Flash Photolytic Generation of Primary, Secondary, and Tertiary Ynamines in Aqueous Solution and Study of Their Carbon-Protonation Reactions in That Medium

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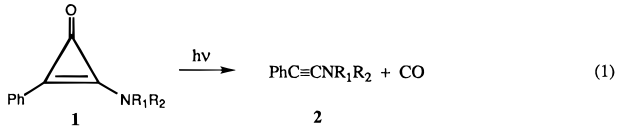
Abstract: A group of nine phenylynamines ($PhC{\equiv}CNH_2$, $PhC{\equiv}CNHCH(CH_3)_2$, $PhC{\equiv}CNHC_6H_{11}$, $PhC{\equiv}CNHC_6H_5$, $PhC{\equiv}CNHC_6F_5$, $PhC{\equiv}CN(CH_2)_5$, $PhC{\equiv}CN(CH_2CH_2)_2O$, $PhC{\equiv}CN(CH_2CH_2CN)_2$, and $PhC{\equiv}CN(CH_3)C_6F_5$) were generated in aqueous solution by flash photolyic decarbonylation of the corresponding phenylaminocyclopropenones, and the kinetics of their facile decay in that medium were studied. This decay is catalyzed by acids for all ynamines—primary, secondary, and tertiary—and also by bases for primary and secondary ynamines. Solvent isotope effects and the form of acid−base catalysis show that the acid-catalyzed path involves formation of keteniminium ions by rate-determining proton transfer to the β-carbon atoms of the ynamines. The ions generated from primary and secondary ynamines then lose nitrogen-bound protons to give ketenimines, and the ketenimines obtained from secondary ynamines are hydrated to phenylacetamides, whereas that from the primary ynamine tautomerizes to phenylacetonitrile. Keteniminium ions formed from tertiary ynamines have no nitrogen-bound protons that can be lost, and they are therefore captured by water instead, and the amide enols thus produced then ketonize to phenylacetamides. The base-catalyzed decay of primary and secondary ynamines also generates ketenimines, but protonation on the β-carbon is now preceeded by proton removal from nitrogen. Rate constants for β-carbon protonation of $PhC{\equiv}CNHCH(CH_3)_2$ and $PhC{\equiv}CN(CH_2)_5$ by a series of carboxylic acids give linear Bronsted relations with exponents $\alpha = 0.29$ and 0.28, respectively, whereas inclusion of literature data for protonation of $PhC{\equiv}CN(CH_2)_5$ by a group of weaker acids gives a curved Bronsted relation whose exponent varies from 0.25 to 0.97. Application of Marcus rate theory to this curved Bronsted relation produces the intrinsic barrier $\Delta G^{\ddagger}_{o} = 3.26 \pm 0.19$ kcal mol^{-1} and the work term $w^{r} = 8.11 \pm 0.15$ kcal mol^{-1}.

1-Aminoacetylenes, commonly called ynamines, are very reactive substances. Primary and secondary ynamines, for example, undergo facile tautomerization to nitriles and ketenimines, and they therefore have been observed previously only in the gas phase or in low-temperature matrices.[1] Tertiary ynamines cannot isomerize in this way, and they have consequently been prepared and characterized,[2] but they are nevertheless quite reactive, and only one previous investigation of their chemistry in aqueous solution has been carried out.[3] We have found that all three classes of ynamines can be generated by photodecarbonylation of phenylaminocyclopropenones, eq 1 (R_1, R_2 = H, alkyl, aryl), and that their reactions in aqueous solutions



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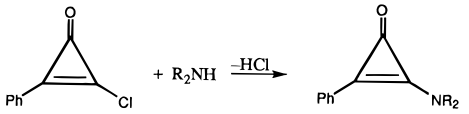
may be studied using flash photolytic techniques. We present here the results of a detailed examination of the representative series of phenylynamines listed in Chart 1.[4]

Chart 1

	R_1	R_2
2a	H	H
2b	H	$CH(CH_3)_2$
2c	H	*c*-C_6H_{11}
2d	H	C_6H_5
2e	H	C_6F_5
2f	$(CH_2)_5$	
2g	$(CH_2CH_2)_2O$	
2h	CH_2CH_2CN	CH_2CH_2CN
2i	CH_3	C_6F_5

Experimental Section

Materials. Phenylaminocyclopropenones were prepared by treating the corresponding amines with phenylchlorocyclopropenone, as shown in eq 2, which was itself obtained either by partial hydrolysis of



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phenyltrichlorocyclopropene,[5] eq 3, or by treatment of phenylhydroxy-

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) Wentrup, C.; Winter, H.-W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 720−721. Buschek, J. M.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 729−731. van Baar, B. L. M.; Koch, W.; Lebrilla, C.; Terlouw, J. K.; Weiske, T.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 827−828. Terlouw, J. K.; Bergers, P. C.; van Baar, B. L. M.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 357−359. Wentrup, C.; Briehl, H.; Lorencak, P.; Vogelbacher, U. J.; Winter, H.-W.; Maquestiau, A.; Flammang, R. *J. Am. Chem. Soc.* **1988**, *110*, 1337−1343. August, J.; Klemm, K.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1841−1844.

(2) See, for example: Viehe, H. G. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; Chapter 12. Gladych, J. M. Z.; Hartley, D. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon: New York, 1979; pp 75−79.

(3) Verhelst, W. F.; Drenth, W. *J. Am. Chem. Soc.* **1974**, *96*, 6692−6697.

(4) A preliminary account of some of this work has appeared in: Chiang, Y.; Grant, A. S.; Kresge, A. J.; Pruszynski, P.; Schepp, N. P.; Wirz, J. *Angew Chem., Int. Ed. Engl.* **1991**, *30*, 1356−1358.

