THE JOURNAL OF Organic Chemistry®

VOLUME 43, NUMBER 3

FEBRUARY 3, 1978

Intramolecular Dipolar Cycloaddition Reactions with Vinylbiphenyl-Substituted 1,3-Dipoles[1]

Albert Padwa,* Hao Ku, and Arthur Mazzu

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

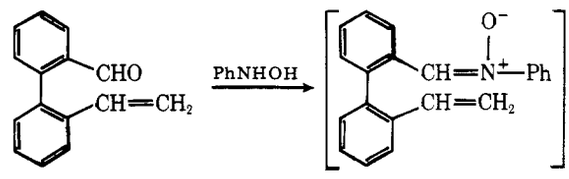
Received July 14, 1977

The intramolecular 1,3-dipolar cycloaddition reactions of several vinylbiphenyl-substituted 1,3-dipoles were studied. Condensation of 2′-vinyl-2-biphenylcarboxaldehyde with *N*-phenylhydroxylamine produced a transient nitrone intermediate which quantitatively cyclized to give phenanthro[9,10-*c*]isoxazole **5**. The regioselectivity of the above cycloaddition is controlled by steric factors and not by HOMO–LUMO interactions. A series of vinylbiphenyl-substituted 2*H*-azirines containing dipolarophile groups in close proximity to the azirine ring were subjected to UV irradiation. The exclusive formation of internal 1,3-dipolar cycloadducts can be attributed to cycloaddition of the initially generated nitrile ylide onto the neighboring double bond of the dipolarophile. A similar mode of cycloaddition occurred when *N*-(*p*-nitrobenzyl)-2′-vinyl-2-biphenylcarboximidoyl chloride (**26**) was treated with base. With these systems there is no particular constraint to attaining the parallel plane approach of addends, and consequently smooth 1,3-dipolar cycloaddition readily occurs. Irradiation of 3,3′-(2,2′-biphenylene)bis[2*H*-azirine] (**18**) with electron-deficient olefins gives cycloadducts derived from a transient diazabicyclo[3.1.0]hexene intermediate. The isolation of imidazole derivative **29** from the irradiation of **18** in the presence of dimethyl fumarate requires the formation of a discrete intermediate, in which transfer of a hydrogen from the ring to the side chain can occur. This process represents a rare example of an ene-type reaction from a 1,3-dipole.

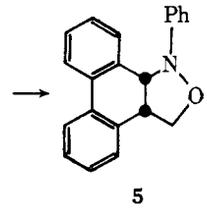
Interest in the chemistry of 2*H*-azirines has increased considerably over the past several years.[2] As a synthetic reagent the 2*H*-azirine ring occupies a position of particular utility. An unusual feature of this three-membered heterocyclic ring is that it is susceptible to attack by both electrophilic and nucleophilic reagents.[2] In addition, the 2π electrons present in the ring can participate in thermally allowed [π4s + π2s] cycloadditions as dienophiles[3,4] or as dipolarophiles.[5] Few reactions rival cycloadditions in the number of bonds that undergo transformation during the reaction, producing products considerably more complex than the reactants. Cycloaddition reactions utilizing 2*H*-arizines include thermal reactions with ketenes,[6,7] ketenimines,[7] nitrile oxides,[5] cyclopentadienones,[8,9] cyclopentadiene,[10] diphenylisobenzofuran[11,12] and diazomethane[5] to yield a variety of unusual heterocyclic ring systems. 2*H*-Azirines also react photochemically with various carbon–carbon and hetero double bonds to give five-membered heterocyclic rings.[13,14] The photoreaction proceeds by way of irreversible opening of the azirine ring to form a nitrile ylide intermediate which is subsequently trapped by a suitable dipolarophile.[13] As part of a research program designed to uncover new cycloaddition reactions of 2*H*-azirines, we initiated a study dealing with the intramolecular cycloaddition reactions of nitrile ylides generated by the photolysis of 2*H*-azirines.[15] In a continuation of these studies, we have recently examined the intramolecular 1,3-dipolar cycloaddition reactions of a series of vinylbiphenyl-substituted 2*H*-azirines. The results which we have encountered with this system are described in this paper.

Results and Discussion

Our initial goal was to determine whether a vinylbiphenyl-substituted 1,3-dipole is capable of undergoing intramolecular 1,3-dipolar cycloaddition. For various reasons, nitrone **4** was chosen as a suitable substrate for our model studies. The preparation of *N*-[*o*-(*o*-vinylphenyl)benzylidene]aniline *N*-oxide (**4**) required the initial synthesis of 2′-vinyl-2-biphenylcarboxaldehyde (**3**). This was accomplished by treating diphenylaldehydic acid methyl ester (**1**)[16] with methyltriphenylphosphorane. Subsequent reduction of the initially formed Wittig product **2** with lithium aluminum hydride followed by oxidation of the resulting alcohol with Corey's pyridinium chlorochromate reagent[17] gave **3** in ex-



3 **4**

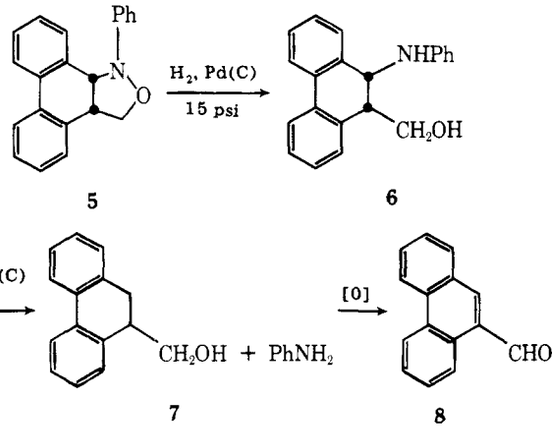


5

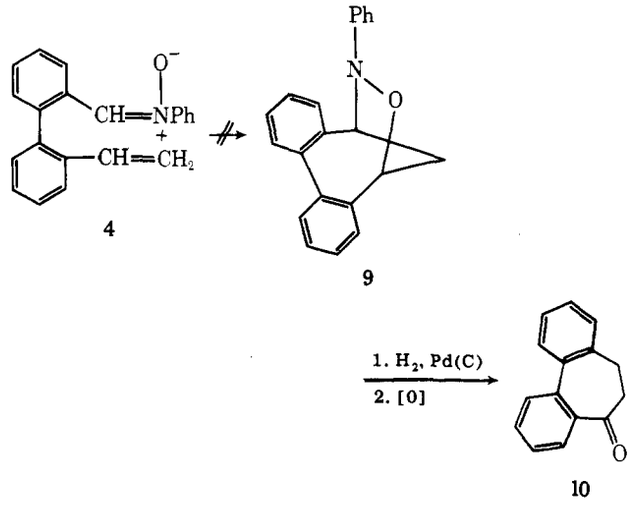
0022-3263/78/1943-0381$01.00/0

cellent yield. Condensation of **3** with *N*-phenylhydroxylamine in absolute ethanol resulted in the transient formation of **4** which immediately cyclized to give *cis*-1,3,3a,11b-tetrahydro-1-phenylphenanthro[9,10-*c*]isoxazole (**5**) as the only detectable product.

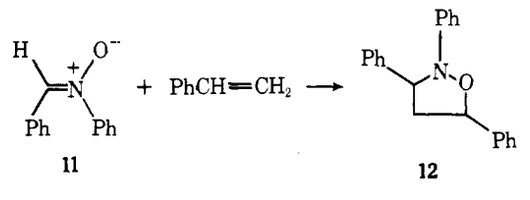
The regioselectivity of the internal cycloaddition was established by hydrogenolysis of **5** to **6** which, in turn, was further hydrogenated to **7**. Oxidation of **7** with pyridinium chlorochromate gave 9-phenanthrene carboxyaldehyde **8**. Thus, the formation of **8** from this series of reactions provides



strong support for the structure of **5**. If the internal cycloaddition of nitrone **4** had proceeded in the opposite direction (i.e., formation of **9**), then the hydrogenation oxidation sequence would have given ketone **10** as the ultimate product.

