

Solvent and Structure Effects on the Rates of Bromine Addition to Acetylene Derivatives. Analogies and Differences in Electrophilic Additions to Double and Triple Bonds

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The rates of bromine addition to phenylacetylene, 1-hexyne, and 3-hexyne were measured in acetic, formic, and trifluoroacetic acids and in methanol-water mixtures and compared to those for the corresponding ethylenic derivatives. From the analysis of solvent effects it is concluded that nucleophilic assistance by the solvent is important in many solvents in the case of hexynes and that typical reactivity ratios k^o/k^a for nucleophilically unassisted brominations are of the order of 10^3 for the pair styrene/phenylacetylene and 10^8 for 1-hexene/1-hexyne. Structural effects on the rate of bromination in methanol for substituted phenylacetylene and diphenylacetylenes indicate a highly asymmetrically charged transition state. The possible reasons for the different k^o/k^a ratios in halogen additions relative to those observed in acid-catalyzed hydrations are discussed.

Following the wave of interest in the chemistry of vinyl cations, several recent studies^{1-10,13,14} have appeared concerning the mechanism of electrophilic additions to acetylene derivatives.

Kinetic and stereochemical evidence has been presented which points to very close mechanistic analogies between electrophilic additions to double and triple bonds. In both cases, the slow step of the reaction is indicated¹ as the formation of cations 1 or 2 (Scheme I) either in the "open" (a) or in the "bridged" (b) geometry, depending on the bridging ability of E.

The analogies are particularly evident⁴ in the case of acid-catalyzed hydration (E = H). The reaction for both ethylene and acetylene derivatives is dominated by a slow proton transfer from the solvent to the substrate and is characterized by very similar mechanistic parameters,⁵ such as the general acid catalysis, solvent isotope effects, and substituent effects.

The addition of halogens, in particular bromine, which has been more widely investigated, is a more complicated case where analogies but also differences between alkenes and alkynes have been observed.⁶⁻¹¹ Here the comparison is made difficult by a variety of factors such as the very high reactivity of alkenes in most solvents and the very large solvent effect.

One of the most debated questions^{1,4,7,10,13,14} in the field of electrophilic additions to unsaturated systems concerns the relative reactivities of olefins and acetylenes, k^o/k^a , observed in the limiting cases of bromination⁶⁻¹⁰ (values ranging from 10^3 to 10^7) and of acid-catalyzed hydration^{4,5} (values close to unity) for typical cognate pairs such as styrene/phenylacetylene and *n*-alkenes/*n*-alkynes. Different hypotheses have been presented^{1a,1c,7,10} to explain the different relative reactivities. However, in our opinion, some of the rate data for bromination reported in the literature and taken as a basis for discussions needed to be revised, particularly those obtained by competition techniques.^{7,10} Moreover, a more systematic

analysis of solvent and substituent effects on the bromination of alkynes was important to obtain the mechanistic information required by a correct comparison of kinetic data with that of the corresponding olefins.

We have therefore investigated the bromination of phenylacetylene,¹² 1-hexyne, and 3-hexyne in a variety of hydroxylic solvents and of that substituted phenylacetylenes and diphenylacetylenes in methanol. The results herein are compared to those available in the literature relative to the corresponding olefinic systems, and an attempt is made to offer a rationale for the widely different reactivity ratios observed for bromination and acid-catalyzed hydrations.

Results

The rates of bromination of phenylacetylene, 3-hexyne, and 1-hexyne in various solvents have been measured by conventional spectroscopic techniques or by a stopped-flow method under pseudo-first-order conditions (except in CF₃CO₂H).

