

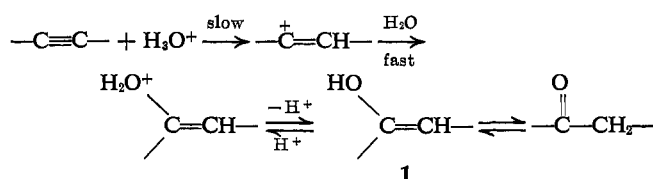
# Polar Additions to Olefins and Actylenes. III. The Kinetics and Stereochemistry of Addition in the System 1-Phenylpropyne–Hydrogen Chloride–Acetic Acid<sup>1</sup>

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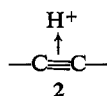
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**Abstract:** The reaction of 1-phenylpropyne with hydrogen chloride in acetic acid follows a third-order rate law, first order in acetylene and second order in hydrogen chloride, and gives 1-chloro-*cis*-1-phenylpropene (3), 1-chloro-*trans*-1-phenylpropene (4), and propiophenone (7) as the principal products. It was found that 1-acetoxy-*cis*- (5) and 1-acetoxy-*trans*-1-phenylpropene (6) are also formed but are converted to propiophenone in a secondary reaction. In 1.0 *M* acid the primary product distribution is 3, 70%; 4, 17%; 5, 5%; 6, 8%. The results are discussed in terms of vinyl carbonium–hydrogen dichloride ion pairs as intermediates.

A number of studies have implicated vinyl cations as intermediates in the addition of acids to acetylenes. Examples include (1) the acid-catalyzed hydration of acetylenic ethers,<sup>2</sup> phenylacetylenes,<sup>3</sup> and phenylpropionic acids;<sup>3b</sup> (2) the addition of trifluoroacetic acid to 1-hexyne, 3-hexyne, and 5-chloro-1-pentyne;<sup>4</sup> (3) the addition of hydrogen halides to 1-propyne.<sup>5</sup> It has been demonstrated that the additions involve a rate-limiting proton transfer<sup>2,3</sup> and that, for phenylacetylene<sup>3a</sup> and phenylpropionic acid,<sup>3b</sup> the transition state possesses considerable positive charge at the benzylic carbon. The results have been interpreted in terms of a slow formation of a vinyl cation which is rapidly attacked by a nucleophilic component of the system. In the hydration of acetylenes to ketones, the enol (1) is assumed to intervene.



The stereochemistry of acid additions to acetylenes is of considerable interest. Burnelle<sup>6</sup> has recently argued on theoretical grounds that *trans* addition is the electronically favored mode for addition to acetylenes. If the intermediate has a  $\pi$ -complex structure (2),

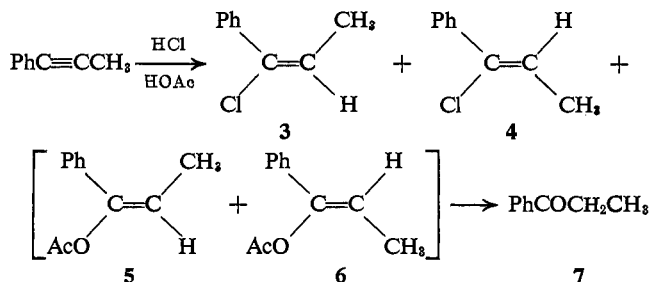


*trans* addition might also be expected. A concerted addition proceeding *via* a cyclic transition state would

require *cis* addition.<sup>7</sup> Experimental results on the stereochemistry of acid additions to acetylenes are scant. Acetylenedicarboxylic acid<sup>8</sup> and methylpropionic acid<sup>9</sup> are reported to add hydrogen halides *trans*, but Peterson<sup>10</sup> has recently found the addition of trifluoroacetic acid to 3-hexyne to be nonstereospecific. We report here a study of the kinetics and stereochemistry of addition in the system 1-phenylpropyne–hydrogen chloride–acetic acid.

## Results

The reaction of 1-phenylpropyne with hydrogen chloride in glacial acetic acid yields as the main products 1-chloro-*cis*- (3) and 1-chloro-*trans*-1-phenylpropene (4) along with propiophenone (7). The chlorides



3 and 4 were isolated by vpc and shown to be identical with previously prepared samples.<sup>11</sup> Careful examination of the reaction mixture by vpc revealed two minor components with retention times identical with those of 1-acetoxy-*cis*- (5) and 1-acetoxy-*trans*-1-phenylpropene (6). Authentic 6 was obtained from the mercuric acetate catalyzed addition of acetic acid to 1-phenylpropyne. A mixture of 5 and 6 was obtained from the reaction of propiophenone with *p*-toluenesulfonic acid in acetic anhydride, pure samples being isolated by preparative vpc. The structures of the acetates were assigned from their nmr spectra; the *trans* acetate 6 exhibited a vinylic proton resonance at lower field than

(7) This type of mechanism has been considered improbable for the hydration of acetylenic thioethers on the basis of the small negative entropy of activation found for *t*-butylthioethyne.<sup>2b</sup>

(8) A. Michael, *J. Prakt. Chem.*, [2] 46, 209 (1892).

