Base Catalysis of the Reaction of Morpholine with 2,4-Dinitrophenyl Phenyl Ether in 10% Dioxane–90% Water

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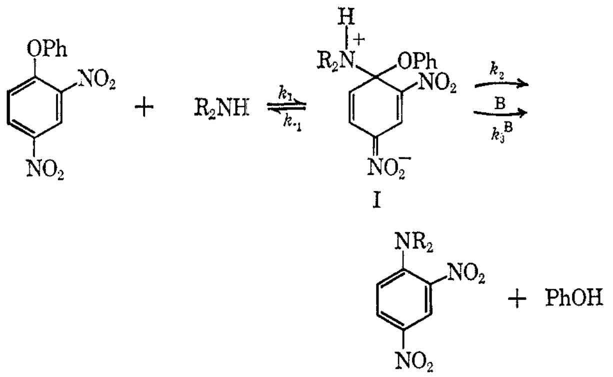
Rate of reactions of 2,4-dinitrophenyl phenyl ether with morpholine to form N-(2,4-dinitrophenyl)morpholine have been measured as a function of sodium hydroxide and morpholine concentration. The reaction is strongly catalyzed by hydroxide ion and moderately by the amine itself; the second-order rate coefficient k_A is curvilinearly related to hydroxide ion concentration. This curved plot is typical for reactions of secondary amines with 2,4-dinitrophenyl phenyl ether in this solvent. The partial rate coefficient k_1 and the ratios k_2/k_{-1} and $k_3{}^B/k_{-1}$ were calculated; they have been discussed in the preceding paper. At high sodium hydroxide concentrations, hydrolysis of N-(2,4-dinitrophenyl)morpholine to form 2,4-dinitrophenol is relatively fast and requires a complete kinetic analysis for a system of two consecutive and parallel reactions (the hydrolysis of 2,4-dinitrophenyl phenyl ether is the parallel reaction). Incidentally, this treatment furnished rate coefficents $k_{OH}{}^P$ for the hydrolysis of N-(2,4-dinitrophenyl)morpholine.

In the preceding paper[2] we reported upon the reactions of benzylamine and N-methylbenzylamine with 2,4-dinitrophenyl phenyl ether. One of the main objectives of this investigation was the search for a correlation between base strength of reacting amine and the sensitivity of the reaction to base catalysis. Such correlation should offer a deeper insight into the mechanistic details of base catalysis.

We took the ratio $k_3{}^{OH}/k_2$ as a measure of sensitivity to base catalysis; $k_3{}^{OH}$ stands for the hydroxide ion catalyzed, and k_2 stands for the uncatalyzed (or water-catalyzed) decomposition of the intermediate I.[3]



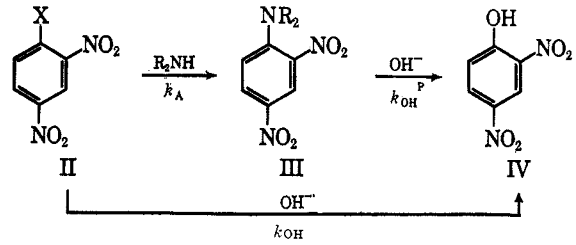
(1)

B = OH⁻ or R₂NH

$k_3{}^B = k_3$ or $k_3{}^{R_2NH}$

In this article an account is given on the reaction of 2,4-dinitrophenyl phenyl ether with another amine, morpholine.

The reaction of morpholine with 2,4-dinitrophenyl phenyl ether is not fundamentally different from the reaction of piperidine,[2,6,7] benzylamine,[2] N-methylbenzylamine,[2] or N-methylaniline[5] with ethers of 2,4-dinitrophenol or with 2,4-dinitrofluorobenzene. In all these systems there are two side reactions taking place: the hydrolysis of the aromatic substrate II and the hydrolysis of the reaction product III, both leading to 2,4-dinitrophenol (IV) (see eq 2). Depending on the specific amine–substrate pair these side reactions play a more or less important role. An example where the hydrolysis of the substrate ($k_{OH}{}^S$) was found to be very rapid is the reaction of N-methylaniline with 2,4-dinitrofluorobenzene.[5] As a consequence the yield of the desired reaction product III varied from 0.72 to 1.61% only, thus introducing a large uncertainty in the evaluation of aminolysis rate coefficients k_A. However, the ratio $k_A/k_{OH}{}^S$ and therewith the yield is usually much higher, making the calculation of k_A much more precise.