The bromine concentration was kept low enough ($<3 \times 10^{-4}$ M) to apply⁶ the proper kinetic law which includes^{9,15,16} the effect of added bromine ion (eq 1). k_ψ is the second-order observed rate constant and K the equilibrium constant for the tribromide ion formation ($\text{Br}_2 + \text{Br}^- \rightleftharpoons \text{Br}_3^-$). The k_2 values were either directly measured, $(k_2)_{\text{dir}}$ (in the absence of Br⁻), or evaluated, $(k_2)_{\text{ext}}$, as the intercept of the plot of the function $k_\psi(1 + K[\text{Br}^-])$ vs. $[\text{Br}^-]$. Where the k_2 constants could be obtained in either way, satisfactorily similar values (see Table I) were obtained.

$$k_\psi = (k_2 + k_{\text{Br}^-}[\text{Br}^-]) / (1 + K[\text{Br}^-]) \dots \quad (1)$$

The solvents of choice were those listed in Table I. The rate of bromination of phenylacetylene in CF₃CO₂H is unaccessible due to the instability of the substrate in the solvent; it is also unstable in HCO₂H, and the rate constant reported in Table I is a very approximate value. The k_2 values are in Table I, and the individual second-order-rate constants, k_ψ , measured in the presence of KBr (and used to calculate, through eq 1 and published¹⁷ K constants, the $(k_2)_{\text{ext}}$ values of Table I) are in Table II (see paragraph at end of paper regarding supplementary material).

The rates in Table I are compared to those available in the literature for the corresponding olefins, i.e., styrene, *cis*-3-hexene, and 1-pentene. The exact analogue of 1-hexyne, namely, 1-hexene, is virtually just as reactive¹⁸ as 1-pentene, but much more data are available^{19,20} for the latter than for the former. Table III shows the k^o/k^a ratios thus evaluated; they are obviously to be taken as approximate values from

Scheme I

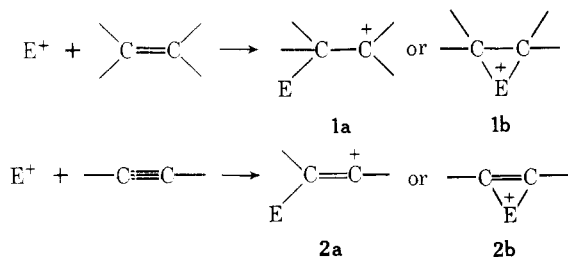


Table V. Minimum^a Estimates of Nucleophilic Assistance, k_s/k_c , for the Bromination of 3-Hexyne and 1-Hexyne

	CF ₃ - CO ₂ H	HC- O ₂ H	CH ₃ - CO ₂ H	MeOH MeOH	MeOH (80%)	MeOH (50%)	H ₂ O
3-Hexyne	1	2	65	225	70	18	6
1-Hexyne	1	9	700	11 250	1314	90	25

^a See ref 27 b.

significant kinetic precursor of the reaction transition state.

Solvent Effects. The slow step of the reaction is indicated as the formation of ionic species **4a** or **4b** and Br⁻ is in the form of ion pairs or free ions, depending on the solvent. Such an indication is confirmed here by the very large increase in the rate observed on going from less polar solvents to water, as expected for reactions proceeding via a rate-limiting ionization process.

The solvent effect is therefore to be discussed in terms of solvation energies of the two ions: cation **4** (a or b) and bromide ion. Small anions like Br⁻ are strongly solvated;²⁵ carbon cations, particularly those with delocalized charge, have low solvation energies. We have recently shown⁴ that vinyl cations resulting from the protonation of aryl- and alkylacetylene derivatives in moderately concentrated sulfuric acid solutions have rather modest solvation requirements which are quite similar to those of their saturated counterparts, i.e., the carbonium ions generated by protonation of aryl- and alkylethylene derivatives. Thus, in this case, since solvation is not important for cations but only for the anion, this being common to all brominations, one should expect very similar solvent effects for cognate pairs of alkenes and alkynes. As anticipated, this is true for aryl derivatives, but not for alkyl derivatives.

Dubois and his co-workers^{11,19,20} have extensively investigated the solvent effects on alkene bromination and have concluded that the process resembles a purely S_N1 process in each case, from 1-pentene, to styrene, and to 1,2-diphenylethylene, and that solvation is essentially electrophilic in character. A plot of log k vs. Y , the Winstein and Grunwald²⁶ parameter, is reasonably linear, although "dispersion"^{27a} is observed; i.e., different slopes are obtained in methanol-water mixtures and carboxylic acids (see Figure 1). The deviations are not serious in view also of the uncertainty on the Y values and of the expected leaving group effect on Y .

