Polar Additions to Olefins and Acetylenes. V. Bimolecular and Termolecular Mechanisms in the Hydrochlorination of Acetylenes[1]

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Abstract: The rate, products, and stereochemistry of addition in the reaction of 3-hexyne with hydrogen chloride in acetic acid have been studied as a function of temperature and reactant concentrations. The addition of hydrogen chloride occurs very predominantly *trans* at 25° but at higher temperatures *cis* addition becomes important. Concurrent addition of acetic acid leads, *via* the intermediate vinyl acetate, to 3-hexanone. The *trans*-hydrochloride to ketone ratio increases with hydrogen chloride concentration. Water and tetramethylammonium chloride (TMAC) specifically accelerate the formation of *trans*-hydrochloride. A comparison of the results for 1-phenylpropyne and 3-hexyne shows that these acetylenes react at comparable rates but by different mechanisms. 1-Phenylpropyne undergoes addition *via* a bimolecular mechanism involving rate-limiting formation of a vinyl cation-chloride ion pair which collapses predominantly to *cis*-hydrochloride. 3-Hexyne reacts *via* a termolecular mechanism involving synchronous C–H bond formation and C–X bond formation on opposite sides of the acetylenic bond.

Much less attention has been given to the study of electrophilic addition to acetylenes than to olefins,[3] a fact which led us, several years ago, to undertake mechanistic studies in this area. Since then a number of studies of acid-promoted additions to acetylenic compounds have appeared which support the existence of vinyl cations as intermediates in these reactions.[4] Our own work on acid additions has been concerned with hydrogen halide promoted addition in acetic acid, our choice of system being dictated by a desire to obtain evidence on the reaction kinetics, the stereochemistry of addition, and the competition between solvent and hydrogen halide addition, all with the same acetylene. Further, we chose to work in relatively concentrated media with the long-range hope of utilizing our results to develop methods of synthetic utility. Early experiments suggested that homolytic addition is not easily suppressed in the hydrobromination of acetylenes in acetic acid;[5] this led us to focus our attention on hydrogen chloride addition for which the homolytic reaction is unfavorable. Studies of the hydrochlorination of 1-phenylpropyne, the first system studied in detail, showed that hydrogen chloride adds mainly, but not completely, *cis* while concurrent addition of acetic acid is essentially nonstereospecific.[6] These results were considered to be consistent with the rate-limiting formation of a resonance-stabilized vinyl cation intermediate which rapidly collapses to products.

We wished to extend our studies to nonconjugated acetylenes where the intermediate cation would not be

resonance stabilized, but, since Peterson and Duddey had shown that the addition of trifluoroacetic acid to 3-hexyne is nonstereospecific,[4] we did not anticipate that such systems would give substantially different results. We were, therefore, somewhat startled to find that 3-hexyne adds hydrogen chloride almost exclusively *trans* in acetic acid. These striking changes in the steric course of addition with substrate and reaction conditions clearly deserved more careful scrutiny. In this paper we report the results of a detailed study of the hydrochlorination of 3-hexyne which serve to clarify the reasons for the variation in stereochemistry with acetylene structure and reaction conditions.

Results

Rate and Products Studies. The reaction of 3-hexyne (H) with hydrogen chloride in acetic acid ([H$_2$O] <0.01 M) proceeds slowly at 25° to yield a mixture of 3-chloro-*trans*-3-hexene (T), 3-chloro-*cis*-3-hexene (C), and 3-hexanone (K). Under comparable
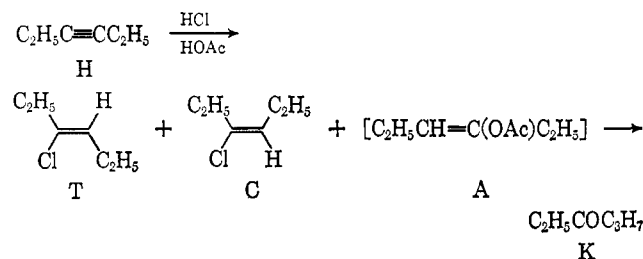
conditions, 3-acetoxy-*trans*-3-hexene was converted to K nearly 10^4 times faster than was 3-hexyne, so that the ketone is reasonably considered to be the secondary product derived from an intermediate vinyl acetate A. The intermediate formation of vinyl acetates was observed directly in the hydrochlorination of 1-phenylpropyne,[6] but their concentration was below the level of detection in the present experiments.

The reaction was studied as a function of reactant concentrations and temperature. Samples of the reaction mixture were worked up by quenching in water

(1) We thank the U. S. Army Research Office (Durham) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This work was reported in part in a preliminary communication: R. C. Fahey and D.-J. Lee, *J. Am. Chem. Soc.*, **89**, 2780 (1967).

(2) Alfred P. Sloan Foundation Research Fellow, 1966–1968.

(3) P. B. D. de la Mare and R. Bolton, "Electrophilic Addition to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966.

(4) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966); D. S. Noyce, M. A. Matesich, and P. E. Peterson, *ibid.*, **89**, 6225 (1967), and references cited in these papers.

(5) D.-J. Lee, Ph.D. Thesis, University of California, San Diego, Calif., 1967.

(6) R. C. Fahey and D.-J. Lee, *J. Am. Chem. Soc.*, **88**, 5555 (1966).

