

**Table XI**  
**Micellar Effects upon the Apparent Dissociation Constants of *n*-Butylxanthic Acid in Water**

Surfactant	" $pK_a$ "	Surfactant	" $pK_a$ "
	1.54	$5 \times 10^{-2} M$ NaLS	2.45
$2 \times 10^{-3} M$ CTABr	1.01	$10^{-2} M$ Triton	1.92

Micellized alkyl sulfates are readily hydrolyzed in moderately concentrated acid; therefore we did not use highly acidic solutions in these experiments, and freshly made solutions were always used.

**Apparent Dissociation Constants.** Micellar effects upon the rates at  $pH > 3$  can be explained qualitatively in terms of changes in the acid dissociation of the alkylxanthic acid. Similar observations have been made on a number of micellar catalyzed or inhibited reactions.<sup>8-10,14b</sup> We have calculated the apparent dissociation constant of *n*-butylxanthic acid in the presence of micelles by rapidly determining the total concentration of xanthate ion. (The values are apparent because we do not know the distribution of xanthic acid or xanthate and hydronium ions between water and the micellar pseudophase.<sup>16</sup>)

Micelles change the dissociation constant in the expected directions (Table XI). Cationic micelles of CTABr should stabilize the xanthate ion relative to xanthic acid, and they increase the dissociation constant, whereas anionic micelles of NaLS and nonionic micelles of Triton should stabilize xanthic acid relative to its anion, and they decrease the dissociation constant.

**Registry No.**—Ethyl xanthate, 151-01-9; *n*-butyl xanthate, 110-50-9; *n*-octyl xanthate, 6253-37-8; CTABr, 57-09-0; NaLS, 151-21-3; Triton X-100, 9002-93-1.

### References and Notes

- (1) Support of this work by the National Science Foundation, The Comision Central de Investigacion of the University of Chile, and the University of Chile—University of California Cooperative Program supported by the Ford Foundation is gratefully acknowledged.
- (2) For a general discussion of xanthate chemistry and the industrial applications of alkyl xanthates, see ref 3.
- (3) S. R. Rao, "Xanthates and Related Compounds," Marcel Dekker, New York, N. Y., 1971.
- (4) I. Iwasaki and S. R. B. Cooke, *J. Amer. Chem. Soc.*, **80**, 285 (1958); *J. Phys. Chem.*, **63**, 1321 (1959); **68**, 2031 (1964).
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- (6) C. A. Bunton, P. Ng, and L. Sepulveda, *J. Org. Chem.*, **39**, 1130 (1974).
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- (8) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).
- (9) E. H. Cordes and C. Gitter, *Progr. Bioorg. Chem.*, **2**, 1 (1973).
- (10) C. A. Bunton, *Progr. Solid State Chem.*, **8**, 239 (1973).
- (11) A. I. Vogel, "Practical Organic Chemistry," Wiley, New York, N. Y., 1956.
- (12) Alkylxanthic acids have  $pK_a \sim 1.5$ .<sup>3-6</sup>
- (13) By pH we mean the value in the reaction mixture as measured using a glass electrode.
- (14) (a) L. K. J. Tong and M. C. Glesmann, *J. Amer. Chem. Soc.*, **79**, 4305 (1957); (b) M. T. A. Behme and E. H. Cordes, *ibid.*, **87**, 260 (1965); (c) C. A. Bunton and M. J. Minch, *J. Phys. Chem.*, **78**, 1490 (1974).
- (15) The residual rate at high concentrations of CTABr decreases with increasing length of the *n*-alkyl group of the xanthate, probably because the longer alkyl groups tend to take the substrate more deeply into the micelle.
- (16) C. A. Bunton and B. Wolfe, *J. Amer. Chem. Soc.*, **95**, 3742 (1973).
- (17) F. M. Menger and C. E. Portnoy, *J. Amer. Chem. Soc.*, **89**, 4968 (1967).
- (18) C. A. Bunton, E. J. Fendler, L. Sepulveda, and K.-U. Yang, *J. Amer. Chem. Soc.*, **90**, 5512 (1968).
- (19) Salt and buffer effects are very small in the absence of surfactants.<sup>4-6</sup>
- (20) C. A. Bunton, M. J. Minch, J. Hidalgo, and L. Sepulveda, *J. Amer. Chem. Soc.*, **95**, 3262 (1973).
- (21) For the equilibrium  $II \rightleftharpoons IV$   $pK_a \approx -1.4$ .<sup>6</sup>

