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Photochromic Aziridines. On the Photochemical Valence Tautomerization and Cycloaddition Reactions of a Substituted Indano[1,2-*b*]aziridine[1]

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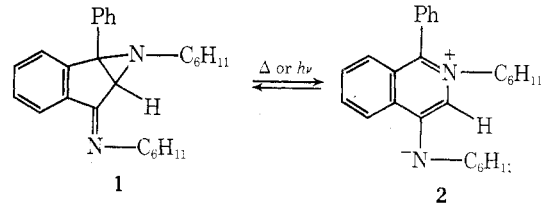
Heat or ultraviolet light partially converts 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine to an aromatic valence tautomer, the red isoquinolinium imine. The red color associated with the 1,3 dipole is rapidly discharged upon exposure to visible light, oxygen, or acetylenic dipolarophiles. The regiochemistry of the initial 1,3-dipolar adducts obtained with acetylenic dipolarophiles is discussed in light of some earlier results published in the literature. The initial cycloadducts were found to undergo a novel rearrangement to a benzazocine derivative whose structure was determined by X-ray crystallography. The details of each reaction are described and evidence is presented demonstrating the existence of transient intermediates in some of the irradiation experiments.

During the past decade, systematic studies of molecules or complexes which undergo reversible photoinduced color changes have contributed greatly to the basic understanding of the factors which govern the behavior of a photochromic system.[2,3] Although these systems have been the subject of valuable and penetrating mechanistic investigations, there are still many gaps in our understanding of this phenomenon.[4] Irradiation of solutions of acyclic[5,6] or bicyclic[7-9] aziridines with ultraviolet light is known to produce red colors which fade spontaneously in the dark. The colored species produced in these photoinduced reversible reactions were assigned as 1,3 dipoles (azomethine ylides).[9] Reactions involving the thermal and photochemical cleavage of aziridines to azomethine ylides and their subsequent 1,3-dipolar additions to reactive carbon–carbon multiple bonds have been studied by several groups of investigators.[10-14] Huisgen and coworkers have firmly established that the thermal ring cleavage of aziridines involves stereospecific, conrotatory ring opening. A disrotatory course has been found to occur from the excited state. Lown and Matsumoto[15] have recently pointed out that when the aziridine ring is constrained in a bicyclic structure of medium size, disrotatory photochemical ring opening is allowed, but thermal conrotatory ring opening is not permitted by the geometry of the system.[16,17] These workers reported, however, that 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine (**1**) undergoes thermal conversion to the tautomeric isoquinolinium imine (**2**), despite the geometrical restrictions imposed by the molecule. The driving

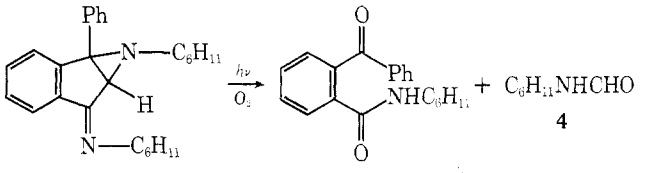


1 2

force for the thermally disallowed valence tautomerization in this system was attributed to the relief of ring strain in **1** and to the gain in resonance energy in **2**. Our interest in 1,3-dipolar cycloaddition reactions also led us to study independently the thermal and photochemical behavior of the phenylindano[1,2-*b*]aziridine ring system.[18] The present paper reports on the photochemical valence tautomerization and cycloaddition reactions of the indano[1,2-*b*]aziridine ring, as well as some of the interesting ground-state chemistry encountered with this system which differs, in

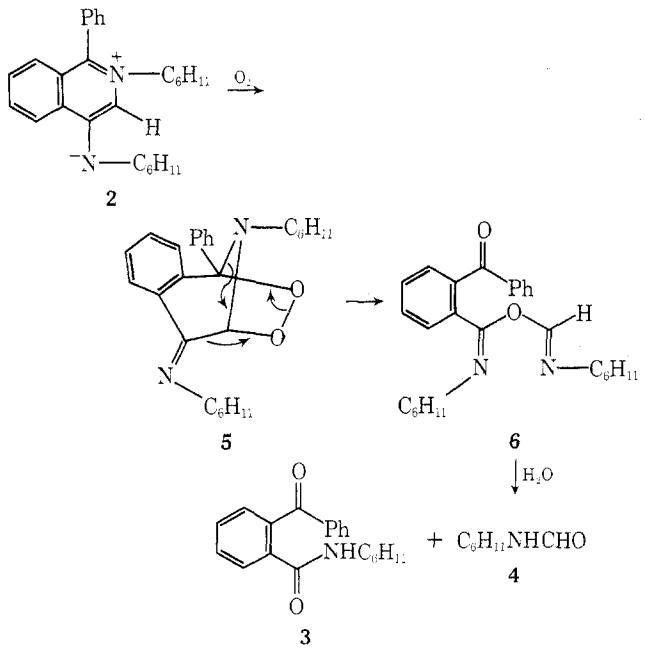
part, from the results described by Lown and Matsumoto.[15]

