

Steady-State and Laser Photolysis Studies of Substituted 2*H*-Azirines. Spectroscopy, Absolute Rates, and Arrhenius Behavior for the Reaction of Nitrile Ylides with Electron Deficient Olefins[†]

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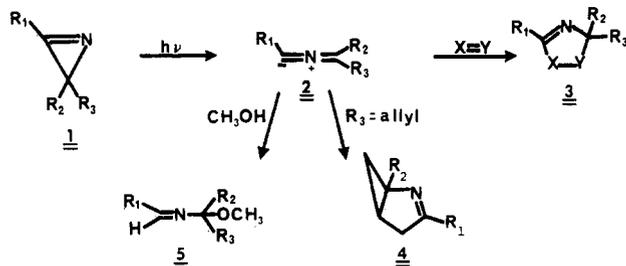
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The photobehavior of 2,2-diphenyl-3-methyl-2*H*-azirine (15) and 2-methyl-2,3-diphenyl-2*H*-azirine (14) was investigated in solution at 298 K. Both azirines undergo ready ring opening on exposure to UV light to give nitrile ylides which can be trapped with methyl acrylate or methanol. In the absence of a trapping reagent, the ylide derived from azirine 15 undergoes 1,5-electrocyclization followed by a 1,3-sigmatropic hydrogen shift to give an isoindole derivative. The transient absorption spectra obtained after pulsed laser photolysis of azirines 14, 15, and 2,3-diphenyl-2*H*-azirine (13) in isoctane at 298 K are in good agreement with those obtained at 77 K in a 3-methylpentane glass. Absolute quenching rate constants for reaction of the ylides derived from azirines 13-15 with acrylonitrile and fumaronitrile are consistent with competitive quenching studies. The Arrhenius behavior for the reaction of the ylide derived from azirine 13 with methyl acrylate and diethyl fumarate gives evidence for reversible formation of an ylide-olefin complex.

Introduction

The ready availability of 2*H*-azirines has spurred considerable activity in the chemistry of these strained heterocycles.^{1,2} Photochemical and thermal cleavage preferences in 2*H*-azirines appear to be quite distinct.³ Photolysis of 2*H*-azirines (1) leads to irreversible ring



opening and the formation of nitrile ylides (2) as intermediates.⁴⁻⁷ These species may be intercepted by a variety of dipolarophiles to form five-membered heterocyclic rings (3). In certain cases the initially formed 1,3-dipole can be intramolecularly trapped to give novel azabicyclohexenes (4).⁸

Frontier molecular orbital theory correctly rationalizes the regioselectivity of most 1,3-dipolar cycloadditions.⁹ When nitrile ylides are used as 1,3-dipoles, the dipole highest occupied (HOMO) and dipolarophile lowest unoccupied (LUMO) orbital interaction stabilizes the transition state. The favored cycloadduct is that formed by the union of the atoms with the largest coefficients in the dipole HOMO and dipolarophile LUMO. An electron-deficient olefin has the largest coefficient on the unsubstituted carbon in the LUMO.⁹ The photoconversion of 2*H*-azirines to alkoxy imines (5) indicates that in the HOMO of the nitrile ylide, the electron density at the disubstituted carbon is greater than at the trisubstituted carbon atom.¹⁰ With this conclusion, all of the regiochemical data found in the photoaddition of 2*H*-azirines with a variety of dipolarophiles can be explained.

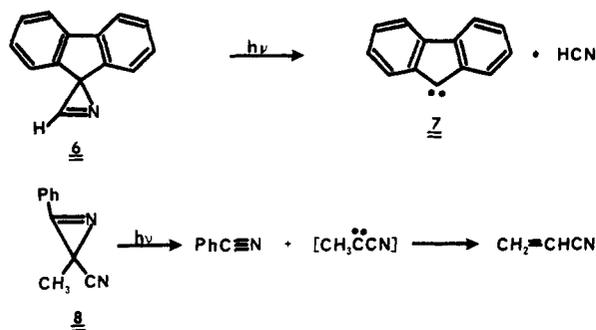
Irradiation of 2*H*-azirines in glassy matrices at 77 K results in the formation of new ultraviolet absorptions.

Direct irradiation of these new absorptions results in their disappearance and the reformation of the azirine absorptions.¹¹ Furthermore, upon warming the photolyzed azirine matrix to 113 K in the presence of a trapping agent, the new ultraviolet absorptions are quenched. Similar behavior was observed for photolysis of 3-phenylazirine.¹² Ultraviolet irradiation of this azirine at 8 K in an argon matrix results in the loss of the azirine IR absorption at 1755 cm⁻¹ and the production of a new IR absorption due to the ylide at 1930 cm⁻¹. When the ylide is irradiated, the new IR absorption at 1930 cm⁻¹ is lost, and the azirine IR absorption at 1755 cm⁻¹ is reformed. These experiments indicate that the new absorptions are, in fact, due to an intermediate nitrile ylide and that cycloadduct formation is derived from a thermal 1,3-dipolar addition of the initially generated nitrile ylide with the added dipolarophile.

A less commonly encountered photoreaction of the 2*H*-azirine ring involves cheletropic fragmentation to a nitrile and carbene. For example, Hafner and Bauer have reported that spiro[2*H*-azirine-2,9'-fluorene] (6) undergoes loss of HCN on irradiation to generate 9-fluorenylidene (7).¹³ A similar fragmentation was reported by Shechter and Magee who found that the irradiation of 2-cyano-2-methyl-3-phenyl-2*H*-azirine (8) gave benzonitrile and acrylonitrile.¹⁴ These two products are derived from

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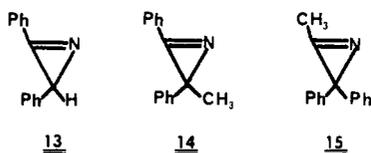
[†] Dedicated to Professor Toshio Mukai on the occasion of his 60th birthday.



carbenic collapse of **8** and hydrogen migration in the methylcyanocarbene generated.

