Mobile Keto Allyl Systems. XI.[1] Kinetic Studies of the Rearrangement–Substitution Reactions of *trans*-β-Benzoyl-γ-phenylallyl Halides

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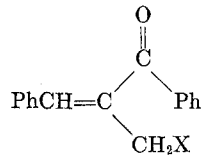
The kinetics of the reactions of *trans*-β-benzoyl-γ-phenylallyl bromide (**1a**) and the corresponding chloride (**1b**) with six primary and secondary amines in *n*-hexane solution are reported. The rate data and product studies indicate that the reactions are bimolecular rearrangement–substitutions. A retardation in the reaction rate with **1a** is observed with increasing bulk at the α-carbon atom of the amine. The leaving group effect suggests a rate-limiting transition state in which there is only a small extension of the carbon–halogen bond.

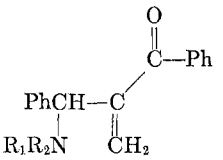
Primary allyl halides have been observed to react with amines to give mainly the normal substitution products.[3] However, it was reported recently that compounds **1a** and **1b** with primary and secondary amines gave exclusively the rearranged substitution products under suitable conditions.[4] Previous work from this laboratory has shown that a secondary halide, 3-bromo-2-benzal-1-indanone, also reacts with primary and secondary amines to give the abnormal substitution products.[5]

It was suggested, as a result of kinetic studies, that, in these reactions of the secondary halide, bond development and bond cleavage were virtually concerted, with some charge localization at the carbonyl group in the transition state.[6] A dipolar transition state structure was also proposed for the reactions of 2-[(α-substituted amino)benzyl]acrylophenones with amines.[7]

The mechanisms of the abnormal nucleophilic substitution reactions of β-benzoyl-γ-phenylallyl halides were of interest to us, and in these initial studies we have investigated the reactions of the bromide **1a** and of the chloride **1b** with primary and secondary amines in order to measure their sensitivity to changes in the size and nucleophilicity of the amine and in the nature of the leaving group.



1a, X = Br
b, X = Cl
c, X = *N*-methylcyclohexylamino



2a, R_1R_2N = *N*-methylcyclohexylamino
b, R_1R_2N = cyclohexylamino
c, R_1R_2N = piperidino
d, R_1R_2N = morpholino
e, R_1R_2N = *tert*-BuNH–
f, R_1R_2N = Et_3CNH–

When stoichiometric quantities of **1a** and *N*-methylcyclohexylamine were allowed to react for 66 hr at room temperature, a pmr spectrum of the crude product indicated the presence of a 1:1 mixture of **2a** and **1c**. Dropwise addition of the amine to **1a** over 24 hr resulted in a 91% yield of **2a**, indicating that **1c** resulted from the further reaction of **2a** with amine.[7]

The rates of reaction of **1a** with the six amines over a range of concentrations of nucleophile and of **1a** were estimated by analysis for bromide ion. The results are given in Table I. Each of the reactions exhibited

Results

trans-β-Benzoyl-γ-phenylallyl bromide and chloride react with primary and secondary amines in nonpolar solvents to give the corresponding 2-[α-(substituted amino)benzyl]acrylophenones.[4] Product and kinetic studies were made in *n*-hexane solution of the reactions of **1a** with *N*-methylcyclohexylamine, cyclohexylamine, piperidine, morpholine, *tert*-butylamine, and triethylcarbinylamine and of **1b** with cyclohexylamine and triethylcarbinylamine. It was established within experimental error that the amount of halide ion produced was equivalent to the yield of abnormal substitution product (**2a–f**).

