Anchimeric Assistance, Rearrangement, and Solvent Addition in the Formolysis of a Nonconjugated Acetylenic (Homopropargylic) Tosylate¹

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Abstract: The rate of formolysis of 2,2-dimethyl-3-pentyn-1-yl tosylate at 75° is six times greater than that of its saturated analog, 2,2-dimethyl-1-pentyl tosylate, as measured by nmr spectroscopy. The triple bond assisted ionization step proceeds with rearrangement to the formate ester of 2-methyl-4-hexyn-2-ol. Addition of formic acid to the triple bond of this ester yields (after elimination) the enol formate of 5-methyl-4-hexen-3-one, which is finally converted to the ketone. Each of these products was identified by following the reaction with nmr. The nmr spectrum of each was separately obtained by dissolving 2-methyl-4-hexyn-2-ol and 2-methyl-2-hexen-4-yne in formic acid.

The substituted propargyl halide 1 solvolyzes (80% ethanol, 25°) at a rate² (5.13 × 10⁻⁴ sec⁻¹) that is about 30 times faster than the rate³ (0.152 × 10⁻⁴ sec⁻¹) at which *t*-amyl chloride solvolyzes under the same conditions. This acceleration suggests a delocalized intermediate 2 that is analogous to the intermediate formed in the solvolysis of the corresponding tertiary allylic halide. We wondered whether this similarity

of behavior between allylic and propargylic compounds would carry over to the next higher homologs; homoallylic compounds are known to solvolyze with double bond participation,^{4,5} whereas homopropargylic compounds had not been examined at the start of the present investigation. Although analogy with the propargyl system suggested that a nonconjugated acetylenic compound might solvolyze with participation by the π electrons of the triple bond, there was the reasonable possibility that, with the introduction of the insulating methylene group, the conjugative, rate-enhancing effect of the triple bond might disappear or fall off faster than would the inductive,6 rate-diminishing effect. A study of the products and rate of formolysis of 2,2-dimethyl-3-pentyn-1-yl tosylate (3) expected to solvolyze without the intervention of SN2 processes, was therefore undertaken.

Results

Starting material **3** was synthesized as outlined below (see Experimental Section).

When a 0.5 M solution of the acetylenic tosylate **3** and sodium formate in formic acid was heated at 60° for 40 hr, a nearly quantitative yield (90-95%) of 5-methyl-4-hexen-3-one (9) was obtained. The structure

(1) Preliminary communication: J. W. Wilson, Tetrahedron Lett., 2561 (1968).

(6) J. K. Kochi and G. S. Hammond, *ibid.*, 75, 3452 (1953).



of **9** was established by comparison with an authentic sample⁷ and by catalytic hydrogenation to 5-methyl-3-hexanone.

When a formic acid solution of 3 and sodium formate was placed in the nmr probe at 75° , it was possible to observe directly not only the disappearance of starting material 3 and the formation of product 9, but also the appearance and disappearance of nmr peaks assigned to two intermediates, 10 first (see Figure 1A) and then 11 (see Figure 1B). Though 10 and 11 were not

$$3 \longrightarrow CH_{3}CH_{2}CH_{2}C \equiv CCH_{3} \longrightarrow CH_{3}C = CHCH_{3} \longrightarrow 9$$

$$CH_{3}C = CHCH_{3} \longrightarrow CH_{3}C = CHCH_{3} \longrightarrow 9$$

$$CH_{3} \qquad CH_{3} \qquad CH_{3}$$

$$10 \qquad 11$$

isolated, their nmr spectra were independently obtained by dissolving 2-methyl-4-hexyn-2-ol (12) and 2-methyl-2-hexen-4-yne (13), respectively, in formic acid. As 12 (prepared from ester 14) was heated in formic acid

$$CH_{3}C \equiv CCH_{2}CO_{2}CH_{3} \longrightarrow CH_{3}C \equiv CCH_{2}C(CH_{3})_{2} \longrightarrow 10 \longrightarrow 9$$

$$14 \qquad 12$$

at 75° several changes in the spectrum, attributed to the formation of ester 10, were noted. These new peaks matched the peaks that appeared (marked at the bottom of Figure 1A) as 3 disappeared during its solvolysis. The spectrum of 13 (prepared from alcohol 15) was recorded in formic acid at room temperature (see Figure 1C). When this solution was placed in the nmr probe at 70°, a new spectrum (see Figure 1D), attributed to the enol formate (11) formed by rapid

(7) Aldrich Chemical Co., Milwaukee, Wisconsin.

 ⁽²⁾ A. Burawoy and E. Spinner, J. Chem. Soc., 3752 (1954).
 (3) H. C. Brown and R. S. Fletcher, J. Amer. Chem. Soc., 71, 1845

⁽³⁾ H. C. Brown and R. S. Fletcher, J. Amer. Chem. Soc., 71, 1845 (1949).

⁽⁴⁾ R. S. Bly and R. T. Swindell, J. Org. Chem., 30, 10 (1965).

