Electrophilic Additions to Acetylenes. Part VI.[1] Addition of t-Butyl Chloride and Benzyl Chloride to Alkynes

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The zinc chloride catalysed addition of t-butyl and benzyl chloride to some mono- and di-substituted alkynes has been studied. The reactions afforded the 1 : 1 addition products, with predominant formation of the isomers of *E*-configuration. This suggested the intervention of a stepwise electrophilic addition mechanism, with the formation of α-alkyl-substituted vinyl cations and the subsequent preferential attack of the nucleophilic Cl^- from the less hindered side of the intermediates. However, some discrepancy in the *E* : *Z* ratios of the addition products and comparison with analogous stereochemical data obtained in the addition of acids to the same substrates suggested that other mechanisms could be involved, though to a small extent. Discussion of the competition among these mechanisms is given.

IN previous work we studied the stereochemistry of the addition of t-butyl and phenylalkyl chlorides [2,3] and bromides [4] to phenyl-substituted acetylenes in the presence of Lewis acids. The results were in agreement with a stepwise electrophilic addition mechanism, implying the formation of vinyl cation intermediates and the subsequent attack by the nucleophilic halide ion from the less hindered side. In a subsequent paper [1] we demonstrated that the intermediates formed in the carbonium ion additions were ' free ' vinyl cations, in the sense that the direction of attack of the nucleophile, and hence the stereochemistry of addition, was independent of the electrophilic species involved in the reaction. This was attributed mainly to the strong resonance stabilisation of the cationic centre by the α-phenyl ring, which rendered the vinyl cations involved in our reactions relatively stable and hence highly selective. We have now extended our study to the addition of alkyl chlorides to alkyl-substituted acetylenes, in order to test the stereochemical behaviour of vinyl cation intermediates stabilised only by inductive, or at most hyperconjugative, effects.

Very few data on this matter are available in the literature. There are reports on the addition of t-butyl

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[1] Part V, F. Marcuzzi and G. Melloni, *J. Amer. Chem. Soc.*, 1976, **98**, 3295.

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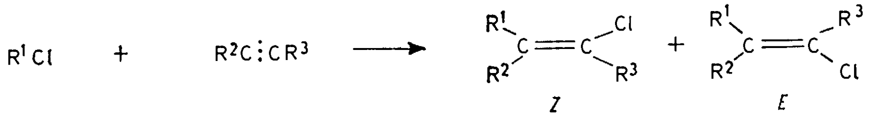
[3] R. Maroni, G. Melloni, and G. Modena, *J.C.S. Perkin I*, 1974, 353.

[4] F. Marcuzzi and G. Melloni, *Gazzetta*, 1975, **105**, 495.

chloride to propyne and hex-1-yne in the presence of aluminium chloride or stannic chloride,[5,6] but no stereochemical data were given. The addition of t-butyl chloride to acetylene in n-pentane catalysed by aluminium chloride was shown to afford only the product of *anti*-addition.[7] The intermediacy of vinyl cations was suggested for the addition of 1-adamantyl cation to acetylene, pent-1-yne, and oct-1-yne in sulphuric acid.[8] We report here the results obtained for the zinc chloride-catalysed addition of t-butyl chloride to some mono- and di-substituted alkynes and of benzyl chloride to propyne and but-2-yne.

RESULTS

The conditions used in the addition reactions investigated were identical with those previously described,[1-3] *i.e.*, dichloromethane as solvent at 40° and in the presence of a small amount of the catalyst, insoluble in the solvent used. Preliminary experiments indicated no variation of the *E* : *Z* ratios in the addition products with the reagent ratio, in accord with the addition of alkyl chlorides investigated previously. Most of the reactions were carried out with an excess of the alkyne.[4] Yields in the range 45—60% of 1 : 1 addition products of the two reagents were obtained, following the general equation (1).



(1)

(I) $R^1 = Bu^t$
(II) $R^1 = PhCH_2$

(III) $R^2 = H, R^3 = Me$
(IV) $R^2 = H, R^3 = Et$
(V) $R^2 = H, R^3 = Bu^n$
(VI) $R^2 = H, R^3 = Bu^t$
(VII) $R^2 = R^3 = Me$
(VIII) $R^2 = R^3 = Et$

(IX) $R^1 = Bu^t, R^2 = H, R^3 = Me$
(X) $R^1 = Bu^t, R^2 = H, R^3 = Et$
(XI) $R^1 = Bu^t, R^2 = H, R^3 = Bu^n$
(XII) $R^1 = R^3 = Bu^t, R^2 = H$
(XIII) $R^1 = Bu^t, R^2 = R^3 = Me$
(XIV) $R^1 = Bu^t, R^2 = R^3 = Et$
(XV) $R^1 = PhCH_2, R^2 = H, R^3 = Me$
(XVI) $R^1 = PhCH_2, R^2 = R^3 = Me$