(9) R. Friedrich, *Ann.*, 219, 368 (1883).

(10) P. E. Peterson and J. E. Duddy, *J. Am. Chem. Soc.*, 88, 4990 (1966).

(11) R. C. Fahey and C. S. Schubert, *ibid.*, 87, 5172 (1965).

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

(2) (a) T. L. Jacobs and S. Searles, *J. Am. Chem. Soc.*, 66, 686 (1944); (b) W. Drenth and H. Hogeveen, *Rec. Trav. Chim.*, 79, 1002 (1960); (c) E. J. Stamhuis and W. Drenth, *ibid.*, 80, 797 (1961).

(3) (a) P. W. Bott, C. Eaborn, and D. R. Walton, *J. Chem. Soc.*, 384 (1965); (b) D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *J. Am. Chem. Soc.*, 87, 2295 (1965).

(4) P. E. Peterson and J. E. Duddy, *ibid.*, 85, 2865 (1963).

(5) (a) K. Griesbaum, *Angew. Chem.*, 76, 782 (1964); (b) K. Griesbaum, W. Naegle, and G. G. Wanless, *J. Am. Chem. Soc.*, 87, 3151 (1965).

(6) L. Burnelle, *Tetrahedron*, 20, 2403 (1964).

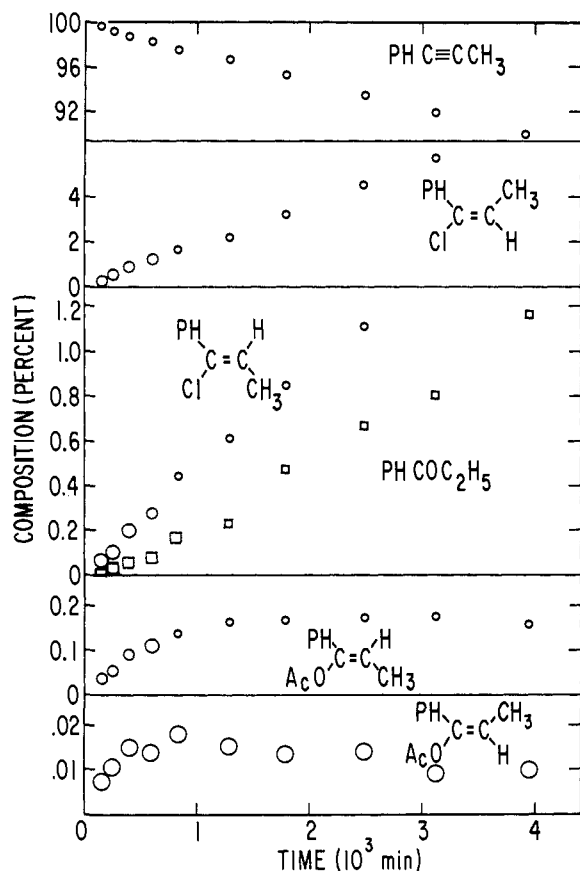


Figure 1. Composition of the reaction mixture as a function of time for an initial HCl concentration of 1.00 M and an initial PhC≡CCH<sub>3</sub> concentration of 0.81 M.

the *cis*-acetate **5**, this feature having been found to be characteristic for 1-phenylpropene derivatives.<sup>11,12</sup>

The composition of the reaction mixture, as determined by vpc, was monitored as a function of time for an experiment in which the initial concentration of acetylene was 0.81 M and that of hydrogen chloride was 1.00 M. The results (Figure 1) show that the concentrations of the acetates increase to a maximum and then slowly decline, and that, paralleling this, there is a slight lag in the formation of ketone. This implies that the ketone is formed *via* the acetates, the latter being formed from acetylene at a lower rate than they are converted to ketone. This was verified by showing that the authentic acetates are stable to the aqueous work-up but are cleanly and rapidly converted to the ketone by hydrogen chloride in acetic acid. The other product of this reaction, by analogy with the reaction of other vinyl acetates with hydrogen chloride in acetic acid,<sup>13</sup> is presumed to be acetyl chloride. Pseudo-first-order rate constants,  $k_1$ , for the conversion were measured at 25.0° with [HCl] = 1.00 M and [acetate] = 0.009 M, values of  $10^5 k_1^5 = 15$  and  $10^5 k_1^6 = 2.3 \text{ sec}^{-1}$  being obtained for **5** and **6**, respectively.

Initial rates,  $R$ , for addition to the acetylene were measured at less than 10% conversion as a function of the acetylene and hydrogen chloride concentrations. A plot of  $\log R$  vs.  $\log [\text{HCl}]$  at constant acetylene concentration (Figure 2) gives a reasonably straight line

(12) M. Barbioux, W. Detay, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belges*, **73**, 716 (1964).

(13) H. J. Hagermayer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949); E. A. Jeffrey and D. P. N. Satchell, *J. Chem. Soc.*, 1876 (1962).

