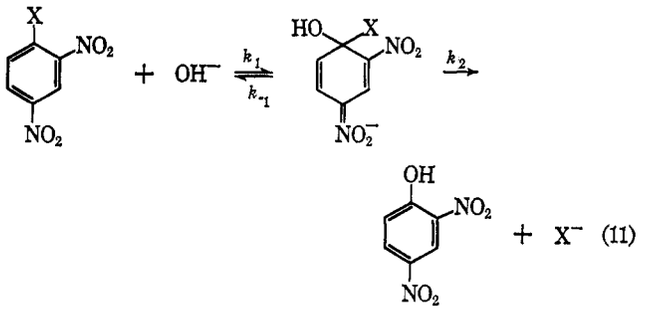
k_{OH}^{P}, the second-order coefficient for formation of 2,4-dinitrophenol from N-(2,4-dinitrophenyl)morpholine, has a considerable scatter among the experiments in Table II. When the sodium hydroxide concentration is low, k_A* is greatly favored over k_{OH}^{P}*; so the latter and, therefore, k_{OH}^{P} 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



(11)

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

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

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 ($k_{OH} = k_1k_2/k_{-1}$).

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

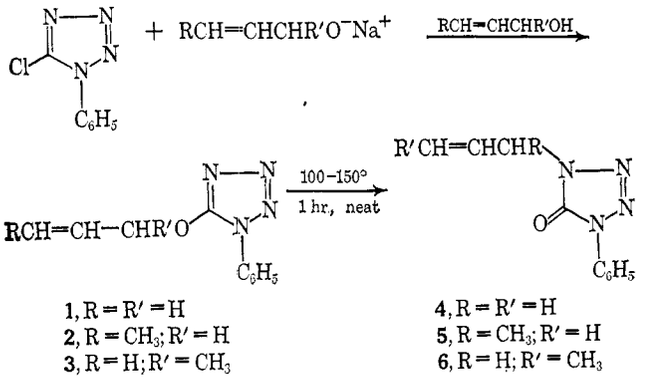
(1) H. J. Minnemeyer, J. A. Egger, J. F. Holland, and H. Tieckelmann, *J. Org. Chem.*, **26**, 4425 (1961).
(2) F. J. Dinan, H. J. Minnemeyer, and H. Tieckelmann, *ibid.*, **28**, 1015, (1963).
(3) H. J. Minnemeyer, P. B. Clarke, and H. Tieckelmann, *ibid.*, **31**, 406 (1966).
(4) R. B. Moffett, *ibid.*, **28**, 2885 (1963).
(5) F. J. Dinan and H. Tieckelmann, *ibid.*, **29**, 892 (1964).
(6) Y. Makisumi, *Chem. Pharm. Bull.*, **12** (7), 789 (1964).
(7) Y. Makisumi, *Tetrahedron Letters*, 699 (1964).
(8) Y. Makisumi, *Chem. Pharm. Bull.*, **12** (12), 1424 (1964).
(9) Y. Makisumi, *J. Org. Chem.*, **30**, 1986, 1989 (1965).
(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).

TABLE I

KINETIC RESULTS OF THE REARRANGEMENTS OF THE 5-ALKYL-1-PHENYLTETRAZOLES

Compd	$k \times 10^6$ sec^{-1}	Temp, °C	Order	Half-life	$\Delta E^{\pm}$, kcal/mole	$\Delta S^{\pm}$, eu
1	21.0 ± 2	110.8 ± 0.2	1	9.2 ± 1 hr	26.3 ± 2.1	−14 ± 5
	36.5 ± 3	116.5 ± 0.2	1	5.25 ± 0.5 hr		
	260.0 ± 30	141.0 ± 1.5	1	44.5 ± 5 min		
3	9.9 ± 0.4	64.6 ± 0.2	1	19.4 ± 0.8 hr	24.6 ± 1.4	−11 ± 4
	40.6 ± 3	77.3 ± 0.2	1	4.7 ± 0.3 hr		
	370.0 ± 30	101.7 ± 1	1	31.2 ± 3 min		
2	Nearly as	64.6 ± 0.4	2−			
	fast as 3	77.2 ± 0.2	1½+			
		101.5 ± 0.7	~1½			

