Substituent Effects on the Solvolysis of α,α'-Dichloroazoalkanes. Evidence for Open Aza-allylic Ion Intermediates on Reaction Pathway[1]

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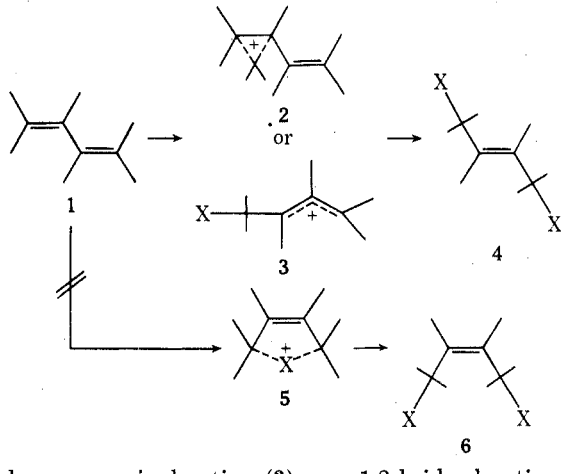
Received January 27, 1975

Reaction of α,α'-dichloroazoalkanes **9** in 7:3 dioxane–water at 25° shows consecutive kinetics. The spectrophotometrically detected intermediate is shown to be a 1-aryldiazoethane (**11** or **13**); this is stable in basic solution but undergoes rapid nitrogen loss in acid. The rate-determining step in the conversion of α,α'-dichloroazoalkanes to diazoalkanes was investigated in detail and shown to be the formation of a stabilized carbonium ion species. This is consistent with a large solvent effect (m = 1.20) and the observation of a rate depression by chloride ion. With symmetrically disubstituted substrates (**9**, $Ar^1 = Ar^2$), electron-donating groups aid reaction ($\rho = -3.68$). However, when the substrates **9** are not symmetrically substituted ($Ar^1 \neq Ar^2$) the data deviate markedly from a simple Hammett relationship and this is rationalized in terms of the formation of an open aza-allylic intermediate (**10**) rather than a symmetrical chloronium ion (**19**). The intermediate **10** does not give the expected diazoalkane (**11**) directly on fragmentation; instead the isomeric material (**13**) is formed preferentially. To explain these results a mechanism for the formation of diazoalkane **13** from **10** is suggested involving the chloronium ion **19** as an intermediate or transition state.

Extensive mechanistic studies have been carried out on the 1,4 addition of halogens to 1,3-dienes (**1**), including butadiene,[2] isoprene,[3] and their 2,3-diaza analogs.[4] In all cases the ionic reaction is stereospecific, leading only to the trans isomer **4**. This observation has been used to rule out the intermediacy of a bridged cyclic intermediate of type **5**, since it has been rationalized that nucleophilic attack by halide ion on **5** would necessarily lead to a cis product **6**. Instead an open vinyl cation (**3**) or a 1,2-bridged cation (**2**) has been proposed as intermediate. However, recent work at low temperature in SbF_5–SO_2 has clearly established the existence of tetramethylenehalonium ions, which are the saturated analogs of **5**.[5,6] Moreover, solvolysis studies have indicated 1,4-halogen participation in the solvolysis of ω-halo-2-alkyl tosylates.[7]

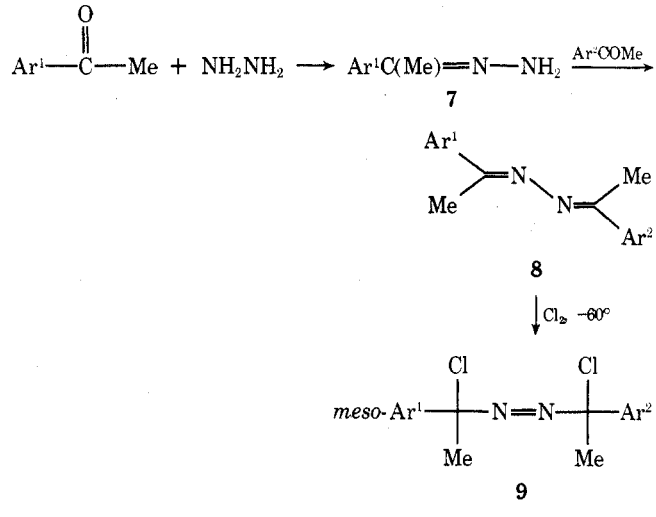


We have investigated in some detail the mechanism of solvolysis of the dichlorides **9**. These are the diaza analogs of the dihalides **4**. It has been suggested[4] that the pathway for the chlorination of the diene and the solvolysis of the dichlorides are similar; thus our observation of both open and bridged chloronium ion species in the solvolysis of **9** is also relevant to the preferred pathway followed in the halogenation of **1**.

Results and Discussion

A. Preparation of α,α'-Dichloroazoalkanes. The symmetrical 2,3-diazabuta-1,3-diene ("ketazine") substrates **8** were prepared directly by the reaction of 2 mol of the appropriate aromatic ketone with 1 mol of hydrazine. However, when a ketazine was required with two different substituents in Ar^1 and Ar^2, the intermediate hydrazone **7** had to be isolated. Such unsubstituted hydrazones are normally unstable, rapidly disproportionating to give the ketazine and hydrazine. However, electron-withdrawing substituents in Ar^1 (e.g., $Ar^1 = p\text{-}NO_2C_6H_4$ or $p\text{-}ClC_6H_4$) provide some stability to the hydrazone and where possible the synthetic route used (Scheme I) took advantage of this.

Scheme I



Several methods are available for the chlorination step. Thus, for example, reaction is reported to proceed well when the ketazine is dissolved in petroleum ether,[8] methylene chloride,[4] sulfur dioxide, or acetyl chloride, and treated with chlorine.[4] Earlier workers[9] chlorinated the ketazine at −60° in the absence of solvent and we have found this to be the preferred procedure for the preparation of the novel unsymmetrical materials **9** ($Ar^1 \neq Ar^2$).

Malament and McBride[4] have shown that in solution the diazabutadiene **8** ($Ar^1 = Ar^2$) exists at equilibrium in the preferred configuration shown, with the bulky aryl groups remote from each other. The chlorination is stereospecific (see below) so that only one product, the meso isomer **9** ($Ar^1 = Ar^2 = Ph$), is formed. Although the stereochemistry of the dichloride formed was not investigated as part of this work, we found no kinetic evidence that mixtures of isomers were present.

