July, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (7), 1931—1936 (1976) 1931

The Reactions of Polychloroethanes with Phenolate and Benzenethiolate Ions in Dipolar Aprotic Solvents

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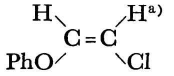
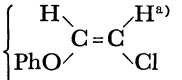
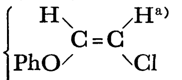
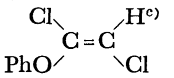
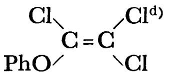
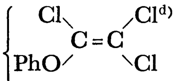
(Received February 26, 1976)

The reactions of several *gem*- and *vic*-polychloroethanes containing 3—5 Cl atoms with PhONa in dimethyl sulfoxide and with PhSNa in *N,N*-dimethylformamide were examined. Either the mono-, di-, or tetra-substituted compounds of polychloroethylenes were obtained as the main products, depending on the kinds of substrates as well as on the amounts of the bases. The reaction products from polychloroethylenes with 2—4 Cl atoms were also examined under similar conditions for the sake of comparison. Reasonable reaction paths leading to these products were given.

Though direct substitution reactions (S_N2) of primary alkyl halides have been widely utilized in the syntheses of various kinds of compounds,[1] the usefulness of alkylidene dihalides in this way is rather limited because of their low reactivities.[2] Thus ,it has been known that the basic substitution of the halogen atom(s) of less-reactive alkylidene dichlorides by nucleophiles other than thiolate ions proceeds only under severe reaction conditions; *e.g.*, the preparation of diphenoxymethane can be accomplished by heating dichloromethane with PhONa in 95% alcohol at 150 °C for 3 h in a sealed tube.[3] We have recently found, however, that this reaction can be conducted even at room temperature by the use of dimethyl sulfoxide (DMSO) as the solvent.[4] Since the basicity of a base is known to be greatly enhanced by the change in solvent from a hydroxylic solvent to DMSO because of the disappearance of a hydrogen-bonding interaction,[5] there is a possibility that, even with a less-basic nucleophile, an olefin-forming elimination might compete considerably with a substitution, at least in basic aprotic solvents. On the other hand, it has been reported that, in the reaction of an alkyl halide with a basic nucleophile, the introduction of an electron-withdrawing group, such as COR, SO_2R, and even Br or Cl, at the *β*-position results in a large increase in the rate of olefin formation.[6] With these points in mind, we examined the reactions of several *gem*- and *vic*-polychloroethanes containing 3—5 Cl atoms with PhONa in DMSO and with PhSNa in *N,N*-dimethylformamide (DMF). The products were mostly the mono- or disubstituted compounds of polychloroethylenes, probably formed by the dehydrochlo-

TABLE 1. REACTION OF POLYCHLOROETHANES WITH PhONa (IN DMSO)

Run	Polychloroethane	Equiv. of PhONa	Reaction temp (°C)	Reaction time (h)	Main products	Yield (%)
1	$CH_2ClCHCl_2$ (I)	2	70	10		28
2	$CH_2ClCHCl_2$ (I)	3	70	10	 $(PhO)_2C{=}CH_2$[b]	49 10
3	CH_3CCl_3 (II)	3	70	10	 $(PhO)_2C{=}CH_2$[b]	50 18
4	$CHCl_2CHCl_2$ (III)	4	70	5		90
5	$CHCl_2CCl_3$ (IV)	2	70	10		23
6	$CHCl_2CCl_3$ (IV)	5	70	10	 $(PhO)_2C{=}CCl_2$[e]	14 52
7	$CH_2ClCHClCH_2Cl$	1	70	10	$CH_2{=}CCl{-}CH_2Cl$[f] $CH_2{=}CCl{-}CH_2OPh$[g]	17 41

