ρ^* and -10.22 for α by the method of least squares.[12] (A σ^* was estimated for $C_2H_5OCOCH_2CH_2-$ by dividing that for CH_3OCO- by 2.8[2].)[3] As the 50% confidence limits[12] on ρ^* are about ± 0.15 in each case, these are not appreciably different from the values of 3.40 and -10.17 obtained using all the data previously available.[2] These parameters were then used in eq. 3 to calculate K_A for mercaptans having other than two α-hydrogen atoms. If there is a significant Baker–Nathan effect, K_A for methyl mercaptan should be higher than calculated and K_A values for mercaptans having less than two α-hydrogen atoms should be systematically lower.[11] It is plain from Table II that

TABLE II

DEVIATIONS FROM EQUATION 3 WITH OTHER THAN TWO α-HYDROGEN ATOMS

Compound	$\log K_A^{obsd} - \log K_A^{calcd\ a}$	$\log K_A^{obsd} - \log K_A^{calcd\ b}$
H_2S[c]	+1.49	+1.48
$HOCH_2C(CH_3)_2SH$	+0.35	+0.17
CH_3SH	0.00	−0.05
t-C_4H_9SH	+0.22	+0.13
	+0.12	+0.03

[a] Calculated using the parameters obtained with groups having two α-hydrogen atoms. [b] Calculated using the parameters of ref. 2. [c] Corrected by a symmetry factor of two.

this is not so. The large deviation for hydrogen sulfide has been discussed previously.[2] It is in the wrong direction for a Baker–Nathan effect. The other deviations, averaging 0.17 log units, are not much larger than those of values used to obtain the correlation and are also in the wrong direction for a Baker–Nathan effect. It seems likely, therefore, that the Baker–Nathan effect is not larger than 0.05 log units per α-hydrogen atom. Steric effects would also appear to be small, apart from the possibility that the H_2S anomaly is to be explained in that way.[2] In fact, as also shown in Table II, the new data seem to be excellently correlated by eq. 3 using the old parameters.

As previously noted[2] thiophenol deviates from eq. 3 by ~1.6 log units. This deviation has been attributed to enhanced resonance stabilization in the anion, and designated $\Delta pK\psi$. For thiolacetic acid $\Delta pK\psi$ is ~1.1 log units. Unfortunately this value is not so reliable as it might be, as the correlation with σ^* is being used well outside of the range in which it was experimentally verified. Nevertheless, these results tend to support the idea[13] that resonance stabilization due to a neighboring unsaturated group is roughly independent of the nature of that group.

The absence of a Baker–Nathan effect, in spite of the presence of a resonance effect due to conjugation, is interesting, since, at least in Hückel approximation, the former is usually predicted to be proportional to the latter.[11] The proportionality constant has been variously estimated as ~1/10[13] and 1/13.[11] The only model which avoids this prediction is one in which *both* the carbon sp^3-orbital holding the α-hydrogen atom *and* the α-hydrogen 1s-orbital have nonzero resonance integrals with a neighboring p-orbital. This model predicts a much larger magnitude for Baker–Nathan effects in electron-deficient systems than in electron-surplus systems, such as the mercaptide ions. Although more data would be very desirable before reaching a final conclusion, this model should probably receive more attention than it has in the past.

(12) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 36–40.

(13) M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 4016 (1957).

