

# Photochemical Transformations of Small-Ring Heterocyclic Compounds. 99. 1,4-Substituent Shifts in the Photorearrangement of 2-Hydroxymethyl-2H-azirine Derivatives to *N*-Vinylimines<sup>1</sup>

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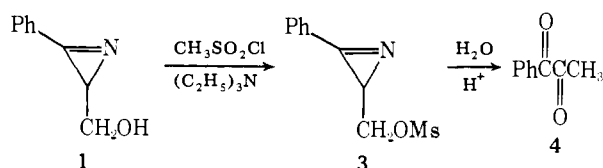
**Abstract:** The photolysis of a series of hydroxymethyl-2H-azirine derivatives results in a novel rearrangement to produce 1-substituted 1-phenyl-2-azabutadienes in essentially quantitative yield. The observation that the rearrangement of the nitrile ylide derived from 3-phenyl-2-trifluoroacetoxymethyl-2H-azirine (**30**) proceeds at a faster rate (200 times) than that of the ylide derived from 3-phenyl-2-acetoxymethyl-2H-azirine (**23**) provides good support for the intermediacy of an ion pair in the rearrangement of these hydroxymethyl-2H-azirine derivatives. Further support for this contention was obtained by studying the rate of rearrangement of a series of substituted 3-phenyl-2H-azirine-2-methanolbenzoate derivatives. Electron-withdrawing substituents in the para position were found to facilitate the rearrangement while electron-donating groups retard the 1,4-substituent shifts. Both the sign and magnitude of the reaction constant ( $\rho = +2.15$ ) indicate that the transition state for the rearrangement has substantial negative charge development. Stern-Volmer treatment of the photoreaction clearly demonstrates that the rate of rearrangement is directly related to the leaving group ability and that the migrating substituent must be a reasonably good leaving group in order for the reaction to occur.

Considerable attention has been focused in recent years on the conjugative interaction of three-ring compounds with adjacent unsaturated centers.<sup>2</sup> Among these studies have been many concerned with the conjugative interaction of small rings with carbonium ions.<sup>3</sup> Cyclopropylcarbinyl derivatives solvolyze with markedly enhanced rates to give rearranged and position-scrambled products. Increased emphasis has also been given during the past few years to the solvolytic behavior of three-ring heterocyclic compounds.<sup>4-9</sup> Replacement of a methylene group in cyclopropane by a heteroatom has been found to severely dampen the ability of the three ring to delocalize the adjacent positive charge. The reactivity of a carbonium ion center adjacent to a cyclopropene ring has also been studied.<sup>10-12</sup> The solvolysis of diphenyl- and dipropylcyclopropenylcarbinyl alcohol derivatives was reported to afford products derived from the cyclobutenyl cation, which results from ring expansion.

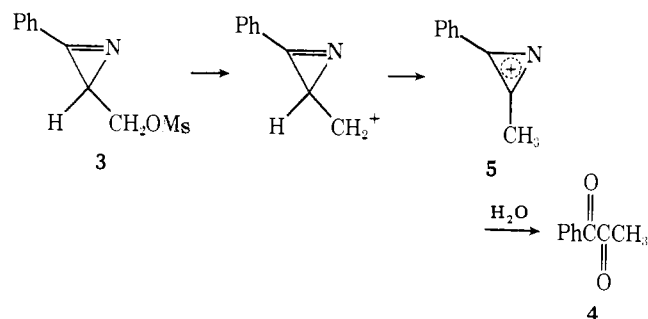
As part of a program designed to delineate the interaction of small-ring heterocycles with adjacent  $\pi$  centers, we sought to define the reactivity of a carbonium ion center adjacent to the three-membered azirine ring. We felt that this would be a particularly interesting species, since its chemical properties would probably be different from those of the related carbocyclic system by virtue of the interaction of the carbonium ion center with the electron pair on the adjacent heteroatom. In this paper we report on the solvolytic and excited state behavior of a series of hydroxymethyl-2H-azirine derivatives which contain good leaving groups. These compounds were found to rearrange to *N*-vinylimines by means of a novel 1,4-substituent shift.<sup>13</sup> The results obtained indicate that the migrating substituent must be a reasonably good leaving group in order for the photorearrangement to occur.

## Results and Discussion

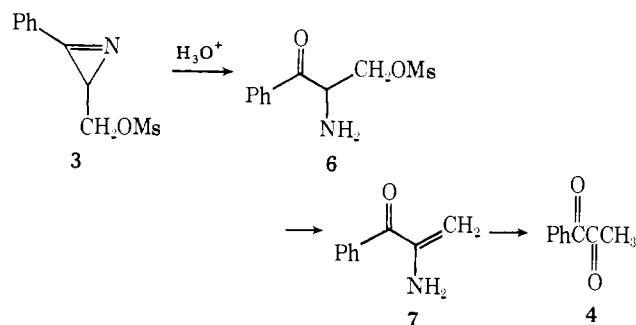
The ready availability of 3-phenyl-2H-azirine-2-methanol (**1**) and  $\alpha$ ,3-diphenyl-2H-azirine-2-methanol (**2**)<sup>14</sup> prompted



us to examine the solvolysis of the corresponding mesylates. Heating an aqueous ethanolic solution of **3** in the presence of a trace of acid resulted in the exclusive formation of 1-phenylpropane-1,2-dione (**4**). One possible explanation to account for the formation of  $\beta$ -diketone **4** involves a 1,2-hydrogen shift of the initially formed carbonium ion. The driving force associated with this process would undoubtedly be related to the stability of the resulting  $2\pi$ -electron azacyclopropenyl ion **5**.<sup>15,16</sup> Hydrolysis of the aromatic cation **5** with aqueous acid would be expected to produce diketone **4**. In fact, a closely

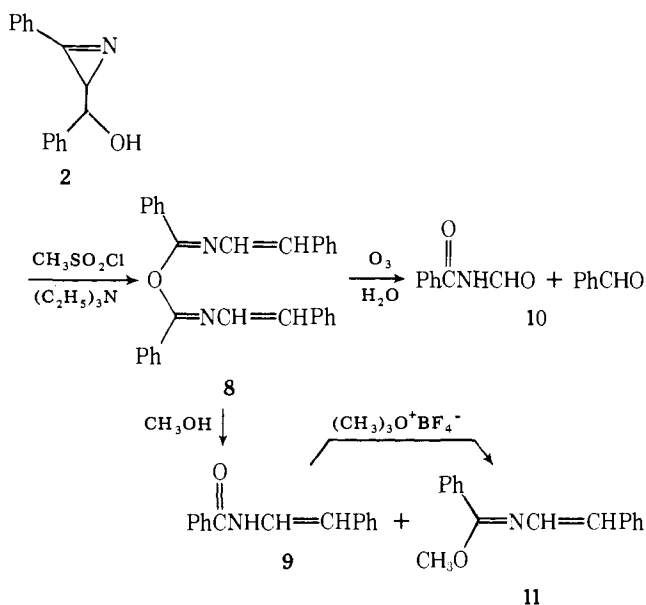


related hydrolytic reaction has been reported by Ciabattini and Cabell in the 3-chloroazirine system and provides reasonable chemical precedent for the formation of diketone **4**.<sup>16</sup> Alternatively, the formation of diketone **4** may be rationalized by an acid-catalyzed opening of the azirine ring followed by the loss of methanesulfonic acid and subsequent conversion of the unsaturated amino ketone **7** to **4**. The acid-catalyzed hy-



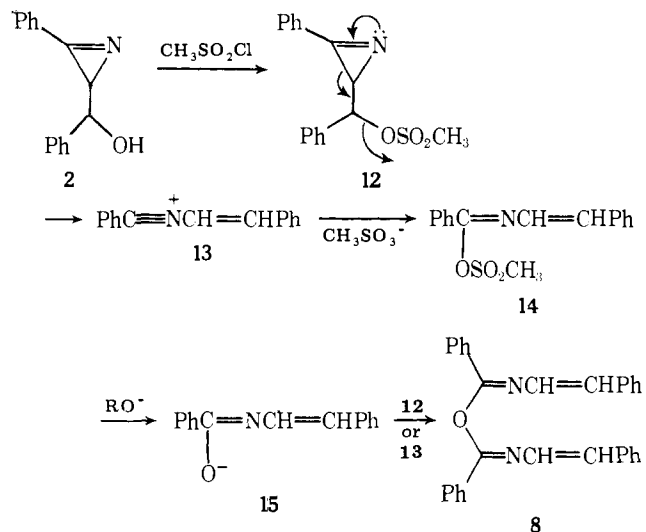
drolysis of **3** to **6** represents one of the best known reactions of 2*H*-azirines.<sup>17</sup> The present evidence does not permit a conclusive choice between the above two possibilities.

Attempts to prepare the methanesulfonate derivative of alcohol **2** resulted in the formation of (*E,E*)-1,4-diphenyl-2-



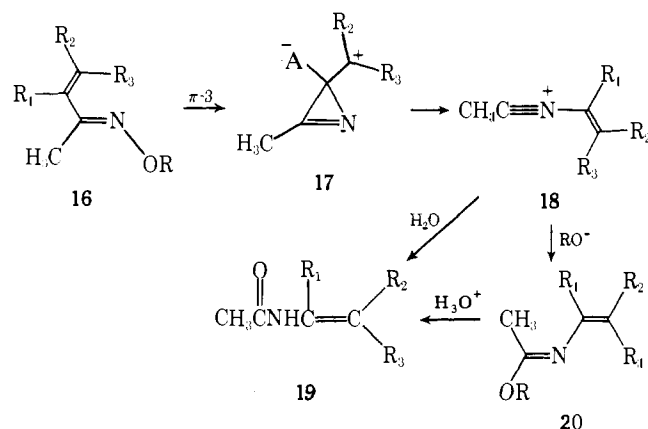
azabutadienyl ether (**8**). The structure of this material was established by its ready hydrolysis to *N*-styrylbenzamide (**9**) and by its ozonization to benzaldehyde and *N*-formylbenzamide (**10**). Recrystallization of a sample of **8** from methanol afforded equal quantities of *N*-styrylbenzamide and (*E*)-1,4-diphenyl-1-methoxy-2-azabutadiene (**11**). The structure of **11** was established by comparison with an independently synthesized sample which was obtained by treating *N*-styrylbenzamide with trimethyloxonium tetrafluoroborate.

The reaction of alcohol **2** with methanesulfonyl chloride is most reasonably explained by assuming initial formation of the benzylic mesylate **12** followed by rapid ring opening to generate nitrilium ion **13**. This species is subsequently trapped by methanesulfonate anion to give **14** as a transient intermediate. Nucleophilic attack on the mesylate group of **14** will generate anion **15** which could react either with **12** or **13** to give the observed product.



