dd, J = 6.2 and 4.0 Hz), 4.64 (1 H, dd, J = 7.6 and 4.0 Hz), 5.49 (1 H, dd, J = 7.6 and 6.2 Hz), 6.40 (2 H, d, J = 7.5 Hz), 6.68 (2 H, d, J = 6.7 Hz), 7.11 (2 H, d, J = 6.7 Hz), and 7.24–7.68 (5 H, m).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.90; H, 5.43.

Photoreaction of 1a with Methyl Benzofuran-2-carboxylate (1d). A solution of **1a** (4.37 g, 37 mmol) and **1d** (1.6 g, 91 mmol) in acetonitrile (180 ml) was irradiated in a Pyrex vessel for 62 hr. After removal of solvent and unreacted **1a** in vacuo, chromatography of the residue on a column of silica gel gave five fractions. The first fraction (*n*-hexane–benzene, 10:1, as eluent) afforded **1d** (450 mg, 2.5 mmol). The second fraction (*n*-hexane–benzene, 10:1, as eluent) yielded **7a** (240 mg, 14%): mp 202–203° (from *n*-hexane–benzene); *m/e* 262 (M^+), 234, 205, and 176; ir (KBr) 1662, 1615, 1385, 1340, 1166, 1113, 1077, 876, 815, and 755 cm^{-1}; NMR ($CDCl_3$) δ 7.20–7.70 (7 H, m). 7.50 (1 H, s), 8.28 (1 H, m), and 10.88 (1 H, s).

Anal. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84. Found: C, 77.66; H, 3.59.

The third fraction (*n*-hexane–benzene, 10:1, as eluent) gave **6** (290 mg, 17%): mp 157–158° (from benzene); *m/e* 262 (M^+), 245, 234, 205, 145, and 117; ir (KBr) 1662, 1620, 1387, 1340, 1164, 1110, 1075, 870, 810, and 750 cm^{-1}; NMR ($CDCl_3$) δ 7.30–7.80 (7, H, m), 7.62 (1 H, s), 8.35 (1 H, m), and 8.84 (1 H, s).

Anal. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84. Found: C, 77.60; H, 3.59.

The fourth fraction (benzene as eluent) afforded **5** (540 mg, 28%): mp 99° (from benzene–diethyl ether); *m/e* 294 (M^+), 176, 145, 118, and 89; ir (KBr) 1750, 1476, 1460, 1232, 1126, 835, 755, and 742 cm^{-1}; NMR ($CDCl_3$) δ 3.80 (3 H, s), AB part of the ABX spectrum at 4.42 (J = 8.0 and 6.6 Hz) and 4.49 (J = 8.0 and 3.8 Hz), X part of the ABX spectrum at 5.63 (1 H, dd, J = 6.6 and 3.8 Hz), and 6.4–7.0 (8 H, m).

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.18; H, 4.77.

The fifth fraction (diethyl ether as eluent) yielded **4b** (160 mg, 7%): mp 166° (from benzene–diethyl ether); *m/e* 352 (M^+), 176, 145, 118, and 89; ir (KBr) 1765, 1730, 1476, 1460, 1430, 1230, 1130, 1075, 1042, 1025, 982, 845, and 750 cm^{-1}; NMR ($CDCl_3$) δ 3.80 (6 H, s), 4.68 (3 H, s), and 6.5–7.0 (8 H, m).

Anal. Calcd for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 68.29; H, 4.38.

Wolff–Kishner Reduction of 7a. A mixture of **7a** (20 mg, 0.077 mmol), potassium hydroxide (50 mg), 90% hydrazine hydrate (50 mg), and diethylene glycol (5 ml) was heated to reflux for 1 hr. After refluxing, water was removed and refluxing was continued for an additional 2 hr. The mixture was then cooled and extracted with benzene. Evaporation of the dried solution and sublimation of the residue at 100–110° (6 mmHg) gave **7b** (17 mg, 88%): mp 126–127° (from *n*-hexane); *m/e* 248 (M^+); NMR (CCl_4) δ 2.60 (3 H, s), 7.04 (1 H, s), 7.10–7.30 (4 H, m), and 7.30–7.60 (4 H, m).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.40, H, 4.90.

Registry No.—**1a,** 271-89-6; **1b,** 7035-06-5; **1c,** 1839-72-1; **1d,** 1646-27-1; **2a,** 52437-49-7; **2b,** 57237-76-0; **3a,** 52169-67-2; **3b,** 57287-76-0; **4a,** 57237-77-1; **4b,** 57237-78-2; **5,** 57237-79-3; **6,** 57237-80-6; **7a,** 57237-81-7; **7b,** 57237-82-8; 3-iodopyridine, 1120-90-7; 4-(3-pyridyl)benzofuran, 57237-83-9.

References and Notes

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(2) C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, **98,** 3102 (1965).
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(5) S. Farid and S. E. Shealer, *J. Chem. Soc., Chem. Commun.*, 296 (1973).
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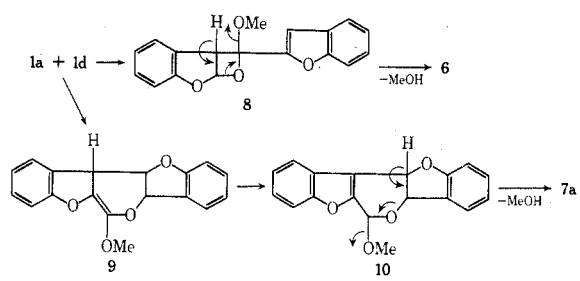
(7) S. Farid, S. E. Hartman, and C. D. DeBoer, *J. Am. Chem. Soc.*, **97,** 808 (1975).
(8) For preliminary accounts of a portion of this work, see K. Takamatsu, H.-S. Ryang, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 903 (1973).
(9) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, p 334.
(10) The decrease in the yield of **2b** and the increase in the yield of **3b** were observed as irradiation time increased. Irradiations of **2b** and **3b** in acetonitrile through Pyrex glass resulted in formation of **1a** and **1c.** Thus, the observed variation in the ratio of **2b:3b** is probably due to the effective photodecomposition of **2b** relative to that of **3b.**
(11) The stereochemistry of **4b,** as well as that of **4a,** has not yet been established. However, **4b** is assigned as one of two possible syn dimers on the basis of its NMR spectrum, in which the strong upfield shift of the aromatic protons was observed. The formation of only one of four possible homodimers from **1d** shown in our present experiments contrasts with the results of the triplet sensitized homodimerization of **1d,** in which three isomers were obtained.[4]
(12) The formation of **6** can be envisaged as occurring via an oxetane intermediate **8** followed by elimination of MeOH. Similarly, a plausible pathway for the formation of **7a** is as follows: 1,4 cycloaddition of **1d** to **1a** followed by aromatization affords an acetal intermediate **10** that may readily lose MeOH to give **7a.**



(13) The possibility of the ground state charge-transfer complex between these benzofurans should be excluded by absorption studies in which no charge-transfer band was observed. In our preliminary mechanistic studies, we found that the fluorescence of **1a** (in cyclohexane) is completely quenched by **1c** (10^{-3} *M*) at room temperature. However, no new emission suggesting the existence of an exciplex has been observed.