More recently, nitrile ylides have been observed to be formed upon photolysis of carbene precursors in nitrile solvent.¹⁵ The nitrile ylides formed in this manner have been trapped by olefinic dipolarophiles. For example, Kende and co-workers have reported that the irradiation of *p*-diazoxide **9** in the presence of methacrylonitrile as solvent leads to cycloadduct **12**.¹⁶ The mechanism for the formation of **12** has been proposed to involve the reaction of the expected carbene **10** with the solvent to yield a nitrile ylide intermediate **11** which undergoes a subsequent 1,3-dipolar cycloaddition to give the stable diadduct **12** (Scheme I). Similar observations have recently been made by Platz and Scaiano^{17a} and Schuster.^{17b,18}

In view of the traditional importance of nitrile ylides as reactive intermediates in azirine photochemistry and the new attention that these species have achieved as intermediates in carbene chemistry, we have studied the pulsed laser transient absorption behavior of azirines **13**–**15**.¹⁹



While the steady-state photochemistry of azirine **13** has been extensively studied, both **14** and **15** are as yet uncharacterized. Azirine **15** is particularly interesting as it represents an independent source for the production of the nitrile ylide which could arise upon photolysis of diphenylcarbene precursors in acetonitrile solvent. The nitrile ylides derived from azirines **13**–**15** have been characterized in terms of their optical absorption, cycloaddition behavior, and absolute rates of reactivity. The Arrhenius behavior for the reaction of the ylide derived from azirine **13** with electron deficient olefins has also been studied.

Results and Discussion

Spectroscopy. The spectroscopic behavior of the nitrile ylide derived from photolysis of azirine **14** was nearly identical with that of azirine **13**.¹¹ Steady-state irradiation of **13** or **14** at 248 ± 10 nm in argon purged 3-methyl-

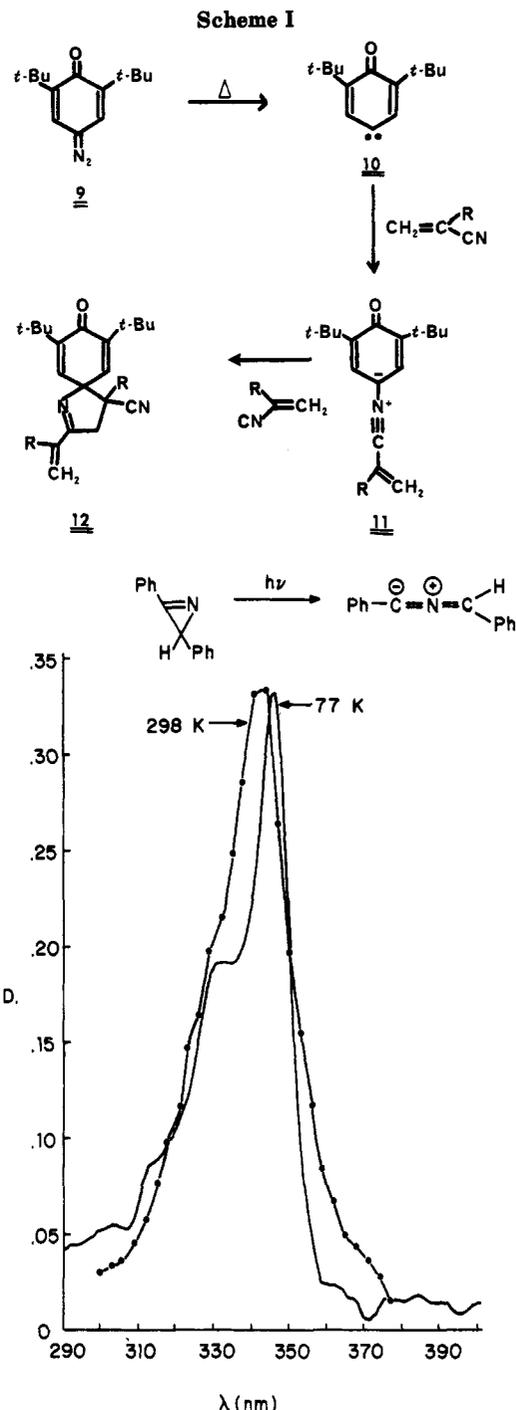


Figure 1. Absorption spectra of the nitrile ylide obtained after steady-state photolysis of azirine **13** at 77 K in 3-methylpentane glass and after pulsed laser photolysis at 298 K in isoctane solution.

pentane glass (77 K) resulted in the production of a new absorption with λ_{\max} 350 nm. Upon 350 ± 10 nm photolysis the new absorption disappeared and the azirine absorption was reformed. This interchange was totally reversible and no absorptions attributable to species other than the ylide or azirine were observed. In contrast to **13** and **14**, photolysis of azirine **15** under the same conditions is not 100% reversible. While steady-state irradiation of **15** produces a new absorption with λ_{\max} 368 nm, photolysis at this wavelength does not result in quantitative reformation of the azirine absorption. In the current study, no emission was obtained upon irradiation of the ylides at 77 K. However, excitation of the residual absorption at 305 nm resulting from the photolysis of **15** produced an

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Table I. Spectroscopic and Rate Constant Data for Azirines 13–15

azirine	13	14	15
λ_{\max} 77 K ^a	346 nm	350 nm	368 nm
λ_{\max} 298 K ^b	345 nm	345 nm	360 nm, 305 nm ^c
k_q , M ⁻¹ s ⁻¹ acrylonitrile ^d	(1.22 ± 0.03) × 10 ⁶	(1.92 ± 0.05) × 10 ⁶	(1.0 ± 0.3) × 10 ⁶
k_q , M ⁻¹ s ⁻¹ fumaronitrile ^d	(1.09 ± 0.07) × 10 ⁹	(1.58 ± 0.05) × 10 ⁹	(5.4 ± 0.3) × 10 ⁸
k_{rel} (fumaronitrile/acrylonitrile)	890 ± 100	820 ± 100	540 ± 200

^a Steady-state photolysis (1000-W Xe-Hg arc lamp equipped with a high intensity monochromator, λ_{ex} 248 ± 10 nm) of ~10⁻⁵ M azirine in argon purged 3-methylpentane. ^b Laser flash photolysis (Lambda Physik EMG 101 Excimer Laser, 248 nm, 15 ns pulse width) of ~10⁻⁵ M azirine in argon purged isooctane. ^c This absorption is quenched by O₂ (see text). ^d Conditions are the same as in b except azirine 1 was excited at 308 nm (20-ns pulse width).

