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] Gycinamide 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 ± 0.2°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_i 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 $k_i/[RNH_2]$ were fit to the steady-state equation (eq 3) by successive approximations as described in the text.

Acknowledgment. This work was supported by Grant GM 20188 from the National Institutes of Health.

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.

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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., $k^A[RNH_3^+]$) 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 (7.9×10^{-4} s^{-1})[2] and k^A values for GA and EDA should be significantly less ($\leq 10^{-4}$ 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 bands[5] at 1550 and 1335 cm^{-1}. The NMR spectra[6] of **2a,b** in Me_2SO-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 Me_2SO-d_6 the NMR signals of $^+NH_3$ in anilinium chloride and of $^+NH_2$ in phenylhydrazinium chloride occur at δ 9.78 and 9.51, respectively.[7]

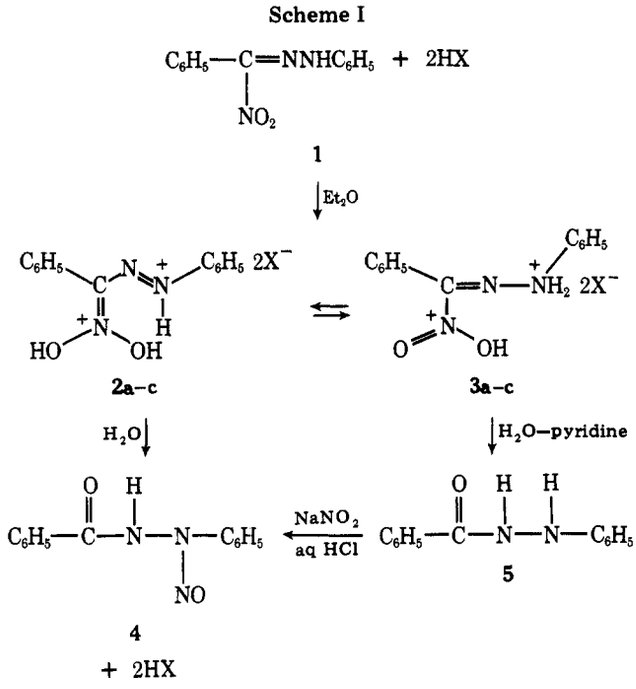
Tautomer **2** can be considered as one of the proposed intermediates in the conversion of primary and secondary nitro compounds to carbonyl compounds in acidic media.[8,9] This viewpoint is supported by the observation that the salts underwent rapid hydrolysis at room temperature to 1-nitroso-2-benzoylphenylhydrazine[10] (**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

Table I. Spectral Data of $C_6H_5C[=^+N(OH)_2]N=^+NHNHC_6H_5$ $2X^-$(2)

X	Infrared spectra, cm^{-1}[a]			NMR spectra, ppm[b]	
	$C=NO_2H_2$	-N=NH-	$=^+NH$	$C=NO_2H_2$	$N=NH^+$
Cl^- (2a)	1550, 1335	1605	3300–2500	14.05 s[e]	11.95 s
$CH_3SO_3^-$ (2b)[c]	1550, 1335	1600	3200–2200	13.50 s	12.10 s
$H_4IO_6^-$ (2c)[d]	1550, 1325	1605	3500–2750		

[a] Spectra were run as potassium bromide wafers. [b] The solvent was Me_2SO-d_6. [c] A $CH_3SO_3^-$ band was present at 1150 and 1060 cm^{-1}. [d] A $H_4IO_6^-$ band was present at 844 cm^{-1}. [e] s = singlet.

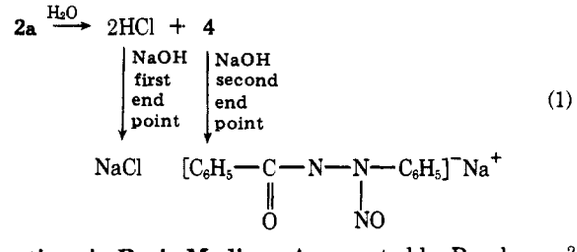
Scheme I



a, X = Cl^-
b, X = $CH_3SO_3^-$
c, X = $H_4IO_6^-$

acid. In a control test, 5 was readily converted to 4 on treatment with sodium nitrite and hydrochloric acid (Scheme I).