The k^o/k^a for styrene and phenylacetylene is virtually unaffected by solvent changes, and therefore the solvent effect for the latter compound describes also an S_N1-like, electrophilically assisted process.

A plot of log k vs. Y for 1-hexyne and 3-hexyne is shown in Figure 1. The type and magnitude of the deviations from linearity are clearly diagnostic of solvent nucleophilic assistance. To evaluate the importance of the solvent nucleophilic assistance there are several criteria very recently discussed.^{27b} The Grunwald-Winstein equation based on the Y and N parameters would allow calculation of m and l , electrophilic and nucleophilic susceptibility parameters. Unfortunately, there are serious discrepancies concerning the Y value for trifluoroacetic acid (1.84;²⁸ but following other estimates it is >4.2 in the *t*-BuCl scale²⁹ and 4.57 in the 2-adamantyl tosylate scale^{27b}) and several uncertainties on other Y and N values for the solvents used.

We will rather follow the approach suggested by Schleyer et al.^{27b} and evaluate the relative importance of the solvent nucleophilically assisted process, k_s , and the solvent electrophilically assisted process, k_c , through eq 2. This is based on the following assumptions and evidence: (a) the bromination of 1-pentene is not accelerated by nucleophilic assistance in

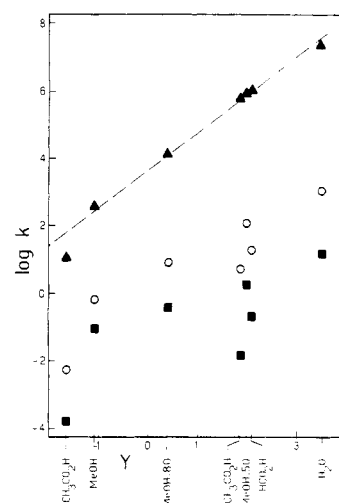


Figure 1. Plot of log k vs. Y for the bromination of 1-pentene (▲), 3-hexyne (○), and 1-hexyne (■). The Y values are taken from ref 24b.

any solvent, and (b) the alkynes do not benefit of any nucleophilic assistance in CF₃CO₂H. The treatment is clearly independent of any solvent parameters. Table V shows the k_s/k_c ratios obtained for the two alkynes. These ratios clearly indicate that the bromination of 3-hexyne in methanol and methanol-water mixtures is mainly nucleophilically assisted and that the same reaction for 1-hexyne, less reactive than for 3-hexyne (see below), is essentially nucleophilically assisted in all solvents but the two strongest acids. The values for 1-hexyne are comparable to those computed^{27b} for the solvolysis of *sec*-alkyl tosylates, and in all solvents except CF₃CO₂H and HCO₂H the reaction should be classified toward the S_N2 end of the S_N spectrum (according to Schleyer et al.²⁷). Therefore, following this analysis, the solvent effect on k^o/k^a for alkyl derivatives can be accounted for. The ratio is close to 10⁸ and may be lowered to 10³ when a good nucleophilic solvent like methanol is used.

$$k_s/k_c = [k(\text{alkyne})/k(1\text{-pentene})]_{\text{any solvent}} / [k(\text{alkyne})/k(1\text{-pentene})]_{\text{CF}_3\text{CO}_2\text{H}} \dots \quad (2)$$

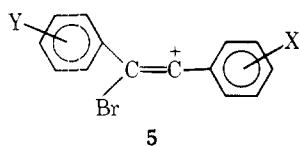
Such a conclusion accords with the results of Dubois et al.⁹ on the effect of bromide ion on the bromination of alkenes and alkynes: the effect is much larger for the latter, particularly in methanol. Following the authors interpretation of the salt effect, alkyne bromination is much more nucleophilically assisted by bromide ions than that of alkenes.

Substituent Effects. The rate constants for the bromination in methanol of the substituted phenylacetylene derivatives reported in Table IV are well ($r = 0.993$) correlated by the Hammett equation, using σ^+ ; no deviation is noticeable in spite of the 10⁵ factor in rates between the two extremes. The ρ^+ value of -4.6 clearly indicates that a large fraction of positive charge is developed at the α -carbon in the transition state.