Intramolecular Reorganization of Some Unsaturated 2*H*-Azirines[1]

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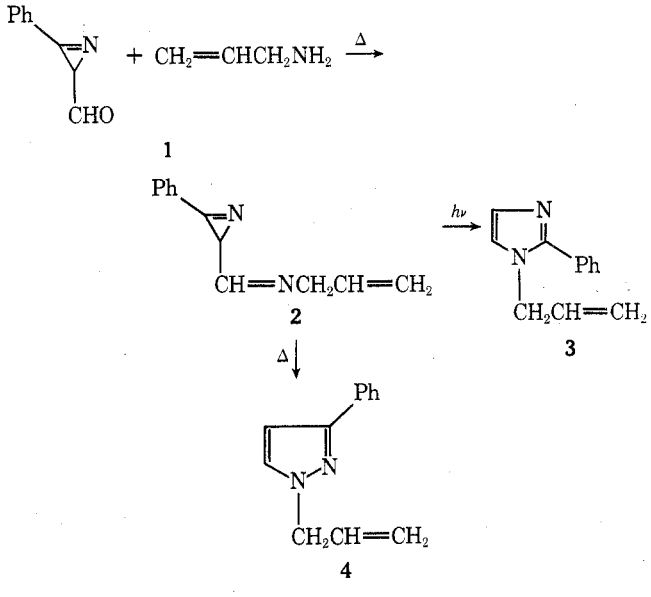
The thermal and photochemical expansion reactions of several unsaturated 2*H*-azirines have been examined. The azirines undergo thermal rearrangement by rupture of the C–N single bond to give a butadienyl nitrene which undergoes cyclization followed by a [1,5]-sigmatropic migration and subsequent tautomerization. The butadienyl nitrene was also found to insert into a neighboring allylic methyl group and the nitrene could also be trapped when the thermolysis was carried out in the presence of tris(dimethylamino)phosphine. The azirine derivatives were found to undergo photochemical reorganization via transient nitrile ylide intermediates which can be trapped with external dipolarophiles.

Previous papers from this laboratory have established that arylazirines undergo irreversible ring opening on electronic excitation to give nitrile ylides as reactive intermediates.[2-6] These species can be intercepted with a variety of

dipolarophiles to form five-membered rings.[1-7] As a result of these early studies, we became interested in determining whether the cycloaddition reaction would occur when the dipolarophile and the azirine ring were constrained to be within the same molecule. In a recent paper we reported that the intramolecular photochemical and thermal cycloadditions of 2-vinyl substituted 2*H*-azirines do indeed take place, the reactions providing clean transformations for the synthesis of five-membered nitrogen-containing heterocycles.[8] This study has now been extended to include other polyunsaturated 2*H*-azirines. The results of this investigation are reported in the present paper.

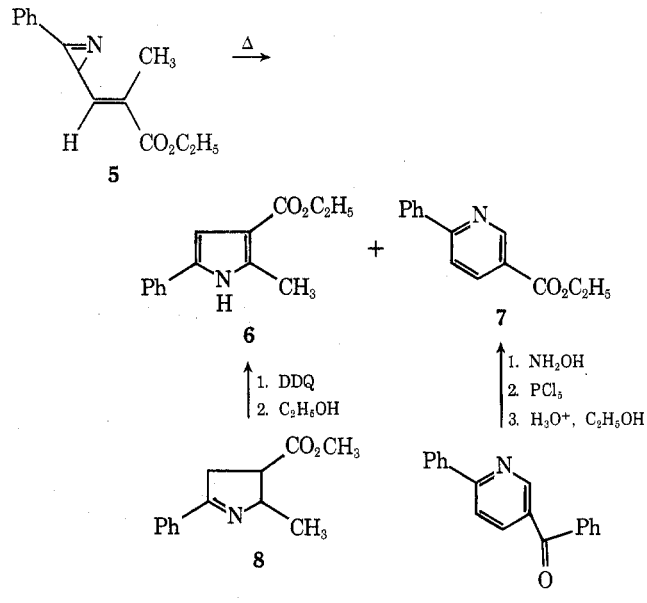
Results and Discussion

2-Formyl-3-phenyl-2*H*-azirine-*N*-allylimine (**2**) was readily prepared by treating 2-formyl-3-phenyl-2*H*-azirine (**1**) with allyl amine in benzene which contained a trace of *p*-toluenesulfonic acid. Photolysis of azirine **2** in benzene afforded 2-phenyl-*N*-allylimidazole (**3**) as the only identifiable product in 85% yield. The structure of **3** is based on analytical and infrared, NMR, and mass spectral data as well as by comparison with an authentic sample synthesized by heating a mixture of 2-phenylimidazole with allyl chloride in the presence of sodium hydroxide. Thermolysis of azirine **2** was found to give *N*-allyl-3-phenylpyrazole (**4**)



as the exclusive thermal product. The structure of pyrazole **4** was readily established by comparison with an authentic sample prepared from the reaction of 3-phenylpyrazole with allyl bromide.

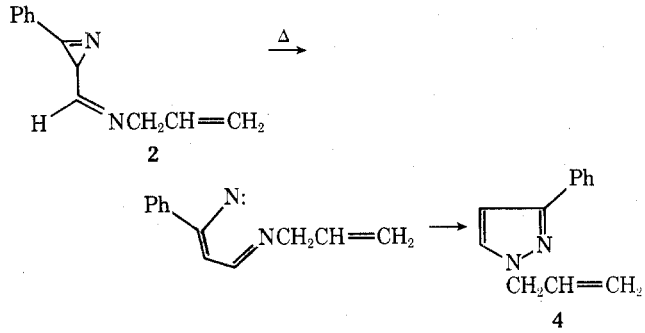
Attention was next turned to the thermal and photochemical behavior of ethyl 3-phenyl-2*H*-azirine-2-(2-methylacrylate) (**5**). This material was formed in high yield from the reaction of **1** with methylcarboethoxymethylenetriphenylphosphorane in benzene at 80°. Heating azirine **5** for 10 hr in xylene at 140° gave a mixture of two products. Separation of the mixture by thick layer chromatography afforded 2-methyl-3-carboethoxy-5-phenylpyrrole (**6**), mp 112–113° (60%), and 2-phenyl-5-carboethoxypyridine (**7**), mp 50–51° (40%). The structure of pyrrole **6** was established from its characteristic spectral data (see Experimental Section) and was further confirmed by its unequivocal synthesis from 2-phenyl-4-carbomethoxy-5-methyl-Δ^1-pyrroline (**8**) by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) followed by transesterification with ethanol. The spectroscopic properties of pyridine **7** were perfectly consistent with the assigned structure (see Experimental Section). Further proof of structure **7** was obtained by comparison with an authentic sample.[9]

