On the Stereochemistry of the Electrophilic Addition of Alkyl Halides and Hydrogen Halides to Phenyl-Substituted Acetylenes[1]

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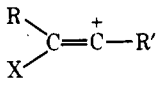
Abstract: The electrophilic addition of *tert*-butyl chloride and of hydrogen chloride to various alkylphenylacetylenes in dichloromethane in the presence of $ZnCl_2$ has been studied. The reactions afforded the 1:1 addition products with high stereoselectivity, in accordance with a stepwise addition mechanism involving the initial formation of open vinyl cation intermediates and the subsequent preferential attack of the chloride ion from the less hindered side. Support for the formation of "free" vinyl cations in the reaction conditions used is given by the result of the addition of benzyl-α,α-d_2 chloride to 1,3-diphenylpropyne, which afforded a 1:1 (*E*:*Z*) ratio of the addition products, showing no preferential direction of attack by the nucleophile on a symmetrically β-substituted vinyl cation. On the other hand, the addition of hydrogen chloride to phenylacetylene-*d* showed a significant intervention of a syn addition process. In light of these results a survey of the data previously obtained in the study of these reactions is made.

Three limiting mechanisms have been considered for electrophilic additions to acetylenes.[2-6] The most common is the stepwise bimolecular addition mechanism (AdE2) involving an unsaturated cationic intermediate, which can be either open (**1**) or bridged (**2**).[3,4,7] A termolecular anti addition mechanism (AdE3) has been found to occur in the hydrohalogenation of alkynes in acetic acid[5,8] and in the bromination of various acetylenes,[9] mostly in the presence of added salt. A molecular syn addition mechanism, possibly concerted, has been discussed from a theoretical point of view,[6] and prevalent formation of syn adducts has been observed in some additions of acids to 1-alkynes[8,10,11] and to phenyl-substituted acetylenes.[8,12-14]

In most cases these mechanisms are concomitant. The balance between them and, in the case of AdE2 addition, between open and bridged intermediates is very delicate, depending both on the structure of the reactants and on the reaction conditions. For this reason all the factors involved in these additions are not as yet fully understood and many studies are still being devoted to the matter.



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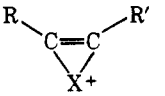


2

A starting point for a better understanding of the competition among the possible mechanisms may be the definition of the steric course of the addition reactions occurring via open vinyl cations **1**. These reactions were once thought to be nonstereospecific;[12,15] subsequent work[16,17a] has shown the importance of the relative size and electronic character of the β groups R and X in determining the direction of the nucleophilic attack to the positive center. A study of this kind must obviously exclude the possibility of formation of cyclic ions **2**; consequently, proton and carbonium ions seem to be the most suitable among the electrophiles exploited so far.

Following this reasoning, in our previous work we have studied the addition of some alkyl chlorides and bromides and, correspondingly, of hydrogen chloride and bromide to phenyl-substituted acetylenes under Friedel-Crafts conditions.[17-19] The reactions afforded in most cases good yields of stable 1:1 adducts which proved to be very useful for the study of the stereochemistry of the addition. In the prosecution of this work we have been faced with the problem of determining whether truly "free"[20] vinyl cations were involved in our additions. In fact, in some of the cross experiments made previously[17,19] [RX + HC≡CPh/HX + RC≡CPh], we had noticed a slight discrepancy between the results of the addition of alkyl halides and those of hydrogen halides, the latter giving larger amounts of the product of formal syn addition. Since most of our previous work was done with hydrogen-substituted systems, i.e., with β groups very different in size, it seemed worthwhile to examine systems less unbalanced and, finally, with identical, though distinguishable, β groups.

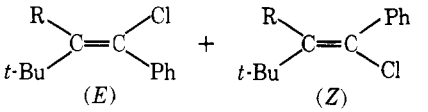
We report here the results obtained in the addition of *tert*-butyl chloride and hydrogen chloride to various alkylphenylacetylenes, of benzyl-α,α-d_2 chloride to 1,3-diphenylpropyne, and of hydrogen chloride to phenylacetylene-*d*. In light of these results, we are now able to draw a comprehensive picture of all our studies on electrophilic additions to acetylenes.

Results

Addition of *tert*-Butyl Chloride to Alkylphenylacetylenes. The additions of *tert*-butyl chloride (**3**) to 1-phenylpropyne (**4**), 1-phenylbut-1-yne (**5**), 3-methyl-1-phenylbutyne (**6**), and 3,3-dimethyl-1-phenylbutyne (**7**) were carried out in boiling anhydrous dichloromethane in the presence of a catalytic amount of anhydrous zinc chloride and afforded mixtures of products derived from 1:1 addition of both *tert*-butyl chloride and hydrogen chloride to the acetylenic compound (eq 1).