The ρ^+ value in methanol is slightly smaller than that (-5.2) reported by Pincock and Yates⁶ for the same system in acetic acid. The same trend was observed for substituted styrenes: ρ^+ is -4.3 in methanol³⁰ and -4.7 in acetic acid.³¹ The small difference in ρ^+ observed on going from acetic acid to methanol is one more argument against nucleophilic assistance by the solvent in the bromination of aryl derivatives. The larger (by ca. 10%) ρ^+ values obtained in the case of phenylacetylenes than in that of styrenes is a commonly observed fact, and the reasons for the trend have been detailed elsewhere.^{1b-d,4}

The effect of substituents on the bromination in methanol of diphenylacetylene derivatives can be simply explained in

terms of a reaction leading to a vinyl cation (5) like transition state, where the positive charge is developed essentially into



the carbon atom next to the better substituted phenyl ring [$(-\sigma^+_x) > (-\sigma^+_y)$]. The type of analysis of rate data described by Dubois and Ruasse³² for the bromination of substituted 1,2-diphenylethylenes allows evaluation of ρ^+_x values of -4.6 ($Y = H$) and -4.2 ($Y = m\text{-Cl}$) for substituents in the better substituted ring and ρ_y values of -1.7 ($X = p\text{-Me}$) and -1.6 ($X = H$) for substituents in the other ring. The above values, although approximate, are comparable to the corresponding ones calculated³² for the *trans*-1,2-diphenylethylenes in methanol at 25 °C: $\rho^+_x = -5.0$ ($Y = H$) and -4.95 ($Y = m\text{-Cl}$); $\rho_y = -1.9$ ($X = p\text{-Me}$) and -1.5 ($X = H$). They are also similar to those observed³³ for the solvolysis of β -bromovinyl aren-sulfonates ($Y\text{-C}_6\text{H}_4(\text{Br})\text{C}=\text{C}(\text{O}_3\text{SAr})\text{C}_6\text{H}_4\text{-X}$) in acetic acid at 25 °C: $\rho^+_x = -4.9$ and $\rho_y = -1.1$.

The basic conclusion from the above analysis is that the transition-state picture in terms of charge distribution is a highly asymmetrical one, much more resembling an open cation like 5 than any bridged species.

The effect of substituents on 1,2-*n*-alkyl-substituted ethylenes in methanol,¹⁸ being defined by the Taft equation, $\log k/k_0 = -3.2\Sigma\sigma^*$, does not reveal any duality such as that observed for 1,2-diarylethylenes and strongly suggests a bridged transition-state structure. Substituent effects for a number of 1,2-dialkylacetylenes have been reported by Kornprobst and Dubois,⁸ however, the structural changes are not so important as to significantly vary the rate constants and offer information on the transition-state geometry. Some of the data of Table I are more informative in this respect when the effect of nucleophilic assistance due to the solvent is taken into account. The $k_2(3\text{-hexyne})/k_2(1\text{-hexyne})$ ratios in the least nucleophilic solvents (350 in $\text{CF}_3\text{CO}_2\text{H}$ and 90 in HCO_2H) are indicative of the effects upon electrophilic bromination due to β -*n*-alkyl substituents. They are of the same order of magnitude as those observed for the corresponding alkenes ($k_2(\text{cis-3-hexene})/k_2(1\text{-hexene or 1-pentene}) = 67$ in $\text{CH}_3\text{CO}_2\text{H}$ ⁷ and 130 in MeOH ^{8,11}) but sharply different from those reported for β -alkyl substitutions in the series of both 1-arylethylenes ($k_2(\text{trans-}\beta\text{-methylstyrene})/k_2(\text{styrene}) = 1.1$ in $\text{CH}_3\text{CO}_2\text{H}$ ³⁴ and 2.5 in MeOH ³⁵) and 1-arylacetylenes ($k_2(1\text{-phenylpropyne})/k_2(\text{phenylacetylene}) = 0.5$ in $\text{CH}_3\text{CO}_2\text{H}$ ⁷). These results, when also compared to those reported for the addition of aren-sulfenyl chloride to alkynes,^{3c} indicate a bridged symmetrically charged transition state for simple alkynes as well as for alkenes.