It should be noted that the above scheme is similar to that proposed in the  $\pi$ -3 assisted Beckmann rearrangement of acyclic *anti*-vinylmethylketoximes.<sup>18-21</sup> Thus, Grob and Wenk have recently shown that derivatives of acyclic *anti*-vinyl-

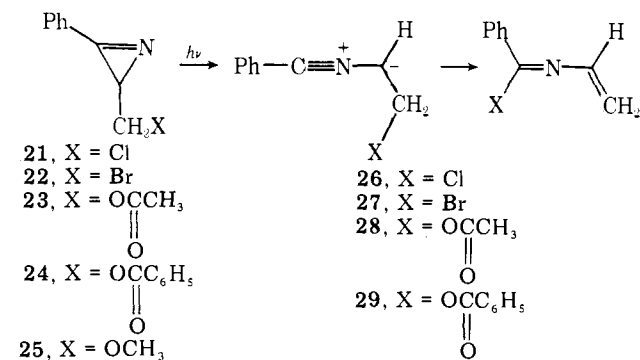
methylketoximes such as **16** which bear electron-releasing substituents ( $R_2$  and  $R_3$ ) undergo  $\pi$ -3 assisted Beckmann rearrangement to enamides **19** by way of azirine (**17**) and nitrilium (**18**) cations.<sup>18</sup> Nucleophilic attack on **18** by water leads



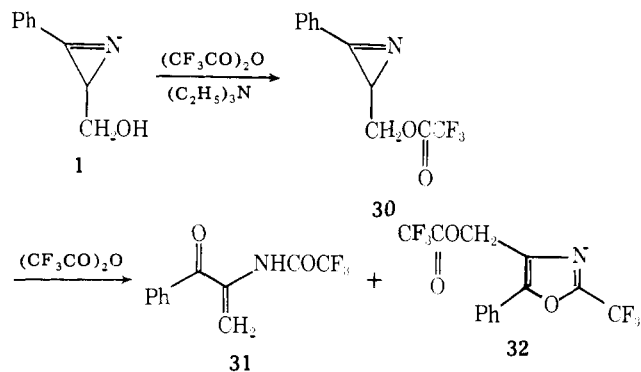
directly to **19** whereas attack by weakly nucleofugal and therefore strongly nucleophilic counterions  $\text{RO}^-$  affords iminol ethers or esters **20**.

The opening of the azirine ring in the solvolysis of mesylate **12** is closely related to the C-C bond scission reaction which occurs on irradiation of this ring system.<sup>22,23</sup> In earlier papers we have shown that 2*H*-azirines undergo photocycloaddition with electron-deficient olefins to give  $\Delta^1$ -pyrroline derivatives.<sup>24</sup> The formation of the adducts was interpreted as proceeding by way of irreversible ring opening of the azirine ring to form a nitrile ylide intermediate which was subsequently trapped by a suitable dipolarophile. As a continuation of our investigations in this area, we were particularly interested in determining whether the irradiation of a series of hydroxymethyl-2*H*-azirine derivatives would also result in the migration of the leaving group. We have found that this reaction does indeed take place and produces *N*-vinylimines in essentially quantitative yield.

3-Phenyl-2*H*-azirine-2-methanol (**1**) provided an easy entry into other substituted 2*H*-azirine derivatives. 2-Chloromethyl-3-phenyl-2*H*-azirine (**21**) was prepared by the reaction

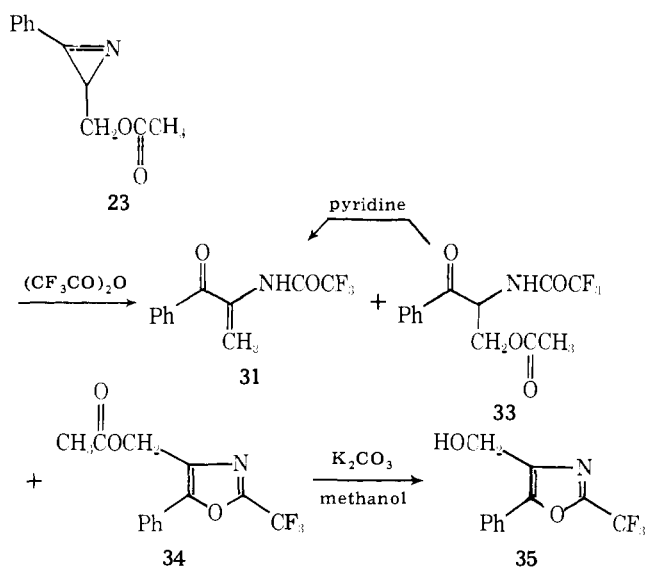


of **1** with tris(dimethylamino)phosphine in carbon tetrachloride.<sup>25</sup> Reaction of mesylate **3** with lithium bromide in ether solution gave azirine **22**. Azirines **23** and **24** were readily prepared by treatment of **1** with acetyl chloride-triethylamine and benzoyl chloride-pyridine. The corresponding methyl ether **25** was prepared from 1-phenyl-3-methoxyprop-1-ene via Hassner's iodine azide route.<sup>26</sup> Attempts to prepare 3-phenyl-2*H*-azirine-2-methanol trifluoroacetate (**30**) by treating **1** with trifluoroacetic anhydride and triethylamine at 25 °C for 12 h produced 1-phenyl-2-*N*-trifluoroacetylaminoprop-2-en-1-one (**31**, 30%) and 2-trifluoromethyl-4-trifluoroacetoxymethyl-5-phenyloxazole (**32**, 60%). When shorter reaction times were used (3 h), trifluoroacetate **30** could be isolated in



high yield. Subsequent studies showed that treatment of **30** with trifluoroacetic anhydride resulted in the formation of **31** and **32**.

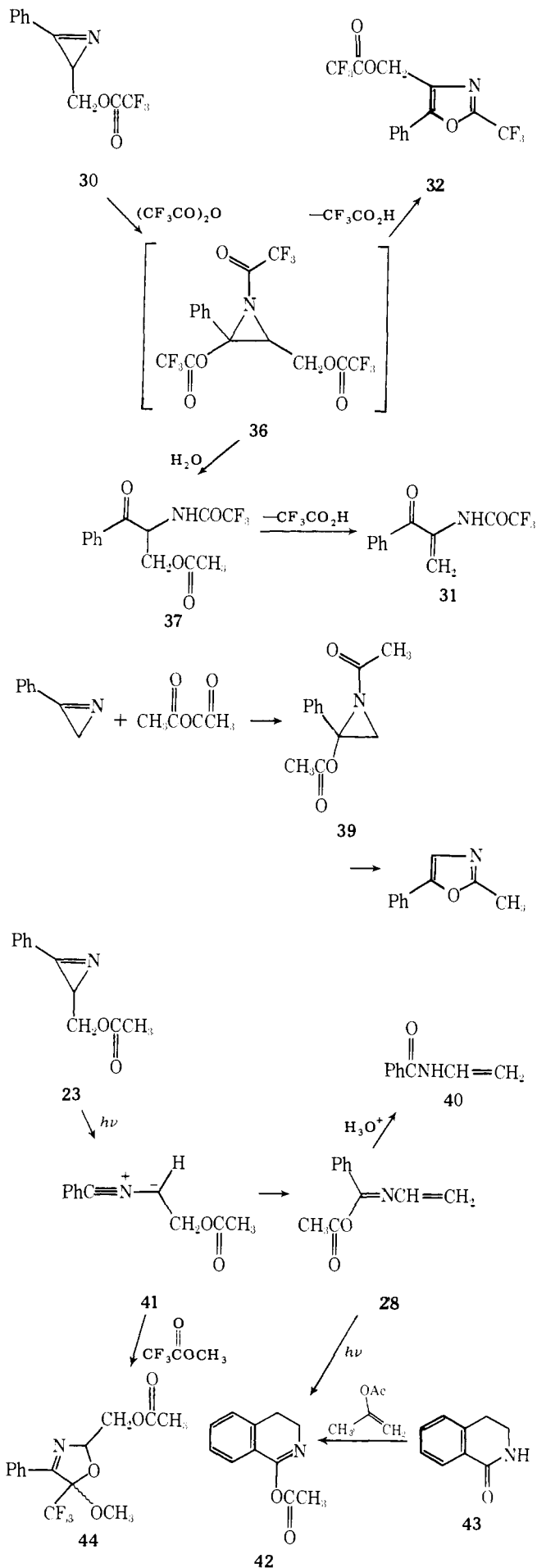
A similar reaction was also found to occur when acetate **23** was treated with trifluoroacetic anhydride under similar reaction conditions. In this case, the three products formed were identified as **31** (22%), 1-*N*-trifluoroacetoxyamino-2-acetoxypropionophenone (**33**, 37%), and 2-trifluoromethyl-4-acetoxymethyl-5-phenyloxazole (**34**, 22%). Oxazoles **32** and **34**



could be readily hydrolyzed to the same alcohol (2-trifluoromethyl-4-hydroxymethyl-5-phenyloxazole, **35**) thereby establishing the nature of the ring system. Verification of the structure of **33** was obtained by its conversion to **31** on treatment with base.

The generation of compounds **31** and **32** from azirine **30** can best be explained in terms of the formation of aziridine **36** as a transient intermediate. This species could easily be converted to oxazole **32** and ketone **37**. The latter compound would be expected to undergo ready loss of trifluoroacetic acid to give **31**. The above scheme is supported by the observation that the reaction of 3-phenyl-2H-azirine with acetic anhydride gives structure **39** which, in turn, is readily converted to 2-methyl-5-phenyloxazole.<sup>27</sup> Similar reactions have also been observed to occur when 2H-azirines are treated with acid chlorides and anhydrides.<sup>28,29</sup>

Irradiation of the above 2-hydroxymethyl-3-phenyl-2H-azirine derivatives **21–24** in benzene for short periods of time afforded azabutadienes **26–29** in essentially quantitative yield. The structures of the products (e.g., **28**) were assigned on the basis of their characteristic NMR spectra (**28** ( $\text{CDCl}_3$ , 100 MHz)  $\tau$  7.76 (3 H, s), 5.49 (1 H, d,  $J = 16.0$  Hz), 5.24 (1 H, d,  $J = 9.0$  Hz), 3.04 (dd, 1 H,  $J = 16.0$  and 9.0 Hz), and 2.10–2.60 (m, 5 H)) and by hydrolysis to *N*-vinylbenzamide (**40**). When the irradiation of **23** was carried out for longer



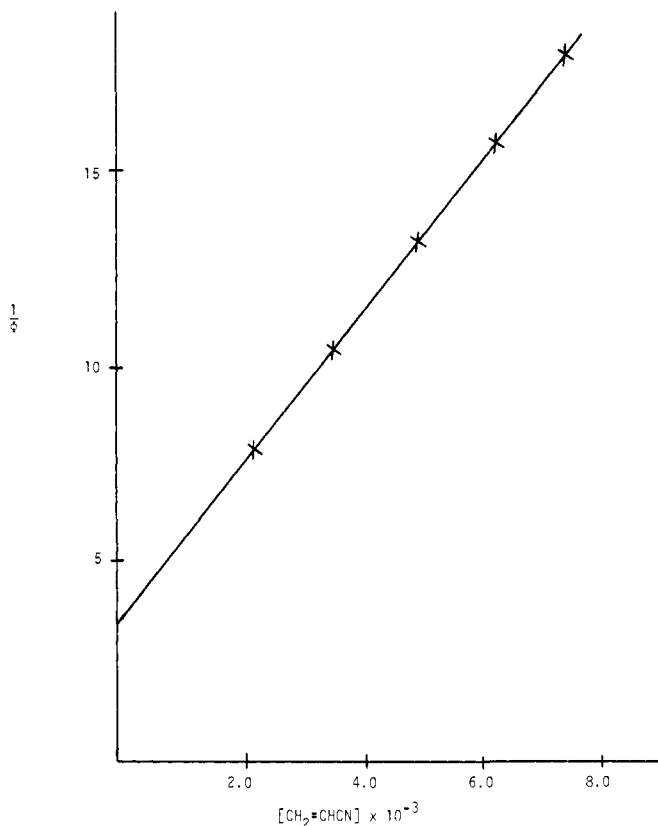
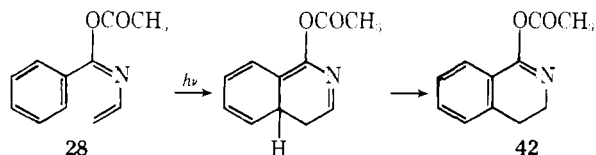


Figure 1. Plot of [quantum yield of rearrangement] against [acrylonitrile] for 3-phenyl-2-acetoxymethyl-2H-azirine (**23**).

periods of time a new compound was obtained whose structure was assigned as 1-acetoxy-3,4-dihydroisoquinoline (**42**). The structure of **42** was unambiguously established by comparison with an independently synthesized sample prepared by treating dihydroisocarbostyryl (**43**) with isopropenyl acetate in the presence of a trace of *p*-toluenesulfonic acid. A control experiment showed that **42** was a secondary photoproduct derived from azabutadiene **28**. The conversion of azabutadiene **28** to dihydroisoquinoline **42** represents a novel reaction and merits some comment. The first step of this process can be viewed as an electrocyclic ring closure of an azahexatriene to a 1,3-azacyclohexadiene. The second step simply involves a symmetry allowed 1,5-suprafacial sigmatropic hydrogen migration.