In the case of the addition to alk-1-ynes the products were always formed in accord with Markownikov rule. Both for the addition of t-butyl chloride and of benzyl chloride no reaction was observed in the absence of catalyst, even after prolonged reaction times. In the case of the addition of t-butyl chloride (I) some dehydrochlorination of (I) in the presence of the Lewis acid occurred. This lowered the yields of products and caused the formation of polymeric substances related to isobutene. Correspondingly, products of addition of hydrogen chloride to the alkyne were formed. This secondary reaction was not studied in detail except in the case of the addition of (I) to hex-3-yne (VIII). No isomerisation of the addition products, of both *E*- and *Z*-configuration, in the reaction conditions was observed.

Addition of t-Butyl Chloride to Alk-1-ynes.—The addition of t-butyl chloride (I) to propyne (III), but-1-yne (IV), and hex-1-yne (V) was studied. Both *E*- and *Z*-isomers of the addition products, with the former predominant, were formed. The results are reported in Table 1.

TABLE 1

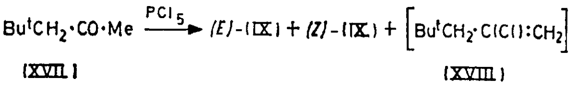
Addition of alkyl chlorides (I) and (II) to alkynes (III)—(V), (VII), and (VIII)

Alkyl chloride	Alkyne	Reagent ratio [a]	Reaction time (h)	Products [Yield (%)]	Products Isomer ratio [b] *E* : *Z*
(I)	(III)	1 : 3	24	(IX) [45]	80 : 20
(I)	(IV)	1 : 3	24	(X) [47]	95 : 5
(I)	(V)	1 : 2	36	(XI) [50]	90 : 10
(I)	(VII)	1 : 1.1	20	(XIII) [45]	100 : 0
(I)	(VIII)	1 : 2	70	(XIV) [60] [c]	90 : 10
(II)	(III)	1 : 5	140 [d]	(XV) [45]	65 : 35
(II)	(VII)	1 : 1	24 [d]	(XVI) [30]	75 : 25

[a] Ratio alkyl chloride : alkyne. [b] Determined by ^1H n.m.r. on the crude reaction mixtures. Estimated error $\leqslant 5\%$. [c] Products of addition of hydrogen chloride to (VIII) were also isolated (see text); the isomer ratio of these products is reported in Table 3. [d] At 60°.

The addition of (I) to 3,3-dimethylbut-1-yne (VI) was also carried out, but no evidence for the formation of the addition products (XII) was obtained, even by carrying out the reactions under more forcing conditions [96 h with a (I) : (VI) ratio of 1 : 5 and, respectively, 5 : 1].[6]

The structure of the addition products was determined on the basis of elemental analysis and spectral data, and in one typical case (addition to propyne) also by comparison with authentic samples synthesised independently. The synthesis of (*E*)- and (*Z*)-(IX) was performed by reaction of 4,4-dimethylpentan-2-one (XVII) with phosphorus pentachloride [equation (2)].



$$\underset{(XVII)}{Bu^tCH_2\cdot CO\cdot Me} \xrightarrow{PCl_5} (E)\text{-(IX)} + (Z)\text{-(IX)} + \underset{(XVIII)}{\left[Bu^tCH_2\cdot CCl{:}CH_2\right]} \qquad (2)$$

The configurations of the three pairs of isomers (IX)—(XI) were assigned by ^1H n.m.r. spectroscopy and were based on the relative chemical shifts of the vinylic protons in the *E*- and *Z*-isomers (see Table 2). It has been shown [9,10] that in

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[5] L. Schmerling, U.S.P. 2,626,962/1953 (*Chem. Abs.*, 1954, **48**, 1407f).

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simple alkyl-substituted vinyl chlorides a small but definite differential shielding between *cis*- and *trans*-vinylic protons is caused by the β-chloro-substituent, and in particular that the *cis*-proton is more deshielded than the *trans*. This observation has been used, for example, to assign the configuration to the isomeric 2-chlorobut-2-enes and 3-chloropent-2-enes.[11] It may be seen in Table 2 that the relative chemical shifts not only of the vinylic but also of the methyl and methylene protons of the *E*- and *Z*-isomers of compounds (IX)—(XI) are strictly in accord with those of such compounds.