We were unable to obtain the normal chlorination products **9** when *both* aromatic rings had strongly electron-withdrawing groups. Thus the ketazine **8** with $Ar^1 = Ar^2 =$

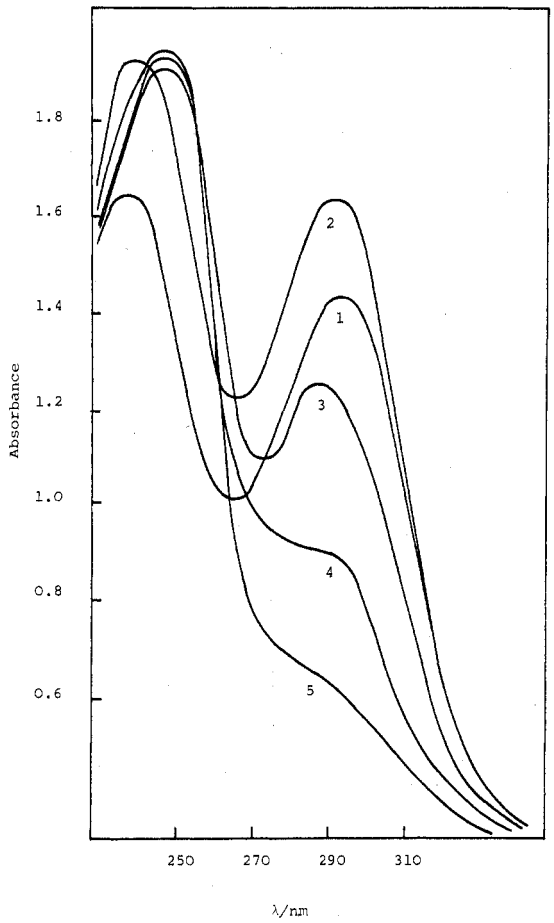


Figure 1. Repetitive scans of the ultraviolet spectrum of **9** (Ar^1 = Ar^2 = p-ClC_6H_4) in 7:3 dioxane–water at 25°; the time interval between the various scans is ca. 2 min.

p-$NO_2C_6H_4$ remained unchanged when treated with chlorine at −60° after 6 hr. At higher temperature extensive decomposition occurred. The m-nitroazine (**8**, Ar^1 = Ar^2 = m-$NO_2C_6H_4$) behaved similarly, but the o-nitro material (**8**, Ar^1 = Ar^2 = o-$NO_2C_6H_4$) gave a high yield of the hydrochloride of the starting ketazine on attempted chlorination.

B. Kinetic Experiments. The solvolyses of α,α'-dichloroazoalkanes **9** were studied in 7:3 (v/v) dioxane–water at 25°. Under these conditions with a typical substrate (**9**, Ar^1 = Ar^2 = p-ClC_6H_4) two consecutive reactions were observed. This is clearly shown by the absence of tight isosbestic points in repetitive scans of the ultraviolet region (see Figure 1 for a typical example). This result is surprising in view of Benzing's report that the solvolysis of 2,2′-dichloro-2,2′-azopropane (followed by N_2 evolution) in 85% aqueous acetone gives good kinetics.[9]

Although the spectral change with time on solvolysis of **9** (Ar^1 = Ar^2 = p-ClC_6H_4) at a single wavelength showed an initial increase in absorbance followed by a decrease (or vice versa), it was possible to follow both reactions by a careful choice of wavelength. Thus no spectral change was observed at 260 nm for the second reaction; the change in optical density at this wavelength was thus used to follow the first reaction. Similarly the first reaction showed little change in optical density at 310 nm and the second reaction was best followed at this wavelength when the first reaction was essentially complete. It was more difficult to estimate the rate constant for the second reaction when its rate was equal to or faster than that of the initial reaction; under these conditions it was usually possible to estimate the rate constant using the τ_{max} technique for series first-order reactions of Frost and Pearson.[10] Normally, however, the reaction conditions could be manipulated (see below) so that just one of the steps was rate determining and good first-order kinetics were then obtained.

Table I
Observed Rate Constants for the Solvolysis of 9 (Ar^1 = Ar^2 = p-ClC_6H_4) in 7:3 Dioxane–Water at 25°

Salt (0.01 M)	$10^3 k_1$,[a] sec^{-1}	$10^3 k_2$,[b] sec^{-1}
NaN_3	7.2	[c]
NaOAc	7.2	[c]
$NaClO_4$	11.0	8.9
NaCl	2.6	3.6
NaOH	4.5	[c]
$HClO_4$	6.0	[c]

[a] Followed at 260 nm. [b] Followed at 310 nm. [c] No subsequent rate observed.

Table II
Rate Constants for the Solvolysis of 9 (Ar^1 = Ar^2 = p-ClC_6H_4) in 7:3 Dioxane–Water at 25° in Presence of Added Chloride Ion

[NaCl], M[a]	[$NaClO_4$], M	$10^3 k_{obsd}$, sec^{-1}
0.00	0.10	11.0
0.02	0.08	6.9
0.05	0.05	4.9
0.08	0.02	3.4
0.10	0.00	2.6

[a] 0.01 M NaOH added to suppress second reaction ($k_2 \sim 0$).

A schematic reaction Scheme II is presented. A is the starting dichlorodiazoalkane **9**; we have carried out a detailed kinetic study to determine the nature of the ultimate products C and the intermediate B and of the rate-determining steps for the first and second reactions, k_1 and k_2, respectively.

Scheme II

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

1. Solvolysis under Neutral and Basic Conditions (k_1). The observed rates of solvolysis of **9** (Ar^1 = Ar^2 = p-ClC_6H_4) in 7:3 dioxane–water in the presence of various added salts are presented in Table I. As regards the first step (k_1), perhaps the most significant observation is that the reaction shows a remarkable insensitivity to the presence of acid or base. Also the rate is increased by salts such as sodium perchlorate and shows a depression in the presence of sodium chloride, a salt with a common ion.[11] The latter effect was examined in more detail (Table II); these measurements were made, for convenience, in the presence of 0.10 M added hydroxide ion in each case since this suppresses the second reaction and good first-order kinetics were obtained in each case.

In addition, the rate of the first reaction is very sensitive to the aqueous fraction of the solvent, increasing sharply with the ionizing power of the medium (Table III). The Grunwald–Winstein m value calculated is 1.20; a value of this magnitude (m for *tert*-butyl chloride is 1.0) is strong evidence for an SN1 dissociative-type mechanism for the first step.[12]

These data, taken together, support a mechanism involving rate-determining C–Cl bond fission for the first step (Scheme III) and confirm the earlier work of Benzing.[9] The charge on the ion formed, **10** (Ar^1 = Ar^2 = p-ClC_6H_4), can be stabilized by delocalization onto the adjacent azo nitro-