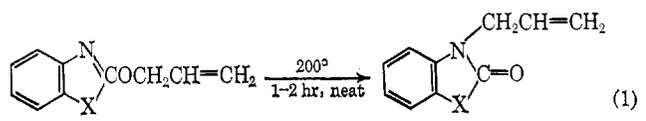
SCHEME I



1, R = R' = H
2, R = CH_3; R' = H
3, R = H; R' = CH_3

4, R = R' = H
5, R = CH_3; R' = H
6, R = H; R' = CH_3

the corresponding alcohols, but in these cases it was necessary to conduct the reactions at room temperature to avoid rearrangements of the ethers. The neat ethers readily rearranged with inversion in the manner of a normal Claisen rearrangement.[12] A kinetic study of these rearrangements is included at the end of the results. 2-Alloxybenzoxazole (**7**) and 2-alloxybenzothiazole (**8**) were prepared from the corresponding 2-chloro derivatives and rearranged easily to the ring nitrogen (eq 1). Ethers **7** and **8** were distillable under



(1)

7, X = O
8, X = S

9, X = O
10, X = S

reduced pressure with only slight rearrangement, whereas the tetrazole ethers **1–3** could not be distilled.

2-Alloxypyrimidine (**11**) was prepared from 2-chloropyrimidine by the standard procedure. This ether was surprisingly stable and under nitrogen at 200° for 2 days only slight rearrangements occurred, as evidenced by the gradual appearance of absorption bands at 1650 and 1525 cm^{-1}. 1-Allyl-2-pyrimidone (**12**), prepared by the alkylation of 2-pyrimidone in ethanol, exhibited its two strongest absorptions at precisely those wavenumbers. The possibility of these bands being due to 2-pyrimidone, the cleavage product, was unlikely since no absorption was observed at 1345 cm^{-1}, where 2-pyrimidone has its strongest absorption. No rearranged product was isolated and, hence, its existence is only suggested by the infrared spectrum. In the reverse experiment there was no evidence of rearrangement of 1-allyl-2-pyrimidone (**12**) to **11**.

3-Alloxy-1-phenylpyrazole (**13**),[13a] like the pyrimidine ether **11**, was stable under the mild conditions employed in the rearrangements of **1**, **2**, **3**, **7**, and **8**. However, at higher temperatures, 4-allyl-3-hydroxy-1-phenylpyrazole[13a] and 1-phenyl-2-allyl-3-pyrazolone (**14**)[13b] were produced, along with decomposition products and unidentified materials. Also, at 185° for 1 day, **14** rearranged to give 15–20% **13**, along with tarry material.

The structures of the ethers and their corresponding N-alkenyl isomers were confirmed by nmr, ultraviolet, and infrared spectroscopy (see Experimental Section). It is interesting to note that each of the tetrazole ethers **1–3** possessed phenyl resonance within the range τ 2.2–2.8, whereas the three N-alkenyl compounds exhibited shifted resonances for the *ortho* hydrogens which are apparently experiencing deshielding from the carbonyl group.

The unusually rapid rates of rearrangement of the tetrazole ethers (**1–3**) created an incentive to carry out a preliminary kinetic investigation of the reactions. The rearrangements were carried out neat. A first-order plot for the conversion of **1** to **4** gave a straight line at each of three temperatures. Activation energies and entropy changes were calculated (see Table I).[14]

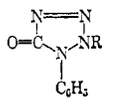
The rearrangement of the neat α-methalloxy ether (**3**) to the N-crotyl isomer (**6**) was first order, but the rearrangement of the crotoxy ether (**2**) was not and the order seemed to vary with the temperature (see Table I). This may mean that changing "solvent" properties are more important in this rearrangement than in the rearrangements of **1** and **3**.