(5) Chickos, J. S.; Patton, E.; West, R. *J. Org. Chem.* **1974**, *39*, 1647−1650.

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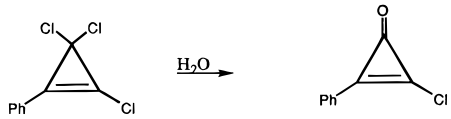
cyclopropenone[5] with thionyl chloride, eq 4. The partial hydrolysis



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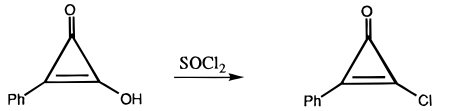


(4)

was carried out by stirring an acetone (25 mL) solution of the trichloride (1.0 g) with ice (10 g) at 0 °C for 2 h. The acetone was then removed under vacuum at room temperature, and the residual white oil was used directly without further purification.

The other synthesis of phenylchlorocyclopropenone was performed by stirring a mixture of phenylhydroxycyclopropenone (0.15 g) and thionyl chloride (1.5 mL), plus a catalytic amount of dimethylformamide (6 μL), in a dry flask under a nitrogen atmosphere at 0 °C for 10 min. The excess thionyl chloride was then removed under vacuum at room temperature to leave a yellowish solid, mp 35−38 °C; this also was used directly without further purification.

The reactions of phenylchloropropenone with amines occurred readily and were effected simply by adding 2−4 equiv of the amine, either neat or dissolved in dichloromethane, to a dichloromethane solution of the chloride. With the more basic amines this usually produced a precipitate of the amine hydrochloride, which was removed by filtration. Evaporation of the solvent from the filtrate then left a crystalline solid, which was purified either by chromatography or by recrystallization. The phenylaminocyclopropenones so produced were characterized by their infrared, mass, and NMR spectra; details are given in Table S1.[6]

***N*-Methylpentafluoroaniline** was prepared by methylating the *N*-(*p*-toluenesulfonyl) derivative of pentafluoroaniline and then removing the sulfonyl group. The methylation was performed using methyl sulfate and the sulfonamide sodium salt, and sulfonyl group removal was effected with sulfuric acid in acetic acid solution. The final product was characterized by its mass and NMR spectra; details are given in Table S1.[6]

1-(*N*-Methyl-*N*-(pentafluorophenyl)amino)-2-phenylacetylene was synthesized by the reaction of phenylchloroacetylene[7] with the lithium salt of *N*-methylpentafluoroaniline, generated by treating the aniline with butyllithium. The ynamine was characterized by its mass and NMR spectra; details are given in Table S1.[6]

***N*-(Phenylacetyl)piperidine and *N*-(phenylacetyl)morpholine** were prepared by treating phenylacetyl chloride with the corresponding amines; their spectral properties are listed in Table S1.[6]

All other materials were the best available commercial grades.

Kinetics. Flash photolysis rate measurements were made using both a conventional flash lamp system and an excimer laser system that have already been described in detail.[8] Excitation in the conventional system[8a] was provided by a pair of xenon lamps that produced light over the entire spectral region from the ultraviolet through the visible; the laser system[8b] operated at $\lambda = 248$ nm. In both cases the temperature of the reacting solutions was controlled at 25.0 ± 0.05 °C.

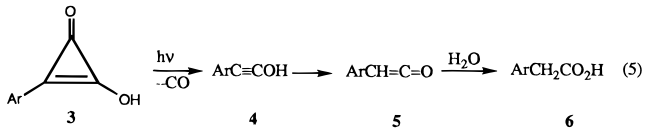
Some reactions were too slow to be monitored accurately by flash photolysis, and these were therefore followed using Cary 118 and 2200 spectrometers. The reactions were first initiated by a single flash from the conventional flash system, and the reacting solutions were then quickly transferred to the Cary instruments, whose cell compartments were also thermostated at 25.0 ± 0.05 °C. Observed rate constants were calculated by nonlinear least-squares fitting of exponential functions.

Rates of reaction of authentic 1-(*N*-methyl-*N*-(pentafluorophenyl)-amino)-2-phenylacetylene were measured using a Hi-Tech SF-S1 stopped-flow spectrometer operating at 25.0 ± 0.05 °C.

Results

Identification of Transients. Flash photolysis of the primary aminocyclopropenone, **1a**, or any of its secondary analogs, **1b**−**e**, in aqueous solution produced an immediate bleaching of the strong absorbance of these substances at $\lambda \cong 310$ nm, followed by a slower but still quite rapid decay of absorbance at this wavelength. This slower decay was accompanied by a simultaneous rise in absorbance at $\lambda \cong 270$ nm that occurred at the same rate, and this new absorbance then decayed away somewhat more slowly. These spectral changes suggest that two transient species are formed in the flash photolysis of these aminocyclopropenones: a substance absorbing at $\lambda = 310$ nm and another, somewhat longer-lived, absorbing at $\lambda = 270$ nm.

Two transient species are also formed in the flash photolysis of arylhydroxycyclopropenones, **3**, eq 5, and the transients there



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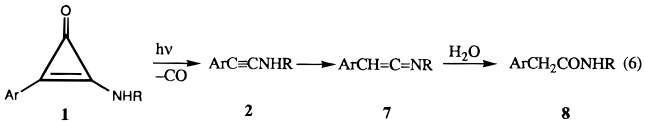
have been identified[9] as the ynol, **4**, produced by photodecarbonylation of **3**, and the ketene, **5**, formed by isomerization of **4**. In aqueous solution the ketene becomes hydrated, giving the arylacetic acid final product, **6**. A similar process can be formulated for the aminocyclopropenone systems studied here, as shown in eq 6: photodecarbonylation of the aminocyclopropenone, **1**, gives the ynamine, **2**, whose isomerization then leads to the ketenimine, **7**, and hydration of that produces the acetamide final product, **8**. Evidence that this sequence of reactions does in fact take place in the presently studied systems comes from a previous investigation of ketenimine hydration.[10] The phenylketenimines investigated there had strong absorption bands at $\lambda \cong 270$ nm, and their hydration to the corresponding phenylacetamides occurred with rate constants numerically identical with the rate constants for decay of the 270 nm absorbance determined here. This establishes the identity of the longer lived of the two transient species observed here as ketenimines.