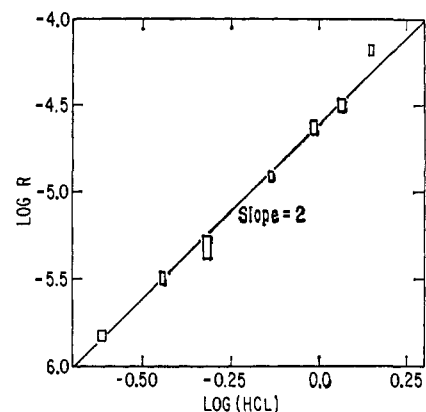


Figure 2. Log-log plot of the initial rate ( $R$ ) as a function of the HCl concentration at a constant initial PhC≡CCH<sub>3</sub> concentration of 0.81 M.

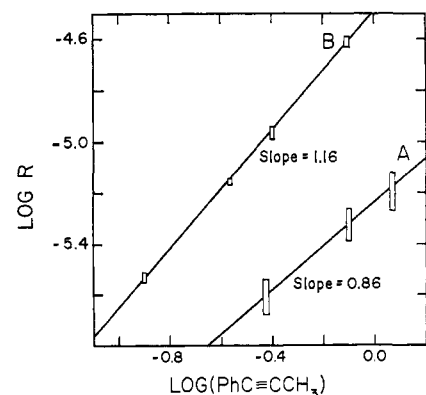


Figure 3. Log-log plot of the initial rate as a function of PhC≡CCH<sub>3</sub> concentration: A, [HCl] = 0.5 M; B, [HCl] = 0.98 M and hydrocarbon content held constant with cyclohexane.

of slope 2. A plot of  $\log R$  vs.  $\log [\text{PhC}\equiv\text{CCH}_3]$  at constant hydrogen chloride concentration has a slope of less than 1, but, if the hydrocarbon content of the solvent is maintained constant with cyclohexane as the acetylene concentration is reduced, a slope of greater than unity is observed (Figure 3). At the high concentrations employed here, an increase in the acetylene concentration decreases the solvent polarity, leading to an apparent kinetic order of less than unity. Since cyclohexane is even less polar than 1-phenylpropyne, the studies at constant hydrocarbon content understandably yield a kinetic order greater than one. From these results it is evident that the rate law is best represented by

$$\text{rate} = k_3[\text{PhC}\equiv\text{CCH}_3][\text{HCl}]^2 \quad (1)$$

Values of  $k^3$  calculated from the integrated form of eq 1<sup>14</sup> are collected in Table I. In Table II are given the results of experiments in which diluents were added to the reaction mixture.

Product compositions were obtained and are included in Tables I and II. The per cent of *cis*- and *trans*-chloride in the product was independent of reaction time, indicating that these products are stable to the reaction conditions. This was also demonstrated in control experiments. Since no increase in the amount of ketone formed was found on adding water to the

(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1963, p 20.

**Table I.** Third-Order Rate Constants and Product Compositions for the Hydrochlorination of 1-Phenylpropyne in Acetic Acid at 25.0°

[PhC≡CCH <sub>3</sub> ], M	[HCl], M	10 <sup>7</sup> k <sub>3</sub> , M <sup>-2</sup> sec <sup>-1</sup>	Product composition, %		
			3	4	(5 + 6 + 7) <sup>a</sup>
0.81	1.40	7.3	67 ± 1	19 ± 1	13 ± 1
0.81	1.20	5.3	72 ± 2	15 ± 1	12 ± 2
0.81	1.00	5.7	70 ± 1	17 ± 1	13 ± 1 <sup>b</sup>
0.81	0.97	5.3	70 ± 2	16 ± 1	12 ± 1
0.81	0.75	5.0	72 ± 2	16 ± 1	12 ± 1 <sup>b</sup>
0.81	0.50	4.7	74 ± 2	14 ± 1	12 ± 2
0.81	0.37	5.3	78 ± 2	11 ± 1	11 ± 2
0.80	0.25	5.5	77 ± 2	12 ± 1	11 ± 2
0.39	0.50	4.8	73 ± 2	14 ± 1	13 ± 2
1.20	0.50	4.0	74 ± 2	13 ± 1	13 ± 2
1.61	0.62	4.3	75 ± 2	15 ± 1	10 ± 2
0.81 <sup>c</sup>	0.98	5.8	71 ± 1	16 ± 1	13 ± 1 <sup>b</sup>
0.41 <sup>c</sup>	0.98	5.2	70 ± 1	17 ± 1	13 ± 1 <sup>b</sup>
0.28 <sup>c</sup>	0.98	4.7	70 ± 1	17 ± 1	13 ± 1 <sup>b</sup>
0.13 <sup>c</sup>	0.98	4.2	70 ± 1	17 ± 1	13 ± 1 <sup>b</sup>

<sup>a</sup> Except as noted, these values are based on the measured amount of 7 corrected to include 5 and 6 using the ratio of 7: (5 + 6) obtained in other experiments. <sup>b</sup> Based on actual measurement of 5, 6, and 7. <sup>c</sup> In this series of experiments, the hydrocarbon content was maintained with cyclohexane as the 1-phenylpropyne concentration was reduced.