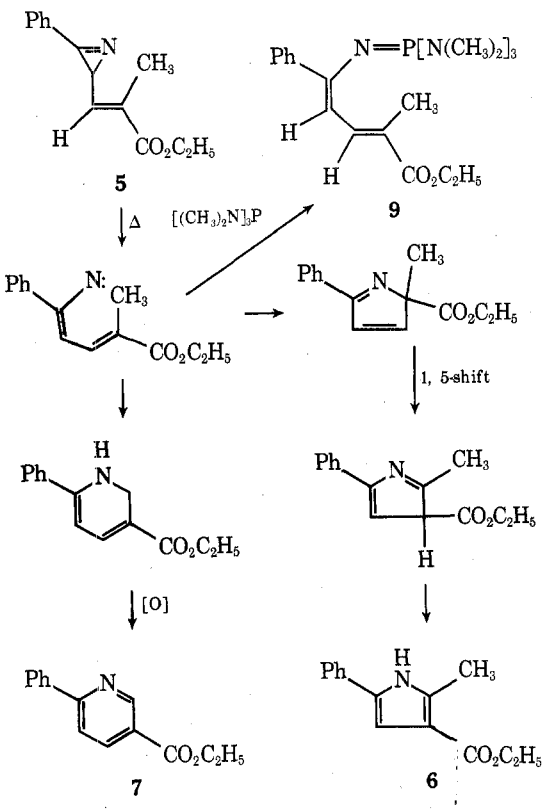


The thermal transformations observed with these systems can best be rationalized in terms of an equilibration of the 2*H*-azirine with a transient vinyl nitrene which subsequently rearranges to the final product. Several examples are available in the literature which provide good analogy for the cyclization of a butadienyl nitrene to a five-membered ring.[10,11]

The rearrangement of azirine **5** to pyrrole **6** is envisaged to occur by a related cyclization followed by a [1,5]-sigmatropic carboethoxy shift and subsequent tautomerization. The presumed carboethoxy shift in this reaction resembles the Van Alphen rearrangement[12] where 3,3,4,5-tetrasubstituted pyrazolenines rearrange into N-substituted pyrazoles, a reaction which was reported to be an uncatalyzed thermal rearrangement.[13] Recently, other examples of the pyrazolenine rearrangement were reported by Dürr and Sergio[14] and by Franck-Newmann and Buchecker,[15] who observed migrations of ester, acyl, and cyano groups which they also explained in terms of [1,5]-sigmatropic migrations.

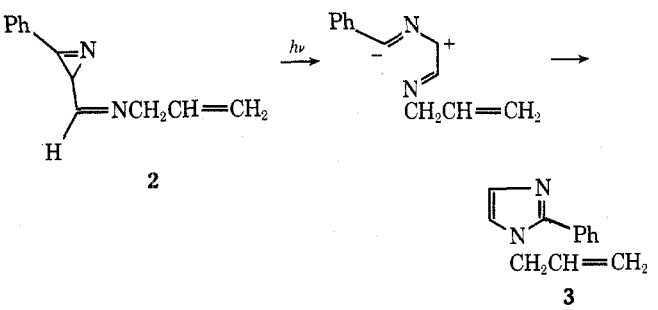
The formation of 2-phenyl-5-carboethoxypyridine (**7**) can be postulated to arise by insertion of the butadienyl nitrene into the neighboring allylic methyl group followed by oxidation of the transient dihydropyridine. Such a reaction pathway is supported by the fact that when the thermolysis of **5** was carried out in the presence of tris(dimethylamino)phosphine, the yield of both **6** and **7** was significantly diminished. Under these conditions, a new compound was obtained and identified as a 1:1 adduct of **5** and tris(dimethylamino)phosphine (i.e., structure **9**). Nishiwaki and



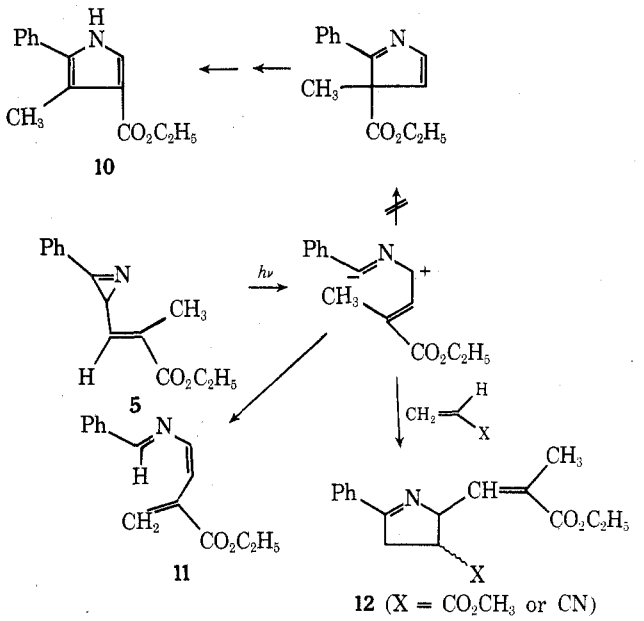


co-workers had previously demonstrated that vinyl nitrenes can be generated and trapped with phosphines during the thermolysis of substituted 2*H*-azirines.[16] Their results provide excellent precedence for the formation of structure **9**.

The photoisomerization of azirine **2** to 2-phenyl-*N*-allylimidazole (**3**) is explicable on the basis of a ring opening to

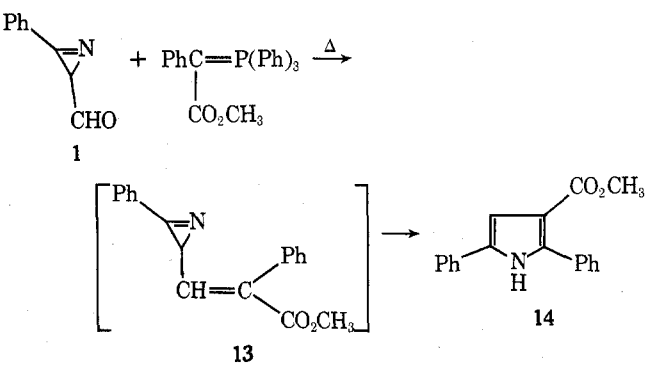


a nitrile ylide which subsequently undergoes intramolecular reorganization to the observed imidazole. Since the photolysis of 2*H*-azirines generally produces nitrile ylides, we anticipated the formation of 2-phenyl-3-methyl-4-carboethoxypyrrole (**10**) from the irradiation of azirine **5**. This pyrrole was expected to be formed by intramolecular reorganization of the initially generated nitrile ylide followed by a [1,5]-sigmatropic carboethoxy migration and subsequent tautomerization. However, all attempts to detect this pyrrole in the crude photolysate failed. Instead, the irradiation of **5** led to a complex mixture of products which resisted all attempts at purification. The crude NMR spectrum of the photolysate showed the presence of imine **11**, which can be envisaged to be formed by an intramolecular hydrogen transfer reaction. When the irradiation of **5** was carried out in the presence of methyl acrylate, a mixture of cis and trans cycloadducts **12** was formed in high yield. Similar results were obtained when acrylonitrile was used



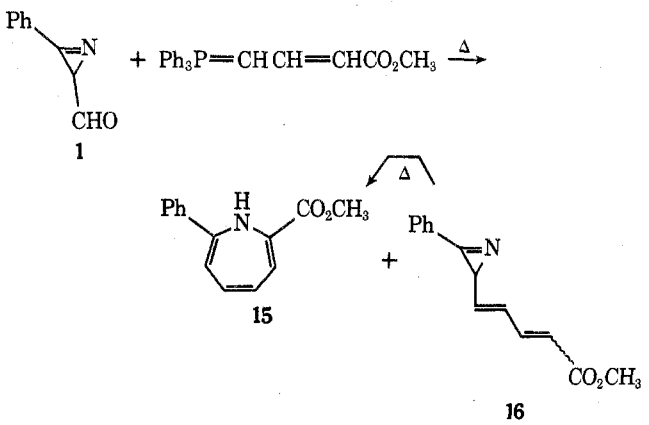
as the dipolarophile. The stereochemical assignments of the cycloadducts were made on the basis of the NMR data (see Experimental Section). The chemical shifts of the carbomethoxy groups are in the same direction as was previously observed for *cis*- and *trans*-2,5-diphenyl-4-carbomethoxy-Δ^1-pyrrolines.[3] The formation of the cycloadducts and the reduction in the yield of the other products formed from the irradiation of **5** strongly argue for the involvement of a nitrile ylide in the photolysis of azirine **5**.