TABLE I

VALUES OF THE SECOND-ORDER RATE COEFFICIENTS k_2 FOR THE REACTIONS OF β-BENZOYL-γ-PHENYLALLYL BROMIDE WITH AMINES IN HEXANE AT 25°

Amine	10^3[amine]	10^3[allyl bromide]	10^2k_2, l. mol^{-1} sec^{-1}
Cyclohexylamine	19.02	5.330	1.32 ± 0.08[a]
	19.02	6.240	1.31 ± 0.08
	14.45	5.330	1.21 ± 0.09
	14.23	5.328	1.29 ± 0.01
	27.50	5.328	1.27 ± 0.06
	27.50	6.076	1.30 ± 0.05
Morpholine	15.54	6.072	6.38 ± 0.04
	15.54	6.368	7.05 ± 0.12
	16.69	6.072	6.08 ± 0.07
	17.87	6.368	6.26 ± 0.09
Piperidine	6.94	3.100	38.7 ± 3.5
	6.94	2.910	38.9 ± 1.9
	6.77	3.100	40.7 ± 3.0
	6.77	2.886	41.1 ± 1.0
N-Methylcyclohexylamine	18.44	5.62	1.45 ± 0.1
	18.44	4.92	1.47 ± 0.1
	14.08	4.92	1.50 ± 0.1
Triethylcarbinylamine	47.00	15.78	0.0685 ± 0.004
	61.80	15.78	0.0710 ± 0.007
	61.80	17.58	0.0718 ± 0.001
tert-Butylamine	48.46	10.84	0.179 ± 0.01
	35.60	10.84	0.187 ± 0.03
	35.60	12.33	0.197 ± 0.03

[a] Standard deviation obtained from at least seven observations.

(1) For paper X in this series, see G. Glaros and N. H. Cromwell, *J. Org. Chem.*, **36**, 3033 (1971).

(2) The author to whom all correspondence concerning this article should be addressed.

(3) (a) F. G. Bordwell and D. A. Schexnayder, *J. Org. Chem.*, **33**, 3240 (1968); (b) G. Valkanas and E. S. Waight, *J. Chem. Soc.*, 531 (1964); (c) R. H. De Wolfe and W. G. Young, "The Chemistry of Alkenes," Vol. 1, S. Patai, Ed., Wiley, New York, N. Y., 1964, p 681.

(4) (a) N. H. Cromwell and R. P. Rebman, *J. Org. Chem.*, **32**, 3830 (1967); (b) *Tetrahedron Lett.*, No. 52, 4833 (1965).

(5) G. Maury, E.-M. Wu, and N. H. Cromwell, *J. Org. Chem.*, **33**, 1900 (1968).

(6) For a discussion of nucleophilic, bimolecular, concerted reactions involving four or more bonds, see F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

(7) N. H. Cromwell, K. Matsumoto, and A. D. George, *J. Org. Chem.*, **36**, 272 (1971).

overall second-order kinetics, first order in **1a** and in amine. No term of higher order in amine was apparent upon increasing the concentrations of cyclohexylamine relative to that of **1a**.

Samples of a mixture of **1a** and cyclohexylamine in *n*-hexane were analyzed concurrently for **1a** and for bromide ion. The results, in Table II, show that the

TABLE II

VALUES OF THE SECOND-ORDER RATE COEFFICIENTS k_2 FOR THE REACTIONS OF β-BENZOYL-γ-PHENYLALLYL HALIDES, PhCH=C(CH_2X)COPh, WITH AMINES IN *n*-HEXANE[a]

X	Amine	Temp, °C	10^3[amine]	10^3[allyl halide]	10^2k_2, l. mol^{-1} sec^{-1}
Br	Cyclohexylamine	41.35	14.87	4.956	2.94
		36.07	14.23	5.260	2.39
		36.07	14.23	4.453	2.31
		31.50	11.09	6.403	1.74[b]
		31.50	11.09	6.403	1.62[c]
		31.50	17.26	5.334	1.75
		31.50	17.26	5.700	1.93
		31.50	19.86	6.476	1.81
		18.40	22.74	6.955	0.60
		18.40	11.37	6.310	0.64
Br	Triethylcarbinylamine	52.50	24.28	8.33	0.304
		41.35	35.45	12.94	0.168
		36.07	31.61	11.50	0.138
		36.07	31.61	15.06	0.137
		31.50	43.50	22.30	0.0802[b]
		31.50	41.10	20.90	0.0942
		31.50	50.67	25.26	0.108
		31.50	50.67	18.15	0.104
Cl	Cyclohexylamine	18.50	22.74	15.61	0.173
		18.50	45.48	15.61	0.166
Cl	Triethylcarbinylamine	25.0	41.47	10.47	0.0122

[a] Rates were measured by the Volhard method for bromide ion unless indicated otherwise. [b] Estimated spectrophotometrically. [c] Estimated concurrently with the preceding rate constant and not included in Table III.