Table I. The Hydrochlorination of 3-Hexyne in Acetic Acid

[HCl], M	[C$_6$H$_{10}$], M	$10^7 \times R$, M sec^{-1}	Product composition, %			Log A^a
			T	C	K	
		At 25.0°				
0.057	0.81	0.0097	24 ± 2	2.0 ± 0.2[b]	74 ± 2	−1.25
0.12	0.81	0.024	29 ± 2	2.4 ± 0.2[b]	69 ± 2	−0.94
0.23	0.81	0.061	32 ± 1	1.4 ± 0.2[b]	66 ± 1	−0.63
0.38	0.81	0.22	41 ± 2	≤1	59 ± 2	−0.32
0.49	0.81	0.30	43 ± 1	≤1	57 ± 1	−0.23
0.59	0.81	0.45	45 ± 3	≤1	55 ± 3	−0.14
0.78	0.81	0.87	47 ± 4	≤1	53 ± 4	0.05
1.14	0.81	2.04	58 ± 2	≤1	42 ± 2	0.32
0.13[c]	0.81	0.043	50 ± 2	≤1	50 ± 2	
0.26[c]	0.81	0.12	50 ± 2	≤1	50 ± 2	
0.42[c]	0.81	0.48	68 ± 2	≤1	32 ± 2	
0.60[c]	0.81	0.92	72 ± 2	≤1	28 ± 2	
0.59	0.81	0.45	45 ± 3	≤1	55 ± 3	
0.59	0.40[d]	0.18	46 ± 1	≤1	54 ± 1	
0.59	0.21[d]	0.082	45 ± 2	≤1	55 ± 2	
0.59	0.20	0.14	44 ± 1	≤1	56 ± 1	
		At 50.0°				
0.12	0.81	0.38	22 ± 2	2.0 ± 0.4	76 ± 2	−0.94
0.23	0.81	0.92	25 ± 2	2.5 ± 0.4	72 ± 2	−0.63
0.39	0.81	2.0	30 ± 2	1.9 ± 0.5	68 ± 2	−0.29
0.82	0.81	7.0	38 ± 1	1.9 ± 0.2	60 ± 1	0.10
		At 80.0°				
0.12	0.81	5.5	23 ± 1	4.6 ± 0.2	73 ± 1	−0.94
0.23	0.81	12.5	25 ± 1	5.2 ± 0.2	70 ± 1	−0.63
0.39	0.81	24.0	25 ± 1	4.3 ± 0.3	71 ± 1	−0.29
0.82	0.81	70.0	30 ± 1	4.8 ± 0.2	65 ± 1	0.10

[a] At 18°. Calculated from data in ref 7. [b] Isomerization tests were not performed for the extended periods involved in these runs. [c] In acetic acid containing 0.08 M water. [d] Pentane added to make hydrocarbon content equivalent to 0.81 M run.

Table II. The Effect of TMAC on the Hydrochlorination of 3-Hexyne in Dry Acetic Acid

[HCl], M	[C$_6$H$_{10}$], M	[TMAC], M	$10^7 \times R$, M sec^{-1}	Product composition, %			Log A^a
				T	C	K	
			At 25.0°				
0.096	0.81	0.214	1.2	97 ± 1	≤0.2	3 ± 1	−1.02
0.19	0.81	0.214	2.4	97 ± 1	≤0.2	3 ± 1	−0.72
0.38	0.81	0.214	6.0	97 ± 1	≤0.2	4 ± 1	−0.32
0.60	0.81	0.214	11.0	96 ± 1	≤0.2	4 ± 1	−0.12
0.78	0.81	0.214	16.7	96 ± 1	≤0.2	4 ± 1	
0.60	0.81	0.054	3.1	91 ± 1	≤0.2	9 ± 1	
0.60	0.81	0.107	6.1	95 ± 1	≤0.2	5 ± 1	
0.60	0.81	0.427	20.0	98 ± 1	≤0.2	2 ± 1	
0.71	0.81	0.214	14.7	95 ± 1	≤0.2	5 ± 1	
0.71	0.41[b]	0.214	7.3	96 ± 1	≤0.2	4 ± 1	
0.71	0.20[b]	0.214	3.6	96 ± 1	≤0.2	4 ± 1	
0.71	0.20	0.214	4.5	97 ± 1	≤0.2	3 ± 1	
0.81	0.81	0.113	9.3	95 ± 1	≤0.2	5 ± 1	
			At 50.0°				
0.81	0.81	0.113	82	92 ± 1	≤0.2	8 ± 1	
			At 80.0°				
0.81	0.81	0.113	670	89 ± 1	0.7	10 ± 1	

[a] For hydrogen chloride in acetic acid at 18°; calculated from data in ref 7. [b] Pentane added to make hydrocarbon content equivalent to 0.81 M run.

and extracting with pentane; the organic fraction was then analyzed by glpc. Control experiments showed that no fractionation occurs in the work-up procedure and that the products (T, C, and K) are stable to the reaction conditions. By employing an internal standard, it was shown that T, C, and K comprise over 90% of the the total product. Initial rates, $R = -\Delta[H]/\Delta t = \Delta[T + C + K]/\Delta t$, were determined at less than 10%

conversion from glpc analysis of the reaction mixture and were corrected for the small changes in reactant concentrations which occur over this interval. The results obtained for the hydrochlorination of 3-hexyne in acetic acid are given in Table I. The reaction was also studied as a function of added tetramethylammonium chloride (TMAC) and the results of these experiments are summarized in Table II. In the
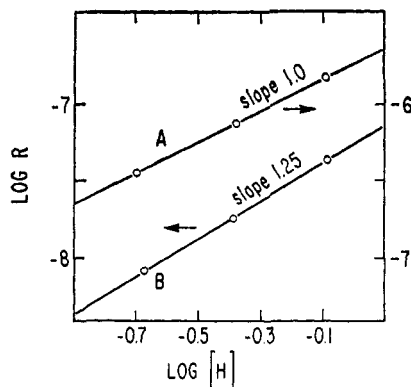
Figure 1. Plot of log R vs. log [H] for the hydrochlorination of 3-hexyne in acetic acid at 25.0° with hydrocarbon content maintained constant with pentane: A, [HCl] = 0.71 M, [TMAC] = 0.214 M; B, [HCl] = 0.59 M, [TMAC] = 0.

absence of hydrogen chloride, 3-hexyne undergoes no significant reaction with acetic acid, either with or without added TMAC.

Analysis of Rate Data. In principle, the rate law for the reaction can be inferred from log–log plots of R vs. reactant concentration, but difficulties arise at the high concentrations employed here. Thus, as the acetylene concentration is varied from 0.2 to 0.8 M, the hydrocarbon content of the solvent increases substantially, decreasing the polarity of the medium and the reaction rate. To counteract this effect, the hydrocarbon content was maintained constant with pentane as the acetylene concentration was varied. A plot of log R vs. log [H] at constant hydrocarbon content is given in Figure 1. In the presence of TMAC the plot has unit slope, but without salt a somewhat higher than unit slope is observed. We conclude that the reaction is first order in 3-hexyne, the deviation from unit slope in the absence of salt resulting from differences in effects of pentane and 3-hexyne on the reaction medium. Similar effects were observed in the hydrochlorination of 1-phenylpropyne.[6]

A plot (not shown) of log R vs. log [HCl] for the data obtained with 3-hexyne at 25° in the absence of salt has a slope of about 2, similar to that found earlier for 1-phenylpropyne, but exhibits curvature over the range of concentration stuided. Satchell[7] has studied the protonation equilibria of aniline bases in HCl–HOAc solutions. With 4-chloro-2-nitroaniline as base he finds that the ratio of protonated to unprotonated base increases linearly with HCl concentration up to 0.1 M but that the ratio increases faster than HCl concentration above 0.1 M acid. Satchell's data with 4-chloro-2-nitroaniline can be employed to define an acidity, A, similar to h_0, applicable to the acid concentrations involved in the present work.