## Kinetics of the Condensation of *N*-Methyl-4-picolinium Iodide with *p*-Dimethylaminobenzaldehyde in Aqueous Ethanol

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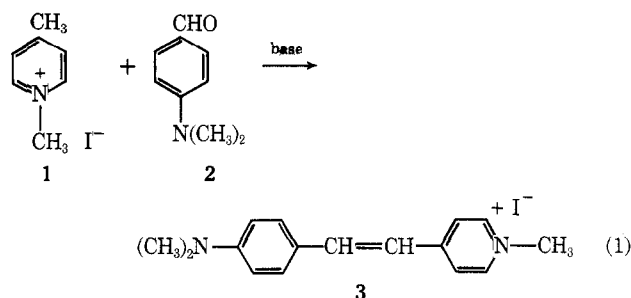
The kinetics of condensation of *N*-methyl-4-picolinium iodide and *p*-dimethylaminobenzaldehyde in 78.2% (v:v) aqueous alcoholic sodium hydroxide were determined at 25° spectrophotometrically by following the appearance of *p*-dimethylamino-4-styrylpyridinium methiodide at 470 nm. The reaction was first order in methiodide, aldehyde, and hydroxide with a third-order rate constant of  $1.67 \times 10^{-2} M^{-2} \text{sec}^{-1}$ . The kinetics of the proton exchanges of *N*-methyl-4-picolinium iodide in methanol-*d*<sub>4</sub>-methoxide-*d*<sub>3</sub> were determined by nmr at 35°. The second-order rate constants for exchange of *N*-methyl, 2,6-, and *C*-methyl protons were  $2.2 \times 10^{-5}$ ,  $1.62 \times 10^{-4}$ , and  $7.5 \times 10^{-2} M^{-1} \text{sec}^{-1}$ , respectively. The second-order rate constant for the *N*-methyl proton exchange of *N*-methylpyridinium iodide was  $16 \times 10^{-5} M^{-1} \text{sec}^{-1}$ . The kinetic data are in accord with a condensation mechanism in which the rate-determining step is carbon-carbon bond formation by reaction of the methylene base with the aldehyde. Nitrogen decoupling experiments showed the  $\beta$  protons of the *N*-methylpyridinium iodide to be coupled to nitrogen. Furthermore, the *N*-methyl group showed a positive nuclear Overhauser effect upon irradiation of nitrogen.

In conjunction with a study of the detection of alkyl halides by reaction with 4-picoline we have examined the rate of the 78.2% (v:v) aqueous alcoholic base induced condensation of *N*-methyl-4-picolinium iodide (1) with *p*-dimethylaminobenzaldehyde (2) to yield the highly colored *p*-dimethylamino-4-styrylpyridinium methiodide (3) (eq 1).

Phillips<sup>1</sup> has reported the analogous piperidine-induced condensation of *N*-methyl-2-picolinium iodide with 2.

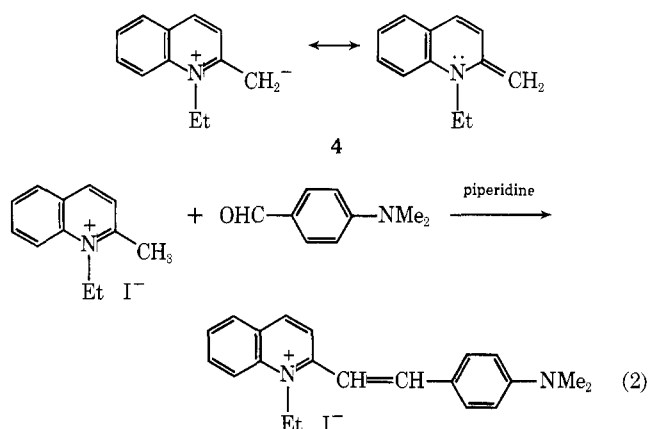
The objective of the kinetic experiments was to determine the reaction mechanism sufficiently to define the optimum conditions for alkyl halide detection. The central mechanistic questions were (1) the role of the conjugate

base of the quaternary ammonium ion (*i.e.*, the methylene base); (2) the role of the dimer of the methylene base; and (3) the identification of the rate-determining step of dye production, whether it is carbon-carbon bond formation or

