spectively. Pmr spectra were recorded on JEOL MH-100 and C-60 HL spectrometers, and chemical shifts are reported with respect to internal TMS. Elemental analyses were performed by G. I. Robertson Laboratory, Florham Park, N. J.

Preparation of 8a.—To a solution of 2.0 g (0.0093 mol) of TNT dissolved in a minimum amount of 1,3-dicarbomethoxyacetone at 25° was added about 3 ml of triethylamine. After standing at room temperature for 10 hr, the reaction mixture was washed with anhydrous ether to remove the unreacted ketone. After several 100-ml washings the oily residue finally solidified to an orange powder, which when recrystallized from a 1:4 ether–ethanol mixture yielded cubic crystals of **8a**: mp 116–117°; λ_{max} (MeOH) 446 nm; ir (KBr) 1730, 1662, 1610, 1555, 1490, 1450 cm^{-1}; pmr ($DCCl_3$) δ 1.36 [t, 9 H, $^{+}HN(CH_2CH_3)_3$], 2.46 (s, 3 H, CH_3), 3.18 [q, 6 H, $^{+}HN(CH_2CH_3)_3$], 3.75 and 3.85 (each a singlet, 3 H each, CO_2CH_3), 4.15 (d, 1 H, $CHCO_2CH_3$), 4.42 (q, 1 H, $CHNO_2$), 5.30 (d, 2 H, bridgehead protons), 11.08 [br, 2 H, $HN(CH_2CH_3)_3$ and OH]. A pmr spectrum of the crude product showed the absence of **9a**.

Anal. Calcd for $C_{20}H_{30}N_4O_{11}$: C, 47.81; H, 6.02; N, 11.15. Found: C, 48.04; H, 6.31; N, 11.09.

Preparation of 8b and 10b.—To a solution of 2.0 g (0.0074 mol) of methyl 2,4,6-trinitrobenzoate dissolved in a minimum amount of 1,3-dicarbomethoxyacetone at 50° was added 2 ml of tetrahydrofuran and 3 ml of triethylamine. After 4 hr at 25° the reaction mixture was washed with 75-ml portions of anhydrous ether. The resulting oil was dissolved in 35 ml of hot methanol and 90 ml of ether was added. After standing for 2 days at 25°, crystals were deposited on the bottom of the flask. Examination of these with a stereomicroscope showed two distinct crystalline forms. The crystals formed in larger quantity (*ca.* 80%) were a dull orange, while a smaller quantity of bright red-orange crystals were also formed (*ca.* 20%). These crystals were separated manually under the microscope, and each was recrystallized from ether–methanol solution. The product formed in the largest amount was **8b**, the remaining amount being **10b**. There was essentially no product left in the mother liquor.

8b had mp 142–143° and was hygroscopic; λ_{max} (MeOH) 499 nm; ir (KBr) 1742, 1725, 1665, 1610, 1555 cm^{-1}; pmr ($CDCl_3$) δ 1.35 [t, 9 H, $^{+}HN(CH_2CH_3)_3$], 3.15 [q, 6 H, $^{+}HN(CH_2CH_3)_3$], 3.80 (s, 3 H, CO_2CH_3), 3.85 (s, 6 H, two CO_2CH_3), 3.82 (d, 1 H, $CHCO_2CH_3$), 4.5 (q, 1 H, $CHNO_2$), 5.26 and 5.46 (two q, bridgehead protons), 12.1 [br, 2 H, $^{+}HN(CH_2CH_3)_3$ and OH].

Anal. Calcd for $C_{21}H_{30}N_4O_{13}$: C, 46.16; H, 5.53; N, 10.25. Found: C, 45.68; H, 5.76; N, 9.99.

10b had mp 142–143°; λ_{max} (MeOH) 497 nm; ir (KBr) 1755, 1740, 1650, 1610, 1555 cm^{-1}; pmr ($CDCl_3$) δ 1.35 [t, 9 H, $^{+}HN(CH_2CH_3)_3$], 3.15 [q, 6 H, $^{+}HN(CH_2CH_3)_3$], 3.70 (s, 3 H, CO_2CH_3), 3.85 (s, 6 H, two CO_2CH_3), 4.80 (s, 1 H, $CHCO_2CH_3$), 5.2 (d, 1 H, $CHNO_2$), 5.38 (br d, 1 H, bridgehead), 8.75 (s, 1 H, nitropropene nitronate), 12.1 [br, 2 H, $^{+}HN(CH_2CH_3)_3$ and OH].

Anal. Calcd for $C_{21}H_{30}N_4O_{13}$: C, 46.16; H, 5.53; N, 10.25. Found: C, 46.96; H, 6.19; N, 9.42

Preparation of 8c.—A solution of 2 g (0.008 mol) of *N*-(2-nitrophenyl)picramide and 3 ml of triethylamine in the minimum amount of 1,3-dicarbomethoxyacetone necessary for dissolution was allowed to stand at room temperature for 4 hr. After washing the resulting reaction mixture with two 125-ml portions of ether an oily residue was obtained, which when recrystallized from a methanol–ether solution yielded orange crystals of **8c**: mp 155°; λ_{max} (CH_3OH) 458 nm; ir (KBr) 1740, 1660, 1610, 1535 cm^{-1}; pmr ($CDCl_3$) δ 1.10 [t, 9 H, $^{+}HN(CH_2CH_3)_3$], 2.85 [q, 6 H, $^{+}HN(CH_2CH_3)_3$], 3.70 and 3.78 (two s, 3 H each, two CO_2CH_3), 4.1 (d, 1 H, $CHCO_2CH_3$), 4.3 (q, 1 H, $CHNO_2$), 5.15 and 5.50 (two q, 2 H, bridgehead), 7.2–7.8 (m, 4 H, *m*-$NO_2C_6H_4$), 12.4 [broad s, 2 H, $^{+}HN(CH_2CH_3)_3$ and OH].

Anal. Calcd for $C_{25}H_{32}N_6O_{13}$: C, 48.10; H, 5.18; N, 13.48. Found: C, 47.93; H, 5.31; N, 13.34.

Registry No.—**8a**, 38218-79-0; **8b**, 38355-40-7; **8c**, 38218-80-3; **10b**, 38413-80-8; TNT, 118-96-7; MTNB, 15012-38-1; NPP, 38229-29-7; 1,3-dicarbomethoxyacetone, 1830-54-2.

Acknowledgments.—The authors wish to thank the Army Research Office at Durham, the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Photochemical Transformations of Small Ring Heterocyclic Compounds. XLVIII. Further Studies on the Photocycloaddition and Photodimerization Reactions of Arylazirines[1]

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Received November 29, 1972

Further evidence for the mechanism of the photodimerization of arylazirines was obtained by irradiating a mixture of phenyl- and diphenylazirine. The formation of a mixture of *endo*- and *exo*-2,4,5-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene is rationalized in terms of 1,3-dipolar addition of the nitrile ylide derived from diphenylazirine onto the C–N double bond of phenylazirine. Irradiation of methyl- and dimethylphenylazirine in an inert solvent gave 1,3-diazabicyclo[3.1.0]hex-3-enes as primary photoproducts. The initial photodimers undergo subsequent photoreaction. The products formed depend on the substituent groups, the time of irradiation, and the particular solvent employed. The photocycloaddition of arylazirines has been found to proceed with a wide variety of dipolarophiles and provides a synthetic route into systems otherwise difficult to prepare.

In earlier papers we have shown that arylazirines undergo photocycloaddition with electron-deficient olefins to give Δ^1-pyrroline derivatives.[1,5] 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. Arylazirines are also known to undergo photodimerization to 1,3-diazabicyclo[3.1.0]hex-3-enes.[6,7] The formation of these dimers was rationalized in terms of 1,3-dipolar addition of the initially generated nitrile ylide onto a ground-state azirine molecule. This conclusion was reached by a study of the variation of the quantum

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[1] Part XLVII: A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *J. Amer. Chem. Soc.*, **95**, 1954 (1973). Part XLVI: *ibid.*, **95**, 1945 (1973).

[2] Alfred P. Sloan Foundation Fellow, 1968–1972; National Institutes of Health Special Postdoctoral Fellow, 1972–1973.

[3] NDEA Title IV Fellow, 1969–1971.

[4] NSF Science Faculty Fellow, 1970–1971; Virginia Military Institute Faculty Fellow, 1971–1973.