(2)

The hydrolysis of the reaction product III had not been found to be very important in the systems investigated so far, because the entering amines were strong nucleophiles or because the leaving group X was a very "good" one, prone to separate from carbon; either condition leads to a large k_A and apparently to a large $k_A/k_{OH}{}^P$ ratio.[8] The product hydrolysis could therefore usually be neglected completely or be allowed for by slightly modifying the infinity values of the spectrophotometric measurements.[9]

The reaction of the relatively weak nucleophile (small k_A) morpholine with 2,4-dinitrophenyl phenyl ether appears to be the first example where $k_A/k_{OH}{}^P$ is so small as to require a complete kinetic treatment as a system of two consecutive and parallel reactions (eq 3). For details see Experimental Section.

Experimental Section

Materials.—1,4-Dioxane was purified by the method of Fieser[10] and was stored over calcium hydride, from which it was distilled as needed; "10% dioxane–90% water" was prepared by diluting one volume of dioxane to a total of ten volumes with distilled

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[1] Address correspondence to Division of Natural Sciences, University of California at Santa Cruz, Santa Cruz, Calif. 95060.

[2] C. F. Bernasconi, *J. Org. Chem.*, **32**, 2947 (1967).

[3] The intermediate complex mechanism (eq 1) for nucleophilic aromatic substitution has frequently been discussed elsewhere.[2,4-7]

[4] J. F. Bunnett, *Quart. Rev.* (London), **12**, 1 (1958).

[5] J. F. Bunnett and J. J. Randall, *J. Am. Chem. Soc.*, **80**, 6020 (1958).

[6] J. F. Bunnett and R. H. Garst, *ibid.*, **87**, 3879 (1965).

[7] J. F. Bunnett and C. F. Bernasconi, *ibid.*, **87**, 5209 (1965).

[8] *A priori* the low mobility of the strongly basic amine moiety as leaving group in III is expected to keep $k_{OH}{}^P$ small and thus be partly responsible for the high value of $k_A/k_{OH}{}^P$. See Discussion, however.

[9] See, *e.g.*, the reactions of benzyl- and N-methylbenzylamine with 2,4-dinitrophenyl phenyl ether.[2]

[10] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 284.

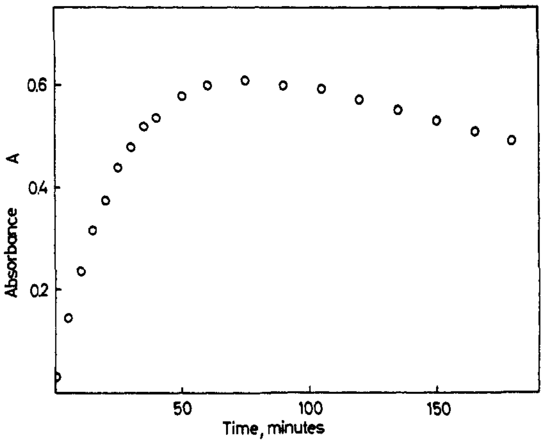

Figure 1.—Absorbance (observed) at 377 mμ in function of time for a representative run. Data are from Table I.

water. Reagent grade morpholine (Fluka) was used without further purification. Morpholine hydrochloride was prepared by standard methods and recrystallized from ethanol, mp 168–171°. 2,4-Dinitrophenyl phenyl ether was available from a previous study.[3] N-(2,4-Dinitrophenyl)morpholine was prepared by the method of Bunnett and Randall[5] used for N-(2,4-dinitrophenyl)-N-methylaniline, and thrice recrystallized from ethanol: mp 118°.

Rate Measurements.—The general photometric procedure described earlier[5,7] was employed. Runs were set up so that morpholine and any added base were in large excess over the substrate (2,4-dinitrophenyl phenyl ether) and the product of aminolysis (N-(2,4-dinitrophenyl)morpholine). Thus pseudo-first-order kinetics were assured for all reactions taking place.

