The Stereochemistry of the Electrophilic Additions to Triple Bonds *via* Linear Vinyl Cations

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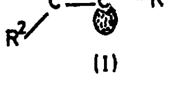
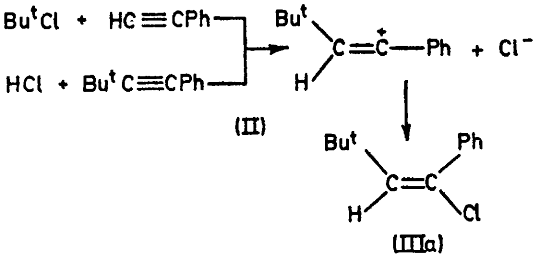
Summary The formation of (*E*)-1-chloro-3,3-dimethyl-1-phenylbutene during the addition both of t-butyl chloride to phenylacetylene and of HCl to t-butylphenylacetylene *via* linear vinyl cations is taken as evidence that the relative size of the β-groups in such intermediates determines the direction of attack of a nucleophile on the positive centre, and therefore the configuration of the product.

THE intermediacy of vinyl cations in unimolecular substitutions at the vinyl carbon and in electrophilic additions to acetylenes and allenes is now well established.[1] Nevertheless, the stereochemical demands of such intermediates and, consequently, the stereochemistry of the reactions involving them have not been well defined. Earlier reports suggested that reactions occurring *via* linear vinyl cations would give equal amounts of the two isomeric products,[2] but later results showed that such reactions are in general stereoselective.[3] Linear vinyl cations (I) have in fact a planar geometry, with the empty *p*-orbital lying in the plane of the molecule.[1] Consequently, the attack of a nucleophile on the positive centre should occur in this plane and be sensitive to the size and electronic character of the groups bonded to the adjacent carbon atom.



(I)

In the course of an extensive study of the electrophilic alkylation of acetylenes, which will be reported elsewhere, we have obtained the first clear evidence that the relative size of the β-groups determines the direction of attack of the nucleophile and therefore the configuration of the products. We observed (Scheme) that the Lewis acid-catalysed addition of t-butyl chloride to phenylacetylene and of hydrogen chloride to t-butylphenylacetylene affords as the only adduct (*E*)-1-chloro-3,3-dimethyl-1-phenylbutene (IIIa). Since the addition to phenylacetylenes of an electrophile like the proton, and therefore reasonably a positive carbon,[1,4] occurs *via* linear vinyl cation, it may be assumed that both reactions proceed through the formation of the same cationic intermediate (II), which leads to the (*E*)-adduct (IIIa) by reaction with the chloride ion.



Scheme

The two reactions were carried out as follows. The addition of t-butyl chloride to phenylacetylene (*ca.* 1 : 3) in boiling dichloromethane in the presence of a catalytic amount of $ZnCl_2$ for 3 h afforded, after chromatography on silica gel, a mixture of the (IIIa) (36%), τ (CCl_4) 2·78 (5H, s), 4·05 (1H, s), and 9·12 (9H, s), and of α-chlorostyrene (18%). The two products were separated by g.l.c. The α-chlorostyrene[5] reasonably arises from the addition to phenylacetylene of hydrogen chloride formed by some dehydrohalogenation of t-butyl chloride by the Lewis acid. The reaction of gaseous hydrogen chloride (saturated dichloromethane solution) with t-butylphenylacetylene[6] in the presence of a catalytic amount of $ZnCl_2$ at 60° for 48 h afforded, after chromatography on silica gel, a 96% yield of the (IIIa) and a small amount of 3,3-dimethyl-1-phenylbutanone. In both reactions no evidence was found of the formation of the other isomer.

For comparison purposes and for the assignment of the configuration an independent synthesis of (*E*) (IIIa) and (*Z*) (IIIb) was also carried out. Dehydrochlorination in the presence of triethylamine of 1,1-dichloro-3,3-dimethyl-1-phenylbutane (V), obtained by treatment with PCl_5 of 3,3-dimethyl-1-phenylbutanone (IV),[6] afforded a mixture of (IIIa) and of its isomer (*Z*)-1-chloro-3,3-dimethyl-1-phenylbutene (IIIb), τ (CCl_4) 2·40—2·88 (5H, m), 3·98 (1H, s), and 8·71 (9H, s), in the ratio of *ca.* 1 : 4, which were separated by g.l.c.

The assignment of the configuration to the two isomers was based on the deshielding effect caused by a phenyl group on a β-*cis*-olefinic proton relative to a *trans*-proton,[7] feature which has been tested previously and found characteristic of a number of styrene derivatives.[8,9] Thus, we assigned the (*Z*)-configuration (IIIb) to the compound with the vinyl proton signal at lowest field. This assignment was also confirmed by the relative chemical shift of the t-butyl protons in the two isomers. It has been shown that a phenyl group has a shielding effect on β- and γ-*cis*-methyl and methylene protons relative to *trans*-protons.[8] The (*Z*)-isomer (IIIb) is the compound with the t-butyl protons signal at lowest field.

It was also proved that compounds (IIIa) and (IIIb) do not isomerise under the reaction conditions.

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