a) Bp 74—77 °C/4 mmHg (lit,[8a] 80—81 °C/4 mmHg). b) Bp 148—152 °C/11.5 mmHg (lit,[10] 115—116 °C/1 mmHg). c) Bp 72—74 °C/4 mmHg (lit,[9] 98—99 °C/13.5 mmHg). d) Bp 91—93 °C/4 mmHg (lit,[8b] 112—113 °C/15 mmHg). e) A new compound. Bp 154—155 °C/4 mmHg. *Anal.* Found: C, 60.21; H, 3.62%. Calcd for $C_{14}H_{10}Cl_2O_2$: C, 59.86; H, 3.58%. f) Bp 92 °C (lit,[11] 92.5 °C). g) A new compound. Bp 68—69.5 °C/2.8 mmHg. *Anal.* Found: C, 63.97; H, H, 5.31%. Calcd for C_9H_9ClO: C, 64.00; H, 5.37%.

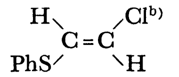
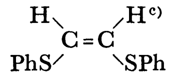
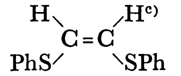
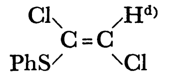
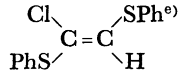
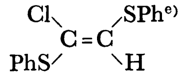
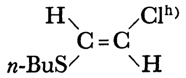
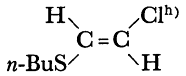
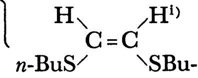
rination of the original polychlorides and by subsequent vinylic substitution(s) of the resulting olefins. Therefore, the reaction products from various polychloroethylenes with 2—4 Cl atoms were also examined under similar conditions for the sake of comparison.

The direct formation of substituted (chloro)ethylenes from polychloroethanes has never been reported so far as we know. However, there are several reports in the literature regarding vinylic substitution(s) of polychloroethylenes, where the reactions are mostly carried out in protic solvents or neat. Previous preparative data indicate that the substitution by RO^- [7] or ArO^- [8] can be achieved only under severe conditions, whereas the reaction with highly nucleophilic RS^- or ArS^- takes place readily under usual reaction conditions. The only study in a polar aprotic solvent was given by Normant; he found that, in DMF, the reaction of trichloroethylene with equimolar PhONa proceeded smoothly on heating at 65—70 °C.[9]

Results and Discussion

The reaction with PhONa was carried out by adding the chloroethanes to a solution of PhONa in DMSO (prepared by dissolving NaOH and PhOH in the solvent on heating) at an appropriate temperature. The reaction with PhSNa was conducted in a similar way, except for the use of DMF as the solvent under a nitrogen atmosphere, because the reaction in DMSO resulted in the formation of substantial amounts of diphenyl disulfide. The results for the two reactions are summarized in Tables 1 and 2. The reactions of the chloroethylenes with PhONa and PhSNa were similarly carried out in DMSO and DMF respectively. Some results are given in Table 3. The recorded yields in these tables are not always those obtained under optimum conditions. As can be seen from Tables 1 and 2, when more than an equivalent amount of the nucleophile was used, the substituted chloroethylenes and/or substituted ethylenes were isolated as the main products,

TABLE 2. REACTION OF POLYCHLOROETHANES WITH PhSNa (IN DMF)

Run	Polychloroethane	Equiv. of PhSNa	Reaction temp. (°C)	Reaction time (h)	Main products	Yield (%)
1	$CH_2ClCHCl_2$ (I)	1	70	5	$CHCl_2CH_2SPh$[a]	49
2	$CH_2ClCHCl_2$ (I)	2	70	5	 [b]  [c]	11 27
3	$CH_2ClCHCl_2$ (I)	3	70	5	 [c]	58
4	$CHCl_2CHCl_2$ (III)	2	70	5	 [d]  [e]	38 14
5	$CHCl_2CHCl_2$ (III)	4	70	5	 [e]	52
6	$CHCl_2CCl_3$ (IV)	5	70	5	$(PhS)_2C{=}C(SPh)_2$[f]	74
7	$CH_2ClCHCl_2$ (I)	1[g]	60	5	 [h]	48
8	$CH_2ClCHCl_2$ (I)	3[g]	60	5	 [h]  [i]	8 63
9	$CH_2ClCHClCH_2Cl$	1	70	5	$CH_2ClCHClCH_2SPh$[j]	58