Since HCl and chloride salts are largely undissociated in acetic acid,[8] the main equilibrium with an indicator base, I, involves HCl (either molecular or ionized but undissociated) and the anilinium chloride ion pair (eq 1). The equilibrium is governed by eq 2, where the

$$I + HCl \rightleftharpoons [IH^+Cl^-] \qquad (1)$$
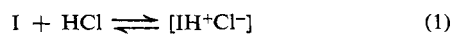
(7) D. P. N. Satchell, *J. Chem. Soc.*, 1916 (1958).
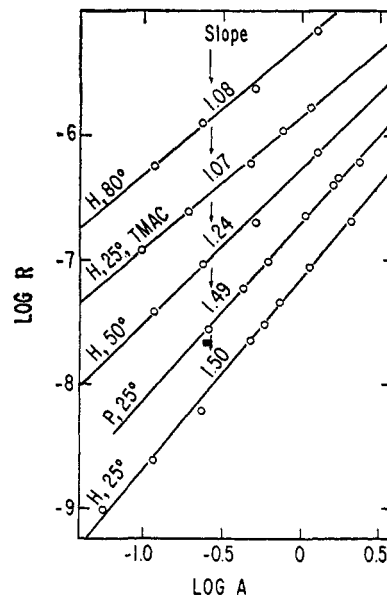(8) I. M. Koltoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956), and references therein.

Figure 2. Plot of log R vs. log A for the hydrochlorination of 3-hexyne (H) and 1-phenylpropyne (P) in acetic acid; acetylene concentration 0.81 M; line labeled TMAC for reaction in the presence of 0.214 M TMAC. Standard deviation of slopes is ±0.03.

$$I_b = \frac{[IH^+Cl^-]}{[I]} = K_b a_{HCl} \frac{\gamma_I}{\gamma_{IH^+Cl^-}} \qquad (2)$$

$$\log A = \log \frac{I_b}{K_b} = \log \left(\frac{a_{HCl}\gamma_I}{\gamma_{IH^+Cl^-}} \right) \qquad (3)$$

equilibrium constant K_b, for 4-chloro-2-nitroaniline as base, is evaluated at 12.8 ± 0.3 from Satchell's data[7] at [HCl] < 0.1 M. Values of log A, as defined by eq 3, were calculated from Satchell's results and are included in Tables I and II.

In Figure 2, log R is plotted vs. log A for the data of Tables I and II. Also included is a plot of the data obtained earlier with 1-phenylpropyne.[6] These plots demonstrate that a reasonably linear dependence of log R upon log A exists, but the slopes of these lines are greater than unity and vary with the reaction conditions.

Addition of TMAC to the reaction medium causes a substantial rate increase. A plot of R vs. [TMAC] is given in Figure 3 and is seen to be reasonably linear while a plot of R vs. [TMAC]$^{1/2}$ (not shown) exhibits substantial curvature. The magnitude of the effect is too large to be attributed to a salt effect so that TMAC must exert a catalytic effect upon the reaction.

It should also be noted (Table I) that small amounts of water significantly accelerate the reaction.

Variations in the Product Composition. The product composition from the hydrochlorination of 3-hexyne is a sensitive function of the hydrogen chloride concentration. This can be seen in Figure 4 where the ratio %T/(%K + %C) is shown to increase sharply with acid concentration. The effect is largest at 25° and decreases with increasing reaction temperature. The results of Table I show that the fraction of C formed increases markedly with increasing reaction temperature. From Tables I and II it is clear that the presence of water or TMAC in the reaction medium causes a marked increase in the amount of trans-hydrochloride
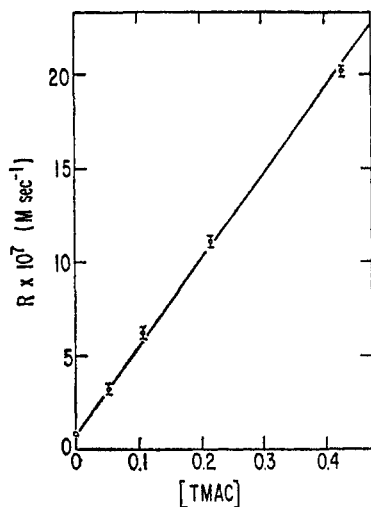
Figure 3. Plot of log R vs. log [TMAC] for the hydrochlorination of 3-hexyne in acetic acid at 25.0° at [HCl] = 0.60 M and [H] = 0.81 M.
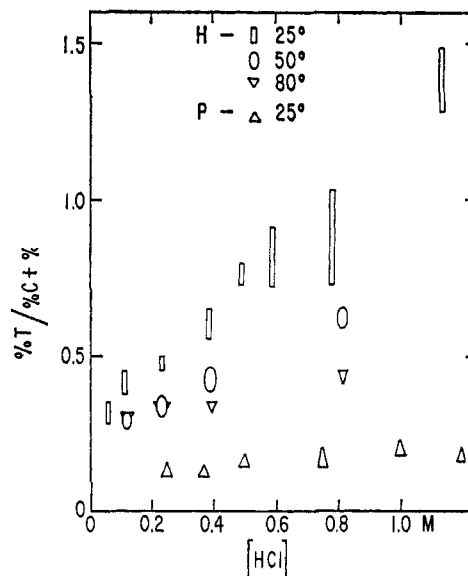

Figure 4. Plot of per cent *trans*-hydrochloride divided by the sum of per cent *cis*-hydrochloride and per cent ketone vs. [HCl] for the hydrochlorination of 3-hexyne (H) and 1-phenylpropyne (P).

(T) formed. In fact, the increase in rate produced by added water or TMAC can be associated almost entirely with an enhanced rate for formation of T.