(6)

This comparison with previous work can be made for three of our ketenimines, those whose nitrogen substituents are isopropyl (**7b**), cyclohexyl (**7c**), and phenyl (**7d**). As did the previous investigators, we found the hydration of these substances to be acid-catalyzed and also to have a significiant uncatalyzed component. Rates of the acid-catalyzed reactions of **7b** and **7d** were measured in dilute perchloric acid solutions over the concentration range 0.02−0.10 M, and rates of the uncatalyzed reactions of **7b** and **7c** were measured in 0.010 M

(6) Supporting information; see paragraph at the end of this paper regarding availability.

(7) *Organic Synthesis*; Wiley: New York, 1973; *Collect. Vol. 5*, pp 921−923.

(8) (a) Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000−4009. (b) Andraos, J.; Chiang, Y.; Huang, G.-C.; Kresge, A. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 10605−10610.

(9) Chiang, Y.; Kresge, A. J.; Hochstrasser, R.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 2355−2357. Chiang, Y.; Kresge, A. J. Popic, V. V. *J. Am. Chem. Soc.* **1995**, *117*, 9165−9171. Wagner, B. D.; Zgierski, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1994**, *116*, 6433−6434.

(10) McCarthy, D. G.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 579−591.

Table 1. Comparison of Rates of Hydration of Ketenimines Studied Here with Literature Values[a]

	$k_H^+/10^3$ M^{-1} s^{-1}		$k_o/10^{-3}$ s^{-1}	
substrate	present study	lit.[b]	present study	lit.[b]
PhCH=C=NCH(CH$_3$)$_2$	2.19	2.20	1.15	1.35
PhCH=C=N-*c*-C$_6$H$_{11}$			2.17	2.20
PhCH=C=NC$_6$H$_5$	0.986	1.00		

[a] Aqueous solution at 25 °C. [b] Reference 10.

sodium hydroxide. Some rate measurements for the *N*-phenyl substrate were also made in more concentrated, 0.1−1.0 M, perchloric acid solutions. The data are summarized in Tables S2 and S3.[6]

Observed rate constants determined in dilute acid solutions proved to be directly proportional to acid concentration, and hydronium-ion catalytic coefficients were determined by linear least-squares analysis. Observed rate constants measured in the more concentrated acid solutions, on the other hand, increased more rapidly than in direct proportion to acid concentration, and the Cox−Yates method[11] using the X_o acidity function[12] was used to correlate the data. The two sets of measurements gave results that agreed well with each other: $k_H^+ = 97.5 \pm 0.3$ M^{-1} s^{-1} from dilute solutions and $k_H^+ = 99.7 \pm 0.8$ M^{-1} s^{-1} from concentrated solutions. Best values of rate constants for the uncatalyzed reactions were obtained by taking averages of the 4−6 replicate determinations made in sodium hydroxide solution.

These results are summarized in Table 1. Comparison with the previously determined values, also listed in Table 1, shows that there is close correspondence between the two sets of measurements.

Tertiary ynamines cannot tautomerize to ketenimines, but evidence that they are formed by photodecarbonylation of our tertiary aminocyclopropenones comes from yet another previous investigation.[3] It was found in this previous work that authentic tertiary ynamines prepared by established methods protonate rapidly on carbon, eq 7, giving keteniminium cations, **9**, which

$$\mathrm{PhC{\equiv}CNR_2} \xrightarrow[-A^-]{HA} \underset{\mathbf{9}}{\mathrm{PhCH{=}\overset{+}{C}NR_2}} \xrightarrow[-H^+]{H_2O} \underset{\mathbf{10}}{\mathrm{PhCH{=}C(OH)NR_2}} \longrightarrow \underset{\mathbf{8}}{\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}NR_2}} \quad (7)$$

upon hydration produce amide enols, **10**; the enols then ketonize to give amides, **8**, as the ultimate reaction products. Reaction rates were measured in this previous work by monitoring the decay of ynamine absorbance at $\lambda \cong 290$ nm. We found that flash photolysis of tertiary phenylaminocyclopropenones produces transient species that absorb light in this same region and decay at rates consistent with those determined in the previous study. Rate comparisons can be made for two sets of substrates: the previous investigation found $k = 1.0$ s^{-1} for the reaction of 1-(piperidino)-2-phenylacetylene (**2f**) and $k = 0.015$ s^{-1} for that of 1-(morpholino)-2-phenylacetylene (**2g**) in basic solution where water is the proton donor, and we found $k = 1.8$ s^{-1} and $k = 0.026$ s^{-1} for decay of the transients formed from the corresponding phenylaminocyclopropenones (**1f** and **1g**) under the same conditions.

Agreement between these two sets of rate constants is not exact because the measurements were made in different solvents: the previous work in water containing 8.6% dioxane and our study in wholly aqueous solution. Although the difference is small and in the direction expected for a change in solvent polarity for such an ion-forming reaction, we nevertheless supplied a more exact comparison by preparing an authentic tertiary ynamine and measuring its rate of reaction in wholly aqueous solution. Figure 1 shows that the results we obtained for 1-(*N*-methyl-*N*-(pentafluorophenyl)amino)-2-phenylacetylene agree well with rates of decay of the transient species formed by flash photolysis of the corresponding aminocyclopropenone. This establishes the identity of this transient and shows that all three classes of ynamines are formed by flash photolysis of corresponding aminocyclopropenones.