Upon brief irradiation of solutions of 1 with ultraviolet light, the red isoquinolinium imine 2 was formed. Intensely colored solutions could also be developed by rapid heating of 1 in toluene or xylene to 135°. The intense red color faded upon cooling or on exposure to visible light. The red color was also sensitive to oxygen and electron deficient olefins or acetylenes. Addition of trace quantities of acid or base also resulted in the rapid bleaching of the color. Two products were obtained when indano[1,2-*b*]aziridine 1 was exposed to ultraviolet irradiation in the presence of oxygen. These were identified as 2-benzoyl-*N*-cyclohexylbenzamide (3) and *N*-cyclohexylformamide (4) by comparison with authentic samples. Structure 3 was independently



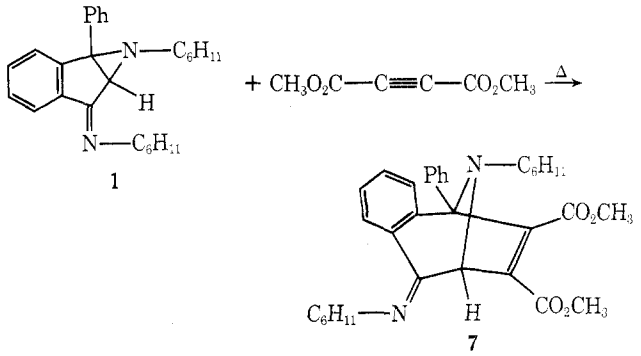
1 3 4

synthesized by treating *o*-benzoylbenzoic acid with thionyl chloride and cyclohexylamine. The formation of these products can be rationalized by assuming that oxygen adds to the initially generated isoquinolinium imine (2) by analogy to the known dipolar additions of reactive olefins and acetylenes to this compound.[15,18] Other six-membered, heteroaromatic betaines have been found to undergo similar cycloadditions with oxygen and provide reasonable chemical precedent for this step.[19-21] The transient peroxide (5) formed undergoes a subsequent Baeyer–Villiger-like rearrangement to a dimine anhydride (6) which readily hydrolyses to the observed products on work-up. The conversion



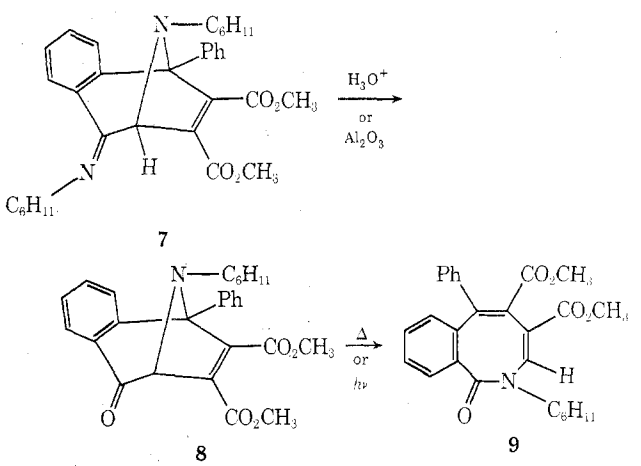
of the ozonide-like structure 5 into 6 parallels findings in the reaction of certain oxazoles with singlet oxygen in which the initial 4 + 2 cycloadduct undergoes a subsequent rearrangement to produce a triamide.[22]

Heating a degassed solution of 1 with an equimolar quantity of dimethyl acetylenedicarboxylate in xylene for 36 hr afforded a crystalline adduct (7), mp 177–179°, in 71% yield, whose structure is assigned as dimethyl 10-cyclohexyl-8,9-dihydro-9-(cyclohexylimino)-5-phenyl-5*H*-



benzocyclohepten-5,8-imine-6,7-dicarboxylate on the basis of the physical and chemical data outlined below. This structure corresponds to the 1,3-dipolar cycloaddition of dimethyl acetylenedicarboxylate across the azomethine ylide system. The elemental analysis obtained for this adduct was consistent with the empirical formula $C_{33}H_{38}N_2O_4$. The nmr spectrum showed multiplets at δ 0.6–2.20 (21 H) and 3.8–4.10 (1 H), singlets at 3.70 (6 H) and 5.50 (1 H) in addition to the aromatic protons at 6.6–8.3 (9 H). The adduct that we have obtained differs from that isolated by Lown and Matsumoto in its melting point (reported[15] mp 68–70°) and nmr spectrum. The nmr spectrum reported by these authors had two distinct singlets for the bridgehead protons at δ 4.90 and 5.55 and two sets of signals for the ester methyl groups at δ 3.57 and 3.78. These authors rationalized their nmr spectrum by assuming the existence of syn–anti stereoisomerism about the 6-cyclohexylimino group. In our hands, the above cycloaddition reaction produced a homogeneous adduct which displayed single absorptions for the carbomethoxy and bridgehead protons in the crude reaction mixture. It is conceivable that under our reaction conditions we have isolated the more stable anti isomer.