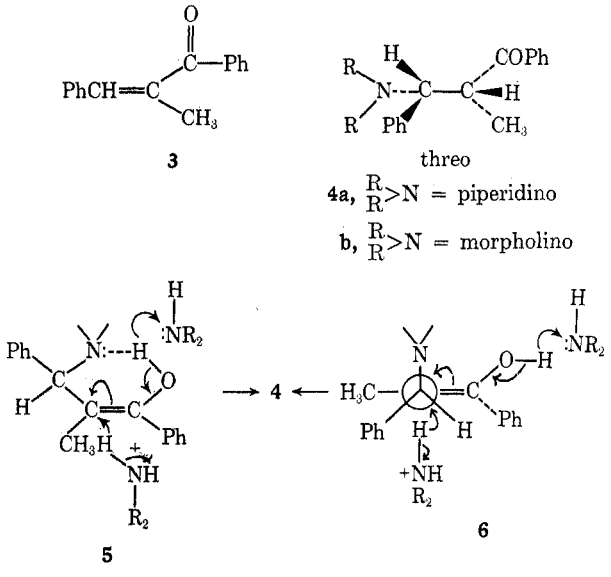
rates estimated by each method were equivalent within experimental error. Similarly, for the reaction of **1a** with triethylcarbinylamine, the spectrophotometric rate constant was approximately equivalent to the volumetric rate constant. Data obtained by the volumetric method gave better correlation over 80–90% of the reaction in a second-order rate plot than the spectroscopic data; hence the volumetric method was preferred.

The effect of varying the leaving groups was examined by comparing the reactivities of **1a** and of **1b** toward cyclohexylamine and triethylcarbinylamine. These results are also presented in Table II.

Activation parameters for the reactions of **1a** with cyclohexylamine and with triethylcarbinylamine were determined and the relevant data are given in Tables II and III.

1-Phenyl-2-benzoylpropene (**3**), an analog of **1a** and **1b** which contains no leaving group, underwent reaction with morpholine and with piperidine *via* a slow 1,4 addition to give the corresponding 2-benzoyl-1-amino-1-phenylpropane, **4a** or **4b**, as indicated in Scheme I. However, 1,4-addition products could not be detected upon similar treatment of **3** with either cyclohexylamine or *tert*-butylamine. The application of either of two models for steric control of asymmetric induction in the reactions between **3** and the secondary

SCHEME I



amines predicts the formation of the threo configuration, as represented in Scheme I. A large vicinal coupling (J = 11 Hz) was observed for protons attached to the adjacent asymmetric centers, suggesting that the conformer in solution contains true trans protons.[8]

Discussion

Three of a number of rate-controlling factors to be considered in nucleophilic substitution reactions are the polarizability and size of the nucleophile and the strength of the new bond between carbon and the nucleophilic atom.[9] The new bond strength is generally proportional to the basicity of the nucleophile toward a proton and, if this parameter is overall rate limiting, we may expect the order of nucleophilicity to parallel that of the basicity.[9]

We observed the following order of nucleophilicity toward **1a**: piperidine > morpholine > *N*-methylcyclohexylamine ~ cyclohexylamine > *tert*-butylamine > triethylcarbinylamine.

The basicities of four of the amines may be written: piperidine > *tert*-butylamine > cyclohexylamine > morpholine.[10] This order is not in agreement with our observed order of nucleophilicity, indicating that the strength of the developing carbon–nitrogen bond is not overall rate controlling. The rate ratio $k(Et_3CNH_2):k(C_6H_{11}NH_2)$ is approximately 0.054 and is indicative of a considerable decrease in reactivity for the reaction with triethylcarbinylamine which originates in a less favorable entropy of activation term, consistent with a more compressed transition state for reaction with the more bulky amine.

