Solvents of Low Nucleophilicity. VIII. Possible Vinyl Cation Intermediates, a 1,4-Chlorine Shift, and Novel Substituent Cleavages in the Reaction of Trifluoroacetic Acid with Alkynes[1]

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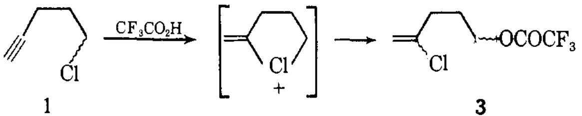
Abstract: The reactions of trifluoroacetic acid with unsubstituted hexynes and with 5-substituted 1-pentynes having chloro, methoxy, acetoxy, trifluoroacetoxy, and cyano substituents occurred readily at rates comparable to those previously determined for the corresponding alkenes. One mole of trifluoroacetic acid added nonstereospecifically to 3-hexyne, presumably *via* a vinyl cation intermediate, to give *cis*- and *trans*-3-hexen-3-yl trifluoroacetate. In a competing reaction, part of the 3-hexyne trimerized to give hexaethylbenzene. 5-Chloro-1-pentyne underwent a novel 1,4-chlorine shift, presumably *via* a chloronium ion intermediate, to give 4-chloro-4-penten-1-yl trifluoroacetate. 5-Methoxy-1-pentyne yielded 5-trifluoroacetoxy-2-pentanone, presumably *via* a cyclic oxonium ion. Rates of the various reactions at 60° were measured and are interpreted in terms of rate-increasing substituent participation, rate-decreasing inductive effects, and a relative ease of formation of vinyl cation intermediates.

The reaction of 5-chloro-1-pentyne with trifluoroacetic acid (eq 1) constitutes the first authenticated example of a 1,4-chlorine shift.[2] The apparent intermediacy of the five-membered cyclic chloronium ion **2** is of particular interest and has prompted us, in the study reported here, to compare the reactions of the chloroalkyne **1** with the analogous reactions of unsubstituted alkynes and other 5-substituted 1-pentynes. Among the questions to which we directed our attention were the following: Are vinyl cation intermediates formed in the addition of trifluoroacetic acid to alkynes, despite the reputed high energy of vinyl cations? What comparisons can be made between vinyl cation intermediates and the more familiar secondary carbonium ion analogs? Will vinyl cations show unusual reactivity, possibly characteristic of hot carbonium ions? (For example, the reaction of eq 1 could conceivably represent abstraction of chlorine by a cation of high reactivity). Will stereospecific addition to triple bonds be observed? Will substituents other than chlorine lead to reactions proceeding *via* cyclic ions, and, if so, what will be the products and rate effects?



1 2 3 (1)

Vinyl Cations as Intermediates. From the reported lack of reactivity of vinyl halides with alcoholic silver nitrate, vinyl cations have been inferred to be high in energy, relative to the halide precursors.[3] However, our preliminary report of the relatively high reactivity of alkynes toward the addition of trifluoroacetic acid may be interpreted as showing that vinyl cations are readily accessible *via* addition of protons to alkynes, possibly as a consequence of the high energy of the starting materials.[2a]

Prior to our own work there were a number of reported reactions in which vinyl cations were considered as intermediates, including the acid-catalyzed hydration of acetylenic ethers[4] and reactions of 2-oxazolidones in basic solution.[5] Robertson's group has shown that halogenation of alkynes in acetic acid involves a positively charged transition state.[6]

Since our preliminary report of the present work vinyl cations have been postulated as intermediates in several other reactions: (1) the addition of hydrogen bromide and hydrogen chloride to allene and propyne;[7] (2) the acid-catalyzed cleavage of (phenylethynyl)triethylgermanes;[8] (3) the solvolysis of α-bromostyrene and α,β-unsaturated β-halocarboxylate ions;[9] (4) the intramolecular addition of carboxylic acids to triple bonds;[10] (5) the deamination of vinylamines;[11] (6) the hydration of 3-hexyne in 90% sulfuric acid;[12] and (7) the acid-catalyzed hydration of phenylacetylenes and phenylpropiolic acids.[13,14] Stable cations having a contributing vinyl cation resonance form have been observed by nmr.[15] Solvolysis of sulfonate esters

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[1] This research was supported by a grant (790A-4) from the Petroleum Research Fund of the American Chemical Society.

[2] (a) For a preliminary report see P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **85**, 2865 (1963). (b) In this paper bonds between carbon and an atom other than carbon usually are shown as a wavy line (∼) to increase clarity.

[3] (a) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 141. (b) The absence of a definitive study of the reactivity of vinyl halides was noted in our preliminary report (ref 2a).

[4] (a) T. L. Jacobs and S. Searles, *J. Am. Chem. Soc.*, **66**, 686 (1944); (b) W. Drenth and H. Hogeveen, *Rec. Trav. Chim.*, **79**, 1002 (1960); (c) E. J. Stamhuis and W. Drenth, *ibid.*, **80**, 797 (1961).

[5] M. S. Newman and A. G. Weinberg, *J. Am. Chem. Soc.*, **78**, 4654 (1956).

[6] P. W. Robertson, W. E. Asent, R. M. Milburn, and W. H. Oliver, *J. Chem. Soc.*, 1627 (1950).

[7] (a) K. Griesbaum, *Angew. Chem. Intern. Ed. Engl.*, **3**, 697 (1964); (b) K. Griesbaum, *J. Am. Chem. Soc.*, **86**, 2301 (1964); (c) K. Griesbaum, W. Naegele, and G. G. Wanless, *ibid.*, **87**, 3151 (1965).

[8] R. W. Bott, C. Eaborn, and D. R. Walton, *J. Organometal. Chem.*, **1**, 420 (1964).

[9] (a) C. A. Grob and G. Cseh, *Helv. Chem. Acta*, **47**, 194 (1964); (b) C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, **47**, 1590 (1964).

[10] R. L. Letsinger, E. N. Oftedahl, and J. R. Nazy, *J. Am. Chem. Soc.*, **87**, 742 (1965).

[11] D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, **87**, 863 (1965).