The method of calculating rate constants from the light absorption measurements at 377 mμ was different from that used in earlier investigations, except for runs where morpholine hydrochloride was added (low hydroxide ion concentration).

The kinetic system is described by eq 3, where A is 2,4-dinitrophenyl phenyl ether, B is 2,4-dinitrophenylmorpholine, C is 2,4-dinitrophenol, $k_A{}^*$ is the pseudo-first-order coefficient for formation of B, and $k_{OH}{}^{S*}$ and $k_{OH}{}^{P*}$ are the pseudo-first-order coefficients for formation of C from A and B, respectively. The differential rate equations are

$$\begin{tikzcd} A \arrow[r, "k_A{}^*"] \arrow[rr, bend right, "k_{OH}{}^{S*}"'] & B \arrow[r, "k_{OH}{}^{P*}"] & C \end{tikzcd} \qquad (3)$$

$$\frac{d[A]}{dt} = -(k_A{}^* + k_{OH}{}^{S*})[A] = -k_\psi[A] \qquad (4)$$

$$\frac{d[B]}{dt} = k_A{}^*[A] - k_{OH}{}^{P*}[B] \qquad (5)$$

$$\frac{d[C]}{dt} = k_{OH}{}^{S*}[A] + k_{OH}{}^{P*}[B] \qquad (6)$$

By integration with the boundary conditions $[B]_0 = [C]_0 = 0$ one obtains

$$[A] = [A]_0 e^{-k_\psi t} \qquad (7)$$

$$[B] = [A]_0 \frac{k_A{}^*}{k_{OH}{}^{P*} - k_\psi}(e^{-k_\psi t} - e^{-k_{OH}{}^{P*} t}) \qquad (8)$$

$$[C] = [A]_0 - [A] - [B] \qquad (9)$$

The measured light absorption A or the ratio $A/[A]_0$ is then a function of the three unknowns $k_A{}^*$, k_ψ, and $k_{OH}{}^{P*}$, of the easily determined extinction coefficients ϵ_A, ϵ_B, and ϵ_C and of time t (eq 10).

$$\frac{A}{[A]_0} = \epsilon_A e^{-k_\psi t} + \epsilon^B \frac{k_A{}^*}{k_{OH}{}^{P*} - k_\psi}(e^{-k_\psi t} - e^{-k_{OH}{}^{P*} t}) + \epsilon_C \frac{1}{k_{OH}{}^{P*} - k_\psi}(1 - ((k_A{}^* + k_{OH}{}^{P*} - k_\psi)e^{-k_\psi t} - k_A{}^* e^{-k_{OH}{}^{P*} t})) \qquad (10)$$

The three pseudo-first-order coefficients for which the experimental data gave the best fit with eq 10 were evaluated by *nonlinear* regression analysis[11,13] (method of least squares). By inserting the values of these coefficients into eq 10, A could be calculated for each experimental time and be compared with the experimental values of A. A representative fit of calculated and found A values is displayed in Table I; Figure 1 shows A as a function of time for a typical run.

TABLE I

REACTION OF MORPHOLINE WITH 2,4-DINITROPHENYL PHENYL ETHER IN 10% DIOXANE–90% WATER AT 29.4°. A REPRESENTATIVE RUN[a]

Time, min	A, calcd[b]	A, obsd[c]
0	0.032	0.032
5	0.147	0.146
10	0.241	0.237
15	0.319	0.318
20	0.383	0.376
25	0.436	0.440
30	0.478	0.481
35	0.512	0.521
40	0.540	0.538
50	0.578	0.579
60	0.599	0.599
75	0.610	0.611
90	0.606	0.600
105	0.593	0.597
120	0.576	0.574
135	0.555	0.555
150	0.534	0.534
165	0.513	0.512
180	0.492	0.494

[a] Initial concentrations: $[\text{substrate}]_0 = 3.41 \times 10^{-5}$ *M*; $[\text{morpholine}]_0 = 0.2$ *M*; $[\text{NaOH}]_0 = 0.2$ *M*. Extinction coefficients at 377 mμ: $\epsilon_A = 446$, $\epsilon_B = 13{,}550$, $\epsilon_C = 75$. [b] Absorbance at 377 mμ, calculated by eq 10 with $k_\psi = 5.69 \times 10^{-4}$ sec^{-1}, $k_A{}^* = 4.69 \times 10^{-4}$ sec^{-1}, and $k_{OH}{}^{P*} = 4.95 \times 10^{-5}$ sec^{-1}. [c] Observed absorbance at 377 mμ.