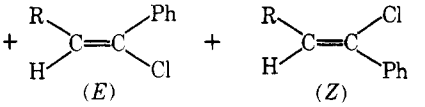
t-BuCl + R—C≡C—Ph →

3 **4**, R = Me; **5**, R = Et; **6**, R = *i*-Pr; **7**, R = *t*-Bu



(*E*) (*Z*)

8, R = Me; **9**, R = Et; **10**, R = *i*-Pr; **11**, R = *t*-Bu



(*E*) (*Z*)

12, R = Me; **13**, R = Et; **14**, R = *i*-Pr; **15**, R = *t*-Bu (1)

Table I. Addition of *tert*-Butyl Chloride (3) to Alkylphenylacetylenes 4–7 (Eq 1)

Acetylene RC≡CPh	Reagent ratio[a]	*t*-BuCl addition products *t*-Bu(R)C=C(Cl)Ph Compd (% yield)	Ratio,[c] % *E*	*Z*	HCl addition products RCH=C(Cl)Ph Compd (% yield)	Ratio,[c] % *E*	*Z*
4, R = Me	1:1	8 (40)	100		12 (23)	70	30
5, R = Et	1:1	9 (28)	95	5	13 (40)	80	20
6, R = *i*-Pr	1:1	10 (trace)[b]			14 (32)	95	5
6, R = *i*-Pr	5:1	10 (trace)[b]			14 (73)	95	5
7, R = *t*-Bu	5:1	11 (none)			15 (79)	100	

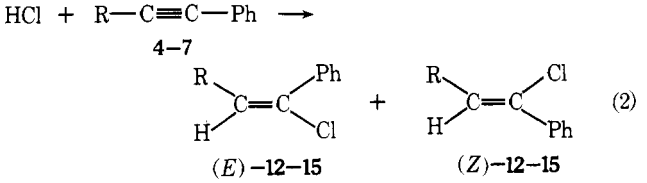
[a] Ratio *t*-BuCl–acetylene. [b] Unknown stereochemistry. [c] Determined by ^{1}H NMR; estimated error ≤5%.

The results of these reactions are reported in Table I. In the case of the addition to acetylene **6**, only a trace of the *tert*-butyl chloride addition products **10** was detected, even using a large excess of **3**; in the case of the addition to **7**, no evidence of the formation of adducts **11** was obtained. For this reason we were unable to use the latter reaction for studying the stereochemistry of the addition of deuterated *tert*-butyl chloride to **7**, which was our original aim.

The formation in these reactions of large amounts of adducts **12–15** has to be imputed to formation of hydrogen chloride by dehydrochlorination of *tert*-butyl chloride (**3**) in the presence of the Lewis acid, in competition with the addition of **3** to the acetylenic compound.[17]

Independent tests showed that no isomerization of the products of addition, both of *tert*-butyl chloride and of hydrogen chloride in the reaction conditions, occurred.

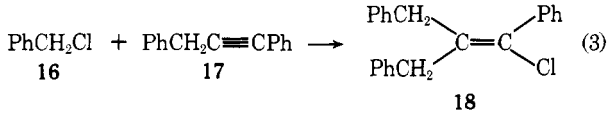
Addition of Hydrogen Chloride to Alkylphenylacetylenes. The addition of hydrogen chloride to acetylenes **4–7** was carried out in tightly stoppered flasks at 40° in the presence of zinc chloride as a catalyst, using appropriate volumes of a saturated solution of dry hydrogen chloride in dichloromethane. The expected 1:1 addition products **12–15** were obtained in good yields, according to eq 2.



(2)

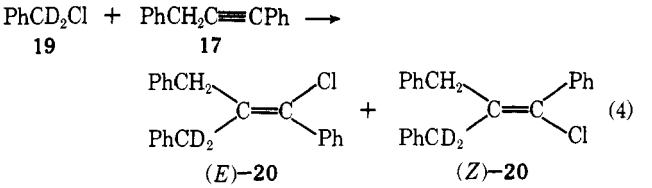
The *E*:*Z* ratios in compounds **12–15** were found to be identical with those obtained in the reactions with *tert*-butyl chloride, where **12–15** were formed as side products (eq 1 and Table I).

Addition of Deuterated Benzyl Chloride to 1,3-Diphenylpropyne. The reaction between benzyl chloride (**16**) and 1,3-diphenylpropyne (**17**) in the conditions described above was very slow. Therefore, a higher boiling solvent (1,2-dichloroethane) was used; with a threefold excess of the acetylenic compound a 58% yield of the 1:1 adduct **18** was obtained after 11 days of reflux (eq 3). The NMR spectrum of **18**



(3)

showed a marked difference between the chemical shifts of the methylenic protons cis and trans to the phenyl group. This reaction seemed, therefore, suitable for the stereochemical study of addition of labeled benzyl chloride. Identical conditions were then used in the addition of benzyl-α,α-d_2 chloride (**19**) to the same acetylene **17**. A 1:1 ratio of the isomeric adducts (*E*)- and (*Z*)-**20** was obtained (eq 4).



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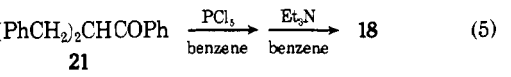
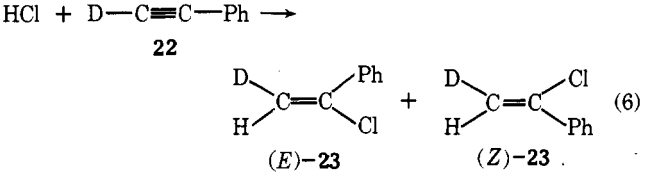
A proof of the structure of compound **18** was obtained by independent synthesis, carried out by chlorination of ketone **21** and subsequent dehydrochlorination in the presence of triethylamine (eq 5).



