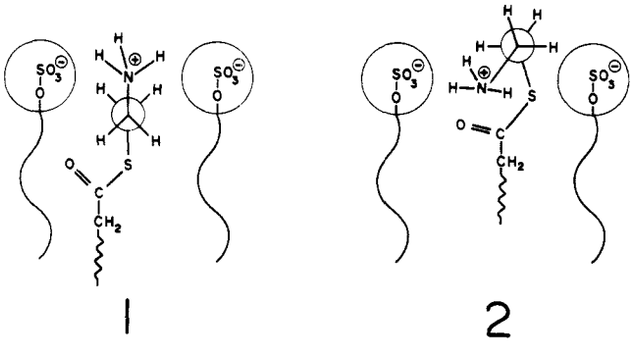
Scheme II



1 2

bution coefficient for this substrate. That this interaction has both electrostatic and hydrophobic components is implied by the 250-fold smaller distribution coefficient for AMA. The hydrophobic, or electrostatic interaction(s), will tend to stabilize the amine segment in the Stern layer; the hydrophobic contribution, on the other hand, will favor the insertion of the long acyl chain in the interior of the micelle. These interactions will favor an elongated configuration of the substrate (form 1, Scheme II). The molecular movement of OMA in SDS micelles will thus be nonisotropic, in the sense that the attainment of the bent conformation, necessary for attack leading to products, will be highly unfavorable (form 2, Scheme II) due, in part, to the exposure of the methylenic bridge to the solvent. Rotational anisotropy of a negatively charged spin probe (*N*-oxyl-4′,4′-dimethyloxazolidine derivative of 5-ketostearic acid) incorporated into a positively charged micelle has recently been described.[22] It has also been proposed, in a SDS inhibited system, that the ionic array of SDS with a positively charged substrate is tight in order to explain the observed stereoselectivity[23] of the reaction.

The rate of S to N transfer in OMA is enhanced about fivefold in the micellar phase of CTAB. The simplest explanation of this (small) effect would be a decrease in the pK of the terminal amine, thus increasing the concentration of the reactive (unprotonated) species. In a related system, it has been shown that micellization of dimethyl dodecyl ammonium chloride produces both an increase in the proton-exchange rate and a decrease in the pK of the ammonium ion of 1.4 pH units.[13] Taking this latter system as references, it would be expected that, in the absence of other effects, the rate acceleration caused by CTAB in the S to N transfer of OMA should be at least 30-fold. The rate acceleration obtained is significantly smaller, and the kinetic results can not be accommodated within the framework of a simple distribution model. This constitutes an indication of the occurrence of a mixed activation–inhibition effect by CTAB on this reaction.

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Registry No.—CTAB, 57-09-0; SDS, 151-21-3; AMA, 17612-91-8; OMA, 17612-92-9; Brij 35, 9002-02-0.

References and Notes

(1) C. A. Bunton, *Progr. Solid State Chem.*, **8**, 239 (1973).
(2) E. H. Cordes, Ed., "Reaction Kinetics in Micelles", Plenum Press, New York, N.Y., 1973.
(3) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular System", Academic Press, New York, N.Y., 1975.
(4) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw Hill, New York, N.Y., 1969.
(5) T. Wieland and H. Hornig, *Ann. Chem.*, **600**, 12 (1956).
(6) R. B. Martin, S. Lowey, E. L. Elson, and J. T. Edsall, *J. Am. Chem. Soc.*, **81**, 5089 (1959).
(7) R. B. Martin and A. Parcell, *J. Am. Chem. Soc.*, **83**, 4830 (1961).
(8) R. B. Martin, R. I. Hedrick, and A. Parcell, *J. Org. Chem.*, **29**, 3197 (1964).
(9) R. B. Martin and R. I. Hedrick, *J. Am. Chem. Soc.*, **84**, 106 (1962).
(10) R. E. Barnett and W. P. Jencks, *J. Am. Chem. Soc.*, **91**, 2358 (1969).
(11) W. O. Foye, R. N. Duvall, and J. Mickles, *J. Pharm. Sci.*, **51**, 168 (1962).
(12) T. Wieland and E. Bokelman, *Ann. Chem.*, **576**, 20 (1952).
(13) I. V. Berezin, K. Martinek, and A. K. Yatsimirski, *Russ. Chem. Rev. (Engl. Transl.)*, **42**, 787 (1973).
(14) T. C. Bruice, J. Katzhendler, and L. R. Fedor, *J. Am. Chem. Soc.*, **90**, 1333 (1968).
(15) C. A. Bunton and L. Robinson, *J. Phys. Chem.*, **74**, 1062 (1970).
(16) F. M. Menger and J. L. Lynn, *J. Am. Chem. Soc.*, **97**, 948 (1975).
(17) S. Ohnishi, T. J. R. Cyr, and H. Fukushima, *Bull. Chem. Soc. Jpn.*, **43**, 673 (1970).
(18) T. Nakagawa and H. Jizomoto, *Kolloid Z. Z. Polym.*, **250**, 594 (1972).
(19) E. Williams, B. Sears, A. Allerhand, and E. H. Cordes, *J. Am. Chem. Soc.*, **95**, 4871 (1973).
(20) M. Shinitzky, A. C. Dianoux, C. Glitler, and G. Weber, *Biochemistry*, **10**, 2106 (1971).
(21) H. Takahashi, Y. Nakayama, H. Hori, K. Kihara, H. Okabayashi, and M. Okuyama, *J. Coll. Interface Sci.*, **54**, 102 (1976).
(22) J. R. Ernandes, S. Schreier, and H. Chaimovich, *Chem. Phys. Lipids*, **16**, 19 (1976).
(23) C. N. Sukenik, B. Weissman, and R. G. Bergman, *J. Am. Chem. Soc.*, **97**, 445 (1975).