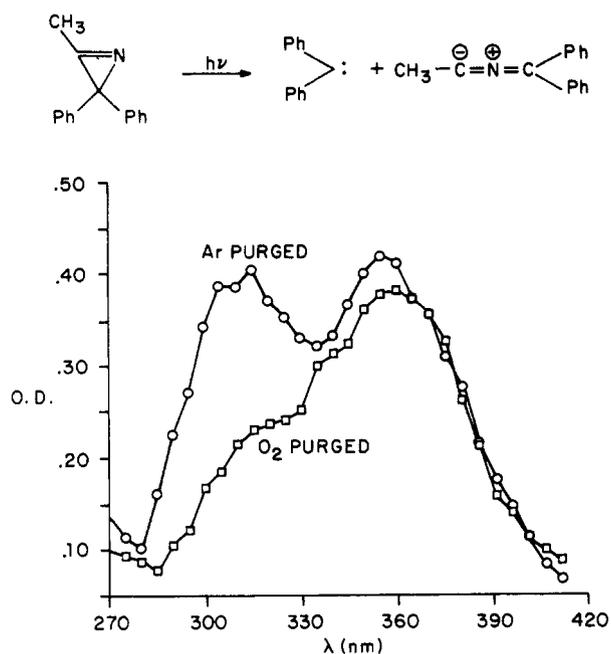


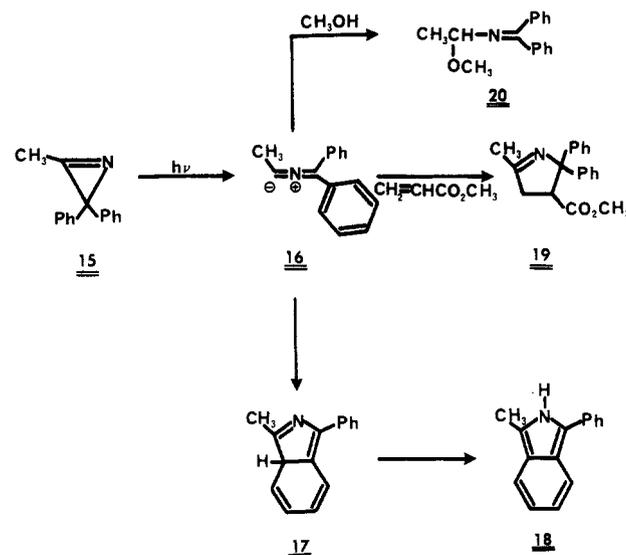
Figure 2. Transient absorption spectra obtained after pulsed laser photolysis of azirine 15 in argon-purged and oxygen-purged isooctane solution.

emission with λ_{\max} 485 nm (sh 520 nm). This corresponds well with that of diphenylcarbene produced by other routes.²⁰

The transient absorption spectra for azirines 13–15 were obtained at 298 K in argon purged isooctane. Laser flash photolysis at 248 nm produced strong, long-lived ($\tau > 100 \mu\text{s}$) absorptions which were in excellent agreement with the spectra obtained at 77 K (Figure 1 and Table I). In the case of azirines 13 and 14, the absorptions obtained were attributable to the nitrile ylides alone. However, the absorption spectrum for 15 showed an additional short-lived absorption between 300–315 nm. While the ylide absorptions were unaffected by oxygen, the short-lived transient was efficiently quenched with a rate constant of $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This is close to $1/9$ the diffusion rate in isooctane and is characteristic of triplet–triplet quenching in fluid solution (i.e., ³diphenylcarbene + ³O₂). The transient absorption spectra in argon and oxygen purged solution are shown in Figure 2. Subtraction of these two

spectra resulted in a spectrum with λ_{\max} 305 nm. This transient could also be quenched by 1,4-cyclohexadiene. However, due to the complex nature of the system, an exact rate constant could not be determined. Concomitant with the quenching of this absorption was the appearance and growth of a new absorption at 330 nm which is characteristic of the absorption of diphenylmethyl radical. These results, along with a linear laser power dependence (over a 10-fold intensity range) on the ratio of the two absorptions, indicate that a cheletropic fragmentation of azirine 15 into diphenylcarbene and acetonitrile is occurring in competition with electrocyclic ring opening to the nitrile ylide. The essentially quantitative production of ylide reaction products suggests that this competing fragmentation is a relatively minor process.

Product Studies. The photochemistry of azirines 14 and 15 was investigated in solution at 298 K. Our initial experiments revealed that 15 was highly photochemically reactive. Irradiation of 15 in benzene for short periods of time gave isoindole 18 in essentially quantitative yield.



The structure of 18 was assigned on the basis of its characteristic spectral data (see Experimental Section). Involvement of a nitrile ylide intermediate (i.e., 16) in the rearrangement of 15 to 18 was demonstrated by carrying out the photolysis of 15 in the presence of methyl acrylate. Under these conditions, the formation of 18, which is produced in quantitative yield in the absence of trapping agent, is entirely suppressed. The only product isolated was Δ^1 -pyrroline 19. Assignment of the structure of the cycloadduct rests on its spectral properties and by comparison with the NMR spectra of model compounds.^{21,22} Nitrile ylide 16 could also be trapped by methanol to give methoxy imine 20. Chemical confirmation of structure 20 was obtained by its acid hydrolysis to benzophenone. The formation of the isoindole ring system from the irradiation of a 2-phenyl-substituted 2*H*-azirine can be interpreted in terms of a formal mechanism, involving 1,5-electrocyclization of nitrile ylide 16 to give 17 followed by a 1,3-sigmatropic hydrogen shift. Related transformations have been observed with 2-vinyl-substituted 2*H*-azirines and provide good analogy for the proposed mechanism.²³