(5)

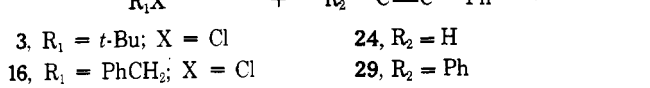
Addition of Hydrogen Chloride to Phenylacetylene-*d*. This reaction, previously reported in a communication,[13] was carried out in the conditions described above for the analogous addition to alkylphenylacetylenes using a twofold excess of acetylene **22**, and afforded the two isomeric α-chlorostyrenes (**23**) in the *E*:*Z* ratio of 2.3:1 (eq 6).



(6)

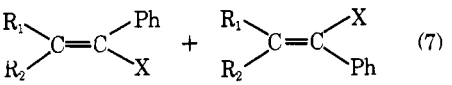
Careful examination of unreacted phenylacetylene **22** showed that no hydrogen–deuterium exchange had occurred. A control experiment was also performed under the same conditions by adding deuterium chloride to phenylacetylene (**24**). An exactly reversed *E*:*Z* ratio of isomers **23** was obtained.

Other Additions of Alkyl Halides and Hydrogen Halides to Acetylenes. The results of a series of addition reactions previously described are reported for comparison purposes in Tables II and III along with those obtained in this work, following the general equations 7 and 8.



3, R_1 = *t*-Bu; X = Cl
16, R_1 = $PhCH_2$; X = Cl
25, R_1 = *t*-Bu; X = Br
26, R_1 = $PhCH_2$; X = Br
27, R_1 = Ph_2CH; X = Cl
28, R_1 = Ph_2CH; X = Br

24, R_2 = H
29, R_2 = Ph

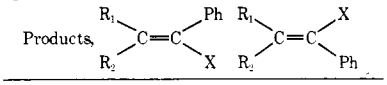

(7)

(*E*)-**15**, R_1 = *t*-Bu; R_2 = H; X = Cl
(*E*)-**30**, R_1 = *t*-Bu; R_2 = H; X = Br
(*E*)-, (*Z*)-**31**, R_1 = *t*-Bu; R_2 = Ph; X = Cl
(*E*)-, (*Z*)-**32**, R_1 = $PhCH_2$; R_2 = H; X = Cl
(*E*)-, (*Z*)-**33**, R_1 = $PhCH_2$; R_2 = H; X = Br
(*E*)-, (*Z*)-**34**, R_1 = $PhCH_2$; R_2 = Ph; X = Cl
(*E*)-, (*Z*)-**35**, R_1 = Ph_2CH; R_2 = H; X = Cl
(*E*)-, (*Z*)-**36**, R_1 = Ph_2CH; R_2 = H; X = Br

Discussion

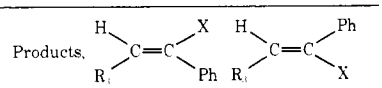
SN1 mechanisms with formation of open vinyl cation intermediates (**1**) have been conclusively demonstrated to operate in solvolyses of α-phenylvinyl halides bearing hydrogen or alkyl groups in the β position[3,4,7,14] (eq 9). The formation of the same intermediates may be equally proposed for our additions of alkyl and hydrogen halides to phenyl-substituted acetylenes, which formally proceed by the reverse path (eq 10).

Table II. Stereochemistry of the Addition of Alkyl Halides to Phenylacetylenes

Alkyl halide R_1X	Acetylene $R_2C{\equiv}CPh$	Products,  Compd	Ratio, %[g]		Ref
3, R_1 = *t*-Bu; X = Cl[a]	**24**, R_2 = H	**15**[c]	100[h]		17
3, R_1 = *t*-Bu; X = Cl[a]	**4**, R_2 = Me	**8**[d]	100[h]		This work
3, R_1 = *t*-Bu; X = Cl[a]	**5**, R_2 = Et	**9**[d]	95[h]	5	This work
3, R_1 = *t*-Bu; X = Cl[a]	**29**, R_2 = Ph	**31**[c]	95[i]	5	18
25, R_1 = *t*-Bu; X = Br[b]	**24**, R_2 = H	**30**[c]	100[h]		19
16, R_1 = $PhCH_2$; X = Cl[a]	**24**, R_2 = H	**32**[c]	80[h]	20	17
16, R_1 = $PhCH_2$; X = Cl[a]	**29**, R_2 = Ph	**34**[c,e]	15[i]	85	18
26, R_1 = $PhCH_2$; X = Br[b]	**24**, R_2 = H	**33**[c]	80[h]	20	19
19, R_1 = $PhCD_2$; X = Cl[a]	**17**, R_2 = $PhCH_2$	**20**[f]	50[h]	50	This work
27, R_1 = Ph_2CH; X = Cl[a]	**24**, R_2 = H	**35**[c]	90[h]	10	17
28, R_1 = Ph_2CH; X = Br[b]	**24**, R_2 = H	**36**[c]	90[h]	10	19

[a] In the presence of 0.1 mol of anhydrous $ZnCl_2$. [b] In the presence of 0.1 mol of anhydrous $ZnBr_2$. [c] See eq 7. [d] See eq 1. [e] 2,3-Diphenylindene (20% yield) was also formed. [f] See eq 4. [g] Determined by ^1H NMR; estimated error ≤5%. [h] *E* isomer. [i] *Z* isomer.

