THE SOLVOLYTIC REARRANGEMENT OF SOME 1,2-DIPHENYL-3,3-DICHLOROAZIRIDINES¹

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Abstract—The solvolytic rearrangement of 1,2-diphenyl-3,3-dichloroaziridine has been studied by stoichiometric, kinetic and isotopic tracer techniques. The heterogeneous reaction occurring in water suspension results in a quantitative yield of α -chloro- α -phenylacetanilide. The homogeneous reaction in dioxan-water mixtures yields α -chloro- α -phenylacetanilide and α -hydroxy- α -phenylacetanilide in nearly equal amounts, also in high total yield. Tracer results using Cl⁴⁴ and C¹⁴ give information on the chlorine atom shift and on the point of ring cleavage respectively. The rate constant increases markedly with increase in the % H₂O in the mixed solvent (Grunwald-Winstein m = 0.88). Kinetic investigations are reported for a series of 1-(*para*-substituted phenyl)-2-phenyl- and 1-phenyl-2-(*para*-substituted phenyl)-3,3-dichloroaziridines. The Hammett reaction constant rho (ρ) for the former series is -3.5, while a value of -1.9 was obtained for the latter series. Mechanistic interpretations based upon our results are discussed in terms of an ion-pair intermediate.

INTRODUCTION

THE compound 1,2-diphenyl-3,3-dichloroaziridine has been isolated from the reaction of benzalaniline and dichlorocarbene-generating reagents.^{8,4} This aziridine was found³ to rearrange to α -chloro- α -phenylacetanilide when placed in boiling water.

As this reaction must involve significant atomic rearrangement, including the possibility of an internal chlorine shift, we decided to investigate certain aspects of the stoichiometry and reaction mechanism. The results are presented herein.

EXPERIMENTAL

General. All m.ps, are corrected and were recorded with a Herschberg apparatus. Radioactivity determinations were obtained with a Geiger-Mueller counter. Radioactive specimens were spread as uniformly as possible over the 5 cm² area of stainless steel planchets. All carbon-14 sample wts were greater than 20 mg/cm² ("infinitely thick samples") so that the counting rate would be independent of sample wt. All chlorine-36 samples were placed in stainless steel planchets, and essentially identical sample wts were taken for each experiment so that self-absorption corrections were minimized.

NMR spectra were recorded on a Varian Model A-60 high resolution spectrometer. The compounds were dissolved in CCl_4 or $CDCl_5$ to make concentrated solutions; tetramethylsilane was used as an internal reference compound.

IR spectra were measured with Perkin-Elmer spectrophotometers PE-21 and Infracord-137 with Nujol mulls or KBr pellets. UV spectra were measured in anhydrous dioxan solutions on a Bausch and Lomb Spectronic 505 spectrophotometer using quartz cells. Elemental analyses were performed by Dr. S. M. Nagy (M.I.T.)

Materials

(a) Solvents. Dioxan was purified according to the method of Hess and Frahm;⁵ all aqueous dioxan mixtures were prepared on a wt/wt basis. Immediately after distillation the dioxan was diluted with an appropriate wt of distilled water.

¹ Taken in part from the Ph.D thesis of R. E. B., Brown University (1965).

- ^a Monsanto Fellow, 1962-64.
- * E. K. Fields and J. M. Sandri, Chem. & Ind. 1216 (1959).
- ⁴ J. O. Edwards and P. K. Kadaba, J. Org. Chem. 25, 1431 (1960).
- ⁵ S. K. Hess and H. Frahm, Ber. Dtsch. Chem. Ges. 71, 2627 (1938).

(b) Schiff bases. Condensation of the appropriate commercially available anilines and benzaldehydes resulted in approximately 80% yield of the corresponding Schiff bases. In a typical reaction, the aniline (0.5 mole) was dissolved in 300 ml dry toluene and the solution brought to reflux in a flask fitted with a Dean Stark Trap. To this solution the aldehyde (0.6 to 0.8 mole) was added over a period of 2 hr. The solution was maintained at reflux until the calculated amount of water had been collected. The solution was then cooled and the solvent removed *in vacuo*. The residue was washed with pet. ether to remove excess aldehyde. The solid was then recrystallized from an appropriate solvent. The Schiff bases prepared included N-benzylidene-p-bromoaniline,⁶ N-benzylidene-p-nitroaniline,⁸ N-benzylidene-p-anisidine,⁷ N-benzylidene-p-chloroaniline,⁶ N-benzylidene-p-toluidine,⁸ benzalaniline, p-methoxybenzylidene-aniline,¹¹ Physical properties and related data on these known compounds are listed elsewhere.¹

(c) 1,2-Diphenyl-3,3-dichloroaziridines. This preparation is representative of the reaction conditions employed to prepare the substituted dichloroaziridines. All apparatus was oven-dried and flamed under a stream of dry N_2 and the N_2 stream was maintained throughout the reaction.

To a cooled (0°) solution of 0.05 mole benzalaniline and 0.2 mole ethyl trichloroacetate (Eastman) in 400 ml anhydrous ether (Mallinckrodt) was added 0.2 mole commercial MeONa (Matheson, Coleman and Bell), in solid form, over a period of 2 hr. The mixture was stirred for an additional 2 hr at 0° and 1 hr at room temp. (R.T.). The mixture was then filtered and the inorganic residue washed with pet. ether (b.p. 30-60°). The combined filtrates were concentrated *in vacuo* (R.T.) until precipitation occurred, and then filtered. The hygroscopic solid was immediately recrystallized from a pet. ether-ether mixture, dried *in vacuo* and stored in this way at 0°. Filtration gave 8.5 g white solid m.p. 99-100° (Lit.¹ m.p. 98-99°). Concentration of the filtrate gave 2 g product m.p. 97-99°; total yield, 80%. For details of compounds, see Table 1. Yields of dichloroaziridines were usually in the range of 50-70%. Deterioration on storage was found to be greater for aziridines with electron-donating substituents on either phenyl group. When pure the aziridines could be stored in vaccuum over P₂O₈ at 0° for periods from 3 days to 6 months depending on the substituent.