TABLE 2

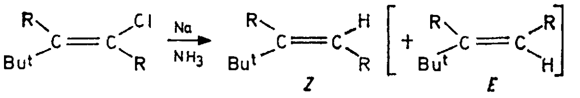
^{1}H N.m.r. data (τ; J/Hz) for the addition products and related compounds

Compound	
(*E*)-(IX)	4.40 (1 H, q, *J* 1.2, C=CH), 7.85 (3 H, d, *J* 1.2, C=CMe), 8.87 (9 H, s, Bu^t)
(*Z*)-(IX)	4.58 (1 H, q, *J* 1.0, C=CH), 7.96 (3 H, d, *J* 1.0, C=Me), 8.83 (9 H, s, Bu^t)
(*E*)-(X)	4.43br (1 H, s, C=CH), 7.57br (2 H, q, *J* 8.0, CH_2CH_3), 8.86 (3 H, t, *J* 8.0, CH_2CH_3), 8.88 (9 H, s, Bu^t)
(*Z*)-(X)	4.58br (1 H, s, C=CH), 8.85 (9 H, s, Bu^t) [a]
(*E*)-(XI)	4.42br (1 H, s, C=CH), 7.59br (2 H, t, *J ca.* 7, $C{=}CCH_2$), 8.30—9.15 (7 H, m, $CH_2CH_2CH_3$), 8.87 (9 H, s, Bu^t)
(*Z*)-(XI)	4.55br (1 H, s, C=CH), 7.75—9.15 (9 H, m, Bu^n), 8.85 (9 H, s, Bu^t)
(*E*)-(XIII)	7.73 (3 H, q, *J* 1.5, C=CMe α to Cl), 8.15 (3 H, q, *J* 1.5, C=CMe β to Cl), 8.82 (9 H, s, Bu^t)
(*E*)-(XIV)	7.46 (2 H, q, *J ca.* 7, $C{=}CCH_2$ α to Cl), 7.68 (2 H, q, *J ca.* 7, $C{=}CCH_2$ β to Cl), 8.81 (9 H, s, Bu^t), 8.88 (3 H, t, *J ca.* 7, CH_2CH_3 α to Cl [b]), 9.00 (3 H, t, *J ca.* 7, CH_2CH_3 β to Cl [b])
(*Z*)-(XIV)	8.99 (s, Bu^t) [c]
(*E*)-(XV) [d]	2.70—3.00 (5 H, m, Ph),[e] 4.54br (1 H, t, *J* 7.5, C=CH), 6.60br (2 H, d, *J* 7.5, $PhCH_2$), 8.00 [f] (3 H, m, C=CMe)
(*Z*)-(XV) [d]	2.70—3.00 (5 H, m, Ph),[e] 4.29br (1 H, t, *J* 8.0, C=CH), 6.86br (2 H, d, *J* 8.0, $PhCH_2$), 8.00 [f] (3 H, m, C=CMe)
(*E*)-(XVI)	2.70—3.00 (5 H, m, Ph),[e] 6.43br (2 H, s, $PhCH_2$), 7.89br (3 H, s, C=CMe α to Cl), 8.39br (3 H, s, C=CMe β to Cl)
(*Z*)-(XVI)	2.70—3.00 (5 H, m, Ph),[e] 6.62br (2 H, s, $PhCH_2$), 7.86br (3 H, s, C=CMe α to Cl), 8.26br (3 H, s, C=CMe β to Cl)
(*Z*)-(XIX)	4.82 (1 H, qq, *J* 6.5 and 2.0, C=CH), 8.30 (3 H, d, *J* 6.5, C=CMe α to H), 8.34 (3 H, d, *J* 2.0, C=CMe β to H), 8.90 (9 H, s, Bu^t)
(*E*)-(XIX)	4.70 (1 H, qq, *J* 6.0 and 1.8, C=CH), 8.42 (3 H, d, *J* 6.0, C=CMe α to H), 8.47 (3 H, d, *J* 1.8, C=CMe β to H), 8.98 (9 H, s, Bu^t)
(*Z*)-(XX)	5.04 (1 H, t, *J* 7.0, C=CH), 7.85 (2 H, q, *J* 7.0, $C{=}CCH_2$ β to H), 7.91br (2 H, approx. quintet, *J ca.* 7, $C{=}CCH_2$ α to H), 8.85 (9 H, s, Bu^t), 9.00 (3 H, t, *J* 7.0, CH_2CH_3 β to H [b]), 9.04 (3 H, t, *J* 7.0, CH_2CH_3 α to H [b])
(*E*)-(XX)	4.91br (1 H, t, *J ca.* 7, C=CH),[a] 9.03 (9 H, s, Bu^t) [a]

[a] Only these shifts could be unambiguously assigned. [b] Uncertain assignment. [c] Only this signal was detected. [d] See ref. 15. [e] Mixture of the two isomers. [f] Coincident signals.