N-Methylcyclohexylamine exhibits a slight but real increase in reactivity relative to cyclohexylamine (by a factor of 1.08). It would appear that favorable electron release from the methyl group is of greater importance in controlling the rate than the steric

(8) For a related study, see C. A. Kingsbury and D. C. Best, *J. Org. Chem.*, **32**, 6 (1967).

(9) (a) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968, Chapter VI. (b) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Organic Chemistry Monographs, Vol. 6, A. T. Blomquist, Ed., Academic Press, London, 1965, Chapter 4.

(10) J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc. A*, 1212 (1969).

TABLE III

ACTIVATION DATA[a] FOR THE REACTIONS OF β-BENZOYL-γ-PHENYLALLYL BROMIDE WITH AMINES IN *n*-HEXANE

Amine	10^2k_2,[b] l. mol^{-1} sec^{-1} 21.5°	21.9°	25°	31.5°	36.07°	41.35°	52.5°	$E^{\ddagger}$, kcal mol^{-1}	10^5A, sec^{-1}
Cyclohexylamine	0.996	1.09	1.28	1.83	2.35	2.94		9.8	1.88
Triethylcarbinylamine			0.0704	0.102	0.138	0.168	0.304	10.3	0.171

[a] $k_2 = Ae^{-E^{\ddagger}/RT}$. [b] From Tables I and II, using arithmetical mean values where appropriate.

requirement of the secondary amine. Piperidine is the most reactive of the amines studied and this result is in agreement with reports by others of facile abnormal substitutions employing piperidine as a nucleophile.[3a]

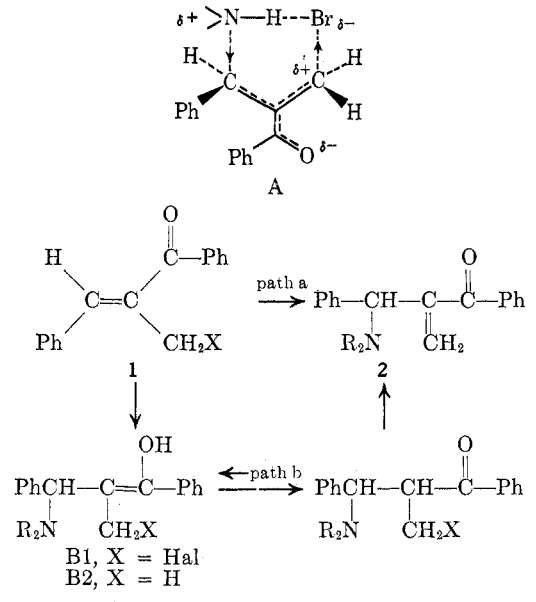
Thus in abnormal substitution reactions with **1a** the relative reactivities of the secondary amines, piperidine and morpholine, which are about equal in size, parallel the order of their basicities (or polarizabilities), whereas the rate data for the primary amines are indicative of a decrease in reactivity with an increase in substitution at the α-carbon atom of the amine.

The ratios of the reactivities of **1a** and **1b**, k(**1a**):k(**1b**), with cyclohexylamine and with triethylcarbinylamine were approximately 3.6 and 5.7, respectively. The leaving group effects of bromine *vs.* chlorine for SN2 reactions show a reactivity ratio of about 50.[11] It is generally accepted that extensive bond breakage occurs in the transition state of an SN2 reaction; thus it would appear that there is only a small extension of the carbon–halogen bond in a rate-limiting transition state for the reactions of **1a** and **1b** with amines. The somewhat greater leaving group ratio with the more polarizable amine is reminiscent of similar effects which have been observed in nucleophilic substitutions at aromatic carbon atoms.[12]

