M). Reaction was started by adding 10 μL of the substrate stock solution with use of a microsyringe into a 3-mL buffer solution equilibrated at 30 ± 0.1 °C in a stoppered quartz cuvette inserted in a water-jacketed cell holder. The reaction was followed by the decrease in the absorption at about 237 nm or the increase in that at 226 nm (at pH >10), using a Shimadzu UV 200 spectrophotometer. The values of pH of buffer and reaction solutions were determined by a Hitachi-Horiba CTE F-5 pH meter.

Acknowledgment. We thank S. Kawao for his assistance in some kinetic measurements.

Registry No. **1a**, 63860-13-9; **1b**, 76334-32-2; **1c**, 76334-33-3; **2**, 35468-63-4; **3**, 928-47-2; $B(OH)_3$, 10043-35-3.

Imidoyl Azide to Tetrazole Cyclization Limited by Internal Hydrogen Bonding and Imine Isomerization

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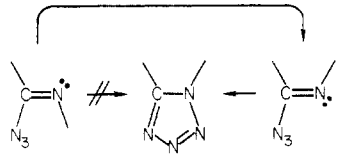
Received September 18, 1980

The rates of cyclization of the 2-azido-3-benzoyl enamine **6** to the corresponding tetrazole **9** have been measured in D_2O as a function of pD at 25 °C. A complex pD–rate profile is observed with a maximum rate at a pD of ca. 2.0. The observed rate constants are reduced (typically 7-fold) in D_2O in those regions where proton transfer to the enamine is rate determining; however, the actual rate of isomerization about the iminium ion intermediate ($C{=}N^+$) remains unchanged in D_2O, indicating that the solvent most likely does not add reversibly in the slow step for isomerization. The imidoyl azide **15** is stabilized in the open-chain azido form by internal hydrogen bonding to the *o*-OH group. Both the neutral (**15**) and anionic (**16**) forms cyclize to the tetrazole **18**, the latter 35-fold more rapidly. The protonated species **17** does not cyclize to the tetrazole and is inert to hydrolysis.

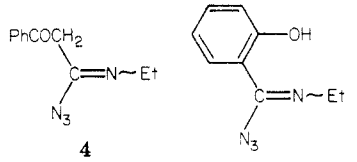
In the previous papers in this series[2,3] we have shown that those imidoyl azides which have been isolated as such, rather than as the isomeric tetrazole **2**, are stabilized in the azido form due to stereochemical factors: the azido group is trans to the lone pair on the adjacent nitrogen (**1**).



1 **2** **3**

Only the *E* isomer **3** is able to cyclize directly to the tetrazole **2**, so that the slow step is $Z \rightarrow E$ (**1** → **3**) isomerization. Reflecting this, most of those imidoyl azides reported in the literature have substitutents which would specifically be expected to slow this nitrogen inversion.

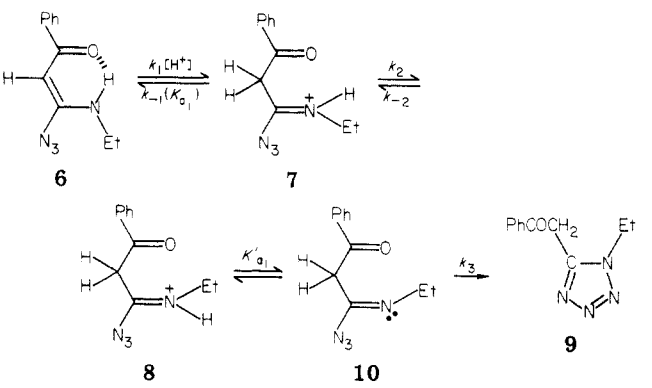
The azide **4** reported by Woodard and co-workers[4] was



4 **5**

an apparent exception to this since, in the absence of other factors, nitrogen inversion should be rapid in this case. We have shown, however,[2] that this group of azides actually has the hydrogen-bonded enamine structure **6**. Cyclization of **6** to the tetrazole **9** occurs only subsequent to proton transfer to carbon (to give **7**) and $Z \rightarrow E$ isomerization of the protonated substrate, which yields an imidoyl azide, **10**, correctly oriented for cyclization to **9** (Scheme I). Either of the precyclization steps (proton transfer, **6** → **7**, or iminium ion isomerization, **7** → **8**) can be rate determining (dependent on pH) but not the cyclization step (**10** → **9**) itself.