Addition of t-Butyl Chloride to Disubstituted Alkynes.—The addition of t-butyl chloride (I) to but-2-yne (VII) and hex-3-yne (VIII) was studied. In the case of (VII) only one addition product was formed, namely (*E*)-2-chloro-3,4,4-trimethylpent-2-ene (XIII), while in the case of (VIII) both (*E*)- and (*Z*)-4-chloro-2,2-dimethyl-3-ethylhex-3-ene (XIV) were isolated, with the *Z*-isomer formed in small amount. The results of these reactions are reported in Table 1.

Structures were assigned on the basis of elemental analysis and spectral data. In addition, the structure of (*E*)-(XIII) and (*E*)-(XIV) was confirmed by transformation into the corresponding alkenes of *Z*-configuration (XIX) and (XX) by reaction with sodium in liquid ammonia, following a method described in the literature [12] [equation (3)].



(3)

(*E*)-(XIII) R = Me
(*E*)-(XIV) R = Et

(XIX) R = Me
(XX) R = Et

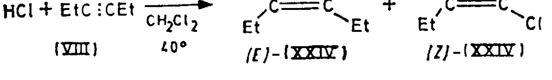
This protiodechlorination was reported to proceed with at least 96% retention of configuration in the synthesis of normal *cis*-pentenes, -hexenes, and -octenes from the corresponding chloro-alkenes of *E*-configuration.[12] Our reactions were somewhat less stereoselective, but still to a satisfactory extent (80–85% retention).

Compounds (XIX) were identified by comparison with an authentic sample of (*E*)-3,4,4-trimethylpent-2-ene, synthesised by a known procedure,[13] *i.e.*, by dehydration of 2,2,3-trimethylpentan-3-ol (XXII), prepared by the reaction of ethylmagnesium bromide with 3,3-dimethylbutan-3-one (pinacolone) (XXI) [equation (4)].

$$\underset{\text{(XXI)}}{Bu^tCO{\cdot}Me} + EtMgBr \longrightarrow \underset{\text{(XXII)}}{Bu^tC(OH)(Me)Et} \longrightarrow (E)\text{-(XIX)} + \underset{\text{(XXIII)}}{Bu^tC(Et){:}CH_2} \qquad (4)$$

The *E*-configuration was assigned to the addition product (XIII) by comparison with the ^{1}H n.m.r. spectra of both isomers (XIX), and also by comparing the ^{13}C n.m.r. spectrum of (*E*)-(XIX) with that recently reported.[14] The comparison between the ^{1}H n.m.r. spectra of isomers (XIX) ascertained that the *Z*-isomer had the signal corresponding to the vinylic proton at higher field and that corresponding to the t-butyl protons at lower field than those of the *E*-isomer. By analogy the configurations of the isomeric alkenes (XX), and therefore of the addition products (XIV), could also be determined.

In the case of the addition of t-butyl chloride (I) to hex-3-yne (VIII) besides the 1 : 1 addition products (XIV) a fraction containing products of addition of hydrogen chloride to (VIII), *i.e.* the 3-chlorohex-3-enes (XXIV), was isolated from the mixture. The *E* : *Z* ratio (40 : 60) was determined both by g.l.c. and by ^{1}H n.m.r. spectroscopy and was identical to that obtained independently by direct addition of hydrogen chloride to hex-3-yne (VIII) [equation (5)].



(5)

(VIII) (*E*)-(XXIV) (*Z*)-(XXIV)

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[14] J. W. de Haan and L. J. M. van de Ven, *Org. Magnetic Resonance*, 1973, **5**, 147.

Addition of Benzyl Chloride to Alkynes.—This addition was studied for two typical alkynes, propyne (III) and but-2-yne (VII). The reactions were much slower than with t-butyl chloride, particularly in the case of (III); consequently, they were carried out at higher temperature in sealed tubes. Under these conditions the yields of addition products (XV) and (XVI) were somewhat improved but, correspondingly, some polymerisation of benzyl chloride (II) occurred, which made purification more difficult. The results are reported in Table 1.