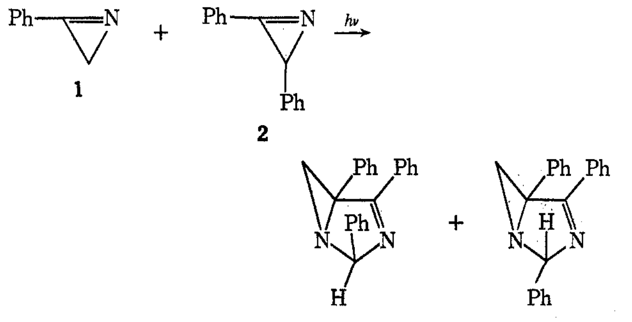
[5] A. Padwa and J. Smolanoff, *J. Amer. Chem. Soc.*, **93**, 548 (1971).

[6] A. Padwa, S. Clough, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *ibid.*, **94**, 1395 (1972).

[7] N. Gakis, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 748 (1972).

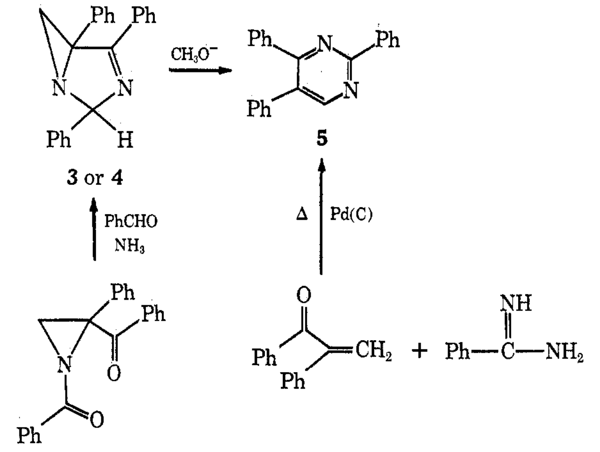
yield for cycloadduct formation as a function of the concentration of added dipolarophile.[6] According to this mechanistic scheme, it should be possible to generate a nitrile ylide from one arylazirine and intercept it with the C–N double bond of another azirine molecule. The present paper describes a reaction of this type which provides additional support for the mechanism of dimerization. To learn more about the effect of substituents in the azirine system, we also chose to study the photodimerization of methyl- and dimethylphenylazirine. An additional objective of this study was to examine the photobehavior of arylazirines with dipolarophiles other than electron-deficient olefins, and we herein report on such reactions. This process provides a synthetic route into systems otherwise difficult to prepare.

Coirradiation of Phenyl- and Diphenylazirine.—Further evidence for the mechanism of the photodimerization of arylazirines was derived by irradiating an equimolar mixture of 2-phenyl- and 2,3-diphenylazirine (1 and 2). At 3130 Å, the extinction coefficient for diphenylazirine is about 20 times that of phenylazirine, so that *ca.* 95% of the light is absorbed by diphenylazirine in the above experiment. Under these conditions a mixture of two 1:1 adducts was isolated. These were separated by liquid–liquid partition chromatography and identified as *endo*- and *exo*-2,4,5-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (3 and 4) on the basis of the evidence presented below.



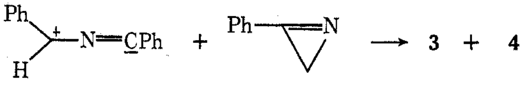
1 **2** **3** **4**

The component of shortest retention time, 3 (20% of the 1:1 adducts), mp 176–177°, had the following nmr spectrum ($CDCl_3$, 100 MHz): aromatic protons at τ 2.70 (15 H, m) and singlets at 8.26 (1 H), 7.42 (1 H), and 3.32 (1 H). The second component (4, 20%), mp 85–87°, displayed an nmr spectrum (100 MHz) consisting of singlets at τ 7.98 (1 H), 6.92 (1 H), and 4.06 (1 H), and a multiplet centered at 2.75 (15 H). Upon treatment with sodium methoxide in methanol, 3 (and/or 4) afforded 2,4,5-triphenylpyrimidine (5), mp 110–111°.[8] Compound 5 was prepared independently by the reaction of α-phenylacrylophenone with benzamidine followed by oxidation over palladium on charcoal. The above structural assignments were further confirmed by an independent synthesis of 3 and 4 from 1,2-dibenzoyl-2-phenylaziridine (6), benzaldehyde, and ammonia. The formation of 3 and 4 can be most economically rationalized in terms of 1,3-dipolar addition of the initially generated nitrile ylide onto phenylazirine.



3 or 4 **5** **6**

On further irradiation (in cyclohexane), 3 and 4 are converted to triphenylpyrimidine (5) in low yield. When the irradiation of 3 (or 4) was carried out in methanol, two new compounds were formed in addition to 5 (5%). These structures have been assigned as *N*-methoxymethyl-2,4,5-triphenyl-2,3-dihydroimidazole (7) and *N*-methoxymethyl-2,4,5-triphenylimidazole (8). Treatment of 8 with aqueous acid afforded triphenylimidazole. The formation of 7 and 8 can be attributed to the addition of methanol to the azomethine ylide[9,10] formed on irradiation of 3 (or 4).



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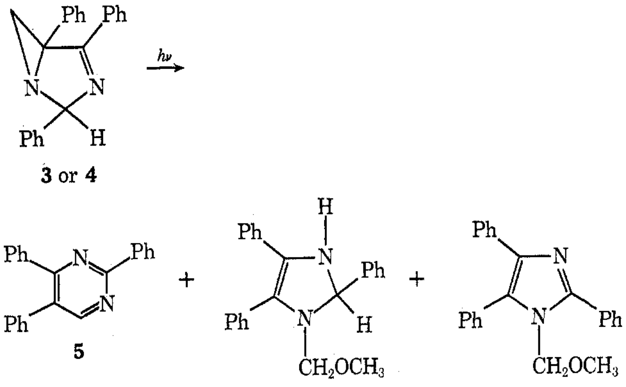

3 or 4 **5** **7** **8**

Photodimerization Reactions of Methyl- and Dimethylphenylazirines.—As part of a study of the effect of substituents on the photoreactions of arylazirines, we have examined the photochemistry of 3-methyl-(9) and 3,3-dimethyl-2-phenylazirine (10). When 3-methyl-2-phenylazirine (9) was irradiated in cyclohexane, a 3:1 mixture of diazabicyclohexenes 11 and 12 was obtained in 45% yield. The structure of the dimers rests firmly on spectroscopic and chemical evidence. Thus, these substances were shown by their elemental analyses and mass spectra to be dimeric. The nmr spectrum of the major dimer 11 ($CDCl_3$) showed two

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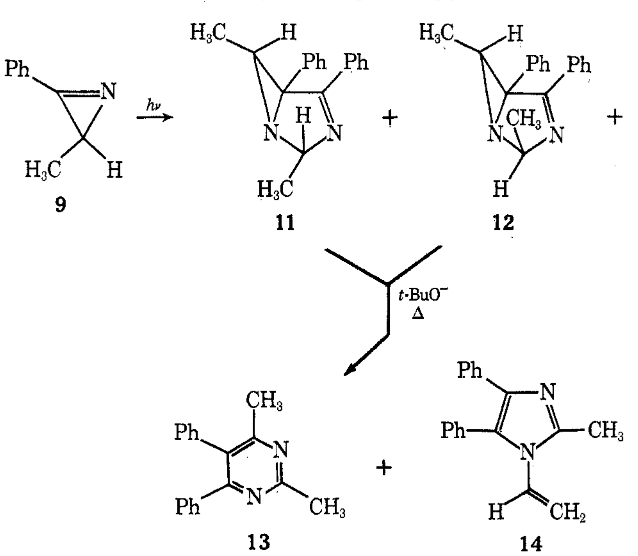
[8] H. Heine, R. Weese, R. Cooper, and A. Durbetaki, *J. Org. Chem.*, **32**, 2708 (1967). These authors were the first to report the base-catalyzed oxidative rearrangement of 1,3-diazabicyclo[3.1.0]hex-3-enes to substituted pyrimidines.