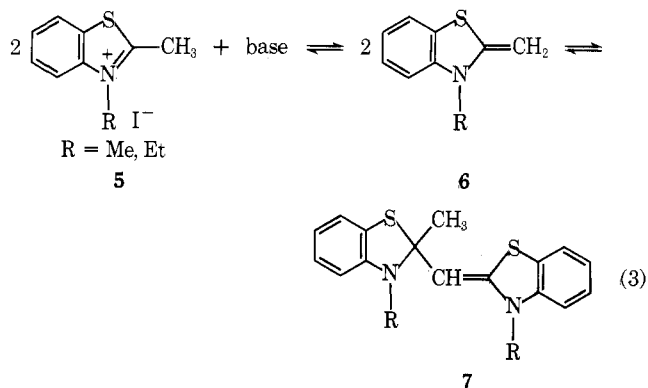


elimination to form the final conjugated system. In ancillary experiments we have measured the rates of exchange of the protons of 1 in methanol-*d*<sub>4</sub>-methoxide-*d*<sub>3</sub>.

Mills and Raper<sup>2</sup> suggested methylene base 4 as an intermediate in the piperidine-catalyzed reaction of 1-ethylquinidinium iodide with 2 (eq 2).

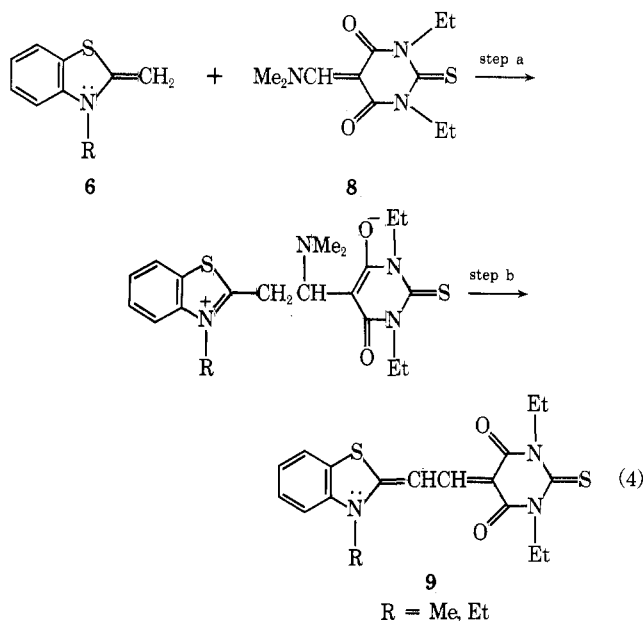


Although Mastagli, Larivé, and Etevenon<sup>3</sup> presented evidence that methylene base 6 is not necessarily an intermediate in the condensation (eq 3) in neutral and acidic media, Brooker<sup>4</sup> invoked methylene base 6 to account for his observations on the condensation of 2-methyl-3-alkylbenzothiazolium iodide (5) with 2. The latter system intro-



duces a complication in that 6 has been shown to form 7 and this dimer can serve as a source of monomeric methylene base 6. The dimer apparently forms by reaction of methylene base with quaternary salt.<sup>5</sup> In elegant experiments Owen<sup>5</sup> isolated the monomeric methylene base 6. This isolation made possible a study of the monomer-dimer equilibrium. Although no data were presented on the rate of approach to equilibrium in solution, the monomer (presumably neat) dimerized within 2 hr at 0° under nitrogen. Spectra of the monomer could be determined without interference from dimerization.<sup>5</sup>

Owen<sup>5</sup> also studied the rate of condensation of methylene base 6 with 1,3-diethyl-5-(*N,N*-dimethylaminomethylene)-2-thiobarbituric acid (8) in acetonitrile containing triethylamine (eq 4).<sup>5</sup> He concluded that carbon-carbon



bond formation (eq 4, step a) was rate determining because the condensation rate was independent of the concentration of excess triethylamine presumably necessary for step b. Furthermore, the rate of formation of 9 from quaternary salt 5 in the presence of a 1000-fold excess of 8 and a 10,000-fold excess of triethylamine was identical within experimental error with the rate of formation of 9 using methylene base 6. This result would suggest that quaternary salt is converted completely to methylene base by triethylamine in a step that is not rate controlling. It seems safe to conclude that dimerization of methylene base is not kinetically significant under Owen's conditions; otherwise the reaction would approach one-half order, instead of the observed first order in methylene base.

While the above-mentioned studies provide an informative guide to the individual steps that might be involved in the condensation in aqueous ethanol, they are at best only suggestive regarding the rate-determining step. We, therefore, have examined the kinetic form of the condensation reaction along with the rates of proton exchange of *N*-methyl-4-picolinium iodide (1) in methanol-*d*<sub>4</sub>-methoxide-*d*<sub>3</sub> to estimate the rate of formation of methylene base derived from 1.