Experimental

Dissociation Constants.—The pH titration, spectrophotometric, and gas solubility methods for determining dissociation constants have been previously described.[2] In determining the dissociation constant of methyl mercaptan it was found desirable to have more basic buffer solutions than those previously used. These were provided by phenol–phenoxide ion buffers. The hydrogen ion concentration of these was estimated using 1.00×10^{-10} as the acid dissociation constant of phenol.[14] In a simple buffer system of this sort the activity coefficients cancel, to a first approximation, and the dissociation constant of the mercaptan is given by eq. 5.

$$K_A^{CH_3SH} = K_A^{C_6H_5OH} \frac{(C_6H_6OH)(CH_3S^-)}{(C_6H_5O^-)(CH_3SH)} \quad (5)$$

Materials.[15]—*Thiolacetic acid* (Eastman Kodak Co., practical grade) was redistilled and the center cut, b.p. 84–85°, was used. Thiophenol (Mathieson Co., reagent grade) was redistilled under vacuum to give b.p. 55–56° at 10 mm. (2-Pyridyl)methyl mercaptan was a gift of the Walter Reed Army Institute of Research through Dr. T. R. Sweeney and was used as supplied. Ethyl β-mercaptopropionate was prepared by the method of Karrer and Schmid[16] from β-mercaptopropionic acid (gift of Evans Chemetics, Inc.) and purified by vacuum distillation to give b.p. 54° at 6 mm. 2-Mercapto-2-methyl-1-propanol was prepared from isobutylene oxide by the method of Davies and Savige[17] and had b.p. 68° at 29 mm. Methyl mercaptan was purchased from Eastman Kodak Co. and was not further purified except that it was distilled into the gas solubility apparatus. *t*-Amyl mercaptan was prepared from *t*-amyl bromide by the method of Backer[18] and had b.p. 104°. *t*-Butyl mercaptan was prepared in essentially the same way from *t*-butyl chloride and had b.p. 63°.

(14) A. J. Biggs, *Trans. Faraday Soc.*, **52**, 32 (1956).

(15) All boiling points are uncorrected.

(16) V. P. Karrer and H. Schmid, *Helv. Chim. Acta*, **27**, 125 (1944).

(17) W. Davies and W. E. Savige, *J. Chem. Soc.*, 774 (1951).

(18) H. J. Backer, *Rec. trav. chim.*, **54**, 216 (1935).

Nucleophilic Heteroaromatic Substitution. I. Pyridazines

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In contrast to the numerous studies of nucleophilic homoaromatic substitutions,[2] kinetic studies of nucleophilic heteroaromatic substitutions have been few. Such studies have been confined mainly to pyridines[3] and pyrimidines[4] where annular nitrogen α and/or γ to the group displaced, generally halogen, facilitates reaction through electron withdrawal.

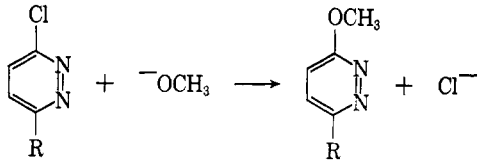
(1) Abstracted in part from the B.S. Honors thesis of J. G. K., Hobart College, 1963.

(2) W. R. Griezerstein, R. A. Bonelli, and J. A. Brieux, *J. Am. Chem. Soc.*, **84**, 1026 (1962), and references quoted therein.

(3) A. Mangini and B. F. Frenguelli, *Gazz. chim. ital.*, **69**, 86 (1939).

(4) N. B. Chapman and D. Q. Russell-Hill, *J. Chem. Soc.*, 1563 (1956).

We have investigated the displacement of chloride by methoxide from a series of 3-chloropyridazines variously substituted in the 6-position (compounds **1**–**9**) and have found that in most cases the reaction follows bi-



1, R = H; 2, R = CH_3; 3, R = OCH_3; 4, R = SCH_3; 5, R = SO_3^-; 6, R = $SOCH_3$; 7, R = CO_2^-; 8, R = CO_2CH_3; 9, R = Cl

molecular kinetics. In these compounds the annular nitrogens are α and β to the leaving group. Methoxide was chosen as the nucleophile to avoid the autocatalysis reported for the reaction of halopyridines with aniline,[5] where protonation of the annular nitrogen by acid liberated during reaction increases the electron-withdrawing power of the annular nitrogen. The pyridazines used are stable in dry methanol for indefinite periods with the exceptions of **1** and **6**, which undergo slow methanolysis to liberate ionic chloride. This methanolysis is sufficiently slow that good second-order plots were obtained to 65% completion of reaction when freshly prepared solutions of **1** and **6** were treated with methoxide in methanol.

