

Formation of α,β -Unsaturated Schiff Bases from β,γ -Unsaturated Ketones. A Change in Rate-Determining Step in the Reactions of 3-Methyl-3-cyclohexenone with Glycinamide and Ethylenediamine

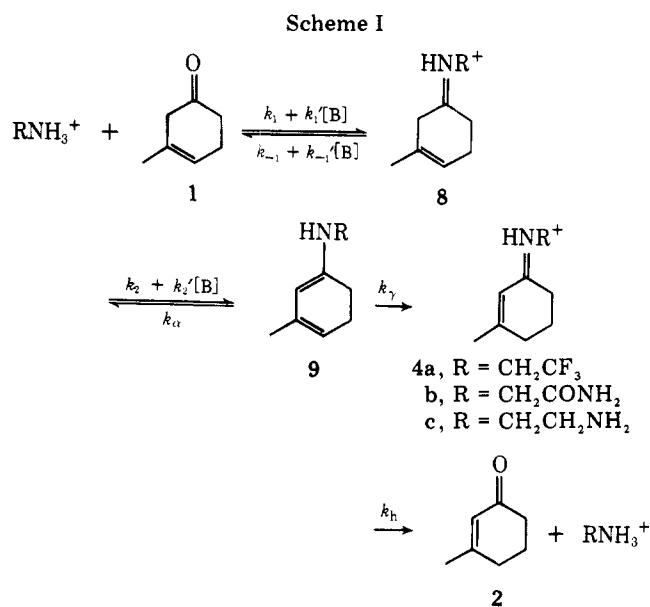
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The isomerization of 3-methyl-3-cyclohexenone (1) to 3-methyl-2-cyclohexenone (2) is catalyzed by glycinamide (GA) and ethylenediamine (EDA) through the intermediate formation of an α,β -unsaturated Schiff base (4). The formation of 4 (k_i) was investigated in detail. A mechanism is proposed which involves formation of a β,γ -unsaturated Schiff base (8) followed by isomerization through a dienamine intermediate (9) to the α,β -unsaturated Schiff base. Nonlinear plots of $k_i/[\text{RNH}_2]$ vs. $[\text{RNH}_3^+]$ are interpreted in terms of a change in rate-determining step from breakdown of 8 at low $[\text{RNH}_2]$ to formation of 8 at high $[\text{RNH}_2]$.

We have previously shown^{1,2} that the isomerizations of 3-methyl-3-cyclohexenone and 1-acetyl-2-cyclohexene to the corresponding α,β -unsaturated isomers are efficiently catalyzed by 2,2,2-trifluoroethylamine (TFEA). The isomerization of 3-methyl-3-cyclohexenone (1) proceeds through the formation of an α,β -unsaturated Schiff base (4a) which is produced by protonation of a dienamine intermediate (9), analogous to the dienol in the corresponding acid-catalyzed³ isomerization (Scheme I). The hydrolysis of 4a is relatively



slow and has been discussed elsewhere.⁴ The overall catalytic efficiency of TFEA in the isomerization of 1 is limited by the rate of hydrolysis of 4a (k_h). Even so, the TFEA-catalyzed reaction shows a rate enhancement of $>10^6$ - and $>10^5$ -fold over the corresponding acid- and base-catalyzed processes, respectively.

In this paper we report on the kinetics of the formation of the corresponding α,β -unsaturated Schiff bases (4b and 4c) from two more basic amines, glycinamide (pK 8.31) and ethylenediamine (pK 7.52). The formation of the α,β -unsaturated Schiff bases from these two amines shows kinetics which suggest a change in rate-determining step with changing amine concentration.

Results

Both glycinamide (GA) and ethylenediamine (EDA) are efficient catalysts for the isomerization of 1 to 2. For catalysis by each amine, ultraviolet spectroscopy showed rapid formation of an intermediate ($\lambda_{\text{max}} \sim 268$ nm) which then slowly

decomposed to 2 ($\lambda_{\text{max}} \sim 240$ nm). By analogy to the corresponding reaction of 1 with trifluoroethylamine (TFEA), this intermediate is considered to be the α,β -unsaturated Schiff base (4) from the amine (GA or EDA) and 3-methyl-2-cyclohexenone.