We next investigated the possibility of obtaining azirine **13** by treating 2-formyl-3-phenyl-2*H*-azirine (**1**) with phenylcarbomethoxymethylenetriphenylphosphorane. Photoly-

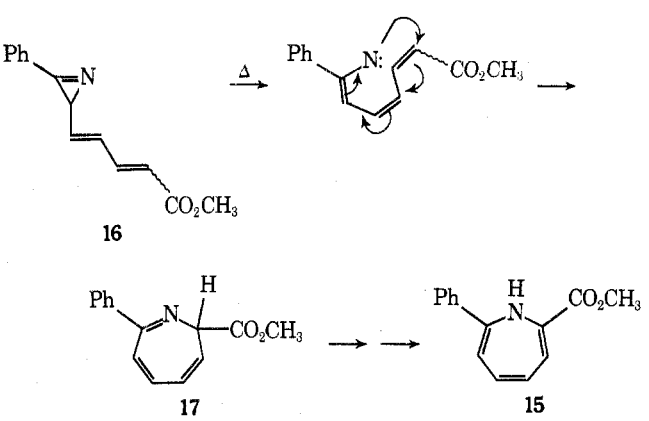


sis of this azirine would avoid the problem of an intramolecular hydrogen transfer. Unfortunately, in order to achieve the desired Wittig reaction between **1** and phenylcarbomethoxytriphenylphosphorane, it was necessary to use elevated temperatures. Under these conditions, we could only isolate 2,5-diphenyl-3-carbomethoxypyrrole (**14**). The formation of this pyrrole presumably proceeds through the intermediacy of azirine **13** followed by C–N ring opening and cyclization of the resulting vinyl nitrene in the same manner as had been previously observed with azirine **5**.

Further examples which would support the generality of intramolecular azirine cycloaddition reactions were sought. With this in mind, we decided to prepare an azirinyl diene system with the expectation that this system might undergo some interesting photochemical behavior. Reaction of 2-formyl-3-phenyl-2*H*-azirine **1** with 3-carbomethoxy-2-propenylidene-1-triphenylphosphorane[17] in benzene afforded a mixture of 2-phenyl-7-carbomethoxy-1*H*-azepine (**15**, 40%), mp 156–157°, as well as azirinyl diene **16** (60%).

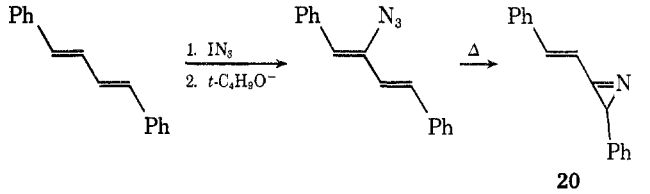


The azepine structure **15** was assigned on the basis of its spectroscopic data. The ultraviolet spectrum of this compound showed an absorption maximum at 388 nm (ϵ 29 300) indicating an extensively conjugated chromophore. The NMR spectrum showed signals at τ 6.28 (3 H, s), 3.70 (1 H, d), 3.40 (1 H, d), and 2.20–2.80 (7 H, m) and is compatible with the structure assignment. The mass spectrum showed the molecular ion peak at *m/e* 227. The azirinyl diene **16** was a mixture of the *EZ* and *EE* isomers which could not be purified since the mixture was extremely heat sensitive and rapidly undergoes isomerization to azepine **15** when allowed to stand at room temperature. The formation of azepine **15** may be formulated as proceeding through a vinyl nitrene intermediate. This species undergoes a subsequent intramolecular reorganization to generate **17**, which



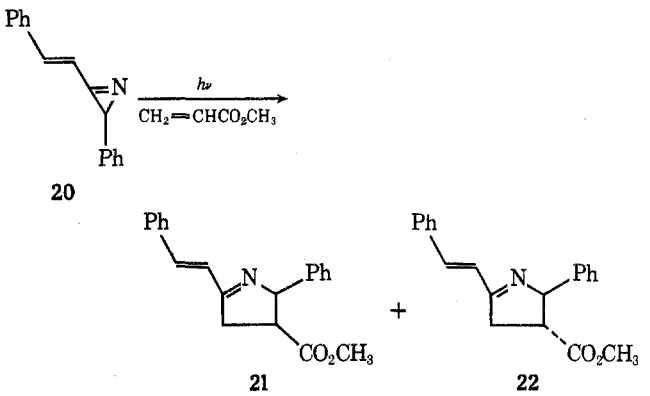
rearranges to the observed product by a series of 1,5-sigmatropic hydrogen shifts. Unlike the novel thermal chemistry encountered with azirine **16**, the photochemical behavior of this system was somewhat disappointing. Irradiation of a dilute solution of **16** through a Pyrex filter gave an extremely complex mixture from which no significant product could be isolated.

We had previously reported[8] an unusual aspect of the intramolecular photocyclization reaction of unsaturated azirines which was uncovered during our studies dealing with the photochemistry of (*Z*)-3-phenyl-2-styryl-2*H*-azirine (**18**). This styryl-substituted azirine was found to rearrange to 1-phenyl-3*H*-2-benzazepine (**19**) in high yield.[8] Our results with azirine **18** prompted an investigation of the chemical behavior of the isomeric 3-styryl-2-phenyl-2*H*-azirine (**20**) system. This compound was synthesized from 1,4-diphenyl-1,3-butadiene by the route shown below.[18]



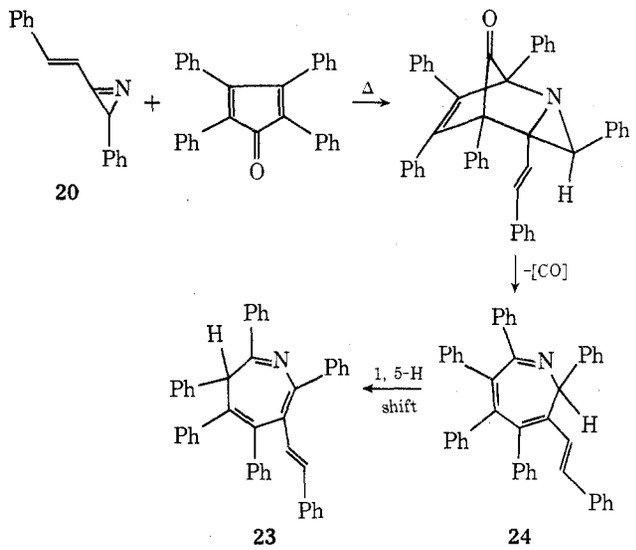
The structure of **20** was based on a parent peak at *m/e* 219 in the mass spectrum, an infrared band at 5.78 μ, uv maximum at 293 nm (ϵ 26 000), and NMR signals at τ 6.92 (1 H, s) and 2.40–3.05 (12 H, m).

