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Chlorination of Acetylenes with Sulfuryl Chloride

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Synopsis. The reactions of some acetylenes with sulfuryl chloride in benzene and carbon tetrachloride at the reflux temperature afford the corresponding (*E*)- and (*Z*)-dichloroalkenes in good to moderate yields *via* homolytic pathway. The kinetically controlled isomer ratios(*E*/*Z*) depended very much on the kind of acetylenes employed; *i.e.*, 93/7 for 1-octyne to 14/86 for 3,3-dimethyl-1-phenyl-1-butyne in benzene.

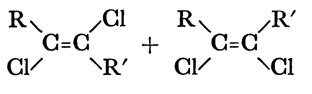
Sulfuryl chloride has long been known to chlorinate olefin homolytically, both chlorine atoms and chlorosulfonyl radicals acting as chain carriers.[1)] To our knowledge, however, the application to acetylenes seems to be so far limited only to divinylacetylene,[2)] 2-butyne,[3)] and phenylpropiolic acid and its methyl ester.[4)] In the last case where sulfuryl chloride itself was used as solvent, the products were the complex mixture and, interestingly, the stereoisomeric ratios (*E*:*Z*) of the produced dichloroalkenes (one of the main products) were 1:4 and 4:1 for the acid and its methyl ester, respectively. Since a systematic study on the stereoisomeric ratios in radical chlorination of acetylenes has been reported only for (dichloroiodo)-benzene,[5)] we undertook the chlorination of some acetylenes with sulfuryl chloride in nonpolar solvent to know whether the reaction proceeds homolytically and what the isomer ratios of dichloroalkenes are. As one of a series of our studies of halogenation of acetylenes by molecular halogen and metal halides,[6)] we wish here to describe the details of the reaction.

Results and Discussion

The reactions of some acetylenes with equimolar amount of sulfuryl chloride in carbon tetrachloride or benzene at the reflux temperature gave a mixture of the corresponding *E*- and *Z*-dichloroalkenes in good to moderate yields [Scheme (1)]. Typical results are shown in Table 1 together with the reported isomer ratios of the chlorination with $PhICl_2$ and of thermodynamic equilibrium. A use of excess sulfuryl chloride resulted in an increase of tetrachloroalkanes with a slight increase of (**2**), the isomer ratio being almost constant. As exemplified from the product yield in the table, the reactions proceeded more smoothly in benzene than in carbon tetrachloride, the isomer ratio being nearly the same in both solvents. Since prolonged reaction time had little effect on the isomer ratios of the products, the reactions must be almost entirely kinetically controlled. We confirmed independently that interconversion between the isomers of (**2**; R=Ph, R′=H or Me) did not occur in both solvents at the reflux temperature for 1—2 h in the presence of 1 equiv. of sulfuryl chloride. The observed kinetically controlled ratio is much different with the ratio of thermodynamic equilibrium and slightly different with the one of radical chlorination using $PhICl_2$. In the case of (**1**; R=Ph, R′=*t*-Bu) the *Z*-isomer was the major product, as has been observed in the chlorination with several chlorinating agents such as Cl_2,[6b)] $CuCl_2$,[6a)] and $SbCl_5$.[6d)]

$$R\text{-}C{\equiv}C\text{-}R' + SO_2Cl_2 \longrightarrow$$

(**1**)



(1)

E-(**2**) *Z*-(**2**)

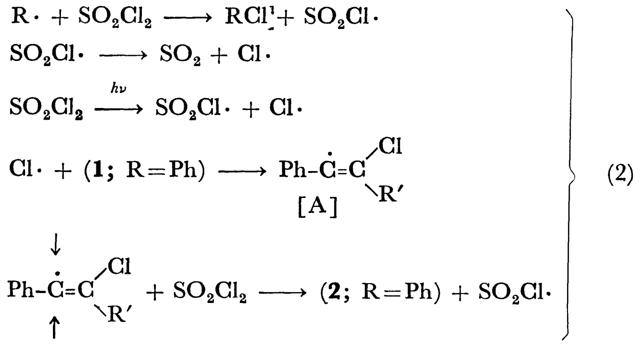
In order to know whether the reaction is homolytic, we have carried out the chlorination of (**1**; R=Ph, R′=H or Me) in the presence of a radical scavenger such as *t*-butylcatechol or phenol and found that the product yield decreased profoundly and the isomer ratio of *E*/*Z* became low. For example, *E*- and *Z*-(**2**; R=Ph, R′=H) were obtained from (**1**; R=Ph, R′=H) in a yield of 11% (*E*/*Z*=76/24) and 17% (*E*/*Z*=63/37) in chloroform (0.5 mmol of *t*-butylcatechol added) and in benzene (0.2 mmol of the catechol added) at reflux for 2 h, respectively. Similarly, the yield of (**2**) in the reaction of (**1**; R=Ph, R′=Me) in benzene at reflux for 2 h decreased to 27% (*E*/*Z*=66/34) by addition of 0.2 mmol of the catechol. On the other hand, when the reaction of (**1**; R=Ph, R′=H) in carbon tetrachloride was carried out by the addition of benzoyl peroxide, a radical initiator, the product yield of (**2**) increased to 58% from 34% without it. This finding also supports the radical nature of the reaction. An ionic chlorination of (**1**; R=Ph, R′=H or Me) with chlorine gas has been reported to give (**2**) in a ratio (*E*/*Z*) of 51/49 or 67/33 respectively. Therefore, a slight increase for the *Z*-isomer in the isomer ratio obtained in the presence of the radical inhibitor may be explained by assuming that this radical chlorination is slightly accompanied with an ionic one with chlorine which may be formed by dissociation of sulfuryl chloride. In fact, when the chlorination of (**2**; R=Ph, R′=Me) with sulfuryl chloride in benzene was carried out at 30 °C for 30 min under UV irradiation, *E*- and *Z*-(**2**; R=Ph, R′=Me) were obtained in a yield of 20%, *E*/*Z* being 91/9. Under similar conditions without irradiation almost no products were obtained. This fact shows that under completely radical condition the formation of the *E*-isomer is much favored.