[12] H. G. Richey, Jr., and N. C. Buckley, as cited by N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 181 (1964).

[13] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.*, 384 (1965).

[14] D. S. Noyce, M. A. Matesich, O.P., M. D. Schiavelli, and P. E. Peterson, *J. Am. Chem. Soc.*, **87**, 2295 (1965).

[15] H. G. Richey, Jr., J. C. Philips, and L. E. Rennick, *ibid.*, **87**,

of 3-pentyn-1-ol[16a] or 6-heptyn-2-ol[16b] accompanied by apparent triple bond participation has led to products which, formally, are derived from vinyl cations. Numerous though they are, these and other similar studies, in general, do not provide the systematic comparison made in the present work and in the work initiated by Noyce and Peterson in 1963[14] between reactions proceeding *via* vinyl cations and those involving secondary cationic intermediates.

Results

Syntheses and Rates. The alkynes were purchased or synthesized as mentioned in the Experimental Section, and rates of reaction, given in Table I, were determined by gas chromatography. Use of the gas chromatographic basic fore-column previously described[17] enabled us to determine the concentration of alkyne as a function of time in dilute solutions (0.1 *M*), as desired. Rate constants obtained in this way are probably accurate to ±5 or 10%, which is adequate in view of the 150-fold variation in *k* values encountered.

Table I. Rates of Reaction of Trifluoroacetic Acid with Alkynes at 60 ± 0.1°

Alkyne	$k \times 10^6$ sec^{-1}	k_H/k_X[a]
1-Hexyne	269	1
2-Hexyne	297	
3-Hexyne[b]	565	
3-Hexyne[c]	605	
5-Chloro-1-pentyne	77.6	3.47
5-Methoxy-1-pentyne	106	2.54
5-Acetoxy-1-pentyne	11.4	23.6
5-Trifluoroacetoxy-1-pentyne	4.48	60.0
5-Cyano-1-pentyne	3.60	74.7

[a] 1-Hexyne was used as the reference compound because of the volatility of 1-pentyne at 60°. It is assumed that substituting a methyl for a hydrogen does not alter the rate significantly. [b] Average of three determinations based on the disappearance of starting material (k = 548, 586, and 586 $\times 10^{-6}$ sec^{-1}, respectively) and one determination based on the appearance of products ($k = 546 \times 10^{-6}$ sec^{-1}). [c] Measured in the absence of added sodium trifluoroacetate.

Products. Our studies of reaction products are summarized by the following equations and brief comments. Characterization of products is described entirely in the Experimental Section. 3-Hexyne reacted as shown in Scheme I. The vinyl trifluoroacetates **4** and **5** were formed in almost identical amounts, and they were shown to be stable under the reaction conditions. Accordingly they arise from *nonstereospecific* addition. The yields of **4** and **5** and **7** vary with hexyne concentration, as shown in Table II.

Scheme I. Reaction of 3-Hexyne

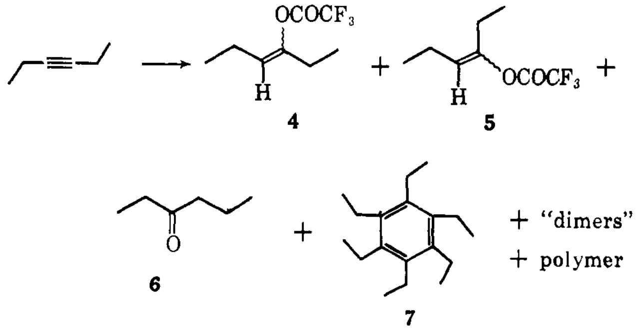


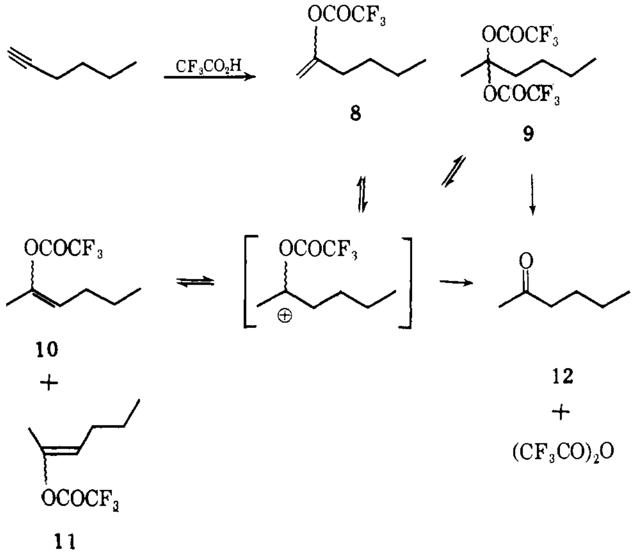
Table II. Effect of the Concentration of 3-Hexyne on the Yields of Products of the Reaction with Trifluoroacetic Acid

Molarity of 3-hexyne	**4** and **5**, mole %	**7**, mole %
0.107	98[a]	~2[a]
0.220	...	4.5[a]
0.640	...	15.5[a]
1.03	24[b]	21.1[a]
1.41	...	24[a]
2.00	18[b]	30[b]
1.00[c]	34[b]	15[b]

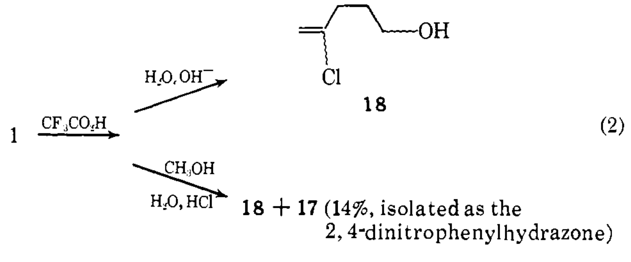
[a] Estimated gas chromatographically by comparison with solutions of known concentration. [b] Isolated from the reaction mixture. [c] Alkyne was added to solution over a period of 12 hr.

In the case of the less fully studied reaction of 1-hexyne, the primary reaction product **8** was not stable and reached a maximum concentration of only 15% (*cf.* Scheme II).

