°C)/methylene chloride (5:1). On the basis of their NMR spectra, the products are the two keto ethers **26b** and **26c**. NMR for (a) **26b** (R = Ph), (b) **26c** (R = Tol): δ (CCl_4) (a) 1.75–2.25, (b) 1.75–2.3, (m, 2 H, $CH_2CH_2CH_2$); (b) 2.42, (s, 3 H, CH_3); (a) 3.10, (b) 3.00, (t, 2 H, CH_2CO, J = 6 Hz); (a) 3.70, (b) 3.67, (t, 2 H, CH_2O, J = 6.5 Hz); (a) 3.78, (b) 3.78, (q, 2 H, CH_2CF_3, J = 8.5 Hz); (a) 7.25–7.60 (5 H), (b) 7.00–8.00, (4 H, m, aryl).

Acid Ring Opening of Aryl Propyl Ketones 7b and 7c. To a solution of 0.5 g of aryl cyclopropyl ketone (**7b**, R = Ph; **7c**, R = Tol) in 10 mL of TFE was added 1 drop of trifluoromethanesulfonic acid (in a 50-mL, round-bottom flask with condenser). *p*-Xylene (100 μL) was added to serve as a GC standard. The reaction was followed by taking aliquots for GC analysis, which showed a steady decline in the concentration of **7b** or **7c** and a corresponding increase in the concentration of ether **26b** or **26c**. After 3 h the content of keto ether **26** was about 30%.

Acknowledgment. One of us (C.J.C.) thanks the Alexander von Humboldt-Stiftung for the generous award that aided in the completion of this work. The senior authors also acknowledge, with thanks, travel funds provided in years past through the Scientific Affairs Division of the North Atlantic Treaty Organization (Research Grant No. 814).

Registry No. **6a**-OTf, 54106-83-1; **6a**-OTs, 3329-88-2; **6b**-OTf, 87639-40-5; **6b**-OTs, 85375-43-5; **6c**-OTf, 87639-41-6; **6c**-OTs, 87639-42-7; **6d**-OTs, 87639-43-8; **6e**-OTf, 87639-44-9; **6e**-OTs, 87639-45-0; **7b**, 3481-02-5; **7c**, 7143-76-2; **10c**, 87639-46-1; **10d**, 70106-27-3; 11-OTf, 70106-33-1; 11-ONf, 83961-10-8; **13b**, 10229-11-5; **13c**, 31208-53-4; **13d**, 52999-15-2; **13e**, 87639-47-2; **14**, 1121-37-5; (*E*)-**15**, 83313-95-5; (*Z*)-**15**, 87639-48-3; (*E*)-**16**, 87639-49-4; (*Z*)-**16**, 87639-50-7; (*E*)-**17**, 87639-51-8; (*Z*)-**17**, 87639-52-9; **18**, 33462-81-6; **19**, 1489-69-6; **20**, 87639-53-0; **21**, 70106-28-4; **22a**, 646-05-9; **22b**, 13633-26-6; **22c**, 30011-66-6; **22d**, 55088-86-3; **22e**, 71452-17-0; **26b**, 87639-54-1; **26c**, 87639-55-2; EtMgBr, 925-90-6; triton B, 100-85-6; phenylacetylene, 536-74-3; *p*-tolylacetylene, 766-97-2; anisylacetylene, 768-60-5; ethylene oxide, 75-21-8; 1-bromo-3-chloropropane, 109-70-6; diphenyl sulfide, 139-66-2; 2,5-dichloropent-2-ene, 20177-02-0; 3-bromopropyltriphenylphosphonium bromide, 3607-17-8; *p*-tolualdehyde, 104-87-0; anisaldehyde, 123-11-5; (*p*-tolylmethylene)cyclopropane, 55088-80-7; (anisylmethylene)cyclopropane, 55088-84-1; *p*-nitrobenzoic acid, 62-23-7; bromobenzene, 108-86-1; 3-chlorobutyronitrile, 53778-71-5; α-cyclopropylbenzylidenimine hydrochloride, 20127-69-9.

Kinetic Study of the Reaction of 2,4,6-Triphenylpyrylium Ion with Amines. Base-Catalyzed Ring-Opening Reaction of 2*H*-Pyran Intermediates