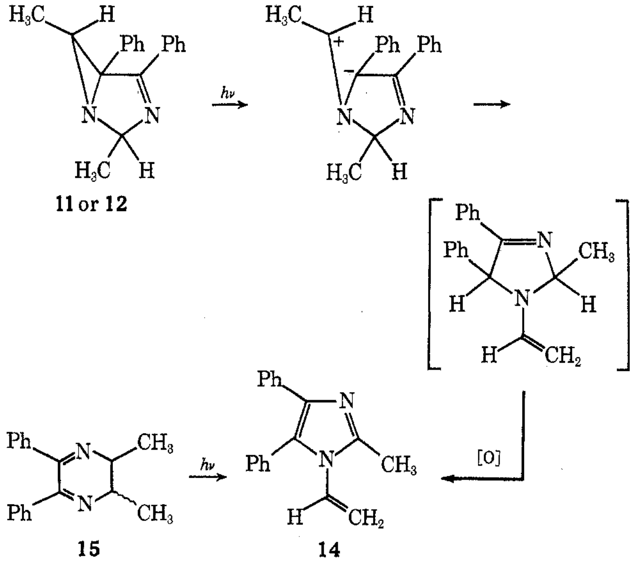
[9] A. Padwa and E. Glazer, *Chem. Commun.*, 838 (1971); A. Padwa and E. Glazer, *J. Amer. Chem. Soc.*, **94**, 7788 (1972).

[10] T. DoMinh and A. M. Trozzolo, *ibid.*, **94**, 4046 (1972); **92**, 6997 (1970).

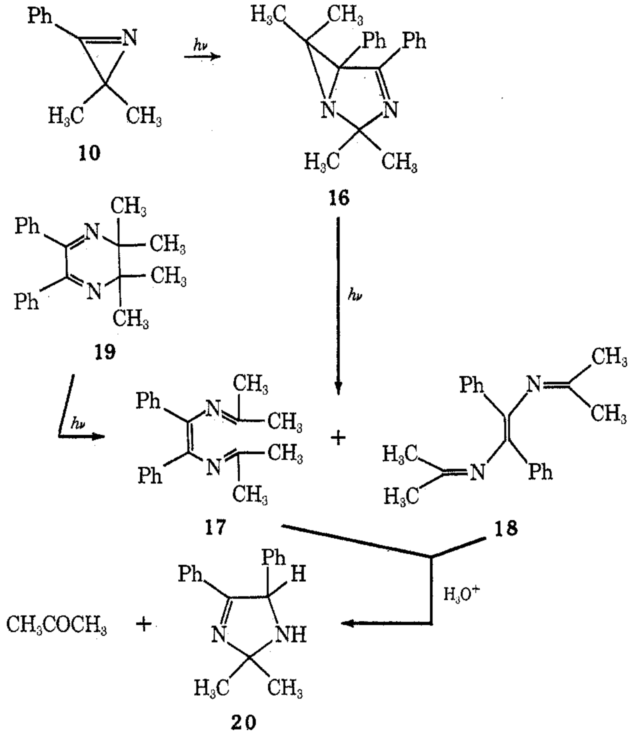
methyl doublets at τ 8.72 (J = 5.0 Hz) and 8.40 (J = 6.5 Hz), two single hydrogen quartets at 8.03 (J = 5.0 Hz) and 5.02 (J = 6.5 Hz), and a multiplet centered at 2.60 (10 H). The minor isomer **12** showed methyl doublets at τ 8.73 (J = 6.0 Hz) and 8.45 (J = 6.0 Hz), single hydrogen quartets at 7.86 (J = 6.0 Hz) and 4.34 (J = 6.0 Hz), and a multiplet centered at 2.60 (10 H). Chemical confirmation of these structures was obtained by treating **11** (and/or **12**) with potassium *tert*-butoxide in refluxing toluene to give 2,4-dimethyl-5,6-diphenylpyrimidine (**13**) (85%), mp 105–106°.

In addition to dimers **11** and **12**, pyrimidine **13** (8%) and *N*-vinyl-3-methyl-4,5-diphenylimidazole (**14**) (12%), mp 83–84°, nmr ($CDCl_3$) τ 7.46 (3 H, s), 5.04 (1 H, d, J = 16.0 Hz), 5.01 (1 H, d, J = 10 Hz), 3.51 (1 H, dd, J = 16 and 10 Hz), 2.56–3.00 (10 H, m), were also isolated from the irradiation of **9**. Imidazole **14** was independently synthesized by irradiating 2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazine (**15**) in cyclohexane according to the procedure of Beak and Miesel.[11] These workers have shown that 2,3-dihydropyrazines rearrange to imidazoles upon photolysis. Suspicion that compounds **13** and **14** are secondary photoproducts was confirmed by the finding that the photolysis of **11** (and/or **12**) in cyclohexane afforded pyrimidine **13** and imidazole **14**. The photoconversion of **11** (or **12**) into **14** may be formulated as proceeding *via* an azomethine ylide, formed by cleavage of the aziridine C–C bond. Proton transfer followed by oxidation of the transient *N*-vinylimidazoline readily accounts for the formation of **14**. The isolation of pyrimidine **13** from the photolysis of **11** (or **12**) can be attributed to cleavage of the aziridine C–N bond followed by loss of hydrogen.





To determine the influence of two methyl substituents on the photodimerization reaction, the photochemistry of 3,3-dimethyl-2-phenylazirine (**10**) was examined. It was felt that, by blocking the remaining position of the azirine ring, the expected diazabicyclic dimer would not be capable of imidazole or pyrimidine formation by the prescribed pathway. Either increased photochemical stability or formation of other valence tautomers[11,12] of the dimer might be expected. Irradiation of **10** for 6 hr in pentane using 2537-Å light gave a complex mixture of photoproducts. By carrying out the irradiation for short periods of time (2 hr), 4,5-diphenyl-2,2,6,6-tetramethyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**16**), mp 71–72°, was obtained in good yield (45%). Irradiation of **10** for 3.5 hr gave **16** as well as two new substances (**17** and **18**). The same two compounds were also obtained from the irradiation of **16** or from the irradiation of 2,3-diphenyl-5,5,6,6-tetramethyldihydropyrazine (**19**). These new photoproducts were separated by fractional crystallization and were identified as *cis*- (**17**) and *trans*-2,7-dimethyl-4,5-diphenyl-3,6-diazaocta-2,4,6-triene (**18**). Both isomers were transformed into 2,2-dimethyl-4,5-diphenyl-3-imidazoline (**20**) and acetone when treated with methanol containing a trace of acid. This observation provides substantial support for the mechanism of imidazoline formation from the irradia-



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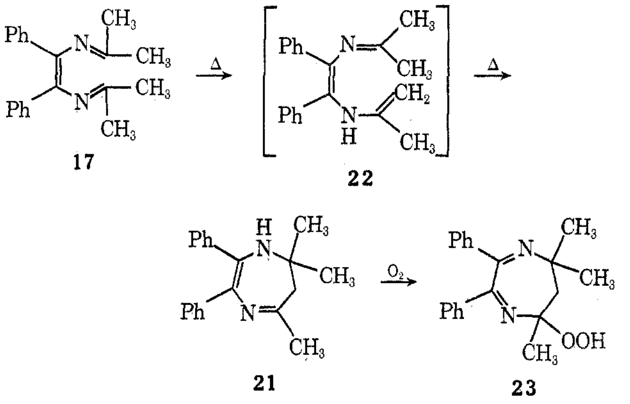
[11] P. Beak and J. L. Miesel, *J. Amer. Chem. Soc.*, **89**, 2375 (1967).

[12] D. R. Arnold, V. Y. Abraitys, and D. McLeod, Jr., *Can. J. Chem.*, **49**, 923 (1971).