**Table II.** The Effect of Diluents on the Rate and Product Composition for the Hydrochlorination of 1-Phenylpropyne in Acetic Acid; [HCl] = 1.00 M, [PhC≡CCH<sub>3</sub>] = 0.81 M<sup>a</sup>

Diluent	Concn, M	10 <sup>7</sup> k <sub>3</sub> , M <sup>-2</sup> sec <sup>-1</sup>	Product composition, %		
			3	4	(5 + 6 + 7) <sup>b</sup>
None	...	5.7	70	17	13
H <sub>2</sub> O	0.05	5.8	70.5	17	12.5
H <sub>2</sub> O	0.1	6.8	68	19	13
HCOOH	1.1	11.8	66	18.5	15.5 <sup>c</sup>
Cyclohexane	0.9	3.5	72.5	16	11.5

<sup>a</sup> These experiments were run concurrently, and the same stock solution of hydrogen chloride in acetic acid was used to prepare all of the solutions. <sup>b</sup> Based on actual measurement of 5, 6, and 7. <sup>c</sup> Includes two unidentified products present in small concentrations.

reaction mixture (Table II), it may be concluded that ketone is not formed from trace amounts of water present in the acetic acid but derives entirely from the intermediate acetates.

From the foregoing results it is possible to estimate the initial product composition at [HCl] = 1.00 M and [PhC≡CCH<sub>3</sub>] = 0.81 M. When the concentration of acetate 5 is at a maximum, its rate of formation must equal its rate of conversion to ketone

$$k_3^5[\text{PhC}\equiv\text{CCH}_3][\text{HCl}]^2 = k_1^5[5][\text{HCl}]^7$$

For [HCl] = 1.00 M

$$k_3^5 = k_1^5 \frac{[5]}{[\text{PhC}\equiv\text{CCH}_3]}$$

Taking the ratio of 5 to acetylene from Figure 1 and the value of k<sub>1</sub><sup>5</sup> reported above, we find 10<sup>8</sup>k<sub>3</sub><sup>5</sup> = 2.7 M<sup>-2</sup> sec<sup>-1</sup>. The corresponding calculation for 6 gives 10<sup>8</sup>k<sub>3</sub><sup>6</sup> = 4.2 M<sup>-2</sup> sec<sup>-1</sup>. The sum of these rates corresponds to 12% of the total rate (10<sup>7</sup>k<sub>3</sub> = 5.7) at [HCl] = 1.00 M which is in good agreement with the fraction of acetate plus ketone (13 ± 1%) obtained from the acetylene under these conditions. With the

ratio of k<sub>3</sub><sup>5</sup> to k<sub>3</sub><sup>6</sup> determining the initially formed ratio of 5 to 6, the primary product composition at [HCl] = 1.00 M is 3, 70%; 4, 17%; 5, 5%; 6, 8%.

In order to interpret the preceding results, it proved of interest to obtain an estimate of the relative stabilities of the isomeric acetates and chlorides. In the course of preparing 1-acetoxy-*cis*-1-phenylpropene, it had already been found that this compound was less stable than its *trans* isomer, converting, in the presence of acidified acetic anhydride, to a mixture containing less than 10% of the *cis* form. The *cis*-chloride was not readily isomerized by acid but was converted to a mixture containing 90% *trans*-chloride by palladium on charcoal activated by a trace of hydrogen. Under similar conditions the *trans*-chloride did not yield significant amounts of the *cis* isomer. From these observations it is evident that the *trans* isomers are favored.

## Discussion

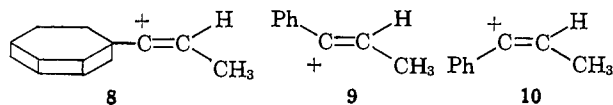
The foregoing results provide a considerably more detailed insight into the product-forming steps involved in acid additions to acetylenes than previous data have allowed. The enol acetates have been clearly identified in the present system as precursors to ketone formation. The fraction of ketone formed (Table I), when linearly extrapolated to zero acid concentration, amounts to 11 ± 2% of the product, not significantly different from the fraction formed at high acid concentrations. This shows that acetate and *cis*-chloride must be very predominantly formed according to the same third-order rate law. Similarly, the fraction of *trans*-chloride extrapolated to zero acid concentration is 10 ± 2% of the product, so that it is also significantly formed according to the third-order rate expression of eq 1. There is, however, a rather substantial variation in the stereochemical composition of the chloride with acid concentration. These observations obviously have important consequences for the mechanism of the reaction.

A concerted *cis*-addition mechanism might seem attractive considering the second-order dependence on acid and predominant formation of *cis*-chloride, but there remains the problem of accounting for the other products. If *cis*-chloride and acetate were both formed *via* a concerted process, formation of *cis*-acetate should involve a lower kinetic order in acid, but there is no evidence for this. Further, it is difficult to envision formation of *trans*-chloride by a concerted process following the same third-order rate law.

