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Vinyl Cation Intermediates in Electrophilic Additions to Triple Bonds. 2. Chlorination of Alkylacetylenes

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The addition of molecular chlorine to 12 alkyl-substituted acetylenes has been studied in anhydrous acetic acid. Disubstituted acetylenes react by predominant anti addition to give both dichlorides and chloro acetates. Monosubstituted acetylenes react by exclusively syn addition and give only 1,2-dichlorides. Acetylene itself does not react at all under the same conditions. Acetylenes substituted with *tert*-butyl groups react by a variety of pathways to give skeletally rearranged products and none of the expected simple addition products. The rates or chlorination are very fast for the disubstituted compounds, and the second-order rate constants follow Taft's polar substituent constant scale with a ρ^* of -3.2. However, the rates for monosubstituted compounds are slower than would be expected from this relationship. The *tert*-butyl derivatives also react more slowly, and some show evidence of steric retardation. The results are consistent with bridged vinyl-cation-like intermediates and transition states only in the case of disubstituted triple bonds. Acetylenes with only one or no alkyl substituents are presumed to react via open vinyl-cation-like species, if at all. Both types of intermediate can react by a variety of pathways to give final products. These include ion-pair collapse, solvent attack, proton abstraction, and 1,2-shifts. The overall mechanisms of chlorination of both alkyl- and aryl-substituted triple bonds are summarized.

As mentioned in the preceding paper,[1] the mechanism of addition of molecular chlorine to the carbon-carbon triple bond has received little systematic attention, despite the current interest in reactions involving vinyl cations as intermediates.[2] The nature of these intermediates, as well as the transition states which precede them, has yet to be established. The major questions to be answered concern whether these cationic species are best represented as open or bridged vinyl cations[3,4] and which of the various mechanistic categories for electrophilic additions best describe these chlorination reactions.[4]

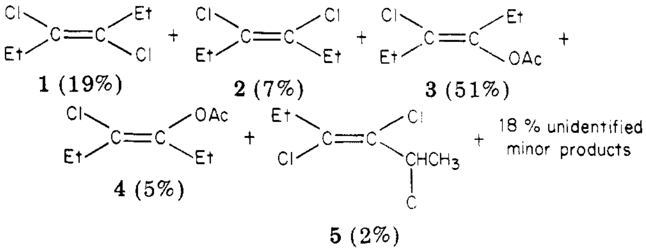
The present paper reports a study of the kinetics and mechanism of chlorination of alkyl-substituted acetylenes.

Results

Products. The procedures and conditions used for the investigation of the products of chlorination of aliphatic acetylenes were exactly the same as those used for the reactions of the arylacetylenes in the preceding paper.[1] The same precautions were taken to prevent possible free-radical reactions. A 10–15% excess of acetylene was maintained to minimize secondary chlorination of the primary products. At least three runs were performed on each substrate, and the product distributions were found not to differ by more than 3%. Because the alkylacetylenes show evidence of reacting by way of different intermediates, they will be treated as three groups: terminal alkynes, disubstituted alkynes, and sterically hindered alkynes.

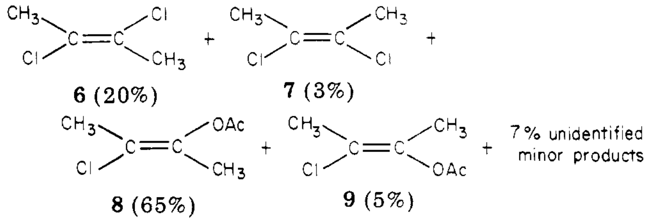
Two simple terminal acetylenes, 1-hexyne and 1-pentyne, were reacted with chlorine in acetic acid. The results are very similar. Only one major product was found in each case. This was isolated and identified to be the dichloride arising from syn addition across the triple bond. The stereochemistry was confirmed by contrast with the *E* isomer which was synthesized via another route. Previous work on the chlorination of 1-hexyne in acetic acid by Hennion and co-workers[5] showed the same stereospecific (*Z*)-dichloride formation. However, in their work, many other more highly chlorinated compounds were also obtained, due to a different experimental procedure. Free-radical pathways have been excluded for the present reactions by control experiments (see Experimental Section).

In contrast, the products of chlorination of dialkylacetylenes show markedly different distributions. Two cases, 2-butyne and 3-hexyne, were examined. These reactions are not clean, and many products were found. In the case of 3-hexyne, more than 20 peaks appeared in the gas chromatogram of the product mixture. The major components were isolated by preparative GC and analyzed. 3-Hexyne reacts with chlorine in acetic acid to give the following product mixture:



1 (19%) 2 (7%) 3 (51%) 4 (5%) 5 (2%)

2-Butyne reacts to give a simpler reaction mixture:



6 (20%) 7 (3%) 8 (65%) 9 (5%)

The reactions of the dialkyl-substituted acetylenes are therefore nonstereospecific, unlike those of the terminal acetylenes, and, furthermore, the products are formed from predominant anti rather than syn additions. This includes the solvent-incorporated chloro acetates, which in both cases are the major products, not the expected 1,2-dichlorides.

Even more complex product mixtures are found for the chlorination of acetylenes carrying *tert*-butyl groups. Of

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[1] K. Yates and T. A. Go, *J. Org. Chem.*, preceding paper in this issue.

[2] G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973); Z. Rappoport, *Acc. Chem. Res.*, **9**, 265 (1976).

[3] P. Bassi and U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, 1283 (1974); G. Modena and U. Tonellato, *J. Chem. Soc. C*, 374 (1974).

[4] G. H. Schmid and D. G. Garratt in "Chemistry of Double Bonded Functional Groups", S. Patai, Ed., Wiley, London, 1977, Suppl. A, Part 2, Chapter 9; G. H. Schmid, "Electrophilic Additions to Carbon-Carbon Triple Bonds. The Chemistry of the Carbon-Carbon Triple Bond", S. Patai, Ed., Wiley, London, 1978, Chapter 8.