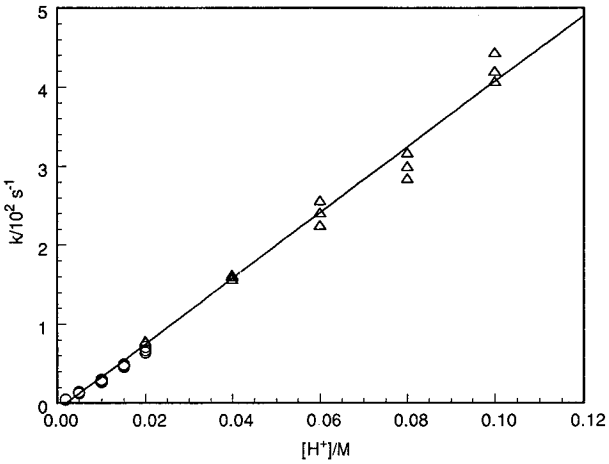


Figure 1. Comparison of rates of reaction of authentic 1-(*N*-methyl-*N*-(pentafluorophenyl)amino)-2-phenylacetylene, ○, with rates of decay of transient formed by flash photolysis of phenyl(*N*-methyl-*N*-(pentafluorophenyl)amino)cyclopropenone, △, in aqueous perchloric acid solutions at 25 °C.

Table 2. Rate Constants for the Carbon Protonation of Ynamines by Hydronium Ion in Aqueous Solution at 25 °C[a]

ynamine	k_H^+/M^{-1} s^{-1}	k_H^+/k_D^+	pK_{BH}^+ [b]
PhC≡CNH$_2$	6.70×10^5	2.95	9.24
PhC≡CNHCH(CH$_3$)$_2$	6.42×10^6	1.98	10.67
PhC≡CNH-*c*-C$_6$H$_{11}$	7.01×10^6		10.64
PhC≡CNHC$_6$H$_5$	2.43×10^4	2.42	4.60
PhC≡CNHC$_6$F$_5$	8.83×10^2	3.25	−0.28
PHC≡CN(CH$_2$)$_5$	7.73×10^6	2.60	11.12
PHC≡CN(CH$_2$CH$_2$)$_2$O	8.12×10^5		8.49
PhC≡CN(CH$_2$CH$_2$CN)$_2$	1.76×10^5	2.63	5.2
PhC≡CN(CH$_3$)C$_6$F$_5$	4.16×10^3	2.71	0.68

[a] Ionic strength = 0.10 M. [b] pK_a of the conjugate acid of the simple amine formed by substituting H for the PhC≡C group of the ynamine.

Ynamine Rate Measurements. Rates of reaction of the ynamines studied here were determined in perchloric acid, sodium hydroxide, and buffer solutions. The measurements in acid solutions were done in H_2O and in D_2O over a range of acid concentrations, usually spanning a 5−10-fold variation, and replicate determinations were made at each concentration. The rate data so obtained are sumarized in Table S5.[6]

In each case, observed first-order rate constants were found to be accurately proportional to acid concentration (see Figure 1), and bimolecular catalytic coefficients were determined by linear least-squares analysis. The results so obtained are listed in Table 2.

The measurements in sodium hydroxide solutions were also done in H_2O and D_2O over a range of base concentrations, and replicate determinations were made at each concentration. The data are summarized in Table S4.[6]

For primary and secondary ynamines, observed first-order rate constants proved to be accurately proportional to base

(11) (a) Cox, R. A.; Yates, K. *J. Am. Chem. Soc.* **1978**, *100*, 3861−3867. (b) Kresge, A. J.; Chen, H. J.; Capen, G. L.; Powell, M. F. *Can. J. Chem.* **1983**, *61*, 249−256.

(12) Cox, R. A.; Yates, K. *Can. J. Chem.* **1981**, *59*, 2116−2124.

(13) Andraos, J.; Chiang, Y.; Grant, A. S.; Guo, H.-X.; Kresge, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 7411−7412.

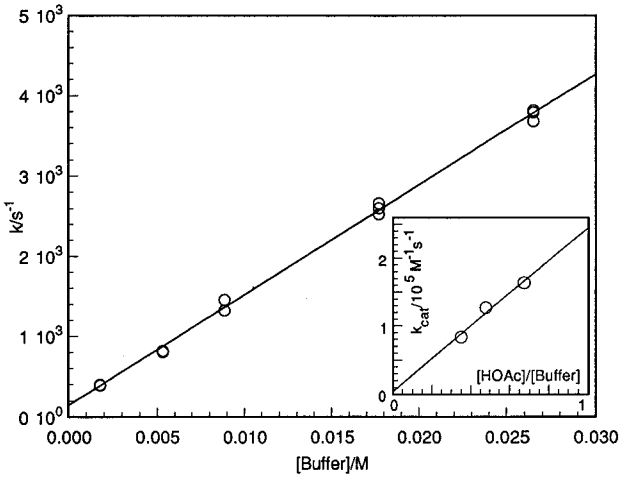


Figure 2. Buffer dilution plot for the reaction of 1-(*N*-isopropylamino)-2-phenylacetylene in acetic acid buffer solutions at 25 °C. Inset: dependence of catalytic coefficients upon fraction of buffer present in acidic form.