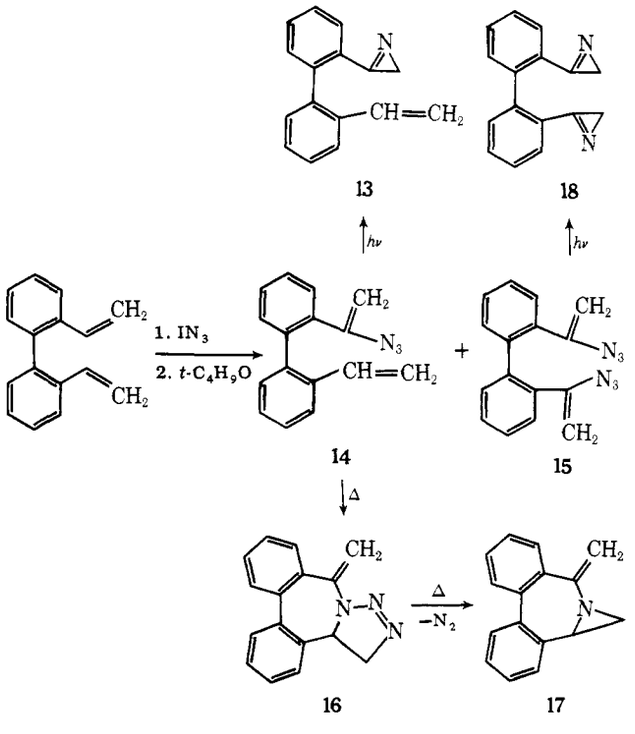


The formation of **5** from **4** is representative of the well-known intramolecular cycloaddition of a nitrone to an olefin.[18,19] Numerous examples of this type of cycloaddition exist in the literature.[19,20] LeBel and co-workers have elegantly demonstrated the utility and synthetic scope of this intramolecular dipolar cycloaddition for the preparation of a variety of polycyclic isoxazolidines.[21] The exclusive formation of **5** is especially interesting in light of Huisgen's work dealing with the bimolecular reaction of *N*-phenylbenzalnitrone (**11**) with styrene.[22] Huisgen's group was able to show that the cycloaddition of nitrone **11** with sytrene gave a single regioisomer whose structure was established as isoxazolidine **12**. Thus, the regioselectivity observed in the reaction of **3** with *N*-phenylhydroxylamine is directly opposite to that encountered by Huisgen. Preferential formation of **5** rather than **9** by a concerted pathway may be due to steric destabilization of the transition state for formation of the latter. It would seem as though the regioselectivity of the intramolecular cycloaddition of nitrone **4** is controlled by steric factors and not by the HOMO–LUMO interaction, which generally control the regioselectivity in bimolecular cycloaddition reactions.[23-25]

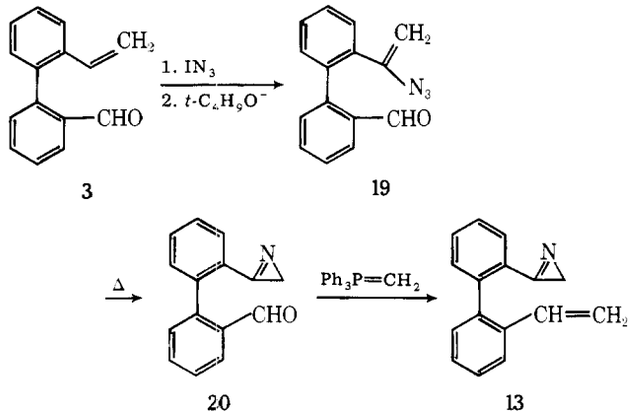


Having established the occurrence of an intramolecular 1,3-dipolar cycloaddition reaction with vinylbiphenyl nitrone **4**, we decided to study the intramolecular photocycloaddition reactions of some related vinylbiphenyl substituted 2*H*-azirines. Irradiation of 2*H*-azirines generates nitrile ylides as reactive intermediates which can undergo both 1,1- and 1,3-intramolecular dipolar cycloaddition.[15] As was pointed out elsewhere,[15] the geometry of the transition state involved in the intramolecular 1,1-cycloaddition reaction is significantly different from that required for concerted 1,3-dipolar cycloaddition. In view of the stringent spatial requirements associated with the intramolecular cycloaddition of nitrile ylides, we thought it worthwhile to examine the photochemical behavior of a series of vinylbiphenyl-substituted 2*H*-azirines in order to determine whether a 1,1- or 1,3-dipolar cycloaddition would occur.

As our first model, we chose to investigate the photochemistry of 3-(2′-vinyl-2-biphenyl)-2*H*-azirine (**13**). Our initial attempt to synthesize **13** involved the classical iodine azide route of Hassner and co-workers.[26] Reaction of 1.1 equiv of iodine azide with 2,2′-divinylbiphenyl followed by treatment of the initially formed iodine azide adducts with potassium *tert*-butoxide resulted in the formation of a mixture of both the monoazide **14** and divinylazide **15**. It would appear as though the initially formed iodine azide adduct undergoes further reaction with IN_3 at a rate competitive with starting material. Monoazide **14** was found to rapidly cyclize to triazolo[1,5-*a*]azepine **16** on standing at room temperature.[27] Further heating of **16** resulted in the loss of nitrogen and formation of vinylaziridine **17**. Since it was not possible to obtain a sample of **13** from the thermolysis of vinyl azide **14**, we subjected the mixture of vinyl azides (i.e., **14** and **15**) to UV

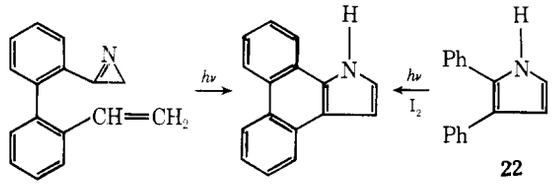


irradiation. Chromatography of the crude photolysate resulted in the isolation of the desired 2*H*-azirine **13** in 13% yield as well as bis(2*H*-azirine) **18** in 60% overall yield. Since the yield of **13** was so low, we decided to use an alternate procedure to prepare azirine **13.** This was accomplished by treating aldehyde **3** with iodine azide followed by reaction with potassium *tert*-butoxide to give **19** in high yield. Thermolysis of this material in refluxing benzene gave 2′-(2*H*-azirin-3-yl)-2-biphenylcarboxaldehyde (**20**) in 85% yield. Treatment of the azirinyl aldehyde with methyltriphenylphosphorane afforded the desired 3-(2′-vinyl-2-biphenyl)-2*H*-azirine (**13**) in good yield.



3 19 20 13

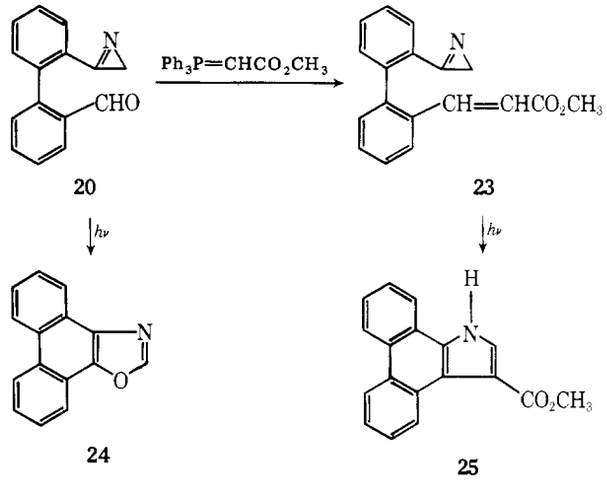
Irradiation of azirine **13** in benzene gave 1*H*-phenanthro[9,10-*b*]pyrrole (**21**) as the only identifiable photoproduct. The formation of this material arises by 1,3-dipolar cycloaddition of the initially formed nitrile ylide onto the double bond followed by air oxidation to pyrrole **21.** No detectable quantities of a 1,1-cycloadduct could be found in the crude photolysate. The structure of **21** was unequivocally established by comparison with an independently synthesized sample obtained by the iodine-catalyzed photooxidation of 2,3-diphenylpyrrole (**22**). Rigidly held stilbene moieties are



13 21 22

known to yield phenanthrene derivatives on irradiation and provide excellent precedent for this latter transformation.[28-31]