Mechanism of the Meyer–Schuster Rearrangement

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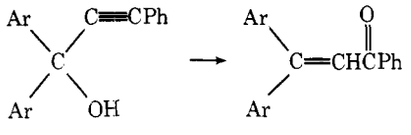
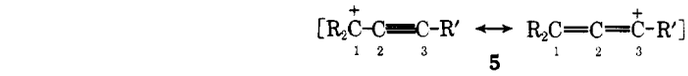
Received January 25, 1977.

The mechanism of the Meyer–Schuster rearrangement of tertiary arylpropargyl alcohols to α,β-unsaturated carbonyl compounds is discussed. The data, inverse solvent isotope effects, k_{H_2O}/k_{D_2O} = 0.36–0.48, ρ vs. σ^+ = −2.3 at the reaction site and −1.6 at the rearrangement terminus, $(k_H/k_d)_\alpha$ at the rearrangement terminus = 0.92, and relatively large negative $\Delta S^\ddagger$, all suggest an ion–dipole intermediate undergoing nucleophilic attack by H_2O as the rate-determining step. The rearrangement of eight triaryl- and diarylpropargyl alcohols is reported.

In 1922 Meyer and Schuster reported that triarylpropargyl alcohols, **1** and **2**, were converted in good yield to α,β-unsaturated ketones **3** and **4** by a variety of acidic catalysts such as CH_3COOH/H_2SO_4, HCl in ether, acetic anhydride, and acetyl chloride.[2] Several reviews concerned with the Meyer–Schuster and related Rupe rearrangements have appeared within the last 10 years.[3,4] Each suggests that alkynyl cations such as **5** are involved in the Meyer–Schuster rear-

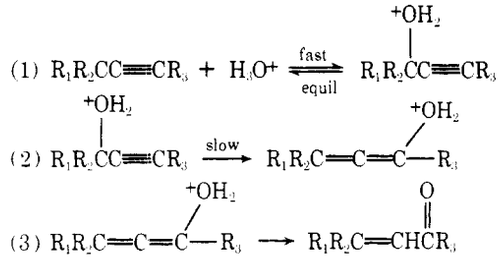


1 Ar = Ph **3**
2 Ar = *p*-ClC_6H_4 **4**

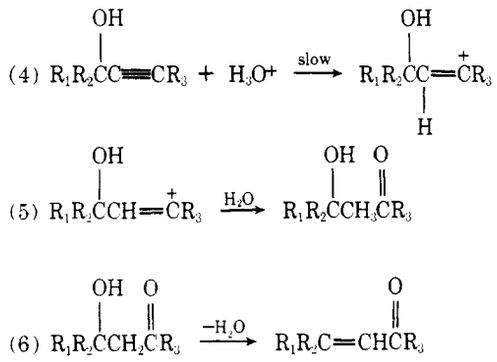


5

Scheme I. Acid-Catalyzed Preequilibrium



Scheme II. Acid-Catalyzed Hydration–Dehydration

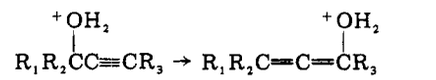


rangement, yet no firm evidence is available to support this contention. Indeed, the mechanistic evidence upon which pathways for the Meyer–Schuster rearrangement have been suggested has been acquired primarily from studies on propargyl alcohols undergoing the related Rupe rearrangement.[5-12] While we did not doubt the intermediacy of a cationic species, we did seek to establish the mechanism of this rearrangement in more detail than had previously been suggested. We therefore used the Schemes I and II as working hypotheses in our study. It should be noted that R_1, R_2, and R_3 must be chosen so that α hydrogens are not available for elimination from carbons adjacent to a cationic center. In our study, we chose R_1 and R_2 = aryl and R_3 = aryl or H in order to satisfy the earlier constraint as well as to avoid skeletal rearrangements known to occur when R_n = branched alkyl.[12]

Scheme I involves a rapid, preequilibrium step followed by slow rearrangement of the conjugate acid. Subsequent ketonization of the resulting allenol is considered rapid. Scheme II involves a rate-limiting proton transfer to carbon followed by rapid hydration of the resulting vinyl cation and subsequent rapid dehydration of the intermediate ketol. While Scheme II appeared unlikely on the basis of mechanistic evidence against its incursion in the Rupe rearrangement of 1-ethynylcyclohexanol to 1-acetylcyclohexene, we noted that the conditions required to effect Meyer–Schuster rearrangement of certain triarylpropargyl alcohols were not dissimilar to those under which arylacetylenes are hydrated to acetophenones via a mechanism involving a carbynium ion.[13]

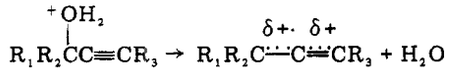
If Scheme I is examined it is apparent that step 2, i.e., the expected rate-limiting step, represents a multitude of kinetically indistinguishable mechanistic possibilities. Three of these are detailed below.