 ^{(5) (}a) K. L. Servis and J. D. Roberts, J. Amer. Chem. Soc., 86, 3773 (1964); (b) K. L. Servis and J. D. Roberts, *ibid.*, 87, 1331 (1965).



Figure 1. (A) Solvolysis in HCO_2H at 75° of 3 after 31 min. (B) Solvolysis of 3 after 110 min. (C) Compound 13 in HCO_2H at room temperature. (D) Compound 11 formed by heating 13 for several minutes at 70°. HMDS used as external reference.

addition of formic acid to 13, appeared.⁸ The absorption in the vinyl region of this spectrum was very similar to the complex absorption pattern (marked by an arrow labeled 3 in Figure 1B) that appeared briefly (and was clearly visible only at high amplifier gain)

$$CH_{3}C \equiv CCHCH(CH_{3})_{2} \longrightarrow$$
15
$$CH_{3}C \equiv CCH = C(CH_{3})_{2} \longrightarrow 11 \longrightarrow 9$$
13

during the solvolysis of 3. Both 12 and 13 were eventually converted to unsaturated ketone 9 in formic acid. In several runs it appeared that 9 was slowly converted to another, as yet unidentified, product. The rate at which this reaction occurred appeared to be affected by trace amounts of water in the formic acid, for in a run using formic acid freshly distilled from boric anhydride the transformation was faster than in another run in which the formic acid contained at least 1% water. Trace amounts of water also appeared to affect the rates at which 10 was converted to 11 and at which 11 was converted to 9 in a way that has not yet been quantitatively defined.

The rate of formolysis of tosylate 3 was determined by nmr spectroscopy using the method of Servis and

Roberts.⁵ A 0.5 *M* solution of **3** and sodium formate in formic acid was prepared in an nmr tube, which was placed in a variable-temperature probe of a Varian HA-60-IL spectrometer at 75.0 \pm 0.5°.⁹ A plot of 1n [x/(x + y)] vs. t (min) was prepared, where x = height of the methyl resonance of tosylate 3 at time t and y =height of the methyl resonance of *p*-toluenesulfonic acid at time t (the arrow in Figure 1A points to these two peaks). As the reaction progressed and the concentration of ketone 9 began to increase, the quartet of the methylene protons of 9 began to overlap with the tosylate methyl peak of 3. Nonetheless, the plot gave a satisfactory straight line during about two half-lives of the reaction before curvature due to the overlap became serious. Three runs yielded the following rate constants, 3.17, 3.07, 2.89 \times 10⁻⁴ sec⁻¹, with an average value of: $k_1 = 3 \times 10^{-4} \text{ sec}^{-1}$. Small amounts of water have little effect on the rate constant for the ionization step. The middle value came from a run in which the formic acid was distilled directly before use, the last value from a run where 1% water was deliberately added and the first from a run where no special precautions were taken.

For comparison purposes the rate of formolysis of the saturated analog of 3, 2,2-dimethyl-1-pentyl tosylate (16), was determined by the same method. Two runs gave the following rate constants: 5.3 and 5.1 \times 10⁻⁵ sec⁻¹, with an average value of: $k_2 = 5 \times 10^{-5}$ sec⁻¹.

⁽⁸⁾ For another example of this reaction see: G. F. Hennion, R. B. Davis, and D. E. Maloney, J. Amer. Chem. Soc., 71, 2813 (1949).

⁽⁹⁾ The absolute temperature is accurate to $\pm 2^{\circ}$ according to ref 5.

Discussion

The course of the formolysis of the homopropargylic tosylate 3 has been shown by nmr spectroscopy to involve: (a) assisted ionization accompanied by rearrangement to 10, (b) addition of formic acid to the triple bond of this intermediate to yield the enol formate 11, and (c) transformation of 11 to the α,β -unsaturated ketone 9.