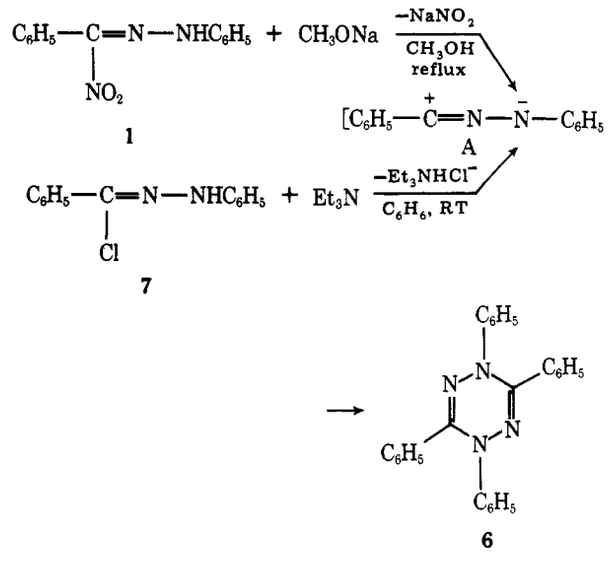
The results of the neutral equivalent determinations of 2a–c are in agreement with these observations. Titrations with base gave curves exhibiting two end points. The first at pK_a 2.65 corresponded to the neutralization of acid liberated in the hydrolysis and the second at pK_a 8.60 resulted from the neutralization of the acidic proton in the nitroso compound 4 (eq 1). Direct titration of authentic 4 gave a pK_a of 8.90.[11]



(1)

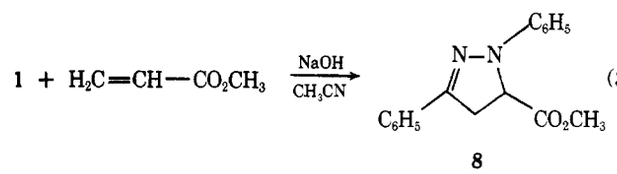
Reactions in Basic Medium. As reported by Bamberger[2] the reaction of 1 with sodium methoxide in methanol gave 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine (6) (eq 2). More recently, Huisgen[12] reported that 6 is also formed when the hydrazidic chloride 7 was treated with triethylamine in benzene at room temperature (eq 2). He considered that the formation of 6 occurred by a 1,3-dipolar head to tail coupling of the diphenyliminonitrile A. Evidence for the intermediacy of A was found when 7 in the presence of triethylamine reacted with dipolarophiles to give 1,3-dipolar adducts.[13]

It was established that 1 could replace 7 as a source of a



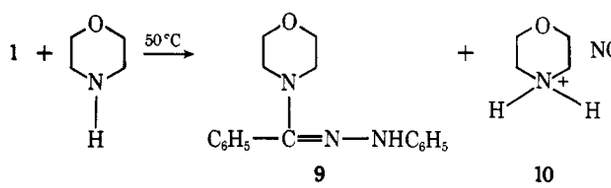
(2)

nitrilimine synthon. Treatment of 1 with sodium hydroxide and methyl acrylate in acetonitrile afforded a 75% yield of 5-carboxymethyl-4,5-dihydro-1,3-diphenyl-2-pyrazoline (8) (eq 3). Compound 8 was previously prepared by the thermolysis of 1,3-diphenyltetrazole in the presence of methyl acrylate.[14]



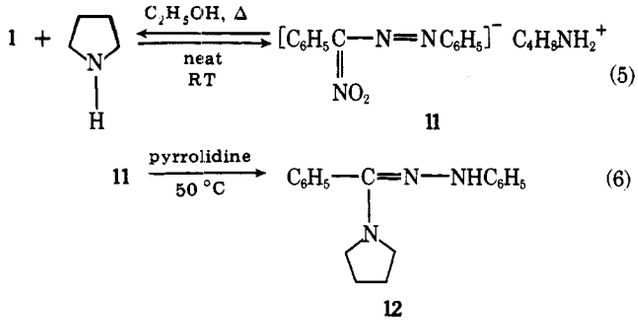
(3)

In contrast to 7, compound 1 did not react with triethylamine in refluxing benzene and was recovered unchanged. However, reactions did take place with secondary amines to give amidrazones. The reaction of 1 with morpholine afforded α-*N*-morpholinobenzylidene phenylhydrazine (9) and morpholinium nitrite (10), each in 85% yield (eq 4). The spectral properties of 9 and 10 were in agreement with their assigned structures.