Table III. Stereochemistry of the Addition of Hydrogen Halides to Phenylacetylenes

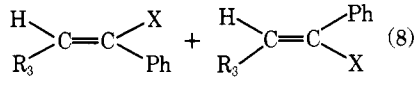
Hydrogen halide HX	Acetylene $R_3C{\equiv}CPh$	Products,  Compd	Ratio (%)[g] (*E*)	(*Z*)	Ref
HCl[a]	**22**, R_3 = D	**23**[d]	70	30	This work
HCl[b]	**22**, R_3 = D	**23**[d]	65	35	13
HBr[c]	**22**, R_3 = D	**38**[e]	75	25	19
HCl[a]	**4**, R_3 = Me	**12**[f]	70	30	This work
HCl[a]	**5**, R_3 = Et	**13**[f]	80	20	This work
HCl[a]	**6**, R_3 = *i*-Pr	**14**[f]	95	5	This work
HCl[a]	**7**, R_3 = *t*-Bu	**15**[e,f]	100		17, this work
HBr[c]	**7**, R_3 = *t*-Bu	**30**[e]	100		19
HCl[a]	**17**, R_3 = $PhCH_2$	**32**[e]	85	15	17
HBr[c]	**17**, R_3 = $PhCH_2$	**33**[e]	90	10	19
HCl[a]	**37**, R_3 = Ph_2CH	**35**[e]	95	5	17
HBr[c]	**37**, R_3 = Ph_2CH	**36**[e]	~98	~2	19
HCl[a]	**29**, R_3 = Ph	**39**[e]	100		18

[a] In the presence of 0.1 mol of anhydrous $ZnCl_2$. [b] In CH_2Cl_2 at 40° in the absence of catalyst. [c] In the presence of 0.1 mol of anhydrous $ZnBr_2$. [d] See eq 6. [e] See eq 8. [f] See eq 2. [g] Determined by ^1H NMR; estimated error ≤5%.

HX + R_3—C≡C—Ph →

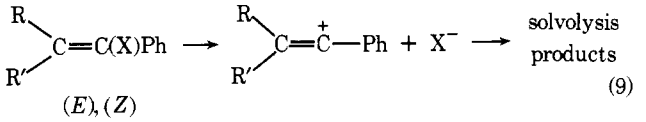
X = Cl, Br

7, R_3 = *t*-Bu
17, R_3 = $PhCH_2$
22, R_3 = D
24, R_3 = H
29, R_3 = Ph
37, R_3 = Ph_2CH

 (8)

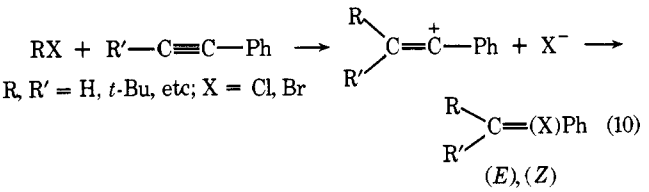
(*E*)-**15**, R_3 = *t*-Bu; X = Cl
(*E*)-**30**, R_3 = *t*-Bu; X = Br
(*E*)-, (*Z*)-**32**, R_3 = $PhCH_2$; X = Cl
(*E*)-, (*Z*)-**33**, R_3 = $PhCH_2$; X = Br
(*E*)-, (*Z*)-**35**, R_3 = Ph_2CH; X = Cl
(*E*)-, (*Z*)-**36**, R_3 = Ph_2CH; X = Br
(*E*)-, (*Z*)-**38**, R_3 = D; X = Br
(*E*)-**39**, R_3 = Ph; X = Cl

All the data obtained in our study, though lacking kinetic analysis, strongly support the two-step bimolecular addition mechanism outlined in eq 10. The observed regiospecificity of the addition according to Markownikoff's rule is an indication

 (9)

(*E*), (*Z*)

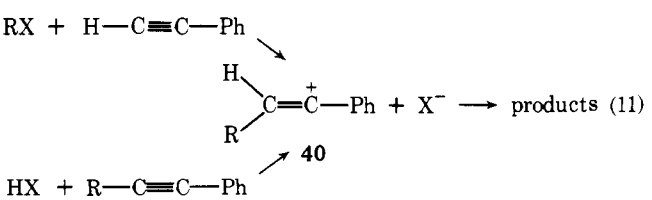
R, R′ = H, Alk; X = Br, I

 (10)

(*E*), (*Z*)

of ionic reaction, in which the electrophilic species is a carbonium ion formed by the action of the Lewis acid on the alkyl halide. In fact, it has to be pointed out that in our conditions products of addition could be obtained only with tertiary or phenyl-substituted alkyl halides, corresponding to stable carbonium ions. We have been unable to obtain any addition product with simple primary or secondary alkyl halides, from which the formation of carbonium ions is difficult, if not impossible, in our reaction conditions.

The most significant evidence in favor of the AdE2 mechanism comes from the comparison of the stereochemical results of the addition of *tert*-butyl, benzyl, and diphenylmethyl chlorides (**3**, **16**, and **27**) and bromides (**25**, **26**, and **28**) to phenylacetylene (**24**) (Table II) with those of the addition of hydrogen chloride and bromide to 3,3-dimethyl-1-phenylbutyne (**7**), 1,3-diphenylpropyne (**17**), and 1,3,3-triphenylpropyne (**37**), respectively (Table III). The formation of the same (or nearly the same) isomer distribution in both kinds of addition reactions is a strong indication of a common product formation step and consequently of a common intermediate (**40**) (eq 11). In these additions, therefore, the formation of the

 (11)