The fact that 3 undergoes dissociation and simultaneous rearrangement to 10 six times faster than its saturated analog 16 undergoes dissociation and rearrangement demonstrates π -electron participation by the carbon-carbon triple bond in the transition state. The fact of a rate acceleration offers confirmation of the earlier arguments for neighboring-group participation by the triple bond in the face of solvolysis rates for acetylenic compounds that were slower^{10,11} than or equal¹² to the rates of solvolysis for the saturated analogs. In these cases the rate-slowing inductive effect of the triple bond apparently overbalanced or just balanced its rate-enhancing conjugative effect. The magnitude of these effects in the present case can be estimated in the manner of Bly, et al., 13 in their recent investigation of the acetolysis of 2,2-dimethyl-3,4-pentadienyl brosylate, a homoallenyl system. From the pK_a for $CH_3C \equiv$ $CCH_2CO_2H^{14}$ (3.59), a value of σ^* for the group $CH_3C \equiv CC(CH_3)_2$ was calculated using the Taft equation as follows: log $[K_A/K_{A_0}] = \sigma^*[CH_3C \equiv CCH_2]\rho^*$; $pK_A = 3.59$, $pK_{A_0} = 4.65$, $\rho^* = 1.4$; $\sigma^*[CH_3C \equiv C-(CH_3)_2] = \sigma^*[CH_3C \equiv CCH_2] + 2\sigma(Et) = 0.76 + 2(0.1)$ = 0.56. To estimate the rate of solvolysis of 3 in absence of π delocalization, the Taft equation was employed as follows: $\log k_1 - \log k_2 = (\sigma_1^* - \sigma_2^*)\rho^*$; $k_2(16) = 5 \times 10^{-5} \sec^{-1}, \sigma_1^* = 0.56, \sigma_2^* = -0.33, \rho^* = -3$; $k_1(\text{calcd}) = 10^{-8} \sec^{-1}, k_1/k_2(\text{calcd}) = 0.0022, k_1/k_2$. (obsd) = 6. Note that the observed solvolysis rate ratio for compounds 3 (k_1) and 16 (k_2) is 3000 times larger than the calculated ratio. Of course, this very rough estimate depends vitally on the very uncertain choice of ρ^* (as well as on the estimated σ^* values), but it serves to indicate a considerable rate enhancement due to π participation by the triple bond. The rate enhancement estimated by Bly, et al., for acetolysis¹⁵ of the homo-

(10) M. Hanack, I. Herterich, and V. Vött, Tetrahedron Lett., 3871 (1967).

(11) See also W. D. Clossen and S. A. Roman, ibid., 6015 (1966).

(12) P. E. Peterson and M. J. Kamat, J. Amer. Chem. Soc., 88, 3152

(1966). (13) R. S. Bly, A. R. Ballentine, and S. U. Koock, ibid., 89, 6993 (1967); Southeast-Southwest Regional Meeting of the American Chemi-

(al Society, Memphis, Tenn., Dec 2-4, 1965, Abstracts, p 46.
 (14) G. H. Mansfield and M. C. Whiting, J. Chem. Soc., 4761 (1956).

(15) Participation is expected to be less in acetic acid.¹⁶

(16) P. E. Peterson, R. J. Bopp, D. M. Chevli, R. L. Curran, D. E.

Dillard, and R. J. Kamat, J. Amer. Chem. Soc., 89, 5902 (1967).

Journal of the American Chemical Society | 91:12 | June 4, 1969

allylic system is in the range 440-2000. That participation in the homopropargylic case should be of the same order of magnitude as in the homoallylic case is in agreement with the findings of Peterson and Duddey,¹⁷ who observed that alkynes and alkenes exhibit similar reactivity with respect to addition of trifluoroacetic acid. For acetolysis of the homoallenyl system, Bly estimates a rate enhancement due to participation in the range 8300-58,000. It is reasonable that participation in that case should be greater than in the homopropargylic case, when contributing structures A and B to the two transition states are considered. Though both involve vinyl cations, the ground state leading to B is more stable¹⁸ than that leading to A. In addition structure B, a



methylene cyclopropane, is more strained¹⁹ than structure A.²⁰

Several mechanisms (shown in Scheme I) for the transformation of 10 to 11 are possible. Direct evidence on this point is not available from the present work.

Scheme I



The product formed from 3 in formic acid is quite different from the products formed in the solvolysis of two other homopropargyl compounds, reported while the present work was in progress.

Hanack and coworkers 10, 21, 22 have examined the solvolyses of several homopropargyl arenesulfonates that differ from our system mainly in their lack of the β -gem-dimethyl groups. For example, the reaction of 3-pentyn-1-yl m-nitrobenzenesulfonate (17) in trifluoroacetic acid gives 2-methylcyclobutanone (18) in good yield. A mechanism involving structures 19 and

(17) P. E. Peterson and J. E. Duddy, *ibid.*, 88, 4900 (1966).
(18) W. R. Moore and H. R. Ward, *ibid.*, 85, 86 (1963).
(19) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, 90, 4315 (1968).

(20) Though the present evidence sheds little light on the question of the absolute stability of vinyl cations and the question of the effect of the gem-dimethyl groups on the solvolysis rate, these questions are considered in ref 13.

(21) (a) M. Hanack, J. Häffner, and I. Herterich, *Tetrahedron Lett.*,
(35) (b) M. Hanack and I. Herterich, *ibid.*, 3847 (1966); (c) M.
Hanack, V. Vött, and H. Ehrhardt, *ibid.*, 4617 (1968).
(22) We regret having overlooked at the time of our preliminary com-

munication the evidence of Professor Hanack and his coworkers in ref 10 for neighboring group participation by the triple bond in a homopropargylic system.

20 was advanced to explain the formation of 18. As mentioned earlier, in our neopentenyl-like system a



structure similar to 19 must contribute to the transition state leading from 3 to the tertiary carbonium ion corresponding to 10. The fact that 3 can yield such a tertiary ion is one explanation for the different products.