(4)

When compound 1 was treated with pyrrolidine at room temperature, a quantitative yield of orange-red pyrrolidinium phenylazophenylmethanenitronate (11) was isolated (eq 5). The infrared spectrum of 11 showed a strong ammonium band at 3100–2300 cm^{-1} and nitronate bands at 1465 and 1210 cm^{-1}. The NMR spectrum indicated pyrrolidinium absorptions at δ 1.6 and 2.9 and ammonium absorptions at δ 6.1. The ultraviolet spectrum in 95% ethanol showed a maximum at 403 nm with a large extinction coefficient (log ϵ 4.10), similar to

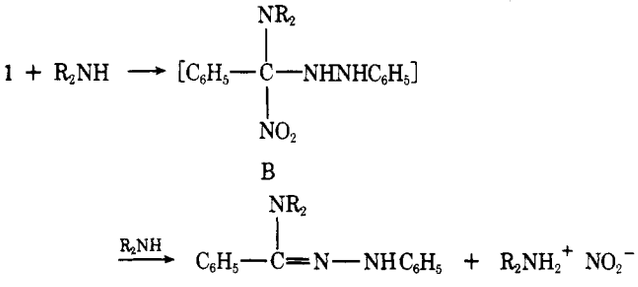


that reported[1] for compound 1. Apparently the extended conjugation in 1 was not changed in salt 11.

Compound 11 reverted to starting materials when placed in refluxing absolute ethanol or when kept in vacuo for several days. The instability of ammonium salts of nitro compounds is well documented in the literature.[15] Upon heating in pyrrolidine at 50 °C, 11 was converted in high yield to α-*N*-pyrrolidinobenzylidene phenylhydrazine (12) (eq 6). However, 12 was unstable and could not be purified. Its infrared and NMR spectra agreed with the proposed structure.

The formation of compounds 9 and 12 might occur by an addition–elimination type reaction as shown in Scheme II.

Scheme II



The formation of the adduct B is very likely preceded by salt formation which is a reversible step as observed in the reaction between compound 1 with pyrrolidine. Our observation that triethylamine, a stronger base than morpholine and slightly weaker than pyrrolidine, did not react with 1 (no formation of tetrazine 6) renders a 1,3-dipolar reaction very unlikely. Moreover, salt 11 underwent dissociation (eq 5) rather then elimination of pyrrolidinium nitrite.

Experimental Section

α-Nitrobenzylidene Phenylhydrazine Dihydrochloride (2a). A 150-mL solution of absolute ether containing 2.41 g (0.01 mol) of α-nitrobenzylidene phenylhydrazine (1) was cooled to 10 °C. Hydrogen chloride was introduced slowly with stirring in 30 min as the temperature rose to 20 °C. A white precipitate formed and the suspension was kept at 0 °C overnight. Filtration and repeated washings with absolute ether gave 2.5 g (78%) of α-nitrobenzylidene phenylhydrazine dihydrochloride (**2a**): mp 70–75 °C dec; IR (KBr) 3100–2500 (N=NHC$_6$H$_5$), 1605 (N=NH), and 1550 and 1335 cm^{-1} (NO$_2$); NMR (Me$_2$SO-d_6) δ 7.2–8.0 (m, 10, ring H), 11.95 (s, 1, N=$^+$NHC$_6$H$_5$), and 14.05 (s, 2, C=NO$_2$H$_2$).

Anal. Calcd for $C_{13}H_{13}Cl_2N_3O_2$: Cl, 21.58; neut equiv, 314. Found: Cl, 21.50; neut equiv, 320.

α-Nitrobenzylidene Phenylhydrazine Dimethanesulfonate (2b). To 25 mL of absolute ether containing 1.0 g (0.004 mol) of 1 was added with stirring 1.48 g (0.05 mol) of methanesulfonic acid at room temperature. After 2 h, a yellow precipitate formed. The suspension was cooled to 0 °C, filtered, and dried in vacuo to give 1.2 g (70%) of α-nitrobenzylidene phenylhydrazine dimethanesulfonate (**2b**): mp >80 °C dec; IR (KBr) 3100–2200 (N=NHC$_6$H$_5$), 1605 (N=NH), 1550 and 1335 (NO$_2$), and 1150 and 1060 cm^{-1} (CH$_3$SO$_3^-$); NMR (Me$_2$SO-d_6) δ 2.5 (s, 6, CH$_3$SO$_3^-$), 7.2–8.0 (m, 10, ring H), 12.1 (s, 1, N=$^+$NHC$_6$H$_5$), and 13.50 (s, 2, C=NO$_2$H$_2$).