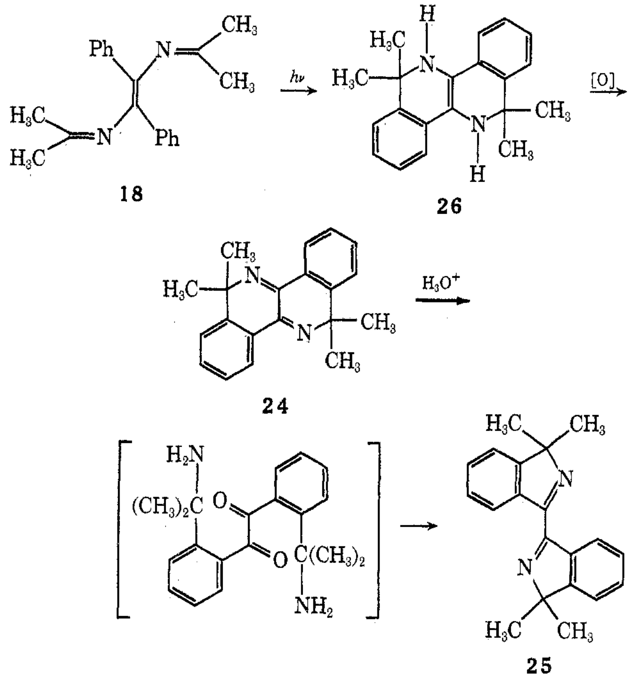
tion of dihydropyrazines as suggested by Beak and Miesel.[11]

When *cis*-enediimine **17** was allowed to stand in the dark at room temperature in a degassed chloroform solution, it was smoothly converted into 2,3-diphenyl-5,7,7-trimethyl-1,4-diazacyclohepta-2,4-diene (**21**) (90%), mp 117–119°. This compound was easily characterized by its nmr spectrum, which showed singlets at τ 9.54 (6 H), 7.70 (3 H), 7.48 (2 H), and 7.30 (1 H, NH). The latter three singlets disappeared within 30 min at 80° on D_2O exchange. The formation of product **21** from *cis*-enediimine **17** can be interpreted in terms of a 1,3-hydrogen shift to give **22** as a transient intermediate which could then lead to **21** by enamine addition across the double bond. Although nmr studies have failed to give evidence for the presence of **22**, it is not unreasonable to suppose that this species is present in such small amounts that it cannot be detected spectroscopically. The passage of **17** to **22** is undoubtedly assisted by the driving force arising from relief of methyl group crowding.



On standing for an additional period of time in an aerated chloroform solution at 25°, **21** underwent smooth conversion to hydroperoxide **23**, mp 142–143°, nmr (pyridine) τ 8.60 (3 H, s), 8.39 (3 H, s), 8.30 (3 H, s), 7.34 (1 H, d, J = 15.0 Hz), and 6.78 (1 H, d, J = 15.0 Hz). This structure was supported by the observation that **23** liberated iodine from an acidified potassium iodide solution. The formation of hydroperoxides from the reaction of enamines and certain Schiff bases with molecular oxygen has been reported in the literature[13-16] and provides good chemical analogy for the above transformation.

Irradiation of dimethylphenylazirine **10** for 5 hr gave a mixture of **16**, **17**, **18**, and a new photoproduct, **24**. Compound **24** was shown to be a secondary photoproduct derived from enediimine **18**. Its structure is assigned as 6,12-dihydro-6,6,12,12-tetramethyl-5,11-diazachrysene (**24**), mp 189–190°, nmr ($CDCl_3$) τ 8.36 (12 H, s) and 1.5–2.6 (8 H, m). Diazachrysene **24** was transformed into isoindole **25**, mp 203–204°, on treatment with aqueous acid. The formation of **24** from **18** is analogous to the photocyclization of stilbenes to phenanthrenes.[17] We have, in fact, been able to detect the presence of **26** as a transient intermediate in the reaction mixture. This material is subsequently oxidized to **24** on work-up.



The above results indicate that the photodimerization of arylazirines to 1,3-diazabicyclo[3.1.0]hex-3-enes is a general reaction which is independent of the nature of the substituent groups attached to the C atom of the azirine ring.[18] The primary photoproducts have been found to undergo subsequent reaction on further irradiation. Our results indicate that the secondary photoproducts formed from the irradiation of the diazabicyclohexenes depend on the substituent groups, the time of irradiation, and the particular solvent employed.

Cycloaddition of Arylazirines with Hetero Multiple Double Bonds.—As was pointed out earlier, photochemically generated nitrile ylides can be trapped with electron-deficient carbon–carbon multiple bonds and, in their absence, with the carbon–nitrogen double bond of unreacted azirine. We felt that the photoaddition of arylazirines would not be restricted to just electron-deficient double bonds, but would also occur with other dipolarophiles. Huisgen has recently demonstrated that nitrile ylides, generated by ground-state reactions, undergo cycloaddition with a wide variety of hetero-multiple bonds.[20] The results outlined below demonstrate that the photoaddition of azirines proceeds with a number of dipolarophiles and provides a convenient route for the synthesis of a variety of five-membered heterocyclic rings.[21]

Irradiation of 2,3-diphenylazirine (**2**) in benzene with an internal water-cooled mercury arc lamp in the presence of an equimolar amount of methyl dithiobenzoate[22] produced a mixture of two Δ^2-thiazolines,

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[13] C. L. Stevens and R. J. Gasser, *J. Amer. Chem. Soc.*, **79**, 6057 (1957).

[14] B. Witkop and J. B. Patrick, *ibid.*, **75**, 4476 (1953).

[15] B. Witkop and H. M. Kissman, *ibid.*, **75**, 1975 (1953).

[16] R. Criegee and G. Lohans, *Chem. Ber.*, **84**, 219 (1951).

[17] For a review, see F. R. Stermitz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 247.

[18] Similar results have been observed by Schmid and coworkers.[7,19]

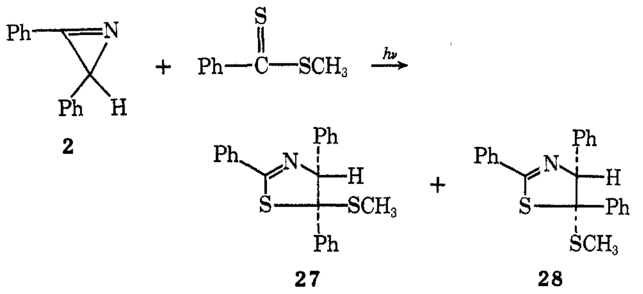
[19] B. Jackson, N. Gakis, M. Marky, H. J. Hansen, W. von Philipsborn, and H. Schmid, *Helv. Chim. Acta*, **55**, 916 (1972).

[20] R. Huisgen, H. Stangl, H. J. Sturm, R. Raab, and K. Bunge, *Chem. Ber.*, **105**, 1258 (1972); K. Bunge, R. Huisgen, R. Raab, and H. Stangl, *ibid.*, **105**, 1279 (1972); K. Bunge, R. Huisgen, R. Raab, and H. J. Sturm, *ibid.*, **105**, 1307 (1972); R. Huisgen, R. Sustmann, and K. Bunge, *ibid.*, **105**, 1324 (1972).

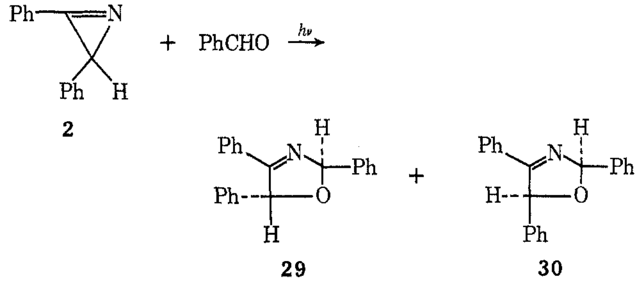
[21] Similar results have recently been reported by B. Jackson, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 919 (1972).

[22] E. J. Hedgley and H. G. Fletcher, *J. Org. Chem.*, **30**, 1282 (1965).

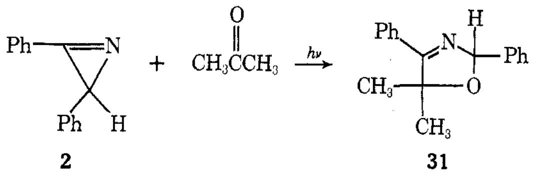
27 (mp 116–117°) and **28** (mp 125–126°). Nmr analysis of the crude photolysate indicated that **28** was the major adduct (**28**:**27** = 1.5:1.0) by comparison of the methyl singlets at τ 7.86 (**27**) and 8.10 (**28**).