Since our interest in this study is in the mechanism of the conversion of the β,γ -unsaturated ketone (1) to an α,β -unsaturated Schiff base (4), we monitored the reaction at the isosbestic point for the subsequent hydrolysis of 4 to 2. This procedure allows rate constants for the reaction 1 \rightarrow 4 to be obtained directly. Rate constants for the hydrolysis of the α,β -unsaturated Schiff bases were not determined. Using this procedure, values for the pseudo-first-order rate constants for the formation of 4 (k_i) were evaluated at $25.0 \pm 0.2^\circ\text{C}$ and constant ionic strength ($\mu = 1.0$, maintained with NaCl). Good first-order kinetics were obtained at all concentrations of amine.

In our previous investigation of this reaction with TFEA,^{1,2} it was found that k_i could be expressed by an equation of the form

$$k_i = k^B[\text{RNH}_2] + k^{AB}[\text{RNH}_2][\text{RNH}_3^+]$$

so that a plot of $k_i/[\text{RNH}_2]$ vs. $[\text{RNH}_3^+]$ was linear. In contrast, similar plots for EDA and GA are not linear. The reaction with GA was studied in detail to determine the reason for the curvature in the buffer plots. Figure 1 shows plots of $k_i/[\text{GA}]$ vs. $[\text{GAH}^+]$ at constant pH for three buffer ratios. Concave buffer plots such as these are indicative of a change in rate-determining step with changing buffer concentration. At low $[\text{GAH}^+]$, k_i is largely second order in amine, while at high $[\text{GAH}^+]$, k_i becomes predominantly first order in amine. In addition, the first-order term at high amine concentration decreases with increasing pH, giving rise to more pronounced curvature of these plots at high pH.

These results may be analyzed in terms of Scheme I. Application of the steady-state equation to Scheme I gives eq 1 for the conversion of 1 to 4 in the absence of external buffer (i.e., $[\text{B}] = [\text{RNH}_2]$)

$$k_i = \frac{(k_1[\text{RNH}_3^+] + k_1'[\text{RNH}_3^+][\text{RNH}_2])(k_2 + k_2'[\text{RNH}_2])R}{(k_{-1} + k_{-1}'[\text{RNH}_2]) + (k_2 + k_2'[\text{RNH}_2])R} \quad (1)$$

where $R = k_\gamma/(k_\alpha + k_\gamma)$. Dividing eq 1 by $[\text{RNH}_2]$ and rearranging gives eq 2, where $K_1 = [8]/[1][\text{RNH}_3^+] = (k_1 + k_1'[\text{RNH}_2])/(k_{-1} + k_{-1}'[\text{RNH}_2])$, $k_1^0 = k_1[\text{RNH}_3^+]/[\text{RNH}_2]$, and $k_2^0 = k_2[\text{RNH}_3^+]/[\text{RNH}_2]$.

$$\frac{k_i}{[\text{RNH}_2]} = \frac{K_1(k_1^0 + k_1'[\text{RNH}_3^+])(k_2^0 + k_2'[\text{RNH}_3^+])R}{(k_1^0 + k_1'[\text{RNH}_3^+]) + K_1(k_2^0 + k_2'[\text{RNH}_3^+])R} \quad (2)$$

Table I. Calculated Rate Constants for the Formation of α,β -Unsaturated Schiff Bases from 3-Methyl-3-cyclohexenone^a

Amine	pH	$10^2 k_1$, $M^{-1} s^{-1}$	$10^2 k_1'$, $M^{-2} s^{-1}$	$10^3 K_1 k_2 R$, $M^{-1} s^{-1}$	$K_1 k_2' R$, $M^{-2} s^{-1}$
GA	7.71	2.90 ± 0.13	3.2 ± 1.4	<i>b</i>	0.55 ± 0.03
	8.31	3.18 ± 0.18	3.5 ± 1.0	4.9 ± 1.6	0.54 ± 0.05
	8.89	4.36 ± 0.16	4.5 ± 0.7	12 ± 1.0	0.57 ± 0.02
	Av		3.7 ± 0.7		0.56 ± 0.02
EDA	7.02	8.2 ± 0.8	<i>b</i>	1.3 ± 0.3	1.10 ± 0.04
	7.52	15 ± 3	<i>b</i>	5.6 ± 3.9	1.05 ± 0.13
	Av				1.08 ± 0.07

^a Errors are standard deviations obtained from linear plots according to eq 3 (see text). ^b Could not be determined.

