Z-Chlorination of Alkylphenylacetylenes with Antimony Pentachloride

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Summary Reaction of alkylphenylacetylenes with $SbCl_5$ in carbon tetrachloride gives the corresponding dichloroalkenes in fair yields, *Z*-addition predominating.

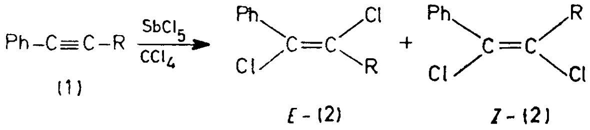
It has recently been reported that $SbCl_5$ reacts with various olefins to give unexpected dichloro-compounds.[1] However, there are no reports on its application to acetylenes, except one by Nesmeyanov *et al.*[2] which describes the formation of tris-(2-chlorovinyl)antimony dichlorides from the reaction of acetylene with $SbCl_5$. We now report the first example of direct chlorination of the triple bond with $SbCl_5$ which proceeds mainly in a *Z*-fashion.

Table. Reaction conditions, yields, and isomer ratios.

(**1**) R	Molar ratio $SbCl_5$/(**1**)	Reaction temp. (°C)	Reaction time (min)	Yield (%) and isomer ratio of (**2**) (*E*:*Z*)[a]
Me	1·23	25	10	28 (13:87)
Me	1·23	30	60	27 (17:83)
Me	1·21	76	10	25 (22:78)
Et	1·08	25	10	32 (16:84)
Pr^n	1·27	25	10	24 (7:93)
Bu^n	1·27	25	10	17 (10:90)
Bu^t	1·08	25	10	25 (0:100)[b]
Bu^t	1·04	76	120	55 (0:100)[c]

[a] Based on (**1**) as determined by g.l.c. Compound (**2**) gave satisfactory analytical data. Identification of (**2**) is described elsewhere.[4] [b] Other product; *E*-PhClC=$CHBu^t$, 31% yield. [c] Other product; *E*-PhClC=$CHBu^t$, 20% yield.

When the alkylphenylacetylene (**1**) (1·1—1·3 mmol) in CCl_4 (1 ml) was slowly added to a CCl_4 solution (4 ml) of $SbCl_5$ (1·4—1·9 mmol) at 25—76 °C and the mixture was stirred for 10—120 min, an isomeric mixture of the corresponding dichloroalkenes, *Z*-(**2**) and *E*-(**2**), was obtained (17—55%) together with some resinous products, the *Z*-isomer being predominant irrespective of the alkyl group (Table). In the case of (**1**, R=Bu^t) the product of *Z* HCl addition,[3] *E*-PhClC=$CHBu^t$, was also formed. Under these conditions tetrachloroalkanes or organoantimony compounds were not obtained. The reaction also proceeded in CH_2Cl_2, $CHCl_3$, and $ClCH_2CH_2Cl$ but significant improvement in the *Z*-selectivity or the yield were not observed.



The reactions were insensitive to radical scavengers such as *m*-dinitrobenzene and oxygen. We confirmed in separate experiments that interconversion between the isomers did not occur under these conditions. Very high *Z*-stereospecificity could be explained by assuming a concerted or near-concerted molecular addition of $SbCl_5$ or its dimer to the triple bond; similar mechanism was suggested for the *Z*-chlorination of simple olefins.[1b]

Chlorination of (**1**, R=Me) and (**1**, R=Bu^t) with chlorine in CCl_4 at 25 °C for 10 min gave a mixture of *E*- and *Z*-(**2**) in 34 (*E*:*Z* 68:34) and 51% (*E*:*Z* 13:87) yields respectively, showing that *Z*-stereospecificity is low compared to that in the $SbCl_5$ case.

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[2] A. N. Nesmeyanov and A. E. Borisov, *Bull. Acad. Sci., U.S.S.R.*, 1945, 251; *Chem. Abs.*, 1946, **40**, 2123.

[3] R. Maroni, G. Melloni, and G. Modena, *J.C.S. Perkin I*, 1973, 2491.

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