Table 3. Rate Constants for the Reaction of Ynamines in Sodium Hydroxide Solution at 25 °C[a]

ynamine	$k_{HO^-}/M^{-1}\ s^{-1}$	k_{HO^-}/k_{DO^-}	k_o/s^{-1}
PhC≡CNH$_2$	3.99×10^6		
PhC≡CNHCH(CH$_3$)$_2$	6.79×10^6	1.91	
PhC≡CNH-*c*-C$_6$H$_{11}$	3.52×10^7		
PhC≡CNHC$_6$H$_5$[b]	2.40×10^9	4.09	6.81×10^5
PhC≡CN(CH$_2$)$_5$			1.84
PhC≡CN(CH$_2$CH$_2$)$_2$O			2.64×10^{-2}

[a] Ionic strength = 0.10 M. [b] Reference 13.

concentration, and bimolecular catalytic coefficients were determined by linear least-squares analysis. Observed first-order rate constants for tertiary ynamines, on the other hand, did not vary with base concentration, and best values here were therefore obtained by taking simple averages. The results are listed in Table 3.

The rate measurements in buffer solutions were made with CNCH$_2$CO$_2$H, ClCH$_2$CO$_2$H, HCO$_2$H, CH$_3$CO$_2$H, C$_2$H$_5$CO$_2$H, $H_2PO_4^-$, $(CH_2OH)_3CNH_3^+$, NH_4^+, and HCO_3^- as the buffer acids. Series of solutions of constant buffer ratio and constant ionic strength (0.10 M) but varying buffer concentration were used; this served to hold hydronium ion concentrations constant along most of the buffer solution series. In the case of CNCH$_2$CO$_2$H and ClCH$_2$CO$_2$H buffers, however, buffer failure[14] occurred, and this was compensated for by adjusting observed rate constants to a common hydronium ion concentration using the hydronium ion catalytic coefficients determined in perchloric acid solutions; hydronium ion concentrations needed for this purpose were obtained by calculation using literature pK_a's of the buffer acids and activity coefficients recommended by Bates.[15] The data are summarized in Table S6.[6]

As Figure 2 illustrates, pronounced buffer catalysis was found in the carboxylic acid solutions, and analysis of results obtained at different buffer ratios showed the catalysis to be completely of the general acid type (see inset to Figure 2). Carboxylic acid catalytic coefficients were evaluated by least-squares analysis of the relationship between observed rate constants and buffer acid concentration. These catalytic coefficients, summarized in Table 4, were used to construct Bronsted plots for

(14) Keeffe, J. R.; Kresge, A. J. In *Techniques of Chemistry, Volume VI, Investigations of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Chapter XI.

(15) Bates, R. G. *Determination of pH Theory and Practise*; Wiley: New York, 1973; p 49.

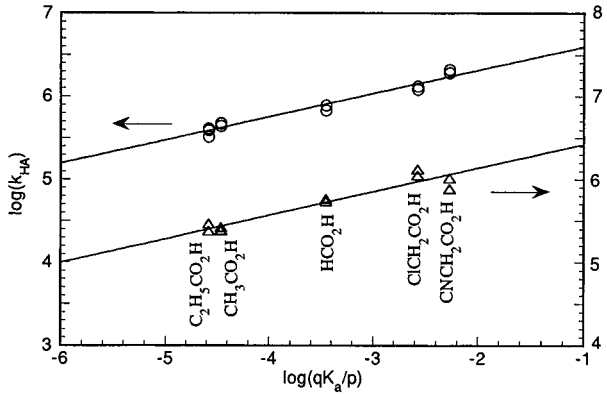


Figure 3. Bronsted relation for the carbon protonation of 1-(*N*-isopropylamino)-2-phenylacetylene (△) and 1-(piperidino)-2-phenylacetylene (○) by a series of carboxylic acids in aqueous solution at 25 °C.

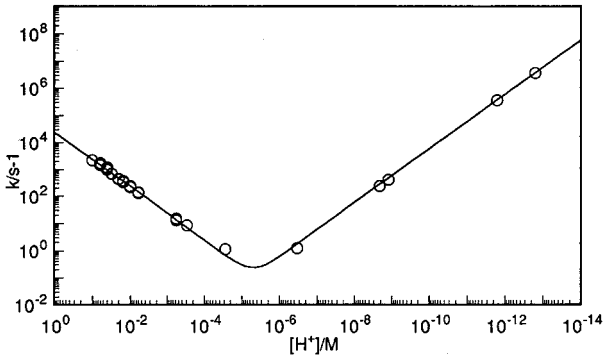


Figure 4. Rate profile for the carbon protonation of 1-(*N*-phenylamino)-2-phenylacetylene in aqueous solution at 25 °C.

Table 4. Carboxylic Acid Catalytic Coefficients for the Carbon Protonation of Ynamines in Aqueous Solution at 25 °C[a]

acid catalyst	$k_{HA}/10^3\ M^{-1}\ s^{-1}$
PhC≡CNH$_2$:	
CH$_3$CO$_2$H	8.47, 6.24
PhC≡CNHCH(CH$_3$)$_2$:	
CNCH$_2$CO$_2$H	769, 1030
ClCH$_2$CO$_2$H	1120, 1310
HCO$_2$H	575, 539
CH$_3$CO$_2$H	242, 264, 239
CH$_3$CH$_2$CO$_2$H	290, 239
PhC≡CNHPh:	
HCO$_2$H	0.628, 0.614
PhC≡CN(CH$_2$)$_5$:	
CNCH$_2$CO$_2$H	2080, 1900
ClCH$_2$C$_2$H	1320, 1200
HCO$_2$H	775, 674
CH$_3$CO$_2$H	468, 471, 436
CH$_3$CH$_2$CO$_2$H	406, 324, 388

[a] Ionic strength = 0.10 M.

1-(isopropylamino)-2-phenylacetylene and 1-piperidino-2-phenylacetylene, shown in Figure 3, whose slopes are $\alpha = 0.29 \pm 0.03$ and $\alpha = 0.28 \pm 0.02$, respectively.