Anal. Calcd for $C_{15}H_{19}N_3O_8S_2$: C, 41.55; H, 4.38; N, 9.69; S, 14.77; neut equiv, 433. Found: C, 42.61; H, 4.39; N, 9.78; S, 15.00; neut equiv, 441.

α-Nitrobenzylidene Phenylhydrazine Diperiodate (2c). A similar procedure was used as described in the preparation of **2b** except that 1.0 g (0.004 mol) of 1 and 2.3 g (0.01 mol) of periodic acid were employed in 25 mL of absolute ether. Filtration gave 2.5 g (90%) of α-nitrobenzylidene phenylhydrazine diperiodate (**2c**): mp 155–160 °C dec; IR (KBr) 3500–2750 (N=NHC$_6$H$_5$), 1605 (N=NH), 1550 and 1325 (NO$_2$), and 844 cm^{-1} (H$_4$IO$_6^-$).

Anal. Calcd for $C_{13}H_{21}I_2N_3O_{14}$: I, 36.41; neut equiv, 697. Found: I, 36.13; neut equiv, 681.

1-Nitroso-2-benzoylphenylhydrazine (4). A. Employing Compound 2a. To 25 mL of water was added with stirring 1.0 g (3 mmol) of compound **2a** at room temperature. The solution rapidly turned cloudy with the formation of a white precipitate. The suspension was filtered, dried, and recrystallized (50 °C) from 75% ethanol to give 0.6 g (80%) of 1-nitroso-2-benzoylphenylhydrazine (**4**): mp 105–110 °C dec (lit.[10] mp 108–110 °C); IR (KBr) 3180 (OH) and 1680 cm^{-1} (C=O); NMR (Me$_2$SO-d_6) δ 7.1–7.8 (m, 10, ring H) and 11.2 (s, 1, NH).

Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.32; H, 4.60; N, 17.42. Found: C, 64.50; H, 4.83; N, 17.29.

B. Employing Compound 5. To a suspension of **5** (5.0 g, 0.023 mol) in absolute ethanol (100 mL) and 12 M hydrochloric acid (5.5 mL) was added at 0 °C a 10-mL aqueous solution of sodium nitrite (1.72 g, 0.025 mol). A yellow color developed with the formation of a homogeneous solution. Addition of 50 mL of water gave a yellow precipitate which after drying and recrystallization from 95% ethanol afforded compound **4** (66% yield), mp 106 °C dec.[16]

Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.32; H, 4.60; N, 17.42; neut equiv, 241.2. Found: C, 64.58; H, 4.78; N, 17.30; neut equiv, 250.2.

5-Carbomethoxy-1,3-diphenyl-4,5-dihydro-2-pyrazoline (8). Compound 1 (1 g, 4 mmol), sodium hydroxide (0.5 g, 12 mmol), and methyl acrylate (1.6 g, 10 mmol) were added to 50 mL of acetonitrile and the mixture refluxed for 30 min. Cooling, filtering, and concentrating the filtrate in vacuo gave 0.8 g (75%) of 5-carbomethoxy-1,3-diphenyl-4,5-dihydro-2-pyrazoline (**8**) (absolute CH$_3$OH): mp 108–109 °C (lit.[14] mp 107 °C); IR (KBr) 1650 (C=O) and 1600 cm^{-1} (C=N); NMR (CDCl$_3$) δ 3.5 (m, 2, CH$_2$CH), 3.75 (s, 3, CH$_3$), 4.8 (m, 1, CHCH$_2$), and 6.8–7.9 (m, 10, ring H).

α-*N*-Morpholinobenzylidene Phenylhydrazine (9). To 10 mL of morpholine was added with stirring 0.65 g (3 mmol) of compound 1 at room temperature. The deep red solution turned bright yellow upon heating for 30 min at 50 °C. Then excess morpholine was removed in vacuo and the residual yellow oil dissolved in 30 mL of ethyl ether. A white precipitate formed which was filtered and dried to give 0.30 g (85%) of morpholinium nitrite (**10**): IR (KBr) 3400–2200 (NH$_2$), 1235 and 860 (NO$_2^-$), and 1185 cm^{-1} (C–NH$_2$).