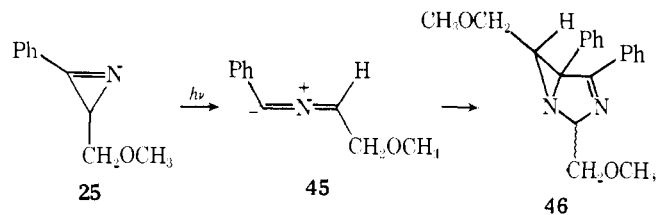


Weber and co-workers have recently observed the all-carbon analogue of this rearrangement<sup>30</sup> and Wendling and Bergman have reported on a closely related thermal rearrangement of a structurally related 1-phenylazabutadiene.<sup>31</sup> The conversion of **28** to **42** is also related to the photocyclization reaction of a number of phenyl unsaturated amides which has been suggested to proceed via a similar pathway.<sup>32-34</sup>

Involvement of a nitrile ylide intermediate (**41**) in the rearrangement of **23** to **28** was demonstrated by carrying out the photolysis of **23** in the presence of the very reactive dipolarophile methyl trifluoroacetate.<sup>35</sup> Under these conditions, the formation of **28**, which is produced in quantitative yield in the absence of a trapping reagent, is entirely suppressed. The only product isolated was the 3-oxazoline **44**. Assignment of the 3-oxazoline structure rather than the isomeric 2-oxazoline structure was made on the basis of the IR spectrum and by

comparison with the NMR spectra of model compounds.<sup>35,36</sup>

In contrast to the above rearrangements, photolysis of the trimethylsiloxy derivative produced only polymeric materials while the methyl ether **25** afforded a mixture of *exo*- and



*endo*-(2,6-dimethoxymethyl)-4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**46**). The formation of the 1,3-diazabicyclohexene system **46** from the irradiation of **25** can be interpreted in terms of 1,3-dipolar addition of the nitrile ylide (**45**) across the C-N double bond of the starting azirine. Other accounts describing the cycloaddition of 1,3-dipoles with azirines have appeared in the literature and provide good chemical analogy for this reaction.<sup>37-42</sup> The fact that a dimer is formed from the irradiation of **25** suggests that the methoxy substituent is such a poor migrating group that the nitrile ylide intermediate prefers to undergo cycloaddition with unreacted starting material rather than undergo a 1,4-substituent shift.

The above results indicate that the migrating substituent (X) attached to the methylene unit of the azirine ring must be a reasonably good leaving group in order for the 1,4-substituent shift to occur. An equally plausible explanation is that the migration is the result of neighboring group participation. The lack of migration for OCH<sub>3</sub> and OSi(CH<sub>3</sub>)<sub>3</sub> could be attributed to the small size of the migrating group leaving it being unable to bridge the three-atom unit of the  $-\text{C}=\text{N}^+=\text{C}-$  dipole, whereas the larger halogens are able to do so, as are the acyloxy and benzyloxy groups.

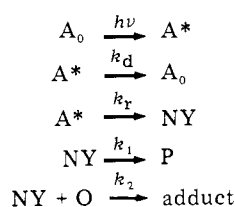
In order to derive additional mechanistic information concerning the intramolecular 1,4-substituent shift, a more quantitative investigation of these rearrangements was undertaken. Quantum yields for product formation were determined using cyclopentanone as the chemical actinometer.<sup>43</sup> Degassed and sealed quartz tubes containing solutions of the azirines were irradiated with actinometer tubes in a rotating photochemical assembly. Reactions were carried out to low conversions to prevent appreciable light absorption by the products, and yields of products were determined by quantitative NMR analysis. The quantum yield for product formation as a function of the concentration of added acrylonitrile was also studied. The data are presented graphically in Figures 1 and 2 for the 3-phenyl-2-acetoxymethyl- (**23**) and 3-phenyl-2-trifluoroacetoxymethyl-2H-azirine (**30**) systems.

Several features become apparent upon examination of the data shown in the figures. Good linear relationships are observed between the inverse of the quantum yield for product formation and the concentration of acrylonitrile. The slopes and intercepts of the plots depend on the structure of the azirine used. At zero dipolarophile concentration, the quantum yield for rearrangement is 0.27 for azirine **23** and 0.45 for azirine **30**. The magnitude of the intercept indicates that rearrangement of azirine **23** is ca. 40% less efficient than the rearrangement of **30**. The results obtained using these azirines as nitrile ylide precursors are consistent with the mechanism outlined in Scheme I. In this scheme, A<sub>0</sub> = azirine **23** or **30**, NY = nitrile ylide, P = product, and O = dipolarophile (i.e., acrylonitrile)

By making the usual steady-state assumption, we can write

$$1/\Phi_P = [(k_d + k_r)/k_f][1 + (k_2[\text{O}]/k_1)]$$

Scheme I

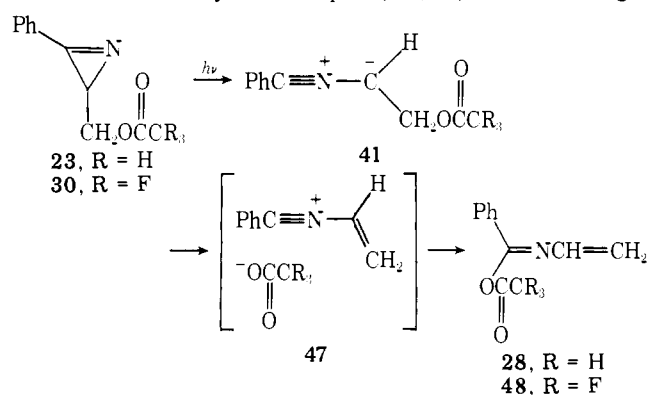


where  $k_d$  represents the nonradiative decay of excited azirine,  $k_r$  is the rate of the 1,4-substituent shift, and  $\Phi_P$  is the quantum yield of product formation.

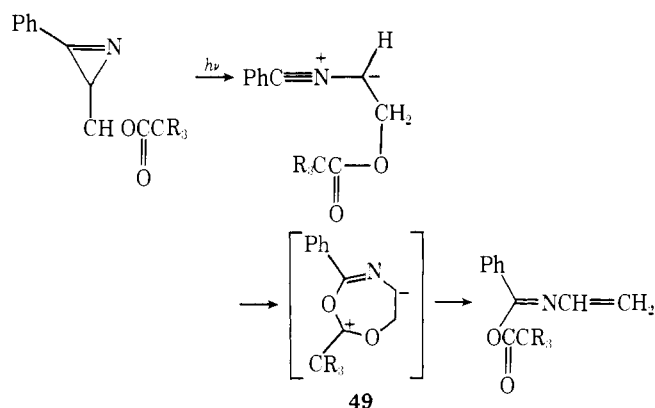
From the slope and intercept of the Stern-Volmer analysis for product formation with a given dipolarophile, we find that the slope/intercept =  $k_2/k_1$ . For the case of azirine **23**,  $k_2/k_1 = 312$ , while with azirine **30**,  $k_2/k_1 = 1.57$ . These values indicate that the nitrile ylide intermediate obtained from azirine **23** is much more easily trapped with an added dipolarophile than the 1,3-dipole derived from the trifluoroacetoxy substituted azirine **30**. If we assume that the rate of cycloaddition (i.e.,  $k_2$ ) of both nitrile ylides with acrylonitrile is the same,<sup>44</sup> we can obtain the relative rate difference for the 1,4-substituent shift of these two azirines:

$$\begin{aligned}
 [k_2/k_1(\text{azirine } \mathbf{23})/k_2/k_1(\text{azirine } \mathbf{30})] \\
 = k_{30}/k_{23} = k_{rel} = 200
 \end{aligned}$$

The observation that the rearrangement of the nitrile ylide derived from azirine **30** proceeds at a faster rate (200 times) than that of the ylide derived from **23** provides good support for the intermediacy of an ion pair (i.e., **47**) in the rearrange-



ment of these hydroxymethyl-2H-azirine derivatives. If the 1,4-substituent shift had occurred by means of neighboring group participation, then the ylide derived from azirine **23** should have undergone rearrangement at the faster rate since this ylide would have given rise to the more stable bridged intermediate **49**. This is clearly not the case. Thus, one can



conclude that both the quantum yields and rates of rearrangement of these hydroxymethyl-2H-azirine derivatives are a function of the leaving group ability.

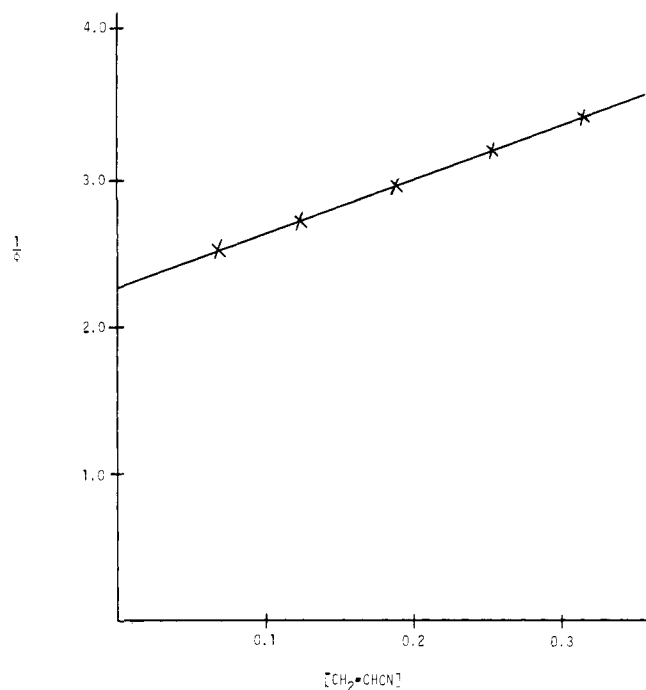
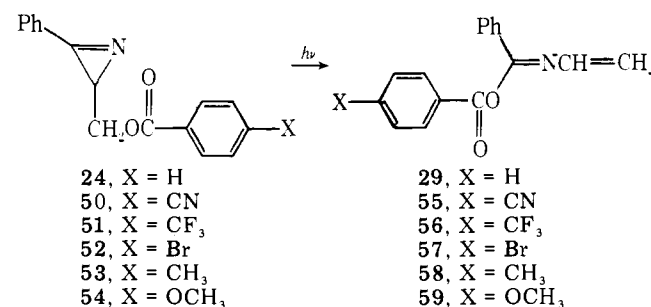


Figure 2. Plot of [quantum yield of rearrangement] against [acrylonitrile] for 3-phenyl-2-trifluoroacetoxy-2H-azirine (**30**).