(d) C¹⁴-Labelled compounds; Benzalaniline. Labelled benzaldehyde (50 microcuries of carbonyl-C¹⁴ in 13·1 mg, from Nuclear Chicago Corp.) was diluted with 6 g Cl₂-free benzaldehyde, b.p. 177-179° (Matheson, Coleman and Bell). To this was added 5.25 g aniline (Baker and Adamson A.C.S. reagent grade) and the mixture heated to 80°. The mixture was permitted to cool and allowed to stand for 15 min. Abs EtOH (10 ml) was added and the solution cooled to 0°. Addition of a seed crystal of benzalaniline caused rapid product separation. The mixture was allowed to come to room temp. and filtered. The yield of product was 86% and had a m.p. range from 49-51°. A 0.4714 g sample gave a counting rate of 7625 c/m.

1,2-*Diphenyl*-3,3-*Dichloroaziridine*-2-C¹⁴. Labelled benzalaniline, hexachloroacetone and MeONa were allowed to interact in dry pet. ether. The work-up afforded a 40% yield (m.p. 98–100°) of 1,2-diphenyl-3,3-dichloroaziridine-2-C¹⁴. A 0.515 g sample gave a counting rate of 2585 c/m.

Procedures; rearrangements of 1,2-diphenyl-3,3-dichloroaziridine

(a) Heterogeneous reaction. Upon the addition of 1,2-diphenyl-3,3-dichloroaziridine to water (2 phase system) and subsequent heating to boiling, the white solid changed to an emerald green oil which over the course of about $\frac{1}{2}$ hr gave a straw-yellow solid. Recrystallization of this product from acetone gave white crystals of a-chloro- α -phenylacetanilide in high yield; m.p. 147–148°.¹

(b) Homogeneous reaction. Solution of the aziridine in dioxan, addition of water (to make 33.3% water) and a brief reflux (5 or 30 min) resulted in the separation, upon the addition of further water, of a mixture of products (m.p. $125-130^{\circ}$). The two products, shown to be α -chloro- α -phenylacetanilide and a α -hydroxy- α -phenylacetanilide, were separable by virtue of the solubility of the hydroxyanilide and insolubility of the chloroanilide in hot water.

- ⁶ A. Hantzsch and O. Schwab, Ber. Dtsch. Chem. Ges. 34, 831 (1901).
- ⁷ C. Phillip, Ber. Dtsch. Chem. Ges. 25, 3248 (1892).
- ⁸ H. D. Law, J. Chem. Soc. 101, 157 (1901).
- ⁹ O. Anselmino, Ber. Dtsch. Chem. Ges. 40, 3474 (1907).
- ¹⁰ O. Fischer, Ber. Dtsch. Chem. Ges. 14, 2525 (1881).
- ¹¹ E. Wayne and J. Cohen, J. Chem. Soc. 127, 450 (1925).

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	Fou	20222222
	N, % Requires	4 4 7 4 4 4 7 4 4 4 7 4 4 4 7 1 4 4 4 1 4 4 1 4 1
	Found	240 240 256 255 255 255 255 255 255 255 255 255
"ES"	CI, % Requires	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
AZIRIDIN	Found	4 436 3 46 3 46 3 46 6 3 46 6 3 46 6 3 16 6 3 16 6 4 3 16 6 4 13 14 14 14 14 14 14 14 14 14 14 14 14 14
3-DICHLORG	H, % Requires	443 471 374 443 443 374 443 374 3726 3726
HENYL-3,	N-Ar Cl	60-79 65-19 55-82 54-30 61-43 65-43 54-14 54-14
UTED DIP	Requires	61-40 64-40 56-29 56-29 61-40 61-40 56-29 56-29
E para-surstit	Formula	Contraction Contra
TABLE 1. TH	6max b	15,000 19,700 19,400 11,000 11,000 15,400 11,400 11,400 11,400 11,400
	$\lambda_{\max}(m\mu)$	220 248 248 223 223 223 222 222 223 223 304 304 304
	а.р., °С	99-100 100-101 75-76 86-87 86-87 104-5-106 92-93 70-71 84-85 1111-112
	titu en ts Ar	H H H H H H H H H H H H H H H H H H H
	Subs	HHHHHHH

^b Dioxan.

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(c) Hydrolysis of α -chloro- α -phenylacetanilide. A 0.01M solution of the chloroanilide was shown not to undergo significant hydrolysis when it was allowed to interact in dil. acidic dioxan-water (2:1) solution for 24 hr at 40°; this is a set of conditions similar to those used in the kinetic runs. Using 140 ml of a 50% solution of H₂SO₄, a yield of about 70% of organic acid was obtained when 2 g of the chloroanilide was refluxed for 20 hr. The organic acid product was shown to be α -hydroxy- α -phenylacetic acid (mandelic acid); no chloro-acid was detected.

(d) Degradation of carbon-labelled compounds-decarboxylation of mandelic acid. Mandelic acid was oxidized by acid permanganate solution¹³ to benzoic acid and CO₂. The CO₂ was absorbed by a 3M NaOH (carbonate-free) solution and precipitated with BaCl₂ as BaCO₂.

After investigating several procedures, stoichiometric amounts of permanganate (assuming an oxidation number change of 3 for Mn) and H_3SO_4 were used for decomposition of the C¹⁴ labelled mandelic acid. The oxidizing agent was added in two equal portions and a fresh scrubbing solution of 3M NaOH was used for the second portion. BaCO₂ from the first portion was regularly more than $\frac{1}{2}$ of the expected total yield and the sum of the yields was generally greater than the predicted yield. BaCO₃ from the second scrubbing solution always had a higher level of radioactivity than the BaCO₃ from the first solution. This is possible if the excess yield of BaCO₃ was due to oxidation of some benzoic acid product (following the desired oxidative decarboxylation of mandelic acid to product CO₃ and the benzoic acid). The calculations of predicted radioactivity in the several compounds were based on the assumption that the dilution of C¹⁴ with Ba Cl and O atoms result in the same decrease in specific activity that an equal wt of C and H atoms would bring about. The observed radioactivities of the several compounds isolated in the hydrolysis and decarboxylation sequence were compared with values calculated using the assumption that all radioactivity was present in each compound. Corrections were made for the differences in mol. wt.

Radiochlorine studies. **Cl was obtained from Union Carbide and Nuclear Corporation in one microcurie lots as a HCl solution with specific activity greater than 0.1 millicuries per g of Cl ion. Specific activities for radiochlorine were calculated in units of counts per min per g Cl (c/m/g) for essentially identical sample wts for all the specimens counted for a given experiment.