The second-order rate coefficients k_A, $k_{OH}{}^S$, and $k_{OH}{}^P$ were obtained by dividing the pseudo-first-order coefficients by the respective effective[14] morpholine and hydroxide ion concentrations. The "yields" were calculated by dividing $k_A{}^*$ by k_ψ.

k_ψ, $k_A{}^*$, and k_A are estimated to be precise within ±2%; $k_{OH}{}^{S*}$ and $k_{OH}{}^S$ are within ±20%. For a discussion of the uncertainty of $k_{OH}{}^{P*}$ and $k_{OH}{}^P$ see the following section.

Results and Discussion

Our kinetic determinations are presented in Tables II and III. Table II presents for each run the observed pseudo-first-order coefficients k_ψ, $k_A{}^*$, $k_{OH}{}^*$, and $k_{OH}{}^{S*}$, the "per cent yield"[16] of N-(2,4-dinitrophenyl)morpholine, and the second-order coefficients for the different reactions, calculated as described in the Experimental Section. Table III only lists the pseudo-first-order coefficients $k_A{}^*$, which are identical with k_ψ, and

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(11) A modified computer program developed by Kaiser[12] was used. The calculations were performed at the computer center of ETH.

(12) A. Kaiser, Ph.D. Thesis, ETH, Zürich, 1966.

(13) For an earlier example of this problem and its solution, see J. F. Bunnett and R. J. Morath, *J. Am. Chem. Soc.*, **77**, 5051 (1955).

(14) As a consequence of the equilibrium reaction of morpholine with water to form the conjugated acid of morpholine and hydroxide ion, the effective amine and hydroxide ion concentrations are not always identical with stoichiometric concentrations. Effective concentrations were calculated by means of a basicity constant $K_b = 1.29 \times 10^{-6}$ estimated from $pK_a = 8.36$[15] by a procedure described elsewhere.[7] Due to the low value of K_b the equilibrium had only significant influence on the run where no sodium hydroxide was added to the reaction solution.

(15) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **78**, 2570 (1956).

(16) The "per cent yield" as used here is not the same as ordinarily understood because it is calculated by an indirect method rather than determined directly. See Experimental Section.

Table II

Reactions of Morpholine with 2,4-Dinitrophenyl Phenyl Ether and of Sodium Hydroxdie with 2,4-Dinitrophenyl Phenyl Ether and 2,4-Dinitrophenylmorpholine in 10% Dioxane–90% Water at 29.4°. Dependence on Hydroxide Ion Concentration[a]

$[NaOH]_{st}$, M	10^4k_ψ, sec^{-1}	% yield	$10^4k_A^*$, sec^{-1}	10^3k_A, l. mole^{-1} sec^{-1}	$10^5k_{OH}^{S*}$, sec^{-1}	$10^4k_{OH}^S$, l. mole^{-1} sec^{-1}	$10^5k_{OH}^{P*}$, sec^{-1}	$10^4k_{OH}^P$, l. mole^{-1} sec^{-1}
Nil[b]	0.238	100	0.238	0.120			0.048	3.53
0.01	0.887	93.8	0.832	0.416			0.189	1.89
0.02	1.61	89.5	1.44	0.719			0.137	0.69
0.05	2.91	87.3	2.54	1.27			0.276	0.55
0.10	4.18	85.2	3.56	1.78	6.21	6.21	1.24	1.24
0.125	4.62	88.9	4.10	2.05	5.13	4.11	1.88	1.50
0.15	5.08	84.7	4.30	2.15	7.78	5.19	2.73	1.82
0.20	5.69	82.5	4.69	2.35	10.0	5.00	4.95	2.48

[a] Total electrolyte concentration maintained at 0.2 M by addition of sodium chloride as required. $[\text{Substrate}]_0 = 3.20 \times 10^{-5}$ M; $[\text{morpholine}]_0 = [\text{morpholine}]_{eff} = 0.2$ M for all but one run; $[OH]_{eff} = [NaOH]_{st}$ for all but one run. [b] $[OH]_{eff} = 0.00136$ M; $[\text{morpholine}]_{eff} = 0.199$ M.