Intramolecular:



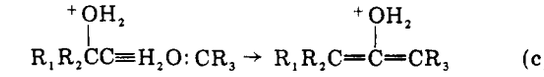
(a)

"Solvolytic":



(b)

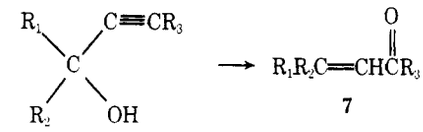
Intermolecular:



(c)

Equations a and b are the classical A-1 and A-2 versions of this rearrangement and imply *covalent* attachment of H_2O in the transition states. Equation b is meant to imply only *electrostatic* interactions, i.e., ion–dipole, of solvent and R^+.

The question of describing the mechanism involved here thus becomes one of deciding first whether proton transfer to the substrate is rate limiting (Scheme II) or not (Scheme I) and secondly, if Scheme I obtains, determining the site(s), i.e., number, and nature, electrostatic or covalent, of the interaction between substrate and associated water molecules. Our task then was to design mechanistic probes which would provide as much detail as possible regarding the rearrangement step. We elected to examine the kinetic behavior of tertiary ethynyl carbinols undergoing the Meyer–Schuster rearrangement exclusively and nearly quantitatively. Compounds **6a–h** were chosen for study.



6 7

a, $R_1 = R_2 = R_3 = C_6H_5$
b, $R_1 = R_2 = C_6H_5$; $R_3 = p\text{-}ClC_6H_4$
c, $R_1 = R_2 = C_6H_5$; $R_3 = p\text{-}CH_3C_6H_4$
d, $R_1 = R_2 = C_6H_5$; $R_3 = p\text{-}CH_3OC_6H_4$
e, $R_1 = R_3 = C_6H_5$; $R_2 = p\text{-}ClC_6H_4$
f, $R_1 = R_3 = C_6H_5$; $R_2 = p\text{-}CH_3OC_6H_4$
g, $R_1 = R_2 = C_6H_5$; $R_3 = H$
h, $R_1 = R_2 = C_6H_5$; $R_3 = D$

Results

Pseudo-first-order rates of rearrangement were measured spectrophotometrically at 3040 or 3100 Å in 40% dioxane:60% aqueous sulfuric acid. Excellent first-order plots were obtained to better than 90% rearrangement. Infinity absorbances indicated that the rearrangement **6** → **7** proceeded to greater than 97% completion in all cases based on molar absorptivities for **7** available in the literature.[14] Values of acidity function, H_0, are available for this medium in the literature.[15] Table I presents the computer-calculated rate data obtained in this study. Figures 1 and 2 display data selected to illustrate the substituent effects and solvent isotope effects observed here. Table II lists the acidity dependence information derived from Table I. Table III contains the secondary isotope-effect data calculated from the paired kinetic runs indicated in Table I, **6g/6h.** The activation parameters calculated from the data in Table I are $\Delta H^{\ddagger} = 20.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7.5$ eu for **6a** and $\Delta H^{\ddagger} = 18.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18.2$ eu for **6g** at 25 °C in 1.5 M H_2SO_4. Substituent effects vs. σ^+ are calculated to be $\rho = -2.3$ ($r = 0.984$) at the reaction center (C-1 in the alkynyl cation, **5**) and $\rho = -1.6$ ($r = 0.973$) at the propargyl position, i.e., C-3. The solvent isotope effects are calculated to be $k_{H_2O}/k_{D_2O} = 0.36$ for **6a** and 0.48 for **6g** in 1.5 M L_2SO_4 at 25 °C. The acidity required to effect measurable rates of rearrangement in these compounds precluded an evaluation of the incursion of specific or general acid catalysis.

Discussion

The inverse solvent isotope effects ($k_{H_2O}/k_{D_2O} < 1$) observed rule out any mechanism in which proton transfer is rate limiting. Consequently, the present discussion is confined to Scheme I.

Table I. Pseudo-First-Order Rate of Acid-Catalyzed Rearrangement 6 → 7 in 40:60 Dioxane/Aqueous H_2SO_4