Scheme III

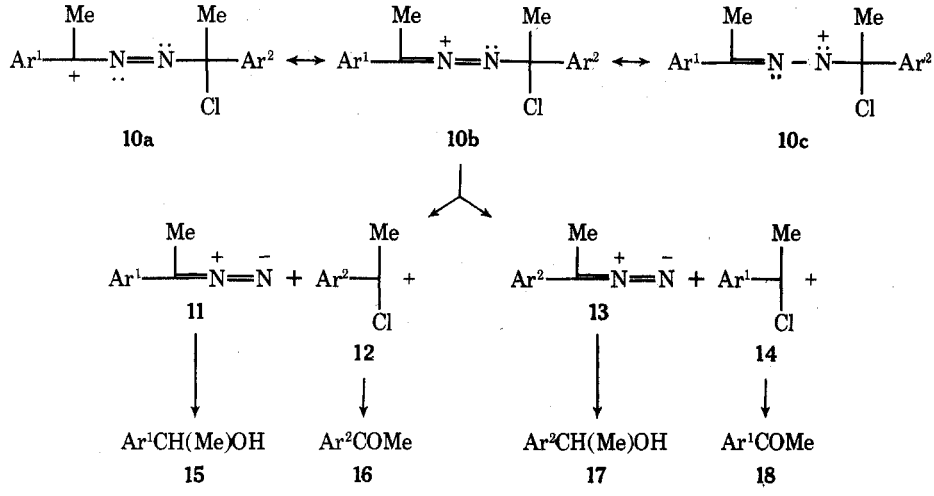


Table III
Rate Constants for the Solvolysis of 9 ($Ar^1 = Ar^2 = p$-ClC_6H_4) in Varying Dioxane–Water Mixtures[a]

Dioxane-water	$10^3 k_{obsd}$, sec^{-1}
55:45	62
60:40	28
65:35	10
70:30	4.5
75:35	2.2

[a] Measured at 25° at 260 nm; 0.01 *M* NaOH added to suppress second reaction ($k_2 \sim 0$).

gens (**10b** and **10c**). The formation of **10** is also consistent with the substituent effects discussed in detail below.

2. The Intermediate B (k_2). The first structure considered for the spectrophotometrically observable intermediate B was the azocarbonium ion **10.** This is, however, unlikely since such a species would be highly reactive in basic solution where B is the observed final product of reaction. Also no second reaction was observed in the presence of acetate or azide ion; the salts (NaN_3 and NaOAc) raise the pH of the medium, slowing the second reaction. In acidic solution no second rate was observed but in this case the final spectrum observed is that of the normal final products of solvolysis, viz., C. It is clear therefore that B is stable in base but reacts rapidly in acid.

The reaction solution containing B in base is pink (indeed Benzing[9] noted the transitory formation of pink solutions during his experiments). This, together with the kinetic data suggested that the intermediate B was in fact the diazoalkane **11,** formed by fragmentation of the carbonium ion **10.** Several pieces of evidence support this. Thus the uv spectrum of B formed from **9** ($Ar^1 = Ar^2 = p$-ClC_6H_4) in 7:3 dioxane–water containing 0.10 *M* NaOH was identical with the spectrum of a mixture of *p*-chlorophenyldiazoethane (**11,** $Ar^1 = p$-ClC_6H_4) and *p*-chloroacetophenone (which would be formed from **12,** $Ar^2 = p$-ClC_6H_4, on reaction with water) measured under the same conditions. In a separate experiment B (formed from **9,** $Ar^1 = Ar^2 = p$-ClC_6H_4) was extracted with methylene chloride and showed a strong absorption at 2043 cm^{-1} in the ir, characteristic of diazoalkanes.[13]

The diazoalkane was actually isolated in one case. Thus 1,1′-dichloro-1-(*p*-nitrophenyl)-1′-phenyl-1,1′-azoethane (**9,** $Ar^1 = p$-$NO_2C_6H_4$; Ar^2 = Ph) was solvolyzed on a large scale in the presence of 0.1 *M* hydroxide. The resulting red solution was extracted with ether and the solid isolated was identical with 1-(*p*-nitrophenyl)diazoethane as shown by melting point, mixture melting point, ir, and uv comparison with an unambiguously prepared sample.

It is well established[13,14] that diazoalkanes are hydrolyzed in aqueous solution by an acid-catalyzed mechanism to give the corresponding alcohol (in the absence of nucleophiles other than water). Thus the ultimate products of hydrolysis of **9** should be a substituted acetophenone and 1-arylethanol formed in a 1:1 ratio in neutral and acidic solution. This was confirmed for **9** ($Ar^1 = Ar^2$ = Ph and $Ar^1 = Ar^2 = p$-ClC_6H_4) by GLC analysis.

Finally the rates of reaction of an unambiguously prepared sample of diazoalkane (**11,** $Ar^1 = p$-ClC_6H_4) in 7:3 dioxane–water were compared with the measured subsequent rate (k_2 values) for the solvolysis of **9** ($Ar^1 = Ar^2 = p$-ClC_6H_4), measured under the same conditions. The observed rate constants were the same in both cases (within experimental error) and varied in the same way with pH (over the pH region 4.9–6.3).

Thus it has been established that **9** solvolyzes by an SN1 mechanism involving the azocarbonium intermediate **10** in aqueous dioxane. This step is neither acid nor base catalyzed, ruling out competing mechanisms involving nucleophilic attack on the substrate. Under neutral or basic conditions diazoalkanes (such as **11**) lie on the reaction pathway. These are also probably formed from **9** in acidic solution but their rapid further reaction (to form alcohols) under these conditions precludes their isolation.

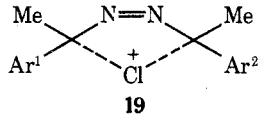
The relative magnitudes of the two rate constants, k_1 and k_2, can, however, be varied since k_1 is very sensitive to the ionizing power of the medium whereas k_2 remains relatively unchanged. Alternatively, changing the pH can also affect the balance between k_1 and k_2; k_1 is insensitive while k_2 is increased in acid and tends towards zero in base. Finally k_1 is depressed by the addition of a salt containing chloride ion, while this has no special effect on k_2.

C. Substituent Effects. 1. Kinetic Studies. In Table IV are summarized the data for the solvolysis of the dichlorides **9** measured under standard conditions (7:3 dioxane–water, 25° in the presence of 0.10 *M* sodium hydroxide); under these conditions $k_2 = 0$ and steady and reproducible infinity values were obtained. When the symmetrically disubstituted substrates (**9,** $Ar^1 = Ar^2$) are taken alone, and log k_1 is plotted against the σ value[15] of the substituent, then an excellent correlation ($r = 0.998$) is obtained (Figure 2). The slope or Hammett ρ value is −3.68, implying a transition state in which there is a build-up of considerable positive charge in the transition state.

Table IV
Observed Rate Constants for the Solvolysis of 9 in 7:3 Dioxane–Water at 25° (μ = 0.10, NaOH)

Ar^1	Ar^2	10^3 k, sec^{-1}	Registry no.
C_6H_5	C_6H_5	35	56688-54-1
p-MeC_6H_4	p-MeC_6H_4	110	56587-95-2
p-ClC_6H_4	p-ClC_6H_4	4.5	56587-96-3
m-ClC_6H_4	m-ClC_6H_4	1.1	56587-97-4
p-BrC_6H_4	p-BrC_6H_4	4.5	56587-98-5
m-BrC_6H_4	m-BrC_6H_4	0.74	56587-99-6
p-ClC_6H_4	m-ClC_6H_4	3.9	56588-00-2
p-ClC_6H_4	p-MeC_6H_4	31	56588-01-3
p-MeC_6H_4	p-$NO_2C_6H_4$	10	56588-02-4
p-ClC_6H_4	p-$NO_2C_6H_4$	0.98	56588-03-5
C_6H_5	p-ClC_6H_4	8.1	56588-04-6
C_6H_5	p-$NO_2C_6H_4$	4.0	56588-05-7

Besides **10** another limiting structure **19** can be visualized for the intermediate carbonium ion. In **19** the charge is



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symmetrically distributed throughout the molecule so that both aryl rings bear an equal fraction of the charge. These two possibilities can be distinguished as follows.