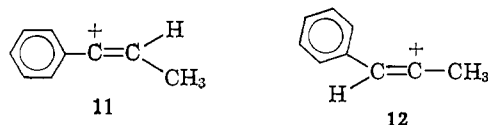
The results are entirely consistent with the formation of a cationic intermediate which partitions among the various observed products. The second-order dependence on hydrogen chloride is understandable if the anion formed is a hydrogen dichloride ion, as has been found for the addition of hydrogen chloride to olefins in nitromethane.<sup>15</sup>

Several possible structures can be considered for the product determining intermediate. The most reasonable structure is a linear vinylic cation 8 with the carbonium p orbital conjugated with the phenyl ring. The bent cations 9 and 10 can be excluded on purely

(15) (a) Y. Pocker, *J. Chem. Soc.*, 1292 (1960); (b) Y. Pocker, A. E. Miller, F. Naso, and K. D. Stevens, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 40S.



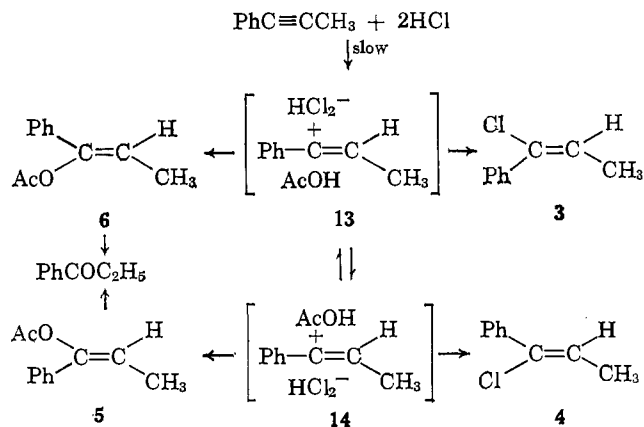
energetic grounds as intermediates having a significant lifetime before conversion to **8**. Cation **8** is favored over **9** or **10** by enhanced charge delocalization resulting from increased overlap of the carbonium p orbital with the phenyl  $\pi$  system, by increased bond energies, and, most importantly, by the promotion energy associated with the difference in a vacant  $sp^2$  orbital and a vacant p orbital.<sup>16</sup> A cation having structure **11**, with the empty p orbital orthogonal to the phenyl  $\pi$  system, is also unacceptable. In this case, the positive charge



is not only localized but is also destabilized by the inductive effect of the phenyl group. If protonation were to occur to yield an intermediate ion in which conjugation of the phenyl ring with the double bond is retained as in **11**, protonation should occur at the  $\alpha$  carbon to yield **12**, but this ion would not lead to the observed products.

The predominant formation of *cis*-chloride is reasonable if, as expected in acetic acid, the cation **8** is initially formed as an ion pair. The simplest possible ion-pair mechanism which can be considered is illustrated in Scheme I. Here, a linear vinyl cation-hydro-

Scheme I



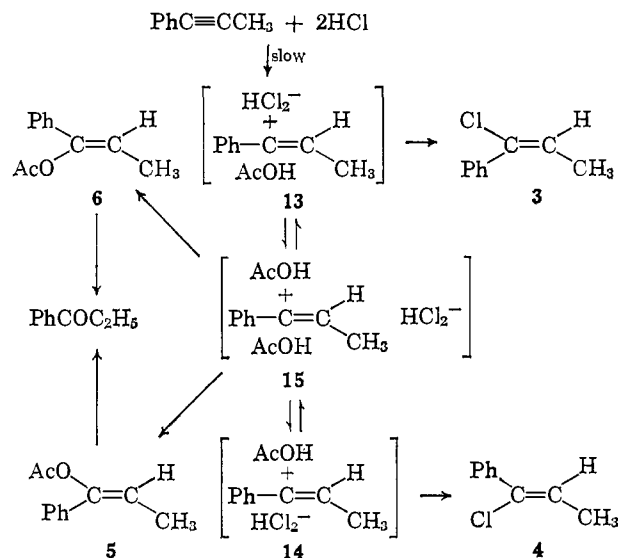
gen dichloride ion pair **13** is formed with the anion associated with one side of the carbonium p orbital and a molecule of acetic acid solvating the other side. Collapse from this intermediate yields *cis*-chloride **3** or *trans*-acetate **6**, while rearrangement to the isomeric ion pair **14** is followed by collapse to *trans*-chloride **4** or *cis*-acetate **5**. This mechanism reasonably accounts for the types of products formed but does not satisfactorily account for the primary product distribution at 1.00 *M* acid concentration. The distribution between chloride and acetate should depend upon the nucleophilicity of the hydrogen dichloride ion relative

(16) An estimate of the promotion energy can be obtained as one-third of the difference in the valence-state ionization potential of a carbon 2s orbital (−21.4 eV) and a carbon 2p orbital (−11.4 eV) or roughly 75 kcal.

to that of acetic acid and upon the relative stability of the products. The *cis* adducts are less stable than the *trans* owing to steric inhibition of conjugation with the olefinic double bond, and yet *cis*-chloride **3** predominates over *trans*-acetate **6** by nearly 9 to 1. This would lead one to conclude that the hydrogen dichloride ion is much more nucleophilic toward the intermediate cation than is acetic acid. If so, then *trans*-chloride **4** should predominate over *cis*-acetate **5** by an even greater margin, but the observed ratio is only 3.4 to 1. Thus, the mechanism of Scheme I is unsatisfactory.