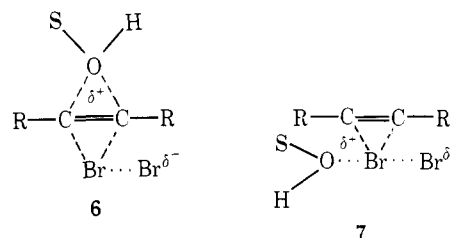
The Nature of the Transition State. The present results and the results of other authors would lead to the following partial conclusions. (1) The rate-limiting step in electrophilic bromination of olefins and acetylenes is the formation of ionic species more or less highly paired. The nucleophilically assisted pathway is limited to the case of alkylacetylene derivatives in good nucleophilic media or in the presence of even low concentrations of Br^- .

(2) The bromination of 1-aryl derivatives in both series proceeds via a very asymmetrically charged transition-state structure. On the other hand, Yates and McDonald³⁶ found that ground-state steric constraints in the case of *cis*-1,2-diphenylethylene are preserved or increased in the transition state of the reaction. From these conflicting indications, the emerging transition-state picture is that of a species with a large fraction of positive charge on the α -carbon but frozen

in a spatial layout similar to that of a bridged (or of π complex) structure.

In our opinion, stereochemical results are of little help in defining the transition state since in following mechanistic Scheme I they are related to the subsequent fast product-determining step of the reaction. Moreover, available stereochemical studies have been carried out under conditions which are too far removed from those under which rate data were obtained. Still they would indicate an essentially open β -bromo-substituted cationic intermediate in both series.

(3) Based on both structural (see above) and stereochemical evidence, there is general agreement concerning the bridged geometry of the transition state of alkylethylene derivatives. The same conclusions can be reached for alkylacetylenes on the basis of the structural effects discussed above. However, in many hydroxylic media, the bromination proceeds via a nucleophilically assisted path and structures 6 or 7 could de-



scribe the transition state. Reports⁷ that bromine addition to 1-hexyne in acetic acid leads to *trans*-dibromo adducts and not to solvent-incorporated products would favor structure 7 were it not for the quite different conditions used for product analyses ($[\text{Br}_2] = 4.15 \text{ M}$) and kinetic measurements ($[\text{Br}_2] < 3 \times 10^{-4} \text{ M}$).

(4) Theoretical studies on $\text{C}_2\text{H}_2\text{F}^+$ ^{37a} and $\text{C}_2\text{H}_2\text{Cl}^+$ ^{37b} and on the corresponding saturated ions³⁸ $\text{C}_2\text{H}_4\text{F}^+$ and $\text{C}_2\text{H}_4\text{Cl}^+$ reveal significant differences. In the case of adducts to acetylene, only the open ions are thermodynamically stable while the bridged structures are in energy maxima. The difference in energy between bridged and open geometries depends on the nature of the halogen (30 kcal mol⁻¹ for F, 10 kcal mol⁻¹ for Cl). On the contrary, in the case of the adducts to ethylene, both open and bridged species are in energy minima and only the relative level changes with the halogen. When this is Cl, the bridged structure is more stable than the open one. These computations parallel the results obtained by Olah and Bollinger³⁹ from ¹H NMR studies.

Calculations on the corresponding brominated cations have not been carried out, but we do not expect dramatic deviations from the trend observed on going from fluorinated to chlorinated ions. Although counterions and solvent have not been included in these models and spectroscopic evidence was obtained in conditions far removed from those of additions, there are clear indications of a large difference in energy between halogen-bridged ions from alkenes and the analogous ones from alkynes. It is noteworthy that theoretical studies carried out on protonated acetylene, C_2H_3^+ , and ethylene, C_2H_5^+ , indicate⁴⁰ that the relative energies of open and bridged structures are rather similar for the two ions. Ab initio computations within the SCF-HF limits indicate the open structure as the more stable species, but when configuration interactions (CI) are included the bridged structure results in lower energy.