Further support for this contention was obtained by studying the rate of rearrangement of a series of substituted 3-phenyl-2H-azirine-2-methanolbenzoate derivatives **50–54**. On irradiation of benzene solutions of the azirines, smooth reorganization occurred to give azabutadienes **55–59** in essentially quantitative yield.



The ratio of rate constants for rearrangement of these substituted benzoate esters was determined from the slope and intercepts of the Stern-Volmer plots. The values are summarized in Table I. To facilitate comparison, all the  $k_1$  values are related to that of 3-phenyl-2H-azirine-2-methanolbenzoate (**24**), which is taken as unity. The data presented in Table I clearly show that the rate of rearrangement is a function of the nature of the substituent group in the para position. Electron-withdrawing groups facilitate the rearrangement while electron-donating groups retard the 1,4-substituent shift. These rate effects are best expressed in terms of a Hammett  $\sigma$ - $\rho$  plot. Figure 3 shows a least-square plot of  $-\log k_1$  vs.  $\sigma$  for the photorearrangement of the 3-phenyl-2H-azirine-2-methanolbenzoates. For this series,  $\rho = +2.15$  with a correlation coefficient of 0.997. The value of  $\rho$  is essentially identical with that observed for the rates of hydrolysis of a series of substituted methyl benzoates by hydroxide ion in aqueous acetone solution ( $\rho = +2.23$ ).<sup>45</sup> Both the sign and magnitude of the reaction constant  $\rho$  indicate that the transition state for the rearrangement has substantial negative charge development and is consistent with our view of the reaction proceeding through a tight ion pair (i.e., **47**).<sup>46</sup> The Hammett correlation

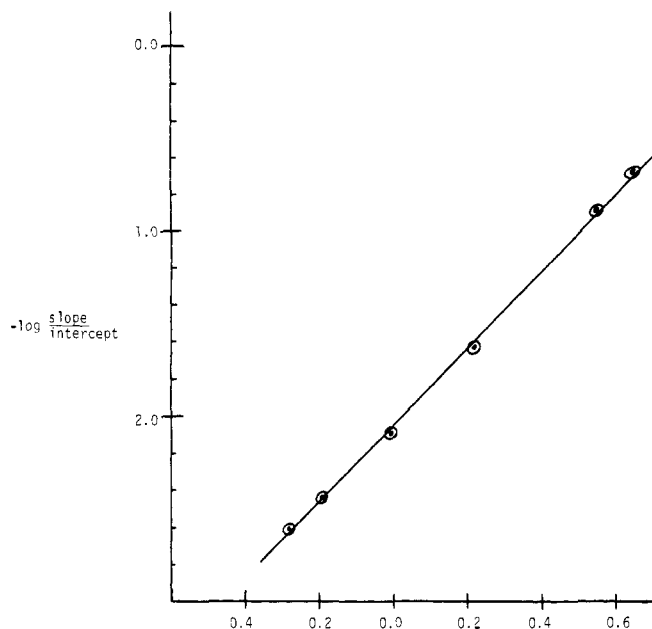


Figure 3. Hammett plot of reaction rate data from Table I.

of Figure 3 clearly shows that neighboring group participation is not involved in these rearrangements. Thus, the Stern-Volmer treatment of the photoreaction demonstrates that the rate of rearrangement is directly related to the leaving group ability and that the migrating substituent must be a reasonably good leaving group in order for the reaction to occur.

#### Experimental Section<sup>47</sup>

**Preparation and Solvolysis of 3-Phenyl-2*H*-azirine-2-methanol Methanesulfonate (3).** To a solution containing 2.35 g of 3-phenyl-2*H*-azirine-2-methanol<sup>14</sup> (**1**) and 1.65 g of triethylamine in 100 mL of methylene chloride at 0 °C was added 1.40 g of methanesulfonyl chloride. The reaction mixture was allowed to stir for 15 min at 0 °C and then 100 mL of water was added. The organic layer was separated and washed with water, a 10% hydrochloric acid solution, a 10% sodium bicarbonate solution, and a saturated salt solution. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to give 3.49 g (90%) of 3-phenyl-2*H*-azirine-2-methanol methanesulfonate (**3**), as a white, crystalline solid; mp 62–63 °C; IR (KBr) 5.70  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  7.42 (1 H, t,  $J$  = 5.0 Hz), 6.95 (3 H, s), 5.76 (1 H, dd,  $J$  = 10.0 and 5.0 Hz), 5.64 (dd, 1 H,  $J$  = 10.0 and 5.0 Hz), 2.2–2.6 (5 H); UV (cyclohexane) 242 nm ( $\epsilon$  12 100);  $m/e$  225, 183, 147, 132 (base), 117, 105, 90, and 77.

Anal. Calcd for C<sub>10</sub>H<sub>11</sub>NO<sub>3</sub>S: C, 53.32; H, 4.92; N, 6.22. Found: C, 53.28; H, 4.83; N, 6.05.

A 300-mg sample of mesylate **3** in 5 mL of a 70% aqueous ethanol solution which contained 1 drop of hydrochloric acid was allowed to reflux for 12 h. The solvent was removed under reduced pressure and the residue was taken up in ether. The ether layer was washed with a 5% sodium bicarbonate solution and was dried over magnesium sulfate. Removal of the solvent left a pale oil whose IR and NMR spectra were identical with those of an authentic sample of 1-phenylpropane-1,2-dione (**4**).<sup>48</sup>

**Reaction of  $\alpha$ ,3-Diphenyl-2*H*-azirine-2-methanol with Methanesulfonyl Chloride.** To a solution containing 330 mg of  $\alpha$ ,3-diphenyl-2*H*-azirine-2-methanol (**2**) in 10 mL of methylene chloride was added 165 mg of triethylamine. The solution was cooled to 0 °C and 240 mg of methanesulfonyl chloride was added dropwise. The reaction mixture was allowed to stir at 0 °C for 15 min and then poured into 25 mL of ice water. The organic layer was separated and washed with a 10% hydrochloric acid solution, a 5% sodium bicarbonate solution, and then water. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give 250 mg (80%) of a white solid, mp 176–177 °C, whose structure was assigned as (*E,E*)-1,4-diphenyl-2-azabutadienyl ether (**8**) on the basis of its chemical

Table I. Relative Reactivity of a Series of Substituted 3-Phenyl-2*H*-azirine-2-methanolbenzoates toward Rearrangement<sup>a</sup>

	$\Phi_0^b$	slope/ intercept	log [slope/ intercept]	$\sigma^c$	$k_{rel}$
X = CN	0.011	4.47	0.65	0.66	38.9
X = CF <sub>3</sub>	0.013	7.26	0.86	0.54	23.9
X = Br	0.023	59.4	1.77	0.23	2.9
X = H	0.031	174	2.24	0.00	1.0
X = CH <sub>3</sub>	0.085	274	2.43	-0.17	0.64
X = OCH <sub>3</sub>	0.06	382	2.58	-0.27	0.45

<sup>a</sup> Stern-Volmer plots used acrylonitrile as the trapping agent.

<sup>b</sup> Quantum yields determined from the intercept. <sup>c</sup> Ordinary Hammett substituent constants: S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973, pp 201–205.

and physical properties: IR (KBr) 6.11  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  2.96 (2 H, d,  $J$  = 15.0 Hz), 2.05 (2 H, d,  $J$  = 15.0 Hz), 1.76–1.90 and 2.40–2.80 (20 H, m); UV (95% ethanol) 310 and 235 nm ( $\epsilon$  26 700 and 17 800);  $m/e$  237, 223, 106, and 77.

In order to verify the structure of this material, an ozonization experiment was carried out. A solution containing 250 mg of the above ether in 40 mL of methylene chloride was cooled to -78 °C and saturated with an ozone stream. The reaction mixture was allowed to warm to -20 °C and 1 mL of dimethyl sulfide was added. After standing for 5 min at -20 °C, the colorless solution was poured into 100 mL of water. The organic layer was separated, washed with water, and dried over sodium sulfate. Removal of the solvent followed by thick layer chromatography afforded 173 mg (80%) of *N*-formylbenzamide (**10**),<sup>49</sup> mp 106–170 °C, and 124 mg (80%) of benzaldehyde.

Further support for the structure of ether **8** was obtained by its ready hydrolysis of *N*-styrylbenzamide (**9**). To a solution containing 60 mg of **8** in 25 mL of tetrahydrofuran was added 15 mL of a 10% hydrochloric acid solution. The mixture was stirred at 25 °C for 12 h and was then neutralized by the addition of solid sodium bicarbonate. The mixture was extracted with methylene chloride, washed with water, and concentrated under reduced pressure to give 45 mg (80%) of *N*-styrylbenzamide (**9**), mp 162–163 °C (lit.<sup>50</sup> 163–164 °C).

Attempts to recrystallize **8** from methanol resulted in a methanolysis reaction. Thus, a sample containing 100 mg of **8** in 1 mL of methanol was heated until it dissolved. The white solid which precipitated on cooling was identified as *N*-styrylbenzamide (**9**). Concentration of the mother liquors afforded 60 mg of an extremely labile oil which could not be purified further as a result of its hydrolytic instability. This material was assigned the structure of (*E*)-1,4-diphenyl-1-methoxy-2-azabutadiene (**11**) on the basis of its spectral data and by an independent synthesis: IR (neat) 6.04 and 6.18  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  5.89 (3 H, s), 3.33 (1 H, d,  $J$  = 15.0 Hz), and 2.24–2.76 (11 H, m). The structure of this material was further verified by treating *N*-styrylbenzamide (**9**) with trimethyloxonium tetrafluoroborate. The material obtained from this reaction was identical in every detail with **11** prepared from the methanolysis of ether **8**.