Scheme I



6 **7** **8** **10** **9**

However, important questions have remained unanswered. At low pH, or in the presence of an "infinite" concentration of general-acid catalysts, the rate-determining step for the conversion of **6** to **9** is the isomerization about the $C{=}N^+$ bond (**7** → **8**).[2] This could occur either as a spontaneous process or via an addition–elimination (involving the solvent or other nucleophilic species). In related iminium salts there is support (sometimes conflicting) for both processes in the literature,[5-8] while the

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(2) P. Ahern, K. J. Dignam, and A. F. Hegarty, *J. Org. Chem.*, **45**, 4302 (1980).

(3) (a) A. F. Hegarty, K. Brady, and M. Mullane, *J. Chem. Soc., Perkin Trans. 2*, 535 (1980); (b) A. F. Hegarty, K. Brady, and M. Mullane, *J. Chem. Soc., Chem. Commun.*, 871 (1978).

(4) R. B. Woodward and R. A. Olofson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).

(5) W. B. Jennings, S. Al-Showiman, M. S. Tolley, and D. R. Boyd, *J. Chem. Soc., Perkin Trans. 2*, 1535 (1975).

(6) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15** 311 (1970).

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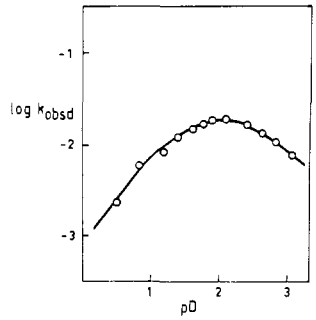


Figure 1. Plot of log k_{obsd} (k_{obsd} in s^{-1}) against pD for the cyclization of the azide **6** to the tetrazole **9** in D_2O (at 25 °C; μ = 1.0, KCl). The points are experimental, and the curve was drawn by using eq 1 with the values of the constants given in Table I.

Table I. Derived Rate Constants for the Cyclization of the Azide 6 to the Tetrazole 9[a]

solvent	k_2	K_1	K_2[d]	K_3	K_{a_1}
H_2O[b]	2.5×10^{-1}	2.29×10^{-2}	5.34×10^{-3}	1.44×10^{-2}	8.49×10^{-3}
D_2O	3.08×10^{-2}	2.63×10^{-2}	2.00×10^{-3}	2.41×10^{-2}	2.18×10^{-3} [c]

[a] At 25 °C (μ = 1.0, KCl). [b] See ref 2. [c] A value of 2.19×10^{-3} was obtained at "infinite buffer concentration" (Figure 2), and 2.24×10^{-3} was obtained spectrophotometrically. [d] Equal to $K_{a_1}K_3/K_1$.

factors which favor a given pathway remain unclear. We have now investigated the involvement of the solvent (water) in the conversion of 7 → 8 by following this reaction in D_2O.

We have also sought an imidoyl azide, isolable in the open-chain form, whose structure is analogous to **4**. This we have found in the *o*-hydroxyphenyl series **5**. This cyclizes to the corresponding tetrazole in aqueous solution, and by investigating the mechanism of cyclization, we have identified a new factor (the presence of intramolecular H bonding to nitrogen) which is responsible for the stabilization of open-chain imidoyl azides.

Results and Discussion

Cyclization of the Azide 6 in D_2O. Figure 1 summarizes the kinetic data obtained by following the rate of cyclization of **6** to **9** at 25 °C as a function of the pD of the solution. As in H_2O, the observed rate constants vary in a complex way with acidity, passing through a maximum at pH (or pD) ca. 2.0. This is attributable[2] to a changeover in the rate-determining step from proton transfer to the carbon of the "enamine" **6** (to give **7**) above pH 2.0 to rate-determining conversion of **7** to **8** (at low pH). The observed rate constants for cyclization are markedly lower at all pH's and are correlated by the empirical equation (eq 1) which can be derived[2,9] on the basis of Scheme I for

$$k_{obsd} = \frac{k_2K_3a_H}{a_H^2 + (K_3 + K_{a_1})a_H + K_3K_{a_1}} \quad (1)$$

a reaction which shows a "bell-shaped" dependency of k_{obsd} on pH. The constants which best fit the kinetic results are summarized in Table I ($K_3 = k_3K_{a'_1}/k_{-2}$; $K_1 = K_3 + K_{a_1}$).