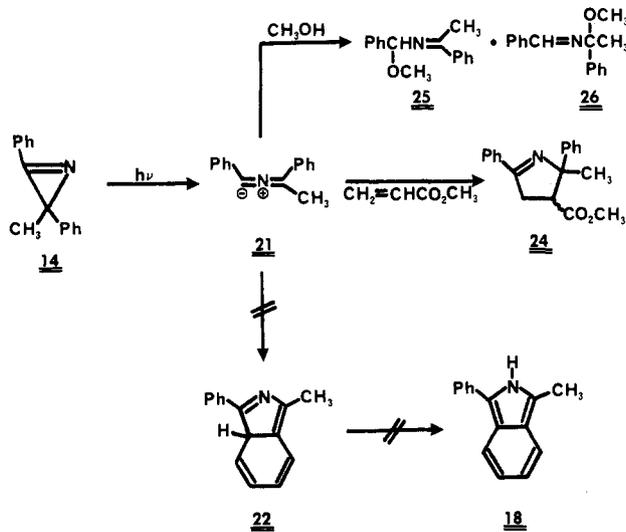
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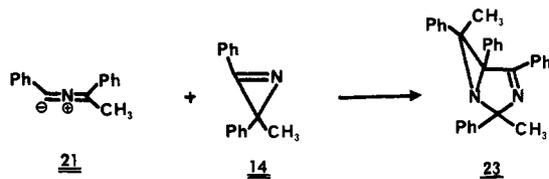
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Attention was next turned to the photochemical behavior of the closely related 2-methyl-2,3-diphenyl-2*H*-azirine (14) system. We assumed that azirine 14 would also produce isoindole 18 on irradiation by a pathway similar to that proposed for the conversion of 15 to 18. Surprisingly, the photolysis of 14 took an entirely different course and gave diazabicyclohexene 23 as the exclusive photo-product. When the irradiation of 14 was carried out in the presence of methyl acrylate, a mixture of stereoisomeric cycloadducts (i.e., 24) was isolated in good yield. Trapping



of the expected nitrile ylide also occurred by carrying out the irradiation of azirine 14 in methanol. Under these conditions, a mixture of methoxy imines 25 and 26 was isolated. The formation of diazabicyclohexene 23 can be interpreted in terms of a 1,3-dipolar addition of the initially generated nitrile ylide on to a ground-state azirine molecule.²⁴

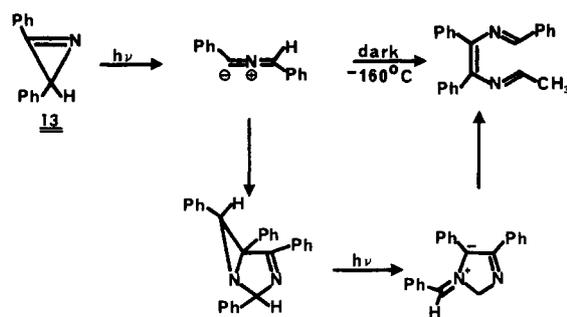


The fact that the nitrile ylide derived from the azirine 14 does not undergo 1,5-electrocyclization to give the isoindole ring system is of some interest and merits comment. Molecular orbital calculations indicate that the parent nitrile ylide system is definitely bent with an HCN angle of 114–116°.^{25,26} The stabilization over the optimized linear form was calculated to be 11.1 (4-31G), 22.4 (STO-3G), 12.9 (MINDO/2), and 16.4 kcal/mol (MINDO/3). These findings indicate that the most stable form of a nitrile ylide resembles a bent allenyl anion rather than a planar propargyl anion. In order for electrocyclization to proceed, the ylide needs to exist in the syn form (i.e., 21a).



However, this represents the more sterically congested isomer and is less likely to be formed in the ring-opening

Scheme II



step. Most probably, the nitrile ylide derived from azirine 14 preferentially exists as the anti isomer (i.e., 21b). With this geometry, electrocyclization is precluded on structural grounds and formation of the dimer occurs instead.

Transient Kinetics and Quenching of Nitrile Ylides. In air-saturated isooctane solution at 25 °C, the observed absorption decays of the nitrile ylides derived from pulsed laser photolysis of azirines 13–15 exhibited both first- and second-order components. This observation is consistent with the previous proposal that the dimeric products obtained from photolysis of azirines 13–15 are derived via two different pathways, ylide–azirine (first order) and ylide–ylide (second order) reactions (Scheme II).^{11b}

As noted earlier, nitrile ylides are quenched efficiently by electron deficient olefins. In fact, at sufficiently high olefin concentrations, the observed transient decay obeyed clean first-order kinetics. The bimolecular quenching rate constant, k_q , could then be obtained from the slope of a plot of the observed first-order rate for ylide decay vs. olefin concentration. The quenching rate constants for acrylonitrile and fumaronitrile are listed in Table I. It should be noted that, for azirine 13, the relative quenching rate obtained from our absolute rates constants (890 ± 100) is the same, within experimental error, as that obtained from steady-state trapping experiments (1070 ± 100).²⁷

Arrhenius Behavior for Azirine 13. The kinetic behavior of the ylide derived from pulsed laser photolysis of azirine 13 with methyl acrylate and diethyl fumarate was examined as a function of temperature. Quenching rates were obtained, after correction of olefin concentrations for solvent contraction, over the range of 313–183 K as described above. The Arrhenius plots (Figure 3) show that k_q for methyl acrylate is essentially insensitive to temperature (e.g., $E_a \approx 0$ kcal/mol), while k_q for diethyl fumarate initially increases with decreasing temperature ($E_a \approx -3.0$ kcal/mol) and begins to decrease at temperatures below 207 K ($E_a \approx 2.5$ kcal/mol). Similar behavior has been observed previously for the quenching of ketone phosphorescence,²⁸ carbenes,²⁹ and singlet oxygen.³⁰ In fact this behavior was observed by Scaiano et al. for quenching of the nitrile ylide produced by the reaction of fluorenylidene with CH_3CN , although the results were misinterpreted at that time.³¹

A kinetic scheme which fits this behavior is given below in which that nitrile ylide (NY) interacts with a quenching