Whereas azirine **18** was smoothly converted to benzazepine **19** on irradiation, photolysis of the isomeric azirine **20** resulted in the formation of polymeric material. When the irradiation was carried out in the presence of methyl acrylate, cycloadducts **21** and **22** were isolated in good yield.



The major isomer (60%) was a crystalline solid, mp 133–134°, whose spectral properties were consistent with 2-styryl-5-phenyl-*cis*-4-carbomethoxy-Δ^1-pyrroline (**21**). The assignment of stereochemistry was made on the basis of analogy to systems previously studied.[3,19] Photoadducts **21** and **22** exhibited absorptions for the carbomethoxy group at τ 6.28 and 6.84, respectively. The marked upfield shift of the carbomethoxy group in the cis adduct **21** can be attributed to shielding by the π electrons of the neighboring phenyl ring.[19] This effect is absent in the trans adduct **22** and the carbomethoxy signal appears at a lower field relative to the signal for cis adduct **21**.

We also studied the thermal behavior of azirine **20** and found that it was perfectly stable in refluxing toluene. However, when azirine **20** was heated in toluene in the presence of 2,3,4,5-tetraphenylcyclopentadienone, a crystalline compound **23** was isolated in 38% yield. The mass spectrum and elemental analysis of this material were consistent with the formula $C_{44}H_{33}N$. The infrared spectrum was devoid of carbonyl and NH absorptions. The ultraviolet spectrum in methylene chloride showed absorption maxima at 283, 315, and 375 nm while the NMR spectrum showed signals at τ 3.80 (2 H, AB quartet, J = 17.0 Hz), 3.72 (1 H, s), and 2.20–3.20 (30 H, m). The above data suggest that the structure of this compound is 6-styryl-2,3,4,5,7-pentaphenyl-3*H*-azepine (**23**). A reasonable mechanism for the formation of this azepine assumes that a normal Diels–Alder reaction initially occurs to produce a strained cycloadduct which then undergoes a chelotropic fragmentation with concomitant aziridine ring opening to give an azacycloheptatriene intermediate (i.e., **24**). This transient intermediate is converted to the thermodynamically more stable 3*H*-azepine by a 1,5-sigmatropic hydro-



gen shift. Such a sequence is closely related to reports by Hassner[20] and Nair,[21] who found that 2*H*-azirines react with substituted cyclopentadienones to give 3*H*-azepines in good yield.

Experimental Section[22]

Preparation of 2-Formyl-3-phenyl-2*H*-azirine-*N*-allylimine. A solution containing 1.45 g of 2-formyl-3-phenyl-2*H*-azirine[8] (**1**) and 0.57 g of allylamine in 125 ml of benzene which contained a trace of *p*-toluenesulfonic acid was stirred in the presence of 15 g of anhydrous sodium sulfate for 1.5 hr. Addition of 1.0 g of sodium bicarbonate followed by filtration and removal of the solvent under reduced pressure left a dark oil. This material was taken up in pentane and separated from the insoluble portion. Removal of the solvent left 1.56 g (85%) of 2-formyl-3-phenyl-2*H*-azirine-*N*-allylimine (**2**) as a light yellow oil: ir (neat) 5.70 and 6.05 μ; NMR ($CDCl_3$) τ 7.04 (1 H, d, J = 7.0 Hz), 5.98 (2 H, m), 4.90 (2 H, m), 4.10 (1 H, m), 2.98 (1 H, d, J = 7.0 Hz), 2.04–2.60 (5 H, m); MS *m/e* 184 (M^+), 183, 105, 90, 89, and 77.

Irradiation of 2-Formyl-3-phenyl-2*H*-azirine-*N*-allylimine. A solution containing 500 mg of *N*-allylimine **2** in benzene was irradiated for 90 min through a Corex filter sleeve. Removal of the solvent under reduced pressure left a dark oil which was distilled at 70° (0.005 mm) to give 425 mg (85%) of a colorless oil whose structure was assigned as 2-phenyl-*N*-allylimidazole (**3**) on the basis of its spectral properties and by an independent synthesis: ir (neat) 6.10 μ; NMR ($CDCl_3$) τ 5.56 (2 H, m), 5.00 (2 H, m), 4.22 (1 H, m), 3.10 (1 H, s), 3.03 (1 H, s), 2.46–2.88 (5 H, m); MS *m/e* 184 (M^+, base), 143, 89, and 75. A picrate derivative was prepared and recrystallized from ethanol, mp 152–153°. An authentic sample of **3** was prepared by heating a mixture which contained 375 mg of 2-phenylimidazole,[23] 206 mg of allyl chloride, and 116 mg of sodium hydroxide in 5 ml of acetonitrile for 3 hr. The mixture was filtered and the solvent was removed under reduced pressure to give a dark oil which was distilled at 90° (0.005 mm) to give 325 mg (65%) of a colorless oil whose spectral properties were identical with those of the major product obtained from the photolysis of azirine **2**.

Thermolysis of 2-Formyl-3-phenyl-2*H*-azirine-*N*-allylimine. A solution containing 200 mg of azirine **2** in 50 ml of xylene was heated at reflux for 30 hr. Removal of the solvent under reduced pressure left a dark oil which was purified by thick layer chromatography using a 1:1 ether–pentane mixture as the eluent. The major band contained 168 mg (84%) of a yellow oil whose structure was assigned as *N*-allyl-3-phenylpyrazole (**4**) on the basis of its spectral properties and by comparison with an authentic sample: ir (neat) 5.96, 6.24 μ; NMR ($CDCl_3$) τ 5.35 (2 H, m), 4.89 (2 H, m), 3.87–4.31 (1 H, m), 3.55 (1 H, d, J = 2.0 Hz), 2.6–3.0 (4 H, m), 2.36 (1 H, m), 2.28 (1 H, d, J = 2.0 Hz). An authentic sample of pyrazole **4** was prepared by treating 5-phenylpyrazole[24] with allyl bromide. To a solution containing 750 mg of 5-phenylpyrazole in 3 ml of absolute ethanol was added 0.28 g of potassium hydroxide in 2 ml of ethanol. The solution was allowed to stir for 30 min at room temperature and was then cooled to 0°. To this mixture was added a solution of 940 mg of allyl bromide in 4 ml of ethanol. After the addition was complete the mixture was heated at reflux for 1 hr. Filtration and removal of the solvent under reduced pressure left a dark oil. This material was purified by thick layer chromatography using a 1:1 ether–pentane mixture as the eluent. The major band corresponded to 626 mg (68%) of a yellow oil whose spectral properties were identical with those of *N*-allyl-3-phenylpyrazole (**4**) obtained from the thermolysis of azirine **2**.