The structure and configuration of (*E*)- and (*Z*)-2-chloro-4-phenylbut-2-enes (XV) were assigned by comparison of their ^1H n.m.r. spectra with those of authentic materials.[15] This also permitted the assignment of the configurations to compounds (XVI), which was done by comparison of their ^1H n.m.r. spectra with those of compounds (XV) and was based on the relative chemical shift of the benzylic protons in the two isomers, the signal for the isomer of *E*-configuration (XV) being at higher field than that for the *Z*-isomer.

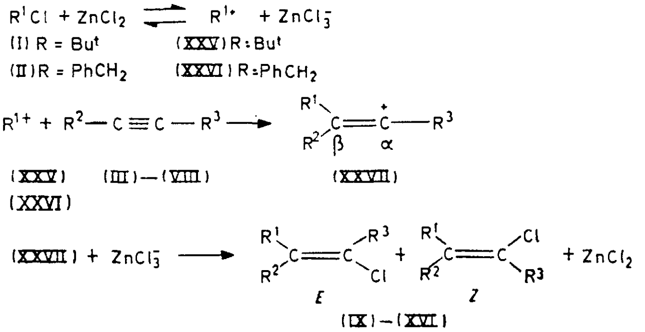
DISCUSSION

The stereochemical data reported in Table 1 clearly show the preferred formation of *E*-adducts, *i.e.* of the adducts with the chlorine and the t-butyl or benzyl group *trans*. This trend is in qualitative agreement with the results previously obtained for the addition of the alkyl chlorides (I) and (II) to phenyl-substituted acetylenes,[1-3] where vinylic adducts of *E*-configuration were also preferentially (in many cases exclusively) formed. This analogy, the Friedel–Crafts-like conditions of reaction, and the observed exclusive formation of the Markownikov adducts in the case of the additions to alk-1-ynes all strongly indicate a stepwise electrophilic addition mechanism, which may be rationalised in terms of formation of vinyl cation intermediates (XXVII) by addition of the stable t-butyl or benzyl carbonium ions (XXV) and (XXVI) to the triple bond of the alkynes, followed by the attack of the chloride ion, complexed by the catalyst, to the positive centre of (XXVII) to give the final products of 1 : 1 addition (Scheme).

The stereochemical course of these additions may thus be rationalised as preferential attack by the nucleophile from the less hindered side of vinyl cations (XXVII). In the cases investigated in this work this corresponds to attack from the side bearing the R^2 group, which is in every case smaller than R^1. In the intermediate (XXVII) R^2 is hydrogen, methyl, or ethyl while R^1 is t-butyl or benzyl; with such β-groups, which are of similar polarity but very different in bulk, steric effects are expected to play a major role in influencing the direction of attack of the nucleophile.

Viewed as a whole, the results obtained may be considered as further evidence of the importance of the relative effects of β-groups in determining the stereochemistry of the reactions occurring *via* vinyl cations, by analogy with the behaviour of the α-phenyl-substituted substrates.[1-4]

A more careful examination of the results, however, indicates that this analogy is not as close as it may seem. In general, the additions to alkynes are less stereoselective: for example, the addition of t-butyl chloride (I) and benzyl chloride (II) to propyne (III) gave *E* : *Z* ratios of adducts of 80 : 20 and 65 : 35 respectively, whereas those to phenylacetylene afforded 100 and 80% respectively of the adduct of *E*-configuration.[2] Furthermore, the stereoselectivity of the addition to disubstituted alkynes (VII) and (VIII) is higher than for alk-1-ynes (III)—(V), whereas on the basis of the relative size of the β-groups in the corresponding intermediates (XXVII) the opposite should be expected. This may be seen by comparing the additions both of (I) and (II) to propyne (III) and but-2-yne (VII), and also by comparing the addition of (I) to but-1-yne (IV) [and to hex-1-yne (V)] with that to hex-3-yne (VII), which gave similar results, whereas the latter should have been less stereoselective.



SCHEME

These discrepancies appear more relevant from a mechanistic point of view if compared with the complex stereochemical trend for the additions of acids to the same, or very similar, substrates.[16-18] For comparison purposes, some selected examples of additions of acids to alkynes are reported in Table 3, together with our data on the addition of hydrogen chloride to hex-3-yne (VIII) in dichloromethane [equation (5)] and in acetic acid.[19]

Examination of the data in Table 3 shows that at least two other mechanisms are involved in these reactions, along with addition *via* a ' free ' [1,20,21] vinyl cation. Participation of a *syn*-addition mechanism [1,22] can be invoked for the additions to alk-1-ynes, whereas the results for the additions to disubstituted alkynes have been interpreted in terms of intervention of *anti*-addition mechanisms, either termolecular [23,24] or *via* a π-complex.[20] The interpretation of the results is further complicated