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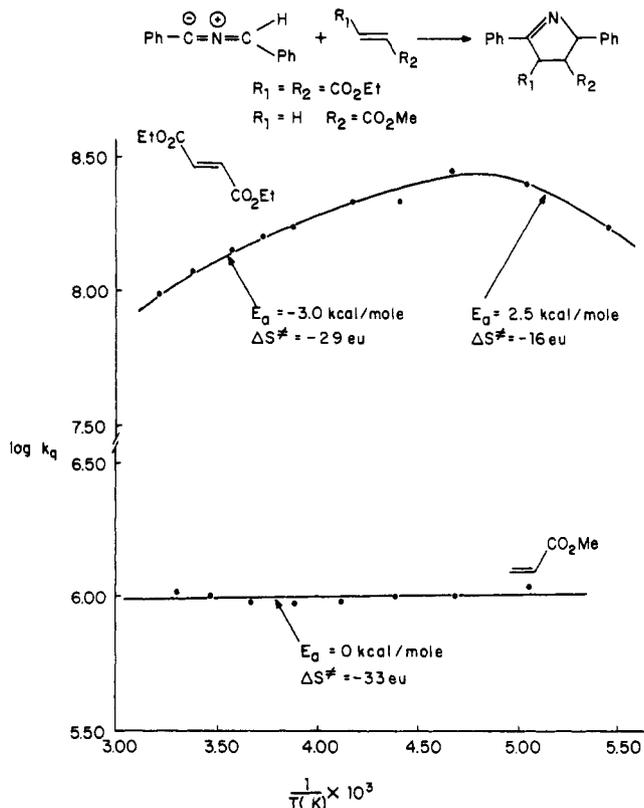
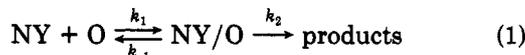


Figure 3. Arrhenius plot for the quenching of the nitrile ylide derived from pulsed laser photolysis of azirine 13 by methyl acrylate and diethyl fumarate in isoctane.

olefin (O) to form an intermediate nitrile ylide/olefin complex (NY/O) (eq 1). For the observed ylide decays



to obey first-order kinetics, this mechanism requires that the steady-state approximation holds for the NY/O complex. With this assumption the observed first-order quenching rate constant, k_q , can be expressed in terms of the above rate constants to give eq 2. Experimentally no

$$k_q = (k_1 k_2) / (k_{-1} + k_2) \quad (2)$$

information can be obtained for the individual rate constants on the right side of eq 2. However, a simple rearrangement yields the ratio of the rates for dissociation and collapse to product for the NY/O complex (eq 3). As-

$$k_{-1}/k_2 = (k_1 - k_q)/k_q \quad (3)$$

suming diffusion controlled complex formation (e.g., $k_1 = k_{\text{diff}}$), values for the ratio k_{-1}/k_2 can be calculated by using the experimentally determined quenching rate constant, k_q , and values for k_{diff} calculated from a modified Debye equation (eq 4). A plot of $\log(k_{-1}/k_2)$ vs. $1/T$ (K) was

$$k_{\text{diff}} = 2 \times 10^5 T/\eta \quad (4)$$

found experimentally to yield a straight line (Figure 4) in accord with eq 6. The slope of the plot yields the dif-

$$\log(k_{-1}/k_2) = \Delta\Delta G^\ddagger / 2.303RT \quad (5)$$

$$\log(k_{-1}/k_2) = (1/2.303R)(\Delta\Delta H^\ddagger/T - \Delta\Delta S^\ddagger) \quad (6)$$

ference in the enthalpy of activation for product formation and dissociation of the complex (e.g., $\Delta\Delta H^\ddagger = \Delta H^\ddagger_{\text{prod}} - \Delta H^\ddagger_{\text{diss}}$). As expected, $\Delta\Delta G^\ddagger$ at 25 °C (eq 5) is larger for methyl acrylate (slow quencher) than for diethyl fumarate (fast quencher). The differential activation enthalpies and entropies, derived thru eq 6, indicate that entropy is the dominant factor influencing $\Delta\Delta G^\ddagger$. It should be noted that

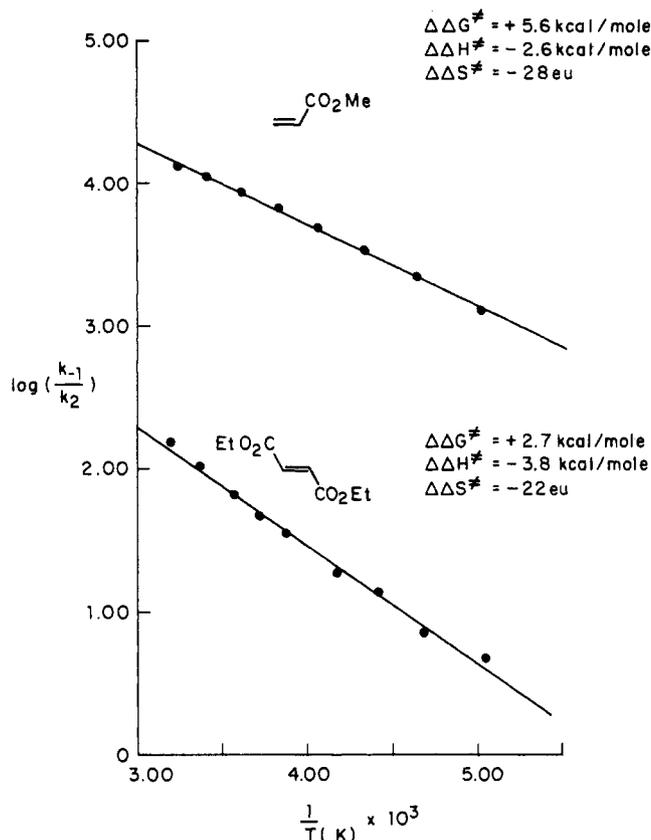


Figure 4. Plot of $\log(k_{-1}/k_2)$ vs. $1/T$ (K) ($\Delta\Delta G^\ddagger$ calculated at 298 K, see eq 5).

the difference in the $\Delta\Delta G^\ddagger$ values for the two quenchers is due in equal parts to both $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$.

Experimental Section

Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer 467 Infrared 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 90 MHz by using a Varian Em-390 spectrometer. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV. All melting points and boiling points are uncorrected.

Isooctane (MCB, OmniSolv) was used as supplied and 3-methylpentane (Aldrich, Gold Label) was passed through neutral alumina prior to use. The olefin quenchers were purified by passage through neutral alumina and distillation immediately prior to use. Fumaronitrile was purified by sublimation. Low temperature (77 K) absorption spectra were recorded on a Perkin Elmer 559A UV/VIS spectrophotometer interfaced to a Perkin Elmer Data Station.

The laser flash photolysis system consisted of a Lambda Physik EMG 101 excimer laser [248 nm (KrF), 15 ns pulse; 308 nm (XeCl), 20 ns pulse]. The transient absorption was monitored at right angles with the laser beam using a pulsed 400 W Xe arc lamp (Photochemical Research Associates, Model 301 power supply, Model M-305 pulser). The transmitted light was passed through an ISA H-10 monochromator and monitored with a RCA 4840 photomultiplier tube. The output from the photomultiplier tube was terminated by using a 50 ohm load resistor and analyzed by using a Tektronix 7912 AD Programmable Digitizer as part of a Tektronix WP2252 signal processing system.

