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EVIDENCE FOR *SYN* ADDITION OF HYDROGEN CHLORIDE TO PHENYLACETYLENE

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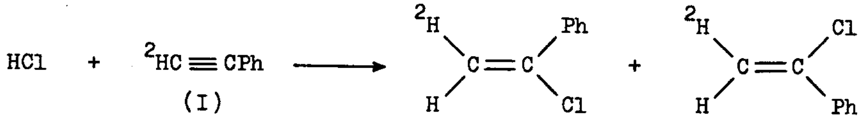
Electrophilic additions to double and triple bonds are generally assumed to occur in an *anti* manner, though several experimental observations indicate that *anti* addition is far to be a general rule.[1,2] Very recently a theoretical explanation of the violations of the forbidden *syn* $[2_\pi + 2_\sigma]$ addition has been offered.[2] In the case of electrophilic additions to acetylenes we have shown that apparent *syn* and *anti* additions are determined by the relative difference in steric and/or electronic properties of the β-groups in a vinyl cation intermediate.[3] Consequently, sound evidence for the occurrence of a *syn* addition is obtainable only with systems where the β-groups are identical.

In order to test this hypothesis we have studied the addition of hydrogen chloride to phenyl[2-$^{2}H_{1}$]acetylene (I) in various solvents. The reactions were carried out at 40° in tightly stoppered flasks with saturated solutions of gaseous hydrogen chloride and afforded the isomeric α-chlorostyrenes (II) and (III) in different ratios depending on the reaction conditions.



(II) (III)

The reactions were carried out with a 50% excess of (I) and were quenched before completion in order to minimize double addition of hydrogen chloride, sometimes observed as a minor side reaction. Careful examination of the unreacted phenyl[2-$^{2}H_{1}$]acetylene[4] by i.r. and ^{1}H n.m.r. spectroscopy showed that no detactable hydrogen-deuterium exchange had occurred. The relative amounts of the α-chlorostyrenes (II) and (III) were determined by integration of the ^{1}H n.m.r. signals (singlets) corresponding to the vinyl protons, which have different chemical shifts whether *cis* or *trans* to the phenyl group.[5] A control experiment was made by adding ^{2}HCl to phenylacetylene (IV) and afforded the expected re-

TABLE

Reactions of addition of hydrogen chloride to phenyl[2-$^{2}H_{1}$]acetylene (I)

Reaction	Solvent	Catalyst [a]	(II):(III) ratio (%) [b]
HCl + (I)	Dichloromethane	$ZnCl_2$	70:30
HCl + (I)	Dichloromethane	==	65:35
HCl + (I)	Acetic acid	==	60:40
HCl + (I)	Nitromethane	$ZnCl_2$	55:45
HCl + (I)	Sulpholane	$ZnCl_2$	50:50
HCl + (I)	Sulpholane	==	75:25
^{2}HCl + (IV)	Dichloromethane	$ZnCl_2$	30:70

[a] Molar ratio catalyst:hydrogen chloride: 0.1. [b] Estimated error: 5%.

versed (II):(III) ratio (see Table).

The results reported in the Table show a considerable participation of a *syn* addition process in most of the reactions investigated. The solvent and the catalyst affect significantly the stereochemistry of the addition; this has probably to be related to the solvation of the chloride ion. In fact, it may be observed that a better solvation of the chloride ion tends to shift the isomers ratio toward the 50:50 value expected for a polar addition *via* a symmetrically substituted free vinyl cation.

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4. Phenylacetylene (I) was prepared by hydrolysis of phenylethynylmagnesium bromide with deuteriated sulphuric acid. The isotopic purity, assayed by i.r. and n.m.r. spectroscopy, was found to exceed 97%.
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