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TABLE 3

Stereochemistry of the addition of acids to alkynes

Alkyne	Acid	Solvent [Temp. (°C)]	Formal addition syn (%)	Formal addition anti (%)	Ref.
MeC⋮CH [a]	FSO_3D	SO_2ClF [−120]	80	20	20
Bu^{n}C⋮CD	HCl	CH_3CO_2H [50] [b]	60	40	23
Bu^{n}C⋮CH	CF_3SO_3D	Pentane [−20]	*ca.* 74	*ca.* 26	21
Bu^{n}C⋮CH [a]	FSO_3D	SO_2ClF [−120]	80	20	20
MeC⋮CMe	CF_3CO_2H	CF_3CO_2H [50]	19.5	80.5	21
MeC⋮CMe	CF_3SO_3H	Pentane [−30]	35	65	21
MeC⋮CMe	FSO_3H	SO_2ClF [−120]	*ca.* 13	*ca.* 87	20
EtC⋮CEt	HCl	CH_3CO_2H [60] [c]	<2	>98	24
EtC⋮CEt	HCl	CH_3CO_2H [40] [d]	15	85	19
EtC⋮CEt	HCl	CH_2Cl_2 [40] [d]	40	60	This work
EtC⋮CEt	CF_3CO_2H	CF_3CO_2H [60]	*ca.* 50	*ca.* 50	21, *f*
EtC⋮CEt	FSO_3H	SO_2ClF [−120] [e]	*ca.* 51	*ca.* 49	20
Pr^{n}C⋮CPr^n	CF_3CO_2H	CF_3CO_2H [75.4]	56.4	43.6	21

[a] The same *syn* : *anti*-ratio was found for EtC⋮CH. [b] In the presence of Me_4N^+ Cl^- the *syn* : *anti*-ratio was 10 : 90. [c] In the presence of Me_4N^+ Cl^- exclusive *anti*-addition was observed. [d] In the presence of $ZnCl_2$. [e] In the presence of pyridinium fluorosulphate the *syn* : *anti*-ratio was 40 : 60 (at −78°). [f] P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, 1963, **85**, 2865; 1966, **88**, 4990.

by the possibility that the vinyl cation intermediates involved deviate from linearity,[21] thus eluding in some way the ' rule ' of the relative effects of the β-substituents, which is followed in the case of linear intermediates.

TABLE 4

Properties of the products of the addition reactions

Compound	G.l.c. data: Column [a] [Temp. (°C)]	G.l.c. data: R_t (min)	Found (%) C	Found (%) H	Found (%) Cl	Formula	Required (%) C	Required (%) H	Required (%) Cl
(*E*)-(IX)	A [100] [b]	9.5	63.05	9.8	26.35	$C_7H_{13}Cl$ [d]	63.4	9.85	26.75
(*Z*)-(IX)	A [100] [b]	8				$C_7H_{13}Cl$ [d]			
(*E*)-(X)	C [135] [b]	17	65.9	10.6	23.95	$C_8H_{15}Cl$	65.5	10.3	24.2
(*Z*)-(X)	C [135] [b]	14				$C_8H_{15}Cl$			
(*E*)-(XI)	C [160] [b]	19	68.8	11.2	20.05	$C_{10}H_{19}Cl$ [e]	68.75	10.95	20.3
(*Z*)-(XI)	C [160] [b]	17				$C_{10}H_{19}Cl$ [e]			
(*E*)-(XIII)	A [140] [b]	9	65.5	10.25	24.15	$C_8H_{15}Cl$	65.5	10.3	24.2
(*E*)-(XIV)	B [180] [c]	15	69.3	10.8	20.0	$C_{10}H_{19}Cl$	68.75	10.95	20.3
(*Z*)-(XIV)	B [180] [c]	11				$C_{10}H_{19}Cl$			
(*E*), (*Z*)-(XV) [f, g]						$C_{10}H_{11}Cl$ [h]			
(*E*), (*Z*)-(XVI) [f, i]			72.95	7.4	19.4	$C_{11}H_{13}Cl$ [f]	73.1	7.25	19.65

[a] See Experimental section. [b] Nitrogen flow rate 150 ml min^{-1}. [c] Nitrogen flow rate 120 ml min^{-1}. [d] See ref. 5. [e] See ref. 6. [f] Mixture of the two isomers. [g] B.p. 81—87° at 5 mmHg (lit.,[15] b.p. 84—94° at 7 mmHg). [h] Described in ref. 15. [i] B.p. 94—100° at 5 mmHg.