Scheme II. Reaction of 1-Hexyne



The "chlorine shift reaction" of 5-chloro-1-pentyne, mentioned previously (eq 1), is more fully characterized as shown in Scheme III. Because the unshifted products may all be hydrolyzed to 5-chloro-2-pentanone (**17**), which is unstable under basic conditions, the reaction products are much simplified by hydrolysis.



(2)

5-Methoxy-1-pentyne (**19**) cleanly underwent an interesting reaction characterized by methoxyl cleavage,

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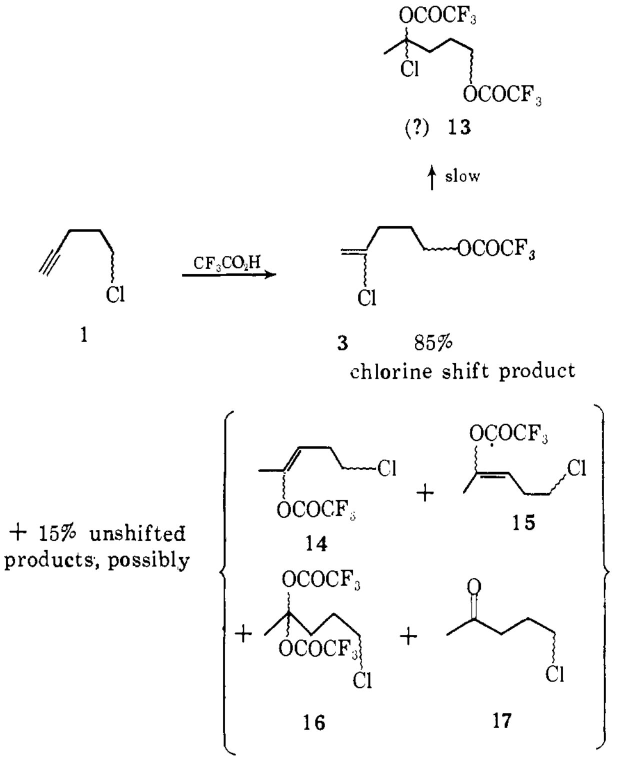
1381 (1965); H. G. Richey, Jr., L. E. Rennick, A. S. Kushner, J. M. Richey, and J. C. Philips, *ibid.*, **87**, 4017 (1965).

(16) (a) M. Hanack, J. Haeffner, and I. Herterich, *Tetrahedron Letters*, 875 (1965); (b) P. E. Peterson and R. J. Kamat, *J. Am. Chem. Soc.*, **88**, 3152 (1966).

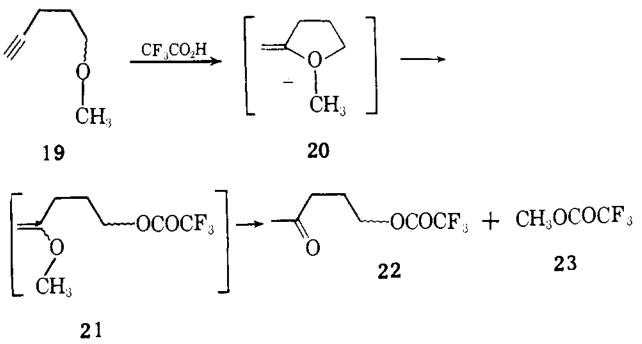
(17) P. E. Peterson and E. Tao, *J. Org. Chem.*, **29**, 2322 (1964).

Scheme III. Reaction of 5-Chloro-1-pentyne

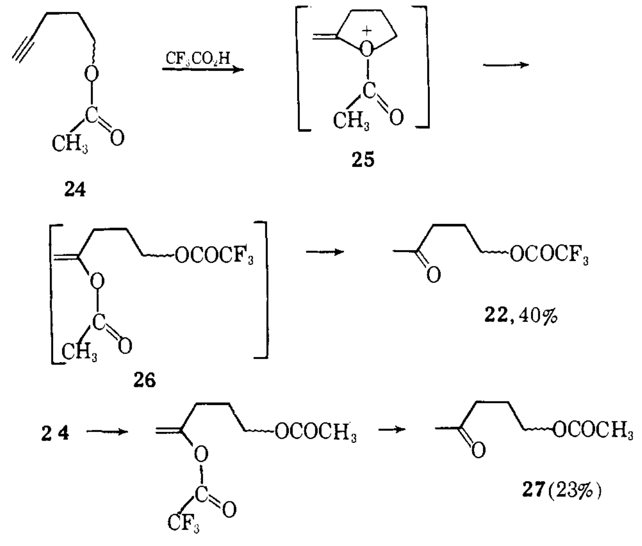


probably by a path involving an intermediate 1,4-methoxyl shift. The observed reaction products are 5-trifluoroacetoxy-2-pentanone (**22**) and methyl trifluoroacetate (**23**) (Scheme IV).

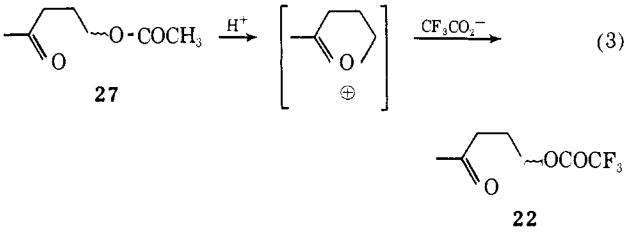
Scheme IV. Reaction of 5-Methoxy-1-pentyne

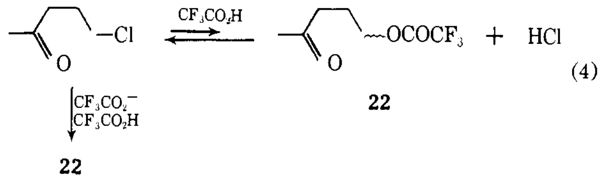


Scheme V. Reaction of 5-Acetoxy-1-pentyne



5-Acetoxy-1-pentyne similarly underwent partial acetoxyl cleavage, very possibly *via* an analogous scheme involving a 1,4-acetoxy acetoxyl shift (Scheme V). It may not be inferred, however, that the 40% yield of 5-trifluoroacetoxy-2-pentanone (**22**) is a measure of the per cent of acetoxyl shift, because the acetoxy ketone **27** is partially converted to **22** under the reaction conditions. Since *n*-butyl acetate was stable under the reaction conditions, the conversion of **27** to **22** appears to represent an interesting example of ketone participation (eq 3). A closely related experiment showed that 5-chloro-2-pentanone underwent a similar reaction. Interestingly, in this case the chloro ketone was the predominant species present when equilibrium had been reached if sodium trifluoroacetate was absent. In the presence of sodium trifluoroacetate, the reaction of the chloro ketone proceeded to completion (eq 4).