The mechanism of Scheme II does offer a plausible explanation of the product distribution. An additional

Scheme II



species **15** is proposed which is envisioned as the intermediate stage between **13** and **14**, with the hydrogen dichloride not associated with either face of the carbonium carbon. In **15**, both sides of the carbonium ion are open to attack by solvent. If this species is considered the primary precursor in acetate formation, the observed 8 to 5 ratio of *trans*- to *cis*-acetate is not unreasonable, and the predominance of *cis*-chloride merely indicates that collapse to product is competitive with the formation of **15**.

The reason for the variation in the chloride composition with acid concentration is difficult to identify with certainty. One possibility is that a fraction of **13** is formed with a molecule of hydrogen chloride replacing the acetic acid. A species of this type would certainly give a product distribution richer in *trans*-chloride. It would be interesting to know whether the variation in *trans*-chloride formation is associated with a different kinetic expression, but medium effects, resulting when high concentrations of reactants are involved, preclude the detection of small components of reaction following a different kinetic law than the main reaction.

The mechanism of Scheme II finds a basis for support in the studies of ion-pair phenomena associated with alkyl carbonium ions in weakly dissociating solvents. Thus, **13** and **14** may be considered as intimate ion pairs<sup>17</sup> and **15** as a solvent-separated ion pair. Recent

(17) S. Winstein, P. E. Klinedinst, and E. Clippinger, *J. Am. Chem. Soc.*, **83**, 4986 (1961), and references therein.

work by Goering and Levy<sup>18</sup> has indicated that solvent-separated ion pairs can be intermediates in the interconversion of stereoisomeric intimate ion pairs, providing some justification for the present proposal.

The stereochemistry of addition to phenylacetylenes is not different from that of the corresponding olefin. Predominant *cis* addition of hydrogen halide to 1-phenylpropene has been observed in methylene chloride<sup>19</sup> and in nitromethane.<sup>15b</sup> It thus appears that vinylic carbonium ions behave very much like their alkyl analogs.

It would obviously be dangerous to generalize the present results to other systems. The structure of the acetylene, the nature of the acid, and the character of the solvent can all influence the mechanism and hence the steric course of additions to acetylenes. The *trans* additions of hydrogen halides to acetylenecarboxylic acids<sup>8,9</sup> and the nonstereospecific addition of trifluoroacetic acid to 3-hexyne<sup>10</sup> are cases in point. Further stereochemical studies in systems where the kinetics are known are required before the types of polar addition mechanism available to acetylenes can be reliably elaborated.

## Experimental Section

Nmr spectra were measured on a Varian Associates HR-60 spectrometer and were calibrated by the side-band technique. Samples were measured as approximately 10% w/v solutions in carbon tetrachloride, and chemical shifts are reported in ppm downfield from TMS as internal standard. Preparative vpc separations were carried out on an Aerograph Autoprep chromatograph using a 10 ft by 3/8 in. 30% diethylene glycol succinate on Chromosorb P column (column 1). An Aerograph Model 200 chromatograph equipped with thermal conductivity detectors and a linear temperature programmer was employed with a 12 ft by 1/8 in. column containing 4 ft of 20% SE52 and 8 ft of 20% diethylene glycol succinate on Chromosorb P-HMDS (column 2) for analytical measurements. Analyses were performed by C. F. Geiger, 312 East Yale St., Ontario, Calif.

**Materials.** 1-Phenylpropyne was obtained from Columbia Organic Chemicals and purified by vpc (column 1 at 150° with a helium flow of 140 ml per min) or spinning-band vacuum fractionation (bp 87°, 12 mm). The purified acetylene (99.9% by vpc) was stored in ampoules sealed under nitrogen. Propiophenone was purchased from Matheson Coleman and Bell. Glacial acetic acid from Allied Chemical was shown to contain less than 0.02% water (w/v) by Karl Fisher titration in methanol and was used without further drying.

**1-Chloro-*cis*- (3) and 1-Chloro-*trans*-1-phenylpropene (4).** Hydrogen chloride (5 g, 0.14 M) and 1-phenylpropyne (16 g, 0.14 M) in 80 ml of glacial acetic acid were allowed to react at 50° for 4 days. The reaction mixture was then diluted with 150 ml of pentane and washed with three 150-ml portions of water and 50 ml of 10% aqueous sodium bicarbonate. After drying over anhydrous potassium carbonate, the pentane was evaporated leaving 19 g of crude product. The chlorides were isolated by vpc on column 1 at 145° with a helium flow of 90 ml per min. 1-Chloro-*cis*-1-phenylpropene (3) had a retention time of 21.5 min,  $\lambda_{\text{max}}^{\text{cyclohexane}}$  246 m $\mu$  ( $\epsilon$  3550), and an nmr spectrum with signals at 7.28 (5 H, singlet), 5.95 (1 H, quartet,  $J = 7$  cps), and 1.70 ppm (3 H, doublet,  $J = 7$  cps).

*Anal.* Calcd for C<sub>9</sub>H<sub>9</sub>Cl: C, 70.83; H, 5.94; Cl, 23.23. Found: C, 69.73; H, 6.00; Cl, 22.11.