Groups other than halogen can be displaced in nucleophilic aromatic substitution[6]; thus it was necessary to confirm that chloride was the only group being displaced in all of our reactions. That this was the case was indicated for compounds **4**, **8**, and **9** by the close parallel between the rate of liberation of chloride and the consumption of methoxide throughout the individual runs. Typical data are presented in Table I. No other product in addition to that expected was isolated from the reactions of compounds **3**, **4**, and **9**. The infrared spectra of the total product from reactions of **4** and **9** showed no change after two crystallizations.

TABLE I

CORRELATION BETWEEN METHOXIDE CONSUMPTION AND CHLORIDE LIBERATION FOR THE REACTION OF 3,6-DICHLOROPYRIDAZINE (20 ML., 0.2396 *M*) AND SODIUM METHOXIDE (20 ML., 0.2396 *M*)[a]

Time, sec.	$^-OCH_3$, moles/l.	Cl^-, moles/l.
40	0.1230	0.1209
300	0.0856	0.0866
600	0.0640	0.0646
900	0.0545	0.0551
1200	0.0402	0.0387
2400	0.0290	0.0284
3600	0.0226	0.0233

[a] In methanol at 40.2°.

The rates of substitution of chloride by methoxide were measured at 25.4 and 40.2° by methoxide consumption and were followed to at least 65% completion and in some cases up to 85% completion. Because of its slow reaction, compound **3** was studied only at the higher temperature and was not followed beyond 40% completion. Reactions of **5** and **7** were carried out with methoxide always present in excess to ensure that

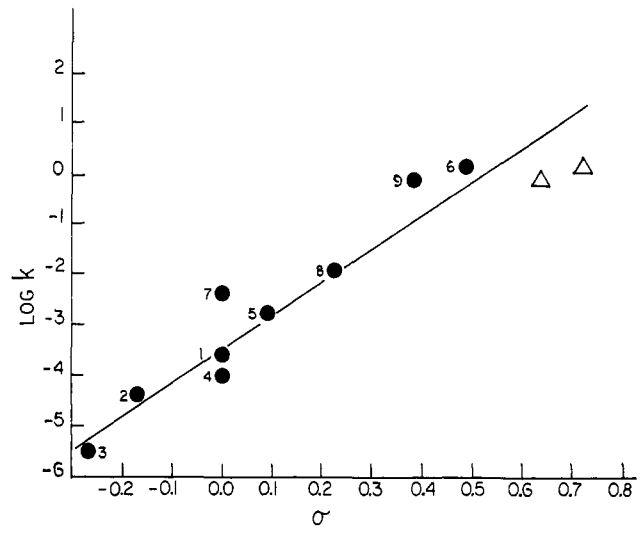


Fig. 1.—Plot of log k against σ (●) or σ^- (△) for the reaction of 3-chloro-6-R-pyridazines with methoxide.

carboxylate and sulfonate ions, instead of the corresponding free acids, were the forms present throughout reaction. Nevertheless, the rate for **7** was faster than anticipated and showed a slight increase as methoxide was consumed. Presumably the more reactive form—the free carboxylic acid—was present in equilibrium with the carboxylate ion, even initially, in sufficient quantities to affect the rate measurements. The increase in rate, then, was due to an increase in the relative amount of free acid as methoxide was consumed. Under the same conditions, the strongly acidic sulfonic acid showed no corresponding enhanced rate nor a change of rate as the reaction progressed. Kinetic data and thermodynamic parameters for the reactions studied are presented in Table II. These thermodynamic parameters are similar to those found by others for nucleophilic substitutions in homo- and heteroaromatic systems.[4,7,8]

A mechanism that may involve a cyclohexadienide intermediate has been proposed for bimolecular nucleophilic aromatic substitutions.[9] This mechanism is supported by spectroscopic, synthetic, and kinetic studies.[10] It seems probable that a similar intermediate is involved in the reaction of methoxide with 3-chloropyridazines.