## Results

**Kinetics of Condensation.** The product of the condensation of 1 and 2 in 78.2% (v/v) aqueous ethanolic sodium hydroxide was 3. This structural assignment was based on melting point comparison (mp 256–258°, lit. mp 255°)<sup>6</sup> and nmr spectral data. Compound 3 showed resonances at  $\delta$  4.28 (s, 3 H, N<sup>+</sup>CH<sub>3</sub>) and 3.2 [s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>], and complex absorptions at  $\delta$  6–7. There were no resonances at higher field than  $\delta$  3.2 in the product 3, indicating the absence of an aromatic methyl group. The *N*-methyl-4-picolinium iodide showed resonances at  $\delta$  1.9 (s, 3 H, CCH<sub>3</sub>) and 3.6 (s, 3 H, N<sup>+</sup>CH<sub>3</sub>). Nitrogen decoupling experiments showed that it was the signal of the  $\beta$  protons of 1 that was broadened considerably by nitrogen coupling. This broadening, which is characteristic of *N*-alkylpyridinium salts, is absent in the free basis. Irradiation of the nitrogen shows a nuclear Overhauser effect for the NCH<sub>3</sub> group, the methyl intensity increasing about 13%. Thus, the nmr spectrum of

**Table I**  
Initial Rate Studies of Reaction Order and the Derived Third-Order Rate Constants for the Base-Catalyzed Condensation of *N*-Methyl-4-picolinium Iodide and *p*-Dimethylaminobenzaldehyde at 25°, 78.2% Aqueous Ethanol (v:v)

[Methiodide], 10 <sup>4</sup> M	d(OD) <sup>a</sup> /dt, min <sup>-1</sup>	[OH <sup>-</sup> ]	10 <sup>2</sup> [aldehyde], M	10 <sup>2</sup> k <sub>3</sub> <sup>b</sup> , M <sup>-2</sup> sec <sup>-1</sup>
0.2	0.013	1.0	2.0	1.63
0.5	0.031	1.0	2.0	1.55
1.0	0.058	1.0	2.0	1.46
1.5	0.080	1.0	2.0	1.33
2.0	0.114	1.0	2.0	1.43
1.0	0.013	1.0	0.5	1.31
1.0	0.028	1.0	1.0	1.41
1.0	0.042	1.0	1.5	1.41
1.0	0.060	1.0	2.0	1.51
2.0	0.026	0.25	2.0	1.30
2.0	0.044	0.375	2.0	1.47
2.0	0.062	0.5	2.0	1.55
2.0	0.119	1.0	2.0	1.49
Average				1.46 ± 0.15

<sup>a</sup> Initial slope of the trace of optical density *vs.* time. <sup>b</sup> Using an extinction for dye 3 of  $3.32 \times 10^4 M^{-1} \text{cm}^{-1}$ .

3 was consistent with condensation at the 4-methyl group and clearly inconsistent with condensation at the *N*-methyl group.

The kinetic order of each factor in the base-catalyzed condensation of 1 and 2 in aqueous ethanol was determined spectrophotometrically by following the rate of appearance of the 470-nm band of 3. The initial slope of the trace of optical density *vs.* time was divided by the extinction coefficient for 3 ( $\epsilon 3.32 \times 10^4 M^{-1} \text{cm}^{-1}$ ) to obtain the initial rate of formation of 3. In any given run the concentration of base was constant. The concentration of 2 was always at least 50 times that of 1, and thus its concentration remained constant. From the behavior of the initial rates as a function of the concentrations of base, aldehyde, and methiodide, the reaction was shown to be first order within experimental error in each of these reagents. The third-order rate constants derived from the initial rates are shown in Table I. The average value of the third-order rate constant from the initial rate data was  $1.46 \times 10^{-2} M^{-2} \text{sec}^{-1}$ .

The reaction was also followed through 1 half-life (or a portion thereof at higher concentrations of 1). Values of optical density and time were read from the trace and optical densities at infinite time were obtained by dilution. Point-by-point pseudo-first-order rate constants were calculated from eq 5 where  $(OD_\infty - OD_0)$  is proportional to the initial methiodide concentration and  $(OD_\infty - OD_t)$  is proportion-

$$k = \frac{1}{t} \ln \left[ \frac{OD_\infty - OD_0}{OD_\infty - OD_t} \right] \quad (5)$$

al to methiodide at time *t*. The pseudo-first-order rate constants were divided by the appropriate hydroxide and aldehyde concentrations to obtain third-order rate constants. Comparison of the third-order rate constants from initial rate studies (Table I) and those from point-by-point determinations (Table II) shows satisfactory agreement.