Considering from the proposed mechanism for olefin chlorination with sulfuryl chloride,[1)] the reaction scheme for the chlorination of phenyl-substituted acetylene seems to be as that shown in Scheme 2 where both chlorine atom and chlorosulfonyl radical act as chain carriers (R· may be derived from organic peroxides). The *E*/*Z* isomer ratio of (**2**) may be determined by the step of sulfuryl chloride attack on the intermediate linear α-phenylvinyl radical [A][7)] where

Table 1. Chlorination of acetylenes with sulfuryl chloride[a)]

1		Time	Yield of **2**	Isomer ratio ($E:Z$)		
R	R′	h	%	This work[b)]	$PhICl_2$[c)]	d)
CCl_4 solvent						
Ph	H	2	34	83 : 17	70 : 30	14 : 86
Ph	H	65	46	84 : 16		
Ph	Me	2	46	87 : 13	51 : 49	54 : 46
Ph	Me	15	68	85 : 15		
Ph	Et	2	37	79 : 21	57 : 43	44 : 56
Ph	Et	15	54	73 : 27		
Ph	*t*-Bu	2	46	14 : 86		
Ph	*t*-Bu	15	49	13 : 87		
Ph	Ph	2	9	55 : 45	76 : 24	28 : 72
Ph	Ph	21	36	56 : 44		
Hexyl	H	2	10	98 : 2	94 : 6	53 : 47
Hexyl	H	20	38	92 : 8		
Benzene solvent						
Ph	H	2	75	85 : 15		
Ph	Me	2	85	84 : 16		
Ph	Et	2	97	75 : 25		
Ph	*t*-Bu	2	87	14 : 86		
Ph	Ph	2	69	57 : 43		
Hexyl	H	2	23	93 : 7		

a) Carried out at reflux temperature (78 °C for CCl_4 and 81 °C for benzene) with **1** (2 mmol), SO_2Cl_2 (2 mmol), and solvent (4 ml). b) Determined by GLC. c) Ref. 5. d) The ratio of thermodynamic equilibrium; Ref. 5.



$$
\left.\begin{aligned}
&R\cdot + SO_2Cl_2 \longrightarrow RCl + SO_2Cl\cdot\\
&SO_2Cl\cdot \longrightarrow SO_2 + Cl\cdot\\
&SO_2Cl_2 \xrightarrow{h\nu} SO_2Cl\cdot + Cl\cdot\\
&Cl\cdot + (\mathbf{1};\ R{=}Ph) \longrightarrow \underset{[A]}{Ph\text{-}\dot{C}{=}C\overset{Cl}{\underset{R'}{<}}}\\
&\quad\downarrow\\
&Ph\text{-}\dot{C}{=}C\overset{Cl}{\underset{R'}{<}} + SO_2Cl_2 \longrightarrow (\mathbf{2};\ R{=}Ph) + SO_2Cl\cdot\\
&\quad\uparrow
\end{aligned}\right\}\quad (2)
$$

the attack by sulfuryl chloride should occur in the plane containing both Cl and R groups.[6b)] When R is sterically smaller than Cl (like H or Me), the *E*-isomer would be favored, while the *Z*-isomer should be the major one when R is a large substituent like *t*-Bu. This assumption is consistent with the experimental results.

Experimental

1-Phenyl-1-alkynes and authentic samples of (**2**) for GLC analyses were prepared as previously described.[6a)] Phenylacetylene, diphenylacetylene, 1-octyne, and other organic materials were commercial products and used without further purification. Sulfuryl chloride was distilled before use. The GLC analyses were carried out on Shimadzu 4BMPF apparatus using EGSS-X(1 or 3 m)-Chromosorb-W columns (N_2 as the carrier gas); the *E*-isomer has a shorter retention time than the *Z*-isomer in all cases except (**2**; R=R′=Ph). The internal standards were ethyl cinnamate for (**2**; R=Ph, R′=H, alkyl, Ph) and *cis*-1,2-dichlorocyclohexane for (**2**; R=n-C_6H_{13}, R′=H). The NMR spectra were recorded with a Varian EM-360 and a JEOL JNM-MH-100 apparatus using CCl_4 solvent (TMS as an internal standard). The UV irradiations were carried out with a high-pressure mercury lamp(Ushio UM-103).

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7) See for example, Ref. 1c pp. 90—92.