spectrometry. Integration of the nmr spectrum (using the C-7-methylene protons as an internal standard) indicated the norbornene (**2**) contained no deuterium, and the mass spectrum confirmed this. All compounds up through the hydroxide **1** were shown to contain one deuterium/molecule by mass spectrometry and nmr spectroscopy.

The fact that the trimethylamine formed from the initial stages of Hofmann elimination of **1** contains 6% trimethylamine-d_1 indicates this reaction proceeds to the extent of not more than 6% by an ylide mechanism. The remaining 94% of the reaction proceeds by some other reaction path, and this can be determined by the following arguments. An E1cb mechanism in this case is unlikely.[3] Equilibration of **1** to give the corresponding *endo* isomer followed by *trans* elimination is also ruled out since it has been shown that the *endo* isomer gives only a trace of norbornene.[5] The only remaining possible mechanism is thus a *cis*-E2 elimination, and this mechanism accounts for 94% of the reaction product. This is analogous to dehydrohalogenations of 2,3-dihalonorbornanes.[9]

The factors affecting this reaction, its occurrence in aliphatic and other alicyclic systems, and the effect of solvents on the mechanism of the reaction will be examined in a full paper.

(9) N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Am. Chem. Soc.*, **85**, 3199 (1963).

(10) Koppers Fellow, 1966; Shell Fellow, 1966–1967.

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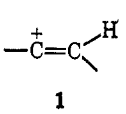
Polar Additions to Olefins and Acetylenes. IV. Evidence for Synchronous C–H and C–Cl Bond Formation in the *trans* Addition of Hydrogen Chloride to 3-Hexyne[1]

Sir:

A somewhat confusing picture has developed regarding the stereochemistry of acid additions to acetylenes. These additions were once thought to be stereospecific *trans* processes based on studies of acetylenecarboxylic acid derivatives,[2] but recent studies have shown that 3-hexyne adds trifluoroacetic acid nonstereospecifically[3] and that the hydrochlorination of 1-phenylpropyne in acetic acid yields a mixture of *cis* and *trans* adducts.[4] Nonstereospecific addition is readily understood if vinyl cations **1** are formed as intermediates in these additions, and for additions in polar media there is substantial evidence[5] to support this hypothesis. The factors leading to stereospecific *trans* addition are less clear. One possibility is that a slow protonation leads to a bridged cation (or π complex) **2** which then collapses rapidly to *trans* adduct. Another explanation, analogous to that proposed by Hammond[6] for olefins, is that *trans* addition occurs *via* transition state **3** in which the C–H and C–X bonds are simultaneously formed. We report here studies of the hydrochlorination of 3-hexyne in acetic acid which show that *trans* addition can occur *via* the latter process.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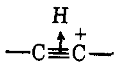
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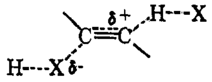
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The hydrochlorination of 3-hexyne in acetic acid yields 3-chloro-*trans*-3-hexene[7] (**4**), 3-chloro-*cis*-3-hexene (**5**), and 3-hexanone (**6**), the latter undoubtedly formed *via* the intermediate vinyl acetate.[4,8] The reaction was followed by quenching samples of the reaction mixture in water, extracting three times with pentane, and analyzing the pentane fraction by vpc. Control experiments showed that **4**, **5**, and **6** are stable under the reaction conditions, that no fractionation occurs in the work-up, and that **4**, **5**, and **6** comprise >95% of the total product. The reaction was studied in the presence and absence of tetramethylammonium chloride (TMAC), and initial rates, R, for total product formation and product compositions were determined at less than 10% conversion. The results are presented in Table I. To these may be added the observations that, in the absence of both TMAC and HCl or in the presence of TMAC and absence of HCl, no reaction occurs.

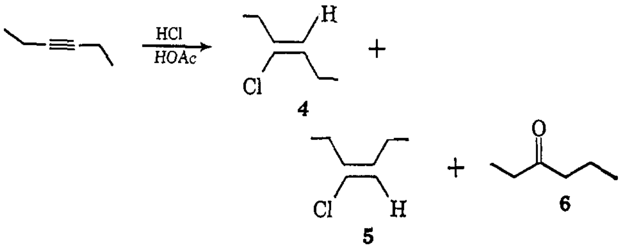

Table I. The Hydrochlorination of 3-Hexyne in Acetic Acid at 25.0°[a]

[HCl], M	[TMAC], M	10^7R, M sec^{-1}	Product composition, % 4	5	6
0.49	...	0.30	42	≤1	58
0.78	...	0.81	48	≤1	52
1.14	...	2.0	58	≤1	42
0.60	0.054	3.0	91	≤0.2	9
0.60	0.11	5.8	94	≤0.2	6
0.60	0.21	11	96	≤0.2	4
0.78	0.21	16	97	≤0.2	3
0.38	0.21	5.7	96	≤0.2	4
0.19	0.21	2.3	97	≤0.2	3

[a] 3-Hexyne concentration 0.81 M.