**Proton Exchange of *N*-Methyl-4-picolinium Iodide.** For convenience the rates of proton exchange of *N*-methyl-4-picolinium iodide (1) were determined in methanol-*d*<sub>4</sub> containing methoxide-*d*<sub>3</sub>. The rates were followed by observing the decay of the nmr signal characteristic of a par-

**Table II**  
Point-by-Point Pseudo-First-Order Rate Constants and Derived Third-Order Rate Constants for the Base-Catalyzed Condensation of *N*-Methyl-4-picolinium Iodide and *p*-Dimethylaminobenzaldehyde at 25°

[Methiodide], 10 <sup>4</sup> M	[Aldehyde], 10 <sup>2</sup> M	10 <sup>4</sup> k <sub>obsd</sub> <sup>a</sup> , sec <sup>-1</sup>	10 <sup>2</sup> k <sub>3</sub> , M <sup>-2</sup> sec <sup>-1</sup>
2	2	3.42	1.72
2	2	3.27	1.63
1	1	1.75	1.75
1	1	1.58	1.59
Average			1.67 ± 0.08

<sup>a</sup> [OH<sup>-</sup>] = 1.0 M in all runs; solvent 78.2% ethanol (v:v).

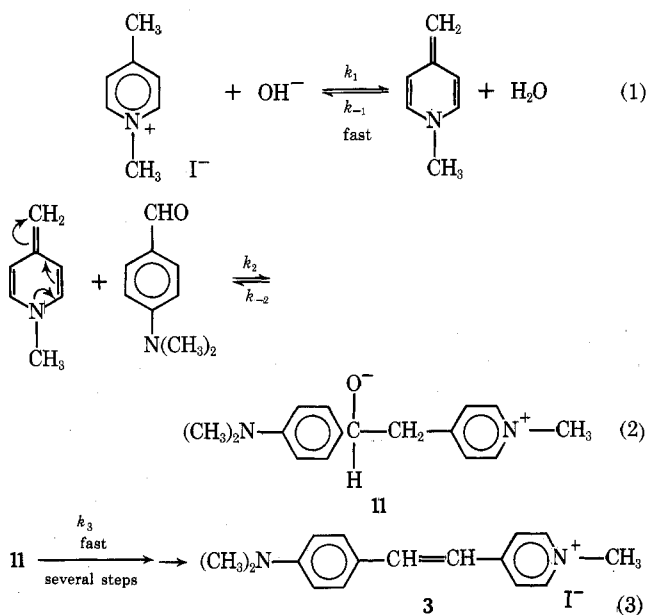
ticular proton. All protons in 1 were exchangeable. The extent of exchange was determined by integration of the particular signal relative to the carbon-bound proton impurity in methanol-*d*<sub>4</sub> as a standard. The exchange measurements were carried out at 35°.

The 4-methyl proton of 1 exchanged too rapidly to measure in 1.47 M methoxide-*d*<sub>3</sub> in methanol-*d*<sub>4</sub>. Under these conditions the *N*-methyl protons ( $\delta$  4.40) exchanged with a pseudo-first-order rate constant of  $3.3 \times 10^{-5} \text{sec}^{-1}$  corresponding to a second-order rate constant of  $2.2 \times 10^{-5} M^{-1} \text{sec}^{-1}$ . The rate constant of *N*-methylpyridinium iodide determined similarly was  $16 \times 10^{-5} M^{-1} \text{sec}^{-1}$ . The inductive effect of the 4-methyl group retards the rate almost eightfold. The rate of exchange of the 2,6 protons of 1 was about ten times faster than that of its *N*-methyl protons, showing a second-order rate constant of  $1.62 \times 10^{-4} M^{-1} \text{sec}^{-1}$  in 0.8 M methoxide-*d*<sub>3</sub>-methanol-*d*<sub>4</sub>. The 4-methyl protons exchanged with a second-order rate constant of  $7.5 \times 10^{-2} M^{-1} \text{sec}^{-1}$  in  $1.47 \times 10^{-4} M$  methoxide-*d*<sub>3</sub>-methanol-*d*<sub>4</sub>.