[5] R. O. Norris, R. R. Vogt, and G. F. Hennion, *J. Am. Chem. Soc.*, **61**, 1460 (1939).

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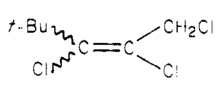
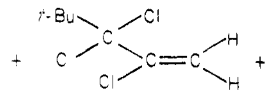
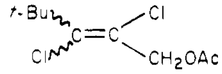
the three substrates studied, *tert*-butylacetylene and di-*tert*-butylacetylene undergo a carbon-skeleton rearrangement, via a 1,2-methyl shift, before the product-determining step. The third substrate, 2,2-dimethyl-3-pentyne, retains the *tert*-butyl group throughout the reaction but undergoes an addition–elimination process instead. This latter case will be discussed first. Again, the product mixture is very complex, and therefore only the major components were separated by column chromatography, distillation, and preparative GC and further analyzed by mass spectrometry and NMR. The products **10–12** were found. It is very difficult to assign geometrical configurations to compounds **10** and **12**. For compounds **12a** and **12b**, the methylene peaks in the NMR are too close together to allow assignment of their individual geometries. Since the isomerism is not crucial to the subsequent discussion of the mechanism, no attempt was made to assign configurations to these compounds. It is to be noted that no simple 1,2-addition products were identified, either dichlorides or chloro acetates, which were the major products in the two previous cases. The major pathway appears to involve an addition–elimination reaction of the type observed previously to give a monochloroallene, followed by addition of Cl_2 to give trichloro olefins as major products.



10 (21%)

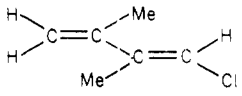


11 (22%)

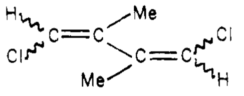


12a (9%)
b (15%)

On the other hand, an addition–elimination process is not possible in the case of *tert*-butylacetylene, since this requires a hydrogen on the carbon next to the triple bond. Consequently, the reaction of this compound and chlorine proceeds via a different pathway, which leads to a very complex product mixture. The molecular weights of the major components in the gas chromatogram were determined by using GC/MS. From the analysis of their fragmentation patterns, compounds **13** and **14** are suggested as the probable major products. It is clear that skeletal rearrangements have taken place, with the probable intermediacy of diene **13** in formation of the other products.

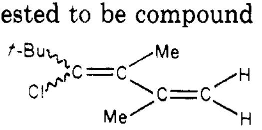


13 (6%)

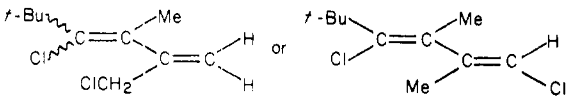


14a (14%)
b (41%)

Similarly, the reaction between chlorine and di-*tert*-butylacetylene gives the same types of products, according to the GC/MS analysis. Thirty percent of the product mixture was suggested to be compound **15**, an analogue of compound **13** in the *tert*-butylacetylene case, and 37% was suggested to be the dichloro diene type product, **16**. For compound **16**, two regioisomers are possible, which are not distinguishable by mass spectrometry. A similar kind of reaction scheme, involving skeletal rearrangement and intermediate diene formation, is probably also applicable here.



15 (30%)



16 (regioisomers, 37%)

Table I. Rates of Chlorination and Bromination of Alkyl-Substituted Acetylenes in Acetic Acid at 25 °C

	chlorination[a]		bromination[b]	
acetylene	k_2, M^{-1} s^{-1}	k_{rel}	k_2, M^{-1} s^{-1}	k_{rel}
HC≡CH	$<10^{-6}$	<0.003	1.94×10^{-5}	0.064
EtC≡CH	2.98×10^{-2}	1.0	3.02×10^{-4}	1.0
n-PrC≡CH	2.45×10^{-2}	0.8	3.06×10^{-4}	1.0
n-BuC≡CH	1.49×10^{-2}	0.5	3.76×10^{-4}	1.2
i-PrC≡CH	2.72×10^{-2}	0.9	6.50×10^{-4}	2.2
t-BuC≡CH	2.60×10^{-2}	0.9	1.33×10^{-3}	4.4
MeC≡CMe	1.06	36	2.33×10^{-3}	7.7
EtC≡CMe	2.75	92	3.87×10^{-3}	13
EtC≡CEt	5.06	170	5.23×10^{-3}	17
i-PrC≡CMe	4.20	140	5.64×10^{-3}	19
t-BuC≡CMe	1.75	59	1.08×10^{-2}	36
t-BuC≡C-*t*-Bu	6.12	160	2.67×10^{-4}	0.9

[a] Estimated error in k_2 is ±2%. [b] Data taken from ref 7.

Kinetics. The rate law for the chlorination of aliphatic acetylenes is the same as that for the arylacetylenes:[1,6] second order overall, first order with respect to each reactant. Table I lists the rate constants for 11 alkyl-substituted acetylenes and the corresponding values recently reported[7] for bromination, for comparison purposes. It can be seen that the rates of chlorination of the disubstituted acetylenes are approximately 100 times those of the terminal acetylenes.

No reaction could be detected between chlorine and acetylene itself in acetic acid at 25 °C. However, in a more polar and nucleophilic solvent system, 50% aqueous acetic acid, the reaction proceeds with a rate constant of 1.2×10^{-3} M^{-1} s^{-1}, which is very slow indeed when compared to the rates of other electrophilic addition reactions in aqueous solvents. It is estimated that an upper limit for the rate of chlorination of acetylene under the present conditions of anhydrous acetic acid would be $k_2 \leq 10^{-6}$ M^{-1} s^{-1}.[8] Thus it is clear that the effects of alkyl substitution on the rate of addition of chlorine to the triple bond are very pronounced, especially in comparison with similar structural effects on the bromination reaction.