The Relative Reactivities of Olefins and Acetylenes.

Let us now face the problem of the different reactivity ratios in the limiting case of protonation and electrophilic bromination. The k^0/k^a values for styrene/phenylacetylene are 0.6 for hydration and 10³ for bromination; for the pair 1-pentene/1-hexyne they are 10 for hydration and 10⁸ for bromination.

For reasons detailed in previous papers,^{1b,1c,4} we prefer to take as "normal" the ratios obtained in the hydration reactions. This implies the assumption that the lower stability of vinyl cations than that of their saturated analogues is almost entirely compensated by the lower strength of the triple bond than that of the double bond being broken in the addition of a proton. As mentioned above, in this case the open or bridged character of the transition state is apparently immaterial since the balance between the two geometries is rather similar in the two series.

To explain the high ratios observed in bromination reactions let us start from the alkyl derivatives. In this case, the transition state and the intermediate are bridged structures. From what theoretical studies clearly indicate a β -chloroethyl (and, by extension, a β -bromoethyl) cation gains in stability by bridging, whereas a β -chlorovinyl (and, perhaps, a β -bromovinyl) cation does not. Therefore, if it is true that there is an even balance between initial and transition-state energies in the case of protonation where neither one of the two systems gains by bridging, this balance must break down in the addition of halogens and strongly favor the ethylene derivatives.

Such an explanation cannot be simply applied to the case of aryl derivatives. However, the available results can be reconciled with the proposed rationale when the following points are considered. (a) The k^o/k^a ratio is much lower (by a factor of ca. 10^5) for aryl derivatives than for alkyl derivatives. (b) Thermochemical data indicate that the transition state for 1,2-diphenylethylene is partially bridged. Such bridging could be energetically more beneficial in the case of ethylene derivatives than in those of acetylene.

Other factors are perhaps to be taken into account to explain the k^o/k^a ratio for 1-aryl derivatives. The balance, fortuitously, even in the case of protonation, may change in the case of formation of destabilized cations such as the β -bromo cations involved in the bromination.⁴¹ As mentioned above, substituent effects are larger in the case of reactions leading to vinyl cations than in those leading to the saturated ones. Scattered data from solvolysis studies^{33,42} would, however, indicate that such effects can not account for a 10^3 factor, but, perhaps, for a factor of 10 in the k^o/k^a ratio.

A more intriguing problem is that of the π -complex transient species. Since the rate of bromine consumption, following Scheme II, may be expressed¹⁹ as $v = K_{\pi}k_2[\text{Br}_2][\text{substrate}]$, where $K_{\pi} = k_1/k_{-1}$, the relative stability of the π complexes from alkene and alkynes may be quite important in explaining the k^o/k^a ratios observed. Such an argument has been brought forward by Olah and Hockswender¹⁰ which argued that it would require more energy for π -complex formation from an alkyne due to the reduced total electron availability. Unfortunately, although evidence of π -complex formation from hexynes and iodine has been reported,⁴³ data on the stability of π complexes from alkynes are not available.

Experimental Section

Materials. Bromine and potassium bromide were of high analytical reagent grade and used without purification. The salt was dried (24 h at 140 °C) before use. The water used was twice distilled from alkaline KMnO_4 solutions. Commercial absolute methanol was treated with bromine (a few drops per liter) and, after standing overnight, fractionally distilled over potassium carbonate and redistilled. Formic acid (>99%) was refluxed for 5 h over phthalic anhydride and then fractionally distilled. Reagent grade trifluoroacetic acid was purified by fractional distillation. Phenylacetylene, 1-hexyne, 3-hexyne, and diphenylacetylene were commercial products which were further purified by standard procedures.