Ward and Sherman²³ have found that the phenylsubstituted homopropargyl system 21 in formic acid yields cyclopropyl ketone 22 by a mechanism that does *not* involve triple bond participation in the ionization

$$\begin{array}{cccc} C_{6}H_{5}C = CCH_{2}CH_{2}OBs \longrightarrow C_{6}H_{5}C = CHCH_{2}CH_{2}OBs \longrightarrow \\ & & & & & \\ 21 & & & & \\ & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & &$$

step. Instead, solvent addition precedes the formation of the rearrangement product. In the case of **3** such a mechanism is excluded by the observation that **3** leads directly to the rearranged *acetylenic* formate **10** before addition of solvent occurs.²⁴ The fact that **3** is different from **21** in two respects, in having a methyl instead of a phenyl group and in being a neopentyl system, makes difficult the explanation of the difference in reactivity. Either or both differences may be important.

Experimental Section²⁵

2,2-Dimethyl-2,3-pentadien-1-ol (5) was prepared by lithium aluminum hydride reduction¹³ of aldehyde 4.²⁶ Its spectral properties were the same as the reported properties.¹³

2,2-Dimethyl-3-pentyn-1-ol (8). The allenic alcohol 5 was first converted to the tetrahydropyranyl ether 6. The work-up of the isomerization product was rendered more convenient by the use of the protecting group because of the low volatility and water insolubility of the protected alcohol 7. A solution of 31 g of 5 (containing a small amount of diethyl ether according to vpc), prepared from 25 g (0.23 mol) of aldehyde 4 and used without further purification, in 100 ml of practical grade dihydropyran and two drops of concentrated hydrochloric acid was stirred at room temperature for 24 hr. The excess dihydropyran was removed on a rotary evaporator leaving 45 g (100% of theoretical based on aldehyde 4) of liquid. The vpc of this material showed one major constituent and several very minor contaminants. Its infrared spectrum was consistent with the expected allenic tetrahydropyranyl ether structure (6), having no OH absorption and a band at 1940 cm^{-1} due to the allene linkage.

Protected allenic alcohol 6 was isomerized to the corresponding acetylenic ether 7 by dissolving 25 g (about 0.12 mol) of 6 in 1 l. of t-butyl alcohol containing 1.1 mol of potassium t-butoxide prepared from 41 g of potassium. The progress of the reaction was followed by transferring 1-ml aliquots into a mixture of 10 ml of water and 10 ml of pentane. Vpc of the pentane extract showed that the isomerization proceeded very slowly at room temperature. However, after the solution had been gently refluxed for 4 hr under nitrogen, the starting material had almost completely disappeared. Most of the t-butyl alcohol was evaporated at reduced pressure. To the slush remaining was added 1 l. of water. This solution was extracted with 800 ml of pentane in three portions and the combined pentane layers were washed with 500 ml of water in two portions. The pentane extracts were dried over sodium sulfate and evaporated. The liquid residue weighing 21 g contained, according to vpc, a single impurity (roughly 20%) in addition to the expected product 7.

The protecting group was removed by dissolving the acetylenic tehydrahydropyranyl ether 7 in 75 ml of benzyl alcohol containing two drops of concentrated hydrochloric acid. The starting ether had practically disappeared (vpc) after 2 hr of stirring at room temperature. In its place appeared vpc peaks that were assigned as benzyltetrahydropyranyl ether, the desired acetylenic alcohol 8 and a low-boiling, unidentified product. Further heating caused no further change in the volatile product composition. Anhydrous potassium carbonate was added to the reaction mixture. After standing for several days this mixture was filtered, the potassium carbonate was washed with benzyl alcohol, and the filtrate was distilled at reduced pressure through an 18-in. spinning-band column. Pure 8, weighing 5.3 g (40% yield based on crude allenic ether 4), was collected at 80° (65 mm); ir (CHCl₃), 3590 and 3360 cm⁻¹ (O-H), and other prominent bands at 1390, 1370, 1360, 1280, 1050, 1040, 1015, and 900 cm⁻¹; nmr (CCl₄), δ 1.10 (6 H singlet, (CH₃)₂C), 1.82 (3 H singlet, CH₃C=C), 2.63 (1 H singlet, O-H), and 3.23 (2 H singlet, CH₂OH).

Anal. Calcd for $C_7H_{12}O$: C, 74.94; H, 10.79. Found: C, 75.03; H, 10.71.

Preparation of 2,2-Dimethyl-3-pentyn-1-yl Tosylate (3). A cold solution of 7.5 g (0.067 mol) of acetylenic alcohol 8 and 14.3 g (0.075 mol) of *p*-toluenesulfonyl chloride in 90 ml of dry pyridine was stirred for 6 hr and then poured over 300 g of ice. The white precipitate that formed was removed by filtration and air dried. The crude tosylate, 13.2 g (75%), mp 39–42°, was recrystallized twice from hexane; mp 42.5–43.5°; ir (CHCl₃), 1600 and 1450 (C₈H₄), 1360, 1190 and 1180 (SO₂), 1150 and 980 cm⁻¹; nmr (HCO₂H, ambient temperature), 0.78 (singlet, (CH₃)₂C), 1.31 (singlet, CH₃C==C), 2.06 (singlet, CH₃Ar), 3.53 (singlet, CH₂O), 7.05 (doublet, J = 8.5 Hz, aromatic H), and 7.50 (doublet, J = 8.5 Hz, aromatic H) ppm from hexamethyldisiloxane.

Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.13; H, 6.81. Found: C, 63.00; H, 6.79.

Formic acid was dried by the method of Winstein and Marshall,²⁷ bp 39° (74 mm). It was stored at room temperature. For several runs it was distilled just before use from fresh boric anhydride. Reagent sodium formate was dried at 140° (0.1 mm) for 2 days and was stored in an oven at 100° .

⁽²³⁾ H. R. Ward and P. D. Sherman, Jr., J. Amer. Chem. Soc., 89, 1963 (1967).

⁽²⁴⁾ The remote possibility that 10 and 11 are formed in parallel rather than sequential steps from 3 cannot be rigorously excluded. However, such a mechanism would require the unlikely possibility that the tertiary formate 10 be in equilibrium with a primary formate corresponding to 3, which would then be converted to 11. The conversion of 3 (or its formate) to 11 would require a stereospecific addition of formic acid to 3 followed by an unlikely rearrangement to 11 (see ref 1). The fact that 3 disappears as 10 is formed and that 10 disappears as 11 is formed indicates that 10 and 11 are formed sequentially, though in the absence of rate data for the last two steps this cannot be rigorously proved.

⁽²⁵⁾ Melting and boiling points are uncorrected. The infrared spectra were determined on a Beckman IR 8 spectrophotometer. The nmr spectra were determined at 60 MHz on a Varian HA-60-IL spectrometer. Chemical shift values are expressed in cycles per second, in δ values (parts per million) relative to a tetramethylsilane internal reference, or in parts per million relative to the hexamethyldisiloxane (HMDS) reference described in the text. Microanalyses were performed by Mr. Daryl Sharp and by Schwartzkopf Microanalytical Laboratories. The gas chromatographic analyses were carried out on Varian Aerograph Model 90-P and Aerograph Autoprep Model A-700 instruments.

^{(26) (}a) A generous supply of 4 was provided by the Tennessee Eastman Company; Kingsport, Tenn.; (b) see B. Thompson, Chem. Abstr.,

Formolysis of 3. A. Product Study. A solution of 9.98 g (0.038 mol) of tosylate 3 and 2.55 g (0.038 mol) of sodium formate in 75 ml of formic acid was heated at 60° for 40 hr. A slow stream of nitrogen that bubbled through the reaction mixture and into a

^{62, 446}h (1965), and D. K. Black and S. R. Landor, J. Chem. Soc., 6784 (1965).

⁽²⁷⁾ S. Winstein and H. Marshall, J. Amer. Chem. Soc., 74, 1120 (1952).

Dry Ice trap yielded no condensable products. The dark reaction mixture was poured into 75 ml of cold water and the mixture was extracted with five 40-ml portions of pentane. The pentane extracts were washed with 50 ml of water and 30 ml of saturated bicarbonate solution. After drying the solution over sodium sulfate, the pentane was removed by distillation. The residue weighed 3.67 g (87% yield) and contained (vpc) a single major product, 9, and several very minor components (ca. 10% of residue). The acidic extract was neutralized with sodium hydroxide and extracted with four 40-ml portions of ether. The residue, 435 mg (98% total)yield, assuming only isomeric products), contained three components, one of which, ketone 9, accounted for about 40% of the total. Continuous extraction of the aqueous extract with ether yielded no further products. The formolysis product was distilled through a 10-cm Vigreux column to yield 1.9 g of 5-methyl-4-hexen-3-one, 9: bp 60–61° (27 mm) [lit.²⁸a 148° (760 mm)]; ir (CHCl₃), 1675 (C=O), 1610 (strong) (C=C), 1440, 1380, 1125, 1020, 880, and 835 cm⁻¹; nmr (CCl₄) δ 1.02 (3 H triplet, J = 7 Hz, CH₃CH₂-), 2.35 (2 H, J = 7 Hz, CH₃CH₂), 1.86 (3 H doublet, J = 1.5 Hz, $CH_{3}C=$), 2.10 (3 H, J = 1.5 Hz, $CH_{3}C=$ C), and 6.00 (1 H multiplet, J = 1.5 Hz, HC=C). A semicarbazone prepared by the method of Suida and Pöll²⁹ melted, after recrystallization from 95% ethanol, at 164-165° (lit. 28b 162°).