When data for unsymmetrically disubstituted substrates **9** ($Ar^1 \neq Ar^2$) are plotted against the sum of the σ values of both substituents, it is seen (Figure 2) that wide scatter results; the datum points lie above and below the correlation line for the symmetrical compounds. No combination of alternative σ values (e.g., σ^+, σ^-, etc.) succeeded in bringing all the data onto the correlation line.

However, when the data in Table IV are broken down as follows certain patterns emerge. Thus when substrates **9** with one p-nitrophenyl group (Ar^1 = p-$NO_2C_6H_4$) are considered then a plot of log k_1 vs. the σ value of the substituent in the other aryl ring (Ar^2) gives a good correlation with $\rho = -2.50$ ($r = 0.997$). Alternatively, when these substrates with Ar^1 = p-MeC_6H_4 are chosen a similar plot (of log k_1 vs. σ value of substituent in Ar^2) gives a very much reduced $\rho = -1.10$ ($r = 0.998$). Good correlations were not always obtained by this technique. Thus when Ar^1 = Ph or Ar^1 = p-ClC_6H_4 plots of log k_1 vs. σ value of the substituent in Ar^2 are curved.

These data are readily explicable only in terms of an unsymmetrical transition state (of type **10**). In the substrate **9** when $Ar^1 \neq Ar^2$, two parallel reactions occur but it is clear that the C–Cl bond cleaved preferentially is that which locates the charge adjacent to the aryl group carrying the most electron-donating group. The p-Me and p-NO_2 substituents are respectively the most electron-donating and -withdrawing groups used. Thus when Ar^2 = p-$NO_2C_6H_4$ the charge is located adjacent to Ar^1 giving the high ρ value for substituents in Ar^1.[16] The opposite situation exists when Ar^1 = p-MeC_6H_4; charge is then located adjacent to Ar^1 (see **10**) and the ρ value for Ar^2 is small. When substrates in which a p-ClC_6H_4 group is present are considered, the second substituent may have a stronger (e.g., p-MeC_6H_4) or weaker (e.g., p-$NO_2C_6H_4$) electron-donating power. Ionization at both sites is then competitive and the position of preferred bond cleavage will therefore change throughout the series leading to the observed curved log k_1 vs. σ plots.

The direct application of the Hammett equation to such curved plots is complex since the observed rate constant

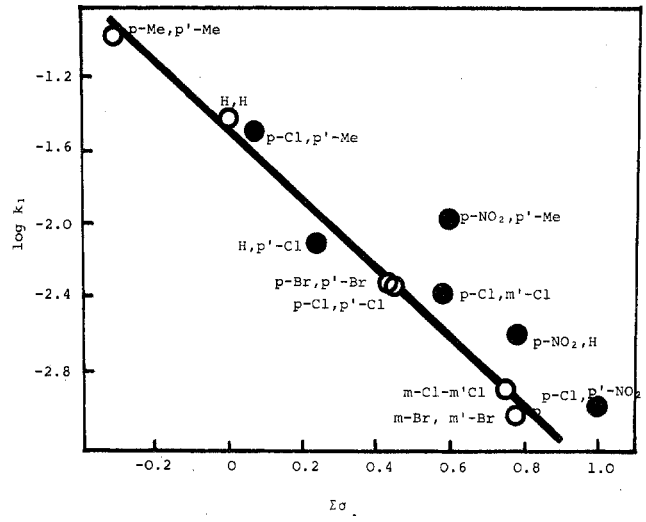
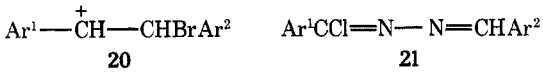


Figure 2. Hammett plot of log k_{obsd} vs. $\Sigma\sigma$ for solvolysis of $XC_6H_4CMeClN{=}NCMeClC_6H_4Y$ in 7:3 dioxane–water at 25° (μ = 1.0, NaOH). The solid line has slope −3.68 and correlates data for symmetrically disubstituted substrates (X = Y, open circles).

represents the *sum* of two rate constants for parallel reactions, each of which varies as the substituent is changed. This difficulty is discussed in detail by Ruasse and Dubois.[17] However, the following simple deduction can be made. In a symmetrically disubstituted substrate the observed ρ value (−3.68) is composite representing the contribution of the remote and adjacent substituent to the stabilization of the ion formed. These individual contributions can be estimated as −2.50 and −1.10 (the ρ values for ionization essentially at a single site adjacent to or remote from aryl group in which the substituent is changed). There is thus unequivocal kinetic evidence available to support the formation of an open (**10**) rather than symmetrical (**19**) carbonium ion intermediate, with preferential C–Cl bond cleavage occurring at a site remote from the most electron-withdrawing group.

The formation of an open carbonium ion (**20**) rather than a bridged bromonium ion has also been noted by Dubois



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and Ruasse in the bromination of stilbenes.[16] In this case the ρ values for electron-withdrawing and electron-donating substituents are different, since the carbonium ion which is preferentially formed always locates the charge adjacent to the most electron-donating aryl group.

The transition state for the formation of **10** may, of course, involve some bridging (i.e., partial **19** formation) but this is unlikely in view of the following evidence. Any degree of bridging by the chlorine in **10** would tend to reduce the ρ value for substituents in Ar^1. A good test would therefore involve comparison with a substrate in which participation is unlikely, e.g., compound **9** in which one of the Cl groups was replaced by Me. We were, however, unable to synthesize such 1-chloroazoalkanes. On the other hand, data are available for the related system **21** and this provides a good model. Thus the ρ values reported for azocarbonium ion formation from **21** are −2.3 and −1.2 for Ar^1 and Ar^2, respectively (measured in 2:3 dioxane–water).[18] These values are remarkably close to those which we have obtained for **9**, and since bridging cannot occur in **21**, neither is it likely to be an important contribution for the reaction of **9**.

On an absolute scale **9** is solvolyzed ca. 120-fold more slowly than the very reactive imidoyl halides.[17] However **9** is still hydrolyzed ca. tenfold more readily than diphenyl-

Table V
Ultraviolet Absorption Maxima for Products Formed in Basic 7:3 Dioxane–Water from Dichlorodiazoalkanes 9

Substrate 9				
Ar^1	Ar^2	λ_{max},[a] nm	Diazoalkane	λ_{max}, nm
C_6H_5	p-$NO_2C_6H_4$	410	11, Ar^1 = p-$NO_2C_6H_4$	410
p-MeC_6H_4	p-$NO_2C_6H_4$	410		
p-ClC_6H_4	p-$NO_2C_6H_4$	410		
p-MeC_6H_4	p-ClC_6H_4	300	5, Ar^1 = p-ClC_6H_4	300

[a] Absorption maximum of diazoalkane formed.