Two main pathways can be envisaged for the reactions of compounds **1a** and **1b** with primary and secondary amines in *n*-hexane and are presented in Scheme II. In path a, we consider that, as the amine approaches the sp^2-hybridized γ-carbon atom, the carbonyl group oxygen accepts much of the developing negative charge resulting in a transition state with structure A, in which there is only a little carbon–halogen bond extension. The approach of the amine could be aided by hydrogen bonding either with the carbonyl oxygen atom, in a manner similar to that proposed for the reactions of amines with α-bromo ketones,[13] or with the halogen atom, resulting in a cis orientation of the amine and the halogen. A cis orientation of the nucleophile and the leaving group was proven for the abnormal substitution reactions of *trans*-6-alkyl-2-cyclohexenyl-2,6-dichlorobenzoates with piperidine,[14] and it is possible that crowding in a similar transition state, A, may explain the lower reactivities of the bulky primary amines in the present work. Alternatively, the steric retardation may originate from an interaction between substituents at the α-carbon atom of the amine and the γ-phenyl ring.

Path b would involve a 1,4 addition of the amine to the α,β-unsaturated ketone grouping of **1** to give an intermediate B, followed by an E2 elimination of hydrogen halide. We would expect the energetics for the formation of B1, with X = Hal, and B2, with X = H, to be similar, and for the formation of B1 to be rate limiting in the absence of any amine catalysis. However, the chalcone, **3**, reacted at an extremely slow rate with amines, and it therefore seems reasonable that the formation of **2** does not proceed *via* this addition–elimination mechanism.

SCHEME II



Experimental Section[15]

2-[α-*N*-Methylcyclohexylamino)benzyl]acrylophenone (2a).—*N*-Methylcyclohexylamine (2.25 g, 0.02 mol) and **1a** (3.0 g, 0.01 mol) in 200 ml of *n*-hexane were stirred for 66 hr at room temperature. A ^{1}H nmr spectrum of the crude products indicated an absence of **1** and the presence of **2c** and **3c** in a 1:1 ratio.

N-Methylcyclohexylamine (1.95 g, 0.017 mol) in 100 ml of *n*-hexane was added dropwise over a period of 24 hr to a stirred solution of **1** (3.0 g, 0.01 mol) at *ca.* 25°; 2.60 g (91%) of **2a** was obtained. Recrystallization from *n*-pentane resulted in long, colorless needles: mp 67–67.5°; $\nu_{C=O}$ (CCl_4) 1656 cm^{-1}; nmr (CCl_4) *ca.* 455 (m, 10 H, aromatic), 378 (t, 1 H, J = 1.2 Hz, vinyl), 352 (t, 1 H, J = 1.2 Hz, vinyl), 310 (s, 1 H, benzyl), 235 (s, 3 H, methyl), and 120–160 Hz (m, 11 H, cyclohexyl).

Anal.[15b] Calcd for $C_{23}H_{27}NO$: C, 82.84; H, 8.17; N, 4.20. Found: C, 82.91; H, 8.16; N, 4.35.

Reaction of β-Benzoyl-γ-phenylallyl Chloride (1b) with Cyclohexylamine.—Cyclohexylamine (0.20 g, 0.002 mol) was added to **1b** (0.26 g, 0.001 mol) in 50 ml of *n*-hexane. The mixture was stirred at room temperature for 4 hr and filtered, and the filtrate evaporated to a white solid. A pmr spectrum of the solid in

(11) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 30.

(12) J. F. Bunnett, *J. Amer. Chem. Soc.*, **79**, 5969 (1957).

(13) (a) P. L. Southwick and R. J. Shozda, *ibid.*, **81**, 5435 (1959); (b) N. H. Cromwell and D. J. Cram, *ibid.*, **65**, 301 (1943).

(14) G. Stork and W. N. White, *ibid.*, **78**, 4609 (1956).