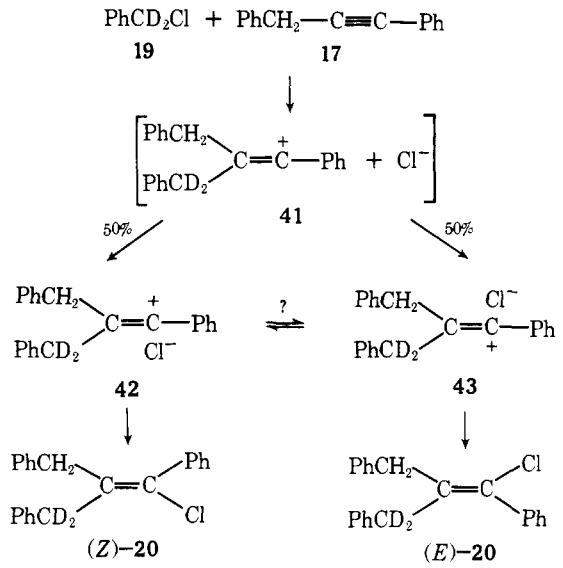
R = $(CH_3)_3$, $PhCH_2$, Ph_2CH; X = Cl, Br

products depends only on the nucleophilic attack of the halide ion or, more properly, of its complex with the catalyst[21] on the intermediate **40**, whose structure determines the stereochemistry of the reaction, regardless of the electrophilic species involved in its formation.

As to the direction of attack of the nucleophilic species on the stable, highly selective vinyl cation **40,** the predominant or exclusive formation of the isomer bearing the halogen atom cis to the smaller β group indicates that the less hindered side of the cation is always preferred. A kinetic control of the nucleophilic attack is also suggested by the fact that the isomer preferentially formed is the less thermodynamically stable, having the two bulkiest groups (alkyl and phenyl) cis to each other.[14] This rules out any alternative interpretation of the results based on product isomerization, which is also excluded by the observed stability of the addition products, both of *E* and *Z configuration, in the reaction conditions, particularly* in the case of chloro derivatives.[17,18]

The exclusive intervention of the two-step mechanism in our carbonium ion additions is indicated by the result of the addition of labeled benzyl chloride (**19**) to 1,3-diphenylpropyne (**17**), which gave a statistical distribution of the isomeric adducts **20,** as expected from a reaction occurring via a symmetrically substituted vinyl cation. This result is particularly significant for the interpretation of all our stereochemical data, since it indicates that the intermediate vinyl cation **41** (see Scheme I) is a free[20] cation; in other terms, referring to the

Scheme I



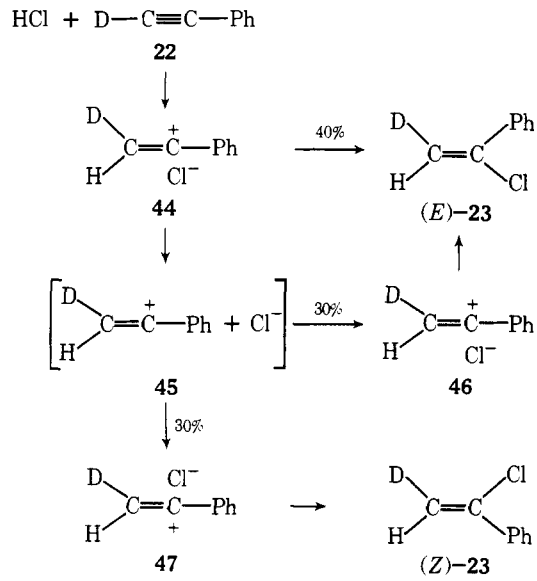
medium of low polarity in which these reactions were carried out, the vinyl cation–chloride ion pair **41** formed at first has a lifetime long enough to allow complete equilibration between the two intimate syn and anti oriented ion pairs **42** and **43** by exchange of the chloride ion[21] with other ions outside the cage of the solvent or, perhaps, by simple rotation of the vinyl cation itself within the solvent cage.

This interpretation can easily be extended to all the carbonium ion additions studied, thus reasonably excluding any preferred collapse of the ion pairs not due to steric or electronic effects of the β substituents.

At variance with the addition of carbonium ions, the addition of hydrogen chloride to labeled phenylacetylene **22** in the same reaction conditions did not afford equal amounts of the isomeric α-chlorostyrenes **23,** but showed the preferred formation (2.3:1) of the adduct of *E* configuration. Following schemes previously proposed for similar additions,[11,12,14] this result might be rationalized in terms of initial formation of a syn oriented ion pair **44** (Scheme II) which in part (40%) collapses to the *E* adduct and in part (60%) forms a free vinyl cation (**45**) which leads to a statistical distribution of the two isomeric adducts.

Also in this case it is conceivable that preferred formation and collapse of a syn oriented ion pair such as **44** occurs in all

Scheme II



the additions of hydrogen chloride (and also of hydrogen bromide)[19] so far studied in our system, thus leading to the formation of *E* adducts in greater amounts than reasonably expected on the basis of the relative effects of the β groups in free vinyl cations.

It has to be pointed out, however, that Schemes I and II do not provide an explanation for the different behavior of alkyl halides and hydrogen halides in our reaction conditions. This could be found in the reasonably low ionization of hydrogen halides in dichloromethane, even in the presence of a Lewis acid, due to poor solvation of the proton. Following this hypothesis, the nucleophile halide ion[21] remains very close to the proton during the attack to the triple bond, giving tight syn oriented ion pairs, while in the additions of carbonium ions, which in our case are stable and therefore less sensitive to poor solvation, less tight ion pairs are formed.