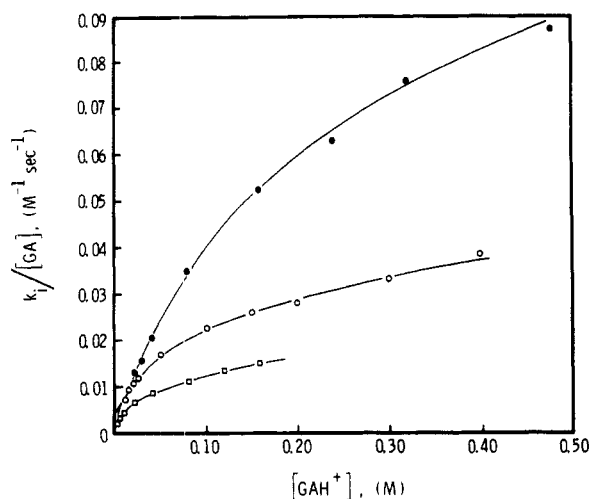


Figure 1. The variation of $k_i/[GA]$ with $[GAH^+]$ for the GA catalyzed formation of 4: (●), pH 7.71; (○), pH 8.31; and (□), pH 8.89. Theoretical curves were calculated from the parameters in Table I.

This rearrangement facilitates fitting the data to the experimental buffer curves.

Initial values of the parameters k_1^0 , k_1' , $K_1 k_2^0 R$, and $K_1 k_2' R$ were obtained at each pH by assuming that the rate-limiting step at low $[RNH_2]$ is the decomposition of 8 (i.e., $k_1^0 + k_1' [RNH_3^+] \gg K_1(k_2^0 + k_2' [RNH_3^+])R$), and at high $[RNH_2]$, the rate-limiting step is the formation of 8 (i.e., $k_1^0 + k_1' [RNH_3^+] \ll K_1(k_2^0 + k_2' [RNH_3^+])R$). Under this assumption, the limiting slope of a plot of $k_i/[RNH_2]$ vs. $[RNH_3^+]$ at low $[RNH_3^+]$ corresponds to $K_1 k_2' R$ and the intercept is $K_1 k_2^0 R$. At high concentration of amine, the slope is k_1' and the extrapolated intercept k_1^0 . Although these limiting cases were not actually observed, estimates of these values could be obtained in this way. Successive approximations enabled a reasonably good fit to the experimental points to be realized. In order to improve the fit, eq 2 was inverted to give

$$\frac{[RNH_2]}{k_i} = \frac{1}{K_1(k_2^0 + k_2'[RNH_3^+])R} + \frac{1}{k_1^0 + k_1'[RNH_3^+]} \quad (3)$$

and the values for k_1^0 and k_1' were substituted into eq 3 leading to values for the quantity $K_1(k_2^0 + k_2'[RNH_3^+])R$ as a function of $[RNH_3^+]$. A plot of this quantity vs. $[RNH_3^+]$ should then yield a straight line with slope = $K_1 k_2' R$ and intercept $K_1 k_2^0 R$. The parameters k_1^0 and k_1' were varied slightly to give the best least-squares fit for this linear relationship. The new values of $K_1 k_2' R$ and $K_1 k_2^0 R$ thus generated were then used in conjunction with eq 3 to recalculate k_1^0 and k_1' in a similar manner. This method was repeated until further iterations showed no change in the parameters. An identical procedure was followed for the reaction with EDA.