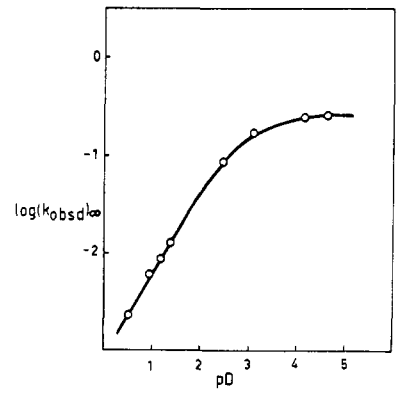
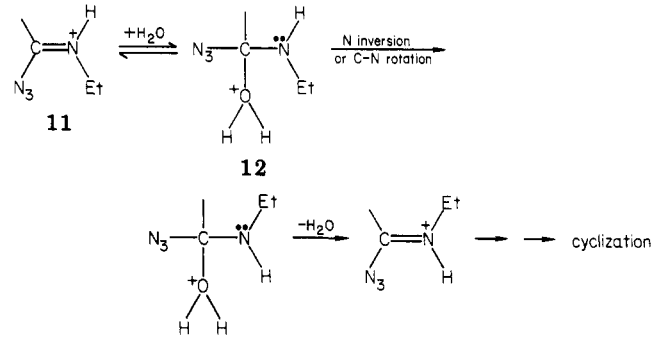


Figure 2. Plot of the observed rate of cyclization of **6** to **9** in D_2O at "infinite buffer concentration" as a function of pD. These values were obtained by extrapolation of double-reciprocal plots (see text). The line was drawn with $(k_{obsd})_\infty = kK_{a_1}/(a_H + K_{a_1})$ where $k = 2.51 \times 10^{-1}$ and $K_{a_1} = 2.19 \times 10^{-3}$.

Scheme II



The pK_a of **6** was also determined spectrophotometrically in D_2O; the value obtained was 2.65. This represents a ΔpK_a on transfer from H_2O to D_2O of 0.59 pK_a unit, which is clearly within the range expected (0.5–0.7) for acids with pK_a's in this region.[10] The value is also in excellent agreement with the value of pK_{a_1} required to fit the observed kinetic data to the theoretical equation derived from Scheme I (see Table I).

Buffer Catalysis in D_2O. General-acid catalysis of the cyclization of **6** to **9** is observed in H_2O over the pH region where proton transfer to **6** is rate determining (or partly rate determining). At low buffer concentration the observed rate constant is directly proportional to the concentration of added acid; as expected general-acid catalysis shows a primary isotope effect, determined as 6.9 for HOAc–DOAc.[2]

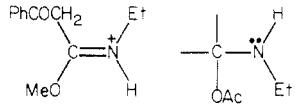
At high buffer concentration, the k_{obsd} vs. buffer plots become nonlinear since the subsequent $Z \rightarrow E$ isomerization (7 → 8) becomes rate limiting. Accurate values of the predicted values of (k_{obsd}) in the presence of "infinite" buffer concentration can be obtained[2] by extrapolation of $1/k_{obsd}$ vs. 1/[buffer] plots. We have shown the values obtained by these extrapolations (as a function of the pD of the solution) in Figure 2. It is seen that they describe a simple titration curve with an apparent pK_a value of 2.65. More importantly, the maximum value of the extrapolated rate constants (which occurs at pD's >4) is 2.52×10^{-1} s^{-1} in D_2O. It has previously been demonstrated that this represents k_2, the rate of $Z \rightarrow E$ isomerization of the protonated substrate (Scheme I). The value for this rate in H_2O has previously been determined as 2.7×10^{-1} s^{-1}.[2]

(7) K. J. Dignam and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, 1437 (1979).
(8) A. C. Satterthwait and W. P. Jencks, *J. Am. Chem. Soc.*, **96**, 7031 (1974).
(9) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms", Vol. 1, W. A. Benjamin, New York, 1966.
(10) R. P. Bell, "The Proton in Chemistry", 2nd ed., Chapman and Hall, London, 1973, Chapter 11.

The values are thus essentially the same in D_2O and H_2O.