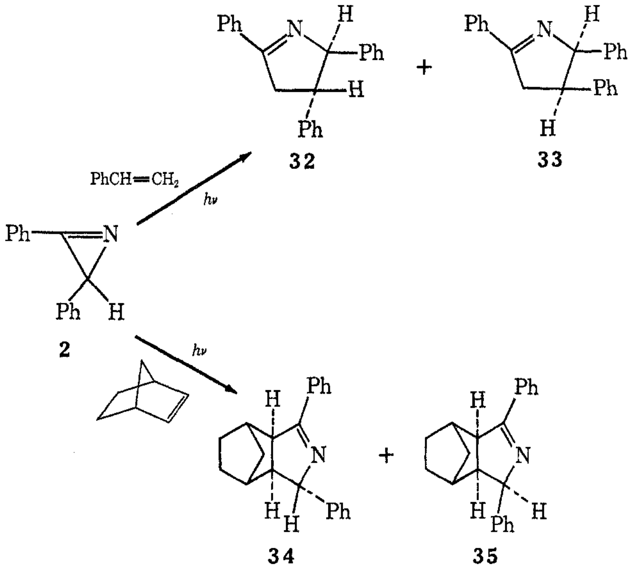
Similar irradiation of a solution of **2** in benzene which contained an excess of benzaldehyde proceeded to give two Δ^3-oxazolines **29** (mp 107–108°) and **30** (mp 30–31°). The ratio of the two cycloadducts (**29**:**30** = 1:2) was determined by nmr analysis of the doublets associated with proton H_5 [τ 3.72 (**29**) and 3.87 (**30**)] in the crude photolysate. Very recently Schmid and coworkers have also reported that arylazirines undergo photochemical cycloaddition with aldehydes to give Δ^3-oxazolines.[23]



The photocycloaddition of diphenylazirine with acetone was not as facile as that encountered with benzaldehyde. When a benzene solution of diphenylazirine was irradiated with a moderate excess of acetone (3 *M*), no photoadduct was obtained; instead tetraphenylpyrazine was produced on extended irradiation.[6] However, when a large excess of acetone was used, a single cycloadduct was isolated in moderate yield. On the basis of its spectral data this material is assigned as 2,4-diphenyl-5,5-dimethyl-Δ^3-oxazoline (**31**). The low-field position of proton H_2 (τ 3.43) supports this orientation of addition.[20]



Photolysis of a solution of **2** and excess styrene gave Δ^1-pyrrolines **32** and **33**. Comparison of the signals of proton H_5, which appeared at τ 4.42 (**33**) and 4.71 (**32**), indicated that **32** was the major component of the mixture (**32**:**33** = 1.5:1.0). The less reactive dipolarophile norbornene also formed a mixture of two adducts with diphenylazirine. Irradiation of a solution of diphenylazirine with norbornene gave a 1:1 mixture of tricyclic Δ^1-pyrrolines **34** and **35**. The nmr spectra of **34** and **35** were essentially identical with those of the adducts obtained from the reaction of *N*-(*p*-nitrobenzyl)benzimidoyl chloride with triethylamine and norbornene.[20]



Experimental Section[24]

Coirradiation of 2-Phenylazirine with 2,3-Diphenylazirine at 3130 Å.—A series of eight Pyrex test tubes, each containing 100 mg of 2,3-diphenylazirine and 70 mg of 2-phenylazirine in 45 ml of benzene, was irradiated with a 450-W Hanovia lamp. The light was filtered by circulation of a solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate in 100 ml of water through the inner jacket.[25] This solution permitted the following wavelength distribution to pass through: 6% 2967 Å, 20% 3025 Å, 62% 3130 Å, 10% 3340 Å. After 14 hr, the tubes were combined and the solvent was removed under reduced pressure. The crude oil was subjected to scanning liquid–liquid partition chromatography. The first peak in the chromatogram (23 mg) was identified as tetraphenylpyrazine. The second fraction contained 224 mg (20%) of *endo*-2,4,5-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**3**): mp 176–177°; ir (KBr) 6.19, 6.35, 6.70, 9.30, 13.25, 14.45 μ; uv (95% ethanol) 247 nm (ε 11,400); nmr ($CDCl_3$, 100 MHz) τ 8.26 (1 H, s), 7.42 (1 H, s), 3.32 (1 H, s), and 2.20–2.76 (15 H, m); *m/e* 310 (M^+), 206, 193, 179, 166, 104 (base), 103, 91, 89, and 77.

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 84.82; H, 5.81; N, 9.06.

The third fraction contained 297 mg (20%) of a clear yellow oil which was purified by preparative thick layer chromatography to give *exo*-2,4,5-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**4**) as a white, crystalline solid: mp 85–87°; ir (KBr) 6.28, 6.38, 6.70, 6.92, and 7.20 μ; uv (95% ethanol) 248 nm (ε 15,200); nmr ($CDCl_3$, 100 MHz) τ 7.98 (1 H, s), 6.92 (1 H, s), 4.06 (1 H, s), and 2.2–2.8 (15 H, m); *m/e* 310 (M^+), 206, 193, 179, 165, 104, 103, 91, 89, and 77.

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 84.54; H, 5.88; N, 9.07.

Treatment of *endo*- and *exo*-2,4,5-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene with Sodium Methoxide.—Confirmation of the structures of diazabicyclohexenes **3** and **4** was obtained by their base-catalyzed rearrangement of 2,4,5-triphenylpyrimidine (**5**).

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(23) H. Giezendanner, M. Marky, B. Jackson, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 745 (1972).

(24) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with a Varian Associates high-resolution spectrometer and at 100 MHz using a Jeol-MH-100 spectrometer.

(25) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

A solution of 75 mg of *endo*- (or *exo*-) bicyclohexene (**3** or **4**) in 10 ml of a freshly prepared 0.13 *N* sodium methoxide-methanol solution was heated at reflux for 10 hr. Removal of the solvent gave a yellow solid, which was thoroughly washed with water. This solid was identified as 3,6-dihydro-2,4,5-triphenylpyrimidine, mp 89–98°, nmr ($CDCl_3$) τ 5.44 (2 H, s), 5.12 (1 H, broad s), 2.20–3.00 (15 H, m).

A mixture of the above dihydropyrimidine and 5% palladium on charcoal in benzene was heated at reflux for 1 hr. The catalyst was separated by filtration and the solvent was removed *in vacuo* to give 2,4,5-triphenylpyrimidine (**5**) (60 mg, 80%) as a crystalline solid: mp 110–111°; ir (KBr) 6.45, 6.60, 7.10, 7.32, 8.55, 9.35, 9.80, 14.45 μ; nmr ($CDCl_3$) τ 2.40–3.00 (15 H, m), 1.34 (1 H, s); uv (95% ethanol) 263 nm (ϵ 30,400); *m/e* 308 (M^+, base), 102, and 77.

Anal. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.09. Found: C, 85.42; H, 5.36; N, 8.88.

Pyrimidine **5** was further confirmed by an independent synthesis. A mixture of 5.0 g of α-phenylacrylophenone[26] and 2.63 g of benzamidine hydrochloride in 50 ml of 95% ethanol was stirred at room temperature. To the above mixture was added a solution containing 1.34 g of potassium hydroxide in 50 ml of 95% ethanol. The resulting solution was heated at reflux for 1.5 hr. The yellow solid which remained was oxidized by heating in benzene in the presence of palladium on charcoal. Removal of the catalyst followed by concentration of the solvent gave white crystals (90%), mp 110–111°. The infrared spectrum of this material was identical in all respects with that of a sample of **5** obtained from the base-catalyzed rearrangement of **3** (or **4**). A mixture melting point was undepressed at 110–111°.

Synthesis of *exo*- and *endo*-2,4,5-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene.—The structure of the mixed photodimer **3** or **4** was further confirmed by an unequivocal synthesis. A solution containing 5.0 g of 1,2-dibenzoyl-2-phenylaziridine[5] (**6**), 0.8 g of ammonium bromide, and 15 ml of benzaldehyde in 100 ml of ethanol was saturated with ammonia. The solution was allowed to stand at room temperature for 6 days, at which time a crystalline precipitate had formed. Fractional crystallization of the crude solid gave *endo*- (**3**) and *exo*-2,4,5-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**4**). The infrared and nmr spectra of both compounds prepared in this fashion were identical in all respects with those of the materials isolated from the coirradiation of mono- and diphenylazirines.

Irradiation of 2,4,5-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene.—A solution containing 700 mg of diazabicyclohexene **3** (or **4**) in 500 ml of absolute methanol was irradiated under a nitrogen atmosphere through a Corex filter for 8 hr. The solvent was removed under reduced pressure and the residual oil was subjected to liquid–liquid partition chromatography. The first peak in the chromatogram was identified as 2,4,5-triphenylpyrimidine (**5**) (15%). The second fraction was a white, crystalline solid, mp 148–149°, whose structure is assigned as *N*-methoxymethyl-2,4,5-triphenyl-2,3-dihydroimidazole (**7**) (9%) on the basis of the following data: ir (KBr) 6.19, 6.89, 7.20, 7.30, 9.24, 10.31, 10.80, 12.05, 12.98, 13.22, 13.79, 13.95, 14.40 μ; nmr ($CDCl_3$, 100 MHz) τ 6.68 (3 H, s), 4.44 (2 H, s), 2.81 (1 H, s), and 1.2–2.6 (15 H, m). The third component in the reaction mixture was identified as *N*-methoxymethyl-2,4,5-triphenylimidazole (**8**) (19%): mp 112–113°; ir (KBr) 6.45, 6.60, 7.10, 8.55, 9.74, 12.08, 13.09, 13.35, 13.80 μ; nmr ($CDCl_3$) τ 6.44 (3 H, s), 4.64 (2 H, s), and 2.0–3.0 (15 H, m). Treatment of imidazole **8** with mild acid or by chromatographing over silica gel gave 2,4,5-triphenylimidazole, thereby providing additional support for the above structural assignments.