Under identical reaction conditions the steric course of addition to 1-phenylpropyne and to 3-hexyne is strikingly different: 1-phenylpropyne yields a mixture of adducts with the *cis* hydrochloride predominating, while 3-hexyne gives nearly equal amounts of ketone and *trans* hydrochloride but only a trace of *cis* hydrochloride. It is found that 3-hexyne reacts about three-

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[1] Acknowledgment is made to the U. S. Army Research Office (Durham) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] R. Friedrich, *Ann.*, **219**, 320, 368 (1883); A. Michael, *J. Prakt. Chem.*, [2] **46**, 209, 289 (1895); A. Michael and G. H. Scadinger, *J. Org. Chem.*, **4**, 128 (1939); G. Drefahl and C. Zimmer, *Ber.*, **93**, 505 (1960).

[3] P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966).

[4] R. C. Fahey and D. J. Lee, *ibid.*, **88**, 5555 (1966).

[5] See D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *ibid.*, **87**, 2295 (1965), and references therein.

[6] G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954); G. S. Hammond and C. H. Collins, *ibid.*, **82**, 4323 (1960).

[7] Authentic samples were prepared as described previously: M. C. Hoff, K. W. Greenlee, and C. E. Boord, *ibid.*, **73**, 3329 (1951).

[8] E. A. Jefferey and D. P. N. Satchell, *J. Chem. Soc.*, 1876 (1962).

fold more slowly than 1-phenylpropyne.[4] The ratio of chloride to ketone is found to increase substantially with the HCl concentration for 3-hexyne but was shown to undergo no significant change for 1-phenylpropyne.[4] These observations indicate that a different mechanism operates for addition to 3-hexyne than for 1-phenylpropyne.

As the results in Table I show, TMAC greatly enhances the rate of formation of *trans* chloride but has little effect on the rate of formation of ketone. At 25° the rates for product formation can be expressed approximately as

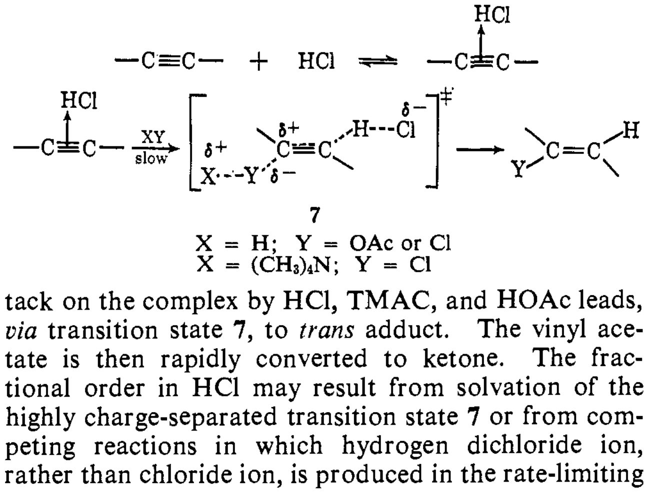
$$d[\mathbf{4}]/dt = kA[\mathrm{HCl}]^{2.6} + k'A[\mathrm{TMAC}][\mathrm{HCl}]^{1.4}$$

$$d[\mathbf{6}]/dt = k''A[\mathrm{HCl}]^{1.8}$$

where A is the concentration of 3-hexyne. The numerical values of the rate constants for these expressions are probably not meaningful since it is not yet clear whether the fractional orders in HCl should be associated with changes in the solvent character at the high concentrations employed here or with rate expressions involving first-, second-, and third-order terms in HCl. In either case it is clear that chloride formation in the absence of TMAC is associated with a rate equation approximately one order higher in HCl than that for ketone formation or for the TMAC-catalyzed reaction. These results are unexpected for a mechanism involving the formation of a cationic intermediate but are in accord with a mechanism involving synchronous formation of the C–H and C–X bonds.