The identity of the rates of $Z \rightarrow E$ isomerization of the protonated imine in D_2O and H_2O is strong evidence that the solvent does not reversibly add to the iminium ion (Scheme II) in a step which is kinetically significant, and we therefore conclude that the iminium ion **7** undergoes spontaneous isomerization. If H_2O was acting as a nucleophile in the slow step (to give, say, **12**), then since D_2O is a significantly weaker nucleophile than H_2O (k_{H_2O}/k_{D_2O} = 2.2, typically for those reactions where water is acting as a nucleophile toward acyl carbon in the slow step[11]), the overall rate of $Z \rightarrow E$ isomerization would be slowed. The only case in which there might be fortuitously the same rate of reaction (while involving the reversible addition of H_2O or D_2O) would occur if loss of H_2O (or D_2O) were rate determining (see Scheme II) and the isotope effects in the addition and elimination steps cancel.

However, rapid nucleophilic attack by water on **11** is unlikely on two further grounds. (a) No hydrolytic products are observed; **6** is smoothly and quantitatively converted to the tetrazole **9**. Moreover, the corresponding protonated methoxy analogue **13** is quite resistant to hydrolysis, even under forcing conditions. (b) At high concentrations of acetate buffer, the observed rate of $Z \rightarrow E$ isomerization tends to a constant value (see Figure 2) which is independent of [AcO^-]. If H_2O were adding reversibly to **11** to promote $Z \rightarrow E$ isomerization, then it would be expected that AcO^- would act even more effectively (indeed, such an addition–elimination mechanism has previously been proposed[5] for the benzoic acid catalyzed isomerization of simple imines) via an intermediate such as **14**. This can, however, be effectively ruled out by the observation that AcO^- does not catalyze $Z \rightarrow E$ isomerization at high [AcO^-].



13 14

Cyclization of *o*-Hydroxy-*N*-ethylbenzimidoyl Azide (5). The method used for the preparation of this azide from *N*-ethyl-5-phenylbenzisoxazolium cation was similar to that described by Kemp and Woodward,[12] except that we isolated the material as a light yellow solid. Otherwise our spectroscopic evidence agrees with that presented by these authors and we also conclude that the major tautomer present is the *o*-hydroxy material **5**. In particular, the absence of a quintet for the NCH_2CH_3 protons (observed for **6**) would seem to rule out any tautomers containing the $NHCH_2CH_3$ grouping. It is clear, therefore, that **5**, unlike **6**, is a true imidoyl azide which is relatively stable in the open-chain (azido) form. The azide **5** could readily be prepared under acidic conditions (where it is relatively stable as shown below) and stored at 0 °C but cyclizes rapidly to the tetrazole **18** on being heated in an inert solvent or at higher pH.

Kinetics of Cyclization of 5 to 18. The rates of cyclization of the imidoyl azide **5** vary in a complex way with pH, as shown by the plot of k_{obsd} against pH in Figure 3. The rate constants were measured at 25 °C in water, with the ionic strength being maintained constant by the addition of KCl and the pH being maintained (where necessary) by a pH stat or by low concentrations of added buffers (with extrapolation to zero buffer concentration).

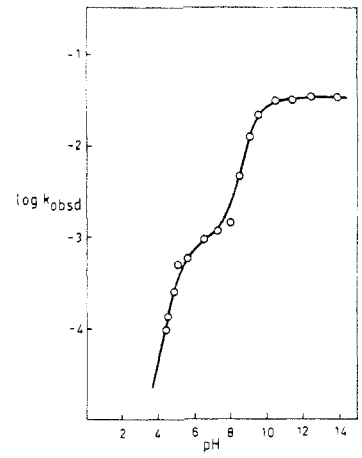
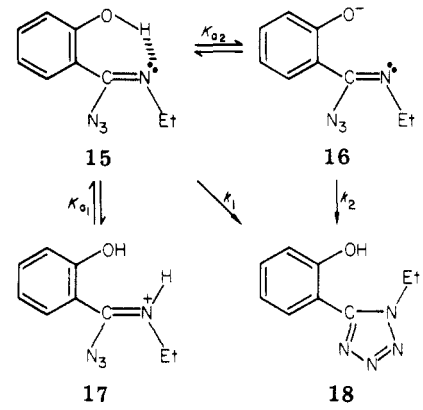


Figure 3. pH–rate profile for the cyclization of the azide **15** to the tetrazole **18** in water at 25 °C (k_{obsd} in s^{-1}; μ = 1.0, KCl). The line was drawn by using eq 2 with the values for the constants given in the text.