a) A new compound. Bp 68—70 °C/3 mmHg. *Anal.* Found: C, 46.39; H, 3.97%. Calcd for $C_8H_8SCl_2$: C, 46.36; H, 3.89%. b) Bp 60—63 °C/3 mmHg (lit,[12] 92 °C/3 mmHg). *Anal.* Found: C, 56.05; H, 4.11%. Calcd for C_8H_7SCl: C, 56.31; H, 4.31%. c) Mp 30—31 °C (lit,[13] 30.5—31.5 °C). d) Bp 82—84 °C/3 mmHg (lit,[14] 140—142 °C/23 mmHg). e) A new compound. Mp 57—59 °C. *Anal.* Found: C, 60.81; H, 3.96%. Calcd for $C_{14}H_{11}S_2Cl$: C, 60.31; H, 3.98%. f) Mp 154—156 °C (Lit,[15] 154.5—155 °C). g) *n*-BuSNa is used in place of C_6H_5SNa. h) A new compound. Bp 80—82 °C/18 mmHg. *Anal.* Found: C, 47.51; H, 7.04%. Calcd for $C_6H_{11}SCl$: C, 47.83; H, 7.36%. i) Bp 88—92 °C/2 mmHg (lit,[16] 120—121 °C/2—3 mmHg). *Anal.* Found: C, 58.43; H, 9.48%. Calcd for $C_{10}H_{20}S_2$: C, 58.76; H, 9.86%. j) A new compound. Bp 92—94 °C/3 mmHg. *Anal.* Found: C, 49.02; H, 4.57%. Calcd for $C_9H_{10}SCl_2$: C, 48.88; H, 4.55%.

Table 3. Reaction of polychloroethylenes with PhONa (in DMSO) or with PhSNa (in DMF)

Run	Polychloroethylene	Equiv. of nucleophile	Reaction temp (°C)	Reaction time (h)	Main products	Yield (%)
1	$CH_2{=}CCl_2$ (V)	PhONa 2	30	40	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}^{a)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhO} & & \mathrm{Cl}\end{array}$	11
2	$CH_2{=}CCl_2$ (V)	PhONa 2	70	5	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}^{a)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhO} & & \mathrm{Cl}\end{array}$ $(PhO)_2C{=}CH_2{}^{b)}$	15 53
3	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}\\ & \mathrm{C{=}C} & \\ \mathrm{Cl} & & \mathrm{Cl}\end{array}$ (VI_c)	PhONa 2	55	20	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}^{a)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhO} & & \mathrm{Cl}\end{array}$	35
4	$\begin{array}{lcl}\mathrm{H} & & \mathrm{Cl}\\ & \mathrm{C{=}C} & \\ \mathrm{Cl} & & \mathrm{H}\end{array}$ (VI_t)	PhONa 2	55	50	No reaction	
5	$CHCl{=}CCl_2$ (VII)	PhONa 3	70	3	$\begin{array}{lcl}\mathrm{Cl} & & \mathrm{H}^{c)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhO} & & \mathrm{Cl}\end{array}$	78
6	$CCl_2{=}CCl_2$ (VIII)	PhONa 4	70	10	$\begin{array}{lcl}\mathrm{Cl} & & \mathrm{Cl}^{d)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhO} & & \mathrm{Cl}\end{array}$ $(PhO)_2C{=}CCl_2{}^{e)}$	28 59
7	$CH_2{=}CCl_2$ (V)	PhSNa 1	60	5	$\begin{array}{lcl}\mathrm{H} & & \mathrm{Cl}^{f)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhS} & & \mathrm{H}\end{array}$ $\begin{array}{lcl}\mathrm{H} & & \mathrm{H}^{g)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhS} & & \mathrm{SPh}\end{array}$	7 34
8	$CH_2{=}CCl_2$ (V)	PhSNa 2	60	5	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}^{g)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhS} & & \mathrm{SPh}\end{array}$	52
9	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}\\ & \mathrm{C{=}C} & \\ \mathrm{Cl} & & \mathrm{Cl}\end{array}$ (VI_c)	PhSNa 1	60	5	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}^{h)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhS} & & \mathrm{Cl}\end{array}$ $\begin{array}{lcl}\mathrm{H} & & \mathrm{H}^{g)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhS} & & \mathrm{SPh}\end{array}$	12 43
10	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}\\ & \mathrm{C{=}C} & \\ \mathrm{Cl} & & \mathrm{Cl}\end{array}$ (VI_c)	PhSNa 2	60	5	$\begin{array}{lcl}\mathrm{H} & & \mathrm{H}^{g)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhS} & & \mathrm{SPh}\end{array}$	54
11	$CHCl{=}CCl_2$ (VII)	PhSNa 3	70	5	$\begin{array}{lcl}\mathrm{H} & & \mathrm{SPh}^{i)}\\ & \mathrm{C{=}C} & \\ \mathrm{PhS} & & \mathrm{Cl}\end{array}$	68
12	$CCl_2{=}CCl_2$ (VIII)	PhSNa 4	70	5	$(PhS)_2C{=}C(SPh)_2{}^{j)}$	78