An alternative explanation for the preferred formation of syn adducts in the hydrogen halide additions could be the intervention of a concerted polar (AX) $2_\pi + 2_\sigma$ cycloaddition. It has been recently suggested[6] that the forbiddenness of suprafacial 2 + 2 cycloadditions according to Woodward–Hoffmann rules may be removed where the two cycloaddends strongly differ in polarity. Although the specific case of phenyl-substituted acetylenes was not discussed,[6] we consider it as an obvious extension of the case of the corresponding ethylenes. At the present stage of our research, however, a decision between this hypothesis and the ion pair scheme cannot be reached.

The interpretation of our stereochemical data in terms of relative effects of the β substituents was mainly based on steric grounds rather than electronic. Polar effects may also be important in the delicate balance between syn and anti nucleophilic attack.[10] Our results do not provide information on this point, even though the stereochemistry of the addition of *tert*-butyl chloride (**3**) to 1-phenylpropyne (**4**) and to 1-phenylbut-1-yne (**5**), i.e., of systems having β substituents of similar polarity but very different in bulk, indicates that a major role is played by steric effects. Both steric and electronic effects of the β groups might also determine deviations from the linearity in the vinyl cation intermediates. Since in α-phenyl-substituted vinyl cations such deviations, if any, are undoubtedly small,[3,4,14] a very little influence on the stereochemistry of the addition is expected.

Experimental Section

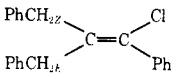
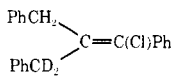
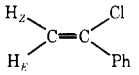
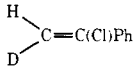
Materials. Solvents and starting materials were purified following

Table IV. ^{1}H NMR Data for Vinyl Chlorides 8–9 and 12–15 (Eq 1)

Compd	Chemical shifts τ (coupling constants in Hz)							
	HC=C	CH_3C=C	CH_3CH_2	CH_3CH_2	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_3C$	Aromatic
(*E*)-8		7.98, s					9.08, s	2.82, s
(*E*)-9			8.78, t (J = 8)	7.54, q[a] (J = 8)			9.10, s	2.85, s[b]
(*Z*)-9			~9, t[c]	8.01, q[a] (J = 8)			8.60, s	2.85, s[b]
(*E*)-12[d]	4.05, q[a] (J = 7)	8.35, d (J = 7)						2.72, s
(*Z*)-12[d]	3.95, q[a] (J = 6)	8.12, d (J = 6)						2.40–2.90, m
(*E*)-13	4.10, t (J = 7.5)		9.05, t (J = 8)	7.93[e] (J = ~8)				2.71, s
(*Z*)-13	3.92, t (J = 7)		8.89, t (J = 8)	7.60[e] (J = ~8)				2.40–2.90, m
(*E*)-14	4.27, d (J = 10.8)				9.03, d (J = 6.6)	7.10–7.90, m[b]		2.70, s[b]
(*Z*)-14	4.12, d (J = 9.3)				8.95, d (J = 6.6)	7.10–7.90, m[b]		2.70, s[b]
(*E*)-15[f]	4.05, s						9.12, s	2.78, s

[a] Quartet. [b] Mixture of the two isomers. [c] The position of this signal could not be determined exactly, since it was submerged by the intense signal of the *tert*-butyl protons of the (*E*) isomer. [d] See ref 12. [e] Approximate quintet. [f] See ref 17.

Table V. ^{1}H NMR Data for Labeled and Related Compounds

Compd	Structure	Type of protons	Chemical shift, τ (J in Hz)	Rel area
18		CH_{2Z}	6.35, s	2
		CH_{2E}	6.72, s	2
		Aromatic	2.35–3.25, m	15
(*E*)-, (*Z*)-20		CH_{2Z}	6.35, s	1
		CH_{2E}	6.72, s	1
		Aromatic	2.35–3.25, m	15
. . .[a]		H_Z	4.58, d (J = 1.8)	1
		H_E	4.39, d (J = 1.8)	1
		Aromatic	2.40–3.00, m	5
(*E*)-, (*Z*)-23[b]		H_Z	4.59, s	0.7
		H_E	4.40, s	0.3
		Aromatic	2.40–3.00, m	5

[a] See ref 17. Owing to a typographical error, the chemical shift of the low-field proton (H_E) was incorrectly reported in this paper. [b] See J. R. Blackborow, *J. Chem. Soc., Perkin Trans. 2*, 1989 (1973). The configurational assignment reported in this paper should be reversed, according to Rappoport and Apeloig (ref 14).

standard procedures. *tert*-Butyl chloride, benzyl chloride, 1-phenylpropyne, and 1-phenylbut-1-yne were commercially available products. 3-Methyl-1-phenylbutyne,[22] 3,3-dimethyl-1-phenylbutyne,[22] 1,3-diphenylpropyne,[23] and 2-benzyl-1,3-diphenylpropan-1-one[24] were prepared by literature methods. Benzyl-α,α-d_2 chloride was prepared by chlorination of benzyl-α,α-d_2 alcohol with thionyl chloride in ether following the procedure described by Clovis and Hammond.[25] Phenylacetylene-*d* was prepared by hydrolysis of phenylethynylmagnesium bromide with sulfuric acid-d_2. The isotopic purity of all the deuterated compounds, assayed by ir and ^{1}H NMR, was found to exceed 98%. In the column chromatographies (silica gel slurries) light petroleum, bp 40–70 °C, was used.