Discussion

From the foregoing results, it is seen that the alloxy derivatives of the tetrazole (**1**), benzoxazole (**7**), and benzothiazole (**8**) easily rearrange, whereas 2-alloxypyrimidine (**11**) and 3-alloxy-1-phenylpyrazole (**13**) do not rearrange under similar conditions.

It is suggested that the rates of rearrangement of the ethers should correlate roughly with the degree of positive character of the ether oxygen together with the degree of nucleophilicity of the nitrogen to which the rearrangement occurs. Thus, the presence of

(12) The possibility that the rearranged products have structures bearing the alkenyl groups in the 2 position has not been rigorously eliminated; however, the structures seem unlikely particularly in view of the high carbonyl frequencies at 1725–1730 cm^{-1}.

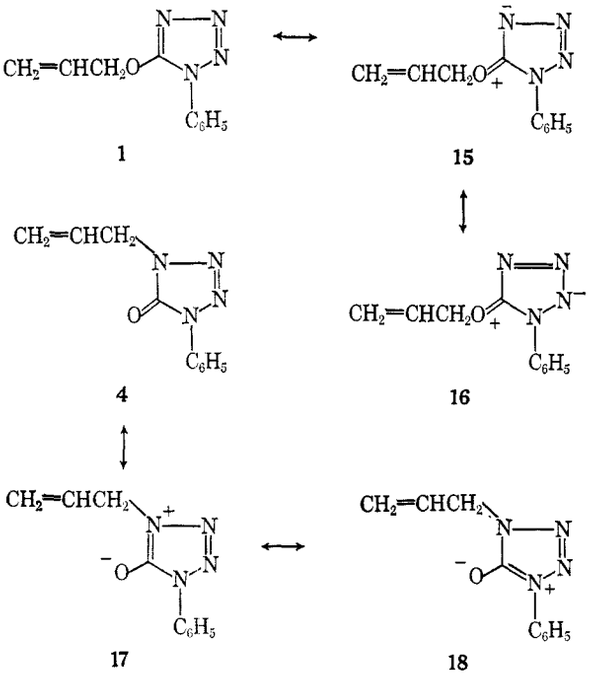


(13) (a) D. F. O'Brien and J. W. Gates, Jr., *J. Org. Chem.*, **31**, 1538 (1966); (b) D. F. O'Brien, private communication.

(14) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 8.

resonance structures such as **15** should accelerate the reaction to the thermodynamically more stable N-alkenyl isomer. An indication of the presence of resonance forms such as **15** in the ground state of **1** is obtained by making a comparison of the allyl allylmethylene (CH_2O) nmr resonance of **1** with that of **4** (CH_2N) (Scheme II). Contributions from resonance

SCHEME II



structures **15** and **16** should increase the chemical-shift differences between the methylene resonances of **1** (CH_2O) and **4** (CH_2N). Conversely, if resonance form **17** were important but only structure **1** were important for the ether, the chemical-shift difference would be decreased. Similar arguments can be applied to the other ethers studied.

The chemical-shift differences found for the tetrazole isomers (**1** and **4**), the benzoxazole isomers (**7** and **9**), and the benzothiazole isomers (**8** and **10**) were τ 0.53, 0.61, and 0.54, respectively. These were the ethers (**1**, **7**, and **8**) which were found to undergo facile rearrangements. However, the chemical-shift difference found for the pyrimidine isomers (**11** and **12**) was only 0.26. In accordance with this low value, 2-alloxypyrimidine (**11**) failed to rearrange under conditions sufficient for the rearrangements of **1**, **7**, and **8** even though 1-allyl-2-pyrimidone (**12**) is the thermodynamically favored product[15] (see Results).