In conclusion, the general features of the addition both of carbonium ions and of protons to alkynes are more complex than those of the corresponding additions to aryl-substituted acetylenes. This is probably related to the lower stability of α-alkyl-substituted vinyl cations compared with that of α-aryl-substituted, as indicated also by the complexity of the solvolysis data for alkyl-substituted vinyl substrates.[21, 25] Therefore, at present further argument on the relative importance of the various pathways would be speculative.

EXPERIMENTAL

The general experimental details are as described in Part I,[2] except for the following additions and modifications. The ^{13}C n.m.r. spectrum of compound (*E*)-(XIX) was recorded for the neat material on a Bruker model WH-90 Fourier transform spectrometer operating at 22.63 MHz; shifts are reported in p.p.m. downfield from Me_4Si. In the preparative g.l.c. separations columns of the following sizes were used: 2 m × 10 mm (A); 3 m × 10 mm (B); 4 m × 10 mm (C).

Addition of t-Butyl Chloride (I) *to Alkynes* (III)—(VIII).—The general procedure was as follows. To a suspension of anhydrous zinc chloride (0.58 g, 4.3 mmol) in a solution of the appropriate alkyne (43—215 mmol) in dichloromethane (30 ml) was added dropwise a solution of t-butyl chloride (I) (3.98 g, 43 mmol) in the same solvent at 0°. The mixture was allowed to warm to room temperature and was then refluxed for 20—96 h (Table 1). In the case of gaseous or low boiling alkynes, *i.e.* propyne (III), but-1-yne (IV), and but-2-yne (VII), the addition of (I) was carried out at dry ice–acetone temperature in a long-necked flask, which was then sealed and allowed to stand at 40° in a thermostatted bath for the time indicated in Table 1, with occasional shaking.

After cooling, the mixture was filtered, and the solvent, the excess of alkyne, and the products of addition of hydrogen chloride to the alkyne, eventually formed, were distilled off at atmospheric pressure, carefully avoiding overheating. The residue was then chromatographed on silica gel, with pentane as eluant in the case of the addition to alkynes (III), (IV), and (VII) and with light petroleum in the other cases. The products were separated and further purified by preparative g.l.c.

The reaction conditions and the yields of products obtained are reported in Table 1, the ^1H n.m.r. spectra in Table 2, and the physical properties and analytical data in Table 4. For most addition products slight decomposition

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[25] R. H. Summerville, C. A. Senkler, P. von R. Schleyer, T. E. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, 1974, **96**, 1100; T. C. Clarke and R. G. Bergman, *ibid.*, p. 7934, and references therein.

occurred in g.l.c. Consequently, poor elemental analyses were obtained in some cases.

(E)- *and* (Z)-2-*Chloro*-4,4-*dimethylpent*-2-*ene* (IX).—4,4-Dimethylpentan-2-one [26] (XVII) (11.42 g, 0.1 mol) was slowly added to phosphorus pentachloride (22.90 g, 0.11 mol) at 0° with efficient stirring. After 2 h the mixture was allowed to warm to room temperature, stirred for a further 7 h, and poured into aqueous sodium chloride containing cracked ice. The organic products were taken into ether, washed, and dried ($CaCl_2$). Careful evaporation of the solvent gave a brown residue, which was chromatographed on silica gel. Elution with pentane gave a mixture of (*E*)- and (*Z*)-2-chloro-4,4-dimethylpent-2-ene (IX) and of 2-chloro-4,4-dimethylpent-1-ene (XVIII) (12.2 g, 92%), which were separated by g.l.c. (Table 4).

The 2-chloro-4,4-dimethylpent-1-ene (XVIII) could not be isolated in pure form since it was present in small amount (*ca.* 10% of the reaction mixture) and its R_t value was very close to that of (*Z*)-(IX). The structure was assigned on the basis of the ^{1}H n.m.r. spectrum, τ *ca.* 4.79 (1 H, m, C=CH), *ca.* 4.98 (1 H, m, C=CH), 7.75 (2 H, s, C=CCH$_2$), and 8.94 (9 H, s, Bu^t).

Protiodechlorination of (E)-2-*Chloro*-3,4,4-*trimethylpent*-2-*ene* (XIII).—The procedure described [12] for the protiodechlorination of various chloroalkenes was followed with slight modifications. To a well stirred solution of sodium (2.0 g, 86.9 mmol) in purified liquid ammonia (*ca.* 30 ml) was added dropwise under nitrogen a solution of compound (*E*)-(XIII) (1.96 g, 13.4 mmol) in pentane (5 ml). The mixture was stirred for 90 min, the excess of sodium was neutralised with solid ammonium chloride, and water was added until all the inorganic materials went into solution. The organic layer was separated, the aqueous layer treated twice with pentane, and the pentane solutions were combined, washed, and dried ($CaCl_2$). Evaporation of the solvent at atmospheric pressure gave a mixture (*ca.* 4 : 1) of (*Z*)- and (*E*)-3,4,4-trimethylpent-2-ene (XIX) (0.68 g, 45%), which were separated by g.l.c. (column B; 75°; nitrogen flow 120 ml min^{-1}) [R_t(*Z*)-(XIX), 16 min; (*E*)-(XIX), 14 min]. The ^{1}H n.m.r. spectra of compounds (XIX) are reported in Table 2.