Mild acid hydrolysis of cycloadduct 7 using Lown's conditions gave a sharp melting keto compound (8), mp 143–145°. The nmr spectrum showed singlets at δ 3.76 (6 H) and 4.84 (1 H). This compound was assigned the structure of dimethyl 10-cyclohexyl-8,9-dihydro-9-oxo-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6,7-dicarboxylate (8). This same compound could also be obtained by passing the initial cycloadduct (7) through an acid-washed alumina column. It is interesting to note the similarity of the nmr spec-



tra of our hydrolyzed product with that reported by Lown but the difference in melting point (lit.[15] mp 134–135°). We are unable to account for this discrepancy.

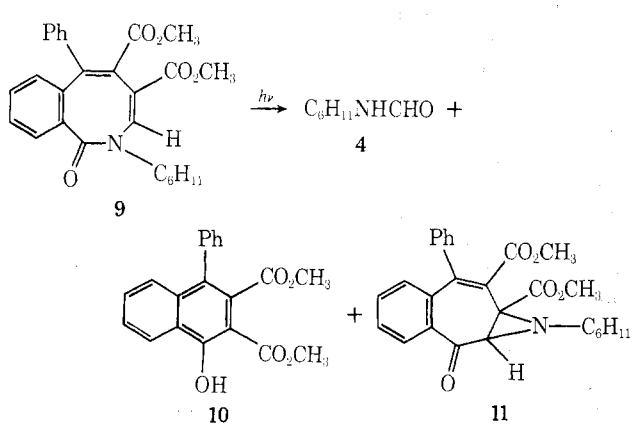
Ketone 8 was found to undergo a novel rearrangement to dimethyl 2-cyclohexyl-1,2-dihydro-1-oxo-6-phenyl-2-benzazocine-4,5-dicarboxylate (9) when heated in toluene or

irradiated with a 450-W Hanovia lamp through a Pyrex filter. The mass spectrum of **9** showed the molecular ion at *m/e* 445 and had an elemental analysis consistent with the empirical formula $C_{27}H_{27}NO_5$. The infrared spectrum showed two different ester carbonyls at 5.80 and 5.85 μ and an amide band at 6.00 μ. The nmr spectrum contained two sets of carbomethoxy protons at δ 3.46 and 3.7 in addition to the cyclohexyl and aromatic protons.

The structure of **9** was unequivocably established by an X-ray single-crystal structure analysis. The three-dimensional intensity data were measured by the stationary–counter-stationary crystal method, using Cu K radiation and balanced filters (Ni *vs.* Co) on a GE-XRD-6 diffractometer equipped with single-crystal orientators. In the range of intensity measurements (0 to 100 in 2θ) 1721 unique reflections of the 2418 unique ones examined for the space group $P2_1/C$ had peak counts significantly greater than their respective background. The structure was derived from Patterson and Fourier synthesis and refined by least squares to an R value of 0.0514, for all the data. The overall geometry of the molecule is shown in Figure 1.

The formation of benzazocine **9** can be postulated to arise by attack of the lone pair of electrons on nitrogen onto the carbonyl group followed by C_8–C_9 and C_5–N_{10} bond cleavage. Alternatively, the thermolysis could proceed *via* diradical intermediates formed by homolytic rupture of the benzoyl carbon–carbon bond. The fact that the thermal rearrangement proceeds at a much faster rate when *n*-amyl alcohol was used as the solvent would tend to support a mechanism where ionic charges are being developed along the reaction coordinate.

The rearranged benzazocine adduct **9** was also found to exhibit interesting photochemistry. Irradiation of a solution of **9** in benzene through a Corex filter for 4 hr gave a mixture of *N*-cyclohexylformamide (**4**, 14%), 1-hydroxy-2,3-dicarbomethoxy-4-phenylnaphthalene (**10**, 23%), and dimethyl-1-cyclohept[1,2-*b*]azirine-8,8a-(1*H*)-dicarboxylate (**11**, 43%). The structure of naphthol **10** was based on a



parent peak at *m/e* 336 in the mass spectrum: infrared absorptions at 5.73 and 6.00 μ; nmr singlets at δ 3.48 (3 H), 3.90 (3 H), 12.18 (1 H–D_2O exchanged), aromatic multiplet at 6.80–8.48 (9 H); elemental analysis ($C_{20}H_{16}O_5$); and its characteristic ultraviolet absorption spectrum which showed bands at 230 (ϵ 30,400), 240 (ϵ 36,100), and 345 nm (ϵ 6200). Structure **11** showed a parent peak at *m/e* 445 in the mass spectrum, infrared bands at 5.75 and 5.88 μ, nmr singlets at δ 3.16 (3 H), 3.80 (3 H), 4.58 (1 H), multiplets at 0.6–2.0 (10 H), 3.4–3.76 (1 H), 7.0–7.9 (9 H), and an elemental analysis which revealed that structure **11** was isomeric with starting material. Treatment of **11** with hydrochloric acid transformed it into anhydride **12**. The structure of **12** was based on its mass spectrum M^+ 431 and $M^+ - CO_2$ at 387 (base); anhydride and ester absorptions at