The probability of incorporation of radiochlorine into the chloroanilide depends upon the specific activity of the radiochlorine (present as external Cl ion) and on the fraction of the rearrangement which occurs via a mechanism involving complete exchange. If the specific activity of Cl ion remained constant the fraction proceeding via a pathway involving loss and reentry of Cl ion would be equal to the ratio of the specific activity of Cl in the chloroanilide to the specific activity of Cl in the solution as Cl ion. However, the Cl ion released from the aziridines during reaction increases the external Cl ion concentration and decreases its specific activity with time. If R_1 is the initial Cl ion specific activity and R_{BOI} the specific activity of the chloroanilide then the ratios

$$\frac{R_{BO1}}{R_1}$$
 and $\frac{R_{BO1}}{R_1}$

bound the actual value for the fraction of the rearrangement proceeding by a mechanism involving complete exchange. Use of calculus and some approximations which are permissible if the percent exchange is small results in the following expression relating the experimentally measureable quantities $(R_1, R_2 \text{ and } R_{RC1})$ to the fraction of aziridine rearrangement (P) which proceeds with chlorine exchange

$$\mathbf{P} = \frac{\frac{\mathbf{R}_{\text{BCI}}}{\mathbf{R}_{1}} \left(\frac{\mathbf{R}_{1}}{\mathbf{R}_{2}} - 1\right)}{\ln \left(\mathbf{R}_{1}/\mathbf{R}_{2}\right)}$$

Kinetic procedure. An appropriate amount of aziridine (sufficient to produce a 10^{-1} M solution) was weighed and introduced into a 100 ml volumetric flask. The sample was then diluted to the mark with a stock solution of 2:1 (wt/wt) dioxan-water mixture at bath temp. Aliquots (5 or 10 ml) were withdrawn at convenient time intervals and quenched in 15 ml dioxan at 0°. The aliquots were then titrated with 0.03M NaOH to a bromthymol blue end point.

Ag ion, when present in the reaction mixtures, was found to accelerate the reaction and therefore could not be used to follow Cl^- production.

Reaction products. The aliquots from a given run were combined and the solvent allowed to ¹³ C. Long, *Biochem. J.* 36, 807 (1942).

evaporate. The residue was extracted with ether, and the extract was dried over Na_2SO_4 . The solid obtained on evaporation of the ether was separated into its pure components by elution chromatography on aluminum oxide (Merck) using in succession pet. ether (60-70°), mixtures of pet. ether and benzene, mixtures of ethyl ether and benzene. The phenylacetanilide compounds so obtained are listed in Table 2. The chloroanilide product was always found to be eluted first (with the less polar solvent).

Stoichiometry. It is heplful in the analysis of the kinetic data to consider the number of protons released per mole of aziridine reacted and to let $N_{\rm H}$ represent this quantity; this quantity is evaluated from the H ion concentration at infinite time divided by the initial aziridine concentration. In a similar manner N_{01} is the number of Cl ions released per mole of aziridine reacted. Provided the reaction involves only the formation of chloroanilide and hydroxyanilide, $N_{\rm H} = N_{01}$ and each value will reflect the ratio of chloroanilide to hydroxyanilide in the products. The percent hydroxyanilide is given by 100 ($N_{\rm H}$ -1) and that of the chloroanilide by 100 (2- $N_{\rm H}$).

Isomerization of dichloroaziridines. Several attempts to isomerize 1,2-diphenyl-3,3-dichloroaziridine under thermal conditions were unsuccessful. Heating above 100° in vacuum or in open glass tubes accomplished only decomposition with liberation of HCl gas and sublimation of starting material. Dissolution of the aziridine in various inert solvents and subsequent refluxing accomplished no significant alteration of starting material. Refluxing the aziridine for 5 hr in ethyl ether, n-butyl ether, cyclohexane, benzene or hexane, resulted in no significant alteration of starting aziridine. The addition of small amount of anhydrous AlCl₈ to the hexane solution caused the formation of tar.

 α -Chloro- α -phenyl-N-phenylacetimidoylchloride. 1,2-diphenyl-3,3-dichloroaziridine (2 g) was dissolved in 50 ml freshly distilled anhydrous dioxan and the solution brought to reflux. The originally colorless solution assumed a yellow color after the first hr. After 12 hr of reflux, the color of the solution began to darken towards a deep red. The heating was arrested and the dioxan removed *in vacuo*. The brown oily residue was distilled at 140° and 0·1 mm but only with considerable decomposition. Three molecular distillations at 120° (external temp) and 10⁻³ mm resulted in a pale yellow liquid. $\lambda_{max}^{dioxan} = 224.7 \text{ m}\mu$ ($\varepsilon = 13200$). (Found: C, 63.50; H, 4.20; Cl, 26.86; N, 5.46. Calc. for C₁₄H₁₁Cl₄N (M.W. = 264.16): C, 63.65; H, 4.20; Cl, 26.83; N, 5.30%.)

The IR spectrum showed major bands at 3.3, 6.0, 6.3, 6.7 and 6.9 μ (CCl₄). This liquid was observed to be extremely hygroscopic. Exposure to air for periods greater than 3 min was sufficient to cause a darkening in color; also, evolution of HCl occurs with the attendant production of a white solid, m.p. 148°, shown to be α -chloro- α -phenylacetanilide by mixed m.p. and IR spectrum. On the basis of the above information, the liquid was identified as the previously unknown α -chloro- α -phenyl-N-phenyl-acetimidoylchloride.¹⁸

 α -Chloro- α -(p-methoxyphenyl)-N-phenylacetimidoylchloride. A solution of 2.9 g 1-phenyl-2-(p-methoxyphenyl)-3,3-dichloroaziridine in 30 ml anhydrous dioxan was boiled under reflux for 3 hr. A yellow hygroscopic oil remained after removal of the dioxan *in vacuo*. The oily residue was dissolved in pet. ether and refrigerated overnight. Two recrystallizations of the yellow precipitate which formed afforded a white diamond-shaped crystalline material, m.p. 63-64°. The IR spectrum contained major absorptions at 6.0, 6.3 and 8.0 μ (CCl₄). The UV spectrum was also different from both the starting aziridine and the Schiff base precursor. $\lambda_{\text{mbx}}^{\text{disx}} = 221.3 \text{ m}\mu$ ($\varepsilon = 15100$). (Found: C, 60.52; H, 4.28; Cl, 23.99; N, 4.94; Calc. for C₁₅H₁₃Cl₅NO(M.W. = 294.17): C, 60.79; H, 4.36, Cl, 24.04; N, 5.01%.)