1-Chloro-*trans*-1-phenylpropene (4) had retention time of 30 min,  $\lambda_{\text{max}}^{\text{cyclohexane}}$  = 249 m $\mu$  ( $\epsilon$  5900), and an nmr spectrum with signals at 7.1–7.6 (5 H, multiplet), 6.09 (1 H, quartet,  $J = 7$  cps), and 1.91 ppm (3 H, doublet,  $J = 7$  cps).

*Anal.* Calcd for C<sub>9</sub>H<sub>9</sub>Cl: C, 70.83; H, 5.94; Cl, 23.23. Found: C, 69.80; H, 5.76; Cl, 21.27.

The chlorides were identical by vpc and nmr with authentic samples prepared previously.<sup>20</sup>

The relative stability of 3 and 4 was established by dissolving 60 mg of the chloride in 1 ml of pentane and adding 10 mg of 10% palladium on charcoal. A catalytic amount of hydrogen was allowed to come in contact with the solution while stirring. Samples were removed after 7 hr and analyzed by vpc. While 4 showed no evidence of isomerization, 3 was 90% converted to 4.

**1-Acetoxy-*cis*-1-phenylpropene (5).** The procedure followed was that of Bedoukian.<sup>21</sup> A mixture of *p*-toluenesulfonic acid (1.0 g), acetic anhydride (47 g), and propiophenone (25 g) was stirred at 155–158°, and the composition of the reaction was monitored by vpc. The *cis*- and *trans*-acetates were both formed, but the former was seen to isomerize to the latter under the reaction conditions, comprising 23% of the product at 11% reaction but only 8% of the product at 40% reaction. Stopping the reaction after 5 hr (25% reaction with 19% of the product being *cis*-acetate), it was possible to obtain a reasonable recovery of *cis*-acetate. The reaction mixture was worked up in water (150 ml) by extracting with pentane (100 ml). The organic layer was washed with water and aqueous sodium bicarbonate, dried over anhydrous potassium carbonate, and then concentrated by evaporation of the pentane. The mixture was separated by vpc on column 1 at 190°, with a helium flow of 150 ml per min. Retention times (min) were: propiophenone, 11; 5, 16; 6, 22. The nmr spectrum of 5 had peaks at 7.29 (5 H, singlet), 5.38 (1 H, quartet,  $J = 7$  cps), 2.08 (3 H, singlet), and 1.73 ppm (3 H, doublet,  $J = 7$  cps).

*Anal.* Calcd for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>: C, 74.98; H, 6.68. Found: C, 74.16; H, 7.04.

**1-Acetoxy-*trans*-1-phenylpropene (6).** Mercuric acetate (1 g) was dissolved in 25 ml of glacial acetic acid with heating, and 20 ml of 1-phenylacetylene was added. The mixture was refluxed under nitrogen for 2 days. After cooling, the solution was shaken with 100 ml of pentane and 100 ml of water. The organic layer was separated, washed twice with water, washed once with 10% aqueous sodium bicarbonate, and dried over anhydrous potassium carbonate. Evaporation of the pentane left 24 g of crude product, part of which was separated by vpc using column 1 at 170° with a helium flow of 155 ml per min. The major product, 1-acetoxy-*trans*-1-phenylpropene (6), had a retention time of 63 min and an nmr spectrum with signals at 7.28 (5 H, singlet), 5.80 (1 H, quartet,  $J = 7$  cps), 2.19 (3 H, singlet), and 1.66 ppm (3 H, doublet,  $J = 7$  cps).

*Anal.* Calcd for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>: C, 74.98; H, 6.86. Found: C, 74.44; H, 6.91.

A second product having retention time of 54 min and nmr signals at 7.28 (5 H, singlet), 5.80 (1 H, narrow multiplet), 2.08 (3 H, singlet), and 2.04 ppm (3 H, doublet,  $J = 1.1$  cps) was presumed to be 2-acetoxy-1-phenylpropene.

**Kinetic and Product Studies.** Solutions of hydrogen chloride (Matheson Co.) in glacial acetic acid were prepared by weight and concentrations checked by addition of a known excess amount of lithium acetate solution in acetic acid followed by potentiometric titration of excess lithium acetate against standard *p*-toluenesulfonic acid in acetic acid. The reaction solutions were prepared in 50-ml volumetric flasks by mixing a stock solution of the acid with the acetylene and diluent (if any) and were transferred to a constant-temperature bath (25.0 ± 0.01°) after thorough and rapid mixing of the solution. Aliquots (3 ml) were withdrawn at intervals and mixed with pentane (20 ml) and water (50 ml). The organic layer was separated, and the water layer was washed with two 10-ml portions of pentane. The combined organic fractions were washed with 10 ml of 10% aqueous sodium bicarbonate and dried over anhydrous potassium carbonate. The residue from evaporation of the pentane was analyzed by vpc on column 2 at 170° with a helium flow of 25 ml per min. Retention times (min) as measured from the air peak were: 1-phenylpropyne, 4; 3, 5.3; 4, 8; 7, 9.3; 5, 13; 6, 16. Reaction mixture compositions were calculated from the peak area ratios (taken equal to mole ratios) measured with a disk integrator attached to the recorder. Pseudo-first-order rate constants for conversion of the acetates 5 and 6 to ketone 7 were measured at 25.0° with initial acetate and hydrogen chloride concentrations of 0.009 and 1.00 M, respectively. No interconversion of the acetates was found under these conditions, and no formation

(20) See ref 11. Owing to an error in the calibration, the chemical shifts of the two low-field peaks of 1-chloro-*cis*- and 1-chloro-*trans*-1-phenylpropene were incorrectly reported in this paper. The corrected values agree well with those given here.