a)—e) See a)—e) in Table 1, respectively. f) See b) in Table 2. g) See c) in Table 2. h) Bp 64—65 °C/3 mmHg (lit,[17] 85—86 °C/3.5 mmHg). *Anal.* Found: C, 56.25; H, 4.20%. Calcd for C_8H_7SCl: C, 56.31; H, 4.31%. i) See e) in Table 2. j) See f) in Table 2.

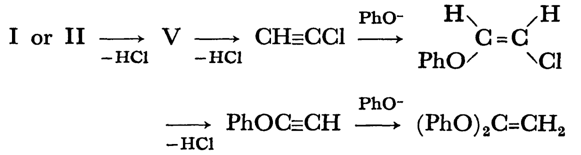
depending on the kinds of reactants and their molar ratios. These products are formed by the initial dehydrochlorination, followed by the vinylic substitution(s) of the resulting chloroethylenes once or several times successively. Indeed, a considerable similarity between some data in these tables and those in Table 3 was noted (compare the product for each pair: Runs 2 and 3, 4, and 6 in Table 1 *vs.* Runs 2, 5, and 6 in Table 3 respectively, and also Runs 2 and 3, 5, and 6 in Table 2 *vs.* Runs 7 and 8, 11, and 12 in Table 3 respectively). In only one case, where 1,1,2-trichloroethane (I) was treated with equimolar PhS^-, was the direct substitution product isolated as the main product (Run 1 in Table 2). On the contrary, the reaction with equimolar *n*-BuS^-, which is similarly nucleophilic but more basic than PhS^-,[18] mainly afforded the product with elimination, *i.e.*, *trans*-1-butylthio-2-chloroethylene (Run 7 in Table 2).

In connection with this, the following observation is also of interest. The reaction of 1,2,3-trichloropropane with equimolar PhS^- gave only the substitution product, 2,3-dichloropropyl phenyl sulfide, while the reaction with equimolar PhO^- (more basic than PhS^-[18]) yielded the elimination products, 2-chloroallyl chloride and 2-chloroallyl phenyl ether (Run 9 in Table 2 *vs.* Run 7 in Table 1).