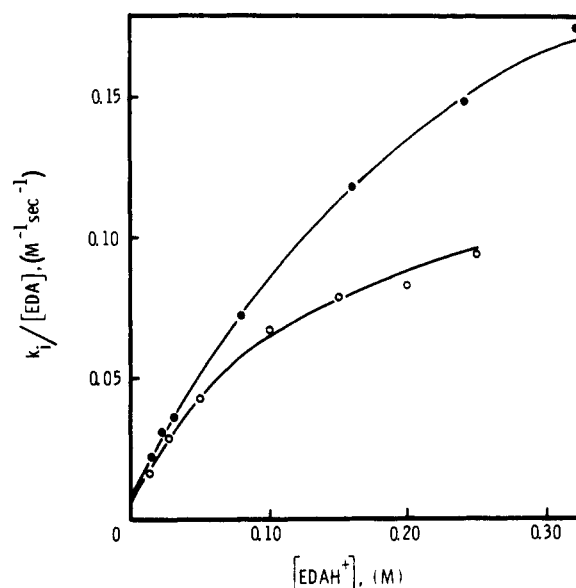


Figure 2. The variation of $k_i/[EDA]$ with $[EDAH^+]$ for the EDA catalyzed formation of 4: (●), pH 7.02; (○), pH 7.52. Theoretical curves were calculated from the parameters in Table I.

With EDA, the curvature in the buffer plots is not as pronounced as with GA, resulting in both relatively large errors for k_1^0 and in k_1' values indistinguishable from zero. Calculated values of k_1 , k_1' , $K_1 k_2 R$, and $K_1 k_2' R$ for both amines are given in Table I. These values, when used in conjunction with eq 1, give excellent fits to the experimental data (Figures 1 and 2).

For both GA and EDA, the rate constant corresponding to the uncatalyzed rate of formation of 8 (k_1) increases with increasing pH. This suggests that these rate constants are composed of a term in hydroxide ion as well as a term independent of pH ($k_1 = k_1^{H_2O} + k_1^{OH^-} [OH^-]$). A plot of k_1 vs. $[OH^-]$ for GA is linear with a slope ($k_1^{OH^-}$) of $2.0 \times 10^3 M^{-2} s^{-1}$ and an intercept ($k_1^{H_2O}$) of $2.8 \times 10^{-2} M^{-1} s^{-1}$. For EDA, only two pHs were used and the values for k_1 are less reliable, but estimates of $k_1^{OH^-}$ ($3.0 \times 10^5 M^{-2} s^{-1}$) and $k_1^{H_2O}$ ($4.5 \times 10^{-2} M^{-1} s^{-1}$) may be obtained. For both amines, the rate of breakdown of 8 (k_2) appears to be linearly dependent on the hydroxide ion concentration with no discernible contribution from a water rate ($k_2 = k_2^{OH^-} [OH^-]$). Although the precision in these numbers is not high, values of $K_1 k_2^{OH^-} R$ may be obtained for both GA ($1.9 \times 10^3 M^{-2} s^{-1}$) and EDA ($15 \times 10^3 M^{-2} s^{-1}$).

Discussion

The complex kinetics for the formation of α,β -unsaturated Schiff bases from 3-methyl-3-cyclohexenone and either glycinamide or ethylenediamine may be rationalized in terms of the mechanism proposed previously² for the corresponding

Table II. Rate Constants for Formation of 4 for Various Amines^a

Amine	pK _a ^b	k ^{AB} , M ⁻² s ⁻¹	10 ³ k ^B , M ⁻¹ s ⁻¹	10 ⁴ K ₁ k ₂ ^{OH⁻} R, ^c M ⁻² s ⁻¹
TFEA ^d	5.77	0.22 ± 0.02	0.19 ± 0.03	3.3 ± 0.3
EDA ^e	7.52 (7.82) ^f	0.54 ± 0.04	2.8 ± 1.2	0.85 ± 0.30
GA	8.31	0.56 ± 0.02	3.8 ± 0.8	0.19 ± 0.04

^a Errors are standard deviations. ^b pH of 1:1 buffer at $\mu = 1.0$; the pK_a for EDA is the first dissociation constant of EDHA₂²⁺. ^c Calculated from identity, $k^B = (K_1 k_2^{OH^-} R) K_w / K_a$. ^d Rate constants from ref 2. ^e All rate constants for EDA have been halved due to the presence of two reactive sites in the diamine. ^f Corrected for statistical effects.