Preparation of 2,2-Diphenyl-3-methyl-2H-azirine (15). To a solution containing 5.0 g of 1,1-diphenylacetone, 25 mL of ethanol, 4 drops of glacial acetic acid, and 2.0 g of sodium acetate was added 5.5 mL of dimethylhydrazine. The reaction mixture was allowed to reflux for 24 h and then 25 mL of water was added. The organic layer was extracted with ether, washed with water,

dried over magnesium sulfate, and concentrated under reduced pressure to give 5.14 g (86%) of 1,1-diphenylpropan-2-one *N,N*-dimethylhydrazone as a pale yellow oil: NMR (CDCl₃, 90 MHz) δ 1.90 (s, 3 H), 2.45 (s, 6 H), 5.05 (s, 1 H) and 7.25 (m, 10 H); IR (neat) 3050, 3008, 2960, 2945, 2870, 2850, 2800, 2750, 1700, 1660, 1595, 1490, 1442, 1360, 1320, 1158, 1080, 1030, 970, 920, 800, 760, 720, and 700 cm⁻¹.

A solution containing 5.0 g of the above hydrazone and 7.5 mL of methyl iodide was allowed to stir at room temperature for 16 h. The excess methyl iodide was removed under reduced pressure and the remaining precipitate was washed with ether to give 6.5 g of 1,1-diphenylpropan-2-one trimethylhydrazonium iodide: mp 171–172 °C; IR (KBr) 3000, 2990, 1630, 1590, 1480, 1440, 1380, 1200, 1120, 1080, 1020, 960, 940, 800, 760, 740, and 700 cm⁻¹.

To a solution containing 6.0 g of the above hydrazonium iodide in 30 mL of dimethyl sulfoxide was added 700 mg of sodium hydride. The reaction mixture was allowed to stir for 4 h at room temperature. At the end of this time the solution was poured into 50 mL of ice water and was extracted with pentane. The extracts were washed with water and dried over magnesium sulfate. The pentane was removed under reduced pressure to give 4.3 g (70%) of a brownish oil. Distillation of this material followed by silica gel chromatography gave 3.4 g (55%) of a pale yellow oil whose structure was assigned as 2,2-diphenyl-3-methyl-2*H*-azirine (15): NMR (CDCl₃, 90 MHz) δ 2.52 (s, 3 H), 7.25 (s, 10 H); IR (neat) 3040, 3000, 2970, 2930, 2840, 2800, 1745, 1700, 1640, 1582, 1480, 1440, 1350, 1270, 1170, 918, 760, and 700 cm⁻¹; *m/e* 207 (M⁺), 197, 182, 166 (base), and 105.

Anal. Calcd for C₁₅H₁₃N: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.87; H, 6.15; N, 6.72.

Irradiation of 2,2-Diphenyl-3-methyl-2*H*-azirine (15). A solution containing 300 mg of azirine 15 in 200 mL of benzene was irradiated under an argon atmosphere for 20 min by using a 450-W Hanovia lamp equipped with a Vycor sleeve. Removal of the solvent under reduced pressure left 300 mg of a reddish oil which was recrystallized from hexane:ether (7:3) to give 285 mg (95%) of 1-phenyl-3-methyl-2*H*-isoindole (18): mp 187–188 °C; NMR (CDCl₃, 90 MHz) δ 1.50 (s, 3 H), 6.9–7.7 (m, 10 H); IR (KBr) 3400, 3030, 2890, 1600, 1590, 1480, 1440, 1380, 1200, 958, 780, 700, and 680 cm⁻¹; UV (hexane) 242 ($\epsilon \approx 13000$), 275 ($\epsilon \approx 10200$), and 395 nm ($\epsilon \approx 3600$); *m/e* 207 (M⁺), 197, 182, 166 (base), 105.

Anal. Calcd for C₁₅H₁₃N: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.85; H, 6.24; N, 6.59.

Irradiation of 2,2-Diphenyl-3-methyl-2*H*-azirine (15) in the Presence of Methyl Acrylate. A solution containing 150 mg of azirine 15 and 3 mL of methyl acrylate in 200 mL of cyclohexane was irradiated for 20 min by using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. The solution was filtered and the solvent was evaporated under reduced pressure to give 215 mg of a colorless residue. The oil was purified by silica gel chromatography using a hexane:ether mixture as the eluent to give 240 mg (93%) of 2-methyl-4-(carbomethoxy)-5,5-diphenyl- Δ^1 -pyrroline (19) as a white solid: mp 67–68 °C; NMR (CDCl₃, 90 MHz) δ 2.10 (s, 3 H), 2.61 (dd, 1 H, *J* = 18.0 and 9.0 Hz), 3.10 (s, 3 H), 3.15 (dd, 1 H, *J* = 18.0 and 6.0 Hz), 3.91 (dd, 1 H, *J* = 9.0 and 6.0 Hz), and 6.8–7.8 (m, 10 H); IR (KBr) 3030, 3000, 2960, 1720, 1640, 1580, 1480, 1420, 1362, 1340, 1305, 1242, 1190, 1160, 1020, 760, and 700 cm⁻¹; UV (hexane) 258 nm ($\epsilon \approx 4700$); *m/e* 293 (M⁺), 207, 166 (base), and 115.

Anal. Calcd for C₁₅H₁₃NO₂: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.72; H, 6.46; N, 4.71.

Irradiation of 2,2-Diphenyl-3-methyl-2*H*-azirine (15) in Methanol. A solution containing 200 mg of azirine 15 in 200 mL of absolute methanol was irradiated through a Vycor filter sleeve for 20 min. The solvent was removed under reduced pressure to afford 270 mg of a yellow oil whose structure was assigned as benzophenone *N*-(methoxyethyl)imine (20) on the basis of its spectroscopic properties: NMR (CDCl₃, 90 MHz) δ 1.31 (d, 3 H, *J* = 6.0 Hz), 3.28 (s, 3 H), 4.61 (q, 1 H, *J* = 6.0 Hz), and 6.9–7.9 (m, 10 H); IR (neat) 3040, 2960, 2900, 2850, 2800, 1650, 1610, 1590, 1575, 1480, 1440, 1360, 1305, 1280, 780, 735, and 700 cm⁻¹.