The chemical-shift difference found for the 1-phenylpyrazole isomers (**13** and **14**) was τ 0.38 and would seem to indicate rearrangement facility intermediate between that of **11** and **1**, **7**, or **8**. However, the value for the methylene (NCH_2) resonance in 1-phenyl-2-allyl-3-pyrazolone (**14**) was probably abnormally high owing to shielding from the twisted phenyl group since the other allyl resonances for **14** were abnormally high (see Experimental Section). Therefore, the chemical-shift difference of τ 0.38 is probably high and ether **13** should be like **11** in rearrangement facility as was observed. At elevated temperatures, **13** leads to a mixture of **13** and **14** in addition to other products. Also **14** rearranges to give some **13**, indicating that at the elevated temperatures the two isomers must be of comparable thermodynamic stability.

(15) D. J. Brown in "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Vol. 16, Interscience Publishers, Inc., New York, N. Y., 1962, pp 249, 372.

Experimental Section

All melting points were run on a Thomas–Hoover Unimelt apparatus and are corrected. Nmr spectra were measured with a Varian A-60 spectrometer using $CDCl_3$ as solvent unless otherwise indicated. Peak positions are expressed in parts per million relative to an internal tetramethylsilane standard (τ 10). The ultraviolet absorption spectra were obtained in ethanol ($\sim 10^{-4}$ *M*) with a Cary 11 spectrophotometer and values are expressed in millimicrons followed by the logarithm of the extinction coefficient. The infrared spectra were taken on a Perkin-Elmer Infracord, Model 137 as potassium bromide pressings or smears and are expressed as wavenumbers (cm^{-1}). The symbols s, d, t, q, or m indicate that resonance appears mainly as a singlet, doublet, triplet, quartet, or multiplet, respectively, at a sweep width of 500 cps.

5-Alloxy-1-phenyltetrazole (**1**).—5-Chloro-1-phenyltetrazole (90.25 g 0.5 mole) was added portionwise to a 50° solution of sodium alloxide prepared by the addition of sodium (12.6 g, 0.55 mole) to 300 ml of cooled allyl alcohol. The addition was conducted at such a rate that the temperature was maintained between 55 and 60°. The resulting solution was heated at 60° for 30 min.

The reaction mixture was cooled, filtered, and evaporated under reduced pressure at 55°. The resulting oil dissolved in ether was washed with water and dried with anhydrous magnesium sulfate. The ether was evaporated under reduced pressure at 55° for 2 hr to give 86.1 g (85.3%): λ_{max} 239.5 (4.02); ν (ROC=N–) 1560; τ 4.89 (d) (CH_2O), 2.2–2.7 (m) (aryl), and 4.6 (m) (CH_2=).

Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.4; H, 4.95; N, 27.7. Found: C, 59.5; H, 5.1; N, 27.6.

5-Crotoxy-1-phenyltetrazole (**2**).—5-Chloro-1-phenyltetrazole (18.1 g, 0.1 mole) was treated with a solution of sodium crotoxide (0.11 mole) in crotyl alcohol and left at room temperature overnight. The salt was filtered and the filtrate was evaporated at 40–45° (<1 mm) for several hours. The crude oil in ether was washed with water, dried with anhydrous magnesium sulfate, filtered, and evaporated. The oil which solidified was recrystallized from petroleum ether (bp 30–35°): mp 32–33°; 12.4 g, 59.5%; λ_{max} 230 (4.03); ν (ROC=N–) 1555; τ 8.26 (m) (CH_3), 4.98 (m) (CH_2O), 2.2–2.8 (m) (aryl) (nmr spectra in CCl_4).

Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.2; H, 5.55; N, 25.9. Found: C, 61.4; H, 5.8; N, 25.5.