(15) Melting points were determined by the capillary method with a calibrated thermometer. The infrared spectra were taken on a Perkin-Elmer Model 21 instrument and ultraviolet spectra were obtained with a Cary Model 11 or a Cary Model 14 instrument. The 60-MHz nmr spectra were determined on a Varian A-60 spectrometer and the chemical shifts were recorded relative to internal tetramethylsilane (0.0 Hz). Elemental analyses were performed by either (a) Micro-Tech Laboratories, Ill., or (b) Alfred Bernhardt, West Germany.

carbon tetrachloride indicated only compounds **1b** and **2b** in a ratio of 1:4 by comparison with pmr spectra of authentic samples of **1b** and **2b** in the same solvent.

Reaction of 1b with Triethylcarbinylamine.—Triethylcarbinylamine (2 equiv) and **1b** (1 equiv) in *n*-hexane were stirred at room temperature for 4 days. A pmr spectrum of the hexane-soluble compounds in carbon tetrachloride indicated only compounds **1b** and **2f** by comparison with pmr spectra of authentic samples in the same solvent.

threo-**2-Benzoyl-1-piperidino-1-phenylpropane** (**4a**).—Piperidine (0.95 g, 0.011 mol) was added to 2.22 g (0.010 mol) of 2-benzoyl-1-phenylpropene and the mixture was allowed to react at room temperature for 7 days. The mixture solidified and was crystallized from 100 ml of a 1:1 ethyl ether–methanol mixture. The white solid which separated weighed 2.96 g (96%): mp 141–142°; λ_{max} (isooctane) 240 mμ (ε 13,900); $\nu_{C=O}$ (CCl_4) 1688 cm^{-1}; nmr peaks ($CDCl_3$) 435–480 (m, 5 H, benzoyl), 428 (s, 5 H, phenyl), 230–280 (m, J = 11, 6.5 Hz, 2 H, methines), 120–170 (m, 4 H α to N), 60–120 Hz (β and γ to N and methyl, J = 6.5 Hz).

Anal.[15a] Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.78; H, 8.29; N, 4.50.

threo-**2-Benzoyl-1-morpholino-1-phenylpropane** (**4b**).—To a 6.66-g (0.030 mol) sample of 2-benzoyl-1-phenylpropene (**7**) was added 2.61 g (0.030 mol) of morpholine and the mixture was allowed to stand at room temperature for 5 days. The mixture was analyzed by nmr spectrometry at various stages of conversion and only one configurational isomer was detected along with starting material. The mixture solidified upon standing and recrystallization of the solid from a 1:1 ethyl ether–methanol mixture yielded 7.24 g (80%) of white crystals: mp 149–150°; λ_{max} (isooctane) 240 mμ (ε 14,100); $\nu_{C=O}$ (CCl_4) 1688 cm^{-1}; nmr peaks 435–480 (m, 5 H, benzoyl), 431 (s, 5 H, phenyl), 230–280 (m, 2 H, J = 11, 6.5 Hz, methines), 210–230 (t, 4 H, J = 5 Hz, α to O), 120–170 (4 H, α to N), and 88 Hz (d, 3 H, J = 6.5 Hz, methyl).

Anal.[15a] Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.43; H, 7.49; N, 4.68.

Materials Used in Kinetic Studies.—β-Benzoyl-γ-phenylallyl bromide (**1a**) and the corresponding chloride (**1b**) were prepared as described previously.[4] Samples of **1a** which were used for kinetics were recrystallized from ether–hexane mixtures, mp 81° (corrected) and λ_{max} 285 mμ (ε 17,100) in *n*-hexane. The purity of **1b** was checked with data recorded previously.[4] Piperidine and cyclohexylamine were distilled from sodium through a 90-cm spinning band. Morpholine, *tert*-butylamine, triethylcarbinylamine, and *N*-methylcyclohexylamine were distilled from barium oxide and redistilled twice. All the compounds used in kinetic studies were purified immediately before use. Fisher Spectro-analyzed *n*-hexane was used as the solvent in the reactions which were monitored by uv spectroscopy. For other kinetic studies Phillip's *n*-hexane was freshly distilled from calcium hydride.