The product distribution obtained in the hydrochlorination of 1-phenylpropyne (P) at 25°[6] differs from that found for 3-hexyne. The major product is the *cis*-hydrochloride (C'). Moreover, the product
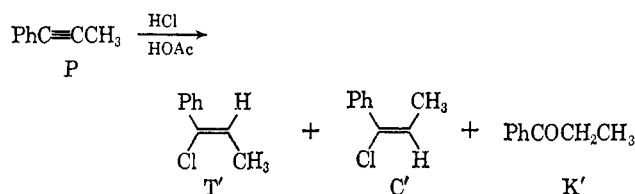
distribution is little affected by the acid concentration. This is evident in Figure 4 where the ratio %T'/(%C' + %K') is seen to vary little with the HCl concentration.

Discussion

Limiting Mechanisms for Addition of Acids to Acetylenes. As an initial working hypothesis, three limiting mechanisms can be considered for the addition of an acid (HA) to an acetylene (Y). The first, molecular addition, involves synchronous attachment of HA across the acetylenic bond and must occur with *cis* stereospecificity.

Molecular addition
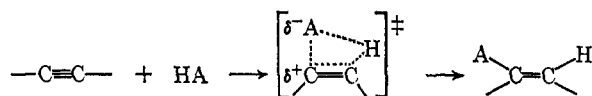
The second mechanism involves stepwise addition *via* a carbonium ion intermediate. In its simplest form this mechanism is bimolecular and can be conveniently denoted as Ad_E2 (addition, electrophilic, bimolecular) using Ingold's system of notation.[9] If the intermediate

cation has bridged structure **1**, *trans* addition might be

Ad_E2 addition

$$Y + HA \xrightarrow{slow} YH^+A^- \xrightarrow{fast} products$$
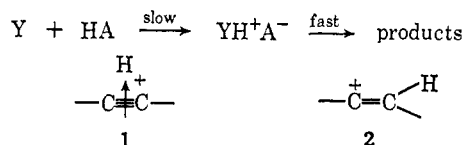

expected to occur, but if an open vinyl cation **2** is involved, nonstereospecific addition should occur. The third mechanism for addition involves a transition state in which both the C–H and C–A bonds are formed in the transition state but in which H$^+$ and A$^-$ derive from different molecular (or ionic) species. This mechanism is termolecular in character and can therefore be classified as Ad_E3.

Ad_E3 addition

$$Y + RA + HA' \longrightarrow [R^+A\cdots Y\cdots HA'^-]^{\ddagger} \longrightarrow$$
$$YHA + R^+ + A'^-$$
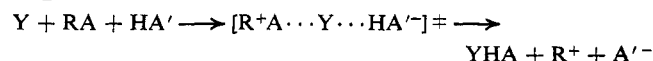
In principle, Ad_E3 addition can occur *cis*, *via* a transition state such as **3**, or *trans* through a transition state resembling **4**. The Ad_E2 and the Ad_E3 mechanisms
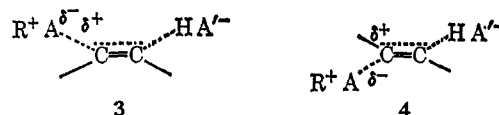
for addition are seen to be closely related to the reverse of the E1 and E2 mechanisms of elimination.[10] If the same stereoelectronic factors which favor E3 *trans* elimination over E2 *cis* elimination are important in addition reactions, then Ad_E3 *trans* addition should be favored over Ad_E3 *cis* addition.

Earlier studies have provided substantial support for an Ad_E2 mechanism involving a vinyl cation intermediate **2** in the addition of acids to acetylenes. The

(9) C. K. Ingold, "Structures and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(10) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963.

present results on the hydrochlorination of 3-hexyne provide strong support for the existence of an Ad_E3 *trans*-addition mechanism.

The Hydrochlorination of 3-Hexyne–Ad_E3 *trans* **Addition.** The main distinction between the Ad_E2 and the Ad_E3 mechanisms for addition lies in whether or not nucleophilic attack occurs in the slow step for addition or in some subsequent fast second step. The fact that the ratio of T to K varies with the HCl concentration and with the concentration of added TMAC does not distinguish between these mechanisms. In principle, the Ad_E2 and the Ad_E3 mechanisms are distinguishable on the basis of kinetic studies. Second-order kinetics should obtain for Ad_E2 addition and third-order kinetics for Ad_E3 addition, but the present results do not allow a clear distinction for the uncatalyzed reaction of 3-hexyne with HCl for two reasons. First, the formation of K depends upon attack by acetic acid as the nucleophile, and, since acetic acid is present in large concentration, it is impossible to demonstrate the kinetic order in this component. Secondly, the actual kinetic order in HCl is uncertain owing to the uncertainties in the interpretation of the slopes of the plots of log R *vs.* log A (Figure 2). The fact that the observed slopes are larger than unity could be taken to indicate that a kinetic dependence on a_{HCl} of greater than one exists for some component of the reaction, or it could be interpreted as indicating that the indicator base, 4-chloro-2-nitroaniline, used to define A is not a suitable model compound with which to compare the protonation of 3-hexyne. Thus, on the basis of these results it is not possible to definitively distinguish between the Ad_E2 and Ad_E3 mechanisms. However, if an Ad_E3 mechanism, in which one molecule of HCl serves as electrophile and another as nucleophile, is involved, then the reaction leading to chloride should be accelerated by chloride salts, since these would serve as more effective sources of nucleophilic chloride than would HCl. That this is so is clearly demonstrated by the result obtained with added TMAC (Table II).

The TMAC-catalyzed reaction can be analyzed in a quantitative fashion by considering explicitly the rate of formation of the *trans*-hydrochloride, $R^T = d[T]/dt = \%T \times R$. In the presence of TMAC, we can express the results

$$R^T = R_0^T + k_3[H][TMAC]A^{1.07}$$

where R_0^T is the rate of formation of T in the absence of TMAC calculated from the data of Table I. From Figure 3 and the fact that T is the major reaction product, it is clear that the second term on the right of this equation dominates the reaction when [TMAC] > 0.05 M. The transition state for the TMAC-catalyzed reaction is composed of 3-hexyne, TMAC, and HCl and has a geometric arrangement favorable to the formation of T. This corresponds to an Ad_E3 *trans*-addition mechanism in which the transition state is described by 4 with $R^+ = (CH_3)_4N^+$ and $A'^- = Cl^-$. From the data of Tables I and II we find $10^6k_3 = 7.7 \pm 0.5, 57 \pm 4$, and 430 ± 30 M^{-2} sec^{-1} at 25.0, 50.0, and 80.0°, respectively. From these values were calculated $\Delta H^\ddagger = 14.5 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -33 \pm 2$ cal/mol deg.