reaction with trifluoroethylamine (Scheme I). Initial formation of a protonated β, γ -unsaturated Schiff base (8) is followed by loss of a proton from the α carbon to give a dienamine (9), which upon protonation at the γ carbon gives the protonated α, β -unsaturated Schiff base (4). Although the curved buffer plots for GA and EDA as reactants show that a change in rate-determining step is occurring as the amine concentration is increased, they do not indicate which steps are rate determining at various amine concentrations. The steady-state equation for Scheme I (eq 2) does not by itself allow a unique solution to this problem. Although we assumed that the change in rate-determining step is from decomposition of 8 at low [RNH₂] to formation of 8 at high [RNH₂], the kinetics alone do not require that this be so. The reverse situation (rate-determining formation of 8 at low [RNH₂] and rate-determining breakdown of 8 at high [RNH₂]) can accommodate the kinetic results equally well. Consequently, it is imperative that other criteria be used to justify our assignment.

At low concentrations of amine, k_i is dominated by a large second-order term ($K_1 k_2' R$) which we assign to abstraction of the α proton from 8, followed by partitioning of the dienamine, analogous to the reaction with TFEA [$(k_{-1} + k_{-1}' [RNH_2]) > (k_\gamma / (k_\gamma + k_\alpha)) (k_2 + k_2' [RNH_2])$]. As the amine concentration is increased, the rate-determining step then becomes formation of 8 [$(k_\gamma / (k_\gamma + k_\alpha)) (k_2 + k_2' [RNH_2]) > (k_{-1} + k_{-1}' [RNH_2])$]. For this explanation to be reasonable, it is necessary that k_{-1} be greater than $k_2 (k_\gamma / (k_\gamma + k_\alpha))$ but that $k_2' (k_\gamma / (k_\gamma + k_\alpha))$ be greater than k_{-1}' . In other words, abstraction of the α proton from 8 must be more sensitive to general base catalysis than the hydrolysis of the Schiff base. In the pH region examined (7.7–8.9) the rate-determining step in the hydrolysis of 8 should be attack of either water or hydroxide ion on the protonated Schiff base.⁵ Although general base catalysis of protonated Schiff base hydrolysis is often observed, the sensitivity of the rate to external general bases is low ($\beta \leq 0.25$ for saturated Schiff bases).^{5–8} Deprotonation of iminium ions, on the other hand, generally shows a greater sensitivity to the presence of external general bases in the solution. For example, a β of 0.4 has been observed for the abstraction of a proton from the protonated Schiff base of acetone and methylamine⁹ and a β of ca. 0.5 may be calculated from the data of Hine et al.¹⁰ for the deprotonation of the *N*-methyliminium ion of isobutyraldehyde. If the change in rate-determining step with increasing amine concentration were in the opposite direction (i.e., formation of 8 at low [RNH₂] and decomposition of 8 at high [RNH₂]), then this would require that the hydrolysis of a protonated Schiff base be more sensitive to general base catalysis than its deprotonation, contrary to what is observed in other systems.

Further evidence for our assignment can be seen by the fact that a change in rate-determining step is only observable with the more basic amines GA and EDA and not with TFEA. Since the rates of hydrolysis of protonated Schiff bases (under conditions where attack of water is rate determining) increase markedly with decreasing amine pK_a ($\beta \sim -1.0$)⁷ it is to be

expected that the rate of hydrolysis of 8 would be much greater for TFEA than either GA or EDA. The rate of breakdown of 8 to products, however, is expected to show a much smaller dependence on amine pK_a, for both $k_2^{OH^-}$ ($\beta \sim -0.5$) and k_2' ($\beta \sim 0$).¹¹ Consequently, the partitioning of 8 should favor return to reactants as the amine pK_a decreases. Since breakdown of 8 is rate determining for TFEA,^{1,2} a change in the rate-determining step would be favored by raising the amine basicity, as is observed.