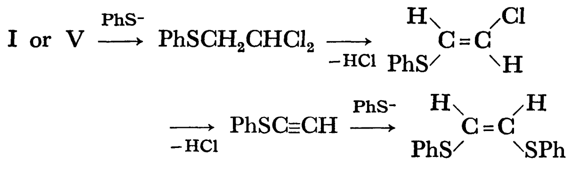
The advantages of the method are the mild reaction conditions and the one-step synthesis of certain substituted (chloro)ethylenes from polychloroethanes. Representative is the synthesis of tetrakis(phenylthio)ethylene from pentachloroethane (IV) or tetrachloroethylene (VIII). In contrast to our method, the reported one for the preparation of tetrakis(alkyl- or arylthio)ethylenes from VIII was carried out under quite drastic conditions, even by means of a two-step synthesis.[19] Further, the formation of 1,1-dichloro-2,2-diphenoxyethylene from IV or VIII in DMSO is noteworthy, because the only reported product from VIII and $\mathrm{PhO^-}$ in a sealed tube is the monosubstituted chloroethylene.[20] Cope has reported that, when 1,1,1-trichloroethane (II) was treated with two moles of PhONa in water, a mixture of *o*- and *p*-hydroxyacetophenones was formed in a slight yield (by the Reimer-Tiemann reaction).[21] The reaction in DMSO, however, afforded 1-chloro-2-phenoxyethylene and 1,1-diphenoxyethylene as the main products.

Next, we will briefly consider a possible reaction path for each case. The reactions of both I and 1,1-dichloroethylene (V) with $\mathrm{PhO^-}$ yielded *cis*-1-chloro-2-phenoxyethylene and 1,1-diphenoxyethylene (Runs 1 and 2 in both Tables 1 and 3), while those with $\mathrm{PhS^-}$ (except for the case of Run 1 in Table 2) afforded *trans*-1-chloro-2-phenylthioethylene and *cis*-1,2-bis(phenylthio)ethylene (Runs 2 and 3 in Table 2 and Runs 7 and 8 in Table 3). Truce *et al.*[22] reported the formation of a similar monosubstituted *trans*-olefin and disubstituted *cis*-olefin from V and $p\text{-}\mathrm{CH_3C_6H_4S^-}$, and proposed a sequence involving an addition-elimination mechanism and an elimination-addition mechanism for two successive substitutions. When I is used as the starting substrate, however, the first intermediate in this sequence, 1,1-dichloro-2-arylthioethane, is not necessarily formed *via* V, since we have observed the formation of this compound from I, without any accompanying elimination product, as has been described above. On the other hand, in the case of the more basic $\mathrm{PhO^-}$, the formation of the monosubstituted *cis*-olefin from V can be explained by assuming an elimination-addition mechanism. The subsequent vinyl substitution leading to the disubstituted olefin may involve an elimination-addition mechanism, as in the case of $\mathrm{PhS^-}$.

There is an additional remark to make on the dehydrochlorination of I with $\mathrm{PhO^-}$. The generation of V rather than *trans*-1,2-dichloroethylene($\mathrm{VI_t}$) may be anticipated from electronic considerations; *i.e.*, the α-H of I is more acidic than the β-H because of the effect of the two electron-withdrawing Cl atoms. The reaction products from I were identical with those from II, supporting this expectation (Runs 1, 2, and 3 in Table 1 and Run 2 in Table 3). Further, $\mathrm{VI_t}$ did not react with $\mathrm{PhO^-}$ to afford any product. Therefore, a route *via* $\mathrm{VI_t}$ is unlikely.



$$\text{I or II} \xrightarrow[-\mathrm{HCl}]{} \text{V} \xrightarrow[-\mathrm{HCl}]{} \mathrm{CH{\equiv}CCl} \xrightarrow{\mathrm{PhO^-}} \underset{\mathrm{PhO}}{\overset{\mathrm{H}}{\mathrm{C}}}{=}\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}} \xrightarrow[-\mathrm{HCl}]{} \mathrm{PhOC{\equiv}CH} \xrightarrow{\mathrm{PhO^-}} \mathrm{(PhO)_2C{=}CH_2} \quad (1)$$