The ethereal solution was concentrated in vacuo and the remaining white solid recrystallized from 80% ethanol to afford 0.65 g (85%) of α-*N*-morpholinobenzylidene phenylhydrazine (**9**): mp 137.5–139 °C; IR (KBr) 3257 (NH), 1597 (C=N), 1269 (>NC=N), 1252 (NC$_6$H$_5$), and 1112 cm^{-1} (COC); NMR (CDCl$_3$) δ 3.10 (t, 4, CH$_2$NCH$_2$), 3.75 (t, 4, CH$_2$OCH$_2$), and 6.6–7.5 (m, 11, ring H and NH).

Anal. Calcd for $C_{17}H_{19}N_3O$: C, 72.57; H, 6.80; N, 14.93. Found: C, 72.31; H, 6.70; N, 14.85.

Pyrrolidinium Phenylazophenylmethanenitronate (11). To 10 mL of pyrrolidine was added 1.0 g (4 mmol) of compound 1 at room temperature. An orange-red precipitate formed immediately which after drying and recrystallization from hexane gave 1.25 g (100%) of pyrrolidinium phenylazophenylmethanenitronate (**11**): mp 103 °C; UV max (95% C$_2$H$_5$OH) 403 nm (log ε 4.10); IR (KBr) 3100–2300 (NH$_2$) and 1465 and 1210 cm^{-1} (C=NO$_2$); NMR (Me$_2$SO-d_6) δ 1.5 (m, 4, CH$_2$CH$_2$), 2.9 (m, 4, CH$_2$NCH$_2$), 6.1 (s, 2, >NH$_2^+$), and 6.6–7.2 (m, 10, ring H).

Anal. Calcd for $C_{17}H_{20}N_4O_2$: C, 65.36; H, 6.45; N, 17.95. Found: C, 65.25; H, 6.32; N, 17.71.

When compound 11 was either refluxed in absolute ethanol or placed in a vacuum desiccator for 1 week, a quantitative yield of 1 was obtained.

α-*N*-Pyrrolidinobenzylidene Phenylhydrazine (12). To 10 mL of pyrrolidine was added with stirring 1.0 g (3 mmol) of salt 11 at room temperature. The solution was heated to 50 °C for 30 min, the excess pyrrolidine removed in vacuo, and the residual yellow oil dissolved in 30 mL of ether. The ethereal solution was washed with 3 × 50 mL of water and dried (MgSO$_4$), and the solvent removed in vacuo to give 0.75 g (95%) of α-*N*-pyrrolidinobenzylidene phenylhydrazine (**12**) as a brown-yellow oil: IR (neat) 3250 (NH) and 1595 cm^{-1} (C=N); NMR (CDCl$_3$) δ 1.4–1.9 (m, 4, CH$_2$CH$_2$), 3.0–3.3 (m, 4, CH$_2$NCH$_2$), and 6.6–7.5 (m, 11, ring H and NH).

Determination of Neutralization Equivalents of Salts 2a–c. Samples (0.1 g) of salts **2a–c** were dissolved with stirring in 40 mL of

50% ethanol and titrated with 0.09 M sodium hydroxide. The end points were determined by plotting the volume of titrant against the millivolts which were read directly from a Beckman Zeromatic pH meter.

Registry No.—**1**, 23157-59-7; **2a**, 62076-89-5; **2b**, 62076-90-8; **2c**, 62076-91-9; **4**, 62076-92-0; **5**, 532-96-7; **8**, 17660-82-1; **9**, 36584-22-2; **10**, 62076-93-1; **11**, 62076-95-3; **12**, 62076-96-4; HCl, 7647-01-0; methanesulfonic acid, 75-75-2; periodic acid, 10450-60-9; morpholine, 110-91-8; pyrrolidine, 123-75-1.

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(11) We should like to thank Mr. S. W. Heinzman for carrying out this experiment.
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(16) Compound **4** decolorized at about 80 °C and then decomposed at about 106 °C.