Any chloro ketone present in the reaction of 5-chloro-1-pentyne with trifluoroacetic acid (Scheme III) presumably underwent further reaction according to eq 4.

Finally it may be noted that the products of reaction of 5-trifluoroacetoxy-1-pentyne and 5-cyano-1-pentyne with trifluoroacetic acid are not reported here. Substituent particlipation would not be detected by a product study in the case of the trifluoroacetoxyalkyne. Preliminary studies have shown that the cyanoalkyne does give several distillable products, suggesting the definite possibility of participation by the nitrile group. The nature of the products appears to be concentration dependent and time dependent, suggesting the need for a separate full study in this instance.

Discussion

Comparison of Alkenes and Alkynes. The possibly novel behavior of vinyl cation intermediates or related positively charged transition states, presumably obtained in our study by addition of protons to the triple bonds of the alkynes, prompts a detailed comparison of alkyne and alkene reactions. Recently the rates of reactions of more than 40 substituted alkenes with trifluoroacetic acid were interpreted in terms of (1) an unusually slow fall-off of the inductive effect with distance between the substituent and the reaction center, (2) substituent participation, including halogen participation, and (3) solvent enhancement of the inductive effect owing to hydrogen bonding.[18] The rates of reaction of alkynes (Table I) are compared with the

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(18) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Am. Chem. Soc.*, 87, 5163 (1965).

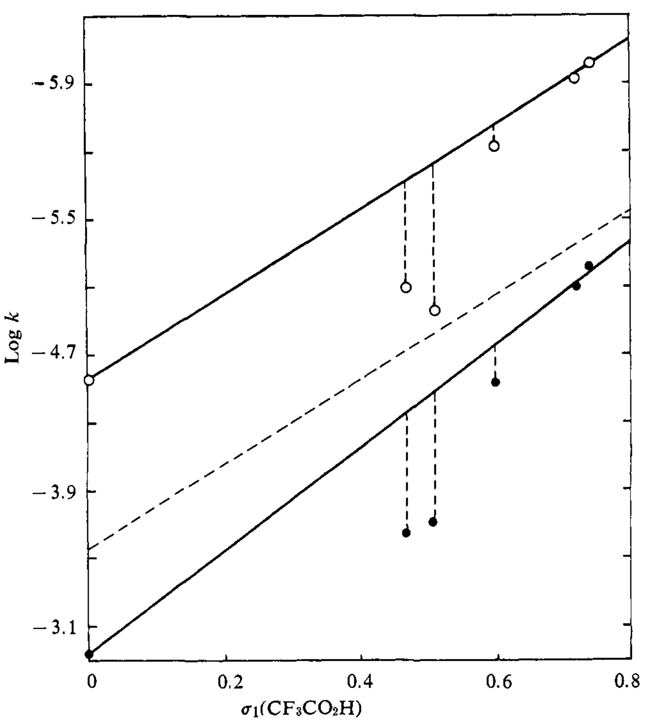

Figure 1. Hammett-Taft plot for reaction of alkynes (open circles, displaced upward one log unit) and alkenes (closed circles) with trifluoroacetic acid. The undisplaced alkyne line is also shown (light dashed line). Substituents are, left to right, hydrogen, chloro, methoxy, acetoxy, trifluoroacetoxy, and cyano.

previously determined values for the corresponding substituted alkenes in the Hammett-Taft plot of Figure 1 in which Taft's σ_I values for trifluoroacetic acid, derived from fluorine nmr frequencies, are employed in the absence of values based on reactivity.[19] The rate constants for the alkynes are seen to be only slightly smaller that those for the alkenes and to exhibit almost the same pattern of substituent effects, indicating a similar cationic nature of the transition states in each instance. The large inductive effects for substituents on the fourth carbon from the cationic site suggest that, as in the alkene series, inductive effects are attenuated only slowly with distance.

In the alkene series substituent participation was previously recognized by deviations from the linearity of "attenuation plots" which were based on the assumption that the inductive effect falls off by a constant factor per methylene group.[18] The trifluoroacetoxy substituent appeared to be nonparticipating by the attenuation plot criterion, and the cyano and acetoxy substituents showed only insignificant rate effects ascribable to participation. In the Hammett–Taft plot, the points for the cyano and trifluoroacetoxy substituents show the least evidence of participation and accordingly are used in both the alkene and the alkyne series to define the line characteristic of purely inductive substituents as shown in Figure 1. A point for a participating substituent falls below the line by an amount which may be used to calculate k_Δ/k_s, the ratio of the rate constant for that part of the reaction which proceeds with participation to the rate constant for the "normal" reaction with solvent. Values of k_Δ/k_s obtained in this way are given in Table III, along with values for the alkene series previously obtained from attenuation plots. The two methods for estimating k_Δ/k_s in the alkene series have not previously been compared. Interestingly the attenuation method is independent of any scale of σ values. Reasonable agreement is obtained, which lends confidence to the over-all separation of inductive and "participation" effects.

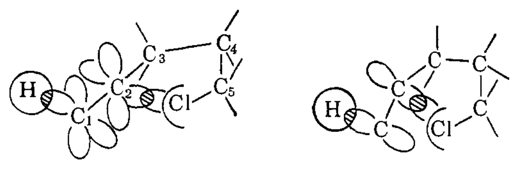

Figure 2. Proposed transition states leading to chloronium ions starting from 5-chloro-1-pentyne (left) and 5-chloro-1-pentene (right).