A solution of 512 mg (4.8 mmol) of formolysis product 9 in 10 ml of absolute ethanol was shaken under 30 psi of hydrogen in the presence of 43 mg of 5% palladium on charcoal in a Parr hydrogenation apparatus. The pressure drop corresponded to the consumption of *ca.* 1 equiv of hydrogen. After removal of the catalyst by filtration and most of the ethanol by distillation, the product, 5-methyl-3-hexanone, was purified by vpc (SF 96, 10 ft \times ³/₈ in, 135°); yield, 213 mg. Its retention time on this column (as well as its ir and nmr spectra) was different from that of a sample of 4-methyl-3-hexanone, which melted at 152–154° (lit.^{28b} 152°), was prepared. This derivative also excluded 4-methyl-2-hexanone, ^{28o} the semicarbazone of which melts at 127–128°, as a structure for the saturated ketone.

B. Nmr Kinetic Study.³⁰ A typical run is described. A solution of 341 mg of dry sodium formate in 10 ml of formic acid (0.5 M) was prepared in a volumetric flask. Tosylate 3 (64.5 mg, 0.242 mmol) was weighed into an nmr tube. By pipet, 0.50 ml of the formic acid solution was added (0.49 M in 3) and the tube was shaken until solution was effected. A fine capillary containing a 50%solution of hexamethyldisiloxane in CCl4 was inserted and the tube was capped. That no reaction took place during this period at room temperature was demonstrated by nmr. To avoid any delay between the insertion of the reaction mixture in the variable temperature probe and the recording of the first spectrum, the spectrometer was locked on the reference signal and the height of the tosylate methyl peak was maximized with a "dummy" sample of tosylate 3 in formic acid at a concentration identical with that of the "real" sample described above. The dummy sample was then removed and replaced by the real sample. At least 20 spectra were recorded, about 15 of them in the first half-life. The spectrum from 0 to 6 ppm was recorded for each point, the time being noted at the appearance of the tosylate methyl resonance.

Peaks from all four compounds, 3, 10, 11, and 9, can be identified in Figure 1B by comparison with reference spectra. The absorption patterns due to 3, 10, and 9 are marked under the spectrum. The strong high-field absorption of 11, present at low concentrations only, is buried under the methyl triplet of 10 and shows up only in the fact that the clean triplet of 10 is now distorted (see arrow).

Preparation of 2-Methyl-4-hexyn-2-ol (12). A. Methyl 3-Pentynoate (14). The procedure of Jones, *et al.*,³¹ was used to prepare 3-pentynoic acid. The concentration of potassium hydroxide necessary to effect isomerization is listed as 9 N in the text of the article and as 2 N in the Experimental Section. The former (9 N) concentration is necessary for completion of the reaction in the stated interval of 1.5 hr at 70°. A solution of 3.32 g of the acid in 50 ml of ether was treated with excess diazomethane in ether. The ether was removed by distillation and the residue was distilled at atmospheric pressure through a 10-cm Vigreux column to yield 2.42 g of pure (homogeneous to vpc on an SF-96 column, 10 ft \times 0.25 in., 135°) ester 14: bp 155–160°; ir (CHCl₃), 1740 cm⁻¹ (ester C=O).

B. Alcohol 12. To methyl magnesium bromide (from 1.04 g of magnesium, 0.043 mol) in 50 ml of cold ether was added 2.42 g of ester 17 (0.022 mol) in 15 ml of ether over 0.5 hr. The reaction mixture, which contained a light yellow solid, was stirred overnight and then hydrolyzed with 6 ml of saturated ammonium chloride solution. After removal of the solid by filtration, the ether was removed from the filtrate by evaporation to yield 2.35 g (97% crude yield) of an orange liquid. It was distilled through a short-path still at 68° (30 mm) [lit. 32 42-44° (5 mm)] to yield 1.362 g (58%) of a clear liquid. Because the infrared spectrum showed a carbonyl band of medium intensity, this material was further purified by vpc (Carbowax 4000, 20 ft \times 0.375 in., 130°); yield 584 mg. Although the ir showed a weak carbonyl band at 1720 cm⁻¹ all other indications of purity were satisfactory (nmr, vpc, CH analysis): ir (CHCl₃), 3570 and 3450 (OH), 2980 and 2930 (CH), 1460, 1380, 1355, 1150 (t-CO), 980, and 910 cm⁻¹; nmr (CCl₄), δ 1.19 (6 H singlet, $(CH_3)_2C$), 1.75 (3 H triplet, J = 2.5 Hz, $CH_3C \equiv C$), 2.28 (2 H quartet, J = 2.5 Hz, CH₂C \equiv C), and 2.43 (1 H singlet, OH). Anal. Calcd for C7H12O: C, 74.94; H, 10.79. Found: C, 74.72; H, 10.85.

Reaction of 12 with Formic Acid. Nmr Study. A solution of 112 mg (1.3 *M*) of **12** and 27 mg (0.7 *M*) of sodium formate in 0.80 ml of formic acid was prepared in an nmr tube in the usual way. The first spectrum recorded at 75° was the same, except for several small changes in chemical shifts, as the spectrum of **10** in CCl₄ at room temperature. After several hours the spectra show peaks due to **13** and **9** as well as the following peaks belonging to the tertiary formate **10**: 1.25 (singlet, (CH₃)₂C), 1.47 (triplet, J = 2.5 Hz, CH₃C=C-), and 2.34 (quartet, J = 2.5 Hz, CH₃C=C-) ppm from HMDS. The chemical shifts of all the protons α to the tertiary center lie further downfield than do those of the alcohol. The more remote acetylenic methyl protons, however, are scarcely affected by the change from alcohol to ester. Ten spectra were recorded in the first 8.5 hr. After approximately 24 hr at 75° the spectrum was that of ketone **9** with several minor contaminant peaks.