The identical compound was observed to form after 1 week at 0° in a stoppered flask originally containing a pet. ether-ether solution of the 1-phenyl-2-(p-methoxyphenyl)-3,3-dichloroaziridine compound. In this case distinct crystalline forms were present. The slow dissolution of the rectangular-shaped prisms of the dichloroaziridine was observed to coincide with the deposition of the other, diamond-shaped, imidoylchloride crystals.

 α -Chloro- α -phenyl-N-(p-chlorophenyl)acetimidoylchloride. Similar treatment of 1-(p-chlorophenyl)-2-phenyl-3,3-dichloroaziridine in boiling dioxan for 12 hr afforded a brown oil. Three molecular distillations at 120° and 10⁻³ mm produced a straw-yellow liquid N³⁵ = 1.6090. The IR spectrum showed a very intense band at 6.0 μ (CCl₄). Analysis of sample showed the presence of an impurity. (Found: C, 54.81; H, 3.32; Cl, 34.94; N, 4.50. Calc. for C₁₄H₁₀Cl₈N: C, 56.29; H, 3.34; Cl, 35.65; N, 4.80%.)

¹⁸ A similar transformation subsequently reported provided independent evidence for this assignment.¹⁴ ¹⁴ H. W. Heine and A. B. Smith, III, Angew. Chem. (Internat. Ed.) 2, 400 (1963).

	Calc. Found Calc. Found	5:45-568 5:13:24 5:39-571 5:32-25:46 5:30-506 13:55-13:43 5:30-506 13:55-13:43 5:30-506 13:55-13:46 5:30-506 13:55-13:43 5:32-26 13:55-13:43 5:30-506 13:55-13:09 5:35-518 5:32-24:77 5:35-518
	H, <u>%</u> Calc. Fou	5-87-5-8 5-43-5-4 6-27-6-6 4-594-45 5-87-5-9 5-87-5-9 5-87-5-9 5-87-5-9 5-87-5-9 3-81-5-9 3-81-5-9 3-81-5-9 3-81-5-9 3-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-9 5-81-5-8 5-81-5-9 5-95-9 5-95-95-9 5-95-95-95-95-95-95-95-95-95-95-95-95-95
NH—Ar'	C, % Calc. Found	70-02-68-83 69-36-69-78 69-36-69-78 60-03-59-43 64-27-63-75 64-27-63-75 65-34-65-75 65-34-65-04 70-02-70-56 69-34-69-87 64-27-64-57 57-84-57-80 57-84-57-80
Ar-CH-C-1	X Formula	00000000000000000000000000000000000000
	I R (2-7 μ region)	3.1, 6.1, 6.3, 6.6, 6.9 3.1, 6.0, 6.2, 6.3, 6.9 3.1, 5.9, 6.2, 6.3, 6.9 3.1, 5.9, 6.2, 6.3 3.2, 6.1, 6.6, 6.8, 7.0 3.0, 3.2, 6.0, 6.5, 6.7 3.1, 6.1, 6.3, 6.5, 6.7 3.1, 6.0, 6.2, 6.5, 6.7 3.1, 5.9, 6.2, 6.5, 6.7 3.1, 5.9, 6.2, 6.5, 6.7
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TABLE 2. THE *a*-CHLORO-*a*-PHENYLACETANILIDES AND THE *a*-HYDROXY-*a*-PHENYLACETANILIDES

• isolated as aniline hydrochloride. ^b isolated as *p*-nitroaniline.

Independent synthesis of α -chloro- α -(p-methoxyphenyl) acetanilide

 α -Hydroxy- α -(p-methoxyphenyl)acetic acid. This compound was prepared according to the method of Knorr.¹⁶ The product obtained had a m.p. of 108° (lit. 108–110°).

 α -Chloro- α -(p-methoxyphenyl)acetanilide. α -Hydroxy- α -(p-methoxyphenyl)acetic acid (3.7 g; 0.02 mole) was dissolved in excess (20 ml) freshly-distilled SOCl₂; b.p. 75.6°). After the initial reaction subsided, the solution was boiled under reflux for 4 hr. The excess SOCl₂ was distilled *in vacuo*. The addition of anhydrous benzene and distillation effected the removal of residual SOCl₃. The oily residue was dissolved in 300 ml anhydrous ether. To this solution with stirring was added an etherial solution of aniline (3.6 g; 0.04 mole). The mixture was stirred for 3 hr and filtered. Concentration of the filtrate and refrigeration produced a white fluffy solid, m.p. 112°. Recrystallization of this material from CHCl₃-CCl₄ resulted in fine white needles m.p. 116°. The IR spectrum showed major bands at 3.1, 5.9, 6.2, 6.4 and 6.6 μ (KBr). $\lambda_{max}^{dioxan} = 247.3 m\mu$ ($\varepsilon = 20500$). (Found: C, 65.38; H, 5.12; Cl, 12.72; N, 5.37; Calc. for C₁₅H₁₄CINO₃ (M.W. = 275.7): C, 65.34; H, 5.12; Cl, 12.86; N, 5.08%.)

Upon heating this material to its m.p. and a few degrees beyond it, the compound was observed to turn blue and evolve HCl gas.

RESULTS

Stoichiometry. The steps in the synthesis of the 1,2-diphenyl-3,3-dichloroaziridines are given in the Experimental Section. In Scheme I, the products of the solvolytic rearrangement are shown. In a heterogeneous mixture of water and aziridine, only the α -chloro- α -phenylacetanilide is formed. In homogeneous solution (dioxan-water solvent), both chloroanilide and α -hydroxy- α -phenylacetanilide in roughly equal amounts are formed. Details on the individual compounds are given in the Experimental section, and quantitative data on relative yields of anilides are given in the Tables which follow. The insensitivity of N_H values to solvent composition, substituents, etc, is quite surprising at first sight.