Substituted phenylacetylenes were prepared from the corresponding acetophenones by literature methods and purified by standard procedures: *p*-methylphenylacetylene, bp 79–81 °C (30 mm) [lit.⁴⁴ bp 79–82 °C (31–33 mm)]; *p*-biphenylacetylene, mp 88 °C (lit.⁴⁵ mp 86–87 °C); *p*-bromophenylacetylene, mp 65 °C (lit.⁴⁶ mp 63.5 °C);

m-chlorophenylacetylene, bp 70–72 °C (15 mm) [lit.⁴⁷ bp 71 °C (15 mm)]; *p*-nitrophenylacetylene, mp 151–152 °C (lit.⁴⁸ mp 149 °C). These were checked by spectroscopic or chromatographic methods, as well as by elemental analysis.

Substituted diphenylacetylenes were obtained by described procedures; the new compounds were obtained from the corresponding 1,2-diphenylethylenes via bromination and dehydrohalogenation: di-*m*-chlorophenylacetylene, mp 81–82 °C (lit.⁴⁹ mp 81.5 °C); (*m*-chlorophenyl)phenylacetylene, bp 150 °C (3.5 mm) [lit.⁵⁰ bp 53 °C (3–5 mm)]; (*p*-chlorophenyl)phenylacetylene, mp 127–128 °C (lit.⁵¹ mp 128 °C); (*p*-methylphenyl)phenylacetylene, mp 79–80 °C (lit.⁵² mp 78–79 °C); di-*p*-methylphenylacetylene, mp 136–137 °C (lit.⁵³ mp 136 °C); (*p*-methoxyphenyl)phenylacetylene, mp 92–93 °C (lit.⁵⁴ mp 89–90 °C); (***m*-chlorophenyl**)-***p*-methylphenylacetylene**, mp 82 °C. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{Cl}$: C, 79.45; H, 4.89; Cl, 15.65. Found: C, 79.59; H, 5.10; Cl, 15.45; (***m*-methylphenyl**)-***p*-methylphenylacetylene**, mp 73 °C. Anal. Calcd for $\text{C}_{16}\text{H}_{14}$: C, 93.16; H, 6.84. Found: C, 93.01; H, 6.62. These compounds were also checked by spectroscopic or chromatographic methods. All solid compounds were crystallized from absolute methanol containing small amounts (2–3% relative to the acetylene derivative) of bromine.

Kinetics. The bromination rates were measured on a Gilford 2400 or a Durrum D-110 stopped-flow spectrophotometer by following the disappearance (a) of bromine in the wavelength region of 450–480 nm for kinetic runs in the absence of KBr and (b) of the tribromide ion in the region around 270 nm for kinetic runs carried out in the presence of KBr. Bromine solutions were freshly prepared and protected from light. The measurements in water were made for solutions containing 3×10^{-3} M H_2SO_4 to prevent bromine hydrolysis and in 1% methanol (v/v) to ensure the solubility of alkynes ($1-5 \times 10^{-4}$ M). The alkyne concentrations in the kinetic solutions were $1-5 \times 10^{-2}$ M in methanol and formic acid and $1-10 \times 10^{-3}$ M in water-methanol mixtures; the ratios $[\text{alkyne}]/[\text{Br}_2]_0$ were in the range 20–100 to ensure pseudo-first-order conditions. Only for trifluoroacetic acid solutions were the rate constants obtained under true second-order conditions, and bromine concentrations were determined spectrophotometrically using published⁵⁵ extinction coefficients.

In the case of some diphenylacetylene derivatives, in methanol the kinetic solutions had to be pretreated as described⁵⁶ with a little bromine (1–2%) before achieving good reproducible results. Quite erratic results, for unexplained reasons, were obtained in the case of *p*-nitrophenylacetylene solutions in the absence of added potassium bromide.

Supplementary Material Available: Kinetic data for the bromination of phenylacetylene, 3-hexyne, and 1-hexyne in MeOH, 80% MeOH, and H_2O in the presence of KBr (Table II, 2 pages). Ordering information is given on any current masthead page.

