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Stereochemistry of Chlorination and Chloroiodination of Alkylphenylacetylenes by $CuCl_2$

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Summary Reaction of alkylphenylacetylenes, PhC≡CR (R = H or alkyl) (**1**), with $CuCl_2$–LiCl or $CuCl_2$–I_2 in acetonitrile gives the corresponding dihalogenoalkenes in good yields; *E*-addition is favoured except in the chlorination of (**1**, R = Bu^t) where *Z*-addition predominates.

THE liquid phase halogenation of olefins by $CuCl_2$ is well known. However, there are no reports on its application to acetylenes, except one[1] which describes the trichlorination of prop-2-ynyl alcohol and aldehyde and dichlorination of methyl propiolate. In order to study the stereochemistry of halogenation of acetylenes by $CuCl_2$ in more detail, we investigated the reaction of alkylphenylacetylenes and phenylacetylene with $CuCl_2$ in the presence or absence of LiCl and I_2.

Reaction of (**1**) (5—10 mmol) with $CuCl_2$ (100—200 mmol) in MeCN (50—100 ml) containing LiCl (100—200 mmol) at 82 °C for 24—48 h gave a mixture of the dichloroalkenes, *E*-(**2**) and *Z*-(**2**), in good yield (Table). The reaction proceeded even without LiCl, but both the yield and the selectivity for *E*-(**2**) were low in the case of (**1**, R = Me). All reactions produced mainly the *E*-isomer, except (**1**, R = Bu^t) where *Z*-addition predominated (Table). Since prolonged reaction time gave improved yields without affecting the isomer ratio, the reactions must be almost entirely kinetically controlled. We also confirmed in separate experiments that interconversion between the isomers did not occur under these conditions. Chloroiodination of acetylenes by a mixture of $CuCl_2$ and I_2 proceeded more smoothly than chlorination and afforded completely regiospecific and highly stereospecific (*E*) chloroiodoalkenes (**3**) in good yields (Table).

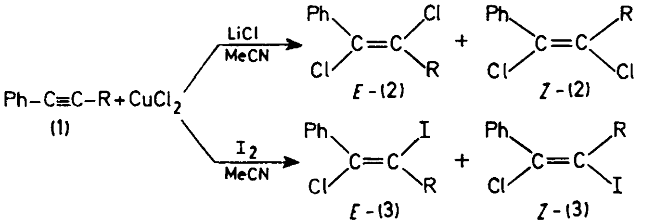
The products were identified by the following data: *E*-(**2**, R = H), b.p. 104 °C at 19 Torr, δ (CCl_4) 6·46 (1H, s, vinylic), and *Z*-(**2**, R = H), δ (CCl_4) 6·62 (1H, s, vinylic) (*cf.* δ 6·75 and 6·98 for *E*- and *Z*-PhBrC:CBrH respectively[2]); *E*-(**2**, R = Me), b.p. 96 °C at 9 Torr, δ (CCl_4) 2·47 (3H, s, Me), and *Z*-(**2**, R = Me), δ (CCl_4), 2·17 (3H, s, Me); *E*-(**2**, R = Bu^t), δ (CCl_4) 1·48 (9H, s, Bu^t), and *Z*-(**2**, R = Bu^t), m.p. 67 °C (from aq. EtOH), δ (CCl_4) 1·05 (9H, s, Bu^t) (*cf.* HCl adducts of **1**, R = Me[3] or Bu^t[4]); *E*-(**3**, R = H), b.p. 112—113 °C at 5 Torr, δ (CCl_4) 6·76 (1H, s, vinylic) [a low-field shift of 0·30 p.p.m. of the vinyl proton in *E*-(**3**, R = H) compared with

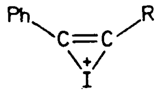
TABLE. Reaction conditions, yields, and isomer ratios

(**1**) R	Molar ratio $CuCl_2$/(**1**)[b]	Reaction time/h	Yield/% and isomer ratio[a]	
			(**2**) (*E*:*Z*)	(**3**) (*E*:*Z*)
H	20	12	65 (93:7)	
H	40	24	95 (94:6)	
H	5	5		93 (100:0)
Me	40	2	22 (97:3)	
Me	40	24	94 (98:2)	
Me	40[c]	24	68 (91:9)	
Me	5	5		93 (100:0)
Et	40	24	94 (95:5)	
Pr^n	40	48	93 (94:6)	
Bu^n	40	48	93 (93:7)	
Pr^i	40	48	95 (80:20)	
Bu^t	40	2	27 (20:80)	
Bu^t	40	48	95 (21:79)	
Bu^t	5	5		95 (90:10)

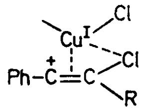
[a] Based on (**1**) as determined by g.l.c. Compounds (**2**) and (**3**) gave satisfactory analytical data and mass spectra. [b] Equal molar amounts of LiCl and I_2 to $CuCl_2$ were added in chlorination and chloroiodination, respectively. [c] LiCl was not added.

E-(**2**, R = H) is consistent with that observed in the case of 1-halogenoprop-1-ene where the difference is 0·23 p.p.m.[5]; E-(**3**, R = Me), b.p. 94—96 °C at 2 Torr, δ (CCl$_4$) 2·70 (3H, s, Me); and E- and Z-(**3**, R = Bu^t) (E:Z = 9:1), b.p. 130—132 °C at 5 Torr, δ (CCl$_4$) 1·57 and 1·15 for E- and Z-respectively (9H, s, Bu^t). G.l.c. analyses [EGSS-X Chromosorb-W (3 m) and Apiezon-L Celite (1 m) columns, 100 ml N$_2$ min^{-1}, 160 °C] showed that the E-isomer had a shorter retention time than the Z-isomer in all cases.





(A)



(B)

It has been reported[6] that (**1**, R = Me) does not undergo homogeneous reaction with chlorine in CCl$_4$, while the reaction of (**1**, R = H) in CH$_2$Cl$_2$ gives roughly equal amounts of E- and Z- (**2**, R = H). No chloroiodination of acetylenes has so far been reported.

Both halogenations were insensitive to radical scavengers such as *m*-dinitrobenzene and oxygen. Very high E-stereospecificity in chloroiodination could be explained by assuming a cyclic iodonium ion (A) as an intermediate, but in chlorination the isomer ratio (E:Z) decreased markedly on changing the alkyl group from primary to secondary and then to tertiary. This cannot be so easily explained unless the reaction proceeds through an open vinyl cation intermediate (B) in which the Cu$^{\rm I}$ salt co-ordinates weakly with the double bond and the chlorine atom. When R becomes sterically large it would hinder attack on its own side in (B) by CuCl$_3^-$ and lead to Z-chlorination. The assumption of a cyclic intermediate in the case of iodine and not in the case of chlorine parallels the result of solvolysis of β-halogenovinyl sulphonic esters.[7]

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