Preparation of 2-Methyl-2-hexen-4-yne (13). A. 2-Methyl-4-hexyn-3-ol (15) was prepared by the addition of propynyl magnesium bromide (0.3 mol) to isobutyraldehyde (0.3 mol).³³ A 71% yield of clear liquid boiling at 60° (15 mm) [lit.³³ 99° (90 mm)], which was homogeneous to vpc (SE-30, 4 ft \times 0.25 in., 110°), was obtained: ir (CHCl₃), 3610 and 3430 (OH), 2210 (C=C), 1460, 1370, 1210, and 1010 (CO) cm⁻¹; nmr (CCl₄), δ 0.92 (6 H doublet, J = 6 Hz, (CH₃)₂CH), 1.75 (1 H octet, J = 6 Hz, CH(CH₃)₂; shift, splitting, and coupling constant only approximate because of overlap with next peaks), 1.80 (3 H doublet, J = 2 Hz, CH₃C=C), and 3.99 (1 H, two overlapping quartets, J = 6 and 2 Hz, C=CCH).

B. Tosylate of 15. To a cold solution of 19.21 g (0.110 mol) of *p*-toluenesulfonyl chloride in 10 ml of dry pyridine was added 10.02 g (0.090 mol) of alcohol 15 over 0.5 hr. Water (60 ml) was added, and the mixture was extracted with three 25-ml portions of ether. The ethereal extract was washed with three 25-ml portions of 10% sulfuric acid, dried, and evaporated to yield 20.3 g (87%) of the clear liquid tosylate: ir (CHCl₃), 2230 (C=C), 1600 (C₆H₄), 1360 and 1175 (SO₂), 1100 and 900 cm⁻¹. This material was used without further purification.

C. En-yne 13. The tosylate of 15 was dissolved in 200 ml of dry pyridine and boiled for 24 hr. The cooled solution was mixed with 700 ml of saturated salt solution and was extracted with three 200-ml portions of ether. The ethereal extracts were washed with five 100-ml portions of 10% sulfuric acid, then dried and distilled through the 18-in. spinning-band column at atmospheric pressure. Of the four fractions collected, the last [bp 112°, lit.³³ 56° (90 mm)] weighing 2.07 g (29% yield), was only slightly contaminated. It was further purified by vpc (Carbowax 4000, 20 ft \times 0.375 in., 145°) to yield 1.03 g of pure en-yne 13: ir (CHCl₃), 2210 (C==C), 1635 (C==C), 1440, 1380, and 820 cm⁻¹ (impurity bands at 1670 and 1720 cm⁻¹ were also present); nmr (CCl₄), δ 1.72 and 1.77 (6 H), 1.87 and 1.91 (3 H), and 5.09 (1 H multiplet, HC==C); each of the peaks between 1.7 and 2.0 looks like a singlet at a 500-Hz sweep width.

^{(28) &}quot;Dictionary of Organic Compounds," Vol. 4, 4th ed, Oxford University Press, New York, N. Y., 1965: (a) p 2224; (b) p 2221; (c) p 2220.

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Reaction of 13 with Formic Acid. A. Product Study. A solution of 138 mg of en-yne 13 in 3.6 ml of formic acid (0.040 M) was heated at 70° for 12 hr. Water (20 ml) was added, and the mixture was extracted with two 10-ml portions of ether. The ethereal extracts were washed to neutrality with saturated sodium bicarbonate solution. After drying and removal of the ether by distillation and evaporation, a liquid weighing 140 mg (85% yield of ketone) remained. It showed a single major vpc peak with very small amounts of impurities. Its nmr, ir, and vpc retention time were almost identical with those of the commercial sample of 5-methyl-4-hexen-3-one (9).

B. Nmr Product Study. A solution of 58 mg (0.62 mmol) of 13 and 42 mg (0.62 mmol) of sodium formate in 0.80 ml of formic acid was prepared in an nmr tube and its spectrum was recorded at room temperature (see Figure 1C). This spectrum is similar to the spectrum of 13 in CCl₄ with single peaks at 1.37, 1.43, 1.52, and 1.55 ppm and a multiplet at 4.79 ppm from HMDS. Another sample prepared in the same way, was inserted in the variable-temperature probe at 70°. The first spectrum recorded at this temperature (see Figure 1D) shows single peaks at 1.20, 1.32, 1.40, and 1.46, a quartet of multiplets centered at 4.96, and a complex multiplet centered at 5.32 (two apparent maxima about 5 Hz apart) ppm from HMDS. Seven spectra were recorded in the first 3 hr, during which interval the conversion to 9 was less than half complete.