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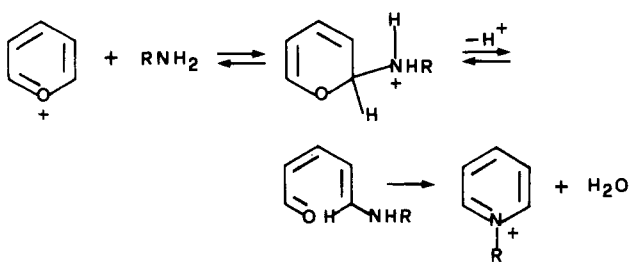
The kinetics of reaction of 2,4,6-triphenylpyrylium ion with butylamine, cyclohexylamine, pyrrolidine, piperidine, and morpholine to yield the corresponding ring-opened divinylogous amides have been studied in methanol at 25 °C. The reactions with the secondary amines are base-catalyzed, whereas those with the primary amines are not. The results are consistent with the formation of a charged 2*H*-pyran as a reaction intermediate. With the primary amines the formation of the intermediate is the rate-determining step, whereas for the secondary amines it is the decomposition of the intermediate toward the ring-opened product that is the slow process. In particular, the sensitivity of the base-catalyzed step to the nature of the secondary amine is shown to indicate that the rate-controlling step is the proton transfer from the charged 2*H*-pyran to the amine to yield the corresponding neutral 2*H*-pyran.

The reaction of primary amines with pyrylium salts is an important route to the synthesis of N-substituted pyridinium salts.[1] A ring-opened divinylogous amide is generally observed as an intermediate in this process. It is presumably formed from the 2*H*-pyran isomer that should be a primary product of the nucleophilic attachment of the amine (see Scheme I). 2*H*-Pyrans are observed in several reactions between pyrylium salts and nucleophiles,[1a] but in the reaction with amines they can be detected only in a few cases.[2]

The synthetic importance of this reaction, in conjunction with our continuing interest in the study of interactions between nucleophiles and heteroaromatic organic cations[3] has led us to investigate the kinetic influence of several primary and secondary amines with varying structural features such as butylamine, cyclohexylamine, pyrrolidine, piperidine, and morpholine on the early stages of the reaction of 2,4,6-triphenylpyrylium ion (**1**) in methanol, i.e., up to the formation of the divinylogous amide. This was a convenient substrate to deal with because of its low tendency to decompose otherwise under the reaction conditions and because of the availability of the rate data for the reaction with MeO^- in the same solvent from previous work.[3]

Scheme I



Experimental Section

Materials. 2,4,6-Triphenylpyrylium perchlorate was available from previous work.[3] All the amines were distilled from sodium and potassium and kept under argon in the dark. Methanol and

(1) (a) Balaban, A. T.; Dinculescu, A.; Dorofeenko, G. N.; Fischer, G. W.; Koblik, A. V.; Mezheritskii, V. V.; Schorth, W. *Adv. Heterocycl. Chem., Suppl.* **1982**, *No. 2*. (b) Zvezdina, E. A.; Zhadonva, M. P.; Dorofeenko, G. N. *Russ. Chem. Rev. (Engl. Transl.)* **1982**, *51*, 469.

(2) (a) Fischer, G. W.; Zimmermann, T. *Z. Chem.* **1981**, *21*, 282. (b) Katritsky, A. R.; Lloyd, J. M.; Patel, R. C. *J. Chem. Soc., Perkin Trans. 1* **1982**, 117.

(3) Doddi, G.; Illuminati, G.; Insam, N.; Stegel, F. *J. Org. Chem.* **1982**, *47*, 960.

0022-3263/83/1948-5268$01.50/0

Table I. Kinetic Data for the Reaction of 1 with Butylamine in MeOH at 25 °C

10^3[$BuNH_2$],[a] M	10^6[MeO^-], M	k_{obsd}, s^{-1}
3.0	2.8	87
4.5	2.8	111
6.0	2.8	128
7.5	2.8	156
9.0	2.8	173
$k_a = 1.4 \times 10^4$ M^{-1} s^{-1} [b]		
5.5	5.7	165
7.0	5.7	192
8.5	5.7	206
10.0	5.7	227
11.5	5.7	241
$k_a = 1.2 \times 10^4$ M^{-1} s^{-1} [b]		
5.8	8.5	208
7.5	8.5	223
9.0	8.5	245
12.0	8.5	298
$k_a = 1.5 \times 10^4$ M^{-1} s^{-1} [b]		

[a] Free amine concentration. [b] Calculated from eq 1.

Table II. Kinetic Data for the Reaction of 1 with Cyclohexylamine ($C_6H_{11}NH_2$) in MeOH at 25 °C

10^3[$C_6H_{11}NH_2$],[a] M	10^6[MeO^-], M	k_{obsd}, s^{-1}
1.2	0.74	16
2.2	0.74	19
3.4	0.74	24
4.8	0.74	29
6.0	0.74	33
$k_a = 3.4 \times 10^3$ M^{-1} s^{-1} [b]		
3.0	3.2	58
4.7	3.2	65
5.5	3.2	72
8.0	3.2	78
11.7	3.2	93
$k_a = 3.9 \times 10^3$ M^{-1} s^{-1} [b]		
9.6	5.9	133
20	5.9	165
30	5.9	201
40	5.9	234
50	5.9	270
$k_a = 3.4 \times 10^3$ M^{-1} s^{-1} [b]		

[a] Free amine concentration. [b] Calculated from eq 1.

methanol solutions of $HClO_4$ were prepared as previously described.[4]

Kinetic Measurements. The kinetics were followed spectrophotometrically with a Durrum 110 stopped-flow apparatus in methanol at 25 °C under pseudo-first-order conditions ([1] ≈ 10^{-5}M) in the presence of buffers prepared by partial neutralization of the amine with a methanol solution of $HClO_4$. The kinetic measurements were carried out separately at the absorption maximum of the substrate (410 nm) and the ring-opened product (~460 nm). The corresponding k_{obsd} values were found to coincide to each other.