Table III

Reactions of Morpholine with 2,4-Dinitrophenyl Phenyl Ether in 10% Dioxane–90% Water at 29.4°.[a] Dependence on Morpholine Concentration

$[\text{Morpholine}]_{st}$, M	$[\text{Mor}\cdot\text{HCl}]_{st}$, M	$10^5k_A^*$, sec^{-1}	10^5k_A, l. mole^{-1} sec^{-1}
0.05	0.025	0.134	2.67
0.075	0.0375	0.295	3.93
0.10	0.050	0.510	5.10
0.125	0.0625	0.760	6.08
0.15	0.075	1.106	7.38
0.175	0.0875	1.456	8.32
0.20	0.10	1.867	9.33

[a] Total electrolyte concentration maintained at 0.2 M by addition of sodium chloride as required. All reactions formed 2,4-dinitrophenylmorpholine quantitatively. $[OH]_{eff} = 2.60 \times 10^{-6}$ M in all runs; $[\text{morpholine}]_{st} = [\text{morpholine}]_{eff}$; $[\text{substrate}]_0 = 3.60 \times 10^{-5}$ M.

k_A, the second-order coefficients of aminolysis. The hydrolysis of both the substrate and the product was negligible and not detectable in the absence of sodium hydroxide.

As can be seen from the results set forth in Table II the reaction is strongly catalyzed by hydroxide ion; k_A is curvilinearly related to the base concentration (Figure 2). Similarly curved plots have been found in the reactions of piperidine with different ethers of 2,4-dinitrophenol,[6,7] of N-methylbenzylamine with 2,4-dinitrophenyl phenyl ether,[2] and of N-methylaniline with 2,4-dinitrofluorobenzene;[5] the mechanistic implications thereof have been discussed in detail elsewhere.[2,5–7]

In Table III the second-order coefficients k_A are displayed in function of a morpholine–morpholine hydrochloride 2:1 buffer of varying concentration. Figure 3 shows that k_A increases almost linearly with buffer concentration, thus demonstrating general base catalysis.[17]

By means of a computer program[11] the values of the partial rate coefficient ($k_1 = 3.33 \times 10^{-3}$ l. mole^{-1} sec^{-1}) and the ratios ($k_2/k_{-1} = 1.5 \times 10^{-3}$, $k_3^{mor}/k_{-1} = 0.13$ l. mole^{-1} (k_3^{mor} is the morpholine-catalyzed transformation of intermediate I to products), $k_3^{OH}/k_{-1} = 11.9$ l. mole^{-1}, and $k_3^{OH}/k_2 = 7900$ l. mole^{-1}) were calculated as described in the foregoing paper.[2] These values have been compared with those of reactions of other amines with the same substrate and discussed by Bernasconi.[2]

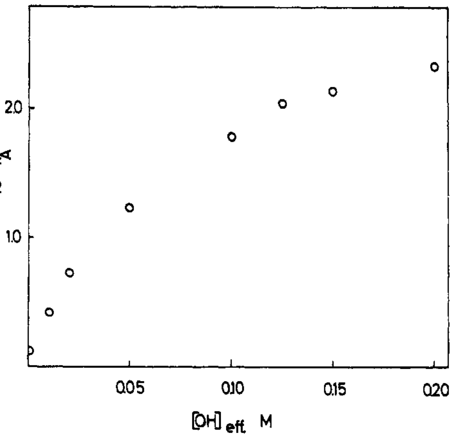

Figure 2.—Reaction of 2,4-dinitrophenyl phenyl ether with morpholine, catalyzed by sodium hydroxide. Data are from Table II.