A plot of log k_2 against Taft's polar substituent constants ($\sum\sigma^*$)[9] gives a good straight line only for the four dialkylacetylenes, with $\rho^* \approx -3.2$. If this line if projected, as shown in Figure 1, the four monoalkylacetylenes have rates which fall well below the line. Even with the estimated upper limit for k_2 for acetylene itself, it is clear that this point would fall considerably below any reasonable line through the other points. Therefore, the chlorination of acetylenes does not follow any simple linear free-energy

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(6) The rates of chlorination were studied under exactly parallel conditions to those used for the arylacetylenes in the preceding paper.[1] No attempt was made to exclude any chloride ion formed during the reactions, since no kinetically significant terms in chloride ion have been reported for chlorine additions to double or triple bonds.[4]

(7) G. H. Schmid, A. Modro, and K. Yates, *J. Org. Chem.*, 44, 4221 (1979).

(8) After 5 days under normal reaction conditions, less than 1% of the initial chloride had been consumed. No products arising from acetylene could be detected, and hence the disappearance of chloride could have been due to a slow reaction with the acetic acid. Thus the estimate of the upper limit for k_2 for acetylene is a conservative one.

(9) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, Chapter 13.

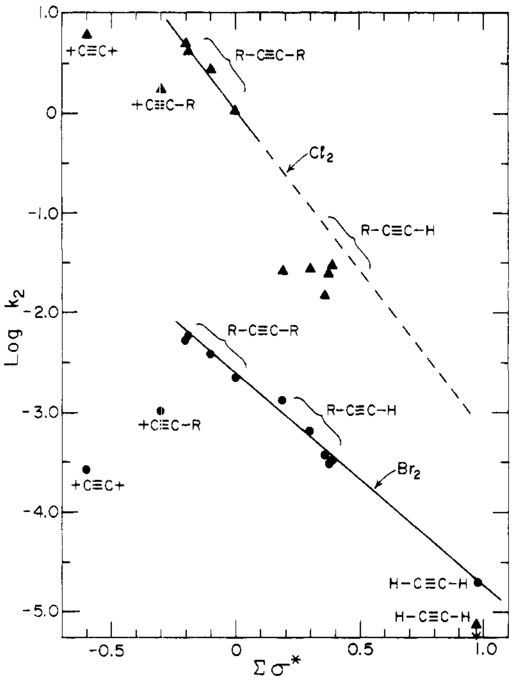

Figure 1. Plot of log k_2 for the chlorination (and bromination) of alkyl-substituted acetylenes vs. Taft's polar substituent constants σ^*.

relationship of the Taft type.[10] This is in marked contrast to the bromination rates, which follow a good log k_2 vs. $\sum\sigma^*$ relationship for all three groups of acetylenes, as reported previously.[7] The points for bromination of the same substituted acetylenes as used in the present chlorination study are shown in Figure 1 for comparison. The ρ^* value for bromination is −2.1.

Although *tert*-butylacetylene itself does not deviate significantly from either line in Figure 1, the points for the *tert*-butylmethyl and di-*tert*-butyl compounds show evidence of marked steric retardation of the addition reaction. This is more pronounced for bromine additions, which is reasonable in view of the larger size of the electrophile. For the chlorination plot, all k_2 values for *tert*-butyl-substituted acetylenes were obtained either from the initial rates or by dividing k_{obsd} by a factor of 2, since these compounds show evidence of intermediate allene or diene formation, followed by rapid uptake of a second mole of chlorine. This will be discussed later.

The rates of chlorination of 1-hexyne and 3-hexyne were measured at several temperatures, and the activation parameters given in Table II were obtained. These are similar to the values previously found for chlorination of arylacetylenes.[1] The values of $\Delta H^‡$ are again lower than those found for analogous bromine additions,[11] although $\Delta S^‡$ values are in the typical range for many bimolecular addition reactions.

Table II. Activation Parameters for Chlorination of Alkylacetylenes

substr	temp, °C	k_2, $M^{-1}\,s^{-1}$	n^a	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, eu
EtC≡CEt	25.0	5.06 ± 0.07	5	6.6 ± 0.1	−33 ± 1
	29.8	6.12 ± 0.08	2		
	40.0	9.07 ± 0.09	2		
	45.1	10.8 ± 0.2	2		
n-PrC≡CH	20.0	(2.15 ± 0.04) × 10^{-2}	3	8.6 ± 0.4	−37 ± 2
	25.0	(2.45 ± 0.05) × 10^{-2}	4		
	31.7	(4.03 ± 0.08) × 10^{-2}	3		
	36.0	(4.55 ± 0.08) × 10^{-2}	3		

[a] Number of kinetic runs.

Discussion

The disubstituted acetylenes (excluding those with *tert*-butyl groups) react predominantly by way of anti addition, whether to give solvent-incorporated chloroacetates or dichlorides. In terms of these simple addition products only, 3-hexyne gives 70% anti addition to 12% syn addition. For 2-butyne the anti and syn product formation is 85 to 8%. It is therefore reasonable to conclude that this type of acetylene reacts predominantly by way of a bridged chlorenium ion intermediate.[3,12] However, the bridging by chlorine must be weak, since some syn adduct is formed in each case. The substituent effects on the rates of chlorination of the disubstituted compounds follow the same kind of simple ρ–σ^* relationship as found for the analogous bromine additions. It therefore appears that both alkyl groups are equally effective in stabilizing the positive charge in the developing vinyl cation and that the transition state is also bridged in these cases. A similar conclusion was arrived at for the bromine additions.[11] However, the slope of the ρ–σ^* relationship is significantly steeper for chlorine addition (−3.2) than for bromine addition (−2.1). This can be taken to indicate less effective charge dispersal by chlorine than by bromine, as seems reasonable, with a consequently greater demand on the two alkyl substituents. This is consistent with the weaker bridging by chlorine[3] at the intermediate stage, leading to predominant rather than exclusive anti addition, as was found for the analogous brominations.