Table VI
Relative Amounts of Two Substituted Acetophenones (16 and 18) Formed from Unsymmetrically Disubstituted Dichloroazoalkanes 9[a,b]

Substrate 3			
Ar^2	Ar^1	Ar^2COMe, %	Ar^1COMe, %
C_6H_5	C_6H_5	50	50
p-ClC_6H_4	C_6H_5	30	70
p-ClC_6H_4	p-MeC_6H_4	17	83
p-$NO_2C_6H_4$	p-ClC_6H_4	8	92
p-$NO_2C_6H_4$	p-MeC_6H_4	2	98

[a] Reaction medium: 7:3 dioxane–water at 25°. [b] Products analyzed by GLC (column: 2 m, 15% Carbowax 20M on Chromosorb 80–100 mesh).

carbinyl chlorides,[19] indicating that the azo group can provide considerable stabilization by electron donation to an adjacent carbonium ion center.

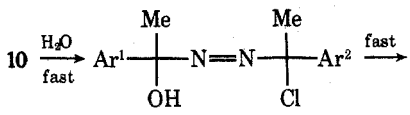
2. Product Analysis. Since it has been demonstrated that the carbonium ion **10** lies on the reaction pathway, it is expected to fragment to give the diazoalkane **11** and ultimately the alcohol **15** and ketone **16.** However, the actual products isolated in major amounts were the isomeric materials **17** and **18.** This result was quite unexpected but was supported by data for several substrates. Two methods of product analysis were used: (a) spectrophotometric determination of the diazoalkanes formed (in base) and (b) GLC analysis of the ketones and alcohols.

Method a gave best results only in those cases in which one of the possible diazoalkane intermediates carried a p-nitrophenyl group, since this absorbed at an appreciably longer wavelength than the other diazoalkanes (typically 410 vs. 290 nm). The results are summarized in Table V and indicate that in all cases the diazoalkane formed preferentially is substituted by the more electron-withdrawing aryl group present in the original dichloroazoalkane **9.** Quantitative studies indicate 80–100% p-nitrophenyldiazoalkane formation.

Method b was more rigorous and could be used with any dichloroazoalkane substrate; for convenience in most cases the relative amounts of the two possible ketones **16** and **18** ($Ar^1 \neq Ar^2$) were estimated, since the separation was better than in the case of the alcohols. However, the results obtained by estimation of either ketone or alcohols were consistent. The results (Table VI) indicate that the ketone formed in largest amount was that with the most electron-donating group. This complements the uv data which indicated that the diazoalkane (and consequently the alcohol) formed has the most strongly electron-withdrawing group.

There is thus an apparent dichotomy between the kinetic results and the product studies. Thus while the kinetics clearly show that, say, **10** is formed preferentially from **9** (Ar^1 more electron-donating than Ar^2), there is equally

Scheme IV



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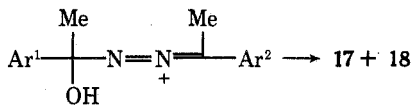

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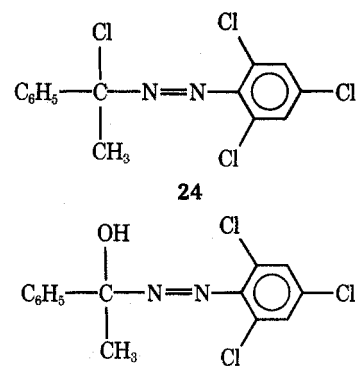
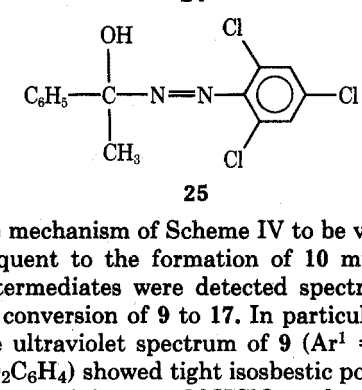
clear evidence that the carbonium ion **10** does not break down to give **11** and **12** preferentially but rather to give **13** and **14.** We therefore propose that an extra step(s) must be involved before the azocarbonium ion fragments; the three most likely are considered below.

(1) Benzing[9] proposed a mechanism (Scheme IV) in which the carbonium ion reacts with water to form the chlorohydroxy material **22.** If this pathway is followed then rapid loss of Cl^- from **22** gives **23** and eventually the correct products **17** and **18** (Ar^1 more electron-donating than Ar^2). The formation of **22** is not unreasonable, since we have found that solvolysis of the chloride **24** under similar conditions also occurs via an azacarbonium ion mechanism and leads to the formation of the azocarbinol **25.**[20] However, for the mechanism of Scheme IV to be viable then all steps subsequent to the formation of **10** must be rapid, since no intermediates were detected spectrophotometrically in the conversion of **9** to **17.** In particular, repetitive scans of the ultraviolet spectrum of **9** (Ar^1 = p-MeC_6H_4; Ar^2 = p-$NO_2C_6H_4$) showed tight isosbestic points in 7:3 dioxane–water containing 0.01 M $HClO_4$ and good first-order kinetics were obtained at all wavelengths [although the spectral difference between the model compounds **24** and **25** is small, there is sufficient difference at 300 nm so that the presence of **22** would be detectable from nonlinear log (absorbance) vs. time plots]. Therefore either (a) the intermediate **22** is not present on the reaction pathway or (b) its further reaction (**22** → **23**) is faster than the formation of **10** from **9.** We regard the latter as unlikely, since this would require that the second ionization, which occurs adjacent to a relatively electron-withdrawing (e.g., Ar^2 = p-$NO_2C_6H_4$) group, should be faster than the first adjacent to Ar^1 (electron donating, such as p-MeC_6H_4). In addition **22** has an OH group in place of the Cl group in **9.** This should, however, have a relatively minor effect on the rates of ionization of the remote C–Cl bond. Thus **26** (X = Cl) actually ionizes 10^2-fold faster to give **27** (X = Cl) than does **26** (X