Carbon tracer. Also in Scheme I, the steps in the degradation of the anilide products from rearrangement of the labelled aziridine are shown. The results obtained for both of the product anilides are similar. The ¹⁴C activity determinations of both the anilides and the degradation products indicate that the phenyl group remains attached to the same carbon atom throughout the course of rearrangement and degradation. In Table 3, data for one set of tracer experiments are presented; these data demonstrate that the molar radioactivities for aziridine, chloroanilide, mandelic acid and benzoic acid are the same within the experimental error. Only a small amount of radioactivity was

		Second	l shelf ^{»,•}	First shelf		
Compound	Wt	obs. c/m	corr. act.	obs. c/m	corr. act.	
Chloroanilide	0.187	897	2.20×10^{5}	2740	6.73 × 10	
Mandelic acid	0.190	1380	2.10×10^{5}	4150	6·31 × 10	
Benzoic acid	0.177	1840	2.24×10^{5}	5445	6·63 × 10	

TABLE 3.	RADIOACTIVITY	OF	HYDROLYSIS	PRODUCTS ⁴
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For chemical reactions, see Scheme I.

These are the shelves for holding planchets below the counter window.

• The observed radioactivity in counts per min (obs. c/m) are given in columns 3 and 5; the corrected activities (c/m times mole wt) are given in columns 4 and 6.

⁴ The corresponding values for the labelled aziridine reactant are 2585 c/m and 6.82×10^{4} .

¹⁵ E. Knorr, Ber. Dtsch. Chem. Ges. 37, 3172 (1904).

observed in the barium carbonate and this amount could be traced to oxidation of some of the mandelic acid beyond the desired stoichiometry.

It can be concluded that the carbonyl carbon in anilide product is the carbon holding both chlorine atoms in the aziridine. It then follows that a chlorine migration from C-3 to C-2 has taken place in the course of rearrangement to chloroanilide.

Chlorine tracer. To ascertain whether the chlorine atom migration occurs via an intramolecular process or via a process involving release and recapture of a free chloride ion, three rearrangements of aziridine were carried out in the presence of radiochloride ion (Table 4). In one experiment (No 3), 10 mmoles 1,2-diphenyl-3,3dichloroaziridine and 4 mmoles tagged hydrochloric acid were dissolved in 200 ml of a 2:1dioxan-water mixture. The temperature was brought quickly to 45° and maintained there for 11 min. The reaction was quenched with 200 ml ice water; 500 ml water was then added and the mixture extracted with three 200 ml portions ether.



The aqueous solution was treated with silver nitrate and, from the silver chloride precipitated, the amount of rearrangement was shown to be approximately 50%.

The ether solution was dried and concentrated. Repeated crystallizations gave thick aziridine crystals which were separated from the anilide products by difference in rate of solution in petroleum ether; the bulky aziridine crystals dissolved more slowly. The recovered aziridine had a m.p. $99-100.5^{\circ}$ and represented an 18% recovery of starting material. There was no detectable radiochlorine present for the counting rate with this sample was in the range of our normal "background" (16 to 20 c/m).

Complete equilibration of radiochlorine would have required a counting rate of 2100 c/m. Therefore no exchange of reactant aziridine with Cl^- took place under conditions which resulted in 50% rearrangement.

The residue of anilide products (approximately 1 g; m.p. 133–136°) was heated for 0.5 hr with 125 ml water and filtered. The m.p. of the remaining crystals, the chloro-anilide, was $147-149^{\circ}$ (0.160 g). The counting rate for a 0.140 g sample was 117 c/m.

The incorporation of ionic chloride into the chloroanilide product (when the solvolytic rearrangement of 1,2-diphenyl-3,3-dichloroaziridine occurs in a 2:1 dioxanuwater solution containing radiochloride ions) apparently becomes increasingly probable as the concentration of chloride ions increases. However, even when the inorganic chloride ions are present at initial concentration three-fold greater than the aziridine (Expt. 2, Table 4), the reaction proceeds predominantly by an intramolecular chlorine shift for the product had only about 10% of activity expected for complete exchange. It was observed that the chloroanilide product did not exchange with external chloride ion under our experimental conditions.

Initial	Expt. 1	Expt. 2	Expt. 3
Aziridine, mmole	1.92	2:00	10.00
Inorganic Cl ⁻ , mmole	0.03	6.00	4.00
Solvent, ml.	60	60	200
Reaction time at 45°	215 min	200 min	11 min
Reaction, per cent	100	100	49
Final			
Aziridine, mmole	0.00	0.00	5.06⁴
R-Cl, mmole	0.93	1.00	2.47
Inorganic Cl ⁻ , mmole	2.80	9.00	11-41
R ₁)	8·7 × 10 ⁴	45,800	209,000
R _a °	87,500	30,100	72,000
R _{B-01} d	9,200	3,800	5,800
$\frac{R_{B-OI}}{R_1} \times 100$	0.11	8.3	2.8
$\frac{\mathbf{R}_{\mathbf{B}-C1}}{\mathbf{R}_{\mathbf{a}}} \times 100$	10.5	12.6	8·1
p [•] × 100	2.3	10-2	4.9

Table 4. Data on and results of radiochloride studies in 66.7% (vol/vol) dioxan at 45°

• Pure aziridine was isolated and found to contain no radiochlorine.

Initial Cl⁻ specific activity.

· Final Cl- specific activity.

Chloroanilide specific activity.

· Fraction of rearrangement proceeding through ionic mechanism.

Kinetic results. First-order rate constants for 1,2-diphenyl-3,3-dichloroaziridine and several of its *para*-substituted phenyl derivatives are given in Tables 5, 6 and 7. In all cases but one (see below), linear plots of log [aziridine] versus time were obtained to about 90% reaction as may be seen in Fig. 1. Tenfold variation in aziridine concentration resulted in first-order rate constants which agree quite well, and the variation in aziridine concentration (entries 5 and 6 of Table 6) did not noticeably influence $N_{\rm H}$ values. The one case where the rate plots showed a slight curvature was the 2-*p*methoxyphenyl compound; this case is discussed below.

Most of the substrate N_{Cl} and N_H values (Table 7) were in the range of 1.50 ± 0.50 indicating that the hydroxy and chloroanilide products were formed in about equal amounts and were independent of the nature of the substrate. The 2-*p*-methoxyphenyl compound again shows individual behavior.

% Dioxan	Yª	k٥	NH
60.0	0.72	2·2 × 10 ^{−a}	1.57
66.7	0.25	$8.3 imes10^{-4.0}$	1·53ª
71.5	-0.10	$3.8 imes 10^{-4}$	1.54
75·0	-0.32	$2.0 imes 10^{-4}$	1.50
87.5	-1.70	1.7×10^{-5}	1.46
97.5	-3.2	$\simeq 3.3 \times 10^{-7}$	—

 TABLE 5. SOLVENT DEPENDENCE OF RATE AND STOICHIOMETRY FOR

 1,2-DIPHENYL-3,3-DICHLOROAZIRIDINE

* A. H. Fainberg and S. Winstein, J. Amer. Chem. Soc. 78, 2770 (1956).