Preparation of 2,2-Dimethyl-1-pentyl Tosylate (16). To a cold solution of 18.0 g (0.095 mol) of p-toluenesulfonyl chloride in 200 ml of dry pyridine was added 10.0 g (0.86 mol) of 2,2-dimethyl-1pentanol (Eastman practical grade). After the reaction mixture has been stirred for 12 hr, 600 ml of ice water was added. The mixture was extracted with two 150-ml portions of pentane-ether (1:1). The organic layers were extracted with two 100-ml portions of cold 5% sulfuric acid, 100 ml of saturated sodium bicarbonate solution, and 100 ml of water. After drying (sodium sulfate) and evaporation of the solvent, the remaining solvent and unreacted starting alcohol were removed by gently heating the residue for 4 hr in vacuo (1 mm). The liquid residue (19.5 g, 84%) was dissolved in 50 ml of pentane and cooled in a Dry Ice-acetone bath until crystals were formed. This recrystallization procedure was repeated seven times. The final liquid product was again taken up in pentane and dried and the solvent was thoroughly removed: weight 12.8 g; ir (CHCl₃), 1603 and 1475 (C₆H₄), 1360, 1190, and 1180 (SO₂), 1600, 965, and 850 cm⁻¹; nmr (CCl₄), δ 0.85 (singlet, (CH₃)₂C), a multiplet between 0.65 and 1.30 that overlaps the gemdimethyl singlet (total area in this region is 13 H), 2.44 (3 H singlet, CH_3Ar), 3.59 (2 H singlet, CH_2O), 7.28 (2 H doublet, J = 8 Hz, ArH), and 7.72 (2 H doublet, J = 8 Hz, ArH). Anal. Calcd for $C_{14}H_{22}SO_3$: C, 62.19; H, 8.20. Found: C,

62.41; H, 8.31

Formolysis of 16. Nmr Kinetic Study. A solution of 77.1 mg (0.286 mmol) of 16 and 21.1 mg (0.21 mmol) of sodium formate in 0.60 ml of formic acid was prepared in an nmr tube. The reaction was followed at 75° by measuring the relative heights of the tosylate methyl peak at 2.11 ppm from HMDS and p-toluenesulfonic acid methyl peak at 2.05 ppm. Thirteen spectra were recorded over 10 hr.

Acknowledgments. Thanks are due to F. Marshall van Meter for preliminary work on this problem, to Daryl Sharp for obtaining the nmr spectra and to Dr. S. L. Smith, J. L. Alderfer, and H. E. Montgomery for help with the nmr work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support.

The Kinetics and Mechanism of the Acid-Catalyzed Rearrangement of 1-Phenyl-3-methylallyl Alcohol and the Hydration of 1-Phenyl-1,3-butadiene¹

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Abstract: The kinetics of the acid-catalyzed rearrangement, racemization, and ¹⁸O exchange of 1-phenyl-3-methylallyl alcohol (1) have been studied in 40% aqueous dioxane at 25.0°. The three reaction rates were found to be identical in a given acid solution, and were further shown to be proportional to the acid concentration with the same second-order rate constant, 6.8×10^{-2} l. mol⁻¹ sec⁻¹. The kinetics of racemization and ¹⁸O exchange of 3phenyl-1-methylallyl alcohol (2) were also studied and the rates shown to be the same within experimental error, with second-order rate constant 1.2×10^{-3} l. mol⁻¹ sec⁻¹. Finally, the rates of dehydration of 2 and hydration of 1-phenyl-1,3-butadiene (3) were followed and shown to correlate with the acidity of the medium, a plot of $\ln k$ vs. H_0 being linear with slope -1.49 in 40% dioxane and -1.22 in water. The mechanism of rearrangement of 1 thus involves protonation of 1 followed by unimolecular dissociation of the protonated species to form the intermediate carbonium ion, which is partitioned almost exclusively in favor of 2. The hydration of 3 proceeds via a ratedetermining protonation of $\mathbf{3}$ to form the same carbonium ion, and the rate of the dehydration of $\mathbf{2}$ is governed by the corresponding deprotonation of the carbonium ion.

The phenomenon of carbonium ion return is well documented in the rearrangement of allylic esters.^{3a,b} The detection of return depends on the

(1) Supported in part by grants from the National Science Foundation (NSF GP-5103) and the Petrolenm Research Fund (PRF 2043-A4) administered by the American Chemical Society. Grateful acknowledgment is made to the donors of these funds.

(2) To whom inquiries should be directed.

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measurement of the rates of racemization, exchange, and rearrangement of the ester. For example, in the acetolysis of 1-phenylallyl acetate the rate of rearrangement to form cinnamyl acetate provides a minimum rate of ionization. However, both the racemization and ¹⁴C-exchange rates are faster, indicating that the initially

unpublished observations; M. H. Andrus, Jr., Ph.D. Thesis, University of Washington, 1967.