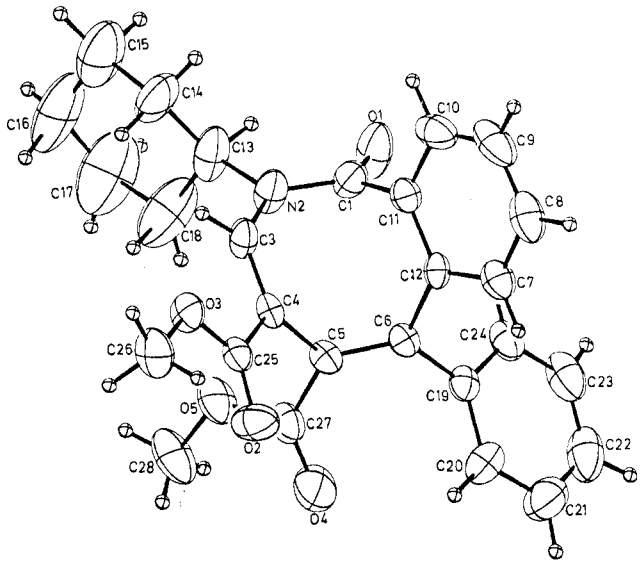
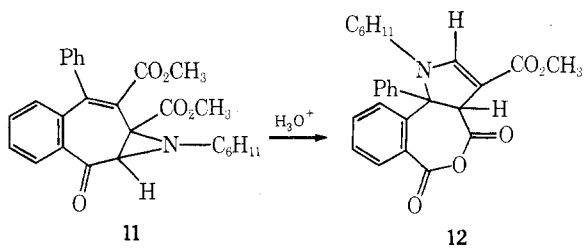
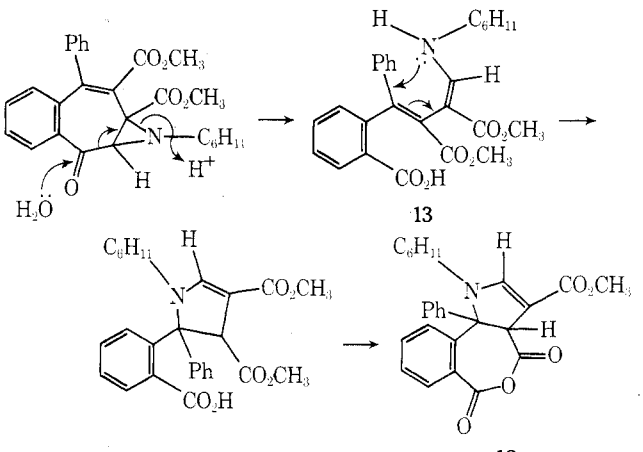


Figure 1. A general view of dimethyl 2-cyclohexyl-1,2-dihydro-1-oxo-6-phenyl-2-benzazocine-4,5-dicarboxylate (**9**).

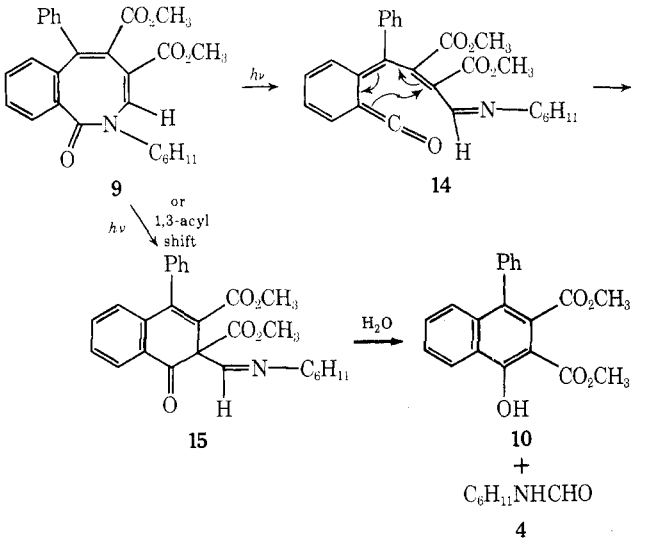


5.60, 5.75, and 5.85 μ in the infrared; nmr singlets at δ 3.04 (3 H), 4.76 (1 H), 6.25 (1 H) in addition to the cyclohexyl and aromatic protons, and an elemental analysis which indicated the molecular formula $C_{26}H_{25}NO_5$.

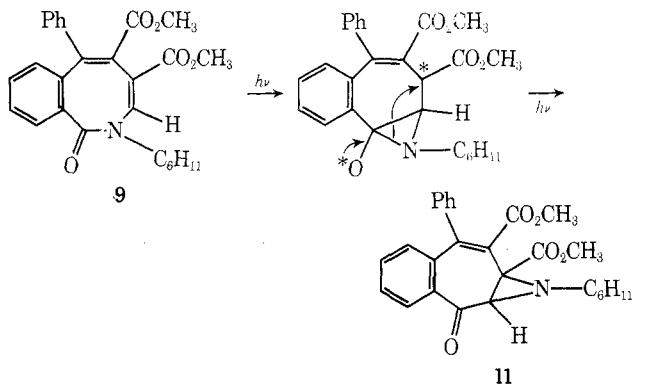
The formation of anhydride **12** is envisaged to occur by protonation of the aziridine ring followed by addition of water to the carbonyl group to produce intermediate **13** which undergoes subsequent ring closure and cyclization.