**Preparation of 3-Phenyl-2-acetoxymethyl-2*H*-azirine (23).** To a solution containing 435 mg of 3-phenyl-2*H*-azirine-2-methanol in 25 mL of benzene were added 1 mL of pyridine and 0.34 mL of acetic anhydride. The reaction mixture was allowed to stir for 12 h at room temperature and was then poured into 50 mL of water. The organic layer was washed with a 10% hydrochloric acid solution and a 5% sodium bicarbonate solution and was dried over sodium sulfate. Removal of the solvent under reduced pressure left 500 mg of a yellow oil which was subjected to silica gel chromatography using a 1:1 ether-pentane mixture as the eluent. The major fraction isolated contained 425 mg of a colorless oil whose structure was assigned as 3-phenyl-2-acetoxymethyl-2*H*-azirine (**23**): IR (neat) 5.70  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  7.99 (3 H, s), 7.51 (1 H, t,  $J$  = 5.0 Hz), 5.80 (1 H, dd,  $J$  = 10.0 and 5.0 Hz), 5.66 (1 H, dd,  $J$  = 10.0 and 5.0 Hz), 2.02–2.50 (5 H, m); UV (cyclohexane) 241 nm ( $\epsilon$  11 000);  $m/e$  189, 147, 146, 130, 104 (base), 103, and 77.

Anal. Calcd for C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.83; H, 5.95; N, 7.64.

**Reaction of 3-Phenyl-2*H*-azirine-2-methanol with Trifluoroacetic**

**Anhydride.** To a solution containing 1.45 g of 3-phenyl-2H-azirine-2-methanol (**1**) in 60 mL of benzene was added 3 mL of pyridine followed by 2.2 g of trifluoroacetic anhydride. The reaction mixture was allowed to stir for 12 h at 25 °C and was then poured over 50 mL of water and the organic layer was separated. The benzene extracts were washed with dilute acid and water, dried, and concentrated under reduced pressure. The resulting yellow oil was subjected to dry column chromatography using a 1:1 ether-pentane mixture as the eluent. The minor component obtained contained 720 mg (30%) of an oil which was distilled at 65 °C (0.01 mm) to give 1-phenyl-2-*N*-trifluoroacetylaminoprop-2-en-1-one (**31**): IR (neat) 2.99, 5.73, 6.00, and 6.02  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  4.12 (1 H, d,  $J$  = 2.0 Hz), 2.88 (1 H, d,  $J$  = 2.0 Hz), 2.19–2.69 (5 H, m), and 0.51 (1 H, singlet, exchanged with D<sub>2</sub>O); UV (95% ethanol) 252 nm ( $\epsilon$  7600);  $m/e$  243 (M<sup>+</sup>), 130, 105 (base), and 77.

Anal. Calcd for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>NO<sub>2</sub>: C, 54.33; H, 3.31; N, 5.76. Found: C, 54.46; H, 3.28; N, 5.65.

The major component (60%) obtained from the column was a white solid, mp 69–70 °C, whose structure was assigned as 2-trifluoromethyl-4-hydroxymethyl-5-phenyloxazole (**35**) on the basis of its spectral properties: IR (KBr) 2.90  $\mu$ ; NMR (CDCl<sub>3</sub>, 60 MHz)  $\tau$  5.20 (2 H, s), 6.12 (1 H, exchanged with D<sub>2</sub>O), 2.19–2.68 (m, 5 H); UV (95% ethanol) 255 nm ( $\epsilon$  17 800);  $m/e$  243 (M<sup>+</sup>, base), 224, 214, 187.4 (metastable), 147, 130, 117, 105, and 77.

Anal. Calcd for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>NO<sub>2</sub>: C, 54.33; H, 3.31; N, 5.76. Found: C, 54.39; H, 3.27; N, 5.61.

It should be noted that structure **35** was not present in the crude reaction mixture. It was subsequently shown that **35** was actually obtained from the hydrolysis of 2-trifluoromethyl-4-trifluoroacetoxymethyl-5-phenyloxazole (**32**) on silica gel chromatography. The trifluoroacetate derivative **32** was isolated from the reaction mixture in the following manner. To a solution containing 145 mg of **1** in 10 mL of benzene were added 440 mg of trifluoroacetic anhydride and 0.5 mL of pyridine. The reaction mixture was allowed to stir at 25 °C for 12 h and was then poured over 20 mL of water. The resulting organic layer was washed with a 5% sodium bicarbonate solution and was dried over sodium sulfate. Removal of the solvent left 257 mg (74%) of a white solid, mp 23–24 °C, which was assigned the structure of 2-trifluoromethyl-4-trifluoroacetoxymethyl-5-phenyloxazole (**32**): IR (neat) 5.53  $\mu$ ; NMR (CDCl<sub>3</sub>, 60 MHz)  $\tau$  4.45 (2 H, s) and 2.63 (5 H, m); UV (95% ethanol) 263 nm ( $\epsilon$  14 700);  $m/e$  339 (M<sup>+</sup>), 243, 103, and 77.

Anal. Calcd for C<sub>13</sub>H<sub>7</sub>F<sub>6</sub>NO<sub>3</sub>: C, 46.03; H, 2.08; N, 4.13. Found: C, 46.20; H, 2.36; N, 4.08.

Chromatography of this material over silica gel resulted in the quantitative formation of 2-trifluoromethyl-4-hydroxymethyl-5-phenyloxazole (**35**).

#### Preparation of 3-Phenyl-2-trifluoroacetoxymethyl-2H-azirine (**30**).

To a solution containing 1.45 g of **1** in 50 mL of benzene was added 4 mL of pyridine followed by the dropwise addition of 2.1 g of trifluoroacetic anhydride. The reaction mixture was allowed to stir for only 3 h and was then concentrated under reduced pressure. The residual oil was subjected to molecular distillation to give 1.97 g of 3-phenyl-2-trifluoroacetoxymethyl-2H-azirine (**30**) as a colorless oil which rapidly darkened on exposure to the atmosphere: IR (neat) 5.67 and 5.78  $\mu$ ; NMR (CDCl<sub>3</sub>, 60 MHz)  $\tau$  7.42 (1 H, t,  $J$  = 5.0 Hz), 5.40 (2 H, d,  $J$  = 5.0 Hz), 2.00–2.58 (5 H, m); UV (cyclohexane) 243 nm ( $\epsilon$  14 100);  $m/e$  243 (M<sup>+</sup>), 130, 105 (base), and 77.

Anal. Calcd for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>NO<sub>2</sub>: C, 54.33; H, 3.31; N, 5.76. Found: C, 54.38; H, 3.46; N, 5.74.

Treatment of this material with trifluoroacetic anhydride for 12 h followed by a normal workup afforded structures **31** and **32** as the only two identifiable compounds.

**Reaction of 3-Phenyl-2-acetoxymethyl-2H-azirine with Trifluoroacetic Anhydride.** To a solution containing 771 mg of 3-phenyl-2-acetoxymethyl-2H-azirine (**23**) and 4 mL of pyridine in 50 mL of benzene was added 0.58 mL of trifluoroacetic anhydride. After stirring for 12 h at room temperature, the mixture was poured onto 50 mL of water and extracted with benzene. The benzene extracts were washed with dilute acid and water, dried over sodium sulfate, and concentrated under reduced pressure to a yellow oil. This material was subjected to silica gel chromatography using a 1:1 ether-pentane mixture as the eluent. The least polar compound (280 mg, 22%) was identified as 1-phenyl-2-*N*-trifluoroacetylaminoprop-2-en-1-one (**31**). The second component isolated from the column was identified as 2-trifluoromethyl-4-acetoxymethyl-5-phenyloxazole (**34**, 285 mg, 22%) on the

basis of its chemical and physical properties: IR (neat) 5.80  $\mu$ ; NMR (CDCl<sub>3</sub>, 60 MHz)  $\tau$  7.88 (3 H, s), 4.80 (2 H, s), 2.20–2.83 (5 H, m);  $m/e$  189, 147, 146 (base), 105, 84, and 77. The structure of this material was further verified by a base-induced hydrolysis to **35**. To a solution containing 80 mg of **34** in 15 mL of anhydrous methanol was added 1.0 g of potassium carbonate. The reaction mixture was allowed to stir for 1 h at room temperature and was then poured into 15 mL of water. Normal workup procedure gave 65 mg of a single component whose structure was identified as 2-trifluoromethyl-4-hydroxymethyl-5-phenyloxazole (**35**).

The last fraction isolated from the column contained 445 mg (37%) of a white solid, mp 61–62 °C, whose structure was assigned as 1-*N*-trifluoroacetoxymethyl-2-acetoxypropiophenone (**33**) on the basis of its spectroscopic properties: IR (KBr) 2.98, 5.71, 5.79, and 5.91  $\mu$ ; NMR (CDCl<sub>3</sub>, 60 MHz)  $\tau$  8.00 (3 H, s), 5.81 (1 H, dd,  $J$  = 11.0 and 6.0 Hz), 5.21 (1 H, dd,  $J$  = 11.0 and 4.0 Hz), 4.00–4.18 (1 H, m), 1.82–2.60 (6 H, m); UV (95% ethanol) 247 nm ( $\epsilon$  13 100);  $m/e$  243, 130, 105 (base), and 77.

Anal. Calcd for C<sub>13</sub>H<sub>12</sub>F<sub>3</sub>NO<sub>4</sub>: C, 51.49; H, 3.99; N, 4.62. Found: C, 51.47; H, 3.91; N, 4.41.

The structure of this material was further verified by a base-induced elimination of acetic acid. A solution containing 100 mg of **33** in 5 mL of pyridine was heated at reflux for 1 h. After cooling, the mixture was taken up in ether, washed with dilute acid, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 72 mg (84%) of a colorless oil which was identical with a sample of **31** obtained previously.

**Irradiation of 3-Phenyl-2-acetoxymethyl-2H-azirine (**23**).** A solution containing 500 mg of **23** in 450 mL of benzene was irradiated for 1.5 h through a Vycor filter sleeve. Removal of the solvent under reduced pressure left 500 mg of a yellow oil whose structure was assigned as 1-acetoxyl-1-phenyl-2-azabutadiene (**28**) on the basis of the following data: IR (neat) 5.92, 6.12, and 6.27  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  7.76 (3 H, s), 5.49 (1 H, d,  $J$  = 16.0 Hz), 5.24 (1 H, d,  $J$  = 9.0 Hz), 3.04 (dd, 1 H,  $J$  = 16.0 and 9.0 Hz), 2.42–2.60 (3 H, m), 2.10–2.26 (2 H, m); UV (cyclohexane) 223 nm ( $\epsilon$  8000);  $m/e$  189, 148, 130, 150 (base), 104, and 77.

Anal. Calcd for C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.76; H, 5.74; N, 7.28.

The structure of this material was further verified by hydrolysis to *N*-vinylbenzamide (**40**).

When the irradiation of azirine **23** was carried out for 3 h, a new compound was produced. Subsequent studies showed that this material was a secondary photoproduct derived from 1-acetoxy-1-phenyl-2-azabutadiene (**28**). Thus, irradiation of a solution of **28** (500 mg) in 400 mL of benzene for 6 h through Pyrex-filtered light followed by evaporation of the solvent and Florisil column chromatography gave 470 mg (94%) of a crystalline solid, mp 99–100 °C, whose structure was assigned as 1-acetoxy-2,3-dihydroisoquinoline (**42**) on the basis of its spectral properties and by comparison with an authentic sample: IR (KBr) 5.90 and 6.20  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  7.36 (3 H, s), 7.00 (2 H, t,  $J$  = 6.0 Hz), 5.88 (2H t,  $J$  = 6.0 Hz), and 2.37–2.84 (4 H, m), and 1.84–1.96 (1 H, m); UV (95% ethanol) 220 nm ( $\epsilon$  8700);  $m/e$  189 (M<sup>+</sup>), 147 (base), 119, 118, 90, and 76. Further verification of this structure was obtained by comparison with an independently synthesized sample. To a solution containing 2,3-dihydroisocarbostyryl<sup>51</sup> (**43**) in 50 mL of isopropenyl acetate was added a catalytic quantity of *p*-toluenesulfonic acid. The solution was heated at reflux for 12 h and the solvent was removed under reduced pressure to give 1.1 g (64%) of a white solid after Florisil column chromatography. This material was identical in every detail with the photoproduct derived from the irradiation of **28**.