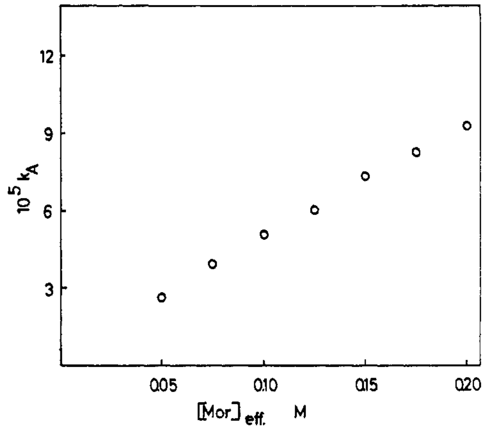

Figure 3.—Reaction of 2,4-dinitrophenyl phenyl ether with morpholine, catalyzed by morpholine. Data are from Table III.

Incidentally, our measurements furnished rate coefficients for the reactions of hydroxide ion with the substrate and the product. The average value of k_{OH}^S, the second-order coefficient for the hydrolysis of 2,4-dinitrophenyl phenyl ether, is 5.12×10^{-4} l. mole^{-1} sec^{-1} among the experiments where the sodium hydroxide concentration was 0.1 M or greater. This compares well with the average value of 4.60×10^{-4} l. mole^{-1} sec^{-1} determined by Bunnett and Bernasconi.[7]

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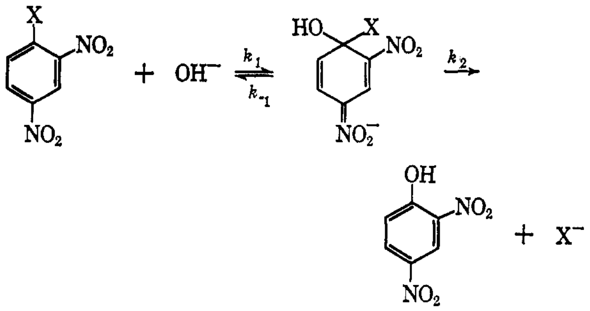
(17) A few preliminary experiments (not listed) have been performed with morpholine–morpholine hydrochloride, 1:1 and 1:2 buffers of varying concentration, showing that catalysis is due to the basic and not to the acidic buffer constituent.

$k_{OH}{}^P$, the second-order coefficient for formation of 2,4-dinitrophenol from N-(2,4-dinitrophenyl)morpholine, has a considerable scatter among the experiments in Table II. When the sodium hydroxide concentration is low, $k_A{}^*$ is greatly favored over $k_{OH}{}^{P*}$; so the latter and, therefore, $k_{OH}{}^P$ cannot be determined precisely. At high sodium hydroxide concentrations, the ratio $k_{OH}{}^P/k_A{}^*$ is more suitable for a calculation; the average value of $k_{OH}{}^P$ among the experiments with 0.15 and 0.2 *M* sodium hydroxide added is 2.15×10^{-4} l. mole^{-1} sec^{-1}.

It is instructive to compare $k_{OH}{}^P$ with the rate coefficients for hydrolysis of other 1-substituted-2,4-dinitrobenzenes, the 1 substituent being the leaving group:[18] chlorine, 3.17×10^{-4} l. mole sec^{-1}; phenoxy, 4.6×10^{-4} l. mole^{-1} sec $^{-1}$; methoxy, 8.2×10^{-4} l. mole $^{-1}$ sec $^{-1}$; thiophenoxy 3.1×10^{-4} l. mole^{-1} sec^{-1}; 4-nitrophenoxy, 14.4×10^{-4} l. mole^{-1} sec^{-1}; 2,4-dinitrophenoxy, 29×10^{-4} [19] l. mole^{-1} sec^{-1}. It has been pointed out[7] that the dependence of the hydrolysis rate coefficient k_{OH} upon the leaving group is not much related to the propensity of the group to separate heterolytically from carbon.[20] The conclusion was that the reactions with hydroxide ion are likely to occur by the intermediate complex mechanism (eq 11) with the first step (k_1) rate determining. As a matter of fact, this mechansim predicts the over-all second-order rate constant to depend on the partial rate coefficients as shown in eq 12. When X is a "good" leaving group, $k_2 >> k_{-1}$ and eq 12 simplifies to $k_{OH} = k_1$. When X is a "poor" leaving group, $k_{-1} >> k_2$ and eq 12 becomes $k_{OH} = k_1k_2/k_{-1}$. For the six leaving groups listed above, the former inequality holds, and $k_{OH} = k_1$. Due to its high basicity, the morpholine moiety is certainly a much poorer leaving group than any one of the six groups listed above and might have been expected to bring about a change in the rate-determining step. However, $k_{OH}{}^P$ for the reaction of hydroxide ion with N-(2,4-dinitrophenyl)morpholine lies in the same order of magnitude as k_{OH} for most of the much better leaving groups. This probably means that the over-all rate is still determined by k_1 alone, a somewhat astonishing fact. Morpholine might be situated at the borderline between the conditions $k_2 >> k_1$ and $k_{-1} >> k_2$; when going to a still more basic leaving group, piperidine, $k_{OH}{}^P$ drops to 2.20×10^{-5} l. mole^{-1} sec^{-1}.[21] It is likely that now the expulsion of the amine moiety becomes partially rate limiting ($k_{OH} = k_1k_2/k_{-1}$).