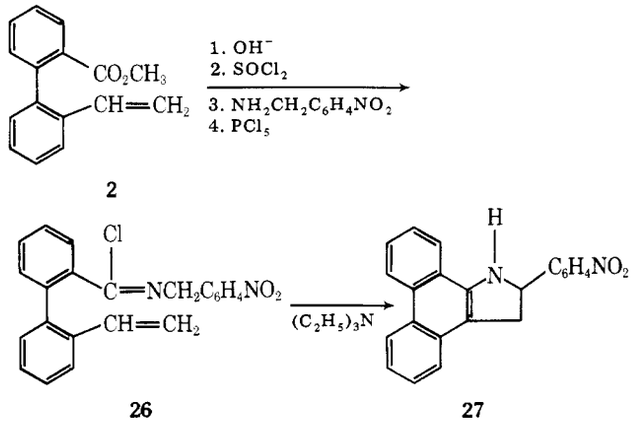
Additional examples of the intramolecular 1,3-dipolar cycloaddition reaction of these vinylbiphenyl-substituted systems were provided by the photolysis of azirines **20** and **23.** Methyl 2′-(2*H*-azirin-3-yl)-2-biphenylacrylate (**23**) was conveniently prepared by treating azirinyl aldehyde **20** with carbomethoxymethyltriphenylphosphorane. Irradiation of **23** in benzene gave methyl 1*H*-dibenz[*e*,*g*]indole-3-carboxylate **25** in 43% yield. Again, no detectable quantities of a 1,1-cycloadduct could be found in the crude photolysate. Similarly, irradiation of azirinyl aldehyde **20** gave phenanthro[9,10-*d*]oxazole (**24**) as the sole photoproduct. The structure of this material was verified by comparison with an independently synthesized sample prepared by the iodine-catalyzed photooxidation of 4,5-diphenyloxazole.[32] The formation of both of these adducts can be attributed to 1,3-dipolar addition of the initially generated nitrile ylide onto the adjacent π bond followed by air oxidation. The regioselectivity encountered here is similar to that normally observed in the



20 23 24 25

photolysis of 2*H*-azirines with benzaldehyde and methyl acrylate.[13,14]

We also studied the intramolecular dipolar cycloaddition reaction of the nitrile ylide generated from the base treatment of imidoyl chloride **26.** *o*-Vinylbiphenyl-substituted imidoyl chloride **26** was conveniently prepared by the series of reactions outlined below. Reaction of triethylamine with a benzene solution of **26** at room temperature produced triethylammonium chloride and an orange-red solution, which presumably contains the unstable nitrile ylide.[33] After stirring for 20 h at room temperature, an orange solid was obtained whose structure was identified as 2,3-dihydro-2-(*p*-nitrophenyl)-1*H*-phenanthro[9,10-*b*]pyrrole (**27**). The formation of **27** can be attributed to 1,3-dipolar addition of the initially generated nitrile ylide across the neighboring double bond followed by a rapid 1,3-H shift. The complete absence of a 1,1-cycloadduct with this system indicates that the transition state involved in the cycloaddition must be flexible enough to allow for maximum orbital overlap in the normal "two-plane" orientation approach required for 1,3-dipolar cycloaddition.[34]

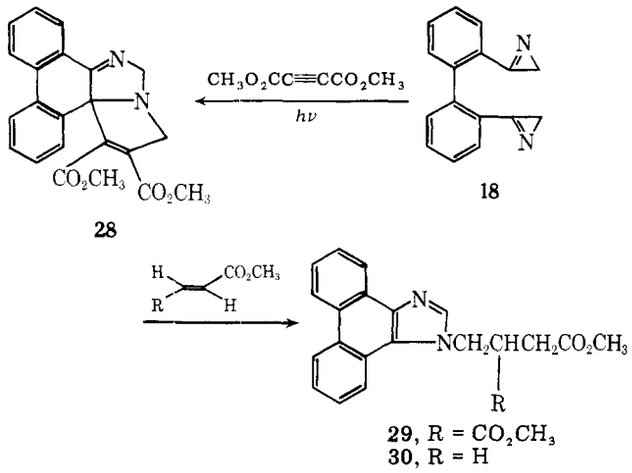


2 26 27

Having verified that vinylbiphenyl-substituted 2*H*-azirines undergo smooth intramolecular 1,3-dipolar cycloaddition, we turned our attention to the photochemical behavior of bis(2*H*-azirine) **18.** Previous work has shown that 2*H*-azirines can be converted to 1,3-diazabicyclo[3.1.0]hex-3-enes when the irradiation is carried out in the absence of an added dipolarophile.[35,36] The formation of these dimers can be rationalized by 1,3-dipolar addition of the initially generated nitrile ylide onto a ground-state azirine molecule. Care is required in the choice of solvent, photolysis time, and substituents since the 1,3-diazabicyclohexenes are themselves photochemically labile.[37] On the basis of these earlier observations, we felt that the irradiation of a representative bis(2*H*-azirine) such as **18** could lead to some interesting photochemistry.

Irradiation of 3,3′-(2,2′-biphenylene)bis[2*H*-azirine] (**18**) in benzene through Pyrex resulted in the formation of a complex mixture of products. However, when the irradiation of **18** was carried out in the presence of dimethyl acetylenedicarboxylate a good yield of a cycloadduct **28** was obtained. The structure of this material was assigned as dimethyl 2*H*,4*H*-phenanthro[9,10-*d*]pyrrolo[1,2-*c*]imidazole-5,6-dicarboxylate (**28**) on the basis of its characteristic analytical and spectral data. Photolysis of **18** with dimethyl fumarate in benzene took an entirely different course and produced cycloadduct **29** as the only detectable photoproduct. The structure of this material was verified by comparison with an independently synthesized sample prepared from the reaction of 4,5-diphenylimidazole with dimethyl itaconate followed by an iodine-induced photooxidation of the imidazole ring of structure **35.** In an analogous manner, photoaddition of **18** with methyl acrylate gave phenanthroimidazole **30** in high yield.

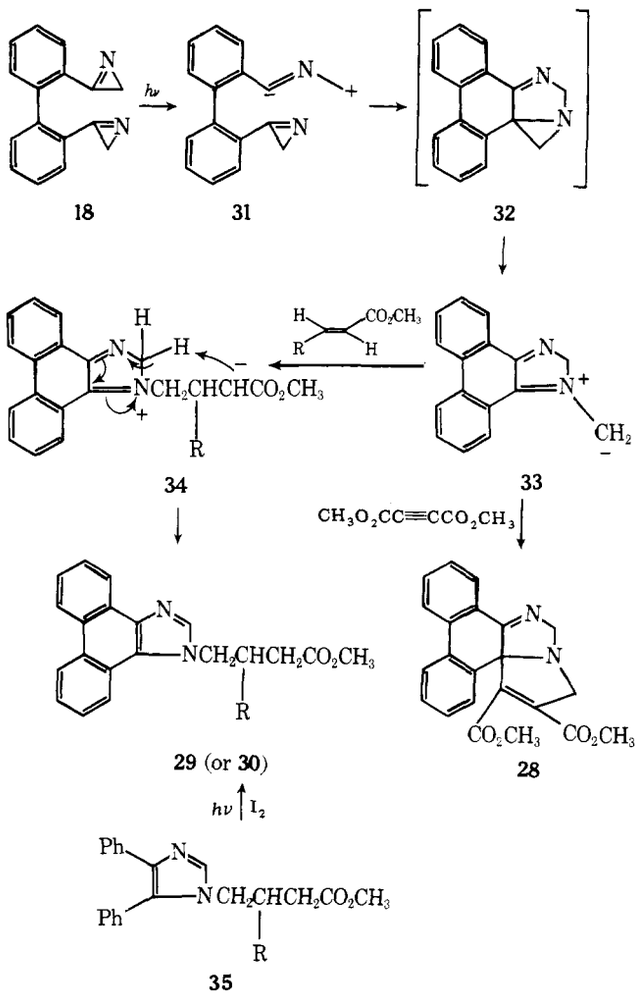
The formation of cycloadduct **28** can be rationalized by the assumption that the initially generated nitrile ylide (i.e., **31**)



29, R = CO_2CH_3
30, R = H

undergoes rapid cycloaddition across the C–N double bond of the adjacent azirine ring to give a transient diazabicyclohexene **32.** The high degree of order already present in the transition state undoubtedly enhances the rate of the intramolecular reaction relative to bimolecular cycloaddition with the added dimethyl acetylenedicarboxylate. The initially generated diazabicyclohexene **32** undergoes a subsequent ring opening to give azomethine ylide **33** which is ultimately trapped with the added dipolarophile. Reactions involving the photochemical cleavage of bicycloaziridines to azomethine ylides[37] and their subsequent additions to reactive multiple bonds are well known and provide good chemical analogy for the above suggestion.