Compd	T, °C	$M_{L_2SO_4}$[a]	H_0	10^4k_{obsd}, s^{-1}	Compd	T, °C	$M_{L_2SO_4}$[a]	H_0	10^4k_{obsd}, s^{-1}
6a	25.03 ± 0.03	0.74	0.85	0.0878	**6e**	25.03 ± 0.03	2.00	−0.02	0.417
		1.06	0.60	0.273			2.30	−0.21	0.881
		1.70	0.18	0.864			2.60	−0.41	1.77
		2.03	−0.03	2.13			2.74	−0.50	1.94
		2.30	−0.21	3.35			3.18	−0.79	5.43
		2.90	−0.63	15.6			3.51	−1.00	12.4
		0.84[b]	0.77[c]	0.432	**6f**	25.03 ± 0.03	0.34	1.18	1.45
		1.06[b]	0.60[c]	0.713			0.57	1.00	2.12
		1.25[b]	0.47[c]	1.04			0.75	0.84	3.70
		1.70[b]	0.18[c]	2.49			1.00	0.64	6.75
		1.95[b]	0.02[c]	3.87			1.35	0.41	16.3
		2.36[b]	−0.25[c]	9.36			1.70	0.18	34.6
	34.62 ± 0.02	0.63	0.93	0.310	**6g**	25.03 ± 0.03	1.15	0.53	0.0794
		0.67	0.90	0.325			1.30	0.43	0.111
		1.06	0.60	0.891			1.53	0.28	0.202
		1.23	0.49	1.23			1.63	0.22	0.235[d]
		1.54	0.28	2.26			1.84	0.08	0.334[d]
		1.84	0.08	4.12			2.12	−0.09	0.605[d]
							2.38	−0.27	1.05[d]
	45.51 ± 0.04	0.43	1.16	0.590					
		0.67	0.90	1.08	**6g**	25.03 ± 0.03	0.71[b]	0.91[c]	0.0592
		0.88	0.78	1.79			0.79[b]	0.80[c]	0.0772
		1.13	0.55	3.09			0.81[b]	0.78[c]	0.0889
		1.30	0.45	4.09			0.97[b]	0.65[c]	0.118
							1.18[b]	0.53[c]	0.189
6b	24.98 ± 0.04	1.06	0.60	0.128					
		1.13	0.55	0.190		35.00 ± 0.04	0.96	0.66	0.166
		1.46	0.33	0.321			1.13	0.55	0.237
		1.85	0.08	0.713			1.28	0.45	0.316
		2.21	−0.15	1.47			1.54	0.28	0.542
		2.60	−0.41	3.21			1.66	0.21	0.676
							1.85	0.07	0.973
6c	25.03 ± 0.03	0.65	0.93	0.465					
		0.66	0.92	0.495		44.10 ± 0.03	0.52	1.06	0.159
		1.02	0.63	1.13			0.58	0.99	0.205
		1.25	0.48	2.11			0.78	0.80	0.337
		1.46	0.33	3.28			1.00	0.63	0.537
		1.55	0.28	3.88			1.17	0.53	0.733
							1.32	0.43	0.976
6d	25.03 ± 0.03	0.40	1.19	0.690			1.54	0.29	1.53
		0.58	0.99	1.20					
		0.88	0.74	2.76	**6h**	25.03 ± 0.03	1.63	0.22[d]	0.262
		0.93	0.69	3.04			1.84	0.08[d]	0.355
		1.30	0.44	7.01			2.12	−0.09[d]	0.667
							2.38	−0.27[d]	1.14

[a] H_2SO_4 unless otherwise indicated. [b] $M_{D_2SO_4}$. [c] D_0, assuming $D_0 = H_0$ at constant M. [d] Paired runs, **6g/6h**, measured simultaneously in identical solutions.

Table II. Summary of Acidity Dependence Data for the Acid-Catalyzed Rearrangement 6 → 7, $\log k_{obsd} = mH_0 + \log k_0$

Compd	Conditions	−m	Log k_0	r
6a	25 °C, 0.74–2.90 M H_2SO_4	1.483	−3.752	0.9981
	25 °C, 0.84–2.36 M D_2SO_4	1.301	−3.368	0.9998
	35 °C, 0.63–1.84 M H_2SO_4	1.335	−3.268	0.9995
	45 °C, 0.43–1.30 M H_2SO_4	1.200	−2.847	0.9968
6b	25 °C, 1.06–2.60 M H_2SO_4	1.338	−4.039	0.9977
6c	25 °C, 0.65–1.55 M H_2SO_4	1.415	−3.018	0.9987
6d	25 °C, 0.40–1.30 M H_2SO_4	1.348	−2.571	0.9993
6e	25 °C, 2.00–3.51 M H_2SO_4	1.461	−4.392	0.9976
6f	25 °C, 0.34–1.70 M H_2SO_4	1.413	−2.227	0.9975
6g	25 °C, 1.15–2.38 M H_2SO_4	1.388	−4.345	0.9984
	25 °C, 0.71–1.18 M D_2SO_4	1.303	−4.052	0.9936
	35 °C, 0.96–1.85 M H_2SO_4	1.314	−3.906	0.9995
	44 °C, 0.52–1.54 M H_2SO_4	1.251	−3.467	0.9994
6h	25 °C, 1.63–2.38 M H_2SO_4	1.341	−4.308	0.9963

Table III. Secondary Isotope Effect Data for Rearrangement 6g, h → 7g, h at 25 °C

$M_{H_2SO_4}$	H_0	k_H/k_D[a]	$\Delta\Delta F^{\ddagger}/D$
1.63	0.22	0.897	64
1.84	0.08	0.941	36
2.12	−0.09	0.907	58
2.38	−0.27	0.921	49

[a] Calculated from paired runs in Table I.