The irradiation of **23** was also carried out in the presence of a trapping agent. A solution containing 300 mg of **23** and 5 mL of methyl trifluoroacetate in 250 mL of benzene was irradiated for 1 h using a Vycor filter. Removal of the solvent followed by silica gel chromatography using a 50% ether-pentane mixture as the eluent gave a mixture (3:2) of *cis*- and *trans*-2-acetoxymethyl-4-phenyl-5-methoxy-5-trifluoromethyl-2,5-dihydro-1,3-oxazine (**44**) in 90% isolated yield. The minor isomer showed signals in the NMR (CDCl<sub>3</sub>, 60 MHz) at  $\tau$  7.95 (s, 3 H), 6.58 (s, 3 H), 5.76 (dd, 1 H,  $J$  = 12.0 and 5.0 Hz), 5.48 (dd, 1 H,  $J$  = 12.0 and 5.0 Hz), 4.08 (t, 1 H,  $J$  = 5.0 Hz), and 1.8–2.7 (m, 5 H), while the major isomer exhibited signals at  $\tau$  7.90 (s, 3 H), 6.63 (s, 3 H), 5.74 (dd, 1 H,  $J$  = 12.0 and 5.0 Hz), 5.46 (dd, 1 H,  $J$  = 12.0 and 5.0 Hz), 3.80 (t, 1 H,  $J$  = 5.0 Hz), and 1.8–2.7 (m, 5 H); IR (neat) of mixture 5.75, 6.15, 6.34, 6.69, 6.90, 7.25, 7.30,

7.57, 7.60, 8.20, 8.40, 9.25, 9.52, 10.60, 11.01, 12.96, 13.58, and 14.35  $\mu$ .

Anal. Calcd for  $C_{14}H_{14}NO_4F_3$ : C, 53.00; H, 4.45; N, 4.41. Found: C, 52.83; H, 4.43; N, 4.28.

**Irradiation of 3-Phenyl-2-trifluoroacetoxymethyl-2H-azirine (30).** A solution containing 110 mg of **30** in 100 mL of benzene was irradiated for 1.5 h through a Corex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil whose structure was assigned as 1-trifluoroacetoxy-1-phenyl-2-azabutadiene (**48**): NMR ( $CDCl_3$ , 100 MHz)  $\tau$  5.28 (1 H, dd,  $J = 16.0$  and  $2.0$  Hz), 5.07 (1 H, dd,  $J = 8.0$  and  $2.0$  Hz), 3.14 (1 H, dd,  $J = 16.0$  and  $8.0$  Hz), 2.10–2.90 (m, 5 H).<sup>52</sup> This material was rapidly hydrolyzed to *N*-vinylbenzamide on treatment with aqueous acid.

**Synthesis and Irradiation of 2-Chloromethyl-3-phenyl-2H-azirine (21).** To a solution containing 2.5 g of 3-phenyl-2-methanol-2H-azirine (**1**) in 80 mL of carbon tetrachloride and 400 mL of ether at 0 °C was added 2.83 g of tris(dimethylamino)phosphine. The reaction mixture was allowed to warm to 25 °C, stirred for an additional 30 min, and then poured into 250 mL of water. The organic layer was separated, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a dark oil. Molecular distillation of the residue at 50 °C (0.002 mm) gave 1.6 g (65%) of a colorless oil whose structure was assigned as 3-phenyl-2-chloromethyl-2H-azirine (**21**) on the basis of its spectral properties:<sup>52</sup> IR (neat) 5.70  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  7.39 (1 H, t,  $J = 5.0$  Hz), 6.53 (1 H, dd,  $J = 11.0$  and  $5.0$  Hz), 6.18 (1 H, dd,  $J = 11.0$  and  $5.0$  Hz), 2.10–2.60 (5 H, m); UV (95% ethanol) 241 nm ( $\epsilon$  14 000);  $m/e$  130, 104 (base), 103, and 77.

A solution containing 350 mg of the above azirine in 250 mL of benzene was irradiated for 8 h using a Vycor filter sleeve. Removal of the solvent under reduced pressure left 342 mg of a yellow oil which was shown to be 1-chloro-1-phenyl-2-azabutadiene (**26**) on the basis of its spectral properties:<sup>52</sup> IR (neat) 6.27 and 6.78  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  4.71 (1 H, d,  $J = 7.0$  Hz), 4.34 (1 H, d,  $J = 15.0$  Hz), 2.40–2.78 (4 H, m), and 1.79–1.96 (2 H, m); UV (cyclohexane) 264 nm ( $\epsilon$  12 800);  $m/e$  167, 165, 130 (base), 105, 104, 103, and 77. The structure of this material was verified by hydrolysis to *N*-vinylbenzamide in quantitative yield, mp 100–101 °C (lit.<sup>50</sup> 101–102 °C). Lithium aluminum hydride reduction of **26** gave *N*-ethylbenzylamide in quantitative yield.

**Synthesis and Irradiation of 3-Phenyl-2-bromomethyl-2H-azirine (22).** To a solution containing 300 mg of 3-phenyl-2H-azirine-2-methanol methanesulfonate (**3**) in 25 mL of ether was added 1.0 g of lithium bromide. The reaction mixture was stirred at room temperature for 23 h, filtered, concentrated under reduced pressure, and taken up in 400 mL of anhydrous benzene. The benzene solution was irradiated for 8 h through a Vycor filter sleeve. Removal of the solvent left 279 mg (93%) of a moisture-sensitive oil whose structure was assigned as 1-bromo-1-phenyl-2-azabutadiene (**27**) on the basis of the following data:<sup>52</sup> IR (neat) 6.08 and 6.25  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  4.67 (1 H, d,  $J = 7.0$  Hz), 4.31 (1 H, d,  $J = 15.0$  Hz), 2.87 (1 H, dd,  $J = 15.0$  and  $7.0$  Hz), 2.48–2.71 (3 H, m), and 1.80–1.99 (2 H, m);  $m/e$  211, 209, 167, 165, 131, 130 (base), 105, 104, 103, and 77. This material was rapidly converted to *N*-vinylbenzamide on treatment with water and was reduced with lithium aluminum hydride to give *N*-ethylbenzylamine in quantitative yield.

**Synthesis of 3-Phenyl-2-methoxymethyl-2H-azirine (25).** To a solution containing 26.8 g of cinnamyl alcohol and 14.4 mL of methyl iodide in 150 mL of anhydrous 1,2-dimethoxyethane was added 5.2 g of sodium hydride in small portions. The reaction mixture was stirred for 3 h at room temperature and then filtered. Removal of the solvent under reduced pressure left an oil which was taken up in ether. The ethereal solution was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a yellow oil which was distilled at 117 °C (20 mm) to give 25.2 g (85%) of 1-phenyl-3-methoxyprop-1-ene as a colorless oil: IR (neat) 6.02  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  6.67 (3 H, s), 5.98 (2 H, d,  $J = 5.0$  Hz), 3.76 (1 H, m), 3.36 (1 H, d,  $J = 16.0$  Hz), and 2.80 (5 H, m).

To a suspension containing 15 g of sodium azide in 100 mL of acetonitrile at 0 °C was added 6 mL of iodine monochloride. The slurry was allowed to stir for 20 min at 0 °C and then 14.3 g of 1-phenyl-3-methoxyprop-1-ene was added in one portion. The reaction mixture was allowed to stir for an additional 9 h and was then poured over 200 mL of water. The aqueous layer was extracted with ether and the ethereal layer was washed with a 10% sodium thiosulfate solution and then water. The organic layer was dried over magnesium sulfate and

the solvent was removed under reduced pressure to give 3-methoxy-2-iodo-1-phenyl-1-azidopropane: IR (neat) 4.75  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  6.60 (3 H, s), 6.14–6.47 (3 H, m), 5.08 (1 H, d,  $J = 7.0$  Hz), and 2.49 (4 H, s).

To an ethereal solution of the above iodoazide adduct at –20 °C was added 13.5 g of potassium *tert*-butoxide. The reaction mixture was stirred for 4 h at –20 °C and then poured into 200 mL of ice water. The organic layer was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent gave 1-phenyl-1-azido-3-methoxyprop-1-ene (78%): IR (neat) 4.72 and 6.10  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  6.71 (3 H, s), 6.08 (2 H, d,  $J = 7.0$  Hz), 4.35 (1 H, t,  $J = 7.0$  Hz), and 2.52 (5 H, s).

A solution containing the above vinyl azide in 500 mL of chloroform was heated at reflux for 7 h. Removal of the solvent under reduced pressure left a red oil which was distilled at 65–70 °C at 0.2 mm to give 12.0 g (70%) of 3-phenyl-2-methoxymethyl-2H-azirine (**25**) as a colorless oil: IR (neat) 5.72  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  7.58 (t, 1 H,  $J = 5.0$  Hz), 6.54 (3 H, s), 6.38 (2 H, d,  $J = 5.0$  Hz), 1.94–2.25 (5 H, m); UV (cyclohexane) 246 nm ( $\epsilon$  16 000);  $m/e$  161, 160, 130 (base), 104, and 77.

Anal. Calcd for  $C_{10}H_{11}NO$ : C, 74.51; H, 6.88; N, 8.69. Found: C, 74.26; H, 6.74; N, 8.73.

**Irradiation of 3-Phenyl-2-methoxymethyl-2H-azirine (25).** A solution containing 500 mg of **25** in 450 mL of benzene was irradiated through a Pyrex filter sleeve for 3 h. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a preparative thick layer plate using ether as the eluent. The major component isolated from the plate contained 233 mg of *exo*-2,6-di(methoxymethyl)-4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**46**) as a colorless oil: IR (neat) 6.01  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  7.79 (1 H, t,  $J = 6.0$  Hz), 6.59 (3 H, s), 6.50 (3 H, s), 6.16 (4 H, m), 4.81 (1 H, t,  $J = 4.0$  Hz), 2.09–2.80 (10 H, m); UV (95% ethanol) 243 nm ( $\epsilon$  19 600);  $m/e$  322 ( $M^+$ ), 321, 283, 269, 238, 165, 117 (base), 104, and 77.

Anal. Calcd for  $C_{20}H_{22}N_2O_2$ : C, 74.51; H, 6.88; N, 8.69. Found: C, 74.68; H, 6.82; N, 8.63.

The minor component obtained from the thick layer plate contained 165 mg (33%) of *endo*-2,6-di(methoxymethyl)-4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**46**):<sup>53</sup> IR (neat) 6.01  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  7.52 (1 H, t,  $J = 6.0$  Hz), 6.56 (3 H, s), 6.52 (3 H, s), 6.12 (4 H, m), 4.25 (1 H, t,  $J = 5.0$  Hz), 2.08–2.75 (10 H, m); UV (95% ethanol) 243 nm ( $\epsilon$  19 600);  $m/e$  322 ( $M^+$ ), 321, 290, 275, 246, 165, 130, 119, 117 (base), 104, and 77.