The monosubstituted acetylenes, on the other hand, react exclusively by syn addition and give only the 1,2-dichloride as product. This is only consistent with an open vinyl cation intermediate, which readily undergoes syn ion-pair collapse and is not easily intercepted by solvent or external anions, as was found to be the case for the arylacetylenes.[1] The fact that the rates for these compounds do not fall on the same type of ρ–σ^* plot as for the disubstituted cases, or for bromination in general, indicates a different type of transition state. It is reasonable to conclude that the rates of chlorination are much slower for the monosubstituted acetylenes because chlorine is less effective at stabilizing positive charge in a bridged transition state and that two alkyl groups are needed to disperse the charge in such a species. Hence the monoalkyl derivatives probably react by way of a less stabilized open vinyl-cation-like transition state,[13] similar in structure to

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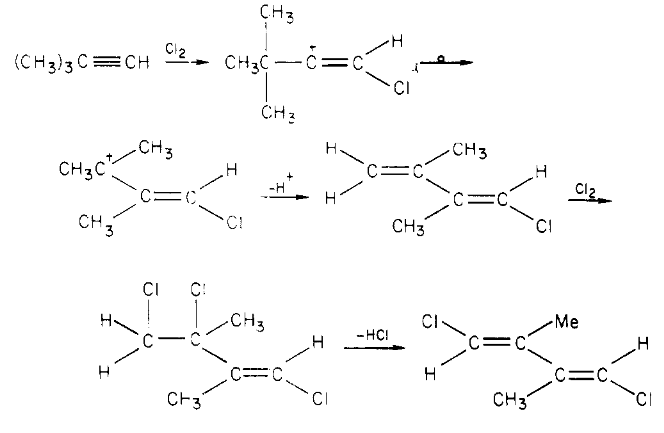
[10] Although, as pointed out by a referee, a rough straight line could be drawn through both the dialkyl and monoalkyl points in Figure 1, it is clear that the latter points would be badly scattered about *any* line drawn. Furthermore, no reasonable line whatever would come anywhere near the upper limit for acetylene itself. A curved relationship therefore seems inevitable if all three classes are included. It seems clear that unlike bromination, these chlorine additions do not go through a common type of intermediate. This is supported by the variable stereochemistry, which ranges from predominantly anti to exclusively syn, unlike bromination which leads to exclusively anti addition for all three classes.

[11] J. A. Pincock and K. Yates, *J. Am. Chem. Soc.*, **90**, 5643 (1968); J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

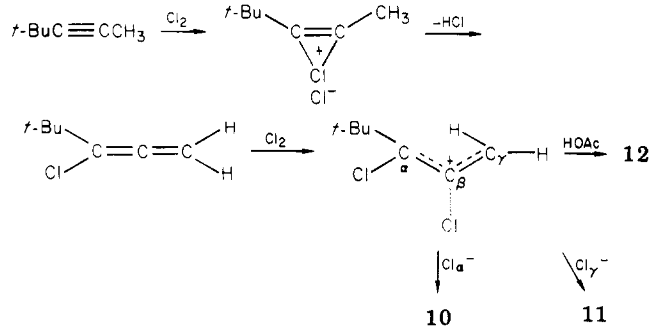
[12] L. C. Allen and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 5350 (1969); V. Lucchini, G. Modena, and I. G. Csizmadia, *Gazz. Chim. Ital.*, **105**, 675 (1975); R. Sustmann, J. E. Williams, M. J. S. Dewar, A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **44**, 385 (1977); T. A. Go, I. G. Csizmadia, and K. Yates, *ibid.*, **49**, 241 (1978).

[13] A referee has suggested that a mechanism involving an open vinyl cation would require a larger substituent effect than that in a bridged ion. It is difficult, however, to compare the magnitudes of the substituent effects in the two series since the monoalkyl points are so badly scattered and the point for acetylene itself is not known accurately.

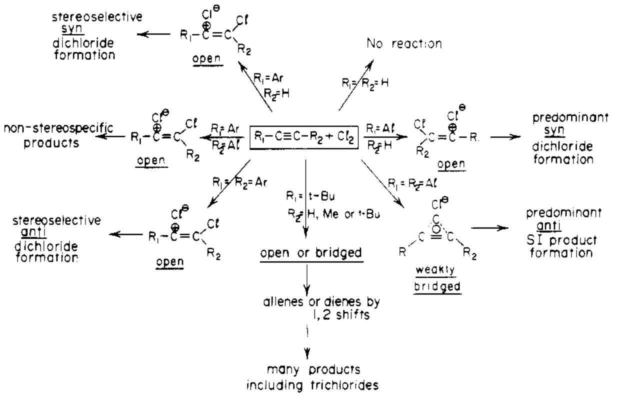
Scheme I



Scheme II



Scheme III



the subsequently formed product-determining intermediate, which is an open vinyl cation.

This is consistent with the fact that acetylene itself does not react at all under similar reaction conditions. With no alkyl substituents and an ineffective bridging atom, the open chlorovinyl cation which would be formed is simply too unstable, since it would be a primary vinyl cation with a strongly electron-withdrawing group at the β-position. For example, the cation formed would be the same as that expected in the solvolysis of 1,2-dichloroethylene. Such a vinyl halide would be expected to be extremely resistant to solvolysis,[14] even in much stronger ionizing solvents than anhydrous acetic acid.

The acetylenes bearing *tert*-butyl groups are somewhat unusual in their pattern of reactivity. Rather than giving predominant 1,2-addition products as do the other acetylenes, they give very complex mixtures, with the major products being either trichlorides or chlorinated dienes. In the case of *tert*-butylacetylene, the results are most easily explained in terms of initial formation of an open vinyl cation, followed by a 1,2-methyl shift to give a more stable carbonium ion and proton loss to give a chloro diene intermediate. This can then react further, as shown in Scheme I.