Preparation of Ethyl 3-Phenyl-2*H*-azirine-2-(2-methyl)acrylate. A solution containing 1.45 g of 2-formyl-3-phenyl-2*H*-azirine (**1**) and 3.6 g of methylcarboethoxymethylenetriphenylphosphorane in 125 ml of benzene was heated at reflux for 12 hr. Removal of the solvent left an oily solid which was triturated with ether and filtered to remove triphenylphosphine oxide. The filtrate was concentrated under reduced pressure to leave an oil which was filtered through a short Florisil column with a 10% ethyl acetate–benzene mixture. Removal of the solvent left a light yellow oil which solidified on standing. This material was sublimed at 45° (0.005 mm) and recrystallized from pentane to give 2.0 g (89%) of ethyl 2-phenyl-2*H*-azirine-2-(2-methyl)acrylate (**5**) as a crystalline solid: mp 43–44°; ir (KBr) 5.73, 5.90, and 6.12 μ; uv (cyclohexane) 243 nm (ε 27 400); NMR ($CDCl_3$) τ 8.84 (3 H, t, J = 6.0 Hz), 7.95 (3 H, s), 7.06 (1 H, d, J = 9.0 Hz), 5.90 (2 H, q, J = 6.0 Hz), 3.94 (1 H, dq, J = 9.0 and 1.0 Hz), 2.07–2.66 (5 H, m); MS *m/e* 229, 200, 184, 156, and 129.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.64; N, 6.06. Found: C, 73.29; H, 6.59; N, 6.11.

Thermolysis of Ethyl 3-Phenyl-2*H*-azirine-2-(2-methyl)acrylate. A solution containing 0.5 g of ethyl 3-phenyl-2*H*-azirine-2-(2-methyl)acrylate (**5**) in 500 ml of xylene was heated at reflux for 10 hr. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on silica gel using a 50% ether–pentane mixture as the eluent. The first material eluted from the column was a crystalline solid, mp 50–51° (40%), whose structure was assigned as 2-phenyl-5-carboethoxypyridine (**7**) on the basis of the following data: ir (KBr) 5.86 and 6.30 μ; uv (95% ethanol) 290 nm (ε 29 000); NMR ($CDCl_3$) τ 8.59 (3 H, t, J = 7.0 Hz), 5.59 (2 H, q, J = 7.0 Hz), 1.55–2.45 (7 H, m), 0.7 (1 H, d, J = 2.0 Hz); MS *m/e* 227 (M^+), 197, 180 (base), 153, 127, and 58. The structure of **7** was unambiguously verified by comparison with an authentic sample synthesized from the corresponding carboxylic acid according to the procedure of Benary and Psille.[9]

The second component isolated from the column was a crystalline solid, mp 112–113° (60%), whose structure was assigned as 2-methyl-3-carboethoxy-5-phenylpyrrole (**6**) on the basis of its spectral properties and by an independent synthesis: ir (KBr) 3.03, 6.02, and 6.29 μ; uv (95% ethanol) 268 nm (ε 20 000); NMR ($CDCl_3$) 8.79 (3 H, t, J = 7.0 Hz), 7.51 (3 H, s), 5.80 (2 H, q, J = 7.0 Hz), 3.26 (1 H, d, J = 3.0 Hz), 2.50–2.94 (5 H, m), and 1.26–1.56 (1 H, broad singlet); MS *m/e* 229 (M^+), 199 (base), 183, and 156. The structure of **6** was verified by comparison with an authentic sample synthesized in the manner described below. To a solution containing 1 g of 2-phenyl-4-carbomethoxy-5-methyl-Δ^1-pyrroline[3] (**8**) in 50 ml of benzene was added 1 g of DDQ. The mixture was refluxed for 3 hr, filtered, and evaporated under reduced pressure. The dark oil obtained was purified by passing it through a short Florisil column with benzene. The crude solid obtained was identified as 2-methyl-3-carbomethoxy-5-phenylpyrrole: NMR ($CDCl_3$) τ 7.44 (s, 3 H), 6.20 (s, 3 H), 3.20 (d, 1 H, J = 3.0 Hz), 2.4–2.8 (m, 5 H), 1.20 (NH, exchanged with D_2O). A solution containing 700 mg of the above carbomethoxypyrrole and a trace of sodium metal was heated at reflux in absolute ethanol for 4 hr. The mixture was diluted with water and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 0.71 g (65%) of a white solid, mp 112–113°, which was identical with the sample of 2-methyl-3-carboethoxy-5-phenylpyrrole (**6**) obtained from the thermolysis of ethyl 3-phenyl-2*H*-azirine-2-(2-methyl)acrylate (**5**). A mixture melting point was undepressed at 112–113°.

The thermolysis of ethyl 3-phenyl-2*H*-azirine-2-(2-methyl)acrylate (**5**) was also carried out in the presence of tris(dimethylamino)phosphine. A solution containing 250 mg of **5** and 1 g of tris(dimethylamino)phosphine in 50 ml of xylene was heated at reflux for 12 hr. Removal of the solvent left an oily solid which was recrystallized from chloroform–ether to give 268 mg (62%) of a yellow solid (**9**): mp 230–235°; NMR ($CDCl_3$) τ 8.06 (3 H, s), 7.20–7.40 (18 H, 4 lines), 6.34 (3 H, 2 lines), 3.42 (1 H, dt, J = 11.0 and 2.0 Hz), 2.12–2.86 (6 H, m). Azirine **5** was also heated in the presence of triphenylphosphine. A solution containing 0.5 g of **5** and 1.72 g of triphenylphosphine in 500 ml of xylene was heated at reflux for 15 hr. Removal of the solvent under reduced pressure gave a yellow oil. All attempts to purify this material resulted in the formation of tri-

phenylphosphine oxide. Under these conditions the normal thermal products (6 and 7) were formed in much lower yields.

Irradiation of Ethyl 3-Phenyl-2*H*-azirine-2-(2-methyl)acrylate. A solution containing 500 mg of ethyl 3-phenyl-2*H*-azirine-2-(2-methyl)acrylate (**5**) in 450 ml of benzene was irradiated for 1 hr using a Pyrex filter sleeve. The solvent was removed under reduced pressure to give a light yellow oil which was extremely sensitive to moisture and readily decomposed on standing at room temperature. The NMR spectrum of the crude photolysate was quite complex and showed a complex pattern of overlapping triplets for the carboethoxy methyl group at τ 8.90, a singlet at τ 8.12, a doublet at τ 6.71 (J = 16.0 Hz), a complex pattern of overlapping quartets for the carboethoxy methylene group at τ 6.12, a triplet at τ 4.72 (J = 10.0 Hz), a doublet at τ 4.26 (J = 8.0 Hz), a doublet at τ 3.90 (J = 10 Hz), a doublet at τ 3.48 (J = 8.0 Hz), aromatic protons at τ 2.39–3.24 (multiplet), and a singlet at τ 2.39. All attempts to separate the mixture into its component parts failed as a result of the ready hydrolysis of the mixture to benzaldehyde and additional components which could not be characterized.