Determination of pK_a in Methanol. The pK_a values of butylamine (11.3) and cyclohexylamine (11.3) in methanol were determined potentiometrically as previously described[5] for the determinations of the pK_a values of pyrrolidine (11.3), piperidine (11.1), and morpholine (9.5).

Results

General Features. When 1 is mixed with the amine buffers in methanol, two well-separated kinetic processes are detected. The first process consists of a fast decrease in the absorbance of 1 until its complete disappearance and a corresponding increase in the absorbance of the ring-opened product. This process can be measured by the stopped-flow method (milliseconds range) and is mainly due to the reaction of 1 with the basic component of the buffer to yield the divinylogous amide if high amine concentrations are used. The reaction is accompanied by the parallel attachment of MeO^- as formed upon interaction of the solvent with the basic amine particularly when buffers with low amine concentrations are used. The kinetic constant of the overall reaction, k_{obsd}, is given by eq 1,

$$k_{obsd} = k_a^0 + k_{MeO}^0 = k_a[\text{amine}] + k_{MeO}[MeO^-] \quad (1)$$

where k_a^0 and k_{MeO}^0 are the pseudo-first-order rate constants for the reaction with amine and MeO^-, respectively, and k_a and k_{MeO} are the corresponding second-order rate constants.

The second process, which can be monitored with a conventional spectrophotometer (minutes range), is shown by a decrease in the absorbance of the ring-opened product. The final spectrum is identical with that of 2-methoxy-2,4,6-triphenyl-2*H*-pyran,[3] whose formation is also confirmed by ^1H NMR measurements. The latter process can be confidently ascribed to the reequilibration process of the ring-opened product back to the more stable 2-methoxy-2*H*-pyran. We have obtained no evidence of nucleophilic attack at the C-4 position of 1.

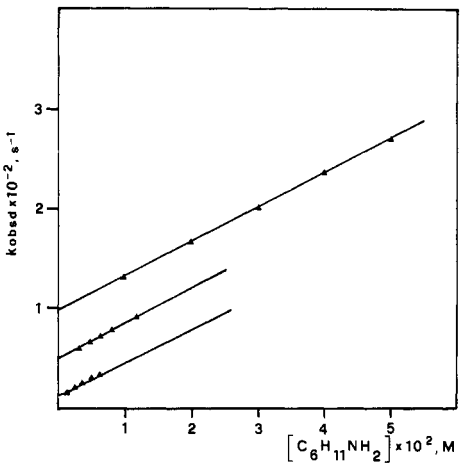


Figure 1. Plot of k_{obsd} vs. free [cyclohexylamine] at [MeO^-] = 5.9×10^{-6} M (upper line), 3.2×10^{-6} M, and 7.4×10^{-7} M (lower line).

In the following we will consider the first process that is related to the formation of the divinylogous amide only.

Primary Amines. The kinetic data of the reaction with butylamine and cyclohexylamine are reported in Tables I and II. For each set of buffers at a constant [amine]/[ammonium] ratio, the plot k_{obsd} vs. free amine concentration is linear, with slope = k_a and intercept = k_{MeO}^0 as shown in Figure 1 for the cyclohexylamine reaction.

Secondary Amines. The kinetic data for the reaction with pyrrolidine, piperidine and morpholine are reported in Tables III–V. As shown in Figure 2 for pyrrolidine the k_{obsd} values increase with the free amine concentration in a curvilinear fashion. Extrapolation to [amine] = 0 yields the corresponding k_{MeO}^0 value. A plot of $k_a = k_a^0/[\text{amine}]$, where k_a^0 is obtained by subtracting k_{MeO}^0 from k_{obsd} according to eq 1, against [amine] is approximatively linear

(4) Doddi, G.; Fornarini, S.; Illuminati, G.; Stegel, F. *J. Org. Chem.* **1979**, *44*, 4496.
(5) Aveta, R.; Doddi, G.; Illuminati, G. *J. Am. Chem. Soc.* **1983**, *105*, 5661.