Photodimerization of 3-Methyl-2-phenylazirine (9).—A solution containing 2.0 g of methylphenylazirine (**9**) in 500 ml of cyclohexane was irradiated with a 550-W Hanovia lamp using a Pyrex filter for 11 hr. The solvent was removed under reduced pressure, giving a crude oil containing two significant components. The mixture was separated by thick layer chromatography. The major component amounted to 600 mg (30%) of a crystalline solid, mp 95–96°, whose structure is assigned as *exo*-2,6-dimethyl-4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**11**) on the basis of the following data: ir (KBr) 3.40, 6.26, 6.94, 7.58, 7.70, 9.19, 9.32, 9.84, 12.84, 13.12, and 14.40 μ; uv (cyclohexane) 230 nm (ϵ 12,300); nmr ($CDCl_3$, 100 MHz) τ 8.72 (3 H, d, J = 5.0 Hz), 8.40 (3 H, d, J = 6.5 Hz), 8.03 (1 H, q, J = 5.0 Hz), 5.02 (1 H, q, J = 6.5 Hz), 2.30–2.90 (10 H, m); *m/e* 262 (M^+), 104 (base), and 77.

Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.40; H, 6.92; N, 10.68. Found: C, 82.21; H, 6.88; N, 10.62.

The minor component (10%) present in the reaction mixture was contaminated with the major dimer (**11**) and all attempts to crystallize this material failed. The structure of this component is assigned as *endo*-2,6-dimethyl-4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**12**) on the basis of its nmr spectrum and chemical behavior: nmr ($CDCl_3$, 100 MHz) τ 8.73 (3 H, d, J = 6.0 Hz), 8.45 (3 H, d, J = 6.0 Hz), 7.86 (1 H, q, J = 6 Hz), 4.34 (1 H, q, J = 6 Hz), 2.30–2.90 (10 H, m).

Base-Catalyzed Isomerization of 2,6-Dimethyl-4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene.—Chemical confirmation of the structures of **11** and **12** was obtained by their base-catalyzed rearrangement to 2,4-dimethyl-5,6-diphenylpyrimidine (**13**). A mixture of 80 mg of **11** (and/or **12**) and 200 mg of potassium *tert*-butoxide was heated at reflux in a 5:1 mixture of toluene and xylene for 3.5 hr. The reaction mixture was washed with water and taken up in ether. The ethereal solution was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crystalline solid that formed (68 mg, 85%), mp 105–106°, was assigned the structure of 2,4-dimethyl-5,6-diphenylpyrimidine (**13**): ir (KBr) 6.59, 7.14, 8.50, 9.94, 11.69, 13.18, 14.31 μ; uv (cyclohexane) 273 nm (ϵ 10,300) and 225 (18,700); nmr ($CDCl_3$, 100 MHz) τ 7.65 (3 H, s), 7.23 (3 H, s), 2.60–3.10 (10 H, m); *m/e* 260 (M^+).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 83.05; H, 6.17; N, 10.72.

Irradiation of 2,6-Dimethyl-4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene.—A solution containing 518 mg of diazabicyclohexene **11** (or **12**) in 125 ml of cyclohexane was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Pyrex filter for 4.5 hr. Concentration of the solution *in vacuo* left a crude mixture of compounds which was separated by thick layer chromatography. One of the many components present was identified as 2,4-dimethyl-5,6-diphenylpyrimidine (**13**) (8%). Another band contained 18 mg (3%) of a crystalline solid, mp 83–84°, whose structure is assigned as *N*-vinyl-4,5-diphenyl-3-methylimidazole (**14**) on the basis of the following data: ir (KBr) 6.05, 7.15, 10.21, 10.87, 12.85, 13.14, 14.40 μ; nmr ($CDCl_3$, 100 MHz) τ 7.46 (3 H, s), 5.04 (1 H, d, J = 16 Hz), 5.01 (1 H, d, J = 10 Hz), 3.51 (1 H, dd, J = 16 and 10 Hz), 2.56–3.0 (10 H, m); *m/e* 260 (M^+).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 82.85; H, 6.36; N, 10.76.

Structure **14** was further confirmed by an independent synthesis. A solution containing 460 mg of 2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazine (**15**)[11] in 125 ml of cyclohexane was irradiated with a 450-W lamp equipped with a Pyrex filter for 1 hr. Concentration of the solution *in vacuo* left a pale yellow oil, which was subjected to thick layer chromatography. One of the bands of the thick layer plate was identified as *N*-vinyl-4,5-diphenyl-3-methylimidazole (**14**) (19%). The infrared and nmr spectra of this compound were identical in every detail with those of a sample of **14** obtained from the irradiation of **11**.

When the irradiation of diazabicyclohexene **11** was carried out in absolute ethanol, the only products identified were pyrimidine **13** and 4,5-diphenyl-1-(1-ethoxyethyl)-2-methylimidazole.[11] Under these conditions there was no detectable signs of vinylimidazole **14**.

Photodimerization of 3,3-Dimethyl-2-phenylazirine (10).—A solution containing 2.2 g of dimethylphenylazirine **10** in 20 ml of pentane was irradiated at 2537 Å using a Rayonet "merry-go-round" apparatus for 160 min. Thick layer chromatography of the residue gave 700 mg (45% based on reacted starting material) of a crystalline dimer, mp 71–72°, whose structure is assigned as 4,5-diphenyl-2,2,6,6-tetramethyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**16**) on the basis of the following data: ir (KBr) 6.24, 6.92, 7.40, 8.22, 13.16, 14.42 μ; uv (cyclohexane) 232 nm (ϵ 13,400); nmr ($CDCl_3$, 100 MHz) τ 8.78 (3 H, s), 8.55 (3 H, s), 8.41 (3 H, s), 8.32 (3 H, s), 2.4–2.9 (10 H, m); *m/e* 290 (M^+).

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.59; H, 7.60; N, 9.63.

Irradiation of 4,5-Diphenyl-2,2,6,6-tetramethyl-1,3-diazabicyclo[3.1.0]hex-3-ene (16).—A solution of 50 mg of diazabicyclohexene **16** in 1 ml of pentane was irradiated at 2537 Å for 105 min. An nmr spectrum of the crude reaction mixture in benzene indicated the presence of two major components. The same two components could also be obtained from an extended irradiation

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[26] L. Mehr, E. J. Becker, and P. E. Spoerri, *J. Amer. Chem. Soc.*, **77**, 984 (1955).

of dimethylphenylazirine. The minor component of the mixture (40%) was isolated by thick layer chromatography using ethyl acetate as the eluent and was assigned the structure of *trans*-2,7-dimethyl-4,5-diphenyl-3,6-diazaocta-2,4,6-triene (**18**), mp 165–166°, on the basis of the following data: ir (KBr) 6.04, 6.74, 6.95, 7.35, 8.14, 12.93, 14.30 μ; uv (cyclohexane) 320 nm (ϵ 11,300) and 230 (12,000); nmr ($CDCl_3$, 100 MHz) τ 8.38 (6 H, s), 8.06 (6 H, s), 2.4–2.8 (10 H, m); *m/e* 290 (M^+).

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64, N, 9.65. Found: C, 82.48; H, 7.68; N, 9.65.

Chemical confirmation of this structure was obtained from some acid hydrolysis experiments. A solution containing 44 mg of **18** in 5 ml of 50% aqueous hydrochloric acid was refluxed for 24 hr. The aqueous system was extracted with chloroform, washed with water, and dried over magnesium sulfate. Removal of the solvent gave a white solid, mp 91–93°, whose structure was identified as benzil by comparison with an authentic sample.