Units in sec⁻¹, temp 45°.

• Ave. value for several runs.

^d $N_{01} = 1.53$.

TABLE 6. EFFECT OF VARIOUS ADDITIVES ON SOLVOLYSIS OF 1,2-DIPHENYL-3,3-DICHLOROAZIRIDINE

					Temp	Rate $\times 10^4$	
Entry	% Dioxan	[imine] \times 10 ^a , M	Additiv	e, M	°C	sec ⁻¹	N _H
1	71.5				25	0·26ª	
2	71.5	1.56	NaClO ₄ ,	0.10	25	0.32	1.55
3	71.5	1.56	NaOH,	0.20	25	0.21	2.23
4	71.5	1.50			45	3.8	1.20
5	71.5	3.1	NaClO ₄ ,	0 ·10	45	4∙0	1.54
6	71-5	0.31	NaClO ₄ ,	0.10	45	3-8	1.54
7	66·7	2.0			45	8·3	1.50
8	66.7	3.33	HCl,	0·10	45		1.51
9	66.7	1.68	NaCl,	0.57	45		1.45
10	66.7	1.58	HCl,	0.020	45	8.5	1.66%
11	66.7	1.58	NaClO ₄ ,	0.20	45	18	1.240
12	66·7	1.58	NaCl,	0.20	45	3.7	1·48°

· Calc from E_a.

^b Data collected before complexity of the reaction was recognized.

TABLE 7. KINETIC DATA FOR VARIOUS *para*-substituted 1,2-diphenyl-3,3dichloroaziridines in dioxan-water (2:1) at 40.6° .

Ar-CH-N-Ar' C							
Substi	tuents	Rate \times 10 ⁴ (sec ⁻¹)	E _a , kcal ^a	∆S≠, e.u.	N _{Cl}	N _H	
Ar	Ar'						
н	н	4.7	23.4	-1.3	1.54	1.53	
CH ₁ O	н	13	17.6	-18		1.98	
CH,	н	9.0	19-1	-9.2	1.52	1.44	
CI	H	1.5	25.0	+1.6	1.53	1.53	
NO,	н	0.13			≃1 ·59	≃ 1·60	
н	CH.O	51	22.8	+1.2	1.48	1.46	
н	CH.	13	22.4	-2.5	1.50	1.49	
н	Cl	1.1	24.5	-0.76		1.50	
н	NO ₃	∼ 0·006				≃1 ·47	

• Determined over 30° range; 3 runs at each of three temps.

The rate constant for the solvolytic rearrangement of 1,2-diphenyl-3,3-dichloroaziridine was found to be essentially unaltered when the solution was initially 0.05M in hydrochloric acid (Table 6). The addition of sodium hydroxide decreases the rate to a slight extent, yet markedly alters the product distribution; the N_{Cl} value goes to 2, and more than two hydrogens are produced per molecule of aziridine reacted (Table 6, entry 3). It seems reasonable to assume that the organic products formed in basic solution are mandelanilide, mandelate ion and aniline, although a thorough study of stoichiometry in base solution was not made.



FIG. 1. The solvolysis of 1,2 diphenyl-3,3-dichloroethyleneimine in 66.7% dioxanwater at 40.6°C.

Solvent dependence. Table 5 summarizes the effect of varying the amount of dioxan in the dioxan-water mixture upon the solvolytic rate of 1,2-diphenyl-3,3-dichloroaziridine at 45°. Application of the Grunwald-Winstein¹⁶ relationship to these data results in a linear plot of log k versus Y with a slope (m) of 0.88.

Salt effects. Preliminary studies (Table 6) of the salt effects on rate with concentrations in excess of 0.1M added salt reveal alterations in rate by a factor of approximately two. Below 0.1M added salt the salt effect, where operative, is too close to the present experimental error to allow adequate discussion.

Substituent effects. A linear correlation of the log k with Hammett¹⁷ σ values was observed for both the 1-(*para*-substituted phenyl)-2-phenyl-3,3-dichloroaziridines and the 1-phenyl-2-(*para*-substituted phenyl)-3,3-dichloroaziridines (Fig. 1). The slope (ρ) of the former plot was -3.5 while that of the latter was -1.9. In both series, reaction is facilitated by electron donation from the *para* position. The best correlation was obtained using the normal Hammett¹⁷ sigma values, and it is to be noted that the 2-*p*-methoxyphenyl compound is not exceptional in rate constant.

¹⁶ E. Grunwald and S. Winstein, J. Amer. Chem. Soc. 70, 846 (1948).

¹⁷ L. P. Hammett, Physical Organic Chemistry. McGraw-Hill, N.Y. (1940).

Activation parameters given in Table 7 are all close to that of the parent compound with the exception of the 2-p-methyl and 2-p-methoxyphenyl derivatives.

The exceptional case. The chemical and kinetic behavior exhibited by 1-phenyl-2-(*p*-methoxyphenyl)-3,3-dichloroaziridine was sufficiently different from the other members of the two reaction series to warrant further study. The results of detailed stoichiometric investigations, plus exploratory exchange and kinetic experiments are given in this section. The results while incomplete and consequently non-definitive, nevertheless contribute to a better understanding and substantiate the complexity of the general solvolysis reaction.

The solvolysis of 1-phenyl-2-(*p*-methoxyphenyl)-3,3-dichloroaziridine in 2:1 dioxanwater mixture was observed to yield two molecules of hydrochloric acid per molecule of aziridine reacted. Several chromatographic examinations of the reaction mixture revealed but one organic compound. The same product was isolated from the heterogeneous reaction in boiling water. By IR and chemical analysis the compound was shown to be α -hydroxy- α -(*p*-methoxyphenyl) acetanilide, therefore the stoichiometry is



This aziridine was observed to be unstable when stored either in anhydrous ether over sodium sulfate or in vacuum over phosphorus pentoxide. Rectangular transparent crystals of the pure methoxyaziridine, on separation from anhydrous ether in the refrigerator, were observed to undergo dissolution over a period of one week with concurrent deposition of diamond-shaped crystals, m.p. 63-64°. This latter compound was found to be isomeric with the starting aziridine and its IR spectrum showed a strong absorption band at $6\cdot 1 \mu$ presumably indicating a carbon-nitrogen double bond. Pure 1-phenyl-2-(*p*-methoxyphenyl)-3,3-dichloroaziridine was found to yield the identical (63-64° m.p.) product when refluxed in anhydrous dioxan for a period of less than 3 hr. The isomeric compound was identified as α -chloro- α -(*p*-methoxyphenyl)-Nphenylacetimiodylchloride on the basis of chemical analysis, IR spectra and reactivity.