A Hammett plot of the logarithms of reaction rates against σ-values (Fig. 1) shows reasonable linearity. The regression line shown in Fig. 1 was obtained from the values for compounds **1**–**5** and **9**. Compound **7** was omitted from the calculation because of the ambiguity regarding the actual nature of the substituent during reaction. Values of σ and σ^- for **6** and **8** are also shown in Fig. 1; the former lie above the regression line and the latter below it, which indicates that carbomethoxy and methylsulfinyl groups exhibit less resonance interaction with the reaction site in the cases under

(5) C. K. Banks, *J. Am. Chem. Soc.*, **66**, 1127 (1944).

(6) J. F. Bunnett, E. W. Garbisch, and K. M. Pruitt, *ibid.*, **79**, 387 (1957).

(7) J. F. Bunnett, F. Draper, Jr., P. R. Ryason, P. Noble, Jr., R. G. Tonkyn, and R. E. Zahler, *ibid.*, **75**, 642 (1953).

(8) E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952). However, values of about −40 e.u. for ΔS^* are reported in ref. 2 for the reaction of piperidine with 5-R-2-nitrochlorobenzenes.

(9) J. Miller, *ibid.*, **85**, 1628 (1963).

(10) For a review of current evidence, see S. D. Ross, "Progress in Physical Organic Chemistry," Vol. I, S. G. Cohen, A. Streitweiser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 31.

TABLE II
KINETIC DATA AND THERMODYNAMIC PARAMETERS FOR THE REACTION OF METHOXIDE WITH 3-CHLORO-6-R-PYRIDAZINES

R	k at 25.4° (l./mole sec.)	k at 40.2° (l./mole sec.)	ΔH^* (kcal./mole)	ΔS^* (e.u.)
OCH_3		$2.90 \pm 0.06 \times 10^{-6}$		
CH_3	$7.42 \pm 0.20 \times 10^{-6}$	$3.85 \pm 0.04 \times 10^{-5}$	19.8	−15.6
SCH_3	$1.89 \pm 0.04 \times 10^{-5}$	$8.31 \pm 0.06 \times 10^{-5}$	19.5	−17.4
H	$5.41 \pm 0.08 \times 10^{-5}$	$2.56 \pm 0.08 \times 10^{-4}$	18.7	−15.4
SO_3^-	$3.34 \pm 0.20 \times 10^{-4}$	$1.43 \pm 0.05 \times 10^{-3}$	17.4	−16.1
CO_2^-	$9.89 \pm 0.30 \times 10^{-4}$	$3.85 \pm 0.40 \times 10^{-3}$	16.3	−17.3
Cl	$2.80 \pm 0.04 \times 10^{-3}$	$1.15 \pm 0.01 \times 10^{-2}$	16.6	−14.5
CO_2CH_3	$3.06 \pm 0.05 \times 10^{-1}$	$9.71 \pm 0.18 \times 10^{-1}$	13.7	−14.9
$SOCH_3$	$4.93 \pm 0.14 \times 10^{-1}$	1.56 ± 0.02	13.7	−13.9

discussion than has been found in most homoaromatic systems.[11]