## Discussion

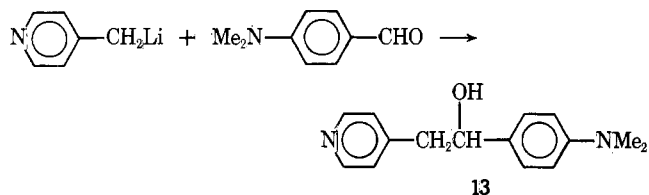
The simplest mechanism that is consistent with the kinetic data is shown in Scheme I in which  $k_{-2} \ll k_3$ . The appearance of the aldehyde in the rate expression suggests

**Scheme I**



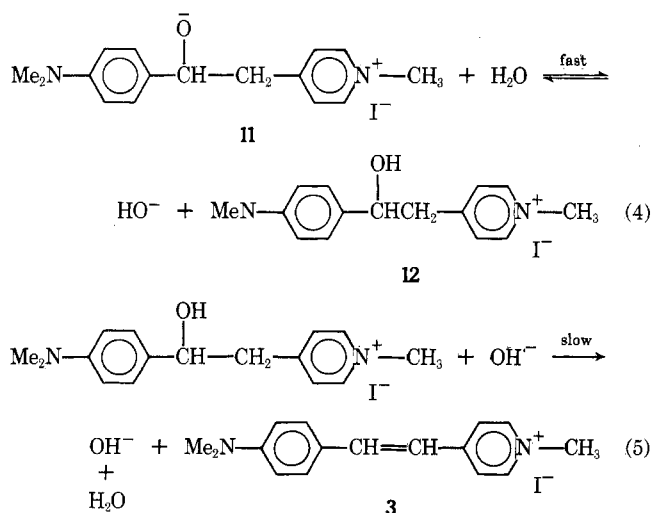
that proton transfer (step 1) cannot be rate determining. This conclusion was confirmed by the nmr exchange experiments, that showed that the 4-methyl protons of *N*-methyl-4-picolinium iodide exchanged much faster than the formation of product 3. The first-order dependence of the condensation rate on base shows that the equilibrium constant for step 1 must be small; *i.e.*, an inappreciable amount of *N*-methyl-4-picolinium iodide is converted to methylene base. In the extreme case, if all picolinium iodide were converted to methylene base, then an increase in the concentration of base would not increase the rate. The conclusion was checked by showing that the uv spectrum of *N*-methyl-4-picolinium iodide was the same in the presence and absence of 1 *M* base. Thus, all of the evidence is consistent with a rapid proton-transfer equilibrium, with step 2 rate determining. Methylene base dimer is not a kinetically significant intermediate.

Another mechanism can be shown to be consistent with the kinetic data if step 3 (Scheme I) is expanded to include the individual steps involved (Scheme II). Thus, if steps 1, 2 (Scheme I), and 4 are rapid and reversible and step 5 (Scheme II) is rate determining, third-order kinetics would result. This mechanism is analogous to that of the condensation of acetophenone with benzaldehyde in ethoxide-ethanol, where it has been shown that the keto alcohol is degraded to acetophenone and benzaldehyde more rapidly than it is converted to benzalacetophenone.<sup>7</sup> To probe this possibility we prepared the alcohol 13 by reaction of the lithium salt of 4-methylpyridine with *p*-dimethylaminobenzaldehyde.<sup>8</sup> Reaction of 13 with methyl iodide failed to



produce 12 in pure form. However, treatment of the solution prepared from 13 and methyl iodide with base gave 10% 3 (based on 13) but less than 1% 2, which was the limit of spectrophotometric detectability of 2. Thus, the balance of the evidence suggests that condensation step 2 is rate determining and not the dehydration step.

Scheme II



Our results show that the condensation reaction is substantially faster than the alkylation of 4-picoline by methyl iodide.

## Experimental Section

Melting points were taken on a Thomas-Hoover capillary apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 in potassium bromide. Routine nmr spectra were determined on a Varian A-60D instrument. Ultraviolet spectra were run on a Cary Model 14 spectrophotometer or a Beckman DB spectrophotometer.