A solution of 30 mg of enediimine **18** in 4 ml of methanol containing 1 drop of dilute hydrochloric acid was allowed to stand at room temperature for several hours. The reaction mixture was made basic with 10% sodium hydroxide and extracted with 10 ml of ether. The ether was dried over magnesium sulfate and the solvent was evaporated under reduced pressure to give a single compound whose structure was shown to be 2,2-dimethyl-4,5-diphenyl-3-imidazoline (**20**):[11] ir (KBr) 6.00, 6.20, 6.40, 6.75, 6.98 μ; nmr ($CDCl_3$) τ 8.52 (3 H, s), 8.39 (3 H, s), 7.44 (1 H, broad s), 4.52 (1 H, s), 2.3–2.8 (10 H, m). Upon standing in the open for several days, imidazoline **20** was quantitatively oxidized to 2,2-dimethyl-4,5-diphenylisoimidazole, mp 75–77° (lit. mp 76–78°).[27]

When the irradiation of diazabicyclohexene **16** was carried out in methanol, a nearly quantitative yield of 2,2-dimethyl-4,5-diphenyl-3-imidazoline (**20**) was obtained.

cis-**2,7-Dimethyl-4,5-diphenyl-3,6-diazaocta-2,4,6-triene (17).**—The major component (50%) formed from the photolysis of diazabicyclohexene **16** was separated from *trans*-enediimine **18** by fractional crystallization from anhydrous ether, mp 82–95°. An nmr spectrum of the purest crop obtained revealed the presence of **18** as a persistent impurity (*ca.* 8%). The structure of the major product is assigned as *cis*-2,7-dimethyl-4,5-diphenyl-3,6-diazaocta-2,4,6-triene (**17**) on the basis of the following data: ir (KBr) 6.05, 6.70, 6.93, 7.33, 8.05, 9.28, 11.25, 12.85, 14.30 μ; uv (cyclohexane) 228 nm (ϵ 15,400) and 312 (10,700); nmr ($CDCl_3$, 100 MHz) τ 8.04 (6 H, s), 8.17 (6 H, s), 2.5–3.9 (10 H, m); *m/e* 290 (M^+), 275, 235 (base), 194, 165, and 104.

cis-Enediimine **17** was rapidly converted to an isomeric compound when it was allowed to stand in deuteriochloroform at room temperature for 50 min. This same compound could also be obtained quantitatively when **17** was heated in benzene at 65° for 45 min. The structure of this compound is assigned as 2,3-diphenyl-5,7,7-trimethyl-1,4-diazacyclohepta-2,4-diene (**21**): mp 114–119°; ir (KBr) 2.98, 3.40, 6.10, 6.25, 6.70, 6.92, 9.32, 10.68, 13.12, 14.30 μ; uv (cyclohexane) 252 nm (ϵ 7700) and 357 (6400); *m/e* 290 (M^+), 288, 275, 234, 194, 172, 165, 105, 104, 77; nmr ($CDCl_3$) τ 8.54 (6 H, s), 7.70 (3 H, s), 7.48 (2 H, s), 7.30 (1 H, broad s), 2.3–3.0 (10 H, m). When **21** was treated with deuterium oxide (containing a catalytic amount of hydroxide ion) at 80° for 0.5 hr, the singlets at τ 7.48, 7.70, and 7.30 were washed out. Replacing the deuterium oxide with water and heating for 4 hr caused the return of these peaks.

When diazacycloheptadiene **21** was allowed to stand in chloroform in an open atmosphere, it was gradually converted into still another new compound. This same material could be prepared in quantitative yield by bubbling oxygen through a chloroform solution of **21**. The white crystalline solid obtained, mp 142–143°, was assigned the structure of 2,3-diphenyl-5-hydroperoxy-5,7,7-trimethyl-1,4-diazacyclohepta-1,3-diene (**23**) on the basis of the following data: ir (KBr) 3.21, 3.45, 6.13, 6.20, 6.91, 8.42, 8.91 μ; uv (methanol) 228 nm (ϵ 12,700) and 259 (8100); *m/e* 288, 287, 162, 122, 105, 103, and 77; partial nmr (100 MHz, pyridine) τ 8.60 (3 H, s), 8.39, (3 H, s), 8.30 (3 H, s), 7.34 (1 H, d, J = 15 Hz), 6.78 (1 H, d, J = 15 Hz).

Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.11; H, 6.85; N, 8.55.

Further support for the structure of hydroperoxide **23** was obtained by the observation that **23** liberated iodine from an acidified methanol solution containing potassium iodide.

The structure of *cis*-enediimine **17** was further verified by the acid-catalyzed hydrolysis of **17** to imidazoline **20** using the same procedure as was described above for *trans*-enediimine **18**. *cis*- and *trans*-enediimines **17** and **18** were also found to be interconverted photochemically.

Irradiation of 2,3-Diphenyl-5,5,6,6-tetramethyldihydropyrazine (19).—A solution of 50 mg of diphenyltetramethyldihydropyrazine **19** in 1.5 ml of pentane was irradiated in a quartz nmr tube with 2537-Å light for 1 hr. Removal of the solvent followed by immediate analysis by nmr ($CDCl_3$) indicated the presence of a mixture of *cis*- and *trans*-2,7-dimethyl-4,5-diphenyl-3,6-diazaocta-2,4,6-triene (**17** and **18**) (ratio 5:4). On standing in the nmr tubes, *cis*-enediimine **17** was converted into **21** and **23**.

Irradiation of *trans*-2,7-Dimethyl-4,5-diphenyl-3,6-diazaocta-2,4,6-triene (18).—A solution containing 226 mg of *trans*-enediimine **18** in 15 ml of absolute methanol was irradiated at 2537 Å for 12 hr. Analysis of the reaction mixture by glpc (5 ft × 0.25 in. column of 5% SE-30 on Chromosorb W) at 205° indicated a trace of 2,2-dimethyl-4,5-diphenylimidazole (3%) and a second photoproduct (53%) which was assigned as 6,12-dihydro-6,6,12,12-tetramethyl-5,11-diazachrysene (**24**). Compound **24** was obtained as a crystalline material, mp 189–190°, by crystallization of the reaction residue from acetone: ir (KBr) 6.27, 7.86, 8.55, 13.10 μ; uv (methanol) 225 nm (ϵ 30,200), 230 sh (29,000), 268 (22,900), 291 (15,700), 302 (14,800), and 365 (400); nmr ($CDCl_3$, 100 MHz) τ 8.33 (12 H, s), 2.40–2.68 (6 H, m), 1.50–1.64 (2 H, m); *m/e* 288 (M^+), 273 (base), and 258.

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99; N, 9.71. Found: C, 83.13; H, 7.03; N, 9.60.

Nmr analysis of the crude reaction mixture indicated that **24** was not a primary photochemical product but rather was derived by subsequent oxidation of a transient intermediate. This species presumably corresponds to 5,6,11,12-tetrahydro-6,6,12,12-tetramethyl-5,11-diazachrysene (**26**), nmr ($CDCl_3$, 100 MHz) τ 8.62 (12 H, s), 7.50 (2 H, broad s), 1.5–2.70 (8 H, m).

Acid-Catalyzed Rearrangement of 6,12-Dihydro-6,6,12,12-tetramethyl-5,11-diazachrysene (24).—To a 46-mg sample of **24** in 5 ml of methanol was added 2 ml of a 50% aqueous hydrochloric acid solution. The mixture was heated at reflux for 3 hr, made basic with 10% sodium hydroxide, and extracted with two 15-ml portions of ether. The extracts were washed twice with water, dried over magnesium sulfate, and concentrated to yield a crude solid. Recrystallization from acetone gave 25 mg (55%) of a white solid, mp 203–204°, which had the following spectral properties: ir (KBr) 6.26, 6.56, 6.88, 7.89, 8.18, 8.58, 10.72, 13.00, 13.67 μ; uv (cyclohexane) 223 nm (19,100), 259 (10,300), 287 sh (5300), and 293 (3700); nmr ($CDCl_3$, 100 MHz) τ 8.38 (12 H, s), 2.3–2.6 (6 H, m), 1.3–1.5 (2 H, m); *m/e* 288 (M^+), 273 (base), 258, and 129.

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99; N, 9.71. Found: C, 83.01; H, 6.91; N, 9.64.

On the basis of the above data this compound is assigned the structure of 3,3′-bis(1,1-dimethyl-1*H*-isoindole) (**25**).