The isolation of cycloadduct **29** (or **30**) from the addition of dimethyl fumarate to azomethine ylide **33** seemingly requires the formation of a discrete intermediate (i.e., **34**) in which transfer of a hydrogen from the ring to the side chain can occur. The results do not seem to be consistent with a process involving 1,3-cycloaddition of **33** with dimethyl fumarate followed by ring opening of the initially formed cycloadduct to give **29,** since there is no reason why the cycloadduct derived from methyl acrylate would be expected to give **30** under the reaction conditions used. The formation of cycloadducts **29** and/or **30** in the reaction of **18** with electron-deficient olefins has some interesting implications in relation to the classical 1,3-dipolar cycloaddition reaction.[25] Current opinion favors a concerted mechanism for dipolar cycloaddition,[25] although an alternate proposal involving a spin-paired diradical intermediate has been advanced by Firestone.[38] The above data appear to provide a rare example of an ene-type reaction from a 1,3-dipole. The possibility that



other ene-reactions can occur from 1,3-dipoles now merits serious consideration. We are further investigating these mechanistic ramifications.

Experimental Section

All melting and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Georgia. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Jeolco-MH-100 and a XL-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc.

Preparation of 2′-Vinyl-2-biphenylcarboxaldehyde (3). To a solution containing 25.0 g of methyltriphenylphosphonium bromide in 150 mL of dry ether was added 28.0 mL of a 2.5 M *n*-butyllithium solution at room temperature under a nitrogen atmosphere. The resulting orange solution was allowed to stir at room temperature for 20 min prior to the addition of 10.2 g of diphenaldehydic acid methyl ester (**1**)[16] in 200 mL of ether. The mixture was stirred at room temperature for 24 h and then 4 drops of water was added, and the solution was filtered to remove the precipitated triphenylphosphine oxide. Removal of the solvent under reduced pressure left a crude brown residue which was chromatographed on a 3 × 50 cm Florosil column using a 40% ether–pentane mixture as the eluent. The major component isolated was a pale oil, 5.0 g (49%), which was identified as 2′-vinyl-2-biphenylcarboxylic acid methyl ester (**2**) on the basis of the following spectral data: IR (neat) 3.39, 5.75, 6.22, 6.78, 6.95, 7.72, 8.82, 9.10, 10.90, 13.23, and 14.00 μm; NMR (60 MHz, $CDCl_3$) τ 6.50 (s, 3 H), 5.00 (dd, 1 H, *J* = 10.0 and 1.5 Hz), 4.49 (dd, 1 H, *J* = 18.0 and 1.5 Hz), 3.62 (dd, 1 H, *J* = 18.0 and 10.0), 2.41–2.99 (m, 7 H), and 2.03–2.26 (m, 1 H).

To a solution containing 360 mg of lithium aluminum hydride in 25 mL of dry ether was added to 4.0 g of the above ester in 25 mL of

ether. The mixture was heated at reflux for 1 h and cooled, and then 1 mL of a 10% sodium hydroxide solution was added dropwise followed by 2 mL of water. The ethereal solution was decanted from the gummy precipitate and washed with water, and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to leave behind 3.0 g (89%) of a clear oil which was assigned as 2′-vinyl-2-biphenylmethanol on the basis of the following spectral data: IR (neat) 2.95, 3.21, 6.10, 6.76, 6.90, 7.04, 8.32, 9.9, 10.90 and 13.22 μm; NMR (60 MHz, $CDCl_3$) τ 8.00 (s, 1 H), 5.71 (s, 2 H), 4.98 (dd, 1 H, J = 10.0 and 1.5 Hz), 4.48 (dd, 1 H, J = 18.0 and 1.5 Hz), 3.66 (dd, 1 H, J = 18.0 and 10.0 Hz), and 2.32–3.07 (m, 8 H). The crude alcohol was not purified but was used directly in the next step.

To a solution containing 2.16 g of pyridinium chlorochromate[17] in 25 mL of methylene chloride at room temperature was added 1.05 g of the above alcohol in 25 mL of methylene chloride. After stirring for 1.5 h, the mixture was filtered through silica gel to remove the chromium salts. The solvent was removed under reduced pressure to leave behind 900 mg (86%) of a pale-yellow oil whose structure was assigned as 2′-vinyl-2-biphenylcarboxaldehyde (**3**) on the basis of its spectral data: IR (neat) 3.28, 3.53, 3.64, 5.90, 6.24, 6.83, 6.95, 7.21, 7.99, 8.35, 10.05, 10.88, 12.05 and 13.21 μm; NMR (100 MHz, $CDCl_3$) τ 4.96 (d, 1 H, J = 11.0 Hz), 4.40 (d, 1 H, J = 16.0 Hz), 3.67 (dd, 1 H, J = 16.0 and 11.0 Hz), 2.33–2.98 (m, 7 H), 1.98–2.12 (m, 1 H), and 0.38 (s, 1 H).

Reaction of 2′-Vinyl-2-biphenylcarboxaldehyde with *N*-Phenylhydroxylamine. A solution containing 550 mg of *N*-phenylhydroxylamine and 1.04 g of **3** in 5 mL of ethanol was allowed to stand at room temperature for 4 h. At the end of this time, a pale-yellow oil had separated which eventually solidified. Recrystallization of the solid from chloroform–hexane gave 998 mg (66%) of 1,3,3a,11b-tetrahydro-1-phenylphenanthro[9,10-*c*]isoxazole (**5**): mp 147–149 °C; IR (KBr) 6.28, 6.77, 6.91, 8.26, 8.84, 9.26, 9.81, 10.25, 10.64, 11.13, 13.15, 13.61, and 14.34 μm; UV (methanol) 266 (ε 17 000) and 301 nm (ε 1710); NMR)100 MHz, $CDCl_3$) τ 6.12–6.61 (m, 2 H), 5.50 (dd, 1 H, J = 16.0 and 12.0 Hz), 4.86 (d, 1 H, J = 6.0 Hz), 2.52–3.11 (m, 11 H) and 2.13–2.36 (m, 2 H); mass spectrum *m/e* 299 (M^+), 269, 206, 205, 191, 179, 178 (base), 177, 176, and 93.

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.24; H, 5.72; N, 4.68. Found: C, 84.24; H, 5.76; N, 4.68.

Addition of $Eu(Fod)_3$ shift reagent to the NMR sample resulted in the conversion of the multiplet at 6.12–6.61 into a doublet of doublets of doublets (τ 6.63, 1 H, J = 7.0, 6.0, and 5.5 Hz) and a doublet of doublets (τ 6.32, 1 H, J = 9.0 and 7.0 Hz). The doublet of doublets at τ 5.50 was slightly compressed [τ 5.72 (dd, 1 H, J = 9.0 and 6.0 Hz)] and the doublet at τ 4.86 remained unchanged except for a slight downfield shift (τ 4.80).