5-α-Methalloxy-1-phenyltetrazole (**3**) was prepared by the procedure used for **2**: mp 34–35° (from petroleum ether); yield 85.2%; λ_{max} 232 (4.02); ν (ROC=N–) 1550; τ 8.40 (d) (CH_3), 2.2–2.7 (m) (aryl), 4.6 (m) (CH_2=).

Anal. Found: C, 61.0; H, 5.9; N, 25.7.

4-Allyl-1-phenyl-5-tetrazolone (**4**).—A few grams of **1** was heated neat at 200° for 1 hr (under these conditions rearrangement was nearly complete): bp 120° (0.55 mm); λ_{max} 249 (4.01), 258 (sh), 271 (sh), 279 (sh); ν (C=O) 1725; τ 5.42 (d) (CH_2N), 1.9–2.2 (m) (aryl *ortho*), 2.4–2.8 (aryl *meta* and *para*), 4.7 (m) (CH_2=).

Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.4; H, 4.95; N, 27.7. Found: C, 59.8; H, 5.1; N, 27.6.

4-α-Methallyl-1-phenyl-5-tetrazolone (**5**).—A few grams of **2** was heated at 120° for several hours: bp 122–123° (0.7 mm); λ_{max} 249 (4.035), 258 (sh), 271 (sh), 279 (sh); ν(C=O) 1725; τ 8.40 (d) (CH_3), 5.1 (m) (CH), 1.9–2.1 (m) (aryl *ortho*), 2.4–2.8 (aryl *meta* and *para*), 4.7 (m) (CH_2=) (nmr spectra in CCl_4).

Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.2; H, 5.55; N, 25.9. Found: C, 61.4; H, 5.7; N, 26.1.

4-Crotyl-1-phenyl-5-tetrazolone (**6**).—A few grams of **3** was heated neat at 120° for 2–3 hr (temperatures >150° led to rapid decomposition): mp 53.5–55.5 (from petroleum ether); λ_{max} 249 (4.03), 258 (sh), 271 (sh), 279 (sh); ν (C=O) 1730; τ 8.30 (m) (CH_3), 5.41 (m) (CH_2N), 1.9–2.2 (m) (aryl *ortho*), 2.4–2.8 (aryl *meta* and *para*).

Anal. Found: C, 61.0; H, 5.9; N, 25.7.

2-Alloxybenzoxazole (7).—2-Chlorobenzoxazole (15.35 g, 0.1 mole) was treated with a cold solution of sodium alloxide (0.11 mole) in allyl alcohol. It was necessary to keep the reaction cold since 2-chlorobenzoxazole reacts exothermically with allyl alcohol, with the separation of 2-benzoxazolinone. The mixture was permitted to warm gradually to room temperature, with stirring, overnight. The reaction mixture was filtered, evaporated, and washed in ether with water as before. The crude dry product was distilled at 71–72° (0.5–0.6 mm) to give 14.0 g (80%): λ_{max} 276 (3.59), 270 (3.64), 229 (4.095), 265 (sh); ν (ROC=N–) 1570, 1620; τ 5.02 (d) (CH_2O), 2.5–3.0 (m) (aryl), 4.6 (m) (CH_2=).

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.6; H, 5.14; N, 8.0. Found: C, 68.9; H, 5.4; N, 8.1.

2-Alloxybenzothiazole (8).—2-Chlorobenzothiazole (16.95 g, 0.1 mole) was treated with sodium alloxide (0.11 mole) in allyl alcohol by the same procedure used to prepare **7**. The oil distilled at 89–90° (0.6–0.7 mm) to give 13 g (68%): λ_{max} 288 (3.03), 278 (3.025), 246 (3.93); ν (ROC=N–) 1530; τ 4.98 (m) (CH_2O), 2.3–3.0 (m) (aryl), 4.7 (m) (CH_2=).

Anal. Calcd for $C_{10}H_9NOS$: C, 62.8; H, 4.7; N, 7.33; S, 16.75. Found: C, 63.0; H, 4.7; N, 7.1; S, 16.5.

