ddagger}$ 191 $[ArSCCl_2]^{+}$ 144 $[CClCCl_2$ $CH_3]^{\ddagger}$ 109 $[ArS]^{+}$	322 M^{+} 225 $ArSCCl_2{}^{+}$ 144 $[CClCCl_2$ $CH_3]^{\ddagger}$ 143 $[ArS]^{+}$ 108 $[C_6H_4S]^{+}$
$(ArS)_2C{=}C(Cl)(CH_3)$ *27–29*	292 $[M]^{\ddagger}$ 183 $[M{-}ArS]^{+}$ 148 $[M{-}ArS{-}Cl]^{\ddagger}$ 109 $[ArS]^{+}$	360 $[M]^{\ddagger}$ 217 $[M{-}ArS]^{+}$ 182 $[M{-}ArS{-}Cl]^{\ddagger}$ 143 $[ArS]^{+}$ 108 $[C_6H_4S]^{\ddagger}$		
ArSSCl *31*				210 $[M]^{\ddagger}$ 175 $[M{-}HCl]^{+}$ 111 $[Ar]^{+}$
$ArSSCH_2CCl{=}CCl_2$ *32*				318 $[M]^{\ddagger}$ 175 $[ArSS]^{+}$ 143 $[CH_2CCl{=}CCl_2]^{+}$ 140 $[C_6H_4SS]^{\ddagger}$



SCHEME 14

fairly ready formation of the allyl radicals $CCl_2{=}CCl\dot{C}H_2$ as compared with the vinyl radicals $CCl{=}CClCH_3$ and $C(CH_3){=}CCl_2$. This results in a more essential role of cleavage of the C—H rather than the C—Cl bond in the fragmentation of the UV-excited $CCl_2{=}CClCH_3$ molecule, the competitive addition of $ArS^{\cdot}$ to $CCl_2{=}CClCH_3$ being the predominant process.

REFERENCES

1. W. E. Vaughan and F. F. Rust (Shell Development Co.), U.S. 2,398,480 (1946); *Chem. Abstr.*, *40*, 3766 (1946).
2. a) T. Hoshino and K. Yamagishi (Tokyo Institute of Technology), Japan. 6480('53); *Chem. Abstr.*, *49*, 9689 (1955). b) T. Hoshino, K. Yamagishi, and Y. Ichikawa, *J. Chem. Soc. Japan, Pure Chem. Sect.*, *74*, 510 (1953).
3. W. H. C. Rueggenberg, W. A. Cook, and E. E. Reid, *J. Org. Chem.*, *13*, 110 (1948).
4. J. F. Harris, *J. Am. Chem. Soc.*, *84*, 3148 (1962).
5. a) N.P. Neureiter and T. G. Bordwell., *J. Am. Chem. Soc.*, *82*, 5354 (1960). b) P. S. Skell and R. G. Allen, *J. Am. Chem. Soc.*, *82*, 1511 (1960).
6. R. Kh. Freidlina , M. Ya. Khorlina, and V. N. Kost, Izv. AN SSSR, *Ser. Khim.*, *1965*, 1788.
7. a) H. L. Goering, D. J. Relyea, and D. W. Larsen, *J. Am. Chem. Soc.*, *78*, 348 (1956), b) H. L. Goering, D. L. Relyea, and K. L. Howe, *J. Am. Chem. Soc.*, *79*, 2502 (1957).
8. a) S. J. Cristol and B. B. Jarvis, *J. Am. Chem. Soc.*, *88*, 3095 (1966). b) W. Schroth and F. Raabe, Ger. (East) 93,552 (1972); *Chem. Abstr.*, *78*, 159211 (1973).
9. C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, *81*, 1144 (1959).
10. A. N. Mirskova, A. V. Martynov, I. D. Kalikhman, V. V. Keiko, V. Yu. Vitkovskii, and M. G. Voronkov, *Zh. Org. Khim.*, *15*, 1834 (1979).
11. S. Tanimoto, R. Taniyasu, T. Takahashi, T. Miyake, and M. Okano, *Bull. Chem. Soc. Japan, 49*, 1931 (1976).
12. E. J. Boonstra, and J. F. *Arens, Rec. Trav. Chim.*, *79*, 866 (1960).
13. A. S. Atavin, N. K. Gusarova, S. V. Amosova, B. A. Trofimov, and G. A. Kalabin, *Z. Org. Khim.*, *6*, 2386 (1970).
14. A. N. Mirskova, A. V. Martynov, and M. G. Voronkov, *Zh. Org. Khim.*, *16*, 2076 (1980).
15. W. E. Parham and S. H. Groen, *J. Org. Chem.*, *30*, 3181 (1965).
16. a) A. S. Atavin, A. N. Mirskova, E. F. Zorina, and Yu. L. Frolov, *Zh. Org. Khim.*, *4*, 1328 (1968). b) A. N. Mirskova, E. F. Zorina, G. G. Levkovskaya, and A. S. Atavin, *Zh. Org. Khim.*, *10*, 28 (1974).
17. a) W. E. Truce and R. Kassinger, *J. Am. Chem. Soc.*, *80*, 1916 (1958). b) G. Modena, and F. Montanari, *Gazz. Chim. Ital.*, *86*, 432 (1956). c) H. J. Backer, J. Strating, and J. F. A. Hazenberg, *Rec. Trav. Chim.*, *72*, 813 (1953). d) J. R. Nooi and J. F. Arens, *Rec. Trav. Chim.*, *81*, 533 (1962).
18. W. Schroth and F. Raabe, Ger. (East) 93,559 (1972); *Chem. Abstr.*, *78*, 136288 (1973).
19. S. Tanimoto, S. Yasuda, and M. Okano, *J. Syn. Org. Chem. Japan, 28*, 1041 (1970).
20. A. V. Martynov, A. N. Mirskova, I. D. Kalikhman, P. V. Makerov, and M. G. Voronkov, *Zh. Org. Khim.*, *15*, 427 (1979).
21. N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, *71*, 2724 (1949).
22. A. V. Martynov , A. N. Mirskova, and M. G. Voronkov, *Zh. Org. Khim.*, *19*, 1869 (1983).
23. R. Aloni, L. A. Rajenbach, and A. Horowitz, *J. Organomet. Chem.*, *171*, 155 (1979).
24. A. N. Mirskova, A. V. Martynov, and M. G. Voronkov, *Zh. Org. Khim.*, *18*, 1555 (1982).
25. A. V. Martynov, A. N. Mirskova, and M. G. Voronkov, *Zh. Org. Khim.*, *20*, 23 (1984).
26. Yu. A. Ol'dekop, R. V. Kaberdin, and E. E. Buslovskaya, *Zh. Org. Khim.*, *17*, 272 (1981).
27. B. A. Shainyan, and A. N. Mirskova, *Zh. Org. Khim.*, *17*, 94 (1981).
28. A. V. Martynov, A. N. Mirskova, V. Yu. Vitkovskii, and M. G. Voronkov, *Zh. Org. Khim.*, *21*, 698 (1985).
29. A. V. Martynov, A. N. Mirskova, V. Yu. Vitkovskii, and M. G. Voronkov, *Zh. Org. Khim.*, *21*, 1159 (1985).
30. A. V. Martynov, A. N. Mirskova, V. Yu. Vitkovskii, and M. G. Voronkov, *Zh. Org. Khim.*, *21*, 1165 (1985).
31. Yu. A. Ol'dekop, R. V. Kaberdin, and V. I. Potkin, *Zh. Org. Khim.*, *16*, 543 (1980).