Table III. Kinetic Data for the Reaction of 1 with Pyrrolidine in MeOH at 25 °C

10^3[pyrr],[a] M	k_{obsd}, s^{-1}	k_a^0, M^{-1} s^{-1}
0.4	12	7[b]
1.2	42	37
2.0	92	87
2.5	140	135
3.0	210	205
3.5	250	245
4.0	318	313
4.5	372	367
5.0	440	435
5.5	520	515
6.0	580	575

[a] Free amine concentration. [MeO^-] = 3.9×10^{-7} in all cases. [b] This value was obtained by obtaining the difference of comparable values ($k_{obsd} - k_{MeO}{}^0$) and therefore was not used for the evaluation of kinetic parameters.

Table IV. Kinetic Data for the Reaction of 1 with Piperidine in MeOH at 25 °C

10^2[pip],[a] M	k_{obsd}, s^{-1}	k_a^0, M^{-1} s^{-1}
0.1	19	4[b]
0.4	37	22[b]
0.8	67	52
1.2	115	100
1.4	140	125
1.6	171	156
1.7	188	173
1.8	203	188
3.0	435	420

[a] Free amine concentration. [MeO^-] = 1.0×10^{-6} M in all cases. [b] This value was obtained by difference of comparable values ($k_{obsd} - k_{MeO}{}^0$) and therefore was not used for the evaluation of kinetic parameters.

Table V. Data for the Reaction of 1 with Morpholine in MeOH at 25 °C

10^2[Mor],[a] M	k_{obsd}, s^{-1}	k_a^0, M^{-1} s^{-1}
0.8	4.5	1[b]
1.5	7.1	3.6[b]
2.5	12.5	9
3.5	20.7	17.2
4.1	27.5	24
4.4	31.2	27.7
7.2	76.1	72.6
8.7	107.0	103.5
9.5	126	119.5
10.5	148	141.5
11.5	180	173.5
12.7	208	203.5
14.0	251	244.5

[a] Free amine concentration. [MeO^-] = 2.6×10^{-7} M in all cases. [b] These values obtained by differences of comparable values ($k_{obsd} - k_{MeO}{}^0$) and therefore were not used for the evaluation of kinetic parameters.

Table VI. Kinetic Parameters Obtained as the Slope ($k' = k_{-1}/k_1k_3{}^{am}$) and Intercept ($k'' = 1/k_1$) from the Plots of $1/k_a$ vs. 1/[Amine] for the Reaction of 1 with Secondary Amines in MeOH at 25 °C (See Also Figure 4)

amine	k', M^2 s	k'', M s
pyrrolidine	3.5×10^{-8}	4.4×10^{-6}
piperidine	1.1×10^{-6}	3.6×10^{-5}
morpholine	6.8×10^{-5}	8.7×10^{-5}

at lower amine concentrations but is curvilinear at higher amine concentrations (See Figure 3). The reciprocal plot of $1/k_a$, as calculated under the latter conditions, vs. 1/[amine] is linear (Figure 4) and characterized by a slope k' and intercept k'' (vide infra and Table VI).

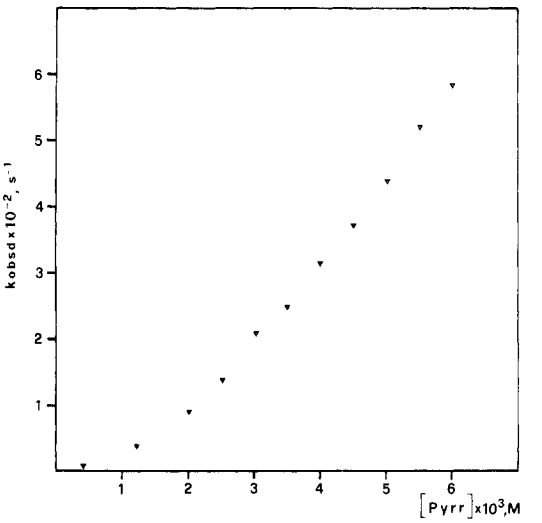


Figure 2. Plot of k_{obsd} vs. free [pyrrolidine] at constant MeO^- concentration (see Table III).

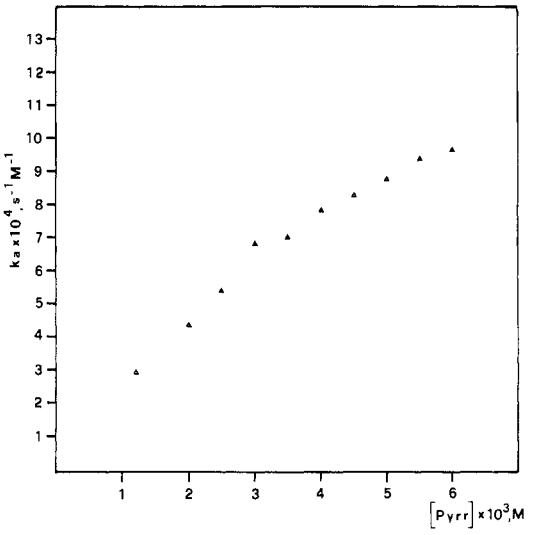


Figure 3. Plot of k_a ($=k_a{}^0/$[Pyrr]) vs. free [pyrrolidine] (see Table III).