(E)-3,4,4-*Trimethylpent*-2-*ene* (XIX).—The procedure described by Whitmore and Laughlin [13] through the synthesis and dehydration of 2,2,3-trimethylpentan-3-ol (XXII) was followed. The dehydration product, analysed by g.l.c., was found to be a mixture of two compounds in the ratio *ca.* 4 : 1.

The main product was identified, according to ref. 13, as a 3,4,4-trimethylpent-2-ene (XIX) by ^{1}H n.m.r. spectroscopy (Table 2). The *E*-configuration was assigned by ^{13}C n.m.r. spectroscopy, δ 12.69 (C-1), 13.80 (3-CH$_3$), 29.46 [(CH$_3$)$_3$], 36.93 (C-4), 115.18 (C-2), and 143.84 (C-3) (lit.,[14] δ 12.48, 13.70, 29.46, 36.37, 115.16, and 143.93).

The secondary product, at variance with the previously assigned structure of 2,3,3-trimethylpent-1-ene (a rearrangement product),[13] was identified as 3,3-dimethyl-2-ethylbut-1-ene [27] (XXIII) on the basis of the ^{1}H n.m.r. spectrum, τ *ca.* 5.18 (1 H, m, C=CH), *ca.* 5.35 (1 H, m, C=CH), 7.93 (2 H, *ca.* q, *J* 7.5 Hz, C=CCH$_2$), and 8.94 (t, *J* 7.5 Hz, CH$_2$C*H*$_3$) and 8.94 (s, Bu^t) (total 12 H).

Protiodechlorination of (E)-4-*Chloro*-2,2-*dimethyl*-3-*ethylhex*-3-*ene* (XIV).—This reaction was carried out as described for compound (*E*)-(XIII). A mixture (*ca.* 5.6 : 1) of (*Z*)- and (*E*)-2,2-dimethyl-3-ethylhex-3-ene (XX) (65% yield) was obtained. The ^{1}H n.m.r. spectra of compounds (XX) are reported in Table 2. By g.l.c. (column B; 100°; nitrogen flow 100 ml min^{-1}) a pure sample of the *Z-isomer* was isolated (R_t 24 min) (Found: C, 85.45; H, 14.85. $C_{10}H_{20}$ requires C, 85.6; H, 14.4%).

Addition of Hydrogen Chloride to Hex-3-*yne* (VIII).—To a solution of dry hydrogen chloride (40 mmol) in dichloromethane (120 ml) were added anhydrous zinc chloride (0.54 g, 4 mmol) and a solution of hex-3-yne (VIII) (4.0 g, 48 mmol) in the same solvent (30 ml). The flask was tightly stoppered, and the mixture was heated at 40° for 70 h with occasional shaking. After cooling, the catalyst was filtered off, the solvent and the excess of (VIII) were removed by careful distillation at atmospheric pressure, and the residue was chromatographed on silica gel. Elution with pentane afforded a mixture (1 : 1.5) of (*E*)- and (*Z*)-3-chlorohex-3-ene (XXIV) (2.94 g, 62%), which were separated by g.l.c. (column B; 160°; nitrogen flow 100 ml min^{-1}) [R_t (*E*)-(XXIV), 7 min; (*Z*)-(XXIV), 6 min], and identified by comparison with authentic materials prepared as described previously.[12,24]

Addition of Benzyl Chloride (II) *to Propyne*(III) *and But*-2-*yne* (VII).—These reactions were carried out as described for the corresponding additions of t-butyl chloride (I) to the same alkynes, except for the reaction temperature (60°). The reaction conditions and the yields of products obtained are reported in Table 1. For both addition reactions separation of the two isomers could not be achieved, either by adsorption chromatography or by g.l.c. In the latter, considerable decomposition of the products was observed. Compounds (XV) and (XVI) were therefore identified on the basis of the ^{1}H n.m.r. spectrum of their mixtures (Table 2) and purified by distillation at reduced pressure. The physical constants and analytical data are reported in Table 4.

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