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of chloride or acetylene was observed. The work-up and analysis procedures were as described above and it was shown that, when the acetates are dissolved in acetic acid and submitted to the work-up procedure, no conversion to ketone results.

The ratio of **3** to **4** did not vary throughout the reaction, indicating that the chlorides are not interconverted under the reaction conditions. This was also demonstrated by showing that an approximately equal molar mixture of **3** and **4** did not significantly change in

composition after 10 hr in a 1.00 M hydrogen chloride solution at 50°. Using known mixtures, it was shown that the vpc procedure was valid (peak area ratios equal mole ratios) and that no product fractionation occurs in the work-up procedure.

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## The N-Decoupled Proton Magnetic Resonance Spectra of Aqueous Pyridine and Pyridinium Ion

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**Abstract:** The proton magnetic resonance (pmr) spectra of neat pyridine and of its aqueous solutions over a range of pH values have been observed under conditions of nitrogen decoupling. With the additional spectral details so obtained, theoretical analyses were carried out leading to complete sets of pmr parameters for neat pyridine, aqueous pyridine, and aqueous pyridinium ion. The effect of protonation on these parameters has been determined, including, in particular, the proton-proton couplings. These results are discussed in terms of electronic and other factors which are likely to be involved.

The earliest reported complete analysis of the proton magnetic resonance spectrum of neat pyridine was carried out in 1957 by Schneider, Bernstein, and Pople,<sup>1</sup> and their results have subsequently provided the initial basis for analyzing the spectra of many pyridine derivatives.<sup>2</sup> The five-spin pyridine system gives rise to a complex spectral pattern which is further complicated by the fact that broadening of the  $\alpha$ -proton resonances by the quadrupolar N atom results in a loss of detailed features necessary for a complete analysis. Recently, Diehl, Jones, and Bernstein have analyzed the  $\beta$  and  $\gamma$  portions of the pyridine spectrum alone by the method of subspectral analysis.<sup>3</sup> Their partial set of parameters differs somewhat from those of Schneider, *et al.*, especially in the case of  $J_{23}$  (in this paper the numbering of ring positions begins with the N atom). Baldeschwieler and Randall demonstrated that the effects of quadrupolar broadening in pyridine could be eliminated by double irradiation but did not report an analysis of the decoupled spectrum.<sup>4</sup>

The pyridinium ion has been examined in trifluoroacetic acid by Smith and Schneider.<sup>5</sup> Their spectrum is broad and poorly resolved, and no complete analysis was attempted. Kotowycz, Schaefer, and Bock have reported chemical shifts for pyridinium salts (Cl, Br, and I) in several nonaqueous media.<sup>6</sup> Neither pyridine nor the pyridinium ion appear to have been studied in detail in aqueous solution, in spite of the widespread interest in the properties of these structures in water.

Interpretations and correlations of results for both pyridine and the ion have been concerned solely with the chemical shifts.<sup>5-8</sup>

This communication describes the results of a detailed study of the pmr spectra of pyridine, both as the neat liquid and in aqueous solution, and of the pyridinium ion in aqueous solution over a wide pH range. Double irradiation at the resonance frequency of the N atom was used when required, and this provided sharp and well-resolved spectra for purposes of refined theoretical analysis, yielding complete sets of spectral parameters for all cases studied. Of particular interest are the values of the H-H coupling parameters for aqueous pyridine and pyridinium ion which are now available for the first time, and which reflect the influence of the positive charge on the electronic (and possibly geometrical) structure of the ring.

### Experimental Section

Matheson Spectrograde, or Reagent Grade, pyridine were used throughout this study without further purification. The aqueous solutions were acidified with concentrated HCl and the volume adjusted to a final concentration of 7 mole % of pyridine. The pH measurements were carried out with a Radiometer TTT-1 pH meter at room temperature ( $\sim 24^\circ$ ).

All spectra were obtained with a Varian Associates Model A-60 spectrometer. The modifications required to provide this instrument with a double-resonance capability are rather extensive and will be reported in detail later. Calibrations were performed by the usual side-band technique using a Krohn-Hite 440-B audio oscillator continuously monitored by a Hewlett-Packard 5245L frequency counter. The peak frequencies are generally the average of two forward and two reverse 50-cps scans taken at 500 cps/sec, with an average deviation of  $\sim 0.1$  cps. The spectra were calibrated relative to external cyclohexane contained in the outer annulus of a precision coaxial sample tube. For the two cases of aqueous pyridine at 0 and 99% protonation the bulk susceptibilities of the

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