Table III. Ratio of "Assisted" to "Unassisted" Rate Constants of 5-Substituted 1-Alkynes and Alkenes

	k_Δ/k_s		
Substituent	Alkynes[a]	Alkenes[a]	Alkenes[b]
Cl	3.4	4.2	7.5 ± 1.5
OCH$_3$	6.5	4.8	5.1

[a] From Hammett-Taft plot. [b] From attenuation plot.

The comparable proportions of substituent participation and the comparable ρ_I values (2.50 and 3.05, respectively) shown in the reaction of trifluoroacetic acid with alkynes and alkenes further emphasize the similarity of the reactivity of these compounds. However, since the rates of reaction reported in our study measure only energy differences between starting materials and transition states, they provide no direct comparison of the energies of vinyl cations and the corresponding secondary carbonium ions. The results do indicate that if vinyl cations are high in energy, the bond reorganization which accompanies protonation of the alkyne provides the extra energy.

Chloronium and Oxonium Ion Intermediates. The similar proportions of reaction proceeding *via* participation in the alkene and alkyne series suggests that the *transition states* resemble the starting materials, in which the relationship of the participating substituents to the relevant p orbitals of the double or triple bonds may be essentially *identical*, as shown for 5-chloro-1-pentyne and 5-chloro-1-pentene (Figure 2).[20] Additions to alkenes have previously been postulated to proceed *via* a geometry resembling the reactants.[21]

In contrast, the cyclic chloronium or oxonium ion *intermediates* obtained from alkynes and alkenes differ markedly in geometry and bonding, as shown for the chloronium ions in Figure 3. These differences are strikingly reflected in the product-determining step. The chloronium ion **28** probably opens essentially entirely by cleavage of the bond to the primary carbon (*cf.* Scheme III) to give the product of over-all 1,4-chlo-

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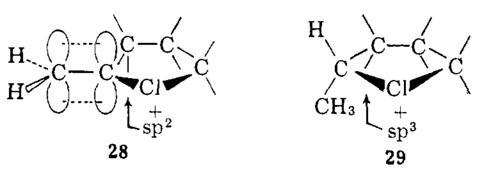
[19] (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963); (b) P. E. Peterson and G. Allen, *J. Org. Chem.*, **27**, 2290 (1962).

[20] The C$_2$–C$_3$ bond distances might, however, be expected to be slightly shorter in the alkyne. Bonding to the C$_2$ p orbital is emphasized, perhaps as an oversimplification. Transition states for *trans* addition are arbitrarily shown. Our argument is independent of the stereochemistry of addition.

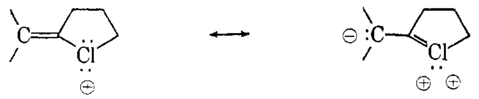
[21] P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *J. Am. Chem. Soc.*, **79**, 3724 (1957).



28 29

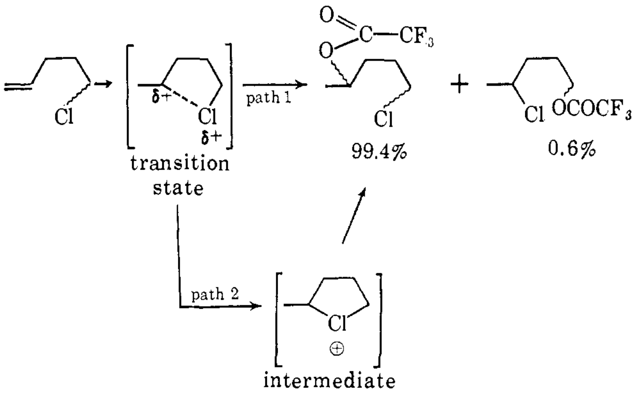
Figure 3. Ionic intermediates derived from 5-chloro-1-pentyne and 5-chloro-1-pentene.

rine shift. This statement is based on the observation that the 15% of "unshifted" products represents somewhat less than the expected amount for that portion of the reaction which, according to the preceding analysis of reaction rates (*cf.* Table III), proceeds without participation. The result is that expected if the strong C–Cl bond to the sp^2 carbon in the ion **28** is unreactive in a ring-opening process which might, *a priori*, have either SN1 or SN2 character. It is interesting that, unlike vinyl halides, the vinyl chloronium ion could hardly show much double bond character in the C–Cl bond because of unfavorable charge repulsion in the second resonance form below.



Accordingly, the unreactivity of vinyl halides may be primarily a consequence of the strength of the σ bond to the sp^2 carbon.

The contrasting behavior of the saturated chloronium ion **29** is shown by the reaction products derived from 5-chloro-1-pentene, in which the chlorine-shifted product has now been shown by capillary column gas chromatography to be present to the extent of only 0.6%. It may be argued that the chloronium ion is never formed in this reaction, since the postulated unsymmetrical transition state might lead directly to the observed major product (path 1) as shown.



Strong evidence against such a scheme (path 1) is the previously reported deuterium-labeling study which indicated that the reaction of 5-chloro-1-hexene, for which rate evidence indicates a closely similar amount of chlorine participation, does proceed with ~40% chlorine shift,[22] indicative of a symmetrical intermediate (path 2). We conclude that in the case of 5-chloro-1-pentene the transition state in which the incipient cationic carbon has only partial bonding to chlorine probably proceeds, as in the hexene case, to a fully formed chloronium ion intermediate, which ultimately reacts in an SN1 reaction to give the secondary trifluoroacetate to the extent of 99.4%.

In the vinyl oxonium ions (**20** and **25**, Schemes IV and V) the vinyl carbon–oxygen bond is probably resistant to cleavage as in the comparable chloronium ion, resulting in the formation of the trifluoroacetate ketone, **22**, *via* cleavage of the primary carbon–oxygen bond. The previously reported[18] products derived from 5-methoxy-1-pentene, however, indicate that the preference for SN1-like cleavage in the intermediate oxonium ion is not as large as that in the chloronium ion, as indicated by the 30% oxygen shift, compared to 0.6% chlorine shift.