The structure of this product was further verified by reduction with palladium on carbon. A 150-mg sample of **5** was taken up in methanol. To this solution was added 5 mg of a 5% palladium on carbon catalyst. The mixture was subjected to hydrogenolysis in a Parr hydrogenation apparatus at 15 psi for 5 h at room temperature. At the end of this time, the catalyst was filtered and the solvent removed under reduced pressure to give 65 mg (62%) of a pale oil which was identified as 10-anilino-9,10-dihydro-9-phenanthrenemethanol (**6**) on the basis of its spectral properties: IR (neat) 2.94, 3.43, 6.21, 6.63, 6.88, 7.59, 8.43, 9.66, 10.93, 13.30, and 14.43 μm; NMR (100 MHz, $CDCl_3$) τ 6.63–6.83 (m, 1 H), 6.20–6.36 (m, 2 H), 5.05 (d, 1 H, J = 4.0 Hz), and 2.13–3.43 (m, 14 H). The amino alcohol **6** was further hydrogenated. A 60-mg sample of this material was taken up in methanol and 5 mg of 5% palladium on carbon was added. The mixture was subjected to hydrogenolysis in a Parr apparatus at 25 psi for 92 h at room temperature. At the end of this time the catalyst was filtered and the solvent removed under reduced pressure. The major component obtained was identified as 9,10-dihydro-9-phenanthrenemethanol (**7**) on the basis of its spectral data: IR (neat) 2.98, 3.41, 6.22, 6.71, 6.88, 9.31, 9.70 and 13.20 μm; NMR (100 MHz, $CDCl_3$) τ 8.31 (br s, 1 H), 6.84–7.18 (m, 3 H), 6.43–6.62 (m, 2 H), 2.60–2.92 (m, 5 H), and 2.11–2.50 (m, 3 H). The crude alcohol was oxidized using 100 mg of pyridinium chlorochromate[17] in 25 mL of methylene chloride to give 9-phenanthrenecarboxyaldehyde (**8**), mp 100–102 °C (lit.[39] mp 100–101 °C). The structure of this material was verified by comparison with an authentic sample.

Irradiation of 2-(1-Azidovinyl)-2′-vinylbiphenyl (14) in Benzene. A 90-mg sample of 2-(1-azidovinyl)-2′-vinylbiphenyl[27] (**14**) in 150 mL of distilled benzene was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a uranium glass filter sleeve for 70 min. The solvent was removed under reduced pressure and the crude photolysate was subjected to preparative thick-layer chromatography using a 1:1 mixture of pentane–ether as the eluent. The major band isolated from the thick-layer plate contained 65 mg (80%) of a pale oil which was identified as 3-(2′-vinyl-2-biphenyl)-2*H*-azirine (**13**) on the basis of the following spectral data: IR (neat) 3.27, 5.75, 6.14, 6.24, 6.80, 6.93, 7.60, 10.02, 10.91, and 13.07 μm; UV (cyclohexane) 300 nm (ε 2060); NMR (100 MHz, $CDCl_3$) τ 8.73 (s, 2 H), 4.95 (d, 1 H, J = 12.0 Hz), 4.46 (d, 1 H, J = 18.0 Hz), 3.68 (dd, 1 H, J = 18.0 and 12.0 Hz), 2.33–2.95 (m, 7 H) and 1.93–2.07 (m, 1 H); mass spectrum *m/e* 219 (M^+), 218 (base), 217, 204, 191, 189, 179, and 178.

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.52; H, 5.76; N, 6.48.

Preparation of 2′-(2*H*-Azirin-3-yl)-2-biphenylcarboxaldehyde (20). To a solution containing 3.26 g of sodium azide in 40 mL of acetonitrile at −5 °C was added a solution containing 3.57 g of iodine monochloride in 5 mL of acetonitrile. The mixture was allowed to stir for 30 min and then 3.34 g of 2′-vinyl-2-biphenylcarboxaldehyde (**3**) dissolved in 10 mL of acetonitrile was added. The mixture was stirred for an additional 30 min at −5 °C and was then stirred for 9 h at room temperature. The resulting orange slurry was added to 200 mL of water and then extracted with ether. The ether extracts were washed with a 5% aqueous sodium thiosulfate solution and then with water. The ethereal layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give 5.51 g (93%) of an orange oil which was used immediately in the next step.

To a solution containing the above iodine azide adduct in 50 mL of dry ether at −5 °C was added 2.24 g of potassium *tert*-butoxide. The mixture was allowed to stir at 5 °C for 14 h, washed with water, and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left 3.10 g (83%) of an orange oil which was identified as 2′-(1-azidovinyl)-2-biphenylcarboxaldehyde (**19**) on the basis of the following spectra characteristics: IR (neat) 3.50, 4.75, 5.88, 6.22, 7.73, 8.33, 11.10, 12.03, and 13.20 μm; NMR (60 MHz, $CDCl_3$) τ 5.31 (d, 1 H, J = 1.5 Hz), 5.29 (d, 1 H, J = 1.5 Hz), 2.42–2.90 (m, 7 H), 1.98–2.18 (m, 1 H), and 0.23 (s, 1 H). The crude oil was used directly in the next step without purification.

A solution containing 3.1 g of the above vinyl azide and 3 mg of 1,4-diazabicyclo[2.2.2]octane in 250 mL of benzene was heated at reflux for 20 h. The solvent was removed under reduced pressure, and the residue was purified by passing it through a 3 × 60 cm Florosil column using a 20% acetone–hexane solution as the eluent. Removal of the solvent under reduced pressure left 2.25 g (85%) of a yellow oil which was subsequently sublimed at 40 °C (0.05 mm) to give 2′-(2*H*-azirin-3-yl)-2-biphenylcarboxaldehyde (**20**) as a pale-yellow solid: mp 67–68 °C; IR (KBr) 3.26, 3.51, 5.75, 5.91, 6.28, 6.94, 7.14, 7.85, 8.33, 10.09, 12.0 and 12.95 μm; UV (cyclohexane) 295 (ε 3380) and 245 nm (ε 19 900); NMR (60 MHz, $CDCl_3$) τ 8.67 (s, 2 H), 1.77–2.68 (m, 8 H), and 0.37 (s, 1 H); mass spectrum *m/e* 221 (M^+), 205, 204, 192 (base), 191, and 165.

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.37; H, 5.05; N, 6.10.

Preparation of 3-(2′-Vinyl-2-biphenyl)-2*H*-azirine (13). To a solution containing 1.43 g of methyltriphenylphosphonium bromide in 50 mL of dry ether was added 1.6 mL of a 2.5 M *n*-butyllithium solution at room temperature under a nitrogen atmosphere. The resulting orange solution was allowed to stir at room temperature for 20 min prior to the addition of 796 mg of 2′-(2*H*-azirin-3-yl)-2-biphenylcarboxaldehyde (**19**) in 30 mL of anhydrous ether. The mixture was allowed to stir at room temperature for 4 days and was then filtered to remove the precipitated triphenylphosphine oxide. Removal of the solvent under reduced pressure left a dark yellow oil which was chromatographed on a 2 × 30 cm Florosil column using a 1:1 pentane–ether mixture as the eluent. The major fraction isolated contained 356 mg (45%) of a pale oil which was identified as 3-(2′-vinyl-2-biphenyl)-2*H*-azirine (**13**). The spectral properties of this compound were identical to those obtained for the major product isolated from the irradiation of 2-(1-azidovinyl)-2′-vinylbiphenyl (**14**).

Irradiation of 3-(2′-Vinyl-2-biphenyl)-2*H*-azirine (13) in Benzene. A 280-mg sample of 3-(2′-vinyl-2-biphenyl)-2*H*-azirine (**13**) in 410 mL of distilled benzene was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Corex filter sleeve for 45 min. The solvent was removed under reduced pressure, and the crude residue was subjected to preparative thick-layer chromatography using a 1:1 pentane–ether mixture as the eluent. The major band isolated contained 123 mg (44%) of 1*H*-phenanthro[9,10-*b*]pyrrole (**21**) as a white solid: mp 155–156 °C; IR (KBr) 2.95, 6.16, 6.49 6.69, 6.88, 7.10, 8.03, 9.15, 11.10, 13.14, and 13.76 μm; UV (cyclohexane) 250 (ε 51 200), 255 (ε 77 600), 287 (ε 14 000), and 298 nm (ε 7440); NMR (60 MHz, $CDCl_3$) τ 2.80–3.04 (m, 2 H), 2.38–2.70 (m, 4 H), 2.06–2.36 (m, 1 H), 1.71–1.98 (m, 1 H), 1.25–1.50 (m, 2 H), and 0.90–1.20 (m, 1 H); mass spectrum *m/e* 218, 217 (M^+ and base), 187, 108.5 (M^{2+}), and 94.

Anal. Calcd for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.63; H, 4.98; N, 6.36.