The intercepts of buffer dilution plots such as those shown in Figure 2 represent reaction through solvent-related species, and these together with the rate constants measured in perchloric acid and sodium hydroxide solutions were used to construct rate profiles. A representative example for a secondary ynamine is shown in Figure 4 and another for a tertiary ynamine is shown in Figure 5.

Product Studies. The hydration of tertiary ynamines is known to produce carboxylic acid amides,[3] as is also the hydration of ketenimines[10] formed by tautomerism of second-

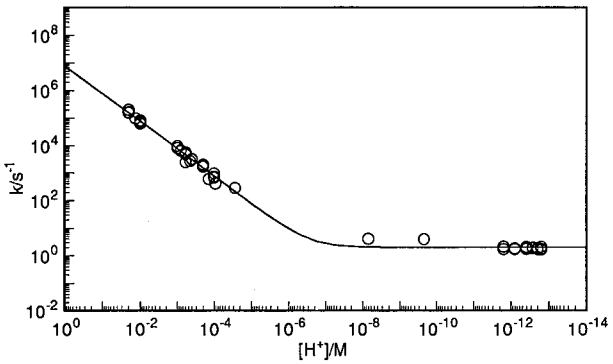
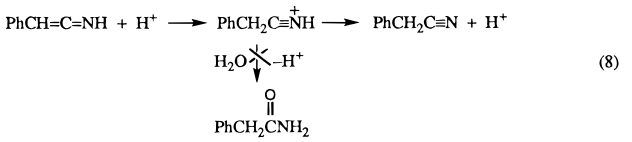


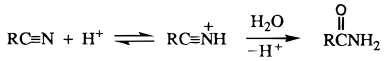
Figure 5. Rate profile for the carbon protonation of 1-(piperidino)-2-phenylacetylene in aqueous solution at 25 °C.

ary ynamines. Carboxylic acid amides are thus expected to be the ultimate products of the reactions we have studied. We verified this by performing HPLC analyses of flashed reaction mixtures, using spiking with authentic amide samples to identify the products. These tests were made for phenylpiperidinocyclopropenone, **1f**, and phenylmorpholinocyclopropenone, **1g**, in acidic, neutral, and basic solutions.

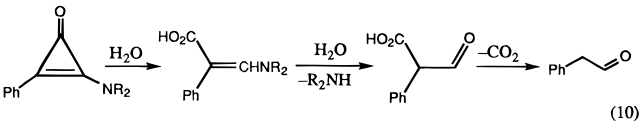
In the case of the primary aminocyclopropenone **1a**, however, the product proved to be phenylacetonitrile rather than phenylacetamide. The cation formed by carbon protonation of the ketenimine here thus loses its nitrogen-bound hydrogen more rapidly than it is captured by water, eq 8. This is consistent


(8)

with the known mechanism for hydrolysis of simple nitriles, which occurs by rapid and reversible protonation on nitrogen followed by reaction of the protonated species with water, eq 9:[16] here again the same cation loses a nitrogen-bound proton more rapidly than it reacts with water.


(9)

We found also that flash photolysis of phenylpiperidinocyclopropenone and phenylmorpholinocyclopropenone produced other products in addition to the corresponding phenylacetamides. One of these additional products proved to be phenylacetaldehyde, which could have been formed by decarboxylation of 2-phenylformylacetic acid, itself made by hydrolysis of the enamine obtained by ring opening of the cyclopropenone, as shown in eq 10. A similar ring-opening reaction has been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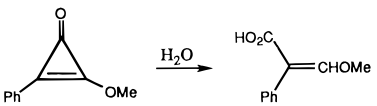
reported for the methyl ether of phenylhydroxycyclopropenone, eq 11,[17] and we have found that treatment of phenylmorpholi-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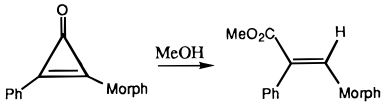
nocyclopropenone with methanol, eq 12, gives the methyl ester of the enamine−acid postulated in eq 10.[18] Unlike the thermal


(12)

ring-opening reactions of eqs 11 and 12, however, our phenylacetaldehyde-producing process must be a photochemical reaction, for our aminocyclopropenones are stable in the solutions we use for flash photolysis. We are currently investigating this additional photochemical process.

Basicity of *N*-Methylpentafluoroaniline. In order to correlate the reactivity of our ynamines with the basic strength of the corresponding simple amines (*vide infra*), we needed to know the pK_a of the conjugate acid of *N*-methylpentafluoroaniline. We determined this by measuring the change in absorbance at $\lambda = 230$ nm that this substance undergoes upon protonation in moderately concentrated aqueous sulfuric acid. The absorbance of solutions containing a constant stoichiometric amount of the aniline was measured at 12 different sulfuric acid concentrations over the range 0−40 wt %, and triplicate determinations were made at each concentration—the results are summarized in Table S7.[6]

These data were analyzed using the Cox-Yates *X* acidity function[11a] in two different ways, one by fitting the expression shown as eq 13 and another by fitting that shown as eq 14. In

$$\log(I/[H^+]) = pK_a + mX; \quad I = [BH^+]/[B] \tag{13}$$

$$A = \frac{A_B + (A_{BH^+}[H^+])10^{(pK_a+mX)}}{1 + [H^+]10^{(pK_a+mX)}} \tag{14}$$

fitting eq 13, the indicator ratio I ($= (A_B - A)/(A - A_{BH^+})$) was calculated using limiting absorbances for the completely unprotonated (A_B) and completely protonated (A_{BH^+}) forms of the substrate measured in water containing no acid and in 40% acid, respectively. In fitting eq 14, on the other hand, A_B and A_{BH^+} were left as parameters to be determined by the least-squares fit. The two methods gave nicely consistent results: p$K_a = 0.676 \pm 0.012$, $m = 1.22 \pm 0.13$ (eq 13) and p$K_a = 0.677 \pm 0.017$, $m = 1.28 \pm 0.29$ (eq 14).