Gas Chromatography. Preparative GLC separations were performed on an Aerograph Autoprep Model 705 gas chromatograph equipped with a 2 m × 10 mm column of 30% Carbowax 20 M on Chromosorb P (60–80 mesh) at 190°, with a nitrogen flow of 240 ml min^{-1}.

^{1}H NMR Analyses. Spectra were recorded in CCl_4 solution with Me_4Si as internal standard on a Perkin-Elmer Model R12 spectrometer operating at 60 MHz, and in some cases on a Bruker Model HFX high-resolution spectrometer operating at 90 MHz. The NMR data for all the reaction products are collected in Tables IV and V.

Addition of *tert*-Butyl Chloride (3) to 1-Phenylpropyne (4). To a suspension of anhydrous zinc chloride (0.58 g, 4.3 mmol) in a solution of 1-phenylpropyne (**4**) (5.0 g, 43 mmol) in anhydrous dichloromethane (30 ml) a solution of *tert*-butyl chloride (**3**) (3.98 g, 43 mmol) in the same solvent (30 ml) was added dropwise, with stirring, at room temperature. The mixture was then refluxed for 24 h. After cooling, the catalyst was filtered off and the solvent evaporated to give a red-dish-brown residue, which was column chromatographed. Elution with light petroleum gave first a mixture of (*E*)-1-chloro-1-phenyl-2,3,3-trimethylbutene (**8**) and of (*E*)- and (*Z*)-1-chloro-1-phenylprop-1-enes[12] (**12**) and then some unchanged **4**. The separation of the three reaction products (pale yellow liquids) was performed by GLC (retention times: (*E*)-**12**, 15 min; (*Z*)-**12**, 20 min; (*E*)-**8**, 36 min).

Anal. for (*E*)-**8**. Calcd for $C_{13}H_{17}Cl$: C, 74.80; H, 8.21; Cl, 16.98. Found: C, 74.60; H, 7.99; Cl, 16.87.

Addition of *tert*-Butyl Chloride (3) to 1-Phenylbut-1-yne (5). The reaction was carried out as described for the addition of **3** to **4**. The column chromatography of the reaction residue, with light petroleum as eluent, afforded a mixture of (*E*)- and (*Z*)-1-chloro-2-ethyl-1-phenyl-3,3-dimethylbut-1-enes (**9**) and of (*E*)- and (*Z*)-1-chloro-1-phenylbut-1-enes (**13**) and some unreacted **5**. The separation of these products (pale yellow liquids) was performed by GLC (retention times: (*E*)-**13**, 18 min; (*Z*)-**13**, 26 min; mixture of (*E*)- and (*Z*)-**9**, ca. 40 min).

Anal. for (*E*)-, (*Z*)-**9**. Calcd for $C_{14}H_{19}Cl$: C, 75.49; H, 8.60; Cl, 15.91. Found: C, 75.54; H, 8.70; Cl, 15.81.

Anal. for (*E*)-**13**. Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65; Cl, 21.27. Found: C, 71.78; H, 6.45; Cl, 21.30.

Anal. for (*Z*)-**13**. Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65; Cl, 21.27. Found: C, 72.22; H, 6.70; Cl, 21.06.

Addition of *tert*-Butyl Chloride (3) to 3-Methyl-1-phenylbutyne (6). The reaction was carried out as described for the addition of **3** to **4**. The column chromatography of the reaction residue, with light petroleum as eluent, afforded a mixture of (*E*)- and (*Z*)-1-chloro-3-methyl-1-phenylbut-1-enes (**14**) and some unreacted **6**. Separation of the two isomers by GLC was not satisfactorily achieved. They were

therefore purified by distillation under vacuum, bp 90–95 °C (2×10^{-2} mm) (pale yellow liquid).

Anal. Calcd for $C_{11}H_{13}Cl$: C, 73.12; H, 7.25; Cl, 19.62. Found: C, 73.23; H, 7.09; Cl, 19.44.

In the NMR spectrum of the mixture of **14** eluted from the column chromatography, signals of very low intensity at τ 9.05, 9.10, and 9.13 were detected, which did not belong to compounds **14** and could indicate the presence of very small amounts of 1-chloro-3,3-dimethyl-1-phenyl-2-isopropylbut-1-enes **10**, i.e., the products of addition of **3** to **6**. An attempt to obtain these compounds in larger amounts by carrying out the reaction with a fivefold excess of **3** has failed.

Addition of *tert*-Butyl Chloride (3) to 3,3-Dimethyl-1-phenylbutyne (7). In this reaction, carried out as described above, no evidence for the formation of 2-*tert*-butyl-1-chloro-3,3-dimethyl-1-phenylbutene (**11**) was obtained. The reaction afforded a high yield of (*E*)-1-chloro-3,3-dimethyl-1-phenylbut-1-ene (**15**), which was identified by comparison with a sample prepared as previously described.[17]

Addition of Hydrogen Chloride to Acetylenes 4–7. To a solution of the appropriate acetylenic compound (20 mmol) in dichloromethane (30 ml) were added anhydrous zinc chloride (0.30 g, 2.2 mmol) and a saturated solution of dry hydrogen chloride (22 mmol) in dichloromethane (ca. 40 ml). The flask was tightly stoppered and the mixture was heated, with occasional shaking, at 40° for 24 h. The mixture was cooled, the catalyst was filtered off, the solvent and the excess hydrogen chloride were removed under reduced pressure, and the residue was column chromatographed. Elution with light petroleum afforded high yields (80–90%) of compounds **12–15**, which were identical with the corresponding products obtained in the additions of *tert*-butyl chloride (**3**) to acetylenes **4–7** (Table I).