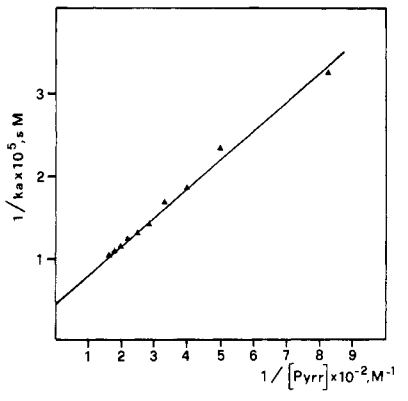


Figure 4. Plot of $1/k_a$ vs. 1/[Pyrr] according to eq 3 (see text).

In experiments carried out at constant amine concentration and variable MeO^- concentration, the $k_a{}^0$ values were found not to change with methoxide ion concentration. The covered range of MeO^- concentrations, as obtained by using amine buffers with different [amine]/[ammonium] ratios, had to be kept within the limits imposed by the stopped-flow technique. Therefore, the observed absence of MeO^- catalysis may be due to the low concentrations used and to the limited range of methoxide

Scheme II

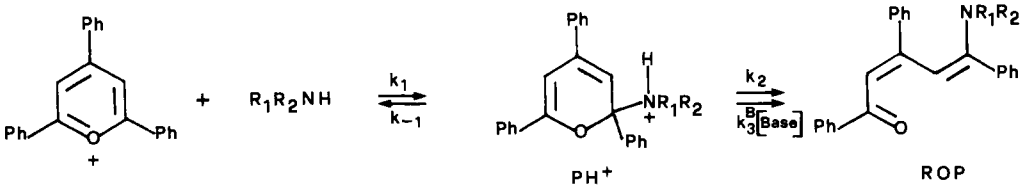


Table VII. Summary of the Kinetic Results for the Reaction of 1 with Amines in MeOH at 25 °C

amine	$10^{-4}k_1$, $M^{-1}\ s^{-1}$	k_3^{am}/k_{-1}, M^{-1}
butylamine	1.4	
cyclohexylamine	0.35	
pyrrolidine	20	125
piperidine	3	33
morpholine	1	1.3

ion concentrations tested (10^{-6}–10^{-5} M).

Discussion

The occurrence of base catalysis in the reaction of 1 with secondary amines and its absence in the reaction with primary amines can be reconciled within the framework of a stepwise mechanism involving a 2*H*-pyran as an intermediate, as shown in Scheme II.

Application of the steady-state approximation to such a scheme leads to eq 2:

$$k_a = \frac{k_1k_2 + k_1k_3^{am}[\text{amine}]}{k_{-1} + k_2 + k_3^{am}[\text{amine}]} \qquad (2)$$

If $k_{-1} \ll (k_2 + k_3^{am}[\text{amine}])$, the rate-controlling step becomes the nucleophilic attack of the amine, and base catalysis is not observed (reaction with primary amines). Under these conditions eq 2 reduces to $k_a = k_1$.

The approximately linear dependence between k_a and amine concentrations, as observed with the secondary amines at lower concentrations, and the downward curvature at higher ones indicate that $k_{-1} \geq k_2 + k_3^{am}[\text{amine}]$. On deriving the reciprocal expression 3 from eq 2, we can evaluate the parameters k_1 and k_3^{am}/k_{-1}

$$1/k_a = k_{-1}/k_1(k_2 + k_3^{am}[\text{amine}]) + 1/k_1 \qquad (3)$$

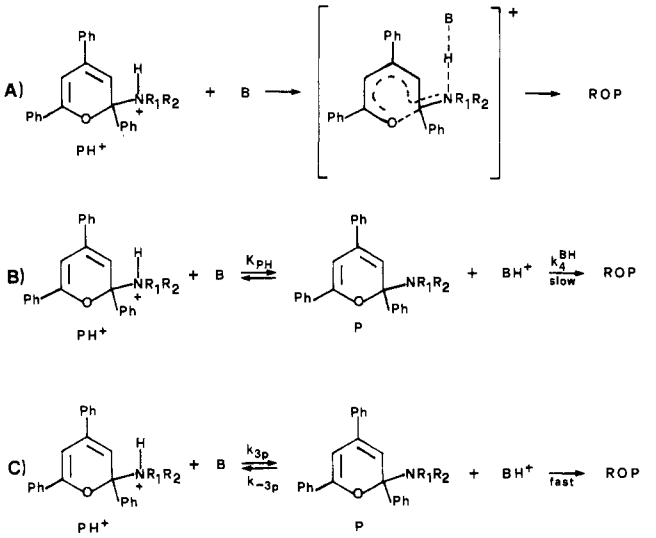
At higher amine concentrations the condition $k_2 < k_3^{am}[\text{amine}]$ can be attained, and a linear dependence between $1/k_a$ and 1/[amine] can be observed, with a slope of $k' = k_{-1}/k_1k_3^{am}$ and an intercept $k'' = 1/k_1$ (Figure 4).