The pK_a of pentafluoroaniline, which we also need for our correlation, had been determined before using an acidity function based on a series of halogenated anilines.[19] However, the Cox-Yates method using the universal acidity function *X* provides a better way of data treatment, and we therefore reanalyzed the original data for pentafluoroaniline[20] and obtained p$K_a = -0.277 \pm 0.014$, $m = 0.92 \pm 0.04$; this result is consistent with, but slightly different from, the originally reported value p$K_a = -0.36 \pm 0.02$.[19]

Discussion

Reaction Mechanism. We have found that primary, secondary, and tertiary phenylynamines are produced by photodecarbonylation of the corresponding phenylaminocyclopropenones, according to eq 1, and that they react with acids in aqueous solution showing general acid catalysis and appreciable hydronium ion isotope effects in the normal direction, $k_H^+/k_D^+ > 1$. This is classic evidence for rate-determining proton transfer to carbon,[14] and it suggests that the process under observation is

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(20) The data was fortunately still available through Dr. R. A. Cox.

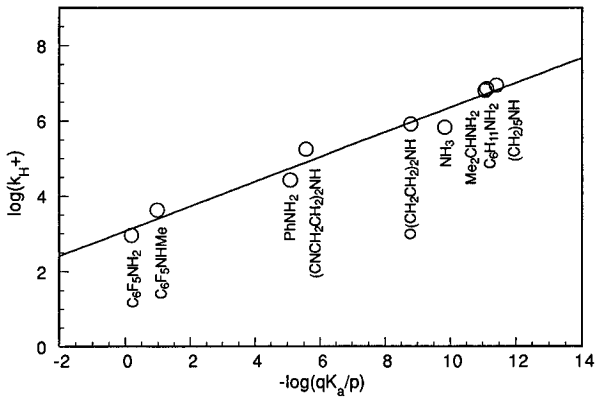

Figure 6. Correlation of hydronium ion rate constants for the carbon protonation of phenlynamines in aqueous solution at 25 °C with the basicity of the corresponding simple amines.

simple protonation of the ynamines on their β-carbon atoms to form keteniminium cations, as shown in eq 15. The cations

$$\mathrm{PhC{\equiv}CNR_2} + \mathrm{HA} \rightarrow \mathrm{PhCH{=}C{=}NR_2^+} + \mathrm{A^-} \quad (15)$$

then react further according to eqs 6, 7, or 8 depending upon whether they have been generated from primary, secondary, or tertiary ynamines.

Further support for the process of eq 15 comes from the fact that the reactions observed are all quite fast (see Table 2), as expected on the basis of the strong ability of amino groups to stabilize adjacent positive charge through their electron donating resonance effects, and that the rates of reaction respond as expected to variations in this electron-donating ability. These variations could be measured by the nitrogen basicity of the ynamines, but that unfortunately is not available (*vide infra*). This basicity, however, will be proportional to the basicity of simple amine analogs of the ynamines in which the phenylethynyl groups have been replaced by hydrogen, and Figure 6 shows that there is indeed a good correlation between this quantity and hydronium ion rate constants. The slope of this correlation is low, 0.33 ± 0.02, consistent with the early, reactant-like transition state expected for a fast process such as this.[21] Primary, secondary, and tertiary ynamines, moreover, obey the same correlation, which implies that proton loss from nitrogen in the case of primary and secondary ynamines is not concerted with proton addition to carbon, for such proton loss cannot occur with tertiary ynamines.

Tertiary ynamines react by the simple process of eq 15 in basic was well as in acidic solution. This is illutrated by the rate profile of Figure 5 for 1-(piperidino)-2-phenylacetylene, where acid catalysis by the hydronium ion can be seen to give way to an "uncatalyzed" reaction in which water serves as the proton donor. The rate-determining proton-transfer nature of this uncatalyzed process is substantiated by the normal solvent isotope effects and general acid catalysis by weak acids observed in this region in the previous investigation of tertiary ynamines.[3]

Primary and secondary ynamimes, on the other hand, give a base-catalyzed reaction. This is illustrated by the rate profile of Figure 4 for 1-(*N*-phenylamino)-2-phenylacetylene, which shows hydroxide-ion catalysis in addition to the hydronium-ion catalyzed process. This base-catalyzed reaction has been identified as a process in which hydroxide ion first removes a nitrogen-bound hydrogen from the ynamine in a rapidly established reversible step, and the very reactive anion thus formed is then protonated on carbon by water, eq 16.[13]

$$\mathrm{PhC{\equiv}CNHR} + \mathrm{HO^-} \rightleftarrows \mathrm{PhC{\equiv}CNR^-} + \mathrm{H_2O} \rightarrow \mathrm{PhCH{=}C{=}NR} + \mathrm{HO^-} \quad (16)$$

In the previous investigation of tertiary ynamines,[3] reactions were observed for 1-(piperidino)-2-phenylacetylene in acetic acid buffers that were believed to be the carbon-protonation process of eq 15, despite the fact that they were several orders of magnitude slower than expected on the basis of results obtained in more basic solutions. It is now apparent that this assignment is incorrect, because we have also observed these slower reactions in addition to the faster changes that we know to be carbon protonation. We are currently investigating these slower processes.

pK_a Limits. At sufficiently high acidities, the carbon-protonation reaction of eq 15 should be accompanied by an equilibrium protonation on nitrogen, eq 17, which will convert

$$\mathrm{PhC{=}CNHR_2^+} \rightleftarrows \mathrm{PhC{\equiv}CNR_2} + \mathrm{H^+} \rightarrow \mathrm{PhCH{=}C{=}NR_2^+} \quad (17)$$

the ynamine into a much less reactive form. This will produce a break in the rate profile, and that break will occur at an acidity corresponding to the acidity constant of the *N*-protonated ynamine. Figures 4 and 5 show that no such break has occurred for the substrates represented there up to an acidity of $[H^+] = 0.1$ M. We have also examined other ynamines in more concentrated acids and have found no breaks up to $[H^+] = 4$ M.[22] This sets an upper limit of $-\log(4) = -0.6$ on the pK_a's of the conjugate acids of these ynamines. If, as seems likely, the protonation of ynamines follows an acidity function rather than $[H^+]$, this upper limit will be even lower than -0.6.