The Hammett plots above suggest an intermediate in which substantial charge is delocalized from the reaction center to the rearrangement terminus. Indeed, the magnitudes of ρ reported here for **6a–f** are similar to those observed in the solvolysis of triarylhaloallenes where ρ_X and $\rho_Y = -2.0$, thus implying a similar intermediate cationic species.[16] These compounds have been shown to solvolyze via a limiting mechanism in aqueous ethanol and aqueous acetone solutions. Indeed, these data do rule out any rearrangement mechanism which does not involve a cationic intermediate. The question remaining, however, is the degree and nature of involvement by H_2O in the transition state. Some information regarding

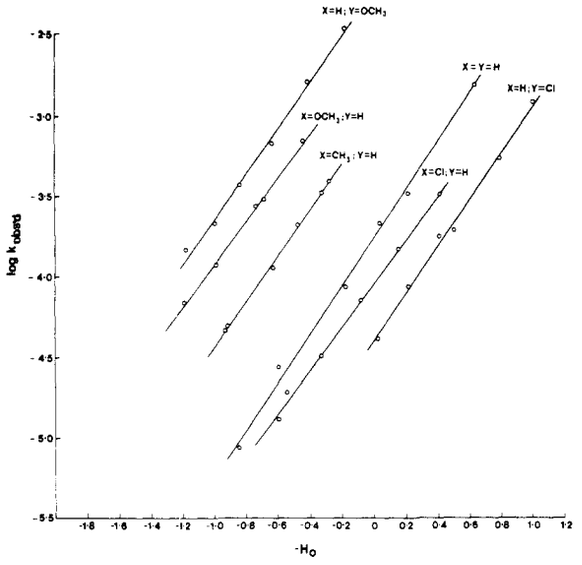


Figure 1. Substituent effects in Meyer–Schuster rearrangement of (*p*-YPh)C(OH)(Ph)C≡C(PhX-*p*).

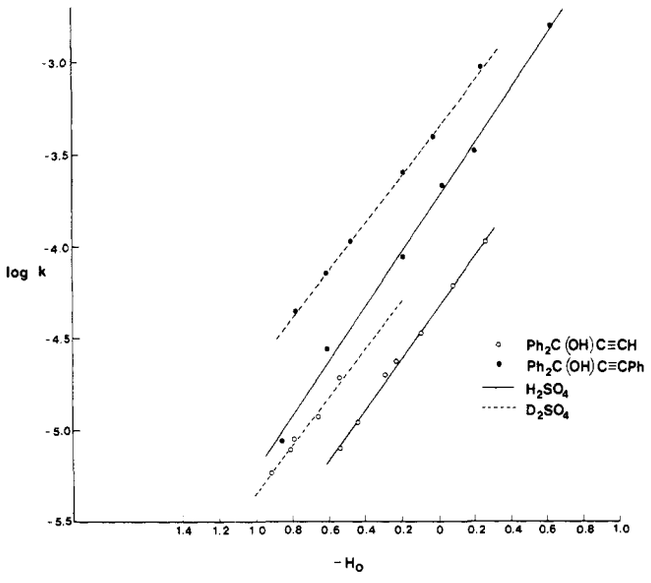


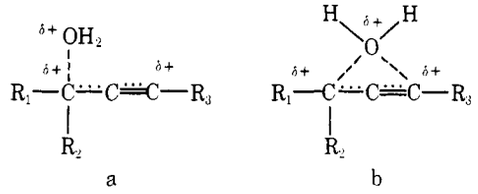
Figure 2. Solvent isotope effects in Meyer–Schuster rearrangement of $Ph_2C(OH)C{\equiv}CH$ and $Ph_2C(OH)C{\equiv}C{-}Ph$ at 25 °C in 40:60 dioxane:aqueous L_2SO_4.

this question can be obtained from a closer examination of the solvent isotope effects observed.

Bunton and Shiner suggested some time ago that a distinction could be made among appropriately chosen models for the transition states of acid-catalyzed reactions by assessing changes in hydrogen bonding strength and number upon formation of the transition-state model and using these changes to calculate the expected solvent isotope effect from a simple empirical expression.[17] While such treatments lead to ambiguous results in a few reported cases, an interesting and distinctive set of predictions is made for six reasonable models, a–f, of the transition state for the present reaction shown in Chart I. These results show that, in general, any covalent attachment of water in the transition state at C-1 or at C-3 leads to an increase in $\Sigma\nu_H - \Sigma\nu^{\ddagger}_H$, i.e., to an increase in k_{H_2O}/k_{D_2O}.[18] Thus, models a, b, and e, which allow covalent interaction by one or two H_2O molecules, exhibit calculated k_{H_2O}/k_{D_2O} ratios of greater magnitude than models c, d, and f which allow only electrostatic interactions of R^+ and H_2O.