There are reasons to believe that the hydrochlorination of 3-hexyne in the absence of TMAC also occurs primarily by an Ad_E3 *trans*-addition mechanism. Since

TMAC is an effective catalyst for Ad_E3 addition, it is reasonable to expect that HCl can serve the same function, albeit less efficiently. The fact that water accelerates the reaction in much the same fashion as TMAC is consistent with this view, since water should serve to promote the ionization of HCl (through formation of $H_3O^+Cl^-$ or more highly solvated species)[8] and thereby increase its effectiveness as a nucleophile. Finally, it is easy to understand why the ratio of T to K exhibits a substantial dependence upon the HCl concentration if an Ad_E3 process is involved for addition to 3-hexyne, but if an Ad_E2 process is involved for addition to both 1-phenylpropyne and 3-hexyne then we are faced with a dilemma. The cation formed from 1-phenylpropyne should be more stable (and therefore more selective) than the cation formed from 3-hexyne, and the product distribution from 1-phenylpropyne should be even more sensitive to the acid concentration than that from 3-hexyne, but just the opposite is observed. On the basis of these arguments it seems probable that the *trans* hydrochlorination of 3-hexyne in the absence of chloride salts occurs largely or completely by an Ad_E3 mechanism. The transition state for this process is considered to resemble 4 with $R^+ = H^+$ and $A'^- = Cl^-$.

We think it likely that the HCl-catalyzed addition of acetic acid to 3-hexyne, which leads ultimately to the formation of 3-hexanone, also occurs largely by an Ad_E3 mechanism. However, there is no direct evidence to support this view and it is based largely on the assumption that the high concentration of acetic acid effectively compensates for its lower nucleophilicity relative to HCl and TMAC.

The Hydrochlorination of 1-Phenylpropyne–Ad_E2 Addition. The hydrochlorination of 1-phenylpropyne was discussed previously[6] in terms of an Ad_E2-type mechanism, but the present results suggest that some modification of the earlier description is needed. At the time the earlier studies were completed, it was considered that the apparent second-order dependence on the HCl concentration was associated with the specific solvation of the chloride ion formed in the slow step of the reaction and that the intermediate formed in the rate-limiting step was best described as a vinyl cation–hydrogen dichloride ion pair. If this description is correct, it implies that a substantial driving force exists for the formation of HCl_2^- from HCl and Cl^-, which would in turn require that the equilibrium lie mainly to

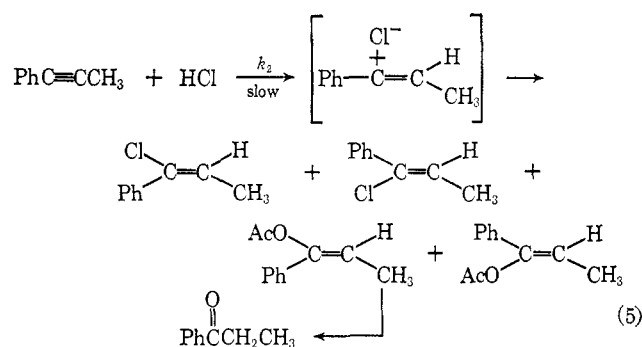$$[(CH_3)_4N^+Cl^-] + HCl = [(CH_3)_4N^+HCl_2^-] \qquad (4)$$
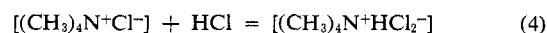
the right in acetic acid. The data of Table II are not consistent with this conclusion, for if TMAC converts a significant fraction of the HCl to the weakly acidic tetramethylammonium hydrogen dichloride, then TMAC at concentrations comparable to the HCl concentration would have a rate-retarding effect upon acid addition. This is indeed the case for the hydrochlorination of olefins in nitromethane as solvent,[11] but the data of Table II show that it is not so for hydrochlorination in acetic acid. It is, therefore, unreasonable to assume that HCl_2^- is the counterion formed in the slow protonation of 1-phenylpropyne in acetic acid.

The plot of log R *vs.* log A (Figure 2) for the hydrochlorination of 1-phenylpropyne is reasonably linear with a slope of 1.49. This observation does not con-

(11) Y. Pocker, *J. Chem. Soc.*, 1291 (1960).

clusively demonstrate the kinetic order in HCl, but shows that the reaction rate is linear in the effective acidity of the medium. The simplest hypothesis is to assume that the reaction is first order in HCl (molecular or ionized, but undissociated) and that the deviation from unit slope reflects the inadequacy of 4-chloro-2-nitroaniline as a model compound for the protonation of 1-phenylpropyne. The Ad_E2 addition to 1-phenylpropyne can then be described in minimum detail by a slow proton transfer from HCl to the acetylene to form a vinyl cation–chloride ion pair which then undergoes rapid conversion to a mixture of cis-hydrochloride ($\sim75\%$), trans-hydrochloride ($\sim10\%$), and a mixture of

$$PhC\equiv CCH_3 + HCl \xrightarrow[slow]{k_2} \left[Ph-\overset{\overset{Cl^-}{+}}{C}=C\overset{H}{\underset{CH_3}{\diagup}} \right] \longrightarrow$$

(5)

acetates ($\sim15\%$).[6] Arguments were presented earlier[6] which suggested that more than one ion-pair intermediate is involved in the mechanism.

Competition between Ad_E2 and Ad_E3 Addition. One of the most striking results of these studies is that the hydrochlorination of 1-phenylpropyne and 3-hexyne occur at comparable rates but by different mechanisms. However, closer examination of the results shows that Ad_E2 and Ad_E3 addition are nearly competitive processes for addition to 3-hexyne. Specifically, the formation of cis-hydrochloride (C) and the increase in the fraction of C formed with increasing reaction temperature (Table I) can be taken as evidence that a small, but significant, fraction of the reaction occurs via an Ad_E2 mechanism.