3-Allyl-2-benzoxazolinone (9).—A few grams of **7** was heated at 200° for 1 hr. The resulting solid was recrystallized from petroleum ether: mp 40–41.5° (lit.[16] mp 41–43°); λ_{max} 274 (ϵ 3.68), 228 (3.95), 280 (sh); ν (C=O) 1770; τ 5.63 (m) (CH_2N), 2.8–3.2 (m) (aryl), 4.7 (m) (CH_2=).

Anal. Found: C, 68.2; H, 5.0; N, 8.0.

3-Allyl-2-benzothiazolinone (10).—A few grams of **8** was heated at 230° for 2 hr: bp 112–114° (0.6–0.65 mm) (lit.[17] bp 155–157° (3 mm)); λ_{max} 288 (3.46), 282 (3.46), 243 (3.75); ν (C=O) 1670; τ 5.52 (m) (CH_2N), 2.5–3.2 (m) (aryl), 4.8 (m) (CH_2=).

Found: C, 62.8; H, 4.9; N, 7.0; S, 16.7.

2-Alloxypyrimidine (11).—2-Chloropyrimidine (11.45 g, 0.1 mole) was treated with sodium alloxide (0.11 mole) in allyl alcohol as before: bp 50–52° (0.5 mm); yield 9.0 g (66.2%); λ_{max} 267 (3.60), λ_{max} (for 2-methoxypyrimidine) 267 (3.66);[18] ν (ROC=N–) 1565; τ 5.08 (m) (CH_2O), 3.02 (t) (5-H aryl), 1.45 (d) (4- and 6-H aryl), 4.7 (m) (CH_2=).

Anal. Calcd for $C_7H_8N_2O$: C, 61.75; H, 5.88; N, 20.60. Found: C, 61.4; H, 5.8; N, 20.4.

1-Allyl-2-pyrimidone (12).—2-Pyrimidone hydrochloride (2.0 g, 0.015 mole) was dissolved in ethanol (50 ml) containing sodium ethoxide (0.03 mole). Allyl bromide (2.2 g, 0.018 mole) was added and the mixture was refluxed until the solution was no longer alkaline. The ethanol was removed and the residue was extracted with chloroform and filtered. The filtrate was chromatographed on alumina, after which the chloroform was removed. The syrup solidified to give crude product which was recrystallized from acetone–petroleum ether: mp 62–64°; yield 1.5 g (73.5%); λ_{max} 216 (3.98), 312 (3.71), λ_{max} (for 1-methyl-2-pyrimidone) 215 (4.0), 302 (3.73);[19] ν (C=O) 1650; τ 5.34 (m) (CH_2N), 1.90 (q), 3.50 (q), 1.33 (t) (aryl), 4.7 (m) (CH_2=).

Anal. Found: C, 61.8; H, 6.1; N, 20.4.

Attempted Thermal Rearrangement of 1-Allyl-2-pyrimidone.—**12** (2 g) was heated neat under nitrogen at 250° for several hours. Only decomposition occurred. The infrared spectrum exhibited no new bands over those of **12** even in regions of absorption of **11**.

3-Alloxy-1-phenylpyrazole (13) was prepared by the alkylation of 3-hydroxy-1-phenylpyrazole with allyl bromide in acetone containing suspended anhydrous potassium carbonate according to the procedure of O'Brien and Gates:[13a] bp 117–120° (0.15 mm); ν (ROC=N–) 1550; τ 5.26 (m) (CH_2O), 2.3–3.0 (m) (aryl), 4.7 (m) (CH_2=).