Scheme III



15 16 17 18

Although the observed behavior of **5** (as shown in Figure 3) is apparently quite different from that of **6** (as shown in Figure 1 in D_2O or in the full pH–rate profile in H_2O; see Figure 1 of ref 2 which also shows base catalysis at high pH), both can be analyzed in terms of the same overall rate law; only the relative magnitudes of the individual rate and equilibrium constants have changed. The solid line in Figure 3 was drawn by using eq 2, with the following values for the rate constants: $k_1 = 8.9 \times 10^{-4}\ s^{-1}$, $k_2 = 3.16 \times 10^{-2}\ s^{-1}$, $K_{a_1} = 5.65 \times 10^{-6}$, $K_{a_2} = 3.98 \times 10^{-10}$.

$$k_{obsd} = \frac{k_1 K_{a_1}}{a_H + K_{a_1}} + \frac{k_2 K_{a_2}}{a_H + K_{a_2}} \qquad (2)$$

A mechanism consistent with this behavior is shown in Scheme III. At low pH the imidoyl system is fully protonated to give **17**, which is inert (does not cyclize). As the acidity of the solution is decreased, the free base **15** is formed; this undergoes uncatalyzed cyclization. Since there is good spectroscopic evidence for the existence of an internal hydrogen bond in **15**, it is likely that it is this factor which slows the rate of nitrogen inversion and consequently stabilizes the azide **15** in the open-chain form. It has been shown[13] that proton transfer from a strongly hydrogen bonded substrate (e.g., salicylate monoanion) occurs via (diffusion controlled to HO^-) reaction of the

(11) See, for example, S. M. Felton and T. C. Bruice, *Chem. Commun.*, 907 (1968).
(12) D. S. Kemp and R. B. Woodward, *Tetrahedron*, **21**, 3019 (1965).
(13) F. Hibbert and A. Awwal, *J. Chem. Soc., Chem. Commun.*, 995 (1976).
(14) See, for example, J. S. Meek and J. S. Fowler, *J. Am. Chem. Soc.*, **89**, 1967 (1967).

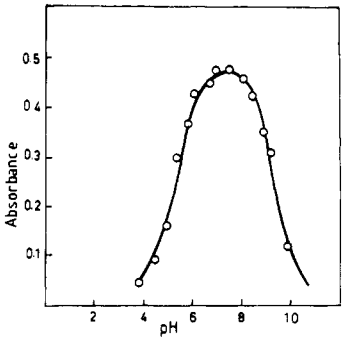
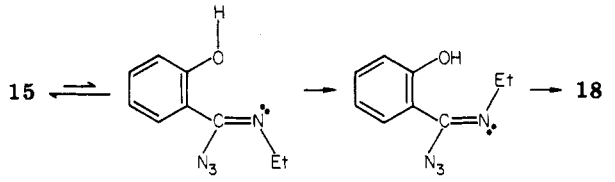


Figure 4. Spectrophotometric determinations of the pK_a's of the azide **15**: the points are experimental, and the line is theoretical (see eq 3) with $pK_{a_1} = 5.25$ and $pK_{a_2} = 9.4$.

non-hydrogen-bonded form which is present in low equilibrium concentrations. On this basis, nitrogen inversion may occur via **19** to give **20** (where the azido group and the lone pair on the adjacent nitrogen have the required cis relationship) and thus the tetrazole **18**.



19 **20**

At higher pH, the concentration of the anion **16** becomes significant, so that at pH >8, essentially all of the reaction occurs via this species. In the anion **16**, the internal hydrogen bond is no longer present so that nitrogen inversion can occur more rapidly than in **15**.

Spectrophotometric determination of the values of pK_{a_1} and pK_{a_2} are consistent with this scheme. At 390 nm the major species absorbing is the neutral material **15**. A plot of optical density at this wavelength against pH is therefore "bell shaped" and shows a maximum at pH ca. 7 (see Figure 4); the decrease at higher and lower pH's is due to the conversion of **15** to **16** and to **17**, respectively. The observed optical density (OD_{obsd}) is related to the maximal value (OD_{max}) by eq 3 to give the line drawn in Figure 4.

$$OD_{obsd} = \frac{OD_{max} K_{a_1} a_H}{a_H^2 + a_H K_{a_1} + K_{a_1} K_{a_2}} \quad (3)$$

The values of pK_{a_1} and pK_{a_2} determined by the fit of eq 2 to the observed data are 5.25 and 9.40, respectively. Thus the two spectrophotometric pK_a's are identical with those required to fit the kinetic data. The assignment of the pK_a's to the ionizations shown in Scheme III is straightforward; a point of interest is the high value (9.4) for pK_{a_2} in spite of the presence of the strongly electron-withdrawing *o*-(C(N_3)=NEt) group. This is undoubtedly attributable to the presence of an internal hydrogen bond in **15**.