It is of interest to compare the rate of cis-hydrochloride formation from 3-hexyne with that from 1-phenylpropyne. From the data of Table I and the previous results[6] it is possible to estimate that cis addition of HCl to 1-phenylpropyne at 25.0° occurs at a rate 250-fold faster than that to 3-hexyne, but this factor neglects the differences in symmetry of the two systems. Thus, addition to 3-hexyne can be initiated by attack at either of the two equivalent acetylenic carbon atoms while attack on 1-phenylpropyne occurs only at C_2. Moreover, attack at a given carbon of 3-hexyne can take place from any one of three directions (5) while attack at C_2 in 1-phenylpropyne can occur at only one position (6) to
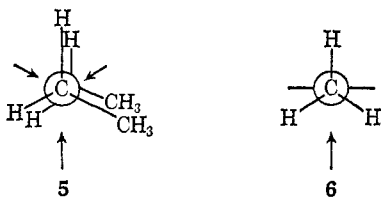
produce a resonance-stabilized vinyl cation. Of course, all three sites of attack in **5** are not equivalent and other conformations than that of **5** may be important, but

these considerations indicate that 3-hexyne should react at least twice as fast, and possibly as much as six times as fast, as 1-phenylpropyne on the basis of the available sites of attack alone. After correction by this factor, 3-hexyne is seen to undergo cis addition of HCl between 500 and 1500 times slower than 1-phenylpropyne, and this is the order of difference of reactivity which would be expected from an Ad_E2 addition via a vinyl cation intermediate. This rate difference can be compared to the nearly 300-fold lower reactivity of t-butylethylene than of styrene toward HCl in acetic acid. There exists good evidence that the latter reactions proceed by an Ad_E2-type mechanism.[12] The data of Table I can be utilized to calculate activation parameters for the cis hydrochlorination of 3-hexyne by assuming a rate law of the form

$$d[C]/dt = k_2{}^C A^n[H]$$

Values of n were assumed to be 1.10 and 1.00 at 50 and 80°, respectively, giving corresponding values for $10^9 k_2{}^C$ of 10 ± 2 and $270 \pm 40 \, M^{-1} \, sec^{-1}$. From these values were calculated $\Delta H^{\ddagger} = 23 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = -20 \pm 6$ cal/mol deg. Comparing these values with those obtained above for the TMAC-catalyzed trans hydrochlorination, we see that cis hydrochlorination has a larger enthalpy and less negative entropy of activation. These differences are consistent with the view that the cis hydrochlorination of 3-hexyne occurs by an Ad_E3 mechanism while the TMAC-catalyzed trans hydrochlorination occurs by an Ad_E3 mechanism.

If Ad_E2 addition is nearly competitive with Ad_E3 addition in the hydrochlorination of 3-hexyne, it might be expected that Ad_E3 addition should nearly compete with Ad_E2 addition in the hydrochlorination of 1-phenylpropyne. Although our previous work[6] provided no definite evidence for an Ad_E3 mechanism, preliminary studies of the effect of TMAC on the reaction show that chloride salts can catalyze Ad_E3 trans addition of HCl to 1-phenylpropyne.[13]

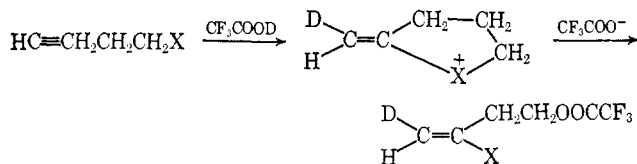**The Factors Affecting Ad_E2 and Ad_E3 Addition.** It is clear that a number of factors affect the balance between Ad_E2 and Ad_E3 addition. From the results on the hydrochlorination of 3-hexyne we see that Ad_E2 addition is favored relative to Ad_E3 addition by an increase in reaction temperature. The observed change from Ad_E3 to Ad_E2 addition upon changing the substrate from 3-hexyne to 1-phenylpropyne shows that the presence of substituents at the acetylenic bond which can delocalize positive charge favors Ad_E2 addition more than Ad_E3 addition. It is expected that Ad_E3 addition should be more subject to steric retardation resulting from the presence of bulky substituents at the acetylenic bond than should Ad_E2 addition, but explicit evidence for this is not yet available.

The Ad_E3 mechanism for acid addition requires the presence in the reaction medium of an effective nucleophile as well as a strong acid. In the absence of a good nucleophile Ad_E2 addition is expected to become relatively more important. The addition of trifluoroacetic acid (TFA) to acetylenes appears to occur quite predominantly by the Ad_E2 mechanism.[4] This is not difficult to understand, however, since TFA is weakly nucleophilic and would serve as a poor nucleophile for

(12) R. C. Fahey and C. A. McPherson, unpublished results.
(13) R. C. Fahey, D.-J. Lee, and M. T. Payne, unpublished results.

Ad_E3 addition. For TFA addition to 5-halo-1-pentynes, Peterson and coworkers[6,14] have shown that the halogen substituent accelerates the rate of addition and that 1,4-halogen shifted products are formed. Especially significant is the observation by Peterson and Bopp[14] that the halogen shift occurs with >92% *trans* stereospecificity when the addition is carried out in deuterated solvent; this corresponds, in effect, to an "internal" Ad_E3-type addition to the triple bond yield-

ing a halonium ion intermediate.

For acid additions to acetylenes that form vinyl cations less readily than 3-hexyne, owing to the presence of electron-withdrawing substituents, the importance of nucleophilic attack in the transition state should be of even greater importance than for addition to 3-hexyne. The hydrochlorination of $CH_3COOC{\equiv}CCOOCH_3$ in acetic acid is reported to occur at a rate which is faster than that found here for 3-hexyne.[15] However, the addition is promoted by either LiCl or HCl, and LiCl is about four times more effective than HCl. Trichloroacetic acid has no effect on the rate but small amounts of water accelerate the reaction. Finally, the rate increases with structure in the order $PhC{\equiv}CCOOCH_3$ < $HC{\equiv}CCOOCH_3$ < $CH_3OOCC{\equiv}CCOOCH_3$. It seems clear that, for acetylenecarboxylic acid derivatives, nucleophilic addition dominates the reaction. Dvorko and coworkers[16] have reported extensive kinetic studies of these additions.