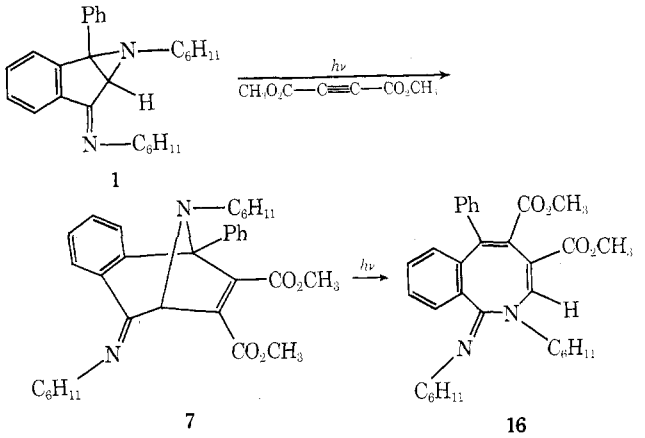
A possible mechanistic rationalization of the photochemistry of benzazocine **9** would involve a photoinduced ring opening to ketene **14** followed by ring cyclization and hydrolysis to *N*-cyclohexylformamide and naphthol **10**. Alternatively, the reaction may be rationalized by a 1,3-acyl shift to generate intermediate **15** which is subsequently converted to **4** and **10** on work-up. This latter process would be analogous to that involved in the photochemical rearrangment of a number of *N*-vinylamides,[23-25] for which evidence has been presented in support of a Norrish Type I cleavage and recombination path.



The formation of aziridine **11** may be considered to be derived from a competing 1,2-acyl shift. This latter process is reminiscent of the formation of substituted cyclopropanes from the irradiation of a β,γ-unsaturated ketones (*i.e.*, oxadi-π-methane rearrangement).[26]

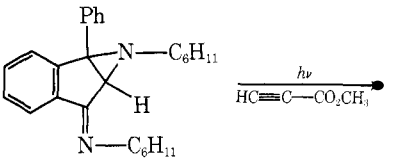


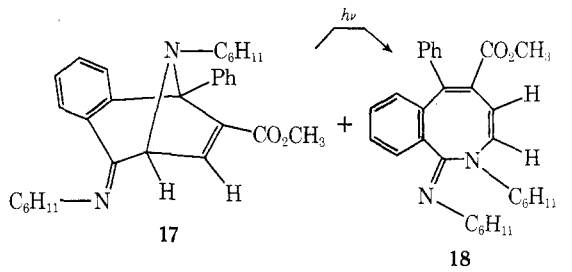
When the irradiation of indano[1,2-*b*]aziridine (**1**) was carried out for 5 hr in a benzene solution containing an equimolar quantity of dimethyl acetylenedicarboxylate, only a trace amount of cycloadduct **7** was isolated. Instead, the major product obtained was identified as dimethyl 2-cyclohexyl-1,2-dihydro-1-(cyclohexylimino)-6-phenyl-2-benzazocine-4,5-dicarboxylate (**16**). The structure of **16** was based on the similarity of its spectral properties with that of benzazocine **9** (see Experimental Section).



A study of product distribution *vs.* extent of irradiation established that the ratio of **7**:**16** varied as a function of time. With short exposures, significant quantities of cycloadduct **7** were found in the reaction mixture by nmr analysis. At longer exposures, owing to a secondary photoreaction of **7**, the amount of **16** increased. This was independently demonstrated by the quantitative conversion of an authentic sample of **7** to **16** in benzene under comparable photolytic conditions.

A similar set of cycloaddition reactions was carried out with indano[1,2-*b*]aziridine (**1**) and methyl propiolate. Irradiation of an equimolar mixture of **1** and methyl propiolate in benzene for 4 hr produced a mixture of two adducts (**17** and **18**) which were readily separated by column chromatography. Examination of the photoreaction as a function



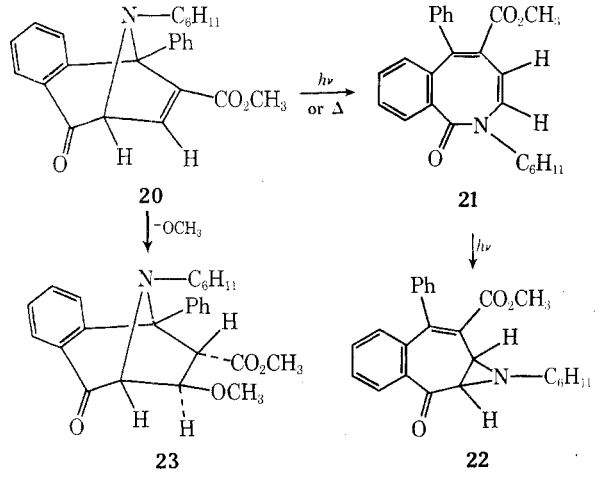


of time clearly showed that **18** was a secondary photoproduct derived from **17**. The structure of **17** was based on its elemental analysis ($C_{31}H_{32}N_2O_2$), mass spectrum (M^+ 468), infrared (5.80 and 6.10μ), and nmr spectrum which showed a singlet at δ 3.60 (3 H) and doublets at 5.16 (1 H, J = 2.5 Hz) and 6.07 (1 H, J = 2.5 Hz) in addition to the cyclohexyl and aromatic protons. This same adduct, mp 147–149°, could also be independently prepared by refluxing a mixture of **1** and methyl propiolate in xylene for 2 days.