In Table VII we report the values of k_1, and k_3^{am}/k_{-1} obtained by this treatment. Our experimental data do not allow us to evaluate safely the k_2/k_{-1} ratios.

Nucleophilic Attachment Step. The rate constants, k_1, for the nucleophilic attachment of the amine are in the following order: pyrrolidine > piperidine > morpholine ≈ butylamine > cyclohexylamine.

The higher reactivity of butylamine with respect to cyclohexylamine, in spite of the identical basicity, indicates that steric effects can affect the amine attack at the cationic substrate. This view is also supported by the lower reactivity of piperidine with respect to pyrrolidine and by the comparable reactivities between piperidine and butylamine.[6] However, severe steric effects do not appear

Scheme III



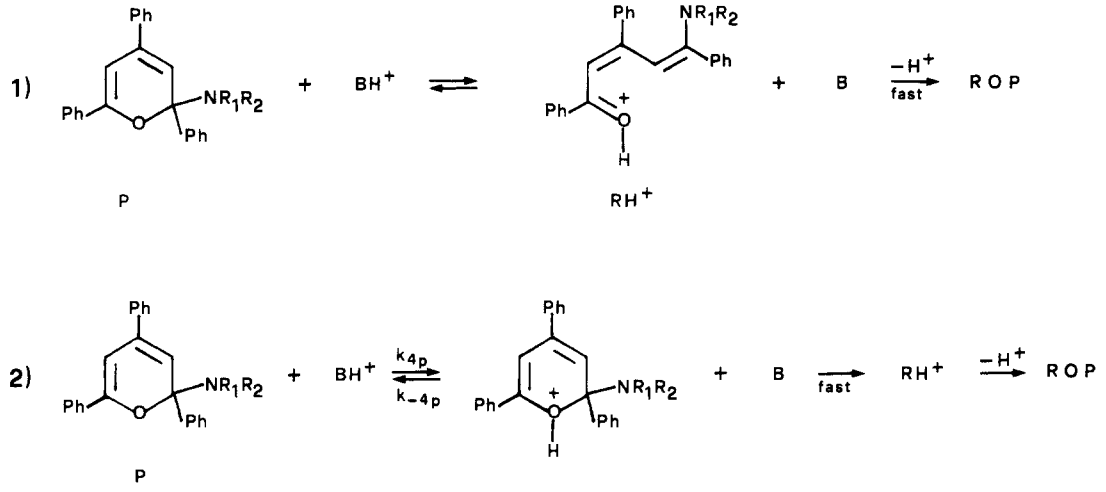
to operate as suggested by the observed reactivity order of secondary amines > primary amines. This order is substantially analogous to that observed for several amine reactions, e.g., the attachment reactions to tri-*p*-anisylmethyl,[7] 2,4,6-triphenylthiopyrylium,[8] and 3,6-bis(dimethylamino)xanthylium[9] ions, activated alkenes,[10] and 1,3,5-trinitrobenzene,[11] but differs from that found for the reaction of the hindered 1,1-dinitro-2,2-diphenylethylene,[12] for which steric effects are reported to be operating on the amine attachment step. The value of $\beta_{nuc} = 0.3$, as evaluated from the piperidine and morpholine reaction, suggests the absence of dramatic steric interactions between the reactants. This parameter is related to the positive charge density developing at the nitrogen atom in the transition state. The observed low value should indicate that only a small amount of the positive charge is transferred to the amino group. Consequently, the formation of the C–N bond should not have made much progress in the transition state.

Mechanism of the Base-Catalyzed Process. In the reactions of the secondary cyclic amines the k_3^{am}/k_{-1} ratios can give some valuable hints about the relative values of the k_3^{am} terms, which refer to the base-catalyzed formation of the product. We suggest that the k_{-1} order of reactivity follows the same trend, i.e., morpholine > piperidine > pyrrolidine, as that observed for the reversal of adduct

(6) Piperidine is generally observed to be more reactive than butylamine by one order of magnitude both in the nucleophilic attack of S_NAr reactions [see: (a) Bernasconi, C. F.; Hoyos de Rossi, R.; Schmid, P. *J. Am. Chem. Soc.* **1977**, *99*, 4090. (b) Bunnett, J. F.; Sekiguchi, S.; Smith, L. A. *Ibid.* **1981**, *103*, 4865] and in the attachment reactions to aromatic compounds and activated alkenes (see ref 8–11).