In aqueous dioxan the methoxyimidoylchloride gave the related α -hydroxy- α -(*p*-methoxyphenyl) acetanilide, m.p. 105-6°, in quantitative yield



This behavior may be contrasted with that of α -chloro- α -phenyl-N-phenylacetimidoylchloride which gave only the related chloroanilide products on similar treatment.

On standing in air, the methoxyimidoylchloride quickly turns first to a blue oil with subsequent evolution of hydrogen chloride and then to a white solid, m.p. 112-115°. The IR spectrum of this material was quite similar to that of the hydroxyanilide product. Chemical analysis and independent synthesis (Scheme II) established this product as α -chloro- α (*p*-methoxyphenyl) acetanilide.

SCHEME II



The chloroanilide prepared according to Scheme II above was found to solvolyze rapidly to the α -hydroxy- α -(*p*-methoxyphenyl) acetanilide in either aqueous acetone or in the solvent of our kinetic conditions, 2:1 dioxan-water.

The possible intervention of the methoxyimidoylchloride and/or the chloroanilide as reaction intermediates was then investigated.

Reaction intermediates. To test for the intermediacy of the methoxyimidoylchloride and/or methoxychloroanilide compounds in the solvolysis of 1-phenyl-2-(p-methoxyphenyl)-3,3-dichloroaziridine, three interrupted hydrolysis experiments were performed in 66.7% dioxan for 3, 7 and 20 min intervals. The arresting procedure was to pour the reaction mixture into a three-fold volume of cold water and extract with ether. Work-up of the dried ether extract always gave a mixture of compounds. In the 3 min experiment, repeated recrystallization showed the presence of methoxyimidoylchloride in addition to starting material and to the final hydroxyanilide product. By a similar procedure both the methoxyimidoylchloride and its chloroanilide product were observed for the 7 min reaction. In the last experiment in which hydrolysis was allowed to proceed for 20 min, only the chloroanilide and hydroxyanilide products could be isolated in pure form. The reaction sequence in aqueous dioxan (Scheme III) is therefore established. However this pathway can not be the only pathway for formation of hydroxyanilides, since the chloroanilides derived from all other aziridines are stable to hydrolysis under the reaction conditions.

Radiochemical studies with chlorine-36 tracer on the solvolysis of the methoxyaziridine gave little new data. This aziridine did not exchange chlorine with external chloride ion; this result is in agreement with already-mentioned results obtained on the unsubstituted aziridine. Both the methoxyl imidoylchloride and the methoxy



chloroanilide were found to exchange chlorine at rates comparable to solvolysis. Because of these exchange processes and because of the difficulty in separation of the products, the observation¹⁸ that the chlorine-containing products from methoxyaziridine solvolysis in the presence of labelled chlorine ion contained radioactivity can not be used as evidence for exchange in the solvolysis steps.

DISCUSSION¹⁹

The product structures and the radiocarbon experiments indicate that no carboncarbon or carbon-hydrogen bonds are broken in the course of the reaction. It is also established that breakage occurs between the C-2 and nitrogen atoms. The radiochloride studies indicate that the chloride shift is predominantly intramolecular.

The kinetic data show that the solvolytic rearrangement is first order in aziridine. Acid catalysis is excluded on two grounds: (1) The first-order plots show no curvature up to approximately 95% reaction in experiments in which the acid concentration increased from zero to 0.06 molar because of the stoichiometries



(2) The addition of acid to the initial reaction mixture results in no rate alteration.

Since reactant aziridine does not exchange chloride (that is, it can be recovered unchanged and without labelled chlorine after one reaction half-life), the rate of ¹⁰ Details may be found in Ref. 1.

¹⁹ Further experimental data, background and discussion may be found in Ref. 1.

disappearance of reactant is apparently equivalent to the rate of product formation. The facts that the rate plots are linear and that no induction period is observed are also consistent with a simple kinetic scheme involving only one rate step.

The reaction sensitivity to solvent polarity as expressed by the value of the Grunwald-Winstein m is typical of S_N solvolytic reactions involving heterolytic cleavage of carbon-chlorine bonds²⁰ as well as similar bonds. The relative insensitivity of product distribution to changes in solvent polarity is also indicative of an S_N type ionization process wherein the product-determining steps are rapid and follow a rate-determining ionization step. Therefore, the primary reaction path seems to involve the formation of a non-exchanging ion pair.

For both of the reaction series, electronic effects are in the same direction with electron-releasing groups accelerating the rate of reaction. The Hammett rho values are negative and of large magnitude; this fact will be discussed below. It is significant that a good linear Hammett plot is obtained for the C-phenyl-substituted aziridines. The rate enhancement of a *p*-methoxy group is correlated with the normal Hammett σ rather than the σ^+ constant.²¹ In recent years, this has been interpreted to denote the lack of direct resonance interaction between the substituent and the reaction center. Accordingly our data suggest that there is no significant localization of positive charge at the benzylic carbon prior to or during the rate determining step.

The case wherein the rate of a unimolecular reaction depends markedly on conditions (solvent nature, temperature and substituents herein) yet the product distribution is little influenced by the same, can be depicted formally by a scheme such as



Here k_1 is the slow step in which reactant A goes to a high energy intermediate B. This intermediate undergoes two competing reactions, both of low activation energy, to form products C and D. In terms of the Hammond postulate²² the endothermic formation of the intermediate should have an activated complex similar to the ion pair; the two competing steps for breakdown of the intermediate presumably are quite exothermic, therefore the activated complexes for steps k_2 and k_3 should also be similar to the intermediate and to each other.