The structure of this material was further verified by its hydrolysis to benzophenone. A solution containing 270 mg of the crude product in 30 mL of a 10% aqueous acetone solution was treated with five drops of concentrated hydrochloric acid at room

temperature and the mixture was allowed to stir for 1 h. The solution was extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a colorless oil which was identified as benzophenone.

Preparation of 2-Methyl-2,3-diphenyl-2*H*-azirine (14). To a solution containing 10.0 g of desoxybenzoin, 6.0 g of sodium acetate, 75 mL of absolute ethanol, and 10 drops of glacial acetic acid was added 12 mL of dimethylhydrazine. The reaction mixture was heated at reflux overnight and then 75 mL of water was added. The organic layer was extracted with ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 9.7 g (80%) of a pale yellow oil whose structure was assigned as 1,2-diphenylethan-1-one *N,N*-dimethylhydrazone: NMR (CDCl₃, 90 MHz) δ 2.50 (s, 6 H), 4.31 (s, 2 H), and 6.9–7.8 (m, 10 H); IR (neat) 3050, 3010, 2950, 2850, 2800, 2760, 1670, 1600, 1490, 1440, 1300, 1270, 1220, 1080, 1025, 980, 920, 760, 740, and 700 cm⁻¹.

To a cooled solution containing 18.27 g of diisopropylamine in 200 mL of tetrahydrofuran was added 118 mL of a 1.6 M *n*-butyllithium solution. After stirring at 0 °C for 30 min, the mixture was cooled to –78 °C and 9.0 g of the hydrazone in 100 mL of tetrahydrofuran was added dropwise. The reaction mixture was stirred at –78 °C for 2 h, was then allowed to reach 10 °C, and was kept at this temperature for one additional hour. The solution was again cooled to –78 °C and 17 mL of methyl iodide was added. The mixture was allowed to stir at –78 °C for 2 h. After warming to room temperature, 200 mL of a saturated ammonium chloride solution was added. The organic phase was extracted with ether, washed with water, and dried over magnesium sulfate. The ether solution was concentrated to a yellow oil which was chromatographed on a silica gel column with a hexane:ether mixture as the eluent to give 8.6 g (91%) of a light yellow oil whose structure was assigned as 1,2-diphenylpropan-1-one *N,N*-dimethylhydrazone: NMR (CDCl₃, 90 MHz) δ 1.45 (dd, 3 H, *J* = 6.0 Hz), 2.6 (s, 6 H), 3.9 (q, 1 H, *J* = 6.0 Hz); IR (neat) 3040, 3000, 2930, 2840, 2755, 2305, 1590, 1480, 1460, 1440, 1370, 1300, 1240, 1020, 950, 905, 760, 740, and 700 cm⁻¹.

A solution containing 8.0 g of the above hydrazone in 12 mL of methyl iodide was allowed to stir for 16 h at room temperature. The excess methyl iodide was removed under reduced pressure and the yellow-brownish paste was washed with ether and was used in the next step without further purification.

To a solution containing the above hydrazonium iodide in 20 mL of dimethyl sulfoxide was added 1.0 g of sodium hydride. The mixture was allowed to stir at room temperature for 4 h and was then poured into 50 mL of ice water and extracted with pentane. The organic layer was washed with water and dried over magnesium sulfate. Evaporation of the pentane under reduced pressure gave 4.3 g of a yellow oil which was purified by silica gel chromatography with a hexane:ether mixture as eluent to give 0.9 g of 2-methyl-2,3-diphenyl-2*H*-azirine (14): NMR (CDCl₃, 90 MHz) 1.78 (s, 3 H), 7.0–8.0 (m, 10 H); IR (neat) 3070, 3045, 3000, 2945, 2900, 2850, 1740, 1670, 1585, 1480, 1370, 1330, 1220, 970, 950, 760, and 695 cm⁻¹; UV (hexane) 245 nm ($\epsilon \approx 20000$); *m/e* 207 (M⁺), 165, 105, and 77.

Anal. Calcd for C₁₅H₁₃N: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.13; H, 6.09; N, 6.58.

Irradiation of 2-Methyl-2,3-diphenyl-2*H*-azirine (14) in Benzene. A solution containing 140 mg of azirine 14 in 200 mL of benzene was irradiated for 5 min by using a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left an oily solid which was recrystallized from benzene–hexane to give 95 mg of a pale yellow solid, mp 203–204 °C, whose structure was assigned as 1,2,4,6-tetra-phenyl-4,6-dimethyl-3,5-diazabicyclo[3.1.0]hex-2-ene (23) on the basis of its spectral properties: IR (KBr) 3000, 1620, 1595, 1575, 1485, 1440, 1360, 1285, 1200, 1120, 1100, 920, and 700 cm⁻¹; NMR (CDCl₃, 90 MHz) δ 1.62 (s, 3 H), 2.05 (s, 3 H), 7.0–7.6 (m, 8 H), 7.7–7.9 (m, 2 H); UV (cyclohexane) 245 nm ($\epsilon \approx 10300$) and 310 nm ($\epsilon \approx 2200$).

Anal. Calcd for C₃₀H₂₆N₂: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.08; H, 6.25; N, 6.41.

Irradiation of 2-Methyl-2,3-diphenyl-2*H*-azirine (14) in the Presence of Methyl Acrylate. A solution containing 140 mg of azirine 14 and 2 mL of methyl acrylate in 200 mL of cyclohexane was irradiated for 10 min by using a 450-W Hanovia

lamp equipped with a Vycor sleeve. The solution was filtered giving 158 mg of a pale yellow oil. The material was subjected to silica gel chromatography with a benzene-acetonitrile mixture (7:3) to give 153 mg of a colorless oil whose NMR showed it to be a mixture of two isomeric cycloadducts. Further purification by silica gel chromatography with a 7:3 hexane-ether mixture as the eluent gave two cycloadducts. The slower moving isomer (40%) was assigned the structure of 2,5-diphenyl-*cis*-4-(carbomethoxy)-5-methyl- Δ^1 -pyrroline (24a) on the basis of its spectral data: NMR (CDCl₃, 360 MHz) δ 1.52 (s, 3 H), 3.23 (dd, 1 H, J = 17.0 and 9.3 Hz), 3.44 (dd, 1 H, J = 9.3 and 7.6 Hz), 3.64 (dd, 1 H, J = 17.0 and 7.6 Hz), 3.80 (s, 3 H), and 7.0-8.0 (m, 10 H); m/e 293, 278, 207 (base), 166, 115, 103, and 77; IR (neat) 3030, 2910, 1720, 1620, 1480, 1440, 1340, 1160, 760, and 700 cm⁻¹; UV (methanol) 245 nm ($\epsilon \approx 13200$).