(7) Bunton, C. F.; Huang, S. K. *J. Am. Chem. Soc.* **1974**, *96*, 515.
(8) Doddi, G.; Ercolani, G., unpublished results. Work presented in part at the 13th Convegno Nazionale di Chimica Organica, Società Chimica Italiana, Milano, Sept 1982.
(9) Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 3573.
(10) Bernasconi, C. F.; Carrè D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2698.
(11) (a) Bernasconi, C. F.; Muller, M. C.; Schmid, P. *J. Org. Chem.* **1979**, *44*, 3189. (b) Crampton, M. R.; Gibson, B. *J. Chem. Soc., Perkin Trans. 2*, **1981**, 533. (c) Crampton, M. R.; Greenhalgh, C. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1175.
(12) Bernasconi, C. F.; Carrè, D. J.; Fox, J. P. In "Techniques and Applications of Fast Reactions in Solution"; Getting, W. J., Wyn-Jones, E., Eds.; Reidel: Dordrecht, Holland, 1979; p 453.

Scheme IV



formation with amines of 2,4,6-triphenylthiopyrylium ion,[8] 3,6-bis(dimethylamino)xanthylium ion,[9] phthalimidium ion,[13] activated alkenes,[10,14] and 1,3,5-trinitrobenzene.[11a,c] According to this hypothesis, we can reasonably expect that the observed changes in the k_3^{am}/k_{-1} values are essentially due to changes in k_{-1} and that the k_3^{am} values do not change appreciably from each other, the differences probably being less than one order of magnitude.

Three routes can be envisaged in order to explain the base-catalyzed formation of the divinylogous amide (Scheme III).

Mechanism A is a sort of concerted elimination if C–N conjugation is taken into account. We believe it is unlikely in view of the existence of stable 2-amino-2*H*-pyrans[2] and also by analogy with the reaction of amines with thiopyrylium ions, whereby 2-amino-2*H*-thiopyrans can be detected and undergo the ring-opening reaction[15] in a separate step. Moreover, we should expect a change in k_3^{am} greater than that estimated above in going from pyrrolidine to morpholine, owing to conjugation to some degree of the amino nitrogen in the transition state (see Scheme III) and to the appreciably greater conjugative ability of pyrrolidine relative to piperidine and morpholine.[16-19]

Mechanism B also appears to be unlikely. In this case, a proton-transfer equilibrium between PH^+ and P is rapidly established, whereas the ring-opening reaction is slow and acid catalyzed (SB-GA mechanism). Any k_3^{am} term is equal to the product of K_{PH}^{am} (the equilibrium constant between the PH^+ intermediate and the corresponding amine) and k_4^{amH}, namely, $k_3^{am} = K_{PH}^{am} k_4^{amH}$. We assume that the equilibrium constant, K_{PH}, is essentially the same for the three diverse amines since the electronic effect of the 2*H*-pyran moiety is likely to be additive, so that the $K_{PH1}^{am1}/K_{PH2}^{am2}$ ratios are expected to be close to unity and the k_3^{am1}/k_3^{am2} ratios to be close to the k_4^{amH1}/k_4^{amH2} ratios. In contrast, the rate constants for the ring-opening acid-catalyzed step, k_4^{amH}, will obviously be dependent on the acidity of the ammonium ion.

Two possibilities can indeed be envisaged for the acid-catalyzed process (see Scheme IV).

The first hypothesis consists of a concerted process involving a proton transfer to the substrate and a ring opening. This is unlikely, however, because in no stage of this process would the proton transfer be thermodynamically favored. The pK_a of the acid catalyst is never intermediate between P and RH^+.[20]

According to the second hypothesis the proton transfer precedes ring opening in a slow step but involves a thermodynamically strongly unfavored charged intermediate. If this is so, any $k_4^{amH_i}$ term coincides with $k_{4p}^{amH_i}$ that should be related to the pK_a's of the acid catalyst by a Brønsted relationship with $\alpha = 1$. Since k_4^{MorH}/k_4^{PipH} was shown to be approximately equal to k_3^{Mor}/k_3^{Pip}, the resulting relationships $k_3^{Mor}/k_3^{Pip} \simeq k_4^{MorH}/k_4^{PipH} \simeq K_a^{Mor}/K_a^{Pip} = 40$ and $k_3^{Mor}/k_3^{Pyrr} \simeq k_4^{MorH}/k_4^{PyrrH} \simeq K_a^{Mor}/K_a^{Pyrr} = 60$ would lead to much too high values for k_3^{Mor}/k_3^{Pip} and k_3^{Mor}/k_3^{Pyrr} as compared to those estimated above.