Although dienes are generally more reactive than acetylenes, some of the first-formed diene is isolated. Scheme I gives only one of the possible pathways available. The complexity of the product mixture shows that the diene can react in different ways, and the above explanation must be regarded as very tentative. The reaction of di-*tert*-butylacetylene presumably follows a similar route, involving a chloro diene **15** formed by addition of a chlorine, a 1,2-methyl shift, and proton loss. The chloro diene can then react with a second mole of chlorine in a similar way to that shown in Scheme I. The methyl *tert*-butylacetylene reacts differently from the above two cases, and it is suspected that the initially formed (and presumably bridged) chlorovinyl cation undergoes proton loss from the methyl substituent to give a highly reactive allene as an intermediate. This allene is not isolated but reacts rapidly with a second mole of chlorine as shown in Scheme II to give the major products observed. Again, the fact that the reaction mixture is so complex illustrates that other pathways are available to the system, and the explanation given in Scheme II must again be regarded as only tentative. A similar scheme can be proposed to explain the minor trichloride product (**5**) formed during the reaction of 3-hexyne.

It is clear from the results in this and the accompanying paper[1] that ionic chlorination of the triple bond is far from simple, especially when *tert*-butyl groups are present. The reactions can take place by a variety of mechanisms, depending on the structure of the starting acetylene. The rate-determining transition states as well as the product-determining intermediates, may be open or bridged vinyl-cation-like species. The cationic intermediates can react in several types of product-forming steps as summarized in Scheme III. These include ion-pair collapse with the initially formed chloride counterion, solvent attack, proton loss, skeletal rearrangement, and in some cases subsequent reaction with a second molecule of chlorine. Perhaps most surprisingly, the parent compound, acetylene, does not react by any of these routes under the present experimental conditions, which are fairly typical for electrophilic addition reactions.

Experimental Section

General Methods. General procedures, instrumentation, and purification of solvents and reagents were as described in the preceding paper.[1] Kinetic measurements were all carried out by the stopped-flow method described previously.

Materials. The aliphatic acetylenes were all commercially available, and samples were purified by distillation before use, when necessary. The purities of all substrates were better than 99.5%, as checked by analytical GC before use. Commercially available acetylene was passed through sulfuric acid and $CaSO_4$ traps prior to use. Concentrations of the gas in acetic acid were determined by two methods. One is based on the change in UV absorption of a standard solution of phenylselenyl chloride on reaction with the acetylene,[16] and the second is a titrimetric

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[14] In solvolytic work on simple alkyl-substituted vinyl systems it has frequently been necessary to use powerful leaving groups such as triflate and nonaflate in order to get the reactions to proceed at reasonable rates.[15]

[15] R. E. Summerville, C. A. Senkler, P. v. R. Schleyer, and T. E. Deuker, *J. Am. Chem. Soc.*, **96**, 1100 (1974); R. H. Summerville and P. v. R. Schleyer, *ibid.*, **96**, 1110 (1974); L. R. Subramanian and M. Hanack, *Chem. Ber.*, **105**, 1465 (1972); L. R. Subramanian and M. Hanack, *J. Org. Chem.*, **42**, 175 (1977).

[16] G. H. Schmid, A. Modro, F. Lenz, D. G. Garratt, and K. Yates, *J. Org. Chem.*, **41**, 233 (1976).

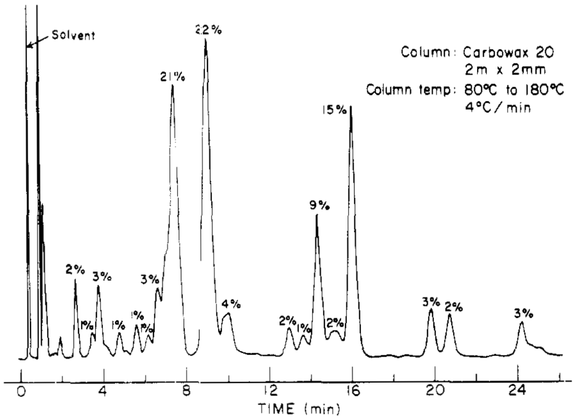

Figure 2.

method based on formation of a cuprous acetylide precipitate, which is reacted with a ferric salt to produce a ferrous solution, which is then titrated with permanganate.[17] The two methods gave reasonable agreement, considering the volatility of the substrate.

Product Analysis. The procedures used to form product mixtures for analysis were exactly as described previously.[1] Control experiments were also carried out to ensure that the products were not being formed as a result of free-radical reactions. These involved use of two known free radical inhibitors: isoamyl nitrite and 2,4-dinitrochlorobenzene. The same mixing procedure as described previously was followed, with the use of approximately equimolar amounts of substrate and inhibitor. After the reaction was complete, the inhibitor was separated from the products by column chromatography on alumina by using hexane as eluant. The product mixture was then analyzed by GC (Figure 2) and NMR, using the same integration procedures as described in the preceding paper.[1] Estimated errors in the product analyses are ±2%. Three substrates were studied: 1-hexyne, 3-hexyne, and phenylacetylene. The product distributions were found to be identical, within experimental error (±3%), with the cases where no inhibitor had been added. Details for each substrate are as follows.

1-Pentyne. The gas chromatogram of the crude reaction mixture showed one major component, 17, which was 90% of the total product, together with numerous minor peaks, each being less than 3% of the total products. The major product was isolated by repeated fractional distillations (73 °C, 20 mm) until its purity was better than 98% as shown by analytical GC. The following spectroscopic data were obtained: NMR δ 0.97 (t, J = 7 Hz, 3 H), 1.67 (tq, $J_1 = J_2$ = 7 Hz, 2 H), 2.77 (d, J = 7 Hz, 2 H), 5.72 (s, 1 H); mass spectrum, m/e (relative intensity) 142 (6), 140 (15), 138 (30), 114 (9), 113 (7), 112 (26), 111 (26), 110 (31), 109 (49), 105 (22), 103 (26), 96 (21), 89 (22), 87 (24), 85 (21), 83 (20), 77 (30), 76 (17), 75 (56), 75 (34), 73 (39), 67 (100); GC retention time, 3.5 min on column B (80–150 °C, flow rate 30 mL/min). Anal. Calcd for $C_5H_8Cl_2$: C, 43.20; H, 5.80; Cl, 51.00. Found: C, 43.33; H, 5.98; Cl, 51.51.