Kinetic Procedures.—The rates of formation of halide ion in the reactions of **1a** and **1b** with amines were obtained by an ampoule technique. The reactions were arrested by cooling to −80° and the contents of the ampoules were extracted into dilute nitric acid. The halide ion content of the aqueous layer was estimated by the Volhard method using a visual end point. The initial concentrations of the amine solutions were estimated by the addition of aliquots to a known excess of hydrochloric acid in methanol and back titration against a standard solution of morpholine in methanol using a pH meter.

The reactions of **1a** and of **1b** with cyclohexylamine and of **1a** with triethylcarbinylamine were also followed by a sampling technique. The rate of disappearance of the band in the 280-mμ region due to the cinnamoyl chromophore of **1a** or **1b** was measured. Absorption in this region due to the products **2b** or **2f** was slight and suitable corrections were made.

The rate constants were evaluated from the following expression, by the method of linear least squares

$$k_2 = \frac{1}{t(a - 2b)} \ln \frac{b(a - 2x)}{a(b - x)}$$

where a and b are the initial concentrations of the amine and allyl halide, respectively, x is the concentration of product, and t is the corresponding time.

Registry No.—**1a**, 14181-92-1; **1b**, 14181-99-8; **2a**, 31893-05-7; **4a**, 31893-06-8; **4b**, 31893-07-9; cyclohexylamine, 108-91-8; morpholine, 110-91-8; piperidine, 110-89-4; *N*-methylcyclohexylamine, 100-60-7; triethylcarbinylamine, 1571-51-3; *tert*-butylamine, 75-64-9.

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1,2,4-Triazines. VI. Tautomerism in Substituted 2,3-Dihydro-3-oxo-1,2,4-triazines

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A series of 2,3-dihydro-3-oxo-1,2,4-triazines have been prepared. It has been established that **4c,e** is the major tautomer, where R_1 and/or R_2 = C_6H_5. When the substituent at C-5 is a methyl group, a methyl–methylene (**8b** ⇌ **9b**; **8d** ⇌ **9d**) tautomeric mixture exists. The equilibrium constants for these equilibria were determined.

We have for some time[1-4] been interested in 1,2,4-triazines and now wish to describe a study of the tautomeric equilibria of some 2,3-dihydro-3-oxo-1,2,4-triazines. These compounds can in principle be prepared either by hydrolysis of 3-amino- (**1**, X = NH_2) or 3-methylthio (**1**, X = SCH_3) derivatives, or by cyclization of semicarbazone derivatives such as **3** (see Scheme I).

The conversions of compounds **3c–e** to compounds **2c–e**, respectively, have been described in the literature.[5,6] However, in our hands, using the described conditions, no product could be isolated from **3d**. This observation substantiates earlier reports to this effect.[7] Base hydrolysis of either 3-amino- or 3-methylthio-1,2,4-triazines (**1a–e**, X = NH_2 or SCH_3) gives the alkali metal salts of the corresponding 3-hydroxy-1,2,4-triazines (**2a–e**).[8]

Since the chemical shifts of the ring protons and the

(1) W. W. Paudler and J. M. Barton, *J. Org. Chem.*, **31**, 1720 (1966).
(2) W. W. Paudler and T. K. Chen, *J. Heterocycl. Chem.*, **7**, 767 (1970).
(3) W. W. Paudler and T. K. Chen, *J. Org. Chem.*, **36**, 787 (1971).
(4) W. W. Paudler and T. K. Chen, *J. Heterocycl. Chem.*, **4**, 224 (1967).
(5) W. Seibert, *Ber.*, **80**, 494 (1947).
(6) S. Rossi, *Rend. Ist. Lomb. Sci. Lett., Cl. Sci. Mat. Natur.*, **83**, 173 (1955); *Chem. Abstr.*, **50**, 10742h (1956).
(7) C. L. Pitzer, "The Chemistry of 1,2,4-Triazine and Some Related Compounds," Ph.D. Thesis, West Virginia University, 1967.
(8) The statement has been made[7] that basic hydrolysis of 3-amino-1,2,4-triazine (**1a**, X = NH_2) does not lead to identifiable products. This observation is now negated by our results.