Synthesis and Configurational Assignment of Some 1-*tert*-Butyl-2-aryl 3-Substituted Azetidines[1]

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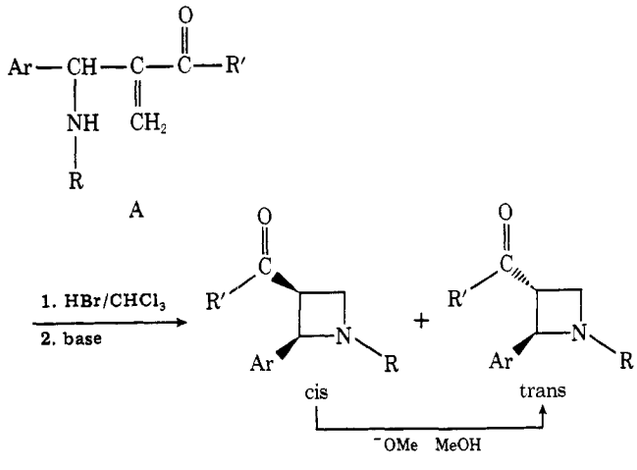
Received November 9, 1976

The kinetically favored products, methyl α-(α-*tert*-butylaminobenzyl)acrylates (**2**), from the reaction of *tert*-butylamine with methyl α-(bromomethyl)cinnamates (**1**), upon treatment with hydrogen bromide in chloroform and then triethylamine gave *trans*-1-*tert*-butyl-2-aryl-3-carbomethoxyazetidine (**7**). Similar treatment of the kinetically favored α-(α-*tert*-butylaminobenzyl)acrylonitrile (**5**), of the reaction of *tert*-butylamine with α-(bromomethyl)cinnamonitrile (**4**) gave a mixture of *cis*- and *trans*-1-*tert*-butyl-2-phenyl-3-carbamoylazetidine (**9** and **10**) and *trans*-1-*tert*-butyl-2-phenyl-3-cyanoazetidine (**11**). ^1H NMR spectroscopic studies, base-catalyzed epimerization, deuterium exchange studies, and chemical correlation of the azetidines were employed to assign the configurations. The mechanism and stereochemistry of the reactions leading to these cyclizations to produce the 1-*tert*-butyl-2-aryl 3-substituted azetidines are discussed.

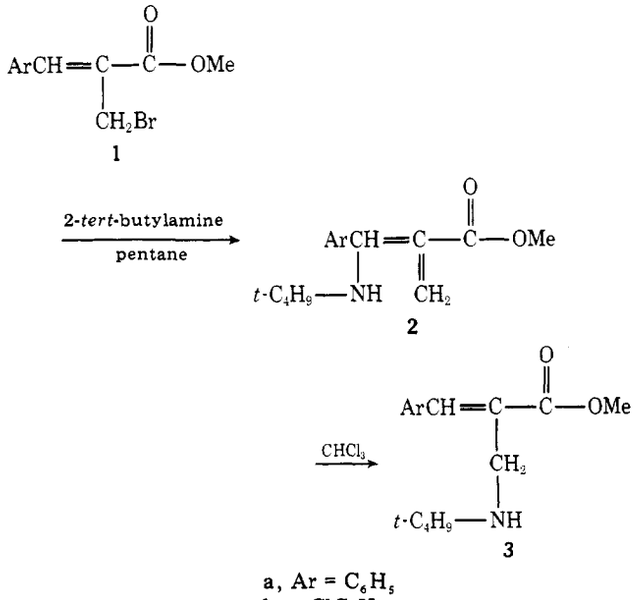
It has been reported[2] that β-carboallylamines A are precursors for the high-yield synthesis of 1-alkyl-2-aryl-3-carboazetidines. The *cis*-azetidine was usually the exclusive or major product, and readily epimerized to the thermodynamically more stable trans isomer in methanol in the presence of sodium methoxide.



R = alkyl
R′ = Ar or CH_3

The cis and trans isomers of the azetidines can be distinguished readily from each other by the ^1H NMR spectra.[2b] Compared to that of the trans isomer, the benzylic (C-2) proton of the cis isomer usually resonates as a doublet at a higher frequency.

In a previous publication,[3] it was reported that the reaction of 2 molar equiv of *tert*-butylamine with β-carbomethoxyallyl bromides **1** gave the substitution–rearrangement products **2**



a, Ar = C_6H_5
b, *p*-ClC_6H_4

exclusively. Compounds **2** isomerized to **3** autocatalytically on prolonged standing in a polar solvent.

It has also been reported[4] that the reaction of *tert*-butylamine with α-(bromomethyl)cinnamonitrile (**4**) yielded the