24



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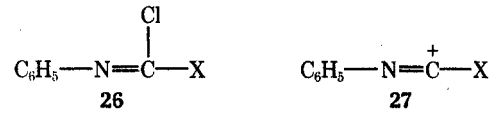
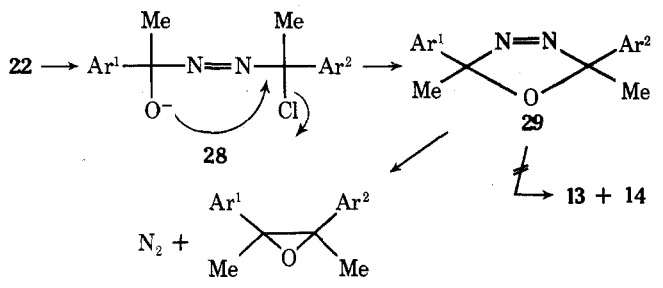
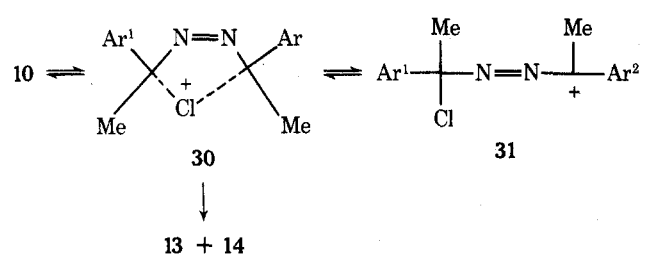


26 **27**

Scheme V



Scheme VI



= –OAr).[21] On the other hand, the Cl group is inductively more electron withdrawing than the OH group (the difference in Taft σ^* values is 0.49),[22] but is insufficient to counter the larger difference in electron-withdrawing power between p-$NO_2C_6H_4$ and p-MeC_6H_4.

(2) The mechanism in Scheme V modifies Scheme IV by inclusion of a rapid intramolecular displacement of Cl^- by the OH group (or its conjugate base **28**) to give the Δ^3-1,3,4-oxadiazoline **29**. Such materials have been reported as unstable;[23] however, nitrogen loss gives rise to epoxides (which are relatively stable and would have been detected) *rather than the observed products* **17** and **18**.

(3) The mechanism presented in Scheme VI is favored on the basis of available evidence. This involves migration (or partial migration) of chloride ion from one carbon site to the other (possibly via the bridged ion **30**). This step must occur *after* the initial rate-determining formation of **10**. Complete transfer (to **31**) is unlikely (since this is *less* stable than **10**) so that fragmentation probably occurs directly from **30**. The extra driving force for bridging by chloride ion is provided by the formation (on fragmentation) of the most stable carbonium ion **14** (Ar^1 is electron donating) and diazoalkane **13** (Ar^2 is electron withdrawing). This is clearly shown in Figure 3, where the log of the relative

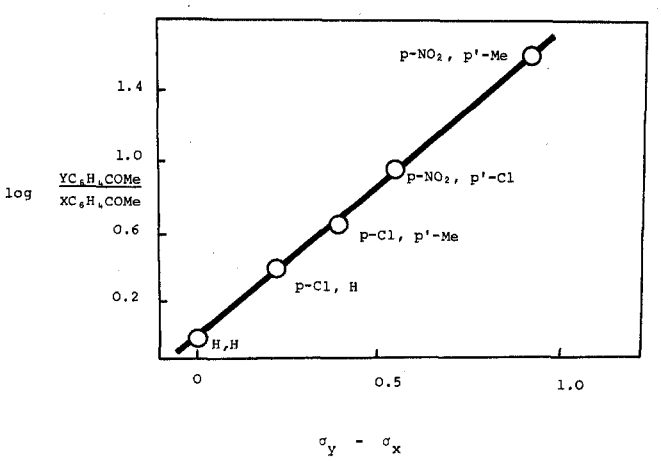
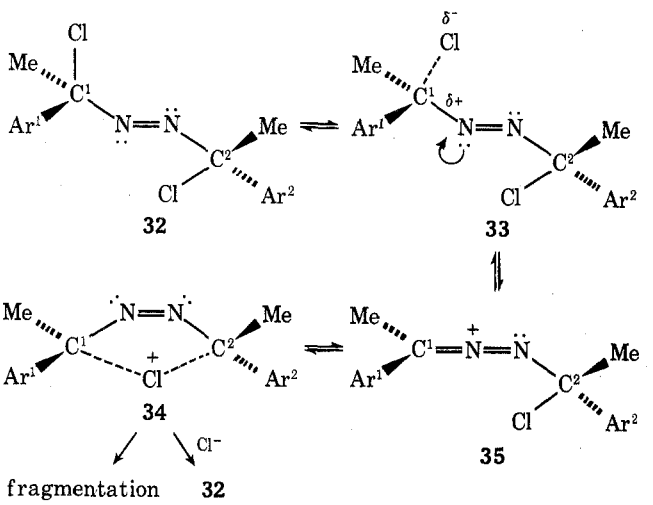


Figure 3. Plot of the log of the relative amounts of ketones formed on solvolysis of dichloroazoalkanes ($XC_6H_4CMeClN{=}NCMeClC_6H_4Y$) vs. the difference in the σ values of substituents X and Y.

Scheme VII



fragmentation **32**

amounts of the two ketones formed [i.e., log ([Ar^1COMe]/[Ar^2COMe])] from **10** is shown to vary with the difference in electron-donating power of Ar^1 and Ar^2. The slope of the correlation (or ρ value) is +1.70; this is most satisfactory, since it indicates that the presence of an electron-withdrawing group in Ar^2 accelerates rearrangement of the initially formed carbonium ion **10**. Since the ρ value (for Ar^1) for the formation of **10** is −2.5 and that for the subsequent rearrangement is +1.70, most of the charge in the transition state for the formation of **10** from **9** is lost in the transition state for the subsequent formation of **13** and **14**. The *proposed chloronium ion* **30**, *either as a transition state or* intermediate, is consistent with this.

The question might be asked: if the chlorine participates in the stabilization of the azocarbonium ion during fragmentation, then why does it not provide stabilization in the initial reaction, loss of Cl^- from **9**.[2] A possible answer arises from the stereochemistry of the system.

There is good evidence[4] that the starting azo materials **9** are in the more stable trans configuration **32** (Scheme VII). In the transition state for azocarbonium ion formation (**33**) there is partial C^1–Cl bond fission; also C^1 has moved partly down into the N–N plane to allow eventual overlap of the vacant p orbital with the filled (lone pair) orbital on nitrogen (**35**). It is clear from molecular models that the distance between the Cl group attached to C^2 and C^1 is too great to allow appreciable bond formation in the transition state **34**. However once the azocarbonium ion **35** is actually formed, the Cl–C^1 bond distance can be further reduced to allow bonding to occur (see **34**). Although it is proposed that both the azocarbonium ion **35** and the chloronium ion **34** lie on the reaction pathway, we have no evidence as to their relative stabilities. However, a priori, there is no reason to expect that **34** is more stable than **35** since (a) in **34**, being a cis configuration, there is some steric interaction between the groups attached to carbon, (b) the possibility of stabilization of the carbonium ion by electron donation from nitrogen is minimized in **34**, and (c) this structure (**34**) places a partial positive charge on C^2, the carbon carrying the most electron-withdrawing substituent (Ar^2).