The irradiation of ethyl 3-phenyl-2*H*-azirine-2-(methyl)acrylate (**5**) was also carried out in the presence of a dipolarophile so as to trap the nitrile ylide. A solution containing 0.5 g of **5** and 10 ml of methyl acrylate in 450 ml of benzene was irradiated for 1 hr through a Pyrex filter sleeve. Removal of the solvent left a yellow oil which was chromatographed on a thick layer plate with a 1:1 mixture of ether–pentane as the eluent. The minor component isolated from the thick layer plate was a crystalline solid, mp 56–58° (38%), whose structure was assigned as *trans*-2-phenyl-4-carbomethoxy-Δ^1-pyrroline-5-(2-methyl)acrylic acid ethyl ester (**12a**) on the basis of the following data: ir (KBr) 5.76, 5.82, 6.02, and 6.16 μ; uv (95% ethanol) 248 nm (ϵ 20 300); NMR ($CDCl_3$) τ 8.79 (3 H, t, J = 9.0 Hz), 8.08 (3 H, s), 6.86–7.18 (1 H, m), 6.56–6.78 (2 H, m), 6.33 (3 H, s), 5.85 (2 H, q, J = 9.0 Hz), 4.79 (1 H, m), 3.40 (1 H, d, J = 10.0 Hz), 2.07–2.80 (5 H, m). The major product isolated from the thick layer plate was a white, crystalline solid, mp 111–112° (62%), whose structure was assigned as *cis*-2-phenyl-4-carbomethoxy-Δ^1-pyrroline-5-(2-methyl)acrylic acid ethyl ester (**12b**) on the basis of the following data: ir (KBr) 5.79, 5.87, 6.05, and 6.14 μ; uv (95% ethanol) 248 nm (ϵ 23 000); NMR ($CDCl_3$) τ 8.78 (3 H, t, J = 7.0 Hz), 8.01 (3 H, s), 6.26–7.08 (6 H, m), 5.87 (2 H, q, J = 7.0 Hz), 4.02 (1 H, m), 3.54 (1 H, d, J = 11.0 Hz), 2.06–2.78 (5 H, m).

The nitrile ylide was also trapped with acrylonitrile. A solution containing 300 mg of **5** and 10 ml of acrylonitrile in 450 ml of benzene was irradiated for 1 hr through a Corex filter sleeve. Removal of the solvent under reduced pressure gave a yellow oil which was chromatographed on a thick layer plate using a 1:1 ether–pentane mixture as the eluent. The minor component obtained (21%) from the thick layer plate was identified as *trans*-2-phenyl-4-cyano-Δ^1-pyrroline-5-(2-methyl)acrylic acid ethyl ester: mp 72–73°; ir (KBr) 4.45, 5.83, 5.95, and 6.17 μ; uv (95% ethanol) 247 nm (ϵ 14 700); NMR ($CDCl_3$) τ 8.70 (3 H, t, J = 7.0 Hz), 7.87 (3 H, s), 6.19–7.20 (3 H, m), 5.78 (2 H, q, J = 7.0 Hz), 4.67 (1 H, m), 3.38 (1 H, d, J = 9.0 Hz), and 2.0–2.3 (5 H, m). The major isomer obtained was identified as *cis*-2-phenyl-4-cyano-Δ^1-pyrroline-5-(2-methyl)acrylic acid ethyl ester: mp 109–110°; ir (KBr) 4.44, 5.72, 6.01, and 6.20 μ; uv (95% ethanol) 247 nm (ϵ 14 900); NMR ($CDCl_3$) τ 8.69 (3 H, t, J = 7.0 Hz), 7.89 (3 H, s), 6.26–7.18 (3 H, m), 5.80 (2 H, q, J = 7.0 Hz), 4.68 (1 H, m), 3.38 (1 H, d, J = 8.0 Hz), and 2.0–2.7 (5 H, m).

Reaction of 2-Formyl-3-phenyl-2*H*-azirine with Phenylcarbomethoxymethylenetriphenylphosphorane. A mixture containing 145 mg of 2-formyl-3-phenyl-2*H*-azirine (**1**) and 480 mg of phenylcarbomethoxymethylenetriphenylphosphorane[25] was heated in the solid state at 170° for 3 hr. Then 10 ml of ether was added to the mixture and the triphenylphosphine oxide which had precipitated was collected. The filtrate was concentrated under reduced pressure and the residue was filtered through a short Florisil column using a 10% ethyl acetate–benzene mixture as the eluent. The major component isolated from the column was a white solid, mp 169–170° (80%), whose structure was identified as 2,5-diphenyl-3-carbomethoxypyrrole (**14**): ir (KBr) 3.10, 6.05, and 6.27 μ; NMR ($CDCl_3$) τ 6.40 (3 H, s), 2.50–3.0 (10 H, m), and 1.3–1.6 (1 H, m). The structure of this material was verified by comparison with an independently synthesized sample. A solution containing 0.35 g of 2,5-diphenyl-4-carbomethoxy-Δ^1-pyrroline[3] and 0.8 g of DDQ in 50 ml of benzene was heated at reflux for 2.5 hr. The solvent was removed under reduced pressure and the residue was filtered through a short Florisil column with benzene. The major product (0.3 g) was identical in all respects with a sample of 2,5-diphenyl-3-carbomethoxypyrrole obtained from the reaction of **1** with phenylcarbomethoxymethylenetriphenylphosphorane. A mixture melting point was undepressed at 169–170°.

Preparation of 3-Phenyl-2-(4-carbomethoxy-1,3-butadienyl)-2*H*-azirine. A solution containing 0.84 g of 2-formyl-3-phenyl-2*H*-azirine (**1**) and 2.16 g of 3-carbomethoxy-2-propenylidene-1-triphenylphosphorane[17] in 100 ml of benzene was heated at 50° under a nitrogen atmosphere for 3 hr. The solvent was removed under reduced pressure and the residual oil was passed through a Florisil column using a 10% ethyl acetate–benzene mixture to give an oily solid. Addition of hexane gave 0.42 g (40%) of 2-phenyl-7-carbomethoxy-1*H*-azepine (**15**): mp 156–157°; ir (KBr) 3.00, 5.92, and 6.12 μ; uv (95% ethanol) 388 nm (ϵ 29 300); NMR ($CDCl_3$) τ 6.28 (3 H, s), 3.70 (1 H, d), 3.40 (1 H, d), and 2.20–2.80 (6 H, m); *m/e* 227 (M^+).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.98; H, 5.70; N, 6.13.

The filtrate consisted of 3-phenyl-2-(4-carbomethoxy-1,3-butadienyl)-2*H*-azirine (**16**, 60%) as a dark oil which exhibited the following spectral characteristics: ir (neat) 5.75, 5.85, and 6.15 μ; NMR ($CDCl_3$) τ 6.84 (1 H, d, J = 10.0 Hz), 6.68 (1 H, d, J = 12.0 Hz), 6.38 (3 H, s), 6.34 (3 H, s), a complex multiplet at τ 5.0–7.0, and aromatic absorptions centered at τ 2.60. The NMR spectrum indicated the presence of two geometric isomers in the ratio of 1.5:1. All attempts to separate and purify the isomeric azirines were unsuccessful as this material is extremely heat sensitive and underwent extensive decomposition on attempted purification. A solution containing 0.4 g of the impure azirines in 75 ml of benzene was heated at reflux for 1 hr. Removal of the solvent left 0.35 g (88%) of crystalline 2-phenyl-7-carbomethoxy-1*H*-azepine (**15**).