Conclusions

The most important feature of the present study is the demonstration of an electrophilic, termolecular, *trans* addition mechanism for acid additions to acetylenes. How general or important this mechanism will prove to be remains to be seen, but it is worth pointing out that analogous evidence to that presented here has been obtained for competing bimolecular (Ad_E2) and termolecular (Ad_E3) mechanisms in the hydrochlorination of cyclohexene[17] and that the *trans* hydrobromination of cyclohexene reported earlier[18] may well involve an Ad_E3 *trans*-addition mechanism. Thus, it is unlikely that the hydrochlorination of 3-hexyne represents an entirely isolated and special case of this type of reaction.

It should be added that the results presented here provide no insight into the steps which precede formation of the transition state for either Ad_E2 or Ad_E3 addition and, in particular, give no hint as to what extent C–H bond formation precedes formation of the

transition state. Thus, rapid reversible formation of a molecular complex between HCl and the acetylene or of a π complex (1) could be involved in either mechanism. Further studies are needed to clarify this aspect of the reaction mechanism.

Experimental Section

An Aerograph Model 200 chromatograph equipped with thermal conductivity detectors and a linear temperature programmer was employed with a 25 ft × $^1/_8$ in. column (A) containing 20% XF-1150 on Chromosorb P-HMDS for analytical measurements and an 18 ft × 0.25 in. column (B) containing 20% XF-1150 on Chromosorb P-HMDS for preparative separations. Analyses were performed by Dr. Franz Pasher, Mikroanalytisches Laboratorium, Bonn, Germany.

Materials. 3-Hexyne was obtained from Farchan Research Laboratory, purified by spinning-band fractionation (bp 80–81°; 99.9% pure by vpc), and stored under nitrogen. 3-Hexanone and *trans*-3-hexene were purchased from J. T. Baker Chemical Company and 2-butanone was bought from Matheson Coleman and Bell. Glacial acetic acid from Allied Chemical was titrated by the Karl Fischer method using methanol as solvent and was prepared for use by adding 1.05 equiv of acetic anhydride (Eastman Chemical, White Label) per equivalent of water. The hydrolysis reaction is slow at room temperature but rapidly goes to completion when the acid stock solutions are prepared (see below). Tetramethylammonium chloride (Matheson Coleman and Bell) was purified by recrystallization from water.[19]

3-Chloro-*cis*- (C) and 3-Chloro-*trans*-3-hexene (T). A modification of the procedure given by Hoff, Greenlee, and Boord[20] was employed. *trans*-3-Hexene (10 g) was chlorinated at 0° by passing a mixture of chlorine (Matheson Company) and oxygen (to inhibit radical addition[21]) through the neat liquid. The resulting *meso*-3,4-dichlorohexane was dehydrochlorinated with potassium *t*-butoxide in *t*-butyl alcohol at 80° to give 3-chloro-*cis*-3-hexene (C). 3-Hexyne (10 g) was hydrogenated in the presence of activated Raney nickel (Cenco) in ethanol at room temperature and atmospheric pressure. Chlorination of the resulting *cis*-3-hexene followed by dehydrochlorination as above gave 3-chloro-*trans*-3-hexene (T).

3-Acetoxy-*trans*-3-hexene. The procedure followed was identical with that used for 1-acetoxy-*trans*-1-phenylpropene described previously.[6] Mercuric acetate (2 g) was dissolved in 50 ml of acetic acid; 16 ml of 3-hexyne was added and the mixture heated for 28 hr. After cooling, the solution was shaken with 100 ml of pentane and 100 ml of water; the organic layer was separated, washed twice with water and washed with 10% sodium bicarbonate aqueous solution, and dried over anhydrous potassium carbonate. Evaporation of the pentane left 13.4 g of crude product. Part of this product was purified by vpc using column B at 140° with a helium flow of 50 cc/min. 3-Acetoxy-*trans*-3-hexene was collected and had a retention time of 31 min.

Anal. Calcd for $C_8H_{13}O_2$: C, 67.57; H, 9.92. Found: C, 67.66; H, 9.88.

Kinetic and Product Studies. Solutions of hydrogen chloride (Matheson Company) in glacial acetic acid were prepared by weight and the concentrations determined by the addition of an excess amount of lithium acetate in acetic acid followed by potentiometric titration of the excess lithium acetate against standard *p*-toluenesulfonic acid in acetic acid. For reactions at 25°, the solutions were prepared in 50-ml volumetric flasks by mixing a stock solution of acid with the acetylene, diluting (if necessary), and transferring to a constant-temperature bath (25.0 ± 0.01°) after thorough and rapid mixing of the solution. For the reactions catalyzed by tetramethylammonium chloride (TMAC), a solution of 2.14 *M* TMAC in acetic acid was prepared and used as a stock solution. For the reactions at higher temperature, 50 and 80°, solutions were prepared in a 50-ml volumetric flask equipped with a special delivery tube. After the solution was mixed thoroughly, the flask was inverted, and 5-ml portions of the solution were delivered into 10-ml ampoules which were sealed quickly. The ampoules were then transferred to the constant-temperature baths (50 ± 0.1, 80 ± 0.2°). It was established that no significant reaction occurred during the preparation of the ampoules.

(14) P. E. Peterson and R. J. Bopp, private communication and results reported at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(15) E. A. Shilov and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **91**, 873 (1953); *Chem. Abstr.*, **48**, 10557 (1954).

(16) G. F. Dvorko and P. F. Miranova, *Ukr. Khim. Zh.*, **32**, 362 (1966); *Chem. Abstr.*, **65**, 7014 (1966), and previous papers in this series.

(17) R. C. Fahey and M. W. Monahan, *Chem. Commun.*, 936 (1967), and unpublished results.

(18) R. C. Fahey and R. A. Smith, *J. Am. Chem. Soc.*, **86**, 5035 (1964).

(19) E. Grunwald and A. F. Butler, *ibid.*, **82**, 5654 (1960).

(20) M. C. Hoff, K. W. Greenlee, and C. E. Boord, *ibid.*, **73**, 3329 (1961).

(21) M. L. Poutsma, *ibid.*, **87**, 4285 (1965).