*N*-Methyl-4-picolinium methiodide was obtained by refluxing equimolar quantities of 4-picoline (Eastman) and methyl iodide in ethanol for 24 hr in the dark. Recrystallization from ethanol afforded material with mp 152° (lit. mp 152°).<sup>9</sup>

*p*-Dimethylamino-4-styrylpyridinium methiodide was prepared by refluxing 2.34 g (0.01 mol) of *N*-methyl-4-picolinium iodide and 1.5 g (0.01 mol) of dimethylaminobenzaldehyde (Eastman) in ethanol containing 0.03 mol of sodium ethoxide for 1 hr. Upon cooling red needles separated, which were crystallized from ethanol, mp 256–258°. *Anal.* Calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>I: C, 52.46; H, 5.19; N, 7.65; I, 34.7. Found: C, 52.48; H, 5.17; N, 7.37; I, 34.8. The nmr, ir, and uv-visible spectral data were in accord with the assigned structure. The extinction coefficient for the styryl methiodide in 95% ethanol was 5.16 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> at 470 nm.

1-(4-Dimethylaminophenyl)-2-(4-pyridyl)ethanol (13) was prepared by a modification of Villani's method<sup>8</sup> using *n*-butyllithium in tetrahydrofuran instead of sodium amide. To 15 ml of a 22% hexane solution of *n*-butyllithium (0.035 mol) at 4° was added dropwise 3.3 g (0.036 mol) of 4-picoline in 20 ml of tetrahydrofuran. After 30 min 4.5 g (0.03 mol) of *p*-dimethylaminobenzaldehyde in 20 ml was added dropwise at 5°. The clear yellow solution was allowed to stand for 18 hr after which time 50 ml of water was added. The solution was extracted with benzene. The resulting solution was dried with magnesium sulfate and the solvent was removed by rotary evaporation. The residue was recrystallized twice from benzene. The product (1 g) had mp 166–168° (lit. mp 165–167°).<sup>8</sup>

**Kinetics.** Stock solutions of *N*-methyl-4-picolinium iodide and *p*-dimethylaminobenzaldehyde were prepared in absolute ethanol. Stock solution of potassium hydroxide were prepared in distilled water. The concentrations of the stock solutions were adjusted so that combination of 0.9 ml of the iodide and aldehyde solutions with 0.5 ml of the aqueous base gave the final concentration of reactants shown in Tables I and II. A run was initiated by addition of temperature-equilibrated base to a cuvette containing iodide and aldehyde. The resulting solution was shaken vigorously and placed in the thermostated compartment of the spectrophotometer.

The initial rate studies (Table I) were carried out on a Beckman DB instrument. Tangents were drawn to the curve and the slopes were determined in the usual way. Corrections were applied where necessary for any reaction that had occurred before the optical density traces could be started. The correction was determined from the initial optical density, the extinction coefficient of the dye, and the stoichiometric concentrations. The experiments were done several times. The results in Table I are representative.

Point-by-point rate data were determined on a Cary 14 instrument. The procedure for preparation and mixing of stock solutions was the same as that for the initial rate studies. The trace of optical density against time was followed from 10 min to 1 hr. The solutions were incubated for 8–10 half-lives before the final optical density reading was taken. Pseudo-first-order rate constants were reproducible to ±5%.

**Proton Exchange of *N*-Methyl-4-picolinium Iodide with Methanol-*d*<sub>4</sub>-Methoxide-*d*<sub>3</sub>.** Sodium metal (67.7 mg, 3 mmol) was dissolved in 2 ml of methanol-*d*<sub>4</sub> (E & M Laboratories, Inc., 99% D, 98.5% CD<sub>3</sub>) to give a 1.5 *M* solution. Addition of 35.5 mg (0.15 mmol) of *N*-methyl-4-picolinium iodide to 0.5 ml of the basic methanol-*d*<sub>4</sub> solution produced a dark green solution. The nmr spectrum showed complete loss of 2,6 aromatic resonance at δ 8.81 (doublet, 2 H) and the high-field methyl resonance at δ 3.68 (singlet, 3 H). The high-field aromatic doublet at δ 7.95 had collapsed to a broad singlet. The exchanged protons appeared in the solvent peak at δ 6.13.

The low-field methyl resonance at δ 4.40 exchanged slowly. The rate was determined by periodic integration of the peak using the carbon-bound proton impurity in methanol-*d*<sub>4</sub> as a standard. The 3 and 5 protons also exchanged but more slowly. The rate of exchange of the 2,6 protons was determined similarly in 0.8 *M* methoxide. For comparison the rate of exchange of the *N*-methyl protons in *N*-methylpyridinium iodide was determined in a similar manner.

The rate of exchange of 4-methyl protons was determined in  $1.47 \times 10^{-4} M$  base by integration of the singlet at  $\delta$  3.68 using the *N*-methyl signal as standard.