An alternate explanation is that the curved buffer plots are due to a change in rate-determining step from k_α at low amine concentration to k_γ at high [RNH₂]. We consider that any appreciable variation in the ratio of k_α to k_γ is unlikely since the corresponding ratio in the TFEA reaction is invariant with changes in both pH and amine concentration.^{1,2}

The derived rate constants for GA and EDA may be compared with those for TFEA in the following way. At very low amine concentration, the slow step is breakdown of the intermediate [i.e., $k_{-1} + k_{-1}' [RNH_2] \gg (k_2 + k_2' [RNH_2]) [R]$], and the overall rate constant k_i can be expressed simply by

$$k_i = K_1 R k_2^{OH^-} [RNH_3^+] [OH^-] + K_1 R k_2' [RNH_3^+] [RNH_2] \quad (4)$$

$$= k^B [RNH_2] + k^{AB} [RNH_3^+] [RNH_2] \quad (4a)$$

Values for k^B and k^{AB} can then be calculated and compared with the corresponding values for TFEA (Table II).^{1,2} The rate constants for EDA have been halved to correct for the presence of two reactive sites in the diamine. The k^{AB} terms reflect proton abstraction by free amine from the iminium ion (8) derived from the same amine; in terms of Scheme I $k^{AB} = K_1 k_2' k_\gamma / (k_\gamma + k_\alpha)$. Several investigations^{9,13} have shown that the equilibrium concentration of Schiff base depends only slightly on the amine pK_a. If the partitioning ratio of the dienamine 9, $k_\gamma / (k_\alpha + k_\gamma)$, does not vary significantly with the identity of the amine, then the relative invariance of k^{AB} with amine pK_a reflects two compensating trends in k_2' . Increasing the pK_a should increase the efficiency of the amine in proton abstraction from 8. However, as the amine pK_a increases, 8 becomes less susceptible to α -proton removal, thus causing little change in k^{AB} for amines of varying base strength.

Evidence that the iminium ion 8 does become less susceptible to α -proton removal with increasing amine pK_a is available from Table II. The sensitivity of the rate of proton abstraction from 8 to the amine pK_a may be estimated from a plot of the statistically corrected values of $\log (K_1 k_2^{OH^-} R)$ vs. amine pK_a (not shown). A reasonable linear correlation with slope of ca. -0.5 is obtained. Since this term corresponds to proton abstraction from 8 by hydroxide ion, this result suggests that for the same base (OH⁻ or, presumably, any general base), an increase in pK_a of the amine forming 8 results in a decrease in the rate of abstraction of the α proton. An analogous plot of k^{AB} vs. the pK_a of the base which is abstracting the proton from 8 in the reaction with TFEA shows a slope of $\beta = 0.55$.² These two trends then balance each other

in the k^{AB} terms, making the effect of amine pK_a on k^{AB} very small. Similar conclusions have been reached previously by Spencer et al.¹¹ for simple α -proton abstractions of Schiff base by the corresponding amine. These authors have extensively discussed the implications of this finding for the mechanism of action of enzymes which function via Schiff base intermediates.

Experimental Section

Materials. 3-Methyl-3-cyclohexenone (1) was prepared and purified as previously described.² Glycinamide hydrochloride was purified by recrystallization from absolute ethanol, and ethylenediamine by distillation of the free amine. Distilled water was used for all kinetic runs.

Kinetic Methods. The kinetics were monitored at $25.0 \pm 0.2^\circ\text{C}$ with an ionic strength of 1.0 maintained by NaCl. Spectra were obtained on a Cary 16K spectrophotometer and rates were followed on either a Gilford 2000 or 2400 spectrophotometer. All first-order rate constants were calculated by a nonlinear least-squares regression analysis. pH values for each series of buffer runs were constant to ± 0.02 pH unit.

The rate constant k_1 was measured at the isosbestic point for the subsequent hydrolysis as described previously.² Good first-order kinetics were obtained for 6–8 half-lives in most cases and yielded stable infinity points. Buffer plots of $k_1/[\text{RNH}_2]$ were fit to the steady-state equation (eq 3) by successive approximations as described in the text.

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Registry No.—1, 31883-98-4; 2, 1193-18-6; 4b, 61915-53-5; 4c, 61915-54-6; GA, 598-41-4; EDA, 107-15-3.