It should be noted that our assignment for structure **17** differs from that made by Lown and Matsumoto.[15] These authors claimed that the reaction of **1** with methyl propiolate produced a different stereoisomer in which the bridgehead and vinyl protons were separated by the carbomethoxy group. Moreover, these workers claim that their adduct (mp 73°) exists as a syn–anti stereoisomeric mixture. This was postulated in order to rationalize the set of doublets (δ 4.46 (0.5 H) and 5.08 (0.5 H)) for the bridgehead protons in the nmr. We were unable to detect these signals in our crude reaction mixture. The magnitude of the vicinal coupling constant corresponds to that reported for norbornadiene in which J_{AB} = 2.9 Hz.[27] Allylic coupling in the model compound has been reported to have a value less than 1.0 Hz (*i.e.*, J_{AC} = 0.95 Hz).[27] Consequently, we believe that the nmr data support our assignment and exclude the alternate structure (which was previously postulated[15]) in which the dipolarophile added to the azomethine ylide in the alternative orientation. We are unable to account for the discrepancy in the melting points and nmr data. It should be pointed out that treatment of cycloadduct **17** with sodium methoxide in methanol resulted in Michael addition of methanol across the double bond and gave a product (**19**), the structure of which is perfectly consistent with our new assignment (see Experimental Section).

The rearrangement of cycloadduct **17** to benzazocine **18** is completely analogous to that observed with the related cycloadduct **7** (*i.e.*, **7** → **16**). It is especially interesting to note that benzazocine **18** contains two doublets in the nmr

for the two vinyl protons (δ 5.52 and 6.00). These hydrogens show a coupling constant of 8.0 Hz. This observation adds further support to our assignment for cycloadduct **17** and strongly argues against the stereochemical assignment made by Lown and Matsumoto.[15] Moreover, hydrolysis of cycloadduct **17** gave the analogous methyl 10-cyclohexyl-8,9-dihydro-9-oxo-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6-carboxylate (**20**) which was smoothly converted to benzazocine **21** on thermolysis or photolysis. The AB quartet observed in the nmr spectrum of **21** (δ 6.0–6.20 (J = 8.0 Hz)) also demands that the bridgehead and vinyl protons of adduct **20** be adjacent to each other.



If the irradiation of **20** was carried out for an extended period of time, aziridine **22** was obtained as the major photoproduct. The formation of **22** was shown to arise from a subsequent photoreaction of benzazocine **21** and probably proceeded *via* a 1,2-acyl shift as had been previously observed with benzazocine **9**. Treatment of **20** with sodium methoxide in methanol gave a product (**23**) which also corresponds to Michael addition across the carbon–carbon double bond.

In summary, these experiments demonstrate that heat or ultraviolet light partially converts the indano[1,2-*b*]aziridine ring system into the red isoquinolinium imine. This reactive 1,3 dipole can be trapped with oxygen or with acetylenic dipolarophiles to give cycloadducts which undergo mechanistically intriguing transformations on further excitation.

Experimental Section

All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 100 MHz using a Jeolco-MH-100 spectrometer.

Irradiation of 1-Cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine (1). A solution containing 500 mg of **1**[28] in 500 ml of cyclohexane was irradiated through a Vycor filter sleeve under a nitrogen atmosphere for 20 min. At the end of this time an intense bright red color had developed. The red solution faded when exposed to visible light. Removal of the solvent under reduced pressure led to the recovery of unreacted starting material.

Different results were obtained when aziridine **1** was irradiated under an oxygen atmosphere. A solution containing 183 mg of **1** in 200 ml of benzene was irradiated with a Hanovia 450-W lamp through a Vycor filter for 3 hr. The solvent was removed under reduced pressure and the residue was subjected to preparative thick layer chromatography. The plate was developed using a 1:1 pentane–ether mixture. Extraction of the lower band with methylene chloride followed by evaporation of the solvent gave 9.0 mg (15%) of *N*-cyclohexylformamide (**4**). This structure was verified by comparison with an authentic sample.