Reported values of ρ for nucleophilic homoaromatic substitution range from +3.874 for the reaction of methoxide with 4-substituted 2-nitrochlorobenzene[12] to the unusually high value of +9.2 for the reaction of methoxide with substituted fluorobenzenes.[13] Our value of +6.82 for ρ ($r = 0.92$) indicates that electron-withdrawing substituents in the 6-position of pyridazines facilitate displacement of chloride by methoxide. This large value for ρ suggests that this reaction is very sensitive to the nature of the substituent. We tentatively ascribe this effect to resonance interaction between the annular nitrogen in the 1-position and the substituent in the 6-position, such that electron withdrawal by the substituent increases the positive character of the nitrogen in the 1-position and thus its electron demand. Although this nitrogen in the 1-position is β to the reaction site and cannot, therefore, affect it by resonance, the influence of its inductive power alone must be great. This can be deduced from comparison of the following reaction rates: 2-chloropyrimidine and ethoxide react 10^6 times as fast as do 2-chloropyridine and ethoxide, both in ethanol and at 20°,[4] and we have found that 2-chloropyridine does not react appreciably with methoxide under the same conditions required for 85% completion of the reaction of 3-chloropyridazine with methoxide.

Experimental[14]

Materials.—Dry methanol and sodium methoxide in methanol were stored in the absence of carbon dioxide and moisture and were dispensed from siphons. The concentration of sodium methoxide in solution was determined by hydrolysis of aliquots and titration with standard acid. The methoxide solution was stable throughout the duration of the experimental work.

The pyridazines were, with two exceptions, prepared by following published procedures and were crystallized from the solvents indicated: 3-chloropyridazine (**1**) from ligroin–ether, m.p. 34–35°, lit.[15] m.p. 35°; 3,6-dichloropyridazine (**9**) from cyclohexane, m.p. 66–68°, lit.[16] m.p. 68°; 3-chloro-6-methoxypyridazine (**3**) from benzene, m.p. 90–91°, lit.[17] m.p. 90.5°; 3-chloro-6-methylpyridazine (**2**) from ligroin, m.p. 61°, lit.[18] m.p. 61°; 3-chloro-6-carboxypyridazine (**7**) from ether, m.p. 145–146°, lit.[15] m.p. 146°; 3-chloro-6-methylthiopyridazine (**4**) from ligroin, m.p. 104°, lit.[19] m.p. 104°; 3-chloropyridazine-6-sulfonic acid (**5**) from ether–ligroin, m.p. 248°, lit.[20] m.p. 248–249°.

3-Chloro-6-methylsulfinylpyridazine (6).—A solution of **4** (16.0 g., 0.1 mole) in glacial acetic acid (200 ml.) was treated with 30% hydrogen peroxide (40 ml.) at room temperature and was left for 24 hr. The reaction was slightly exothermic during the first 3 hr. The solution was concentrated *in vacuo* at room temperature to a small volume and was chilled in ice. The solid that precipitated was filtered and recrystallized twice from absolute ethanol. The white crystals, 13.0 g. (74%), had m.p. 110–112°. The infrared spectrum of the product in chloroform exhibited a strong absorption at 9.58 μ, which is characteristic of the sulfoxide group.[21]

Anal. Calcd. for $C_5H_5ClN_2OS$: C, 34.00; H, 2.84; Cl, 20.11. Found: C, 33.84; H, 2.76; Cl, 19.8.

3-Chloro-6-carbomethoxypyridazine (8).—A solution of **7** (6.3 g., 0.04 mole) in ether (500 ml.) was treated with a solution of diazomethane in ether until only a slight excess of diazomethane remained. The mixture was stored overnight and the ether was distilled. The residue was crystallized from ligroin to yield fine white needles, 5.1 g. (73%), m.p. 104–105°.

Anal. Calcd. for $C_6H_5ClN_2O_2$: C, 41.8; H, 2.90; Cl, 20.57. Found: C, 41.61; H, 2.79; Cl, 20.19.

Kinetics.—For 3 at 40.2° and for 2 and 4 at 25.4°.—Solutions of known concentration of the pyridazine in dry methanol and of sodium methoxide in methanol were mixed, and 5-ml. portions of the well-shaken solution were transferred into glass ampoules which were sealed and immersed in the thermostated bath. The time of immersion was taken as zero time. Each ampoule was removed at a different time interval, opened, and its contents were flushed into about 150 ml. of ice–water. The alkali was titrated with standard acid.

