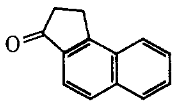
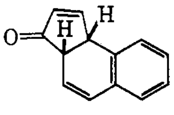
Irradiation of adduct II by a medium-pressure mercury lamp (glass filter, acetonitrile solvent, 20°, nitrogen atmosphere) resulted in the gradual formation of a carbonyl maximum near 1704 cm^{-1} with concomitant decrease in the original carbonyl peak near 1675 cm^{-1}. Silica gel chromatography of the reaction products, followed by sublimation at 80° of the principal chromatographic fraction, gave a new crystalline compound: mp 119–120°; mass spectrum: *m/e* 182, 153, 126, 76; $\nu_{\text{max}}^{\text{CHCl}_3}$ 1707 cm^{-1}; $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ (mμ) 250 (ϵ 61,800), 274 (8700), 284 (10,200), 296 (6600), 330 (2930), 342 (3250); nmr spectrum: A_2B_2 pattern (4 H) with δ_A 2.85, δ_B 3.32, and an aromatic multiplet (6 H) at δ 7.5–8.2. *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.70; H, 5.53; mol wt, 182. Found: C, 85.99; H, 5.75. Taken with the fact that sodium borohydride reduction of this photoproduct generated the ultraviolet spectrum of a 1,2-dialkylnaphthalene, the above data require the photoisomer to contain a conjugated ketone within a five-membered ring fused to the naphthalene nucleus. Three such ketones are possible; all are known and only isomer IV (lit. mp 120–121°) is compatible with the observed melting point. Moreover, the highly structured ultraviolet spectrum of the photoproduct is superimposable with that depicted for authentic ketone IV,[12] and identity was confirmed by comparison with an authentic sample.


IV


V

It can be shown spectroscopically that ketone IV is not present in the photolysis solution during irradiation but can be instantly generated therein by addition of base. We propose that the primary step in the photoisomerization is the rearrangement of II to the diolefinic ketone V,[13] with ultimate isomerization to the aromatic IV taking place during the work-up procedure. Further studies of the ground-state and excited-state chemistry of II and its derivatives are in progress.

(12) R. Huisgen and U. Rietz, *Tetrahedron*, **2**, 274 (1958). We are grateful to Professor Huisgen for providing us with a sample of ketone IV prepared by Friedel–Crafts cyclization of β-(1-naphthyl)propionic acid.

(13) The photoequilibrium between 1,4,4-trimethylbicyclo[3.2.0]-hept-6-en-2-one and 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one discussed by G. Büchi and E. M. Burgess (*J. Am. Chem. Soc.*, **82**, 4333 (1960)) may offer formal analogy to this type of isomerization.

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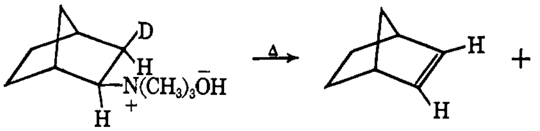
Hofmann Elimination. I. An Example of a *cis*-E2 Mechanism[1]

Sir:

Hofmann elimination of quaternary ammonium hydroxides to give olefins has long been thought to proceed by a *trans* elimination.[2] Only two proven exceptions to this have been reported. One of these involves a *cis*-E2 elimination of N,N,N-trimethyl-*trans*-2-phenylcyclohexylammonium hydroxide to give 1-phenylcyclohexene.[3] This *cis* elimination presumably takes place because of the activating influence of the phenyl group on the β proton (increased acidity). The other exception involves a predominantly *cis*-ylide elimination of N,N,N-trimethyl-2-*t*-butyl-3,3-dimethylbutylammonium-2-d_1 hydroxide to give trimethylamine-d_1.[4]