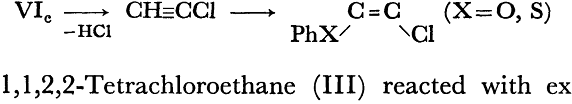


$$\text{I or V} \xrightarrow{\mathrm{PhS^-}} \mathrm{PhSCH_2CHCl_2} \xrightarrow[-\mathrm{HCl}]{} \underset{\mathrm{PhS}}{\overset{\mathrm{H}}{\mathrm{C}}}{=}\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}} \xrightarrow[-\mathrm{HCl}]{} \mathrm{PhSC{\equiv}CH} \xrightarrow{\mathrm{PhS^-}} \underset{\mathrm{PhS}}{\overset{\mathrm{H}}{\mathrm{C}}}{=}\underset{\mathrm{SPh}}{\overset{\mathrm{H}}{\mathrm{C}}} \quad (2)$$

Here, the attack of the second $\mathrm{PhS^-}$ occurred exclusively at an electronically unexpected position. Such an unusual orientation may be ascribed to the resonance stabilization of the resulting carbanion with a S atom at the α-position:[23]

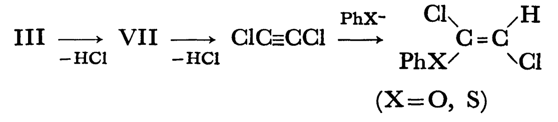
$$\mathrm{PhS\text{-}\bar{C}{=}CH\text{-}SPh} \longleftrightarrow \mathrm{Ph\bar{S}{=}C{=}CH\text{-}SPh}$$

cis-1,2-Dichloroethylene ($\mathrm{VI_c}$) has a favorable geometry for *trans* elimination, as has V, and both olefins afforded the identical *cis*-olefin as the monosubstituted product upon treatment with $\mathrm{PhO^-}$, suggesting the involvement of a common intermediate. The reaction of $\mathrm{VI_c}$ with $\mathrm{PhS^-}$ also afforded *cis*-1-chloro-2-phenylthioethylene, which was isomeric with the product from V. Such a difference may arise from an increased sensitivity toward $\mathrm{PhS^-}$ at the β-C of V. The formation of the *cis*-products from $\mathrm{VI_c}$ in both reactions may be explained by assuming an elimination-addition mechanism:[24]



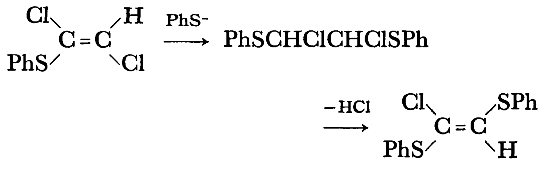
$$\mathrm{VI_c} \xrightarrow[-\mathrm{HCl}]{} \mathrm{CH{\equiv}CCl} \xrightarrow{\mathrm{PhX^-}} \underset{\mathrm{PhX}}{\overset{\mathrm{H}}{\mathrm{C}}}{=}\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}} \quad (\mathrm{X{=}O,\ S}) \quad (3)$$

1,1,2,2-Tetrachloroethane (III) reacted with excess $\mathrm{PhO^-}$ or $\mathrm{PhS^-}$ to give the *trans*-isomer of 1-substituted 1,2-dichloroethylene as the monosubstituted product, implying that both reactions proceed by the same sequence. Trichloroethylene (VII) also afforded the same *trans*-olefin in the reaction with excess $\mathrm{PhO^-}$, but when $\mathrm{PhS^-}$ was used as the nucleophile the main product was a disubstituted one. A reaction path involving an elimination-addition sequence is probable. The same mechanism has already been proposed by Truce *et al.* for the reaction of VII with $p\text{-}\mathrm{CH_3C_6H_4SNa}$:[25]



$$\text{III} \xrightarrow[-\mathrm{HCl}]{} \text{VII} \xrightarrow[-\mathrm{HCl}]{} \mathrm{ClC{\equiv}CCl} \xrightarrow{\mathrm{PhX^-}} \underset{\mathrm{PhX}}{\overset{\mathrm{Cl}}{\mathrm{C}}}{=}\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}} \quad (\mathrm{X{=}O,\ S}) \quad (4)$$