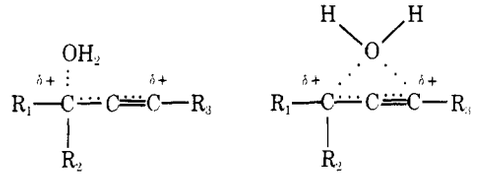
Chart I. Transition-State Models for Meyer–Schuster Rearrangement[a]

Unimolecular, covalent attachment of H_2O, calcd $k_{H_2O}/k_{D_2O} = 0.74$



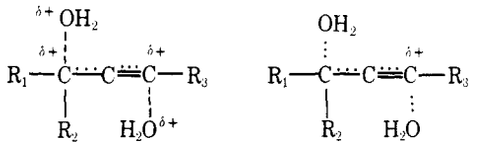
a b

Unimolecular ion–dipole interaction of R^+ and H_2O, calcd $k_{H_2O}/k_{D_2O} = 0.40$

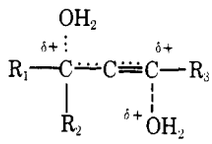


c d

Bimolecular



e, covalent calcd $k_{H_2O}/k_{D_2O} = 1.36$ f, ion–dipole calcd $k_{H_2O}/k_{D_2O} = 0.40$



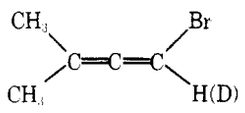
g, ion–dipole at reaction center partially covalent at rearrangement terminus, for calcd k_{H_2O}/k_{D_2O} see text

[a] (---) Covalent interaction; (···) electrostatic interaction.

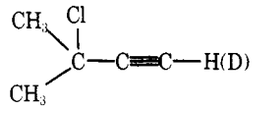
Model g, which corresponds to nucleophilic attack, i.e., partial covalent attachment of H_2O at the rearrangement terminus, on a solvated ion, also predicts an isotope effect of large magnitude (vide infra). These calculations thus suggest that an ion–dipole pair is an intermediate in this rearrangement. That is to say, the covalent attachment suggested by transition-state models a, b, e, and to some extent g appears inconsistent with the low values of k_{H_2O}/k_{D_2O} observed here as well as with the magnitude of ρ reported above. Models c, d, and f all represent a solvated cation, and it is doubtful whether any chemical distinction should be made among them.[17]

The inverse α-secondary isotope effect, **6g/6h,** observed strongly supports the view that some rehybridization (sp → sp^2), i.e., covalent attachment at the rearrangement terminus, has occurred. The calculated maximum $(k_H/k_D)_\alpha$ for complete rehybridization sp → sp^2 is 0.78.[19-21] Thus, the present value $k_H/k_D = 0.92$ suggests substantially less (~34% of maximum) than complete rehybridization has taken place at the transition state. If one assumes that this represents an approximation of the degree of covalent attachment at the rearrangement terminus in **6g** and further assumes that the solvent isotope effect measured in **6a,** $k_{H_2O}/k_{D_2O} = 0.36$, is completely free of any covalent component, then an expected solvent isotope

effect of $k_{H_2O}/k_{D_2O} = 0.46$ for **6q** is calculated.[22] It is not unreasonable to expect the degree of covalent attachment of H_2O at the rearrangement terminus to increase with decreasing stability of the cation formed, as is likely to be the case between **6a** and **6g**. Indeed, the more negative entropy activation calculated for **6g**, −18.6 vs. −7.5 eu for **6a**, is also consistent with this view. Thus, the transition state for the Meyer–Schuster rearrangement of **6g** is apparently an event occurring between the formation of an electrostatically solvated cation and complete covalent attachment of H_2O at the rearrangement terminus. In solvolytic terminology this would be described as nucleophilic attack by solvent on an ion pair or in this case an ion–dipole pair. It is interesting to note that it has been shown recently that 8 undergoes solvolysis via nucleophilic attack of solvent on a tight ion pair of retained configuration and exhibits $(k_H/k_D)_\alpha$ ratios dependent upon solvent nucleophilicity being 1.20 in 60E and 1.28 in 97T.[20,23] Isotopic substitution in **9** as indicated results in no observable isotope effect.[24]

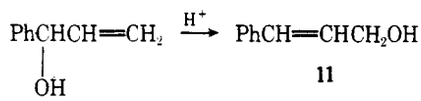


8



9

Finally, an alternative transition-state model involving a covalent or electrostatic interaction of one water molecule with two cationic centers similar to that suggested in the acid-catalyzed rearrangement of 1-phenyl-2-propen-1-ol (**10**) to 3-phenyl-2-propen-1-ol (**11**) appears unlikely in the present



10 11

case owing to the linearity of the alkynyl cation, **5**, and the longer distance between cationic centers not present in the allylic cation intermediate involved in rearrangement of **10**.[25–28] Such a transition state is not ruled out by the present data. Our preference for the rate-limiting step, however, is a highly solvated delocalized cation undergoing nucleophilic attack by solvent or returning to starting alcohol by collapse to the conjugate acid. The reaction is thus controlled by formation of the thermodynamically favored allenol ⇌ α,β-unsaturated carbonyl tautomeric pair. This is further supported by noting that triarylchloroallenes yield only triarylpropargyl alcohols upon solvolysis. Unsaturated ketones are not observed under these conditions. Since the propargyl position is the exclusive site of nucleophilic attack by water on the R^+ generated solvolytically, the R^+ formed by loss of H_2O from the protonated alcohol must return faster than it forms the conjugate acid of the allenol, thus supporting the conclusion above that attack of H_2O at the rearrangement terminus is rate limiting in the present case.