(11)

$$k_{OH} = k_1k_2/(k_{-1} + k_2) \qquad (12)$$

Registry No.—Morpholine, 110-91-8; 2,4-dinitrophenyl phenyl ether, 2486-07-9; dioxane, 123-91-1; water, 7732-18-5.

Acknowledgment.—We thank Professors J. F. Bunnett and H. Zollinger for criticism and discussions.

[18] Taken from ref 7.

[19] Statistically corrected.

[20] The chloro compound, *e.g.*, has nearly the lowest k_{OH} value, lower than 2,4-dinitroanisole, although chlorine is probably the best and methoxy certainly is, by far, the poorest leaving group among the six.

[21] C. F. Bernasconi, unpublished data.

Some Claisen Rearrangements in Heterocyclic Systems

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The preparations and thermal rearrangements of 2-alloxybenzoxazole, 2-alloxybenzothiazole, 5-alloxy-1-phenyltetrazole, 5-crotoxy-1-phenyltetrazole, and 5-α-methalloxy-1-phenyltetrazole are described. 2-Alloxypyrimidine was prepared and upon heating it gave only traces of rearranged product. Neither 2-alloxypyrimidine nor 3-alloxy-1-phenylpyrazole underwent rearrangement at temperatures sufficient for the rearrangements of the alloxy derivatives of benzoxazole, benzothiazole, and 1-phenyltetrazole. The kinetics of the rearrangements of the three tetrazole ethers were each studied at three temperatures. The results are discussed with the aid of nuclear magnetic resonance, infrared, and ultraviolet spectroscopy.

Relatively little work has been conducted involving Claisen rearrangements within heterocyclic ring systems. Studies which have been made were carried out with substituted pyrimidines,[1-3] pyridines,[4,5] quinolines,[6-10] α-pyrones,[11a] and flavones.[11b] Other Claisen rearrangements have been studied in which a heterocyclic ring was present; however, the rearrangement sites were located in other portions of the molecule.

Results

5-Alloxy-1-phenyltetrazole (**1**) was prepared by the reaction of 5-chloro-1-phenyltetrazole with sodium alloxide in allyl alcohol at 60° (Scheme I). 5-Crotoxy-1-phenyltetrazole (**2**) and 5-α-methalloxy-1-phenyltetrazole (**3**) were prepared in a similar manner from

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[1] H. J. Minnemeyer, J. A. Egger, J. F. Holland, and H. Tieckelmann' *J. Org. Chem.*, **26**, 4425 (1961).

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[7] Y. Makisumi, *Tetrahedron Letters*, 699 (1964).

[8] Y. Makisumi, *Chem. Pharm. Bull.*, **12** (12), 1424 (1964).

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[10] A. E. Tschitschibabin and N. J. Jeletzsky, *Ber.*, **B57**, 1158 (1924).

[11] (a) V. M. Dashunin and M. S. Tovbina, *Zh. Obshch. Khim.*, **34** (5), 1438 (1964); (b) W. Heimann and H. Baer, *Chem. Ber.*, **98** (1), 114, (1965).