However, the existence of some bridging by chlorine such as **30** on the reaction pathway provides an elegant explanation for Malament and McBride's observation[4] that the chlorination of diazabutadienes is stereospecific. Chlorination of the diazabutadiene **8** under ionic conditions leads to the formation of the same azocarbonium ion (**34, 35**) as formed in the solvolysis of the dichloride **32**. If the stereochemistry of the intermediate is maintained by bridging by the remaining chlorine on the side remote from the depart-

Table VII
The Ketazines 8 ($Ar^1 \neq Ar^2$)

Substituent			Calcd, %				Found, %		
Ar^1	Ar^2	Mp, °C	C	H	N	Formula	C	H	N
p-$NO_2C_6H_4$	p-MeC_6H_4	138	69.15	5.76	14.23	$C_{17}H_{17}N_3O_2$	68.80	5.43	14.41
p-$NO_2C_6H_4$	C_6H_5	125	68.32	5.33	14.94	$C_{16}H_{15}N_3O_2$	68.00	5.48	15.14
p-$NO_2C_6H_4$	p-ClC_6H_4	155	60.95	4.44	13.33	$C_{16}H_{14}ClN_3O_2$	61.20	4.52	13.30
p-MeC_6H_4	p-ClC_6H_4	138	71.83	5.98	9.75	$C_{17}H_{17}ClN_2$	71.49	5.96	9.85
p-ClC_6H_4	m-ClC_6H_4	112	62.95	4.59	9.18	$C_{16}H_{14}Cl_2N_2$	62.75	4.62	9.54

Table VIII
The Dichlorides 9

Substituent			Calcd, %					Found, %			
Ar^1	Ar^2	Mp, °C	C	H	Cl	N	Formula	C	H	Cl	N
m-BrC_6H_4	m-BrC_6H_4	88	41.74	3.01	49.66[a]	6.02	$C_{16}H_{14}Br_2Cl_2N_2$	40.83	3.02	49.26	6.31
m-ClC_6H_4	p-ClC_6H_4	106	51.06	3.72	37.76	7.44	$C_{16}H_{14}Cl_4N_2$	50.32	3.57	38.00	7.55
p-MeC_6H_4	p-ClC_6H_4	115	57.46	4.78	29.85	7.88	$C_{17}H_{17}Cl_3N_2$	56.97	4.84	29.92	8.31
p-$NO_2C_6H_4$	C_6H_5	75	54.54	4.26	20.17	11.43	$C_{16}H_{15}Cl_2N_3O_2$	54.01	4.27	20.33	11.88

[a] Total halogen (Br + Cl).

ing Cl^- (see 34) then chloride ion attack on 34 gives (by microscopic reversibility) the product of chlorination with the observed trans configuration.

Experimental Section

Substrates. 1,4-Diaryl-1,4-dimethyl-2,3-diazabuta-1,3-dienes. The symmetrically disubstituted ketazines (8, $Ar^1 = Ar^2$) were prepared by the reaction of 1 mol of hydrazine hydrate with 2 mol of substituted acetophenone in 95% ethanol and recrystallized to constant melting point in this solvent. The following hydrazones were also prepared: p-nitroacetophenone hydrazone, mp 152° (lit.[24] 151°); p-chloroacetophenone hydrazone, mp 51° (lit.[24] 55°); m-nitroacetophenone hydrazone, mp 75° (lit.[24] 77°). The unsymmetrical azines (8, $Ar^1 \neq Ar^2$) were prepared from these using 1 mol of the hydrazone and 1 mol of substituted acetophenone; analytical and melting point data are summarized in Table VII.

1,1′-Dichloro-1,1′-diaryl-1,1′-azoethanes. The following is a typical example. Acetophenone azine 8 ($Ar^1 = Ar^2 = Ph$) (2.36 g) was thoroughly dried and finely ground; liquid chlorine at −60° (Dry Ice–acetone) was added and the mixture was maintained at this temperature for 30 min. The apparatus was protected from moisture and light was excluded. The mixture was then allowed to warm to room temperature and the residual chlorine was removed in vacuo to give the dichloride 9 ($Ar^1 = Ar^2 = Ph$) in near-quantitative yield, mp 110°. The other dichlorides were prepared similarly; melting point and analytical data were in agreement with literature values where available;[8] otherwise the data are summarized in Table VIII.

Kinetic Studies. Measurements were made in 7:3 dioxane–water at 25°, unless otherwise stated. The ionic strength was maintained at 0.10 M by the addition of sodium perchlorate or sodium hydroxide. The dioxane was BDH Analar grade, used without further purification. The water used was deionized and then twice distilled from alkaline permanganate. The rates of reaction were measured spectrophotometrically using Unicam SP800 or SP1800 ultraviolet spectrometers; initial repetitive scans established suitable wavelength at which the reactions could be followed. The analytical wavelengths used are noted in the tables. The substrate was dissolved initially (ca. 10^{-2} M) in dioxane and a drop of this solution was added to the reaction solution in a 3-ml cuvette. The apparatus and treatment of results have been described in detail elsewhere.[25]

Product Analysis. p-Nitrophenyldiazoethane was prepared by a literature procedure[14] involving the oxidation of p-nitroacetophenone hydrazone with silver oxide and had mp 87° (70%) (lit.[14] 87–88[6]). The p-bromophenyl and p-chlorophenyl diazoethanes were similarly prepared but not actually isolated from the ethereal solution; ir analysis showed the presence of a strong absorption at 2049 cm^{-1} and the absence of absorption at ca. 3200 cm^{-1} which are present in the starting hydrazones. p-Nitrophenyldiazoethane was also isolated as a solvolysis product of a dichloride 9 as follows. 1,1′-Dichloro-1-phenyl-1′-(p-nitrophenyl)-1,1′-azoethane (9, Ar^1 = Ph; $Ar^2 = p$-$NO_2C_6H_4$) (0.328 g) was dissolved in dioxane (25 ml) and added dropwise at 25° to 7:3 dioxane–water (75 ml) containing sodium hydroxide (0.10 M) over 30 min. The red reaction mixture was extracted with ether. Evaporation of the dried ethereal extracts gave p-nitrophenyldiazoethane, mp 84–87°; on recrystallization from ether this had mp 87° (59% yield) and was shown to be identical with an authentic sample.

Solvolysis of Dichlorides 9, under Neutral or Acidic Conditions. The following represents a typical procedure. 1,1′-Dichloro-1,1′-diphenyl-1,1′-azoethane (9, $Ar^1 = Ar^2 = Ph$) (0.307 g) was dissolved in dioxane (70 ml) and water (30 ml) was added dropwise with stirring over 30 min. After 4 hr, stirring was discontinued and the reaction mixture was extracted with ether (3 × 100 ml). The combined ether extracts were dried and reduced to ca. 50 ml. Samples (5 μl) were analyzed using a Perkin-Elmer F11 gas chromatograph with a 2 m 15% Carbowax 20M on Chromosorb 80–100 mesh at 110°. Authentic samples of the ketone and alcohol were similarly made up in ether and analyzed; integration then gave the relative amounts of the two (or four) products formed. The ketones were also analyzed by the formation of p-nitrophenylhydrazone or 2,4-dinitrophenylhydrazone. Control experiments showed ca. 90% product recovery in this case and when allowance was made for this the results were in agreement with those reported for the GLC method (Table VI).