Preparation of 3-Styryl-2-phenyl-2*H*-azirine. To a stirred ice-cold solution of iodine azide (0.1 mol) in 200 ml of acetonitrile was added 20.6 g of *trans,trans*-1,4-diphenyl-1,3-butadiene. The mixture was allowed to warm to room temperature overnight prior to work-up. The resulting red-brown mixture was poured onto 500 ml of water and was extracted with ether. The combined organic extracts were washed successively with 700 ml of 5% aqueous sodium thiosulfate and 500 ml of water. The solvent was dried over magnesium sulfate and removed under reduced pressure to give a yellow oil which was passed through a neutral alumina column with a 1:1 ether–hexane mixture to give 13.6 g (37%) of a colorless oil. A solution containing 13 g of the iodine azide adduct in 300 ml of ether at 0° was treated with 23 g of potassium *tert*-butoxide. The reaction mixture was allowed to stir at 0° for 24 hr and was then diluted with 200 ml of water. The ethereal layer was dried over magnesium sulfate and concentrated under reduced pressure to give a yellow oil. This material was filtered through a column of neutral alumina and the resulting vinyl azide was heated in chloroform at 60° for 8 hr. Removal of the solvent left 4.6 g (21%) of a crude solid which was sublimed at 50° (0.05 mm) and recrystallized from hexane to give 3-styryl-2-phenyl-2*H*-azirine (**20**):[18] mp 66–67°; ir (KBr) 5.78 μ; uv (95% ethanol) 293 nm (ϵ 26 000); NMR ($CDCl_3$, 100 MHz) τ 6.96 (1 H, s) and 2.40–3.00 (12 H, m); MS *m/e* 219, 218 (base), 217, 204, 191, 115, 108, 90, 89, and 77.

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.34; H, 5.96; N, 6.26.

Irradiation of 3-Styryl-2-phenyl-2*H*-azirine. A solution containing 0.5 g of 3-styryl-2-phenyl-2*H*-azirine (**20**) in 500 ml of benzene was irradiated through a Pyrex filter sleeve for 1 hr. Removal of the solvent under reduced pressure left a viscous oil which resisted all attempts at purification. No characterizable material could be obtained on extensive chromatography. The photolysis of **20** was also carried out in the presence of methyl acrylate. A solution containing 0.65 g of 2-styryl-3-phenyl-2*H*-azirine and 20 ml of methyl acrylate in 500 ml of benzene was irradiated through a Pyrex filter sleeve for 2.5 hr. Removal of the solvent and excess methyl acrylate under reduced pressure afforded a yellow oil. Liquid–liquid partition chromatography[26] of the oil indicated the presence of two adducts. The minor adduct (40%) was a pale yellow oil whose structure was assigned as 2-styryl-5-phenyl-*trans*-4-carbomethoxy-Δ^1-pyrroline (**22**): ir (neat) 5.70, 6.05, and 6.18 μ; NMR ($CDCl_3$) τ 6.80 (2 H, m), 6.28 (3 H, s), 4.56 (1 H, d), and 2.40–3.05 (12 H, m). A picrate derivative was prepared and recrystallized from ethanol, mp 171–172°.

Anal. Calcd for $C_{26}H_{22}N_4O_9$: C, 58.42; H, 4.15; N, 10.48. Found: C, 58.23; H, 4.18; N, 10.39.

The major adduct (60%) was assigned the structure of 2-styryl-5-phenyl-*cis*-4-carbomethoxy-Δ^1-pyrroline (**21**) on the basis of the following data: mp 134–135°; ir (KBr) 5.70, 6.08, and 6.20 μ; uv (95% ethanol) 287 nm (ϵ 22 000); NMR ($CDCl_3$) τ 6.84 (3 H, s), 6.40

(2 H, m), 4.32 (1 H, d), and 2.20–3.10 (12 H, m); MS *m/e* 305, 246, 218, 201 (base), 170, 169, 141, 115, 114, and 77.

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.63; H, 6.23; N, 4.59.

The combined yield of *cis*- and *trans*-Δ^1-pyrrolines (**21** and **22**) was 68%.

Thermolysis of 3-Styryl-2-phenylazirine in the Presence of Tetraphenylcyclopentadienone. A solution containing 0.324 g of 3-styryl-2-phenylazirine and 0.538 g of tetraphenylcyclopentadienone in 50 ml of toluene was heated at reflux for 4 days. The toluene solution was concentrated under reduced pressure and the residual oil was chromatographed on a silica gel column with a 1:1 pentane–benzene mixture as the eluent to afford 0.31 g (38%) of a bright yellow, crystalline compound whose structure was assigned as 6-styryl-2,3,4,5,7-pentaphenyl-3*H*-azepine (**23**) on the basis of the following data: mp 229–231°; ir (KBr) 6.25 μ; uv (methylene chloride) 283, 315, and 375 nm (ϵ 32 400, 18 200, and 14 500); NMR ($CDCl_3$) τ 3.80 (2 H, AB quartet, J = 17.0 Hz), 3.72 (1 H, s), and 2.20–3.20 (30 H, m); *m/e* 369 (base).

Anal. Calcd for $C_{44}H_{33}N$: C, 91.18; H, 5.84; N, 2.44. Found: C, 91.08; H, 5.89; N, 2.37.

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Registry No.—**1,** 42970-55-8; **2,** 57443-65-9; **3,** 14967-25-0; **3** picrate, 15139-33-0; **4,** 57443-66-0; **5,** 57443-67-1; **6,** 3652-48-0; **7,** 57443-68-2; **8,** 57443-69-3; **9,** 57443-70-6; *cis*-**12** (X = CO_2CH_3), 57443-71-7; *cis*-**12** (X = CN), 57443-72-8; *trans*-**12** (X = CO_2CH_3), 57443-73-9; *trans*-**12** (X = CN), 57443-74-0; **14,** 13901-74-1; **15,** 57443-75-1; (*EZ*)-**16,** 57443-76-2; (*EE*)-**16,** 57443-77-3; **20,** 57152-43-9; **21,** 57443-78-4; **22,** 57443-79-5; **23,** 57443-80-8; allylamine, 107-11-9; 2-methyl-3-carbomethoxy-5-phenylpyrrole, 28168-20-9; phenylcarbomethoxymethylenetriphenylphosphorane, 1106-06-5; 3-carbomethoxy-2-propenylidene-1-triphenylphosphorane, 53236-02-5; *trans,trans*-1,4-diphenyl-1,3-butadiene, 538-81-8; triphenylphosphine, 603-35-0; phenylcarbomethoxymethyltriphenylphosphonium bromide, 1106-05-4; methyl α-bromophenylacetate, 3042-81-7.

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(23) F. L. Pyman and R. G. Fargher, *J. Chem. Soc.*, 217 (1919).
(24) K. V. Auwers and W. Schmidt, *Ber.*, **58,** 537 (1925).
(25) A sample of phenylcarbomethoxymethylenetriphenylphosphorane was prepared by stirring 86.5 g of triphenylphosphine with 68.7 g of methyl α-bromophenylacetate in 1 l. of anhydrous benzene for 30 hr at room temperature. The phosphonium bromide which crystallized out of solution (132 g, 89%) was filtered and dried to give a white solid, mp 154–155°. To a solution of 40 g of the above phosphonium salt in 1.75 l. of water was added 2 drops of methanolic phenolphthalein and the mixture was titrated to the end point with a 10% sodium hydroxide solution. The reaction mixture was cooled in an ice bath and filtered to give 30 g (75%) of phenylcarbomethoxymethylenetriphenylphosphorane: mp 151–152°; ir (KBr) 6.30, 8.05, and 10.21 μ.
(26) A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, **89,** 102 (1967).