Finally, the rapid exchange rates of carbonyl compounds with $H_2{}^{18}O$ preclude meaningful labeling studies regarding the inter- or intramolecularity of the rearrangement step. Exchange rates of unlabeled starting material and polarimetric rates on optically active starting materials are being undertaken, in an attempt to assess the freedom of the intermediate carbon ion. However, the resolution of aryl tertiary propargylic alcohols presents a demanding task. Rearrangement of aliphatic propargyl alcohols is also being studied.

Experimental Section

Materials. All melting points are uncorrected. IR spectra were obtained using a Perkin-Elmer Model 457 spectrophotometer. ^1H NMR spectra were obtained using a Hitachi Perkin-Elmer Model R-20B spectrometer, 60 MHz. Dioxane was ACS certified reagent grade and was used without further purification. Triarylpropargyl alcohols **6a–f** were prepared as described previously.[16] 1,1-Diphenyl-2-propyn-1-ol was prepared according to the method of Beumel and Harris.[29] This alcohol was deuterated by three exchanges in 0.20 M NaOD/D_2O solution. No detectable ^1H NMR signal was observed at 100× amplitude. Deuterium oxide was obtained from Bio-Rad Laboratories, isotopic purity 99.88%. Deuteriosulfuric acid was obtained from Mallinckrodt Chemical Works, isotopic purity 99.5%.

Kinetic Measurements. All kinetic studies were performed on a Gilford Instruments Model 240 spectrophotometer. The cell compartment was thermostated using a PRT-regulated proportional temperature controller. Temperature measurement was accomplished with a Hewlett-Packard quartz thermometer.

A 1.25×10^{-4} M stock solution of the alcohol was prepared in dioxane. In a typical kinetic run, 10 mL of the stock solution was diluted with exactly 15.0 mL of aqueous sulfuric acid, resulting in a final concentration of approximately 5×10^{-5} M in propargyl alcohol. After mixing the solution thus obtained (10 s), a 1-cm quartz cell was rinsed twice, filled, and allowed to equilibrate in the cell compartment (10 min). The appearance of product absorbance at 3040 or 3100 Å was recorded vs. time against a blank identical with the sample except for the presence of substrate. Solvent deuterium isotope effects were measured identically except that a total volume of 10 mL was utilized.

A volumetrically measured and weighed portion of the kinetic solution was titrated against standard NaOH. The Hammett acidity function, H_0, was determined by reference to the scale of Torck, Hellin, and Coussemant for H_2SO_4 in 40:60 aqueous dioxane. Rate constants were calculated as described earlier.[19]

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Registry No.—**6a,** 1522-13-0; **6b,** 35556-63-9; **6c,** 1522-14-1; **6d,** 35476-69-8; **6e,** 62698-34-4; **6f,** 62698-35-5; **6g,** 3923-52-2; **6h,** 62698-36-6.

References and Notes

(1) On leave 1976–77, Department of Chemistry, University of Aberdeen, Scotland, to whom the senior author is indebted for the use of facilities and gracious hospitality.
(2) K. H. Meyer and K. Schuster, *Chem. Ber.*, **55,** 819 (1922).
(3) S. Swaminathan and K. V. Narayan, *Chem. Rev.*, **71,** 429 (1971).
(4) S. A. Vartanyan and Sh. O. Banbanyan, *Russ. Chem. Rev.*, **36,** 670 (1967).
(5) H. Rupe and H. Werdenburg, *Helv. Chim. Acta*, **18,** 542 (1935), and 12 preceding papers in this series.
(6) C. D. Hurd and R. E. Christ, *J. Am. Chem. Soc.*, **59,** 118 (1937).
(7) J. D. Chanley, *J. Am. Chem. Soc.*, **70,** 244 (1948).
(8) W. S. Macgregor, *J. Am. Chem. Soc.*, **70,** 3953 (1948).
(9) Y. F. Hennion, R. B. Davis, and D. E. Maloney, *J. Am. Chem. Soc.*, **71,** 2813 (1949).
(10) I. Issei and O. Jokutero, *J. Pharm. Soc. Jpn.*, **79,** 866 (1960).
(11) R. Heilmann and R. Glenat, *Ann. Chim. (Paris)*, 175 (1963).
(12) M. Apparu and R. Glenat, *Bull. Chim. Soc. Fr.*, 1106, 113 (1968).
(13) D. S. Noyce and M. D. Schiavelli, *J. Am. Chem. Soc.*, **90,** 1020, 1023 (1968).
(14) G. Quinkert, M. Hintzmann, P. Michaelis, P. Jürges, H. Appelt, and V. Krüger, *Ann. Chim. (Paris)*, 38 (1971).
(15) B. Torck, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 1657 (1962).
(16) M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. A. Boswell, *J. Am. Chem. Soc.*, **93,** 6989 (1971).
(17) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83,** 42, 3207, 3214 (1961).
(18) The values shown in Chart I arise from utilizing Bunton and Shiner's values of O–H stretching frequencies for hydrogen-bonded H_2O and H_3O^+, i.e., 3400 and 2900 cm^{-1}, respectively. The initial state here assumes a pK_a for the alcohol equal to that given for H_2O, i.e., 16. Covalently bound water molecules are assumed to be comparable to hydronium ion, while electrostatically bound water molecules are free to accept an additional hydrogen bond. Bunton and Shiner's notation has been retained; i.e., covalent interactions are indicated by dashed lines (- - -) and electrostatic interactions by dotted lines (• • •).
(19) M. D. Schiavelli, T. C. Germroth, and J. W. Stubbs, *J. Org. Chem.*, **41,** 681 (1976).
(20) M. D. Schiavelli and D. Ellen Ellis, *J. Am. Chem. Soc.*, **95,** 7916 (1973).
(21) S. R. Hartshorn and V. J. Shiner Jr., *J. Am. Chem. Soc.*, **94,** 9002 (1972); and V. J. Shiner, Jr., private communication.
(22) The observed $RT \ln (k_H/k_D)_\alpha = -49$ cal is 0.34 times the calculated maximum $RT \ln (k_H/k_D)_\alpha = -146$ cal at 298 K. Thus, the expected $RT \ln (k_{H_2O}/k_{D_2O})_{6g}$ should equal $RT \ln (k_{H_2O}/k_{D_2O})_{6a} + 0.34\ RT[\ln (k_{H_2O}/k_{D_2O})_{(covalent)} - \ln (k_{H_2O}/k_{D_2O})_{6a}] = -605$ cal $+ 0.34[-178 - (-605)] = -460$ cal.