The mechanistic evidence suggests that B is a non-exchanging ion-pair in which a carbon-chlorine bond has been broken heterolytically with the positive charge on the ring being stabilized by delocalization of the type

 ²⁰ ^a A. Fainberg and S. Winstein, J. Amer. Chem. Soc. 79, 1597, 5937 (1957); ^b A. Fainberg, S. Winstein and E. Grunwald, *Ibid.* 79, 4146 (1957); ^c J. B. Hyne and R. Wills, *Ibid.* 85, 3650 (1963); ^d A. Fava, A. Iliceto, U. Mazzucato and O. Rossetto, *Ibid.* 83, 2729 (1961).

²¹ H. C. Brown and Y. Okamato, J. Amer. Chem. Soc. 80, 4979 (1958).

²³ G. Hammond, J. Amer. Chem. Soc. 77, 334 (1955).



The importance of this type of delocalization in the activated complex for aziridine rearrangement is shown by the observation that the strained bicyclic monochloroaziridine



is stable.²³ It is presumably necessary for the configurations at the cationic carbon and at the nitrogen to become coplanar for effective overlap and therefore for lowering the energy of the activated complex. In this compound with its bridgehead nitrogen, there can be little overlap.

The chloride ion formed by heterolytic cleavage in the rate step must be held by coulomb attraction in close proximity to the ring cation; the reasons for this conclusion are the lack of radiochloride in most of the chloroanilide product and the probable intermediacy of the chloroimidoyl chloride with its two non-identical chlorine atoms.

There is no evidence that the C-2-N bond is broken in the rate step. The fact that the 2-*p*-methoxyphenyl aziridine reacts at a rate which fits on a regular Hammett plot would not be expected if a significant C-2-N heterolytic bond cleavage occurred in this step. The negative sign and large magnitude observed for substituent effects on both phenyl groups also would not be expected for a mechanism involving significant C-2-N heterolytic bond breakage in the rate step.

Recently Deyrup and Greenwald²⁴ have found that nucleophilic substitutions on chloroaziridines can occur by a S_N path to give products with intact aziridine rings. The nature of their products and the rates found for various substituted aziridines fit well into the ion-pair mechanism that we have deduced herein.

Because of the multiplicity of structural changes the ion-pair intermediate B can not break down to products in a simple fashion. The formation of the chloroanilides must occur in a sequence of steps such as



since chloroimidoylchlorides have been observed in the isomerization of several aziridines when water is absent and since one member of this class (the 2-p-methoxyphenyl

²³ R. Nicoletti and M. L. Forcellese, Tetrahedron Letters 153 (1965).

²⁴ ^a J. A. Deyrup and R. B. Greenwald, submitted to J. Amer. Chem. Soc.; * J. A. Deyrup, personal communication.

case) was isolated under conditions quite similar to those of normal solvolytic rearrangement.

The hydroxyanilide must for the most part be formed by a sequence of steps starting independently at B. Some of the possible intermediates are



As would be expected both the chlorimidoyl chloride and hydroxyimidoyl chloride hydrolyze very rapidly to form chloroanilide and hydroxyanilide respectively. We obtained no evidence for the intermediate 1,2-diphenyl-3-hydroxy-3-chloroaziridine. The chloroimidoyl chlorides and chloroanilides can not be intermediates in the sequence of steps leading to hydroxyanilides (except in the 2-*p*-methoxyphenyl case) as the benzylic carbon-chlorine bond does not hydrolyze under the conditions of our rate experiments.

The 2-*p*-methoxyphenylaziridine shows an initial rate constant that is normal on the Hammett plot, therefore the rate determining step is presumably the same as for the other aziridines. In other ways, however, this aziridine is exceptional. The $N_{\rm H}$ and $N_{\rm Cl}$ values (determined at essentially infinite time) are both near two; this indicates that hydroxyanilide is the only significant product. Nevertheless, the curvature in the rate plots and the fact that this chloroanilide hydrolyzes at a rate comparable to the rearrangement suggest that chloroanilide is indeed formed in this case too. Our data can not give a definite amount for the hydroxyanilide formed via chloroanilide. A relatively fast release of the chloride ion by chloroanilide is expected in this case because of the possibility of resonance interaction between the *p*-methoxy substituent and the benzylic carbon.

The magnitude of the Hammett rho values deserves comment. For the N-phenylsubstituted compounds, a large negative value for rho is understandable if this phenyl ring can strongly interact with the reaction site of the activated complex for formation of intermediate B. Such an interaction is reasonable if the three-membered ring and the N-phenyl ring are coplanar in the activated complex for an extended π -system is thereby formed. Because of angle strain, it is unlikely that the two rings are coplanar in the ground-state but data on rates of ethylenimine ring inversion at nitrogen indicate that planarity is easily attained.²⁵

The rho value of -1.9 for the C-phenyl series is surprisingly large for an electronic effect wherein the reaction site and phenyl group are separated by a four-coordinate carbon. It seems probable that this represents another example of the oft-observed but poorly-understood "unsaturated character" of three-membered ring systems,²⁶

³⁵ A. T. Bottini and J. D. Roberts, J. Amer. Chem. Soc. 80, 5203 (1958); and ^b A. Loewenstein, J. F. Neumer and J. D. Roberts, *Ibid.* 82, 3599 (1960).

 ¹⁴ • A. D. Walsh, *Trans. Faraday Soc.* 45, 179 (1949); ⁴ C. A. Coulson and W. Moffitt, *Phil. Mag.* 40, 1 (1949); ⁶ N. Cromwell, *Record Chem. Progress* 19, 215 (1958); ⁴ H. Jaffe, *Z. Elektochem.* 59, 823 (1955); ⁶ N. Cromwell, F. Schumacher and J. Adelfang, *J. Amer. Chem. Soc.* 82, 974 (1961); ⁷ L. Strait, R. Ketcham, D. Jambotkar and V. Shah, *Ibid.* 86, 4682 (1964); ⁶ C. E. O'Rourke, L. B. Clapp and J. O. Edwards, *Ibid.* 78, 2159 (1956).

which shows up usually as an electronic response larger than would be observed with a comparable alkyl system.

The rearrangement of the dichloroaziridines appears to have possibilities as a way to prepare compounds that are otherwise difficult to synthesize. From our work it appears possible to prepare chloro and hydroxy substituted imidoyl chlorides and anilides. It seems likely that the rearrangement could be run in other protonic solvents to give various amides, amines, esters, ethers and even peroxides. The study of Deyrup and Greenwald²⁴ elaborates other useful modifications and syntheses.

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