In the work-up procedure, aliquots (5 ml) were mixed with pentane (5 ml) and 10% aqueous sodium chloride solution (25 ml). The organic layer was separated, and the aqueous layer was washed with two 5-ml portions of pentane. The last two organic layers were combined and mixed with a dilute aqueous sodium bicarbonate solution (2 ml). The pentane was removed from the collected organic layer by evaporation, and the first organic layer was then added to the residue. The resulting solution was analyzed by vpc. Control experiments showed that this procedure provided quantitative isolation of the products.

The product mixture from 3-hexyne was analyzed using column A at 108° with a helium flow at 25 cc/min. Retention times (minutes) were: 3-hexyne, 2; 3-chloro-*trans*-3-hexene, 4; 3-chloro-*cis*-3-hexene, 5.5; 3-hexanone, 13. The conversion of 3-acetoxy-*trans*-3-hexene to 3-hexanone was followed using column A at 110° with a helium flow of 30 cc/min. Retention times were: 3-hexanone, 7.5; 3-acetoxy-*trans*-3-hexene, 10. Reaction mixture compositions were calculated from the peak ratios (taken as equal to mole ratios),

measured with a disk integrator attached to the recorder. It was established that this method was valid by calibration with mixtures of known composition.

In a control experiment it was shown that pure 3-chloro-*cis*-3-hexene treated in 1.16 M hydrogen chloride solution at 25° underwent no appreciable isomerization. Similarly, neither chloride C nor T, in a solution of 0.8 M hydrogen chloride, or in a solution of 0.8 M hydrogen chloride and 0.21 M TMAC, showed significant isomerization (more than 1%) after 5 hr at 80°. A solution of 3-hexyne in acetic acid containing 0.214 M TMAC showed no product formation after 24 hr at 80°. A pseudo-first-order rate constant of 7×10^{-4} sec^{-1} for conversion of 3-acetoxy-*trans*-3-hexene to 3-hexanone was measured at 25° with initial acetate and hydrogen chloride concentrations of 0.057 and 1.16 M, respectively.

Addition of Electronegatively Substituted Azides to Allenes

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio. Received December 11, 1967

Abstract: Addition of azides to allenes yields alkylidenetriazolines IV and/or isomers of allenimines III. Picryl azide and tetramethylallene (IX) give 4-isopropylidene-5,5-dimethyl-1-picryl-Δ^2-1,2,3-triazoline (XI) which thermolyzes to N-(1,2,3-trimethyl-2-butenylidene)picramide (XII). Reactions of benzenesulfonyl azide and p-toluenesulfonyl azide with IX yield N-(1,2,3-trimethyl-2-butenylidene)benzenesulfonamide (XV) and N-(1,2,3-trimethyl-2-butenylidene)p-toluenesulfonamide (XVI). The nuclear magnetic resonances of XV and XVI indicate that they suffer severe steric restriction. Thermolysis of ethyl azidoformate in IX results in ethyl 4-isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XX) and 2-ethoxy-4-isopropylidene-5,5-dimethyl-2-oxazoline (XXI). XXI is formed on photolysis of XX. Irradiation of ethyl azidoformate in 1,1-dimethylallene (XXIV) leads to 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (XXV). The chemistry of the products of reaction of azides and allenes is described.

O lefins react with organic azides to give 1,2,3-Δ^2-triazolines I, aziridines II, and imines III.[2] The aziridines II and the imines III result from decomposition of the 1,2,3-Δ^2-triazolines I or from reaction of the olefins with nitrenes derived from decomposition of the azides.[2]

I   II   III
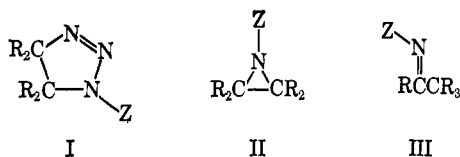
The present investigation is concerned with thermal and photochemical reactions of various azides and allenes and studies of the chemistry of the products obtained therein. Objectives of this research include possible (1) addition of azides to allenes (eq 1) to give alkylidenetriazolines IV which can be decomposed to allenimines[3] V, their isomeric cyclopropanonimines[3] VI, or related isomers VII; and (2) capture of nitrenes by

$$\text{(1)}$$

V   VI   VII

$$N_3Z \longrightarrow NZ + N_2 \quad (2)$$

$$\text{>C=C=C<} + NZ \longrightarrow V + VI + VII \quad (3)$$
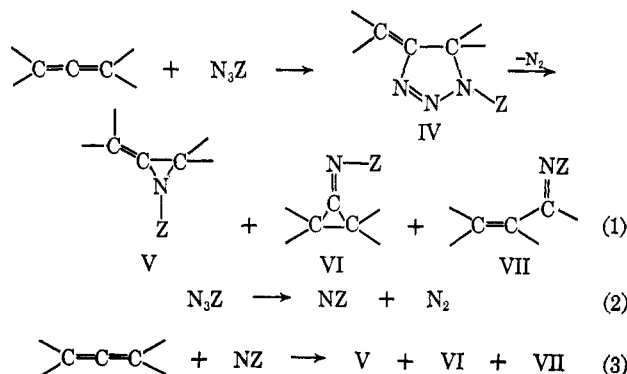
(1) (a) Abstracted from the Ph.D. thesis of R. F. Bleiholder, The Ohio State University, Columbus, Ohio, 1966; (b) to whom inquiries should be addressed.

(2) L. Wolff, *Ann.*, **394**, 23, 59, 68 (1912); K. Alder, and G. Stein, *ibid.*, **485**, 211 (1931); **501**, 1 (1933); P. Scheiner and W. R. Vaughan, *J. Org. Chem.*, **26**, 1923 (1961); P. K. Kadaba and J. O. Edwards, *ibid.*, **26**, 2331 (1961); W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 277 (1962); W. Lwowski, T. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963); L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963); F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964); P. Scheiner, J. Schomaker, S. Deming, W. Libbey, and G. Norwack, *ibid.*, **87**, 306 (1965); P. Scheiner, *J. Org. Chem.*, **30**, 7 (1965).

(3) N-Propylallenimine (A. T. Bottini and R. E. Olsen, *J. Am. Chem. Soc.*, **84**, 195 (1962)) and tetramethylcyclopropanone (N. J. Turro, W. B. Hammond, and P. A. Leermakers, *ibid.*, **87**, 2775 (1965)) are isolable compounds. Their isomers or structures of type VI and VII are as yet unreported.

VIII