For All Other Pyridazines at 25.4° and 40.2°.—Accurately measured volumes of a solution of known concentration of the pyridazine in dry methanol and of sodium methoxide solution were pipetted into separate chambers of a divided flask which was immersed in a bath thermostated at 25.4 or at 40.2°. After thermal equilibrium had been attained, the contents of the flask were mixed at zero time. Aliquots were removed with a calibrated pipet, quenched in ice–water, and titrated with standard acid. Between sample removals, the flask was tightly stoppered.

Stock solutions of the pyridazines (0.2396 M) were freshly prepared for each series of runs and the concentrations of reactants were varied by using different volumes of these solutions with or without addition of dry methanol. The ratio of concentrations of reactants was thus varied by at least a factor of four with respect to each other, and three independent runs were made inside this concentration range for each compound.

Calculations.—The rate constants were obtained graphically from a plot of $1/(a - x)$ or $[1/(b - a)] \log [a(b - x)/b(a - x)]$ against time. ΔH^* and ΔS^* were determined as described by Bunnett.[22]

Product Analyses.—The products of reaction of **2**, **3**, **4**, and **9** were obtained from the reactions of 0.01 mole of these pyridazines with an equimolar amount of sodium methoxide in refluxing methanol. The solvent was distilled, and the product

(11) H. van Bekkum, P. K. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).
(12) J. Miller, *J. Am. Chem. Soc.*, **79**, 93 (1957).
(13) J. Miller, *Australian J. Chem.*, **9**, 61 (1956).
(14) Melting points were determined on a Fisher-Johns block and are uncorrected.
(15) R. F. Homer, H. Gregory, W. G. Overend, and L. F. Wiggens, *J. Chem. Soc.*, 2195 (1948).
(16) R. H. Mizzoni and P. E. Spoerri, *J. Am. Chem. Soc.*, **73**, 1873 (1951).
(17) N. Takahayashi, *J. Pharm. Soc. Japan*, **75**, 776 (1955).
(18) W. G. Overend and L. F. Wiggens, *J. Chem. Soc.*, 239 (1947).
(19) G. R. Duffin and J. D. Kendall, *ibid.*, 3789 (1959).
(20) N. Takahayashi, *J. Pharm. Soc. Japan*, **75**, 1245 (1955).
(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen, London, 1958, p. 358.
(22) J. F. Bunnett, "Techniques of Organic Chemistry," Vol. VIII, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p. 199.

was extracted into boiling hexane. Partial evaporation of the hexane and cooling in ice yielded the product which was crystallized from hexane. The product obtained in each case was as follows: from **3**, 3,6-dimethoxypyridazine, 74%, m.p. 107–108°, lit.[23] m.p. 108°; from **4**, 3-methoxy-6-methylthiopyridazine, 89%, m.p. 86°, lit.[24] m.p. 87°; from **9**, 3-chloro-6-methoxypyridazine (**3**), 78%, m.p. 90–91°, lit.[17] m.p. 90.5°. From **2**, 3-methoxy-6-methylpyridazine hydrochloride was obtained by addition of dry hydrogen chloride to a solution of the reaction product in hexane, m.p. 130–132°, lit.[25] m.p. 131–132°.

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(23) J. Druey, K. Meier, and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).
(24) Noboru Takahayashi, *J. Pharm. Soc. Japan*, **75**, 778 (1955).
(25) W. G. Overend, L. M. Turton, and L. F. Wiggens, *J. Chem. Soc.*, 3500 (1950).