We conclude that the differences in reaction products derived from substituted alkynes and alkenes can be well ascribed to the differing reactivities of the cyclic chloronium and oxonium ions which are involved. The differences provide no evidence for any unusual properties of vinyl cations. On the contrary, the competition between carbonium ion formation (secondary or vinyl) and chloronium or oxonium ion formation is similar in the alkene and alkyne and leads to a similar proportion of products derived from each type of intermediate (according to our interpretation).

Stereochemistry. In a recent paper Burnelle, extending work of Ingold and King, has presented a theory which predicts that additions to acetylene (and, by implication, substituted acetylenes) will proceed in a *trans* fashion.[23] An addition is presumed to involve the reagent-facilitated mixing of a "*trans* bent" excited-state wavefunction with that of the ground state. The known reactions of alkynes were reported invariably to involve *trans* addition.[24]

Interesting though it is, Burnelle's theory fails to predict the stereochemistry of addition of trifluoroacetic acid to 3-hexyne, which probably constitutes by far the most satisfactory available test of the theory. As mentioned earlier (*cf.* Scheme I), equal amounts (50 ± 2%) of the *cis* and *trans* isomers are obtained. A control experiment (0.1 *M* alkyne, 60°) showed that the isomer ratio was constant for samples taken at intervals through several half-lives. Under the reaction conditions, each isomer separately underwent only a trace of isomerization to the other. In view of these results it appears likely that the stereochemistry of additions to alkynes will prove to be as complex as additions to alkenes, where varying proportions of *cis* and *trans* addition are found, except in some instances where halonium ions intervene.[25]

Secondary Reactions. The formation of the "di-addition" products **9**, **13**, and **16** is postulated from studies of the simple analogs, formally derived from propyne.[26] The isolation of these compounds is hindered by their tendency to decompose, with liberation of acid, upon gas chromatography.

The formation of the ketones **6** and **12** and presumably others appears to occur in the absence of water,

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(22) P. E. Peterson and E. V. P. Tao, *J. Am. Chem. Soc.*, **86**, 4503 (1964).

(23) L. Burnelle, *Tetrahedron*, 20, 2403 (1964).

(24) Burnelle's references to *trans* addition are too old to be reliable by modern standards, however. Furthermore both halonium ion intermediates and carboxyl participation may usually be involved in the instances cited.

(25) (a) R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965); (b) R. C. Fahey and R. A. Smith, *ibid.*, **86**, 5035 (1964), and references contained therein.

(26) P. E. Peterson and R. Bopp, unpublished work.

as shown by reaction in sealed nmr tubes containing some trifluoroacetic anhydride. In the absence of water, trifluoroacetic anhydride is presumably a reaction product, along with ketone. Comparable reactions in the acetate series are known.[27] The formation of ketone from the vinyl ether **21** presumably occurs *via* protonation of the double bond to give an ion having an oxonium ion resonance form. The ketone participation reactions of eq 3 and 4 are comparable to similar reactions recently reported.[28]

In our preliminary report,[2a] the possible formation of hexaethylbenzene (Scheme I) *via* a homoallylic vinyl cation obtained from reaction of the first-formed vinyl cation derived from 3-hexyne with a second molecule of alkyne was discussed. Here we add only that the apparent lack of formation of 1,3,5-tributylbenzene from 1-hexyne (absence of aromatic hydrogen in the spectrum) perhaps lends support to the somewhat exotic resonance forms previously written.[2a] The additional alkyl substituents derived from 3-hexyne (compared to 1-hexyne) would stabilize the postulated resonance structures.

Conclusion. The slightly lower reactivity of terminal alkynes compared to alkenes observed in our study may be contrasted with the moderately greater reactivity toward aqueous sulfuric acid observed for phenylpropiolic acids and phenylacetylenes, compared to their alkene analogs.[14,29] This modest reversal of reactivity in the two series only serves to emphasize the closely balanced reactivity of alkenes and alkynes which we have noted in this paper. However, our study does show that reactions in the two series lead to interesting differences in the reaction products—particularly those products arising from 1,4-halogen participation.

Experimental Section

Compounds. The aliphatic alkynes listed in Table I were purchased from Farchan Research Laboratories or synthesized. Modifications of reported syntheses were used to prepare 5-cyano-1-pentyne[30] and 5-methoxy-1-pentyne.[31] The latter compound was prepared in 28% yield from lithium acetylide–ethylenediamine complex (Foote Mineral Co.) and 3-methoxypropyl bromide in dimethyl sulfoxide at 25°.

5-Trifluoroacetoxy-1-pentyne. 4-Pentyn-1-ol was trifluoroacylated with trifluoroacetic anhydride.[18] Isolation and distillation gave 7.63 g (82%) of a product, bp 64° (51 mm).

Anal. Calcd for $C_7H_7F_3O_3$: C, 46.67; H, 3.88. Found: C, 46.94; H, 4.07.

Rate Determination. Solutions of the alkynes (0.1 *M*) were prepared in trifluoroacetic acid, 0.125 *M* in sodium trifluoroacetate, and allowed to react at 60°. Samples were removed at intervals and stored in a dewar flask filled with Dry Ice. On completion of a reaction, the samples were analyzed using an F & M Model 609 gas chromatograph equipped with a flame ionization detector and a Disc integrator. Carefully measured 1- or 2-μl aliquots of the samples in a 10-μl syringe were injected on a column containing either 1 or 2 in. of a basic packing[17] in the front of the column or an 8-in. detachable section filled with the basic packing. Use of an internal standard or of a 1-μl syringe was found to be no better than the procedure employed. First-order rate plots were prepared, based on the decrease in area with time of the peak due to the starting alkyne.

Product Studies. Spinning-band columns were used for distillations. All nmr data is given in δ units (ppm with respect to internal tetramethylsilane).

Reaction of 3-Hexyne with Trifluoroacetic Acid. In a typical experiment 3-hexyne (20 g, 0.25 mole) was added to 150 ml of refluxing trifluoroacetic acid over a period of 12 hr. The mixture was allowed to reflux 4 hr and excess acid was removed by distillation at 35° (155 mm). The resulting concentrate was dissolved in 100 ml of ether, washed with potassium carbonate solution, dried, and flash distilled to give 13.9 g of volatile material and 5.1 g of residue.