Uemura and co-workers[18] have recently studied the stereochemistry of the chlorination of β-alkylphenylacetylenes by cupric chloride ($CuCl_2$) and found that the dichloride products obtained were trans in configuration. This reaction has been extended to the alkyl substrates, so that the trans chloride products could be obtained and a comparison made with the dichloride adducts from the chlorinations in acetic acid. 1-Pentyne reacts with cupric chloride in the presence of lithium chloride in acetonitrile to give one major product. This product, 18, was found to have the following spectroscopic properties: NMR δ 0.97 (t, J = 7 Hz, 3 H), 1.67 (tq, $J_1 = J_2$ = 7 Hz, 2 H), 2.50 (t, J = 7 Hz, 2 H), 6.12 (t, J = 0.4 Hz, 1 H); mass spectrum, similar to that of compound 17; GC retention time, 1.6 min on column B (80–150 °C, flow rate 30 mL/min). Anal. Calcd for $C_5H_8Cl_2$: C, 43.20; H, 5.80; Cl, 51.00. Found: C, 43.64; H, 5.78; Cl, 50.87.

Table III

component	retn time, min	% of pdts
6	1.5	20
7	2.3	3
8	5.3	65
9	6.8	5

Table IV

component	retn time, min	% of pdts
1	2.5	18
2	3.5	7
3	6.1	51
4	9.4	5
5	4.8	2

Comparison of the data for these two dichlorides obtained from the two different routes reveals the following contrast. First, in the NMR spectrum, the chemical shift of the olefinic signal of compound 17 is found at a higher field than that for compound 18. In addition, there is a small coupling constant (0.4 Hz) for the long-range allylic coupling for compound 18 while no observable allylic coupling is found for compound 17. It has been shown in related compounds that the long-range allylic coupling is larger in the trans isomer.[19] Second, the polarities of these two compounds are different. In a polar column such as Carbowax, the less polar trans isomer would have a shorter retention time than the cis isomer. Compound 18 has a shorter retention time. Therefore, on the basis of the above analysis, compounds 17 and 18 are deduced to be the (Z)- and (E)-dichlorides, respectively.

1-Hexyne. The results of the product analysis for the chlorination of 1-hexyne are very similar to those for 1-pentyne. The identity of the products was deduced by analogy with the 1-pentyne case. 1-Hexyne reacts with chlorine in acetic acid to give a complex product mixture, but with one major component representing 80% of the total products as estimated by analytical GC. After purification, this major product, 19, was analyzed by NMR, GC, and elemental analysis, in comparison with the product obtained from the cupric chloride reaction (as described previously). The distinguishing feature in the NMR of the dichloride obtained from chlorination in acetic acid is the proton signal at δ 5.77 (s, 1 H), in contrast to the signal at δ 6.13 (t, J = 0.4 Hz, 1 H) for the dichloride 20 obtained from the cupric chloride route. Compound 19 has a longer retention time (3.7 min) than compound 20 (1.1 min) on column B (110–220 °C, flow rate 40 mL/min). The elemental analyses are consistent with the proposed empirical structural formula of $C_6H_{10}Cl_2$. On the basis of the evidence presented above, compounds 19 and 20 are assigned to be the (Z)- and (E)-dichlorides, respectively.

2-Butyne. The gas chromatogram of the crude mixture had the major components shown in Table III (80–150 °C, flow rate mL/min). Two fractions were collected by using preparative GC on column C (100–200 °C, flow rate 75 mL/min). The first fraction was shown to contain two components in the ratio of approximately 4:1. Their retention times are identical with those of compounds 6 and 7, with the major component having a shorter retention time, which indicates that it is less polar. The NMR spectrum shows two peaks at δ 2.13 and 2.50 (singlets) in the ratio of 4:1 in favor of the lower field signal. The mass spectrum of this mixture shows molecular ions of the dichlorides (at m/e 124, 126, and 128, 2-chlorine pattern)[20] as the base peaks. On the basis of the above evidence, compounds 6 and 7 are assigned to be the (E)- and (Z)-dichlorides, respectively. The second fraction was found to contain two major components whose retention times

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(20) The isotope ratio for chlorine is 3:1 for ^{35}Cl–^{37}Cl, and, therefore, a 2-chlorine pattern would be 9:6:1.

were identical with those of compounds **8** and **9** in the ratio of approximately 9:1 in favor of compound **8**. The NMR spectrum of this mixture shows peaks at δ 2.1 (s, 3 H) and 1.93 (s, 6 H). The mass spectrum shows peaks at *m/e* 116 and 118 which correspond to the chloro ketone moiety and the molecular ion peaks of the chloro enol acetates at *m/e* 158 and 160. On the basis of the data presented above, compounds **8** and **9** are assigned to be the two chloro enol acetates, the *E* and *Z* isomers, respectively.

3-Hexyne. 3-Hexyne reacts with chlorine in acetic acid to give many products. More than 20 peaks appeared in the gas chromatogram of the crude product mixture. Table IV lists the GC data of the major components on column B (90–180 °C, flow rate 30 mL/min) which have been identified.