when X=S



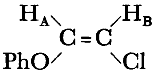
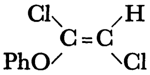
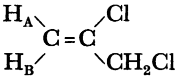
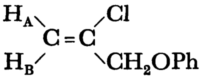
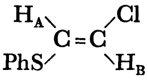
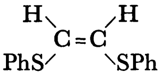
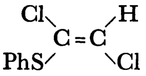
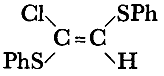
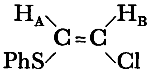
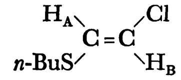
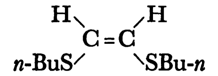
$$\underset{\mathrm{PhS}}{\overset{\mathrm{Cl}}{\mathrm{C}}}{=}\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}} \xrightarrow{\mathrm{PhS^-}} \mathrm{PhSCHClCHClSPh} \xrightarrow{-\mathrm{HCl}} \underset{\mathrm{PhS}}{\overset{\mathrm{Cl}}{\mathrm{C}}}{=}\underset{\mathrm{H}}{\overset{\mathrm{SPh}}{\mathrm{C}}} \quad (5)$$

During the experiments of the reactions of III and VII, we occasionally experienced small explosions. This may be an indication of the intermediate formation of dichloroacetylene, since its exploding property has already been reported.[26]

In the reaction of excess $\mathrm{PhO^-}$ with IV as well as with VIII, the products were 1,1,2-trichloro-2-phenoxyethylene and 1,1-dichloro-2,2-diphenoxyethylene. Since VIII is incapable of dehydrochlorination, consecutive addition-elimination must take place for the formation of polysubstituted (chloro)ethylenes. Truce *et al.* previously proposed the same sequence for the reaction of VII with $p\text{-}\mathrm{CH_3C_6H_4S^-}$:[27]

$$\text{IV} \xrightarrow[-\mathrm{HCl}]{} \text{VIII} \xrightarrow{\mathrm{PhX^-}} \mathrm{PhXCCl_2CHCl_2} \xrightarrow[-\mathrm{HCl}]{} \mathrm{PhXCCl{=}CCl_2} \quad (\mathrm{X{=}O,\ S})$$

Table 4. NMR of substituted (chloro)ethylenes

Compound	Vinylic H (δ ppm) (J_{Hz})	Aromatic and aliphatic H (δ ppm)
 $\mathrm{(H_A)(PhO)C{=}C(H_B)(Cl)}$	H_A 6.72 (1H, d), H_B 5.47 (1H, d), $J_{AB}=4.3$	6.90—7.50 (5H, m)
$\mathrm{(PhO)_2C{=}CH_2}$	3.84 (2H, s)	6.90—7.45 (10H, m)
 $\mathrm{(Cl)(PhO)C{=}C(H)(Cl)}$	5.90 (1H, s)	6.95—7.50 (5H, m)
$\mathrm{PhOCCl{=}CCl_2}$	—	6.95—7.55 (m)
$\mathrm{(PhO)_2C{=}CCl_2}$	—	6.90—7.40 (m)
 $\mathrm{(H_A)(H_B)C{=}C(Cl)(CH_2Cl)}$	H_A 6.11 (1H, d), H_B 5.90 (1H, d), $J_{AB}=1.6$	4.50 (2H, s)[a]
 $\mathrm{(H_A)(H_B)C{=}C(Cl)(CH_2OPh)}$	H_A 5.38 (1H, m), H_B 5.50 (1H, m)	6.80—7.40 (5H, m) 4.52 (2H, t)[a]
 $\mathrm{(H_A)(PhS)C{=}C(Cl)(H_B)}$	H_A 6.47 (1H, d), H_B 6.20 (1H, d), $J_{AB}=13.0$	7.15—7.40 (5H, m)
 $\mathrm{(H)(PhS)C{=}C(H)(SPh)}$	6.50 (2H, s)	7.12—7.50 (10H, m)
 $\mathrm{(Cl)(PhS)C{=}C(H)(Cl)}$	6.50 (1H, s)	7.10—7.45 (5H, m)
 $\mathrm{(Cl)(PhS)C{=}C(SPh)(H)}$	6.91 (1H, s)	7.15—7.55 (10H, m)
$\mathrm{(PhS)_2C{=}C(SPh)_2}$	—	7.16—7.50 (m)
 $\mathrm{(H_A)(PhS)C{=}C(H_B)(Cl)}$	H_A 6.58 (1H, d), H_B 6.18 (1H, d), $J_{AB}=6.5$	7.20—7.55 (5H, m)
 $\mathrm{(H_A)(\textit{n}\text{-}BuS)C{=}C(Cl)(H_B)}$	H_A 6.38 (1H, d), H_B 5.97 (1H, d), $J_{AB}=13.0$	2.46—2.93 (2H, m)[a] 0.73—1.94 (7H, m)
 $\mathrm{(H)(\textit{n}\text{-}BuS)C{=}C(H)(SBu\text{-}\textit{n})}$	6.13 (2H, s)	2.44—2.90 (4H, m)[a] 0.72—1.88 (14H, m)