**Acknowledgment.** The authors express their appreciation to Dr. Louis Berkowitz for preparation of compound 13. They are also indebted to Mr. Thaddeus Novak for technical assistance and to Mr. Harold Klapper for the nmr spectra and their interpretation.

**Registry No.**—1, 2301-80-6; 2, 100-10-7; 3, 959-81-9.

## References and Notes

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# Notes

## N-Monochlorination and N-Monobromination of Carbamates and Carboxamides by Sodium Hypochlorite and Hypobromite<sup>1a</sup>

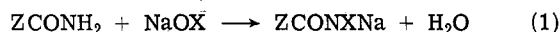
Carol Bachand, Hughes Driguez,<sup>1b</sup> John M. Paton,<sup>1c</sup> Daniel Touchard,<sup>1d</sup> and Jean Lessard\*

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Our studies on the chromous chloride promoted addition of *N*-chlorocarbamates to olefins<sup>2</sup> led us to devise a convenient method for the preparation of *N*-monochlorocarbamates in high yield, free from the *N,N*-dichloro derivatives. This method was also applied to the preparation of *N*-monochlorocarboxamides and of *N*-monobromocarbamates and -carboxamides needed for the chromous chloride promoted addition studies<sup>2c</sup> and some photochemical work.<sup>3</sup> The recent publication of Swern and coworkers<sup>4</sup> on the preparation of ethyl and methyl *N*-chlorocarbamates prompted us to report our results.

The method consists of the formation of the sodium salt of the monohalo derivative followed by careful neutralization. The salt is prepared by treating a slight excess (0.5–2%) of the amide with sodium hypochlorite or hypobromite<sup>5</sup> (5–6% solution) at *ca.* 0° (eq 1). After the addition of



methylene chloride, dilute (1–2 *N*) sulfuric acid is added slowly until the sodium salt (eq 2) and the excess sodium hydroxyde are neutralized (an excess of acid must be avoided). The solvent is removed at reduced pressure at 20–25°. The results are recorded in Table I.

***N*-Chlorocarbamates.** The yields of the *N*-monochlorocarbamates 1–6<sup>7</sup> are excellent (86–98%) with the purity of the crude reaction products being satisfactory for use in reactions without further purification. The method is thus very efficient.

***N*-Chlorocarboxamides.** The *N*-monochlorocarboxamides 8–16 were obtained in good yield, the purity of the

crude reaction products being satisfactory for use in reactions. The method was not successful with the sterically hindered 2,2-dimethylpropionamide nor was it convenient for the preparation of the water-soluble *N*-chloroformamide (7). Beckwith and Goodrich<sup>8</sup> have prepared *N*-monochlorocarboxamides in good yield by the bromine-catalyzed reaction of primary carboxamides with *tert*-butyl hypochlorite.

***N*-Bromocarbamates.** We have studied the bromination of ethyl, 2,2,2-trichloroethyl, and benzyl carbamates (17, 18, and 19) and, to our knowledge, this is the first reported preparation of *N*-bromocarbamates. It appears that the disproportionation of the *N*-bromocarbamates 17 and 18 (eq 3) does occur to a significant extent ( $K^{\text{eq}} \approx 0.08$  and



0.1, respectively, at *ca.* 37°). Indeed, although both the iodometric and neutralization analyses of the crude *N*-bromocarbamates 17 and 18 indicated a purity of 100%, their ir and nmr spectra showed the presence of nonbrominated carbamate. A careful examination of the integration for the various protons of the nmr spectra indicated clearly the presence of a third product, most probably the *N,N*-dibromocarbamate, the aliphatic protons of which had the same chemical shift as those of the *N*-monobromocarbamate, the molar ratio being approximately equal to that of the nonbrominated carbamate (see Experimental Section for details).

The crude benzyl *N*-bromocarbamate (19) was found to decompose rapidly under reduced pressure, as evidenced by continuous evolution of gas within the oily product, the loss of active bromine, and reduction in weight of material (the yield and active bromine content reported in Table I refer to a crude product kept under reduced pressure for 10 min after evaporation to dryness). The crude *N*-bromocarbamates 17, 18, and 19 could be stored in the refrigerator for several days without any loss of active bromine.

***N*-Bromocarboxamides.** Kergomard<sup>6</sup> has prepared *N*-bromoacetamide by adding a sodium hypobromite solution<sup>5</sup> to a solution of acetamide in acetic acid. *N*-Bromobenzamides have been prepared by using bromine in aqueous alkaline solution with subsequent rapid acidification