Amino Derivatives of Pyrazine N-Oxides[1]

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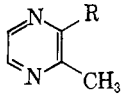
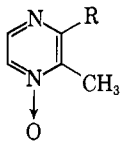
In connection with a program of synthesis of a variety of pyrazine derivatives, we had occasion to prepare several pyrazine N-oxides. The treatment of 2-chloro-3-methylpyrazine[2] (Ia) with hydrogen peroxide afforded the N-oxide IIa,[3] melting at 74–76°, in fair yield. IIa reacted exothermically with piperidine to give a crystalline derivative (IIb) melting at 98–100°. The latter showed a very slight basicity as reflected in the low ionophoretic mobility in 5 *M* acetic acid. The



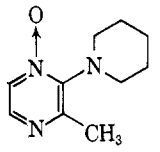
Ia, R = Cl
b, R = 1-piperidyl



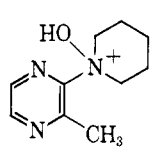
IIa, R = Cl
b, R = 1-piperidyl

piperidino derivative IIb was smoothly deoxygenated by phosphorus trichloride to give 2-piperidino-3-methylpyrazine (Ib). The properties of the free base and its hydrogen sulfate salt were found to be identical with authentic materials prepared by a different route.[4] This shows that the N-oxide obtained from commercial 2-chloro-3-methylpyrazine has structure IIa and is not derived from 2-chloro-6-methylpyrazine known to be present in significant amount in commercial Ia.[4] Similarly, reaction of the N-oxide IIa with dimethylamine resulted in dimethylamino-3-methylpyrazine N-oxide.

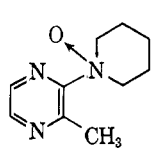
When 2-piperidino-3-methylpyrazine was treated with hydrogen peroxide in acetic or formic acid, two products were formed. One of these, obtained in very small yield, melted at 47–49° and showed an ionophoretic mobility similar to IIb. Elemental analyses were in good agreement with values calculated for an N-oxide isomeric with IIb. Since both the ultraviolet and infrared spectra differed widely from that of IIb, structure III was assigned. The bulk of the material obtained from the reaction mixture was a compound much less soluble in ligroin than III and with a high iono-



III



IV

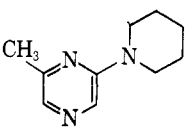


V

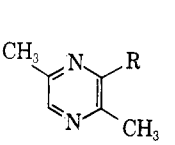
phoretic mobility. Elemental analyses were in agreement with a hydrate of a structure isomeric with IIb or III. Aqueous solutions showed a distinctly alkaline reaction. The ultraviolet spectrum was quite different from either IIb or III and was very similar to that of 2-methylpyrazine. It is well known[5,6] that, although the ultraviolet spectra of aniline and benzene differ greatly, the spectrum of the anilinium ion is very much like that of benzene. The structure of the compound in question must then be IV in which the "onium" center prevents participation of the amino nitrogen in resonance with the ring. Dehydration of IV to V by sublimation was not quite complete as the elemental analysis showed a small residual water content. The strong tendency for V to exist as the hydrate IV is characteristic of aliphatic-type N-oxides.[7]

The oxidation of 2-piperidino-6-methylpyrazine (VI) with hydrogen peroxide in formic acid gave a much more complicated reaction mixture than in the case of the isomeric Ib. However, on the basis of ionophoretic data it is clear that the compound to which structure III has been assigned did not arise from VI, conceivably present as a contaminant in starting material Ib.

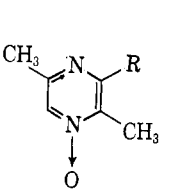
In the 2,5-dimethylpyrazine series, 2-chloro-3,6-dimethylpyrazine (VIIa) was converted to the oxide VIIIa[8] and the latter to the dimethylamino derivative VIIIb. The ultraviolet spectrum of VIIIb was very similar to that of IIb but unlike that of III. In boiling acetic anhydride, VIIIb was converted to the ester IXa which was not isolated but was saponified directly to the alcohol IXb. Structure Xc is excluded because this compound was prepared as described below and shown



VI



VIIa, R = Cl
b, R = $N(CH_3)_2$



VIIIa, R = Cl
b, R = $N(CH_3)_2$

(1) Presented at the 144th Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.
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