The distillate was shown to contain mostly *trans*-3-hexen-3-yl trifluoroacetate (**4**) and *cis*-3-hexen-3-yl trifluoroacetate (**5**), along with some 3-hexanone (**6**). The trifluoroacetates were separated by careful distillation followed by preparative gas chromatography on a neopentyl glycol succinate column.

The first eluted isomer showed infrared maxima (CCl_4) at 1805 cm^{-1} (trifluoroacetoxy carbonyl) and 1708 cm^{-1} (double bond?). The nmr spectrum showed a vinyl hydrogen triplet at δ 4.95 (pure liquid). The second eluted isomer had infrared maxima at the same positions and a vinyl triplet at δ 5.08 (pure liquid).

Anal. Calcd for $C_8H_{11}F_3O_2$: C, 48.98; H, 5.83. Found (first eluted isomer): C, 49.29; H, 5.83. Found (other isomer): C, 49.08; H, 5.72.

Both isomers gave 3-hexanone, free of 2-hexanone, upon hydrolysis, as shown by gas chromatography and by preparation of the 2,4-dinitrophenylhydrazone.

The pot residue, described above, contained hexaethylbenzene and unidentified materials. In other experiments in which larger concentrations of 3-hexyne were employed, hexaethylbenzene crystallized upon cooling the reaction mixture.

Reaction of 1-Hexyne with Trifluoroacetic Acid. 1-Hexyne (5.12 g) was allowed to react with 50 ml of trifluoroacetic acid at 60° for 22 hr. Preparative gas chromatography of the distilled products (4.41 g) and nmr analysis showed that the two possible 2-hexen-2-yl trifluoroacetates (**10** and **11**, vinyl triplets at δ 5.12 and 5.28, 10% in CCl_4) and 2-hexanone were present. Analytical gas chromatography showed the relative amounts of **10**, **11**, and ketone to be 1.8:1:1.95, respectively (based on uncorrected flame ionization detector response.)

Reaction of 5-Chloro-1-pentyne with Trifluoroacetic Acid. (a) **Without Subsequent Hydrolysis.** 5-Chloro-1-pentyne (10.0 g) was allowed to react with 100 ml of trifluoroacetic acid at 60° for 13 hr. Distillation gave 20.4 g of material, bp 55–65° (23 mm). The yield, based on the assumption that all products have the molecular weight of the major product, 4-chloro-4-penten-1-yl trifluoroacetate (**3**), is 94%. Analysis by nmr showed the presence of terminal trifluoroacetates (triplet at δ 4.37) and terminal chlorides (triplet at δ 3.65) present to the extent of 86 and 14%, respectively, based on integrated areas. Preparative gas chromatography gave a sample of the chlorine-shifted product, **3**, which showed a $CH_2O_2CCF_3$ triplet at δ 4.37 and "sharp" peak having some fine structure at δ 5.20 arising accidentally from almost equivalent hydrogens of the $H_2C{=}$ group.

Anal. Calcd for $C_7H_8ClF_3O_2$: C, 38.82; H, 3.72. Found: C, 38.85; H, 3.81.

Other small peaks were collected whose nmr spectra indicated them to be mixtures of components shown in Scheme III.

(b) **Acidic Hydrolysis.** Reaction of 8 g of the above distillate with 24 ml of methanol and 6 ml of concentrated hydrochloric acid gave 4.1 g of a mixture of 4-chloro-4-penten-1-ol (**18**) and 5-chloro-2-pentanone. The latter was found to be present to the extent of 14.7% (gas chromatography on terephthalic acid–Carbowax 20 M) or 13.8% (based on isolation of the 2,4-dinitrophenylhydrazone). These results confirm the previously mentioned nmr analysis and indicate the per cent of chlorine shift to be ~85%.

(c) **4-Chloro-4-penten-1-ol from Basic Hydrolysis.** The ether extract of the products obtained by reaction of 10.34 g of 5-chloro-1-pentyne with trifluoroacetic acid was hydrolyzed with 2.5 *M* sodium hydroxide to give 5.95 g (50% over-all) of 4-chloro-4-penten-1-ol, bp 83.5° (18 mm).

Anal. Calcd for C_5H_9ClO: C, 49.79; H, 7.52. Found: C, 49.58; H, 7.60.

The alcohol was identical with a reference sample prepared in low yield by addition of iodine chloride to 4-penten-1-ol, followed by basic elimination.

Reaction of 5-Methoxy-1-pentyne with Trifluoroacetic Acid. Reaction of 2.5 g of the alkyne and 25 ml of the acid for 24 hr

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(27) (a) H. H. Wasserman and P. S. Wharton, *J. Am. Chem. Soc.*, **82**, 661 (1960); (b) G. Eglinton, E. R. H. Jones, B. L. Shaw, and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954).

(28) D. J. Pasto and M. P. Serve, *J. Am. Chem. Soc.*, **87**, 1515 (1965).

(29) Increased charge delocalization into the phenyl group, attributable to increased overlap of p orbitals in the short sp^2–sp bond between the benzene ring and the side chain, may be postulated in the phenylacetylenes to explain their increased relative reactivity. Similar considerations may apply to vinyl and ethynyl ethers; *cf.* ref 4a.

(30) (a) K. E. Schulte and K. R. Reiss, *Chem. Ber.*, **86**, 777 (1953); (b) G. Eglington and M. C. Whiting, *J. Chem. Soc.*, 3052 (1953).

(31) R. Lespieau, *Compt. Rend.*, **194**, 287 (1932).

at 60° gave 1.7 g (53%) of methyl trifluoroacetate, bp 41–43°, δ, CCl_4, 4.00. Removal of trifluoroacetic acid by distillation, extraction with ether–aqueous potassium carbonate, and distillation of the ether layer gave 5-trifluoroacetoxy-2-pentanone (2.3 g 45%), bp 86° (15 mm), identical with a center distillation fraction from trifluoroacetylation of 5-hydroxy-2-pentanone.