Anal. Calcd for C₁₉H₁₉NO₂: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.58; H, 6.48; N, 4.65.

The major cycloadduct was assigned the structure of 2,5-diphenyl-*trans*-4-carbomethoxy-5-methyl- Δ^1 -pyrroline (24b) on the basis of its spectral data: NMR (CDCl₃, 360 MHz) δ 1.58 (s, 3 H), 3.23 (s, 3 H), 3.31 (dd, 1 H, J = 7.8 and 5.2 Hz), 3.33 (dd, 1 H, J = 15.0 and 7.8), 3.55 (dd, 1 H, J = 15.0 and 5.2 Hz), and 7.2-8.0 (m, 10 H); m/e 293, 278, 207 (base), 166, 115, 103, and 77; UV (hexane) 242 nm ($\epsilon \approx 15400$); IR (neat) 2910, 1722, 1615, 1562, 1480, 1440, 1340, 1260, 1200, 1160, 1120, 1060, 1020, 920, 860, 760, and 695 cm⁻¹.

Anal. Calcd for C₁₉H₁₉NO₂: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.64; H, 6.37; N, 4.59.

Irradiation of 2-Methyl-2,3-diphenyl-2H-azirine (14) in Methanol. A solution containing 80 mg of azirine 14 in 175 mL

of methanol was irradiated through a Vycor filter sleeve for 10 min. Removal of the solvent under reduced pressure left 110 mg of a pale yellow oil whose structure was assigned as a 2:3 mixture of acetophenone *N*-(methoxyphenylmethyl)imine (25) and benzaldehyde *N*-(1-methoxy-1-phenylethyl)imine (26) on the basis of its NMR spectrum and by its hydrolysis to acetophenone and benzaldehyde: NMR (CDCl₃, 90 MHz) δ 25 2.02 (s, 3 H), 3.31 (s, 3 H), 5.67 (s, 1 H), and 7.0-8.0 (m, 10 H); 26 1.58 (s, 3 H), 3.02 (s, 3 H), 7.0-8.0 (m, 10 H), and 8.42 (s, 1 H).

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Registry No. 13, 16483-98-0; 14, 22752-16-5; 15, 65817-54-1; 18, 90968-49-3; 19, 90968-50-6; 20, 70509-13-6; 23, 90968-51-7; 24a, 90968-52-8; 24b, 90968-53-9; 25, 90968-54-0; 26, 90968-55-1; 1,1-diphenylacetone, 781-35-1; dimethylhydrazide, 57-14-7; 1,1-diphenylpropan-2-one *N,N*-dimethylhydrazone, 90968-56-2; methyl iodide, 74-88-4; 1,1-diphenylpropan-2-one trimethylhydrazonium iodide, 69543-13-1; desoxybenzoin, 451-40-1; 1,2-diphenylethan-1-one *N,N*-dimethylhydrazone, 33785-81-8; 1,2-diphenylpropan-1-one *N,N*-dimethylhydrazone, 90968-57-3; methyl acrylate, 96-33-3; methanol, 67-56-1; acrylonitrile, 107-13-1; fumaronitrile, 764-42-1; diethyl fumarate, 623-91-6.

A Novel Friedel-Crafts Reaction of Hindered Ketones

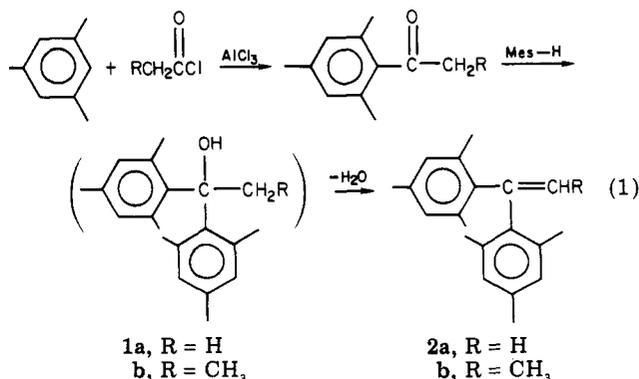
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Mesitylene has been shown to react with acetyl chloride in the presence of aluminum chloride to form 1,1-dimesitylethene. Acetomesitylene has been demonstrated to be an intermediate in the reaction, which proceeds in the second step by nucleophilic attack by the arene on the carbonyl group of acetomesitylene, which is activated by the formation of a polarized complex with aluminum chloride. Mesitylene reacts similarly with propionyl chloride, forming 1,1-dimesitylpropene; propiomesitylene is an intermediate. Steric and electronic factors responsible for this unique Friedel-Crafts reaction are discussed.

Although in the past we have commented on the fact that Friedel-Crafts alkylations have often been conducted at higher temperatures than are necessary, thereby leading to complications,¹ nevertheless one of us carried out an acylation under more strenuous conditions than apparently are required,² with interesting results. With the aim of preparing acetomesitylene, mesitylene, acetyl chloride, and aluminum chloride were heated at 100 °C for 6 h in a molar ratio of 2:1:0.25, respectively. The desired product was obtained in low yield (17%), but the major product (41% yield) was 1,1-dimesitylethene (2a). Under similar conditions, the reaction of propionyl chloride with mesitylene gave propiomesitylene (54%) and 1,1-dimesitylpropene (2b, 31%). We suspected that the dimesitylalkenes were produced by reaction of initially formed acylmesitylenes with a second mole of mesitylene, followed by dehydration of the intermediate alcohols 1a and 1b (eq 1). This was confirmed by preparing acetomesitylene and propio-



mesitylene at low temperature and then heating the pure acylmesitylenes with mesitylene and aluminum chloride at 150-160 °C. The dimesitylalkenes (2a and 2b) were

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