Addition of Benzyl Chloride (16) and Benzyl-α,α-d_2 Chloride (19) to 1,3-Diphenylpropyne (17). A solution of benzyl chloride (**16**) (1.26 g, 10 mmol) in 10 ml of anhydrous 1,2-dichloroethane was added dropwise at room temperature to a suspension of zinc chloride (0.14 g, 1 mmol) in a solution of 1,3-diphenylpropyne (**17**) (5.77 g, 30 mmol) in the same solvent (30 ml). The mixture was then refluxed for 11 days. After cooling, the catalyst was filtered off and the solvent evaporated to give a brown residue, which was column chromatographed. Elution with light petroleum–benzene 8:1 gave 1.62 g (52% yield) of 2-benzyl-1-chloro-1,3-diphenylprop-1-ene (**18**), which was recrystallized from absolute ethanol, mp 92–93 °C, and identified by comparison with a sample synthesized independently (vide infra).

Anal. Calcd for $C_{22}H_{19}Cl$: C, 82.87; H, 6.00; Cl, 11.12. Found: C, 82.85; H, 5.93; Cl, 11.17.

The same conditions were used for the addition of deuterated benzyl chloride (**19**) to **17**, which afforded a 54% yield of a 1:1 mixture of (*E*)- and (*Z*)-2-benzyl-1-chloro-1,3-diphenylprop-1-ene-*3,3*-d_2 (**20**).

Synthesis of 2-Benzyl-1-chloro-1,3-diphenylprop-1-ene (18). A solution of 2-benzyl-1,3-diphenylpropan-1-one (**21**) (15.02 g, 50 mmol) in anhydrous benzene (120 ml) was slowly added to phosphorus pentachloride (10.41 g, 50 mmol) at room temperature, and the mixture was heated on a steam bath with stirring for 6 h. The $POCl_3$ formed and most of the solvent were then distilled off under reduced pressure. A large excess of triethylamine (20.24 g, 0.2 mol) was added, and the mixture was refluxed for 3 h. The hot mixture was poured into concentrated HCl containing cracked ice, benzene was added, and the organic layer was separated, washed with water, and dried ($CaCl_2$). Evaporation of the solvent gave a brown residue, which was column chromatographed. Elution with light petroleum–benzene 8:1 gave 2-benzyl-1-chloro-1,3-diphenylprop-1-ene (**18**) (12.1 g, 76%), which was recrystallized from absolute ethanol, mp 92–93 °C.

Anal. Calcd for $C_{22}H_{19}Cl$: C, 82.87; H, 6.00; Cl, 11.12. Found: C, 83.06; H, 6.16; Cl, 11.19.

Addition of Hydrogen Chloride to Phenylacetylene-*d* (22). This reaction was carried out as described for the addition of hydrogen chloride to acetylenes **4–7**, using an HCl–**22** molar ratio of 1:2 (15 h). Column chromatography of the reaction residue, with light petroleum as eluent, afforded a mixture of (*E*)- and (*Z*)-α-chlorostyrene-β-*d* (**23**) (85% yield, calculated on HCl) and of unchanged acetylene **22**, which were separated by GLC (retention times: **22**, 5 min; (*E*)-, (*Z*)-**23**, 10 min).

Examination of the unreacted **22** by ir and ^{1}H NMR showed that no hydrogen–deuterium exchange had occurred. The deuterated α-chlorostyrenes (**23**) were identified by comparison with an authentic sample of α-chlorostyrene prepared as previously reported.[17]

Acknowledgment. We wish to thank Mr. Roberto Salmaso for technical assistance in recording the high-resolution ^{1}H NMR spectra.

Appendix. Stereochemical Assignments.

The assignment of configuration to all the compounds prepared in this work was made by ^{1}H NMR spectroscopy (see Tables IV and V). For the compounds having a vinyl proton the assignment was based on the deshielding effect caused by the phenyl group on a β-*cis*-vinyl proton relative to a trans proton, a feature which is characteristic of styrene derivatives.[26,27] Thus, we assigned the *Z* configuration to the isomer having the vinyl proton signal at lowest field. Characteristic of these systems is also the shielding effect caused by the phenyl group on β- and γ-*cis*-methyl, methylene, and methine protons relative to the trans protons.[27,28] Thus we assigned the *E* configuration to the compounds having the signals relative to these protons at highest field. This behavior also permitted the assignment of configurations to the compounds having no vinyl protons, and in particular to compound (*E*)-**8**, for which the comparison between the *E* and *Z* isomers was not possible. The *E* configuration of compound **8** was therefore assigned on the basis of the similarity of the chemical shift of the *tert*-butyl protons with that of compounds (*E*)-**9** and (*E*)-**15**.[17]

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(21) Throughout the paper, and in particular in Schemes I and II, the nucleophilic species has been formulated for simplicity as a chloride ion. On account of the catalysis by $ZnCl_2$ it should more correctly be considered as a complex, such as $ZnCl_3^-$.
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