The second band isolated from the thick layer plate amounted to 15 mg (10%) of a compound whose structure is assigned as 2-benzoyl-*N*-cyclohexylbenzamide (**3**): mp 203–205°; ir (KBr) 3.10, 6.02, and 8.30 μ; nmr ($CDCl_3$) δ 0.7–2.80 (m, 10 H), 3.2–3.5 (m, 1 H), 6.8–7.7 (m, 9 H), and 8.50 (s, 1 H); uv (methanol) λ_{max} 285 (ε 1560) and 258 nm (ε 4230); *m/e* 307 (parent), 209 (base), 105, and 98. The structure of this compound was verified by an independent synthesis described below.

A solution containing 2.26 g of 2-benzoylbenzoic acid and 4 ml of thionyl chloride was heated for 30 min at 50°. Removal of the excess thionyl chloride under reduced pressure gave a crystalline compound which was characterized by a major band at 5.60 μ in its infrared spectrum. This material was dissolved in 5 ml of benzene and the above solution was added dropwise to a stirred solution of 2 g of cyclohexylamine in 5 ml of benzene. The mixture was allowed to stand at room temperature overnight. The cyclohexylamine hydrochloride that formed was filtered and the solvent removed under reduced pressure to leave a solid, mp 203–205°, whose infrared and nmr spectra were identical with 2-benzoyl-*N*-cyclohexylbenzamide prepared from the irradiation of **1**. No other characterizable compounds could be obtained from the thick layer plate.

Thermal Cycloaddition of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Dimethyl Acetylenedicarboxylate. A solution of 0.5 g of **1** and 0.2 g of dimethyl acetylenedicarboxylate was refluxed in 100 ml of xylene for 36 hr. The solvent was removed under reduced pressure and the residue was triturated with hexane to give 500 mg of a crystalline product which was recrystallized from hexane to give a white solid, mp 177–179°. This material was characterized as dimethyl 10-cyclohexyl-8,9-dihydro-9-(cyclohexylimino)-5*H*-benzocycloheptene-5,8-imine-6,7-dicarboxylate (**7**) on the basis of the following data: ir (KBr) 5.80, 6.10, 8.00, 8.83, 10.21, 10.70, 11.20, 13.02, 13.47, and 14.17 μ; uv (95% ethanol) 245 nm (ε 19,400); nmr ($CDCl_3$) δ 0.6–2.20 (m, 21 H), 3.70 (s, 6 H), 3.8–4.10 (m, 1 H), 5.50 (s, 1 H), 6.6–8.30 (m, 9 H); *m/e* 526 (parent) and 344 (base).

Anal. Calcd for $C_{33}H_{38}N_2O_4$: C, 75.25; H, 7.27; N, 5.32. Found: C, 75.26; H, 7.25; N, 5.26.

Photochemical Cycloaddition of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Dimethyl Acetylenedicarboxylate. A solution containing 0.5 g of **1** and 0.2 g of dimethyl acetylenedicarboxylate in 500 ml of benzene was irradiated for 5 hr using a 450-W Hanovia Mercury arc fitted with a Corex filter sleeve. Removal of the solvent under reduced pressure followed by trituration of the residue with hexane gave 470 mg (73%) of dimethyl 2-cyclohexyl-1,2-dihydro-1-(cyclohexylimino)-6-phenyl-2-benzazocine-4,5-dicarboxylate (**16**): mp 222–224°; ir (KBr) 5.73, 5.90, 6.00, 6.35 (s), 6.92, 7.02, 7.50, 8.12, 8.25, 8.90, 9.45, 9.55, 11.12, 11.90, 12.65, 13.00, 13.75, and 14.15 μ; uv (95% ethanol) 245 (ε 14,500) and 310 nm (ε 9600); nmr ($CDCl_3$) δ 1.8–2.3 (m, 21 H), 2.87 (s, 3 H), 3.60 (s, 3 H), 3.82–4.20 (m, 1 H), 7.0–8.2 (m, 10 H); *m/e* 526 (parent) and 344 (base).

Anal. Calcd for $C_{33}H_{38}N_2O_4$: C, 75.25; H, 7.27; N, 5.32. Found: C, 75.27; H, 7.29; N, 5.30.

This same product could be obtained in quantitative yield from the irradiation of **7** in benzene for 1 hr using a 450-W Hanovia lamp equipped with a Corex filter.

Acid Hydrolysis of Dimethyl 10-Cyclohexyl-8,9-dihydro-9-(cyclohexylimino)-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6,7-dicarboxylate (7). A solution containing 550 mg of **7** in 2 ml of benzene was chromatographed through a column containing 30 g of alumina (acid washed, Merck) using benzene as the eluent. The main fraction was collected, the solvent was removed under reduced pressure, and the residue was triturated with pentane to give 300 mg (68%) of dimethyl 10-cyclohexyl-8,9-dihydro-9-oxo-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6,7-dicarboxylate (**8**): mp 143–145°; ir (KBr) 3.45, 5.80, 5.85, 6.07, 7.57, 7.70, 7.93, 8.02, 8.20, 12.50, 12.70, 12.90, and 14.00 μ; uv (methanol) 240 (ε 15,100) and 305 nm (ε 1600); nmr ($CDCl_3$) δ 0.6–2.20 (m, 11 H), 3.76 (s, 6 H), 4.84 (s, 1 H), and 6.80–8.00 (m, 9 H); *m/e* 445 (parent), 414, 320, 304, 289, and 276 (base).