(23) M. D. Schiavelli et al., submitted for publication.
(24) V. J. Shiner, Jr., J. W. Wilson, G. Heinemann, and N. Soliday, J. Am. Chem. Soc., 84, 2408 (1962).
(25) H. L. Goering and R. E. Dilgren, J. Am. Chem. Soc., 81, 2556 (1959).
(26) H. L. Goering and R. E. Dilgren, J. Am. Chem. Soc., 82, 5744 (1960).
(27) H. Kwart and J. Herling, J. Am. Chem. Soc., 85, 226 (1963).
(28) See also Y. Pocker and M. J. Hill, J. Am. Chem. Soc., 91, 3243 (1969); M. Stiles and A. L. Longroy, J. Org. Chem., 32, 1095 (1967), for studies on related rearrangements.
(29) O. F. Beumel and R. F. Harris, J. Org. Chem., 29, 1872 (1964).

Thiyl Radical and Mercuric Ion Induced Cyclizations of Dimethyl Dipropargylmalonate and Dimethyl Propargyl-3-thiylallylmalonates

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The first examples of radical-initiated cyclizations of a 1,6-diyne were found in the photochemical reactions of dimethyl dipropargylmalonate with thiophenols. The reactions are accompanied by formation of acyclic monothioenol ethers, which also undergo cyclization on reaction with thiophenols or with mercuric chloride. Cyclopentane products are formed in all of these reactions. Alternatively, the dipropargyl compound on direct reaction with aqueous mercuric chloride yields a diketone which can be cyclized to 5,5-dicarbomethoxy-3-methylcyclohex-2-enone.

Geminal diallyl compounds undergo cyclization to cyclopentyl products in high yields on reaction with thiyl and other radicals.[1] However, 1,6-heptadiyne was reported to yield no radical induced cyclization but only an acyclic radical addition product.[2] While we also found that dimethyl dipropargylmalonate (1) gave only traces of cyclized material on photochemically initiated reaction with ethanethiol or butanethiol, a 2:1 mixture of the cyclized to uncyclized diadducts (**2, 3, 4**) and the uncyclized monoadduct **5** were formed in photochemical reactions with benzenethiol or *p*-toluenethiol.

A reaction of the monoadduct **5** with benzenethiol in the dark did not lead to any cyclization products, but on irradiation a mixture of the acyclic adduct **4** and the cyclization product **3** was formed. None of the encocyclic double bond isomer **2** could be detected in this reaction mixture, in contrast to the above thiol addition to the dipropargylmalonate, where as much endocyclic double bond isomer **2** as exocyclic double bond isomer **3** was obtained. Thus it was found that the cyclization product **2** does not arise from the acyclic adduct **5**, but that it is generated from the diacetylene **1** by direct cyclization to a presumed dimethylenecyclopentane intermediate **6**, which in turn can undergo 1,4 radical addition of benzenethiol to give **2** and probably 1,2 addition to give product **3**. The reactive intermediate **6** could not be isolated. While cyclizations of a cyanomalonyl radical with a terminal acetylenic group[3] and of a vinyl radical with a terminal vinyl group[4] have been shown to yield methylenecyclopentane products, the present result seems to be the first cyclization reaction of a vinyl radical with a terminal acetylene (i.e., the first example of a direct radical-initiated cyclization of a diacetylene).

Reductive desulfurization of the cyclization product mixture of **2** and **3** yielded the dimethylcyclopentene **7** and an epimeric mixture of the dimethylcyclopentanes **8a,b**. Hydrogenation of the olefin **7** also led to a cis/trans mixture of the dimethylcyclopentanes **8a,b**. Reductive desulfurization of the acyclic diadduct **4** and of the monoadduct **5** gave dimethyl di-*n*-propylmalonate (**9**). Since irradiation (a radical process) was required for the cyclization of the thioenol ether **5** with thiophenol, it was of interest to explore alternative ionic