The structure of this material was further established by comparison with an independently synthesized sample. A solution containing 75 mg of 2,3-diphenylpyrrole[40] (**22**) and 3 mg of iodine in 135 mL of cyclohexane was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 45 min. The solvent was removed under reduced pressure, and the crude photolysate was subjected to preparative thick-layer chromatography using a 20% ether–pentane mixture as the eluent. The major band isolated contained 31 mg (40%) of 1*H*-phenanthro[9,10-*b*]pyrrole (**21**): mp 155–156 °C. The spectral properties of this compound were identical to those obtained for the major product isolated from the irradiation of 3-(2′-vinyl-2-biphenyl)-2*H*-azirine (**13**).

Preparation of Methyl 2′-(2*H*-Azirin-3-yl)-2-biphenylacrylate (23). A solution containing 350 mg of 2′-(2*H*-azirin-3-yl)-2-biphenylcarboxaldehyde (**20**) and 560 mg of carbomethoxymethyltriphenylphosphorane[41] in 25 mL of methylene chloride was heated at reflux for 6 h. The solvent was removed under reduced pressure and the resulting residue was chromatographed on a 1 × 30 cm Florosil column using a 40% ether–pentane mixture as the eluent. The major fraction isolated contained 300 mg (68%) of an orange oil which was identified as *trans*-methyl 2′-(2*H*-azirin-3-yl)-2-biphenylacrylate (**23**) on the basis of the following spectral data: IR (neat) 5.74, 6.08, 6.21, 6.93, 7.54, 7.81, 8.29, 8.47, 10.13, and 13.00 μm; UV (cyclohexane) 272 nm (ε 16 500); NMR (100 MHz, $CDCl_3$) τ 8.68 (s, 2 H), 6.33 (s, 3 H), 3.61 (d, 1 H, J = 16.0 Hz), 2.14–2.76 (m, 8 H), and 1.81–1.96 (m, 1 H); mass spectrum m/e 277 (M^+), 246, 245, 244, 219, 218, 217, 204, 203, 191, 190, 179, 178 (base), 177, 176, 165, and 142.

Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.16; H, 5.48; N, 5.20.

Irradiation of *trans*-Methyl 2′-(2*H*-Azarin-3-yl)-2-biphenylacrylate (23) in Benzene. A 390-mg sample of *trans*-methyl 2′-(2*H*-azirin-3-yl)-2-biphenylacrylate (**23**) in 400 mL of distilled benzene was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Corex filter sleeve for 30 min. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a 2 × 30 cm Florosil column using a 1:1 pentane–ether mixture as the eluent. The major component isolated was a white solid, 165 mg (43%), which was recrystallized from acetone–pentane to give methyl 1*H*-dibenz[*e*,*g*]indole-3-carboxylate (**25**) as a white crystalline solid: mp 219–220 °C; IR (KBr) 2.99, 5.92, 6.18, 6.50, 6.91, 7.28, 7.72, 8.35, 8.50, 8.81, 8.98, 9.22, 9.89, 10.49, 10.70, 13.34 and 13.88 μm; UV (cyclohexane) 254 (ε 27 400), 261 (ε 38 000), 286 (ε 5640), 293 (ε 5660), and 306 nm (ε 3430); NMR (60 MHz, acetone-d_6) τ 6.12 (s, 3 H), 2.35–2.60 (m, 5 H), 2.02 (s, 1 H), 1.68–1.88 (m, 1 H), 1.23–1.48 (m, 2 H), and 0.18–0.40 (m, 1 H); mass spectrum m/e 276, 275 (M^+ and base), 245, 244, 214, 189, 137.5 (M^{2+}), 122, 107.5, and 94.5.

Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.37; H, 4.97; N, 5.08.

Irradiation of 2′-(2*H*-Azirin-3-yl)-2′-biphenylcarboxaldehyde (20) in Benzene. A 130-mg sample of azirinyl aldehyde **20** in 150 mL of distilled benzene was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Corex filter sleeve for 30 min. The solvent was removed under reduced pressure, and the crude residue was subjected to preparative thick-layer chromatography using a 1:1 pentane–ether mixture as the eluent. The major band isolated contained 54 mg (41%) of an orange solid which was recrystallized from cyclohexane to give phenanthro[9,10-*d*]oxazole (**24**), mp 145–147 °C. The structure of the photoproduct was assigned on the basis of its elemental analysis and spectral properties: IR (KBr) 6.14, 6.65, 8.08, 8.53, 9.28, 9.61, 10.38, 11.60, 13.40 and 13.87 μm; UV (cyclohexane) 252 (ε 55 300), 277 (ε 11 500), 287 (ε 8030), and 300 nm (10 300); NMR (60 MHz, $CDCl_3$) τ 1.88–2.56 (m, 5 H), 1.85 (s, 1 H), and 1.20–1.61 (m, 2 H); mass spectrum m/e 220, 219 (M^+ and base), 191, 190, 164, 163, 109.5 (M^{2+}) and 82.

Anal. Calcd for $C_{15}H_9NO$: C, 82.17; H, 4.14; N, 6.39. Found: C, 82.15; H, 4.24; N, 6.17.

The structure of the photoproduct (**24**) was unambiguously established by comparison with an authentic sample which was prepared by the iodine-catalyzed photooxidation of 4,5-diphenyloxazole.[32]

Preparation of *N*-(*p*-Nitrobenzyl)-2′-vinyl-2-biphenylcarboximidoyl Chloride (26). A solution containing 2.24 g of 2′-vinyl-2-biphenylcarboxylic acid,[42] 2.4 g of thionyl chloride, and 3 drops of pyridine in 100 mL of benzene was heated at 70 °C for 1 h. The solvent and excess thionyl chloride were removed under reduced pressure to leave behind 2.30 g (95%) of 2′-vinyl-2-biphenylcarboxylic acid chloride as a pale-yellow oil: IR (neat) 5.59, 6.26, 6.39, 6.82, 8.37, 8.91, 10.05, 11.54, and 12.94 μm. The crude product was used immediately in the next step. To a solution containing the above acid chloride in 50 mL of ether at 0 °C was added 1.67 g of *p*-nitrobenzylamine[43] in 30 mL of ether. After the addition was complete, the mixture was allowed to warm to room temperature and then 20 mL of a 1 M sodium hydroxide solution was added. After stirring at 25 °C for 30 min, 20 mL of water was added and the ethereal layer was separated from the basic aqueous layer. The ether extracts were washed with a 5% aqueous hydrochloric acid solution, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to give 2.90 g (81%) of *N*-(*p*-nitrobenzyl)-2′-vinyl-2-biphenylcarboxamide as a white solid: mp 111–112 °C; IR (KBr) 3.09, 6.15, 6.65, 7.45, 7.69, 7.79, 8.67, 9.09, 9.85, 10.19, 10.98, 11.73, 12.72, 13.19, and 14.40 μm; NMR (60 MHz, $CDCl_3$) τ 5.78 (d, 2 H, J = 6.0 Hz), 4.97 (dd, 1 H, J = 10.0 and 1.5 Hz), 4.53 (dd, 1 H, J = 18.0 and 1.5 Hz), 3.31–3.90 (m, 2 H), 3.10 (d, 2 H, J = 8.0 Hz), 2.20–3.05 (m, 8 H), and 2.11 (d, 2 H, J = 8.0 Hz); mass spectrum m/e 358 (M^+), 328, 219, 208, 207, 180, 179 (base), 178, 165, 152, 151, 149, 121, 120, and 106.

Anal. Calcd for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.56; H, 4.93; N, 7.65.

To a solution containing 250 mg of *N*-(*p*-nitrobenzyl)-2′-vinyl-2-biphenylcarboxamide in 5 mL of dry benzene under a nitrogen atmosphere was added 166 mg of phosphorus pentachloride in 5 mL of dry benzene. The mixture was heated at 60 °C until the evolution of hydrogen chloride gas had ceased. The solvent and phosphoryl chloride were removed under reduced pressure leaving behind a pale-yellow oil which was identified as *N*-(*p*-nitrobenzyl)-2′-biphenylcarboximidoyl chloride (**26**) from the following spectral properties: IR (neat) 3.26, 5.94, 6.20, 6.56, 7.41, 8.97, 9.78, 11.56, and 12.99 μm; NMR (60 MHz, $CDCl_3$) τ 5.40 (s, 2 H), 4.96 (dd, 1 H, J = 10.0 and 1.5 Hz), 4.50 (dd, 1 H, J = 18.0 and 1.5 Hz), 3.51 (dd, 1 H, J = 18.0 and 10.0 Hz), 3.09 (d, 2 H, J = 8.0 Hz), 2.16–2.93 (m, 8 H), and 2.08 (d, 2 H, J = 8.0 Hz). The unstable imidoyl chloride was used immediately for the next step.