Weak buffer catalysis of cyclization is noted for borate and phosphate buffers in the pH region <10. From plots of k_{obsd} against buffer concentration, it is clear (see Figure 5) that the basic component of the buffer is the active species; i.e., apparent general-base catalysis is being observed. Above pH 10 where the substrate is converted to the anion **16**, no catalysis is observed (e.g., $k_{obsd} = 3.22 \pm 0.02$ at pH 11.5 and 3.21 ± 0.01 at pH 12.5 when phosphate buffer concentration is varied from 0.001 to 0.5 M). This would eliminate an addition–elimination mechanism for isomerization (analogous to that described above for **6**) involving either addition of the buffer species itself or

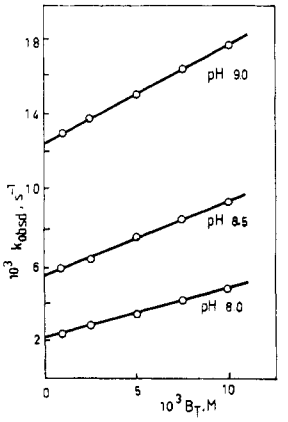


Figure 5. Plot of k_{obsd} against total borate buffer concentration for the cyclization of the azide **15** in water at 25 °C.

assisted addition of water to **15**. While several modes of the involvement of the general base could be envisaged, the most likely is the stabilization of the intermolecularly hydrogen bonded form **19**, thus enhancing nitrogen inversion.

It is interesting to compare the relative rates of cyclization of **5** and **6**, which are present in different tautomeric forms. The most obvious difference is the absence of an acid-catalyzed cyclization pathway for **5**; thus while moderate acidities increase the rate of $Z \rightarrow E$ isomerization of **6** (and thus cyclization), **5** is inert in acid. This may be due to the presence of an internal hydrogen bond with the *o*-OH group in the protonated substrate which therefore resists isomerization about the C=N^+ bond. In basic solution, the cyclization of **6** to **9** also shows a term in the rate equation which is proportional to [HO^-]; however, the rate of cyclization does not become pH independent, even at pH 13 (where $t_{1/2}$ for cyclization is <1 s). Clearly, therefore, the pK_{a_2} of **15** (loss of the phenolic OH) is lower than the corresponding value for **6** (loss of NH), and the rate of cyclization of the conjugate base (with more negative charge concentrated on nitrogen) is consequently faster.

Conclusions

In conclusion, therefore, the azide **6** cyclizes to the tetrazole **9** more slowly at all pH's (pD's) in D_2O than in H_2O. However, when the individual rate constants are analyzed, it is clear that the rate of $Z \rightarrow E$ isomerization of the iminium ion **7** remains unchanged, making it unlikely that solvent is involved (through an addition–elimination mechanism) in the slow step. At those pH's (pD's) where proton transfer to the enamine **6** is rate determining, a large primary isotope effect is observed (as expected).

The imidoyl azide **5**, which exists in another tautomeric form, is stabilized by the presence of an internal hydrogen bond (**15**) and behaves quite differently; although **15** itself slowly cyclizes (probably through the intermolecularly hydrogen bonded form **19**), the conjugate base **16** cyclizes rapidly (though at a measurable rate) at high pH. In contrast to **6** which shows acid catalysis and then inhibition at low pH, the presence of the protonated iminium ion **17** does not aid the rate of $Z \rightarrow E$ isomerization (and thus conversion to the tetrazole).

Experimental Section

The general experimental procedures are as previously described.[2] Deuterium oxide for kinetic experiments was used as received (Aldrich Gold Label, 99.7 atom % D). The pD values were determined by using the formula pD = pH (meter reading) + 0.4.

Substrates. The synthesis of *N*-ethyl-2-azido-3-benzoyl enamines has been described previously.[2] *o*-Hydroxy-*N*-ethylbenzimidoyl azide **6** was prepared by the procedure of Woodward and Kemp[12] and had the following: $\bar{\nu}_{max}$ 2119 and 1610 cm^{-1}; NMR (CCl_4) δ 1.2 (3 H, t), 3.5 (2 H, q), 6.6-7.6 (4 H, m) 9.9 (1 H, s).

p*Ka* Determination. The pK_a of *o*-hydroxy-*N*-ethylbenzimidoyl azide **6** was determined spectrophotometrically by using the method previously described[2] for reactive azides. A bell-shaped pH-optical density curve resulted which was treated by adapting the basic empirical equation for a "bell-shaped" pH-rate profile (see eq 3) and fitted to the observed data by using the method outlined in ref 9.