Anal. Calcd for  $C_{20}H_{22}N_2O_2$ : C, 74.51; H, 6.88; N, 8.69. Found: C, 74.58; H, 6.91; N, 8.46.

**Synthesis of Substituted 3-Phenyl-2H-azirine-2-methanol Benzoates.** The desired aryl-substituted benzoates of 3-phenyl-2H-azirine-2-methanol were prepared by treating a solution of **1** and pyridine in benzene with an appropriate aryl chloride. The resulting mixture was allowed to stir at room temperature for 8 h. The benzene solution was then washed with 10% hydrochloric acid, 5% sodium bicarbonate, water, and a saturated salt solution. After drying over magnesium sulfate the solvent was removed under reduced pressure and the residue was recrystallized from pentane. In this manner the following substituted benzoates were prepared.

**3-Phenyl-2H-azirine-2-methanol benzoate (24)** was prepared in 63% yield: mp 77–78 °C; IR (KBr) 5.82  $\mu$ ; NMR ( $CDCl_3$ , 60 MHz)  $\tau$  7.40 (1 H, t,  $J = 4.5$  Hz), 5.52 (2 H, d,  $J = 4.5$  Hz), and 2.0–2.8 (m, 10 H); UV (cyclohexane) 243 nm ( $\epsilon$  14 000);  $m/e$  251 ( $M^+$ ), 221, 193, 186, 165, 146, 131, 130, 105, 104, 90, and 77.

Anal. Calcd for  $C_{16}H_{13}NO_2$ : C, 76.47; H, 5.22; N, 5.57. Found: C, 76.06; H, 5.29; N, 5.66.

**3-Phenyl-2H-azirine-2-methanol *p*-cyanobenzoate (50)** was prepared in 80% yield: mp 102–103 °C; IR (KBr) 4.50 and 5.88  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  7.58 (1 H, t,  $J = 4.5$  Hz), 5.62 (2 H, d,  $J = 4.5$  Hz), 2.20–2.69 (m, 9 H); UV (cyclohexane) 242 nm ( $\epsilon$  10 000);  $m/e$  276, 211, 172, 144, 135, 104 (base), and 72.

Anal. Calcd for  $C_{17}H_{12}N_2O_2$ : C, 73.90; H, 4.38; N, 10.14. Found: C, 73.51; H, 4.29; N, 10.14.

**3-Phenyl-2H-azirine-2-methanol *p*-trifluoromethylbenzoate (51)** was prepared in 68% yield: mp 69–70 °C; IR (KBr) 5.79  $\mu$ ; NMR ( $CDCl_3$ , 100 MHz)  $\tau$  7.45 (1 H, t,  $J = 4.5$  Hz), 5.48 (2 H, d,  $J = 4.5$  Hz), 1.79–2.51 (9 H, m); UV (cyclohexane) 243 nm ( $\epsilon$  12 000);  $m/e$  300, 173, 144, 130 (base), 104, and 77.

Anal. Calcd for  $C_{17}H_{12}NO_2F_3$ : C, 63.95; H, 3.79; N, 4.38. Found: C, 63.78; H, 3.65; N, 4.07.



**3-Phenyl-2H-azirine-2-methanol p-bromobenzoate (52)** was prepared in 65% yield: mp 64–65 °C; IR (KBr) 5.81  $\mu$ ; NMR (CDCl<sub>3</sub>, 60 MHz)  $\tau$  7.40 (1 H, t,  $J$  = 4.5 Hz), 5.52 (2 H, d,  $J$  = 4.5 Hz), 2.0–2.9 (9 H, m); UV (cyclohexane) 242 nm ( $\epsilon$  14 300);  $m/e$  331, 329, 229, 273, 271, 230, 216, 191, 131, 130, 115, 105, 104 (base), 103, and 77.

Anal. Calcd for C<sub>16</sub>H<sub>12</sub>NO<sub>2</sub>Br: C, 58.20; H, 3.66; N, 4.24. Found: C, 57.85; H, 3.76; N, 4.12.

**2-Phenyl-2H-azirine-2-methanol p-methylbenzoate (53)** was prepared in 68% yield: mp 64–65 °C; IR (KBr) 5.87  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  8.00 (3 H, s), 7.45 (1 H, t,  $J$  = 4.5 Hz), 5.51 (2 H, d,  $J$  = 4.5 Hz), 2.18–2.55 (9 H, m); UV (cyclohexane) 239 nm ( $\epsilon$  12 800);  $m/e$  235, 230, 130, 119, 104 (base), 91, and 77.

Anal. Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>2</sub>: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.81; H, 5.62; N, 5.24.

**3-Phenyl-2H-azirine-2-methanol p-methoxybenzoate (54)** was prepared in 81% yield: mp 88–89 °C; IR (KBr) 5.87  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  7.40 (1 H, t,  $J$  = 4.5 Hz), 6.21 (3 H, s), 5.55 (2 H, d,  $J$  = 4.5 Hz), 2.81–3.30 (9 H, m); UV (cyclohexane) 244 nm ( $\epsilon$  10 000);  $m/e$  251, 135 (base), 131, 130, and 103.

Anal. Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>3</sub>: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.30; H, 5.32; N, 4.93.

**Irradiation of 3-Phenyl-2H-azirine-2-methanol Benzoate (24).** A solution containing 400 mg of **24** in 450 mL of benzene was irradiated for 1 h through a Corex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was filtered through a Florisil column using benzene as the eluent. The major component contained 145 mg (36%) of a solid, mp 124–125 °C, whose structure was assigned as 1-benzoyloxy-1-phenyl-2-azabutadiene (**29**) on the basis of its spectral data: IR (KBr) 5.90, 6.10, and 6.25  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  5.15 (1 H, dd,  $J$  = 16.0 and 1.0 Hz), 5.01 (1 H, dd,  $J$  = 8.0 and 1.0 Hz), 1.90–3.10 (11 H, m);  $m/e$  251, 145, 104, and 77.

Anal. Calcd for C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub>: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.40; H, 5.18; N, 5.46.

The structure of this material was further verified by hydrolysis to *N*-vinylbenzamide. A solution containing 50 mg of **29** in 10 mL of methanol was treated with 1 drop of triethylamine. The mixture was allowed to stir for 24 h at room temperature and was then taken up in ether. The ethereal layer was washed with a 10% aqueous hydrochloric acid solution followed by a 5% sodium bicarbonate solution and water. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give a quantitative yield of *N*-vinylbenzamide.

**Irradiation of 3-Phenyl-2H-azirine-2-methanol p-Bromobenzoate (52).** A solution containing 100 mg of **52** in 125 mL of benzene was irradiated for 20 min through a Vycor filter sleeve. Removal of the solvent under reduced pressure left a yellow oil whose structure was assigned as 1-*p*-bromobenzyloxy-1-phenyl-2-azabutadiene (**57**):<sup>52</sup> NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  5.14 (d, 1 H,  $J$  = 16.0 Hz), 5.06 (d, 1 H,  $J$  = 8.0 Hz), 2.98 (dd, 1 H,  $J$  = 16.0 and 8.0 Hz), 2.0–2.8 (m, 9 H). This material was rapidly hydrolyzed to *N*-vinylbenzamide on treatment with aqueous acid.

**Irradiation of 3-Phenyl-2H-azirine-2-methanol p-Trifluoromethylbenzoate (51).** A solution containing 110 mg of **51** in 150 mL of benzene was irradiated for 20 min through a Vycor filter sleeve. Removal of the solvent under reduced pressure left a yellow oil whose structure was assigned as 1-trifluoromethylbenzyloxy-1-phenyl-2-azabutadiene (**56**):<sup>52</sup> NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  5.10 (1 H, d,  $J$  = 16.0 Hz), 5.02 (1 H, d,  $J$  = 8.0 Hz), 3.10 (1 H, dd,  $J$  = 16.0 and 8.0 Hz), 1.58–2.54 (9 H, m). This material was rapidly hydrolyzed to *N*-vinylbenzamide on treatment with aqueous acid.

**Irradiation of 3-Phenyl-2H-azirine-2-methanol p-Cyanobenzoate (50).** A solution containing 110 mg of **50** in 150 mL of benzene was irradiated for 15 min using a Vycor filter sleeve. Removal of the solvent under reduced pressure left a yellow oil whose structure was assigned as 1-*p*-cyanobenzyloxy-1-phenyl-2-azabutadiene (**55**):<sup>52</sup> NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  4.81 (1 H, dd,  $J$  = 16.0 and 1.0 Hz), 4.71 (1 H, dd,  $J$  = 8.0 and 1.0 Hz), 2.71 (1 H, dd,  $J$  = 16.0 and 8.0 Hz), 1.46–2.44 (9 H, m). This material was rapidly hydrolyzed to *N*-vinylbenzamide on treatment with aqueous acid.

**Irradiation of 3-Phenyl-2H-azirine-2-methanol p-Methylbenzoate (53).** A solution containing 225 mg of 3-phenyl-2H-azirine-2-methanol *o*-methylbenzoate (**53**) in 150 mL of benzene was irradiated for 20 min with Vycor-filtered light. Removal of the solvent under reduced pressure left a yellow oil whose structure was assigned as 1-*p*-methylbenzyloxy-1-phenyl-2-azabutadiene (**58**):<sup>52</sup> NMR (CDCl<sub>3</sub>, 100

MHz)  $\tau$  8.48 (3 H, s), 5.22 (1 H, dd,  $J$  = 16.0 and 1.0 Hz), 5.18 (1 H, dd,  $J$  = 8.0 and 1.0 Hz), 1.92–3.16 (m, 10 H). This material was rapidly hydrolyzed to *N*-vinylbenzamide on treatment with aqueous acid.

**Irradiation of 3-Phenyl-2H-azirine-2-methanol p-Methoxybenzoate (54).** A solution containing 100 mg of **54** in 150 mL of benzene was irradiated for 20 min through a Vycor filter sleeve. Removal of the solvent under reduced pressure left a yellow oil whose structure was assigned as 1-*p*-methoxybenzyloxy-1-phenyl-2-azabutadiene (**59**):<sup>52</sup> NMR (CDCl<sub>3</sub>, 100 MHz)  $\tau$  6.16 (3 H, s), 5.45 (1 H, dd,  $J$  = 16.0 and 1.0 Hz), 5.37 (1 H, dd,  $J$  = 9.0 and 1.0 Hz), 2.04–3.24 (10 H, m). This material was rapidly hydrolyzed to *N*-vinylbenzamide on treatment with aqueous acid.

**Quantum Yield Determinations.** All quantitative measurements were made on a rotating assembly at room temperature using a Rayonet reactor equipped with 2537-Å lamps. Samples were degassed to  $5 \times 10^{-3}$  mm in three freeze-thaw cycles and then sealed. Cyclopentanone solutions were used as the chemical actinometer for which a quantum yield of 0.38 was used,<sup>43</sup> giving a reproducible lamp output of  $1.73 \times 10^{17}$  quanta s<sup>-1</sup>. After irradiation, the degree of reaction was determined by quantitative NMR analysis using a Varian XL-100 FT instrument. The conversions were run to 20% or less and deoxybenzoin and 1,4-dimethoxybenzene were used as internal standards.