1-Phenyl-2-allyl-3-pyrazolone (14).[13b]—A solution of 3-hydroxy-1-phenylpyrazole (16.0 g, 0.1 mole), allyl bromide (12.0 g, 0.1 mole) and sodium hydroxide (4.0 g, 0.1 mole) in 200 ml of water was stirred under nitrogen at room temperature for 3 days. The reaction mixture was acidified and extracted with benzene. The aqueous phase was saturated with sodium chloride and continuously extracted with ether for 2 days. The extracts were combined, washed with 10% sodium hydroxide, washed with water, and then were dried with anhydrous magnesium sulfate. After removal of the solvents, the resulting yellow liquid was fractionated to give 35% yield of **13**: ν (C=O) 1655; τ 5.64 (m) (CH_2N), 2.4–2.9 (m) (aryl), 5.1 (m) (CH_2=); the (=CH–) resonance region was higher than that of any of the other compounds discussed.

Thermal Rearrangement of 3-Alloxy-1-phenylpyrazole (13).—Compound **13** was heated at 190° for 1 day. The infrared spectrum of the crude reaction mixture indicated the presence of a considerable amount of **14**. O'Brien and Gates have prepared 4-allyl-3-hydroxy-1-phenylpyrazole[13a] by heating **13** at 265° for 1 hr neat or in N,N-diethyl-*m*-toluidine. Careful analysis of this reaction mixture has yielded unreacted **13** (10.3%) and **14** (28.6%), as well as the 4-allyl-3-hydroxy-1-phenylpyrazole (53.9%).[13b]

Thermal Rearrangement of 1-Phenyl-2-allyl-3-pyrazolone (14).—Compound **14** was heated at 190° for 1 day. The infrared spectrum of the crude reaction mixture suggested the presence of some **13**. When the nmr spectrum of the crude reaction mixture was compared with that of pure **14**, it was apparent that some **13** was present from the appearance of the two doublets owing to the 4-H (τ 4.12) and 5-H (2.26) pyrazole ring hydrogens of **13**. These resonances are well separated from the corresponding resonances of **14** and 3-hydroxy-1-phenylpyrazole, as well as from the 5-H (2.55) of 4-allyl-3-hydroxy-1-phenylpyrazole.

Kinetic Measurements of the Rearrangements of the Tetrazole Ethers (1–3).—The rearrangements were carried out neat in a tube suspended in vapors over refluxing liquids and thoroughly checked to give the indicated temperature precisions. Actually, the limiting factor in the accuracy of the results was the determination of the concentrations, not the temperature control. In all cases the samples were open to the air during rearrangement.

The rearrangement of **1** was followed by a change in the index of refraction. Pure **1** exhibited an $n^{25.6}D$ 1.5527, whereas the N-allyl isomer (**4**) possessed an $n^{25.6}D$ 1.5608. Measurements of the indices of refraction of a series of known mixtures of the two pure isomers, when plotted *vs.* concentration, furnished a straight line and indicated a maximum deviation of ±2% for the method.

A first-order plot of the rearrangement of **1** gave a straight line at each of the three temperatures. The rate constants and corresponding temperatures were used to construct an Arrhenius plot from which the activation energy was obtained. Also the frequency factor of the Arrhenius equation was used to obtain the entropy of activation[14] (see Table I).

The rearrangement of **2** was followed in the ultraviolet at 278 mμ where **2** has ϵ ~83.5 and the N-methallyl isomer (**5**) has ϵ ~1837. Plots of known mixtures indicated that an accuracy of ±1–2% was obtainable. The rearrangement of **3** was followed at 279 mμ where **3** has ϵ ~71 and the N-crotyl isomer (**6**) has ϵ ~1847. An accuracy of ~±1–2% was obtainable.

Registry No.—**1**, 13437-77-9; **2**, 13449-06-4; **3**, 13444-09-2; **4**, 13444-10-5; **5**, 13449-07-5; **6**, 13444-11-6; **7**, 13444-12-7; **8**, 13444-13-8; **9**, 13444-14-9; **10**, 13449-08-6; **11**, 13444-15-0; **12**, 13444-16-1; **13**, 7409-27-0; **14**, 13444-18-3.

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