The mechanism can be formulated as shown in Scheme I. Since acetylenes[9] and other unsaturated hydrocarbons[10] are known to form weak complexes with HCl, the first step in the reaction is postulated as rapid, reversible complex formation. Competing attack on the complex by HCl, TMAC, and HOAc leads, *via* transition state 7, to *trans* adduct. The vinyl acetate is then rapidly converted to ketone. The fractional order in HCl may result from solvation of the highly charge-separated transition state 7 or from competing reactions in which hydrogen dichloride ion, rather than chloride ion, is produced in the rate-limiting step. The results show that, in the apparent rate equation, k' is over 100 times larger than k, which is consistent with TMAC being a better nucleophile than HCl.

Scheme I



7

X = H; Y = OAc or Cl
X = (CH$_3$)$_4$N; Y = Cl

The observation that 3-hexyne in refluxing trifluoracetic acid undergoes nonsterospecific addition[3] suggests that the stepwise vinyl cation mechanism and the synchronous mechanism are both accessible for addition to 3-hexyne depending upon the reaction conditions. Trifluoroacetic acid, being polar and strongly acidic but weakly nucleophilic, should favor addition *via* a vinyl cation intermediate. There is, in fact, evidence suggesting that a vinyl cation mechanism may be competitive with the synchronous process for the hydrochlorination in acetic acid. Thus, although chloride 5 is a negligible product for addition at 25°, we find that at 80° it amounts to 5% of the total reaction product under kinetically controlled conditions. The present study is being extended to lower acid concentrations and higher temperatures in order to further delineate this apparent competition between stepwise and synchronous addition mechanisms.

[11] Alfred P. Sloan Foundation Research Fellow, 1966–1968.

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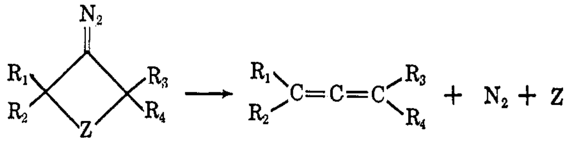
Synthesis of Allenes by Means of Cycloelimination Reactions

Sir:

Although cycloeliminations of the type shown in eq 1 would be of synthetic and theoretical interest, no such reactions have been recorded in the literature. We wish to report the first examples of this type of reaction.



(1)

When an ethereal solution of 4-keto-3,3,5,5-tetramethylpyrazoline hydrazone[1] (1) was treated at room temperature, under nitrogen, with a 10–20% molar excess of nickel peroxide,[2] a transient yellow color was formed and vigorous nitrogen evolution ensued, ceasing after *ca.* 10 min. Analysis of the colorless supernatant by glpc[3] indicated the presence of tetramethylallene (2) in yields of 87–91% (eq 2). Freshly prepared silver(I) oxide is less effective, allene 2 being produced in poor (2.5–3.5%) yield. The tetramethylallene thus produced was identified by comparing its glpc retention times (three different columns) and its infrared, nmr, and mass spectra with those of authentic tetramethylallene. Solutions of the intermediate diazo compound 3 are stable at 0° for at least 30 min, 3 being detectable by its yellow color and by the presence of a strong infrared diazo absorption[4] (2075 cm^{-1} in *n*-decane; 2060

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[9] D. Cook, Y. Lupien, and W. G. Schneider, *Can. J. Chem.*, **34**, 957 (1956).

[10] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, 71, 3573 (1949).

[1] W. L. Mock, Ph.D. Thesis, Harvard University, Cambridge, Mass., Sept 1964. A referee has suggested that, owing to the general inaccessibility of this thesis, the general procedures developed by Mock for the preparation of 1 and 4 be outlined. The 4-keto-3,3,5,5-tetramethylpyrazoline precursor of 1 is obtained from the hypobromite oxidation of the 2,4-diamino ketone resulting from reduction of 2,4-diazido-2,4-dimethyl-3-pentanone with hydrogen sulfide. The diazide may be prepared from the corresponding dibromo ketone [A. Favorsky and A. Umnova, *J. Prakt. Chem.*, **88**, 679 (1913)]. Compound 4 may be prepared from the corresponding ketone which is obtained from the peracetic acid oxidation of the known 2,2,4,4-tetramethyl-3-thietanone [G. Claeson, A. Thalén, and L. Schotte, *Arkiv Kemi*, 21, 295 (1963)].

[2] (a) K. Nakagawa, H. Onoue, and K. Minami, *Chem. Commun.*, 730 (1966); (b) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, 27, 1597 (1962).

[3] Glpc analysis was done on an Aerograph A 90-P3 gas chromatograph using a 5 ft × 0.25 in. column of 20% SE-30 on 60–80 mesh Chromosorb W. Both tetramethylallene and toluene, the internal standard used for the yield determinations, are stable to nickel peroxide under the reaction conditions.