Mechanism C is the only one left which seems to be consistent with a little change in $k_3^{am_i}$ values. We first note that such a mechanism requires that the proton abstraction from the PH intermediate by the corresponding amine be rate-controlling and that, therefore, $k_3^{am_i} = k_{3p}^{am_i}$. Even though in a protic solvent a thermodynamically favored proton transfer from a NH^+ acid to a nitrogen base should be diffusion controlled,[21] there are known reactions whereby proton abstraction from ammonium ions by amine is slower than for a diffusion controlled process as found in the reaction between amines with 1,3,5-trinitrobenzene[11] and activated alkenes.[14a,b] This behavior was ascribed to steric hindrance to the approach of the base to the bulky ammonium ion. Since the investigated secondary amines have comparable or identical steric requirements, they should display similar reactivity toward proton abstraction, i.e., $k_{3p}^{Pip} \simeq k_{3p}^{Mor} \simeq k_{3p}^{Pyr}$, which is indeed the case since we have pointed out that the equilibrium constants for the reaction $PH^+ + B \rightleftarrows P + HB^+$ are also comparable to each other.

The absence of base catalysis in the reaction of primary amines, that is bound to the condition $k_{-1} \ll k_2 + k_3^{am}[\text{amine}]$, can be related to a decrease in k_{-1} and/or to

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an increase in k_3^{am}. The k_2 term probably does not give a large contribution since the linear correlation shown for pyrrolidine in Figure 4 is only possible if k_2 is negligible, and this term should not be greatly affected by the structural change that is involved in going from the secondary amine to the investigated primary amines. Also, at the lower amine concentrations the first portion of the plot reported in Figure 3 for pyrrolidine is approximately linear, a condition that can only be possible if $k_{-1} > k_2 + k_3^{am}$[amine]. On comparing the above-mentioned inequalities in a simplified form (neglect of k_2), i.e.,

$$k_{-1} \ll k_3^{am}[\text{amine}] \quad \text{for cyclohexylamine}$$

$$k_{-1} \simeq k_3^{am}[\text{amine}] \quad \text{for pyrrolidine}$$

which hold at similar amine concentrations, we conclude that k_{-1}(pyrr)/k_{-1}(cyclohex) must be on the order of at least 10^2. Thus, in such a case the disappearance of base catalysis can well be caused by a decrease in k_{-1} alone.

In contrast, with other substrates such as 2,4,6-triphenylthiopyrylium, though very similar to 1, the k_{-1} (secondary amine)/k_{-1} (primary amine) ratio has been found to be lower than 14 (secondary amine = piperidine; primary amine = cyclohexylamine);[8] it should be even lower were pyrrolidine considered. An increase in k_3^{am} would then effectively contribute to the disappearance of base catalysis in the reaction of primary amines. This behavior provides further support to mechanism C because primary amines are less hindered than secondary amines and would hardly reconcile with a SB-GA mechanism because butylamine and cyclohexylamine have the same pK_a as that of pyrrolidine.

Registry No. 2,4,6-Triphenylpyrylium perchlorate, 1484-88-4; butylamine, 109-73-9; cyclohexylamine, 108-91-8; pyrrolidine, 123-75-1; piperidine, 110-89-4; morpholine, 110-91-8.

Anomaly in Palladium-Catalyzed Phenylethynylation of 2,2′-Dihalobiphenyls: Formation of Alkylidenefluorenes

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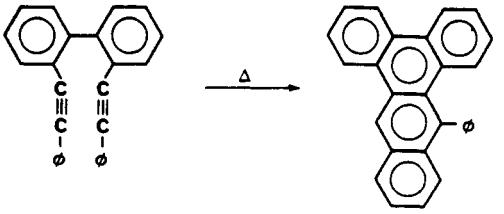
2,2′-Diiodobiphenyl and 5,5′-dinitro-2,2′-dihalobiphenyls underwent palladium-catalyzed phenylethynylation with 2 mol of phenylacetylene to yield 3-(fluoren-9-ylidene)-1,3-diphenylpropyne and 3-(3,6-dinitrofluoren-9-ylidene)-1,3-diphenylpropyne, respectively. These fluorenyl compounds exhibited well-defined splitting patterns for the fluorenyl ring protons in the 250-MHz proton NMR spectra. The structure of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne was further confirmed by an independent synthesis via the thermolysis of diethyl 3-(fluoren-9-ylidene)-1,3-diphenylpropen-1-yl phosphate. The mechanistic importance of the complex iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium(II) in the catalytic cycle was established on the basis of its reaction with phenylacetylene to give 3-(fluoren-9-ylidene)-1,3-diphenylpropyne.

The palladium-catalyzed coupling reaction[1] between an aryl halide and a terminal acetylene in the synthesis of arylalkylacetylenes,[2] tolanes,[3,4] and heteroarylacetylenes[5,6] has received considerable attention in recent years. In similar syntheses of acetylenic compounds, an alternative organocopper method[7-10] is also widely accepted. These two approaches have been shown to be superior to many tedious classical methods.[11]

We became interested in the thermally induced intramolecular cycloaddition of 2,2′-bis(phenylethynyl)biphenyl[12] (1) to a highly fused aromatic nucleus, i.e., 9-



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