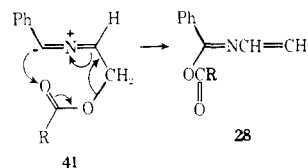
**Competitive studies** were carried out photochemically on mixtures of an arylazirine, an internal standard, and acrylonitrile as the trapping reagent. Since cycloaddition rates varied considerably between systems, tubes were removed periodically and analyzed periodically by NMR until optimum conversion times for analysis had been determined. All measurements were made on a "merry-go-round" assembly at room temperature using a 2537-Å source. Varying quantities of acrylonitrile were added to solutions of the azirine. The amount of rearranged product was determined by NMR analysis after ca. 20% of starting material had been consumed.

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## References and Notes

- Photochemical Transformations of Small Ring Heterocyclic Compounds. 99. For part 98, see A. Padwa, U. Chiacchio, and N. Hatanaka, *J. Am. Chem. Soc.*, **100**, 3928 (1978).
- M. Y. Lukina, *Russ. Chem. Rev. (Engl. Transl.)*, 419 (1962).
- R. Breslow in "Molecular Rearrangements", Vol. I, P. de Mayo, Ed., Interscience, New York, N.Y., 1963, Chapter 4.
- V. R. Gaertner, *Tetrahedron Lett.*, 5919 (1969); *J. Org. Chem.*, **35**, 3952 (1970).
- J. A. Deyrup and C. L. Moyer, *Tetrahedron Lett.*, 6179 (1969).
- A. Padwa, P. Cimiluca, and D. Eastman, *J. Org. Chem.*, **37**, 805 (1972).
- M. Sander, *Monatsh. Chem.*, **96**, 896 (1965).
- E. P. Adams, K. N. Ayad, F. P. Doyle, D. O. Holland, W. H. Hunter, J. H. C. Naylor, and A. Queen, *J. Chem. Soc.*, 2665 (1960).
- H. G. Richey, *Tetrahedron Lett.*, 5919 (1968).
- R. Breslow and M. Battiste, *J. Am. Chem. Soc.*, **82**, 3626 (1960); R. Breslow, J. Lockhart, and A. Small, *ibid.*, **84**, 2793 (1962).
- R. Breslow, H. Bozimo, and P. Wolf, *Tetrahedron Lett.*, 2395 (1970).
- A somewhat specialized case of the reverse rearrangement, i.e., cyclobutenyl to cyclopropenylcarbinyl, has recently been reported; see J. Ciabattoni and A. E. Feiring, *J. Am. Chem. Soc.*, **94**, 5113 (1972); **95**, 5266 (1973).
- For a preliminary report, see A. Padwa, J. K. Rasmussen, and A. Tremper, *J. Chem. Soc., Chem. Commun.*, 10 (1976).
- A. Padwa, J. K. Rasmussen, and A. Tremper, *J. Am. Chem. Soc.*, **98**, 2605 (1976).
- Simple Hückel LCAO-MO calculations indicate a delocalization energy of 1.58 $\beta$  for the parent system: G. R. Harvey and K. W. Ratts, *J. Org. Chem.*, **31**, 3907 (1966), footnote 13.
- J. Ciabattoni and M. Cabell, Jr., *J. Am. Chem. Soc.*, **93**, 1482 (1971).
- F. W. Fowler, *Adv. Heterocycl. Chem.*, **13**, 45 (1971).
- C. A. Grob and P. Wenk, *Tetrahedron Lett.*, 4191, 4195 (1976).
- T. Sato, W. Wakatsuka, and K. Amano, *Tetrahedron*, **27**, 5381 (1971).
- I. Fleming and R. B. Woodward, *J. Chem. Soc., Perkin Trans. 1*, 1653 (1973).
- C. A. Grob, H. P. Fischer, W. Raudenbusch, and J. Zergenyi, *Helv. Chim. Acta*, **47**, 1003 (1964).
- A. Padwa, *Acc. Chem. Res.*, **9**, 371 (1976).
- P. Gilgen, H. Heimgartner, H. Schmid, and H. J. Hansen, *Heterocycles*, **6**, 143 (1977).
- A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *J. Am. Chem. Soc.*, **95**, 1945 (1973).

- (25) B. Castro, Y. Chapleur, B. Gross, and C. Selve, *Tetrahedron Lett.*, 5001 (1972); *Bull. Soc. Chem. Fr.*, 3034 (1973).
- (26) A. Hassner and L. A. Levy, *J. Am. Chem. Soc.*, **87**, 4203 (1965).
- (27) S. Sato, H. Kato, and M. Ohta, *Bull. Chem. Soc. Jpn.*, **40**, 2938 (1967).
- (28) F. W. Fowler and A. Hassner, *J. Am. Chem. Soc.*, **90**, 2875 (1968).
- (29) S. Sato, *Nypon Kagaku Zasshi*, **90**, 113 (1969).
- (30) P. B. Valkovich, J. L. Conger, F. A. Castiello, T. D. Brodie, and W. P. Weber, *J. Am. Chem. Soc.*, **97**, 90 (1975).
- (31) L. A. Wendling and R. G. Bergman, *J. Org. Chem.*, **41**, 831 (1976).
- (32) I. Ninomiya, T. Naito, and T. Kiguchi, *Tetrahedron Lett.*, 4451 (1970); *J. Chem. Soc., Perkin Trans. 1*, 1720, 762 (1975).
- (33) Y. Ogata, K. Takagi, and J. Ishino, *J. Org. Chem.*, **36**, 3975 (1971).
- (34) N. C. Yang and G. R. Lenz, *Tetrahedron Lett.*, 4897 (1967).
- (35) A. Orahovats, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, **57**, 2626 (1974).
- (36) P. Claus, P. Gilgen, H. J. Hansen, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, **57**, 2173 (1974).
- (37) A. Padwa, S. Clough, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *J. Am. Chem. Soc.*, **94**, 1395 (1972).
- (38) A. Padwa, J. Smolanoff, and S. I. Wetmore, Jr., *J. Org. Chem.*, **38**, 1333 (1973).
- (39) N. Gakis, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 748 (1972).
- (40) N. S. Narasimhan, H. Heimgartner, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **56**, 1351 (1973).
- (41) A. L. Logothetis, *J. Org. Chem.*, **29**, 3049 (1964).
- (42) V. Nair, *J. Org. Chem.*, **33**, 2121 (1968); *Tetrahedron Lett.*, 4831 (1971).
- (43) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 1318 (1970).
- (44) Previous work in our laboratory has shown that the relative reactivities of the nitrile ylides generated from different 2*H*-azirine precursors are very similar toward a given dipolarophile, thereby justifying this assumption; see A. Padwa, J. Smolanoff, and A. I. Tremper, *J. Am. Chem. Soc.*, **97**, 4682 (1975).
- (45) H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
- (46) It should be noted that the available data do not exclude the alternate electronic description shown below. However, the magnitude of the reaction



- constant  $\rho$  seems to be more consistent with the ion pair description. Further experiments with  $^{18}\text{O}$ -labeled esters are planned to distinguish between these two possibilities.
- (47) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Varian XL-100 and a Jeolco MH-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All preparative irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc.
- (48) W. Borsche, *Ber.*, 737 (1907).
- (49) Q. E. Thompson, *J. Am. Chem. Soc.*, **73**, 5914 (1951).
- (50) D. Ben-Ishai and R. Giger, *Tetrahedron Lett.*, 4523 (1965).
- (51) P. T. Lansbury, J. G. Colson, and N. R. Mancusco, *J. Am. Chem. Soc.*, **86**, 5225 (1964).
- (52) Owing to the extreme hydrolytic sensitivity of this system, it has not been possible to obtain satisfactory elemental analyses.
- (53) The stereochemical assignment was based on the fact that proton  $\text{H}_2$  in the exo isomer ( $\tau$  4.81) appears at a higher field than the related proton in the endo isomer ( $\tau$  4.25). This is compatible with the anisotropic shielding of this proton by the adjacent aziridine ring<sup>54</sup> and is also consistent with the assignments made for related azabicyclo[3.1.0]hex-3-enes.<sup>55</sup>
- (54) K. Tosi, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 868 (1965).
- (55) A. Padwa and E. Glazer, *J. Am. Chem. Soc.*, **94**, 7788 (1972).

## Effects of pH in Photoreduction by Hydrazine

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**Abstract:** Quantum yields,  $\phi_{\text{ketyl}}$ , for photoreduction of 0.005 M 4-benzoylbenzoate by 0.04 M hydrazine rise from 0.12 at pH 5.8 to 0.35 at pH 7.3 and fall to 0.03 at pH 12. Added ammonium ion and *tert*-butylammonium ion do not affect the reduction. Values of  $k_d$ , from phosphorescence decay, are  $5.6 \times 10^4 \text{ s}^{-1}$  at pH 7 and  $8.0 \times 10^4 \text{ s}^{-1}$  at pH 11.2, and are concentration dependent owing to quenching by ground-state ketone,  $k_q = 6.2 \times 10^6$  and  $8.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at pH 7 and 12. Quenching of phosphorescence, at pH 5.6–11.7, leads to  $k_{\text{ir}} = 6.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for interaction with hydrazine, and  $k'_{\text{ir}} = 4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for interaction with hydrazinium ion. From the effects of concentration of hydrazine on quantum yields, ratios of kinetic constants are obtained,  $k_{\text{ir}}/k_d = 7200 \text{ M}^{-1}$ ,  $k'_{\text{ir}}/k_d = 9.9 \text{ M}^{-1}$ ,  $k'_{\text{ir}}/k_{\text{ir}} = 1.4 \times 10^{-3}$ . The effects of pH on quantum yields are considered in terms of quenching and reduction by both hydrazine and protonated hydrazine, accompanied by regeneration of starting materials by oxidation of ketyl radical anion by hydrazyl radical, importantly at high pH, and by oxidation of ketyl radical by protonated hydrazyl radical, importantly at low pH. Interaction of triplet with protonated hydrazine may lead only to quenching. Free hydrazine is the major reducing agent. A detailed kinetic scheme is developed, which leads to calculated quantum yields essentially the same as those observed over the entire range of pH. Earlier mechanistic proposals are corrected and remaining ambiguities are discussed.

While alcohols are effective photoreducing agents for aromatic carbonyl compounds with  $n, \pi^*$  excited triplets, amines may be quite general photoreducing agents, acting also on the generally less reactive  $\pi-\pi^*$  and charge-transfer triplets.<sup>1</sup> Hydrogen on an atom  $\alpha$  to the nitrogen is essential for reduction, while amino hydrogen is not. We have proposed that amines are both quenchers and photoreducing agents: the reaction proceeds via rapid initial formation,  $k_{\text{ir}}$ , of a charge-transfer complex, CTC; this may be followed either by transfer of an  $\alpha$  hydrogen, rendered acidic by the radical-cationic nitrogen, or by spin inversion and return to the ground state, facilitated by mixing of the triplet carbonyl and singlet amine states,  $k_{\text{h}}$  and  $k_{\text{e}}$ , respectively, eq 1.<sup>2,3</sup>

Formation of the CTC facilitates both reduction and

quenching, and makes reduction more general, but with inherent potential inefficiency.