Acknowledgment. We are grateful to Dr. D. S. Malament for helpful discussion.

Registry No.—8 ($Ar^1 = Ar^2 = C_6H_5$), 56587-83-8; 8 ($Ar^1 = Ar^2 = p$-MeC_6H_4), 56587-84-9; 8 ($Ar^1 = Ar^2 = p$-ClC_6H_4), 56587-85-0; 8 ($Ar^1 = Ar^2 = m$-ClC_6H_4), 56587-86-1; 8 ($Ar^1 = Ar^2 = p$-BrC_6H_4), 56587-87-2; 8 ($Ar^1 = Ar^2 = m$-BrC_6H_4), 56587-88-3; 8 ($Ar^1 = p$-ClC_6H_4; $Ar^2 = m$-ClC_6H_4), 56587-89-4; 8 ($Ar^1 = p$-ClC_6H_4; $Ar^2 = p$-MeC_6H_4), 56587-90-7; 8 ($Ar^1 = p$-MeC_6H_4; $Ar^2 = p$-$NO_2C_6H_4$), 56587-91-8; 8 ($Ar^1 = p$-ClC_6H_4; $Ar^2 = p$-$NO_2C_6H_4$), 56587-92-9; 8 ($Ar^1 = C_6H_5$; $Ar^2 = p$-ClC_6H_4), 56587-93-0; 8 ($Ar^1 = C_6H_5$; $Ar^2 = p$-$NO_2C_6H_4$), 56587-94-1; hydrazine, 302-01-2; acetophenone, 98-86-2; p-methylacetophenone, 122-00-9; p-chloroacetophenone, 99-91-2; m-chloroacetophenone, 99-02-5; p-bromoacetophenone, 99-90-1; m-bromoacetophenone, 2142-63-4; p-nitroacetophenone hydrazone, 28153-22-2; p-chloroacetophenone hydrazone, 40137-41-5; m-nitroacetophenone hydrazone, 56588-06-8; p-nitrophenyldiazoethane, 30009-48-4.

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Acid-Catalyzed Isomerization of 1-Acyl- and 1-Thioacylaziridines. III. 2-Phenylaziridine Derivatives

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Received April 7, 1975

Acid-catalyzed isomerizations of (*R*)-1-(*N*-phenylcarbamyl)- (**1a**) and (*R*)-1-(*N*-phenylthiocarbamyl)-2-phenylaziridine (**1b**) were investigated to see the effect of the ring phenyl group on the orientation of the ring opening and the stereochemistry at the asymmetric carbon atom. Throughout the isomerizations of **1a** and **1b**, exclusive N–CHPh bond cleavage was observed. With protonic acids, **1a** gave partially (40%) racemized 2-anilino-5-phenyl-2-oxazoline (**2a**), and with boron trifluoride etherate, it gave highly (95%) racemized **2a**. The thiourea **1b** gave 2-anilino-5-phenyl-2-thiazoline (**2b**) in good yields with protonic acids and in a poor yield with boron trifluoride etherate.

A variety of acid-catalyzed isomerizations of 1-acyl- and 1-thioacylaziridines to 2-oxazolines[1] or thiazolines[1a,f,2] have been observed, and mechanistic studies of these reactions have been done by several workers. Heine and coworkers[1e] found that 1-aroyl-2,2-dimethyl- or 1-aroyl-2-phenylaziridine isomerized in cold sulfuric acid to 2-aryl-5,5-dimethyl- or 2-aryl-5-phenyl-2-oxazoline, respectively. Deutsch and Fanta[2a] reported that the isomerization of 1-(*N*-phenylthiocarbamyl)-2,2-dimethylaziridine with hot concentrated hydrochloric acid gave 2-anilino-5,5-dimethyl-2-thiazoline. These reactions were considered to proceed via a carbonium ion from the orientation of the ring opening (so-called "abnormal" cleavage).

Our previous study[3] was planned to see if an "abnormal" cleavage would always give rise to a carbonium ion in the acid-catalyzed isomerizations of 1-acyl- or 1-thioacylaziridines, and further to correlate the orientation with the mechanism of the ring opening. (*S*)-1-(*N*-Phenylcarbamyl)-2-methylaziridine (**1a'**) isomerized to 2-anilino-5-methyl-2-oxazoline (**2a'**) with 100% retention of configuration either with protonic acids or with boron trifluoride etherate in refluxing benzene. This means that the conversion of (*S*)-**1a'** to (*S*)-**2a'** ("abnormal" cleavage) has not proceeded via a free carbonium ion. As for the orientation of the ring opening, very puzzling results were obtained and no correlation could be found between the orientation and the mechanism of the ring opening deduced from the stereochemistry: **1a'** gave **2a'** as the major product (80–90%), while 1-(*N*-phenylthiocarbamyl)-2-methylaziridine (**1b'**) gave nearly equal amount of 2-anilino-5-methyl-2-thiazoline (**2b'**) and 2-anilino-4-methyl-2-thiazoline (**3b'**). Optically active **1b'** gave racemic **2b'** in some cases in contrast with **1a'**.

Replacing the 2-methyl group with a phenyl group seemed interesting from the following two points: (1) whether in this case, also, the "abnormal" cleavage would give the oxazoline with retention of configuration, and (2) what would be the orientation of the ring opening especially with the thiourea derivative. Heine and Kaplan[1e] reported that the thermal isomerization of *cis*-1-(*p*-nitrobenzoyl)-2,3-diphenylaziridine gave *cis*-2-(*p*-nitrophenyl)-4,5-diphenyl-2-oxazoline, and the corresponding trans compound gave the trans oxazoline. So far, no stereochemical investigation of the acid-catalyzed isomerization of 2-aryl- or 2,3-diarylaziridine derivatives has been reported.

The present study deals with the isomerization of (*R*)-1-(*N*-phenylcarbamyl)- (**1a**) and (*R*)-1-(*N*-phenylthiocarbamyl)-2-phenylaziridine (**1b**). (*R*)-2-Phenylaziridine was prepared from (*R*)-2-amino-2-phenylethyl alcohol by the Wenker method. Reaction of (*R*)-2-phenylaziridine with phenyl isocyanate gave **1a**. (*R*)-1-(*N*-Phenylthiocarbamyl)-2-phenylaziridine (**1b**) which was prepared from the same aziridine and phenyl isothiocyanate could not be recrystallized owing to the tendency to polymerize in solution.

Authentic samples of the isomerization products (**2a, 2b, 3a,** and **3b**) were prepared. Optically pure samples of (*R*)-2-anilino-4-phenyl-2-oxazoline (**3a**) and (*R*)-2-anilino-4-phenyl-2-thiazoline (**3b**) were prepared from (*R*)-1-(1'-phe-