Photoaddition of Methyl Dithiobenzoate with Diphenylazirine.—A solution of 0.3 g of diphenylazirine and 0.26 g of methyl dithiobenzoate in 150 ml of benzene was irradiated for 3 hr through a Pyrex filter sleeve. Analysis of the mixture by nmr showed that it contained two components (**27** and **28**, ratio 1:1.5). Chromatography of the residue on 27 g of silica gel using a 2:1 benzene–cyclohexane mixture gave 85 mg (18%) of *trans*-5-methylmercapto-2,4,5-triphenyl-Δ^2-thiazoline (**28**): mp 125–126°; ir (KBr) 6.25 μ (C=N); nmr τ 1.96–2.87 (m, 15 H), 4.28 (s, 1 H), and 8.10 (s, 1 H); *m/e* 313, 210, and 193. The second component isolated from the chromatography amounted to 65 mg (13%) of *cis*-5-methylmercapto-2,4,5-triphenyl-Δ^2-thiazoline (**27**): mp 116–117°; ir (KBr) 6.27 μ (C=N); nmr τ 1.95–3.20 (m, 15 H), 4.13 (s, 1 H), and 7.86 (s, 1 H); *m/e* 313, 210, and 193.

Photoaddition of Benzaldehyde with Diphenylazirine.—A solution of 0.3 g of diphenylazirine and 0.38 g of benzaldehyde in 150 ml of benzene was irradiated for 2 hr through a Pyrex filter. The crude residue showed the presence of two components by nmr analysis. The minor component (11%) was separated by liquid–liquid partition chromatography[28] and was assigned as *trans*-2,4,5-triphenyl-Δ^3-oxazoline (**29**): mp 107–108°; ir (KBr) 6.12 (C=N), 9.46, and 9.70 μ; nmr ($CDCl_3$) τ 2.17–2.82 (m 15 H), 3.02 (d, 1 H, J = 5.3 Hz), and 3.72 (d, 1 H, J = 5.3 Hz); uv (cyclohexane) 247 and 288 nm (ϵ 17,500 and 540). The

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major component (20%) from the irradiation was identified as *cis*-2,4,5-triphenyl-Δ^3-oxazoline (**30**): mp 30–31°; ir (neat film) 6.18 (C=N), 9.40, and 9.76 μ; nmr ($CDCl_3$) τ 2.22–2.87 (m, 15 H), 3.15 (d, 1 H, $J = 4.7$ Hz), and 3.87 (d, 1 H, $J = 4.7$ Hz).

Photoaddition of Acetone with Diphenylazirine.—A solution of 0.3 g of diphenylazirine in 150 ml of a 2:1 benzene–acetone mixture was irradiated for 1.5 hr under a nitrogen atmosphere using a 550-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left a dark oil which was purified by preparative thick layer chromatography using a 2:1 benzene–cyclohexane mixture. The major component isolated from the preparative thick layer plate amounted to 130 mg (39%) of a colorless oil whose structure is assigned as 2,4-diphenyl-5,5-dimethyl-Δ^3-oxazoline (**31**) on the basis of the following data: *m/e* 251 (parent) and 193 (P − acetone); ir (neat film) 6.14 (C=N), 9.1, and 9.65 μ (CO); nmr τ 8.35 (s, 6 H), 3.43 (s, 1 H), 2.10–3.10 (m, 10 H). The low-field position of proton H_2 supports this orientation of addition.

Photoaddition of Styrene with Diphenylazirine.—A solution of 0.5 g of diphenylazirine and 0.5 g of styrene in 500 ml of benzene was irradiated for 22 hr under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Pyrex filter. The nmr spectrum of the crude reaction mixture revealed the presence of two major photoadducts in a ratio of 1.5:1 (combined yield 50%). The two components could not be separated by chromatography on all columns tried. Characterization was accomplished by nmr spectroscopy. The major adduct showed a doublet at τ 4.71 while the minor component had a doublet at τ 4.42 (1 H). The remaining portion of the spectrum was essentially identical with the spectrum of the adducts obtained from the reaction of *N*-(*p*-nitrobenzyl)benzimidoyl chloride with triethylamine and styrene.[20]

Photoaddition of Norbornene with Diphenylazirine.—A solution containing 579 mg of diphenylazirine and 5.8 g of norbornene in 500 ml of benzene was irradiated for 22 hr through a Pyrex filter using a 450-W Hanovia immersion lamp. Removal of the solvent and excess norbornene under reduced pressure left a yellow oil. The crude reaction mixture contained two major photoadducts as evidenced by vpc analysis (combined yield 36%). The mixture could be partially separated by liquid–liquid partition chromatography. The trans tricyclic -Δ^1-pyrroline (**34**) was a crystalline solid: mp 141–143°; ir (KBr) 6.15 μ (C=N); nmr ($CDCl_3$) τ 8.6 (6 H, m), 7.9 (1 H, m), 7.68 (2 H, m), 6.7 (1 H, m), 5.3 (1 H, m), and 2.0–3.0 (10 H, m); uv (95% ethanol) 246 nm (ϵ 10,700); *m/e* 287 (base), 246, 193, 168, 130, 105, 91, and 77. The *cis*-Δ^1-pyrroline (**35**) could not be completely separated from the trans isomer. The nmr spectra of both **34** and **35** were essentially identical with the spectra of the adducts obtained by Huisgen from the reaction of *N*-(*p*-nitrobenzyl)benzimidoyl chloride with triethylamine and norbornene.[20]

Registry No.—**3**, 37428-95-8; **4**, 37428-96-9; **5**, 37428-97-0; **7**, 37428-98-1; **8**, 37428-99-2; **9**, 16205-14-4; **10**, 14491-02-2; **11**, 36879-68-2; **12**, 36879-69-3; **13**, 38202-09-4; **14**, 38202-10-7; **16**, 38202-11-8; **17**, 38215-47-3; **18**, 38215-48-4; **20**, 16340-36-6; **21**, 38202-13-0; **23**, 38202-14-1; **24**, 38202-15-2; **25**, 38202-16-3; **27**, 38215-49-5; **28**, 38215-50-8; **29**, 36879-78-4; **30**, 36879-77-3; **31**, 38202-17-4; **34**, 38215-53-1; **35**, 38215-54-2; 2-phenylazirine, 7654-06-0; 2,3-diphenylazirine, 16483-98-0; 3,6-dihydro-2,4,5-triphenylpyrimidine, 38202-18-5; methyl dithiobenzoate, 2168-78-7; benzaldehyde, 100-52-7; acetone, 67-64-1; norbornene, 498-66-8.

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The Preparation and Photolytic Decomposition of Tetrabromodiazocyclopentadiene[1]

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Tetrabromodiazocyclopentadiene (**3**) was prepared in a 45% yield from hexabromocyclopentadiene. Photolysis of **3** in a variety of olefins produced spiro[2.4]heptadienes in good yields. The products were heat and light sensitive and several were isolated as viscous liquids. Products due to insertion into C–H bonds were not detected by nmr analysis of the crude reaction mixtures. Photolysis in *trans*-4-methyl-2-pentene produced only the trans addition product, while photolysis in *cis*-4-methyl-2-pentene produced a mixture of the trans (55%) and the cis adducts (45%). It is concluded that the carbene adds to olefins while in the triplet spin state.

The photolytic decomposition of diazocyclopentadiene is known to yield a carbene which has a triplet ground state,[2] but which reacts in solution while in the singlet state.[3,4] In fact, the carbene is so reactive that attempts to produce the triplet state in solution by collisional deactivation were unsuccessful.[4]

We studied the decomposition of tetrachlorodiazocyclopentadiene and found that the carbene also reacted primarily while in the singlet state.[5,6] However, the presence of the four chlorine atoms allowed facile study of the triplet state by collisional deactivation with hexafluorobenzene.[6,7]

Tetrabromodiazocyclopentadiene (**3**) had been previously prepared,[8] but its decomposition to the carbene had not been studied. We thought that it would be of interest to study what effect four large bromine atoms would have on the reactions of the carbene. Thus, we now wish to report a new synthesis of **3** and a study of its photolytic decomposition in the presence of olefins.

Synthesis of Tetrabromodiazocyclopentadiene (3).—In 1963, a small amount of **3** was prepared in 15% yield from cyclopentadiene.[8] We devised an alternate synthesis to avoid the preparation of large quantities of diazocyclopentadiene, which has reportedly undergone

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(1) Taken in part from the Ph.D. Thesis of K. J. Sienkowski, Purdue University, 1972. Acknowledgment is made to the Stauffer Chemical Co. and the Viol Memorial Fellowship Fund for partial support of this research.

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