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- Part of our kinetic data on the bromination of phenylacetylene has been included in a recent note by Schmid et al.¹³ The data are in substantial agreement with data in a publication by Ruasse and Dubois,¹⁴ which appeared after this paper was submitted for publication.
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 (21) The $k(\text{styrene})/k(\text{phenylacetylene})$ value in water (Table III) is probably underestimated.¹⁴ The k_2 constant for styrene in water,¹¹ $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, appears too small also from the plot of $\log k_2$ vs. Y for methanol-water mixtures or from the fact that the $k(\text{styrene})/k(1\text{-pentene})$ ratio is 3.05 in MeOH, 2.5 in 50% MeOH, and only 0.44 in H₂O.
 (22) This argument has been advanced again, very recently, by Schmid et al.¹³ and by Berliner et al. [S. De Young, S. Erlich, and E. Berliner, *J. Am. Chem. Soc.*, **99**, 290 (1977)] on the basis of the closely similar reactivity of *trans*-cinnamic and phenylpropionic acids and their esters. However, as shown by Weiss [H. Weiss, *J. Am. Chem. Soc.*, **99**, 1970 (1977)], the bromination of these unsaturated acids is probably not a simple electrophilic addition to carbon-carbon multiple bonds. Further doubts on the electrophilic character of the reaction are provided by the negligibly small (twofold) rate retardation observed¹³ on going from unsubstituted to 4-nitro-substituted acids when compared to that observed (see Table IV; factors greater than a thousand) in the case of styrene and phenylacetylene.
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Synthesis of Alkenes from Carbonyl Compounds and Carbanions α to Silicon. 6. Synthesis of Terminal Allenes and Allyl Chlorides^{1,2}

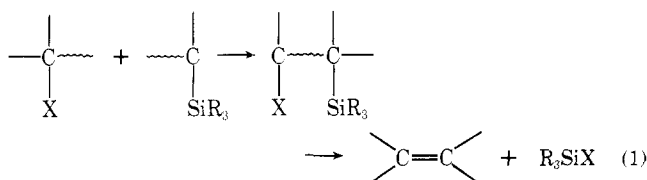
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Aldehydes and ketones can be converted into terminal allenenes or allylic chlorides by reactions with α -silylvinyl carbanions **2** followed by subsequent transformations. The mechanisms and the stereoselectivity of these reactions are discussed.

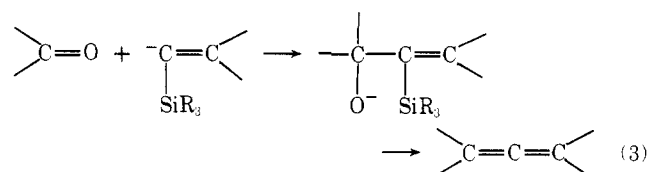
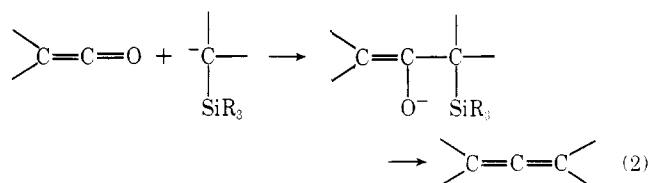
Reactions which lead to the synthesis of alkenes are of great importance to organic chemistry. Numerous named reactions (Hofmann, Saytzeff, Cope, Wittig) have been developed for this purpose. Recently, an alkene synthesis, based on the propensity of β -functionalized organosilicon compounds to undergo elimination, has been introduced.³⁻⁵ The generality of the reaction can be expressed by eq 1 in that any



union of two fragments which brings together the β relationship of the silyl group and a good leaving group can be considered as an alkene synthesis.⁵ A useful version of eq 1 involves the condensation of carbonyl compounds with carbanions α to silicon.³⁻⁵ The reaction bears obvious similarity to the Wittig reaction⁶ and its many modifications.

In the course of developing the synthetic utility of the silicon-based alkene synthesis, we became interested in extending the reaction to the preparation of allenenes.¹ A priori, two ap-

proaches exist. One is to employ ketene as the starting material (eq 2), and the other is to react a carbonyl compound with a vinyl carbanion α to silicon (eq 3). We have chosen to explore the second approach (eq 3) not only because of the ready



availability of the carbonyl compounds in general, but also because of the recognition that the vinylsilane moiety is a latent functionality which can be manipulated subsequently.⁷