Anal. Calcd for $C_7H_9F_3O_3$: C, 42.42; H, 4.54. Found: C, 42.21; H, 4.45.

The nmr spectrum of this fraction showed no nmr evidence for the presence of trifluoroacetates arising from the hemiketal present in 5-hydroxy-2-pentanone.

5-Trifluoroacetoxy-2-pentanone 2,4-Dinitrophenylhydrazone. The derivative melted at 102°.

Anal. Calcd for $C_{13}H_{13}F_3N_4O_6$: C, 41.27; H, 3.43. Found: C, 41.42, H, 3.47.

Reaction of 4-Pentyn-1-yl Acetate with Trifluoroacetic Acid. From the alkyne (12.6 g) in 500 ml of acid maintained at 60° for 110 hr there was obtained 11.2 g of flash distillate and 1.17 g of residue. The distillate contained 5-trifluoroacetoxy-2-pentanone (**22**) and 5-acetoxy-2-pentanone (**17**) in the molar ratio 64:36 (nmr analysis) identified as the 2,4-dinitrophenylhydrazones after separation by gas chromatography. Calculation shows the yields of **22** and **27** to be 40 and 23%, respectively, based on the weight of flash distillate and the observed molar ratio.

5-Acetoxy-2-pentanone 2,4-Dinitrophenylhydrazone. A center distillation fraction (spinning-band column) from acetylation of the alcohol gave the noncyclic acetate as shown by nmr, bp 96–99° (10 mm) [lit.[32] bp 93–95° (10 mm)]. The 2,4-dinitrophenylhydrazone melted at 89–90° (lit.[33] mp 77.6–78°).

Anal. Calcd for $C_{13}H_{16}N_4O_6$: C, 48.15; H, 4.94. Found: C, 48.22; H, 4.82.

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(32) M. A. Volodena, A. P. Terent'ev, L. G. Roshchupkina, and V. G. Mishina, *Zh. Obshch. Khim.*, **34**, 469 (1964); *Chem. Abstr.*, **60**, 13241*c* (1964).

(33) U. S. Patent 2,506,770, U. S. Rubber Co.; *Chem. Abstr.*, **46**, P9, 584*d* (1951).

Reactions of Phosphorus Compounds. XIV.
The Reactions of Halovinylphosphinimines

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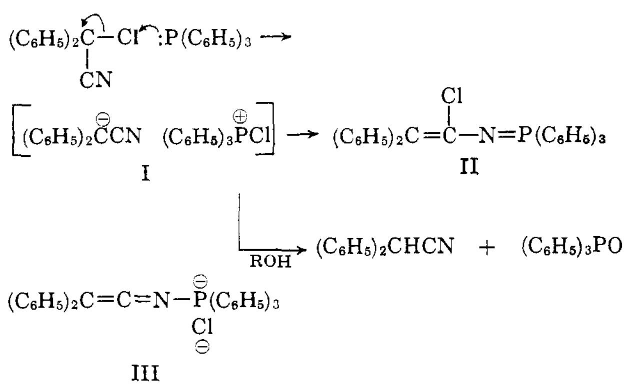
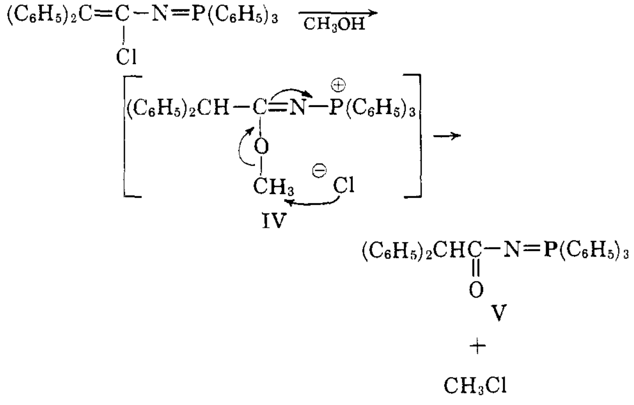
Contribution from the Monsanto Company, Agricultural Division, Research Department, St. Louis, Missouri 63166. *Received June 30, 1966*

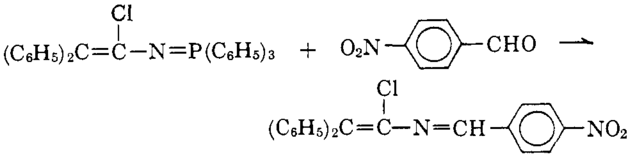
Abstract: The reactions of N-(1-chloro-2,2-diphenylvinyl)triphenylphosphinimine (II) with mercaptans, amines, and benzoic acid are discussed. Mercaptans form isolable phosphonium salts which decompose thermally to diphenylacetonitrile and triphenylphosphine sulfide, probably *via* a thioacylphosphinimine. Amines form amidine-derived phosphonium salts which may be dehydrohalogenated to iminophosphinimines. Benzoic acid yields triphenylphosphine oxide, diphenylacetonitrile, and benzoyl chloride, probably *via* a pentacovalent phosphorus intermediate.

A recent publication[1] from these laboratories described the reaction of chlorodiphenylacetonitrile and triphenylphosphine. Nucleophilic displacement of phosphorus on halogen led to the ion pair I. In the presence of a prototropic solvent, I was converted to diphenylacetonitrile and triphenylphosphine oxide, whereas, in the absence of a protropic solvent, ion pair I was transformed to the halovinylphosphinimine II. (An alternate structure, III, seems unlikely because of the absence of a ketenimine band in the infrared spectrum.) Treatment of II with methanol led to the acylphosphinimine V, presumably *via* the phosphonium salt IV.





Since the favored structure, II, is that of an ylide, its reaction as a Wittig reagent was investigated. Indeed, treatment of II with *p*-nitrobenzaldehyde afforded N-(1-chloro-2,2-diphenylvinyl)-*p*-nitrobenzaldimine (VI). The nuclear magnetic resonance (nmr)



VI

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(1) R. D. Partos and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 5068 (1965).