Registry No. **6**, 74724-91-7; **9**, 68375-95-1.

Formation of (1-Adamantylcarbinyl)arenes from 3-Azidohomoadamantane-Aluminum Chloride-Aromatic Substrates[1]

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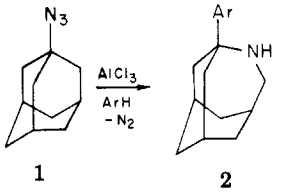
Received September 25, 1980

Reaction of 3-azidohomoadamantane with aromatic substrates catalyzed by aluminum chloride at 80 °C gave the corresponding (1-adamantylcarbinyl)arene in >90% yield. The reaction proceeds exclusively with elimination of azide ion. Competitive reaction with toluene (T)-benzene (B) gave an average k_T/k_B of ~14/1. The results indicate that a straightforward primary cation is probably not the actual attacking electrophile. The possible intervention of a bridged ion is discussed.

In a previous paper,[2] we reported that the reaction of 1-azidoadamantane (**1**) with aromatic substrates in the presence of aluminum chloride proceeded exclusively with the loss of nitrogen gas to give the rearranged product, 3-aryl-4-azahomoadamantane (**2**; eq 1). The results were

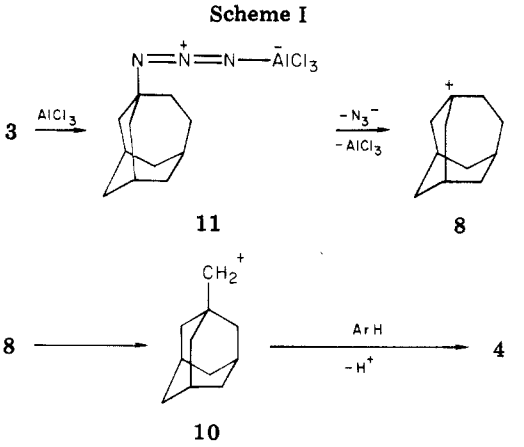


1 2 (1)

consistent with those reported for the photolytic[3] or sulfuric acid catalyzed[4] decomposition of **1**, in which a similar rearrangement was observed. In contrast, in the aluminum chloride catalyzed decomposition of primary and secondary alkyl azides in benzene,[5] both azide ion and nitrogen gas are eliminated to give alkylbenzenes and imines from rearrangement. Hence, elimination of azide ion has been observed only with nonbridgehead alkyl azides. Aryl,[6-8] acyl,[6,9] sulfonyl,[6] α-carbonyl,[10] and alkoxycarbonyl[11,12] azides are all reported to react under similar conditions, primarily with evolution of nitrogen gas, to yield N-substituted anilines.

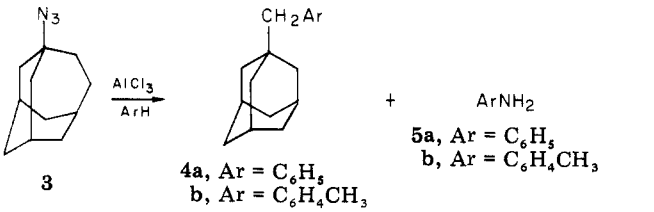
In the present study, we report the reaction of 3-azidohomoadamantane (**3**) with aromatic compounds catalyzed by aluminum chloride, resulting in exclusive elimination of azide ion, followed by rearrangement and alkylation of the aromatic substrate. In addition, we discuss the nature of the cation formed and present data on selectivity in the Friedel-Crafts alkylation.

Scheme I



Results and Discussion

Experimental Results. 3-Azidohomoadamantane (**3**) when exposed at 80 °C for 1.5 h to aluminum chloride and aromatic substrate gave the corresponding (1-adamantylcarbinyl)arene product (**4**) in >90% yield (eq 2). In addition, aminated aromatic product **5** was isolated



(2)

in minor amounts. When the reaction of **3** is carried out in the absence of the Lewis acid catalyst (24 h at 80 °C),

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0022-3263/81/1946-1346$01.25/0