We wish to report an example of a *cis*-E2 elimination mechanism involving a trimethylammonium hydroxide in which there is no activating group other than the trimethylammonium group. It has been shown[5] that N,N,N-trimethyl-*exo*-2-norbornylammonium hydroxide is smoothly converted to norbornene on heating. We have examined this reaction and find that it proceeds by a *cis*-E2 elimination, as deduced from the following evidence. 2-*exo*-Norbornylamine-3-*exo*-d_1 (bp 159–163° (760 mm); n^{24}D 1.4752; acetamide mp 141.5–142.5°) was prepared from norbornene using diborane-d_6 and chloramine[6] and was then converted consecutively by standard procedures to N,N-dimethyl-2-*exo*-norbornylamine-3-*exo*-d_1 (bp 50–52° (6 mm); n^{25}D 1.4690), N,N,N-trimethyl-2-*exo*-norbornylammonium-3-*exo*-d_1 iodide (mp 297–299°), and then to the hydroxide **1**. Compound **1** was heated (as the dry solid) at 120° under vacuum until trimethylamine could just be detected in the vapors. This initially produced trimethylamine was analyzed by mass spectrometry[7] and was found to contain 6% trimethylamine-d_1. When the pyrolysis was carried to completion the total trimethylamine was found to contain 17% trimethylamine-d_1, with the last traces of vapors containing 21% trimethylamine-d_1. This increase in incorporation of deuterium into the trimethylamine after the initial stages of the reaction has been studied by Cope and co-workers[8] and is due to exchange between the methyl hydrogens of the quaternary hydroxide and the water (containing some deuterium) produced during the reaction. In another experiment the pyrolysis of **1** was carried to completion and the norbornene (**2**) that was formed was purified and examined by nmr and mass



1 2

$(CH_3)_3N$ + $(CH_3)_2NCH_2D$
94% 6%

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(1) This work was supported in part by a Public Health Service Research Grant, HE 07050, from the National Heart Institute, U. S. Public Health Service.

(2) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

(3) G. Ayrey, E. Buncel, and A. N. Bourns, *Proc. Chem. Soc.*, 458 (1961); A. C. Cope, G. A. Berchtold, and D. L. Ross, *J. Am. Chem. Soc.*, **83**, 3859 (1961); S. J. Cristol and F. R. Stermitz, *ibid.*, **82**, 4692 (1960); J. Weinstock and F. G. Bordwell, *ibid.*, **77**, 6706 (1955); R. T. Arnold and P. N. Richardson, *ibid.*, **76**, 3649 (1954).

(4) A. C. Cope and A. S. Mehta, *ibid.*, **85**, 1949 (1963).

(5) A. C. Cope, E. Ciganek, and N. A. LeBel, *ibid.*, **81**, 2799 (1959).

(6) H. C. Brown, W. R. Heydkamp, E. Breuer, and W. S. Murphy, *ibid.*, **86**, 3565 (1964); H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 130. The fact that we find total loss of deuterium on Hofmann elimination precludes the possibility of scrambling at the chloramine reaction stage.

(7) For the method used see A. S. Mehta, Ph.D. Thesis, Massachusetts Institute of Technology, 1963.

(8) A. C. Cope, N. A. LeBel, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **83**, 3861 (1961).

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.

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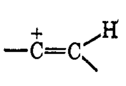
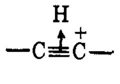
Polar Additions to Olefins and Acetylenes. IV. Evidence for Synchronous C–H and C–Cl Bond Formation in the *trans* Addition of Hydrogen Chloride to 3-Hexyne[1]

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.



1



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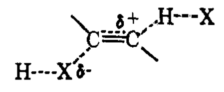

3

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.

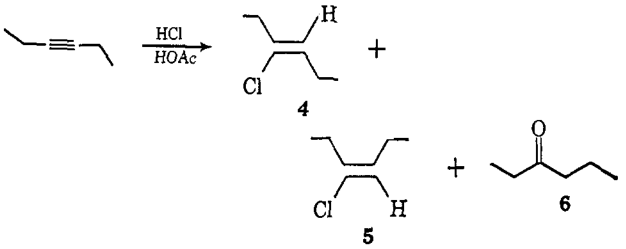

Table I. The Hydrochlorination of 3-Hexyne in Acetic Acid at 25.0°[a]

[HCl], *M*	[TMAC], *M*	10^7R, *M* sec^{-1}	Product composition, % **4**	**5**	**6**
0.49	...	0.30	42	$\leqslant 1$	58
0.78	...	0.8_1	48	$\leqslant 1$	52
1.14	...	2.0	58	$\leqslant 1$	42
0.60	0.054	3.0	91	$\leqslant 0.2$	9
0.60	0.11	$5._8$	94	$\leqslant 0.2$	6
0.60	0.21	11	96	$\leqslant 0.2$	4
0.78	0.21	16	97	$\leqslant 0.2$	3
0.38	0.21	$5._7$	96	$\leqslant 0.2$	4
0.19	0.21	$2._3$	97	$\leqslant 0.2$	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).