Reaction of *N*-(*p*-Nitrobenzyl)-2′-biphenylcarboximidoyl Chloride (26) with Triethylamine. To a solution containing 260 mg of the previously prepared imidoyl chloride in 5 mL of dry benzene at 5 °C under a nitrogen atmosphere was added 140 mg of freshly distilled triethylamine. The color of the solution turned yellow-green immediately and then began to turn orange as it slowly warmed to room temperature. After stirring at 25 ° C for 20 h, the solution was passed through a 2 × 30 cm Florosil column using benzene as the eluent. The major component isolated contained 70 mg (30%) of an orange-red solid: mp 167–168 °C, whose structure was assigned as 2,3-dihydro-2-(*p*-nitrophenyl)-1*H*-phenanthro[9,10-*b*]pyrrole (**27**) on the basis of the following spectral data: IR (KBr) 2.98, 6.25, 6.64, 6.95, 7.38, 9.10, 9.81, 10.55, 11.70, 13.33, 1384 μm; UV (cyclohexane) 255 (ε 42 000) and 324 nm (ε 6300); NMR (60 MHz, acetone-d_6) τ 6.83 (dd, 1 H, J = 14.0 and 8.0 Hz), 6.00 (dd, 1 H, J = 14.0 and 10.0 Hz), 4.58 (dd, 1 H, J = 10.0 and 8.0 Hz), 3.87 (br s, 1 H), 1.78–2.76 (m, 10 H), and 1.22–1.77 (m, 2 H); mass spectrum m/e 340 (M^+), 310, 205, 204, 180, 179 (base), 178, 154, 149, 105, and 77.

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.50; H, 4.68; N, 7.84.

Photoaddition of 3,3′-(2,2′-Biphenylylene)bis[2*H*-azirine] (18) with Dimethyl Acetylenedicarboxylate. A 100-mg sample of **18**[27] in 150 mL of benzene which contained 61 mg of dimethyl acetylenedicarboxylate was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 30 min. Removal of the solvent left a dark residue which was subjected to thick-layer chromatography using a 1:1 ether–hexane mixture as the eluent. The major component isolated (43 mg) was a crystalline solid, mp 169–170 °C, whose structure was assigned as dimethyl 2*H*,4*H*-phenanthro[9,10-*d*]pyrrolo[1,2-*c*]imidazole-5,6-dicarboxylate (**28**) on the basis of the following data: IR (KBr) 5.84, 6.04, 6.94, 7.03, 7.57, 7.94, 8.74, 9.30, 10.42, 13.04, 13.18, and 13.66; UV (methanol) 242 nm (ε 39 250); NMR ($CDCl_3$, 60 MHz) τ 6.88 (s, 3 H), 6.32 (s, 3 H), 6.10 (d, 1 H, J = 17.0 Hz), 5.56 (d, 1 H; J = 17.0 Hz), 5.30 (d, 1 H, J = 14.0 Hz), 4.36 (d, 1 H, J = 14.0 Hz), 2.0–2.8 (m, 8 H).

Anal. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.42; H, 4.78; N, 7.27.

Photoaddition of 3,3′-(2,2′-Biphenylylene)bis[2*H*-azirine] (18) with Dimethyl Fumarate. A 100-mg sample of **18** in 150 mL of benzene which contained 62 mg of dimethyl fumarate was irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 30 min. Removal of the solvent left a dark oil which was subjected to thick-layer chromatography using a 15% methanol–benzene mixture as the eluent. The major fraction isolated from the thick-layer plate (81 mg) was a white crystalline solid, mp 132–133 °C, whose structure was assigned as dimethyl (1*H*-phenanthro[9,10-*d*]imidazol-1-yl-

methyl)succinate (**29**) on the basis of the following data: IR (KBr) 5.80, 6.55, 6.90, 7.25, 7.40, 7.75, 8.20, 8.58, 9.23, 13.14, and 13.76 μm; UV (methanol) 255 nm (ε 97 000); NMR ($CDCl_3$, 100 MHz) τ 7.45 (d, 2 H, J = 6.0 Hz), 6.30–6.60 (m, 1 H), 6.40 (s, 3 H), 6.35 (s, 3 H), 5.30 (dd, 1 H, J = 15.0 and 8.0 Hz), 5.10 (dd, 1 H, J = 15.0 and 8.0 Hz), 2.2–2.4 (m, 4 H), 2.15 (s, 1 H), 1.7–1.8 (m, 1 HO), 1.2–1.4 (m, 3 H); mass spectrum m/e 376 (M^+), 232, 219, 187, 186, and 169.

Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 70.20; H, 5.70; N, 7.13.

The structure of this photoproduct was further verified by comparison with an independently synthesized sample. To a solution containing 220 mg of 4,5-diphenylimidazole in 20 mL of benzene was added 35 mg of sodium hydride. The mixture was allowed to stir at room temperature for ½ h and then 158 mg of dimethyl itaconate in 5 mL of benzene was added. After stirring at 25 °C for 9 h, the excess sodium hydride was destroyed by the addition of water. The organic layer was extracted with chloroform, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting yellow residue was subjected to silica gel chromatography using a 1:1 ether–hexane mixture as the eluent. The major fraction contained 55 mg of dimethyl (4,5-diphenylimidazol-1-ylmethyl)succinate (**35**) as a clear oil: NMR ($CDCl_3$, 100 MHz) τ 7.60 (d, 2 H, J = 7.0 Hz), 6.90–7.20 (m, 1 H), 6.44 (s, 3 H), 6.40 (s, 3 H), 6.04 (dd, 1 H, J = 13.0 and 7.0 Hz), 5.72 (dd, 1 H, J = 13.0 and 7.0 Hz), 2.40–2.96 (m, 11 H). A 75-mg sample of **35** in 200 mL of benzene containing 254 mg of iodine was irradiated through Pyrex for 48 h. The excess iodine was destroyed by washing with a 10% sodium thiosulfate solution. After drying the organic layer, the solvent was removed under reduced pressure to give a sample of **29** which was identical in every detail with that obtained from the irradiation of bis(azirine) **18** with dimethyl fumarate.

Photoaddition of 3,3'-(2,2'-Biphenylylene)bis[2*H*-azirine] (18) with Methyl Acrylate. A 100-mg sample of **18** in 150 mL of benzene which contained 5 mL of methyl acrylate was irradiated with a 450-W hanovia lamp equipped with a Pyrex filter sleeve. Removal of the solvent left an orange oil which was subjected to thick-layer chromatography using a 15% methanol–benzene mixture as the eluent. The major band isolated from the thick-layer plate (85%) was a crystalline solid, mp 76–77 °C, whose structure was assigned as methyl (1*H*-phenanthro[9,10-*d*]imidazole-1-yl)butyrate (**30**) on the basis of the following data: IR (KBr) 5.74, 6.54, 7.00, 7.33, 7.85, 8.50, 10.09, 11.70, 12.08, 13.50, and 13.90 μm; UV (methanol) 255 nm (ε 75 000); NMR ($CDCl_3$, 100 MHz) τ 7.80 (m, 4 H), 6.35 (s, 3 H), 5.60 (m, 2 H), 2.4–2.7 (m, 4 H), 2.35 (s, 1 H), 1.3–2.2 (m, 4 H); mass spectrum m/e 318 (M^+), 232, 219, 218, and 178.

Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80; Found: C, 75.30; H, 6.01; N, 8.49.

Acknowledgment. We gratefully acknowledge the National Science Foundation for financial support. Aid in the purchase of the NMR spectrometer (XL-100) used in this work was provided by the NSF via an equipment grant.