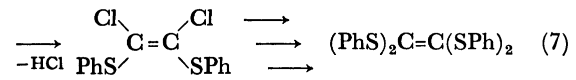
a) Aliphatic H

when X=O

$$\mathrm{PhOCCl{=}CCl_2} \xrightarrow{\mathrm{PhO^-}} \mathrm{(PhO)_2CClCHCl_2} \xrightarrow[-\mathrm{HCl}]{} \mathrm{(PhO)_2C{=}CCl_2} \quad (6)$$

when X=S

$$\mathrm{PhSCCl{=}CCl_2} \xrightarrow{\mathrm{PhS^-}} \mathrm{PhSCHClCCl_2SPh}$$



$$\xrightarrow[-\mathrm{HCl}]{} \mathrm{(Cl)(PhS)C{=}C(Cl)(SPh)} \longrightarrow \longrightarrow \longrightarrow \mathrm{(PhS)_2C{=}C(SPh)_2} \quad (7)$$

Experimental

Illustrative examples of the reactions will be given below.

a) Reaction of 1,1,2,2-Tetrachloroethane (III) with PhONa. In a three-necked flask equipped with a reflux condenser and a mechanical stirrer we placed 200 ml of DMSO, 37.6 g (0.40 mol) of phenol, and 16.0 g (0.40 mol) of NaOH. The mixture was gently warmed up to 70 °C with stirring to dissolve most of the NaOH. To the nearly homogeneous solution we then slowly added 16.8 g (0.10 mol) of III at 70 °C. The stirred mixture was then kept at 70 °C for an additional 5 h, after which the mixture was cooled, diluted with *ca.* 500 ml of water, and saturated with NaCl. The organic layer was extracted with three 100 ml portions of ether. The combined ethereal extracts were washed with water, dried over anhydrous Na_2SO_4, and then distilled to yield 17.0 g of crude *trans*-1,2-dichloro-1-phenoxyethylene; bp 72—74 °C/4 mmHg (yield, 90%).

b) Reaction of Pentachloroethane (IV) with PhSNa. In a similar way, a nearly homogeneous solution of 27.5 g (0.25 mol) of benzenethiol and 10.0 g (0.25 mol) of NaOH in 125 ml of DMF was prepared. Then a 10.1 g portion (0.05 mol) of IV was gradually added at 70 °C, after which the stirring was continued for 5 h at that temperature. All these procedures were carried out under a nitrogen atmosphere to prevent the oxidation of benzenethiol to diphenyl disulfide. The reaction mixture was cooled and diluted with *ca.* 300 ml of water. The resulting precipitate was collected and recrystallized from chloroform to afford 17.0 g of tetrakis(phenylthio)ethylene; mp 154—156 °C (yield, 74%).

The NMR spectra of all the olefinic products are summarized in Table 4.

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