Three fractions were collected by using preparative GC on column C (110–200 °C, flow rate 75 mL/min). The first fraction was found to contain two major components, which have identical retention times with compounds **1** and **2** under the same GC conditions. Compound **1** has a shorter retention time, indicating that it is less polar than compound **2**. The NMR spectrum of this mixture shows a triplet at δ 1.17 (*J* = 7 Hz, 6 H) and two sets of quartets at δ 2.35 (*J* = 7 Hz, 2 H) and 2.95 (*J* = 7 Hz, 2 H), in the ratio of 4:1 in favor of the quartet signals at lower field. These peaks are attributed to the ethyl groups of the dichlorides, with the lower field quartet corresponding to the methylene protons of the *E* isomer. The mass spectrum shows molecular ion peaks at *m/e* 172, 174, and 176 (2-chlorine pattern) for the dichlorides. The base peak occurs at *m/e* 117. Thus, the spectroscopic data are consistent with the assigned structure of compounds **1** and **2**. The second fraction was found to contain two major peaks. The retention times of these components correspond to those of compounds **5** and **3**, in a ratio of approximately 10:1. The NMR spectrum shows two sets of triplets at δ 1.00 and 1.07 of equal intensity, a singlet at δ 2.12, a set of multiplets in the range δ 2.00–2.60, and a quartet at δ 5.40. The intensities of these peaks were too small to integrate accurately. The mass spectrum of this mixture shows molecular ions of the chloro enol acetates at *m/e* 176 and 178 (1-chlorine pattern), but peaks at *m/e* 186, 188, 190, and 192 (3-chlorine pattern) were also found. On the basis of this evidence, compounds **5** and **3** are postulated to be the trichloride and the *E* chloro enol acetate, respectively, with the assigned structures shown previously. The third fraction was found to contain only one component. Its GC retention time, on reinjection, was identical with that of compound **4**. The NMR spectrum is very similar to that of compound **3** in that the two sets of triplets of equal intensities are found in the δ 1.00 region and are attributed to the two ethyl protons in different chemical environments. In addition, a singlet at δ 2.10 is found, showing the presence of the methyl protons on the acetoxy function. The mass spectrum is again similar to that of compound **3** in that the molecular ion of the chloro enol acetate is found and that the base peak can be attributed to the chloro ketone ion. On the basis of the evidence presented above, compound **1** is deduced to be the *Z* chloro enol acetate.

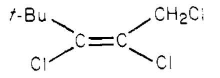
***tert*-Butylacetylene.** *tert*-Butylacetylene gave a very complex mixture. By use of GC/MS, the molecular weights of the three major components were determined. From the fragmentation patterns of the compounds in the mass spectra, possible structures are suggested. The first component, **13**, shows molecular ion peaks at *m/e* 116 and 118 (1-chlorine pattern). The base peak appears at *m/e* 81, which corresponds to a loss of a chlorine atom from the molecular ion. On the other hand, a loss of a methyl group from the molecular ion results in peaks at *m/e* 101 and 103 (1-chlorine pattern). On the basis of this more limited evidence and consideration of possible chemical pathways for this reaction, compound **13** is suggested to be the monochloro diene, with the structure shown previously. Compounds **14a** and **14b** (retention times of 4.8 and 12.3 min, respectively) have identical mass spectra. The base peak is found at *m/e* 81. Molecular ion peaks appear at *m/e* 150, 152, and 154 (2-chlorine pattern). From the molecular ion, a loss of a methyl group gives peaks at *m/e* 135, 137, and 139 in very low abundances, while loss of a chlorine atom gives peaks at *m/e* 115 and 117 (1-chlorine pattern). On the basis of this evidence, compounds **14a** and **14b** are suggested to be the geometrical isomers of the dichloro diene, with the structures shown previously. Detailed structural assignments are not possible, but an NMR spectrum of the product mixture provides evidence for the proposed structures in that no signals attributable to the *tert*-butyl group are observed. Furthermore, the NMR spectrum of the mixture is consistent with the suggested structures for the major products in that several singlets are observed in the δ 2.0 region which can be assigned to the methyl protons on the dienes, and smaller singlets are also observed in the olefinic proton region 5–6.

Table V

components	retn time, min	% of pdts
11	7.7	22
12	9.3	21
13	14.6	9
14	16.3	15

2,2-Dimethyl-3-pentyne. Table V lists the GC data of the major components which were analyzed on column B (80–250 °C, 4 °C/min, flow rate 30 mL/min). After distillation (150 °C, 10 μm), the mixture was passed through a silica gel column with hexane as the eluant. Three fractions were collected and subjected to further analysis. The first fraction contained a major product whose retention time was identical with that of compound **11** under the same GC conditions. Compound **11** is suggested to be the trichloride with the structure shown previously, on the basis of the following spectroscopic observations. The mass spectrum shows molecular ions at *m/e* 200, 202, 204, and 206 (3-chlorine pattern). From the molecular ion, a loss of a methyl group gives peaks at *m/e* 185, 197, 189, and 191 (3-chlorine pattern), and a loss of a chlorine atom gives peaks at *m/e* 165, 167, and 169 (2-chlorine pattern). In addition, loss of HCl is facile for this compound, giving peaks at *m/e* 164, 166, and 168 (2-chlorine pattern). The NMR is consistent with the proposed structure in that two types of protons are found. A signal at δ 1.33 (s, 9 H) is assigned to the *tert*-butyl protons, and two sets of doublets at δ 5.33 and 6.00 (*J* = 2 Hz, 2 H), which are typical coupling patterns for geminal hydrogens, are assigned to the two olefinic protons.

The second fraction contains a major component whose retention time is identical with that of compound **10** under the same GC conditions. The structure of **10** is shown and is suggested



10

to be the geometrical isomer of this trichloride, on the basis of the following observations. The mass spectrum shows the same molecular ion peaks at *m/e* 200, 202, 204, and 206 (3-chlorine pattern) as that for compound **10**, but with a slightly different fragmentation pattern. A similar loss of a methyl group gives peaks at *m/e* 185, 187, 189, and 191 (3-chlorine pattern), and loss of a chlorine atoms gives peaks at *m/e* 165, 167, and 169 (2-chlorine pattern). However, no loss of HCl is found for this compound. The base peak is at *m/e* 165, indicating that a stable ion is formed after a loss of a chlorine from the molecular ion. The NMR is again consistent with such a structure for compound **10**. A signal at δ 1.40 (s, 9 H) is assigned to the *tert*-butyl protons, and a signal at δ 4.45 (s, 2 H) is assigned to the methylene protons.