Registry No.—**1**, 16231-67-7; **2**, 64024-87-9; **3**, 63626-12-0; **5**, 64024-90-4; **6**, 64024-91-5; **7**, 64024-93-7; **13**, 64024-95-9; **14**, 63375-55-3; **18**, 63626-10-8; **19**, 64024-97-1; **20**, 64024-96-0; **21**, 235-96-1; **22**, 26093-30-1; **23**, 64024-98-2; **24**, 64024-99-3; **25**, 64025-00-9; **26**, 64025-01-0; **27**, 64025-02-1; **28**, 64024-84-6; **29**, 64024-85-7; **30**, 64024-86-8; **35**, 64024-88-0; 2'-vinyl-2-biphenylmethanol, 64024-89-1; *N*-phenylhydroxylamine, 100-65-2; sodium azide, 26628-22-8; carbomethoxytriphenylphosphosphorane, 2605-67-6; 2'-vinyl-2-biphenylcarboxylic acid, 64024-92-6; thionyl chloride, 7719-09-7; *N*-(*p*-nitrobenzyl-2'-vinyl-2-biphenylcarboxamide, 64024-94-8; dimethyl acetylenedicarboxylate, 762-42-5; dimethyl fumarate, 624-49-7; 4,5-diphenylimidazole, 668-94-0; dimethyl itaconate, 617-52-7; methyl acrylate, 96-33-3; methyltriphenyl phosphonium bromide, 1779-49-3.

References and Notes

(1) Photochemical Transformations of Small Ring Compounds. 92. For part 91, see: A. Padwa, A. Au and W. Owens, *J. Org. Chem.*, **43**, 303 (1978).
(2) F. W. Fowler, *Adv. Heterocycl. Chem.*, **12**, 45 (1971).
(3) A. Hassner and D. J. Anderson, *J. Am. Chem. Soc.*, **93**, 4339 (1971); *J. Org. Chem.*, **38**, 2565 (1973).
(4) V. Nair, *J. Org. Chem.*, **37**, 802 (1972).
(5) V. Nair, *J. Org. Chem.*, **33**, 2121 (1968); *Tetrahedron Lett.*, 4831 (1971).
(6) A. Hassner, A. S. Miller and M. J. Haddadin, Tetrahedron Lett., 1353 (1972).
(7) F. P. Woerner, H. Reimlinger , and R. Merenyi, *Chem. Ber.*, **104**, 2786 (1971).
(8) A. Hassner and D. J. Anderson, *J. Am. Chem. Soc.*, **94**, 8255 (1972); *J. Org. Chem.*, **39**, 3070 (1974).
(9) D. J. Anderson, A. Hassner, and D. Y. Tang, *J. Org. Chem.*, **39**, 3076 (1974).
(10) H. Hemetsberger and D. Knittel, *Monatsch. Chem.*, **103**, 205 (1972).
(11) V. Nair, *J. Org. Chem.*, **37**, 2508 (1972).
(12) A. Hassner and D. J. Anderson, *J. Org. Chem.*, **39**, 2031 (1974).
(13) A. Padwa, *Acc. Chem. Res.*, **9**, 371 (1976).
(14) P. Gilgen, H. Heimgartner, H. Schmid, and H. J. Hansen, *Heterocycles*, **6**, 143 (1977).
(15) A. Padwa and P. H. J. Carlsen, *J. Am. Chem. Soc.*, **99**, 1514 (1977); A. Padwa and N. Kamigata, *J. Am. Chem. Soc.*, **99**, 1871 (1977).
(16) P. Bailey and R. Erickson, *Org. Synth.*, **41**, 46 (1961).
(17) E. J. Corey and J. Suggs, *Tetrahedron Lett.*, 2647 (1975).
(18) For some leading references, see: A. Padwa, *Angew. Chem., Int. Ed. Engl.*, **15**, 123 (1976).
(19) D. St. C. Black, R. F. Crozier, and V. C. Davis, *Synthesis*, 205 (1975).
(20) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **16**, 10 (1977).
(21) (a) N. A. LeBel and J. J. Whang, *J. Am. Chem. Soc.*, **81**, 6334 (1959); (b) N. A. LeBel, M. E. Post, and J. J. Whang, *ibid.*, **86**, 3759 (1964); (c) N. A. LeBel and T. A. Lajiness, *Tetrahedron Lett.*, 2173 (1966); (d) N. A. LeBel, G. M. J. Slusarezuk, and L. A. Spurlock, *J. Am. Chem. Soc.*, **84**, 4360 (1962); (e) N. A. LeBel, N. D. Ojha, J. R. Menke, and R. J. Newland, *J. Org. Chem.*, **37**, 2896 (1972); (f) N. A. LeBel and E. G. Banucci, *J. Org. Chem.*, **36**, 2440 (1971).
(22) R. Huisgen, R. Grashey, and H. Leitermann, *Tetrahedron Lett.*, 9 (1960).
(23) (a) K. N. Houk, *J. Am. Chem. Soc.*, **94**, 8953 (1972); (b) K. Houk, R. Duke, J. George, J. Sims, and R. Strozier, *ibid.*, **95**, 7287 (1973); (c) K. Houk, J. Luskus, J. Sims, and C. Watts, *ibid.*, 95, 7301 (1973); K. Houk and J. Sims, *ibid.*, **95**, 5798 (1973).
(24) R. Sustmann, *Tetrahedron Lett.*, 2727 (1971).
(25) R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976); *ibid.*, **33**, 2291 (1968).
(26) A. Hassner and L. A. Levy, *J. Am. Chem. Soc.*, **87**, 4203 (1965); F. W. Fowler, A. Hassner, and L. A. Levy, *ibid.*, **89**, 2077 (1967).
(27) A. Padwa, A. Ku, H. Ku, and A. Mazzu, *Tetrahedron Lett.*, 551 (1977); *J. Org. Chem.*, **43**, 66 (1978).
(28) G. R. Lappin and J. S. Zanucci, *J. Org. Chem.*, **36**, 1808 (1971).
(29) A. Schoenberg and M. M. Sidky, *Chem. Ber.*, **107**, 1207 (1974).
(30) C. A. Mudry and A. R. Frasca, *Tetrahedron*, **30**, 2983 (1974).
(31) A. Couture, A. Lablache-Combier, and H. Ofenberg, *Tetrahedron Lett.*, 2497 (1974).
(32) Y. Ito and T. Matsuura, *Tetrahedron*, **31**, 1373 (1975).
(33) R. Huisgen, H. Stangl, H. J. Sturm and H. Wagenhofer, *Angew. Chem.*, **74**, 31 (1962).
(34) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963).
(35) A. Padwa and S. I. Wetmore, Jr., *J. Org. Chem.*, **38**, 1333 (1973); **39**, 1396 (1974); *J. Am. Chem. Soc.*, **96**, 2414 (1974); *J. Chem. Soc., Chem. Commun.*, 409 (1972). For a preliminary report of this work, see: A. Padwa and H. Ku, *J. Chem. Soc., Chem. Commun.*, 551 (1977).
(36) (a) B. Jackson, N. Gakis, M. Maerky, H. J. Hansen, W. V. Philipborn and H. Schmid, *Helv. Chim. Acta*, **55**, 916 (1972). (b) A. Orahovats, H. Heimgartner, H. Schmid, and W. Heinzelmann, *Helv. Chim. Acta*, **58**, 2662 (1975).
(37) A. Padwa and E. Glazer, *J. Am. Chem. Soc.*, **94**, 7788 (1972); *ibid.*, **92**, 1778 (1970); *J. Chem. Soc. D*, 838 (1971); *J. Org. Chem.*, **38**, 284 (1973).
(38) R. A. Firestone, *J. Org. Chem.*, **33**, 2285 (1968); **37**, 2181 (1972); *J. Chem. Soc. A*, 1570 (1970).
(39) I. Heilbron, Ed., "Dictionary of Organic Compounds", Vol. 4, Oxford University Press, New York, 1953, p. 84.
(40) A. Padwa, J. Smolanoff, and A. Tremper, *J. Am. Chem. Soc.*, **97**, 4682 (1975).
(41) H. Gutman, O. Isler, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta.*, **40**, 1242 (1957).
(42) Z. Chugunova and L. Kulev, *Izv. Sib. Otd. Akad. Nauk. SSSR*, **11**, 144 (1962).
(43) N. Dudykina and N. Kochetkov, *Zhur. Obschei. Khim*, **26**, 2612 (1956).