This limit is much below the estimate p$K_a \cong 5$ made for the conjugate acid of 1-piperidino-2-phenylacetylene on the basis of what we now know to be a misidentification of the reactions of this substance in acetic acid buffers.[3] The present limit also makes ynamines remarkably weakly basic substances. Theoretical calculations suggest that this weak basicity is caused by strong destabilization of ynamine conjugate acids.[23]

Bronsted Relations and Marcus Theory. In the previous investigation of tertiary ynamines,[3] a Bronsted relation was constructed for the carbon protonation of 1-piperidino-2-phenylacetylene whose exponent was $\alpha = 0.74$. This is quite different from the Bronsted exponent for the same reaction obtained in the present study, $\alpha = 0.28$. The previous correlation, however, was based on a group of acids much weaker than the presently used series of carboxylic acids. The previous reactions were consequently considerably slower, and they could be expected to have had later, more product-like transition states in which proton transfer would have been further advanced.[21] Since the Bronsted exponent α is believed to measure the extent of proton transfer at the transition state,[24] it is not unreasonable that α for the previous correlation would be greater than that for the present one. This idea is reinforced by the fact that the previous and present sets of data form a self-consistent group. As Figure 7 shows, a smooth continuous curve can be drawn through all of the data, and least-squares fitting of a quadratic expression gives the relationship $\log(k_{HA}/p) = 6.69 \pm 0.08 + (1.29 \pm 0.26) \times 10^{-1} \log(qK_a/p) - (2.62 \pm 0.15) \times 10^{-2}(\log(qK_a/p))^2$.

Curved Bronsted relations such as this are a direct consequence of the hypothesis that the structure of transition states

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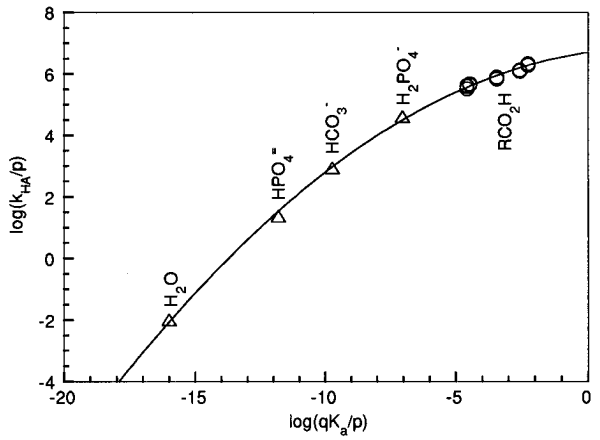

Figure 7. Extended Bronsted relation for the carbon protonation of 1-(piperidino)-2-phenylacetylene in aqueous solution at 25 °C: ○, present work; △, ref 3.

varies with the energetics of the reaction, being reactant-like in exoergic processes and product-like in endoergic ones.[21] The idea is given quantitative expression by Marcus rate theory,[25] which formulates reaction barriers as shown in eq 18, where

$$\Delta G^{\ddagger} = w^{r} + (1 + \Delta G°/4\Delta G^{\ddagger}_{o})^{2}\Delta G_{o}^{\ddagger} \qquad (18)$$

$\Delta G^{\ddagger}$ is the observed free energy of reaction, w^{r} is the work required to assemble the reactants into a reaction complex, $\Delta G°$ is the free energy of reaction within that complex, and $\Delta G^{\ddagger}_{o}$ is the intrinsic barrier. The Bronsted exponent α can be identified with the first derivative of $\Delta G^{\ddagger}$ with respect to $\Delta G°$, eq 19, and the rate of change of α is given by the second derivative, eq 20. This shows that α will change more sharply over a given

$$\alpha = d\Delta G^{\ddagger}/d\Delta G° = (1 + \Delta G°/4\Delta G^{\ddagger}_{o})/2 \qquad (19)$$

$$d\alpha/d\Delta G° = 1/8\Delta G^{\ddagger}_{o} \qquad (20)$$

interval of $\Delta G°$ for intrinsically fast reactions with low values of $\Delta G^{\ddagger}_{o}$ than for intrinsically slow reactions with large values of $\Delta G^{\ddagger}_{o}$, and intrinsically fast reactions will consequently have more sharply curved Bronsted plots.

It is possible to evaluate Marcus theory parameters from the coefficients of a quadratic Bronsted correlation.[26] For the combined data of Figure 7, this leads to $w^{r} = 8.11 \pm 0.15$ kcal mol^{-1} and $\Delta G^{\ddagger}_{o} = 3.26 \pm 0.19$ kcal mol^{-1}. The rather low value of $\Delta G^{\ddagger}_{o}$ implies that this is an intrinsically fast reaction. Even so, however, appliction of eq 20 leads to the prediction that α should change by only 0.12 over the range of ΔG_{o} provided by our series of carboxylic acid protonating agents. The good linearity of the Bronsted plots illustrated in Figure 3 shows that this change in α is too small to be seen, which underscores the difficulty of detecting curvature in Bronsted plots of even intrinsically rather fast reactions.

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Supporting Information Available: Tables S1−S7 (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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