Supplementary Material Available. Observed rate constants for formation of the α,β -saturated Schiff base intermediate (4) from ethylenediamine and glycinamide (Table III) (2 pages). Ordering information is given on any current masthead page.

References and Notes

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- (12) This treatment assumes that proton abstraction from **8** by water makes no contribution to k_2 for GA and EDA. The neglect of any terms in protonated amine in eq 4a (i.e., $k^A[\text{RNH}_3^+]$) cannot be rigorously justified because of the uncertainty in most k_2 values for GA and EDA. However, the k^A term for TFEA is small ($7.9 \times 10^{-4} \text{ s}^{-1}$)² and k^A values for GA and EDA should be significantly less ($\leq 10^{-4} \text{ s}^{-1}$) if k^A decreases with increasing amine pK_a as expected.
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Reactions of α -Nitroarylidene Phenylhydrazines in Acid and Basic Media

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The reaction of α -nitrobenzylidene phenylhydrazine (1) in absolute ether with hydrogen chloride, methanesulfonic acid, and periodic acid affords diprotonated salts which have been proposed as one of the intermediates in the conversion in acidic medium of primary and secondary nitroalkanes to carbonyl compounds (Nef reaction). These salts are rapidly hydrolyzed to 1-nitroso-2-benzoylphenylhydrazine (4). The reaction of 1 with secondary amines gives rise to amidrazones.

In continuation of our studies of α -nitroarylidene phenylhydrazines, which recently have become readily available by the direct alkyl nitration of arylidene phenylhydrazines,¹ we are now reporting on their reactions in acidic and basic media. Although this class of compounds has been known for a long time, very little is known about their reactivity. Bamberger^{2,3} reported that α -nitroarylidene phenylhydrazines were converted to the corresponding aroyl phenylhydrazines on treatment with aqueous base, and to tetrazines on treatment with methanolic sodium methoxide.

Reaction with Acids. The reaction of α -nitrobenzylidene phenylhydrazine (1) in absolute ether with hydrogen chloride, methanesulfonic acid, and periodic acid afforded α -nitrobenzylidene phenylhydrazine dihydrochloride (**2a**), α -nitrobenzylidene phenylhydrazine dimethanesulfonate (**2b**), and α -nitrobenzylidene phenylhydrazine diperiodate (**2c**) in yields of 78, 70, and 90%, respectively (Scheme I). The spectral properties of these salts are in accord with a diprotonated structure.⁴ As shown in Table I, the infrared spectra of **2a–c** showed weak ammonium absorption in the range 3500–2200 cm^{-1} and strong nitronate bands⁵ at 1550 and 1335 cm^{-1} . The

NMR spectra⁶ of **2a,b** in $\text{Me}_2\text{SO}-d_6$ exhibited, respectively, absorptions of OH at δ 14.05 and 13.50 and of NH^+ at δ 11.95 and 12.10, which integrated to three protons in a ratio of 2:1. Although structure **2** is well supported by the nitronate bands in the infrared and the low field absorptions of OH in the NMR spectra, the presence of the tautomeric structure **3** (Scheme I) cannot be excluded. It is of interest that in $\text{Me}_2\text{SO}-d_6$ the NMR signals of $^+\text{NH}_3$ in anilinium chloride and of $^+\text{NH}_2$ in phenylhydrazinium chloride occur at δ 9.78 and 9.51, respectively.⁷

Tautomer **2** can be considered as one of the proposed intermediates in the conversion of primary and secondary nitro compounds to carbonyl compounds in acidic media.^{8,9} This viewpoint is supported by the observation that the salts underwent rapid hydrolysis at room temperature to 1-nitroso-2-benzoylphenylhydrazine¹⁰ (**4**) in quantitative yield (Scheme I). It is believed that compound **4** was formed from the reaction of 2-benzoylphenylhydrazine (**5**) with nitrous acid, these being possible intermediates in the hydrolysis of **2**. In fact, compound **5** was isolated when the hydrolysis of **2a** was carried out in the presence of pyridine, which scavenged the nitrous