The third fraction was shown to contain two fractions by analytical GC whose retention times correspond to compounds **12a** and **12b**. The mass spectrum of this mixture shows molecular ion peaks at *m/e* 224, 226, and 228 (2-chlorine pattern). The base peak appears at *m/e* 189 which corresponds to a loss of a chlorine atom from the molecular ion. The NMR shows the *tert*-butyl protons at δ 1.57 (s, 9 H), the methyl protons on the acetoxy function at δ 2.05 (s, 3 H), and the methylene protons at δ 4.83 (s, 2 H) and at δ 9.90 (s, 2 H), showing the presence of two isomers. Thus, compounds **12a** and **12b** are suggested to be the isomeric solvent-incorporated products, whose structures were given previously.

Di-*tert*-butylacetylene. The product analysis for the chlorination of di-*tert*-butylacetylene was again performed by GC/MS. Two major components were analyzed. The first component, **15**, which was 30% of the total products, gives the molecular ion at *m/e* 172, 174 (1-chlorine pattern). From the molecular ion a loss of a methyl group gives peaks at *m/e* 157 and 159 (1-chlorine

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pattern), and a loss of a chlorine atom gives a peak at m/e 137. The base peak appears at m/e 121 which corresponds to a loss of CH_3Cl and an H atom from the molecular ion. On the basis of the fragmentation pattern, compound **15** is suggested to be the monochloro diene type compound of the structure shown previously.

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Registry No. 1, 51430-68-3; **2**, 51430-67-2; **3**, 73496-77-2; **4**, 73496-78-3; **5**, 73496-79-4; **6**, 1587-29-7; **7**, 1587-26-4; **8**, 73496-80-7; **9**, 73496-81-8; **10**, 73496-82-9; **11**, 73496-83-0; (*Z*)-**12**, 73496-84-1; (*E*)-**12**, 73496-85-2; **13**, 35140-57-9; **14**, 24172-03-0; **15**, 73496-86-3; **17**, 73496-87-4; **18**, 73496-88-5; **19**, 59697-55-1; **20**, 59697-51-7; HC≡CH, 74-86-2; EtC≡CH, 107-00-6; PrC≡CH, 627-19-0; BuC≡CH, 693-02-7; *i*-PrC≡CH, 598-23-2; *t*-BuC≡CH, 917-92-0; MeC≡CMe, 503-17-3; EtC≡CMe, 627-21-4; EtC≡CEt, 928-49-4; *i*-PrC≡CMe, 21020-27-9; *t*-BuC≡CMe, 999-78-0; *t*-BuC≡CBu-*t*, 17530-24-4; Cl_2, 7782-50-5.

Prediction of Substituent Sensitivities (ρ_R^+) for Carbocations. Correlation with Charges or HOMO–LUMO Interactions

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A dual substituent parameter equation, using σ_I and σ_R^+ constants, is applied to substituent effect data from the solvolysis of 1-arylethyl derivatives to obtain ρ_R^+ values as a measure of the sensitivity to resonance effects at various positions. From a comparison of ρ_R^+ values with ^{13}C chemical shift data for stable arylcarbenium ions, it is concluded that the values of ρ_R^+ are proportional to the amount of charge developed at the site of substitution. The ρ_R^+ values are also discussed in relation to MO calculations of charge distribution and HOMO–LUMO interactions.

The interpretation of sensitivities to substituent effects indicated by ρ values in Hammett-type correlations has been a subject of continuing interest. For reactions such as the solvolysis of phenylcarbinyl derivatives in which carbocation intermediates are formed, the slope, ρ^+, of a plot of log k/k_0 against Brown σ^+ constants is usually interpreted as a measure of electron demand.[2] The negative sign of ρ^+ signifies that electron-donating substituents accelerate the reaction, and the magnitude of ρ^+ indicates the magnitude of the electron demand and the extent to which the substituents are able to interact with the electron-deficient reaction center.

Attempts to ascribe a quantum mechanical meaning to ρ^+ have led to distinct viewpoints. An interpretation based on charge is that electron demand is determined by the extent of positive charge development in the system and, specifically, that ρ^+ should depend on the amount of positive charge developed *at the site of substitution*.[3-6] Thus, charges obtained from MO calculations or some other measure of charge distribution in the carbocation should be sufficient to predict the trends of ρ^+ (eq 1, where a is the proportionality constant and b is the intercept).

$$\rho^+ = a\Delta q + b \tag{1}$$

Another interpretation, based on perturbation theory, holds that the substituent effect can be described as an interaction between the HOMO of the substituent and the LUMO of the cation.[7-10] Jorgensen[10] suggested the use of an expression equivalent to eq 2, derived from second-order perturbation theory for the energy of the HOMO–LUMO interaction.

$$\rho^+ = a\frac{c^2}{E_L - E_H} + b \tag{2}$$

Here the key factors are the delocalization of the LUMO, represented by c^2, the square of the appropriate LUMO coefficient, and the relative energies of the cation LUMO (E_L) and the substituent HOMO (E_H).

In this paper, we examine the suitability of eq 1 and 2 for predicting ρ_R^+ values in solvolysis reactions of 1-arylethyl derivatives. The ρ_R^+ values we will discuss in this context are those determined from application of a dual substituent parameter (DSP) equation (eq 3) which uses

$$\log k/k_0 = \rho_I\sigma_I + \rho_R^+\sigma_R^+ + i \tag{3}$$

the parameters of Brownlee, Ehrenson, and Taft.[11] The DSP treatment is used because only the resonance effect, not the field (or inductive) effect, should be described by the second-order perturbation expression for the energy of the HOMO–LUMO interaction. The field effect would be accounted for by a separate electrostatic term in the full perturbation theory expression.[9a,12-15] Similarly, in

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[1] (a) Northeastern University. (b) Franklin and Marshall College.

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