Anal. Calcd for $C_{27}H_{27}NO_5$: C, 72.79; H, 6.11; N, 3.14. Found: C, 72.58; H, 6.03; N, 3.11.

This same product could also be formed by treating **7** with aqueous hydrochloric acid (2 *N*) in 10 ml of methanol at room temperature for 5 hr.

Thermal Rearrangement of Dimethyl 10-Cyclohexyl-8,9-

dihydro-9-oxo-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6,7-dicarboxylate (8). A solution containing 70 mg of 8 in 15 ml of toluene was heated at reflux for 4 hr. Removal of the solvent under reduced pressure gave 66 mg (93%) of a crystalline solid, mp 189–191°, whose structure is assigned as dimethyl 2-cyclohexyl-1,2-dihydro-1-oxo-6-phenyl-2-benzazocine-4,5-dicarboxylate (9) on the basis of the following data: ir (KBr) 5.80, 5.85, 6.00, 7.80, and 8.20 μ; uv (methanol) 245 nm (ϵ 14,500); nmr ($CDCl_3$) δ 1.0–2.0 (m, 10 H), 3.46 (s, 3 H), 3.70 (s, 3 H), 4.4–4.80 (m, 1 H), 6.8–7.4 (m, 10 H); *m/e* 445 (parent), 320, 305, 289, and 276 (base).

Anal. Calcd for $C_{27}H_{27}NO_5$: C, 72.79; H, 6.11; N, 3.14. Found: C, 72.69; H, 6.10; N, 3.16.

This same compound could also be formed (73%) by irradiating 8 in 100 ml of benzene through a Pyrex filter sleeve for 1 hr.

X-Ray Crystal Structure Analysis of Dimethyl 2-Cyclohexyl-1,2-dihydro-1-oxo-6-phenyl-2-benzazocine-4,5-dicarboxylate (9). The molecular structure of dimethyl 2-cyclohexyl-1,2-dihydro-1-oxo-6-phenyl-2-benzazocine-4,5-dicarboxylate (9) was unequivocally determined by an X-ray crystal structure analysis. The crystals used in the structure determination were obtained from methanol as needles. The crystal data obtained are a = 7.855 ± 0.002, b = 18.816 ± 0.002 Å, and c = 17.629 ± 0.002 Å, space group P_{21}/C, d_m = 1.268 g/cm^3, d_c = 1.252 g/cm^3, and Z = 4 molecules. The intensities were measured by the stationary technique using balanced Ni Co filters. A General Electric XRD diffractometer was utilized for this purpose. In the range of measurement (0–100 in 2θ), 1721 unique reflections out of a possible number of 2413 had intensities significantly greater than their background counts. These data were corrected for Lorentz and polarization factors of α_1–α_2 splitting. An adjustment for the anisotropy of transmission of X-rays as a function of the angle φ was made as a means of correcting for absorption. The crystal used to collect the data was approximately 0.5 mm along a (which in turn was parallel to the φ axis) and with a 0.1 mm i.d. The $|F$'s$|$ were put on an absolute scale by use of Wilson statistics[29] and then converted to their respective normalized structure factors, $|E$'s$|$. The phases of 236 normalized structure factors, all having values of E greater than 1.6, were determined using the Sayre equation[30] which is the same as the Σ_2 formula of Hauptman and Karle.[31] A program written by Long was utilized for this purpose.[32] An E-Fourier map was calculated from the solution with the highest consistency index (0.69). The whole molecule was recognized from this map. The positional and thermal parameters were refined by least squares using a block-diagonal approximation to the thermal equations. After anisotropic temperature factors were introduced, the usual reliability index (R value) was found to be 0.149. The positions of the hydrogen atoms were found from a three-dimensional Fourier difference synthesis. These atoms were included in the final cycles of least squares and were refined to a final R value of 0.0514. The positional and thermal parameters obtained from the least-squares refinement are given in Tables I and II. (See paragraph at end of paper regarding supplementary material.) A view of the molecule along with the atomic labeling used is shown in Figure 1. There are no intermolecular contacts that suggest forces stronger than normal van der Waals are operative in the crystal.

Irradiation of Dimethyl 2-Cyclohexyl-1,2-dihydro-1-oxo-6-phenyl-2-benzazocine-4,5-dicarboxylate (9). A solution containing 580 mg of 9 in 500 ml of benzene was irradiated through a 450-W Hanovia lamp fitted with a Corex filter sleeve for 4 hr. The solvent was removed under reduced pressure and the residue was subjected to preparative thick layer chromatography using a 1:1 pentane–ether mixture as the eluent. The slowest moving band was identified as *N*-cyclohexylformamide (14%) by comparison with an authentic sample. The band with the second lowest R_f contained 247 mg (43%) of a crystalline solid, mp 155–157°, whose structure is assigned as dimethyl 1-cyclohexyl-1a-2-dihydro-2-oxo-7-phenylbenzo[4,5]cyclohept[1,2-*b*]azirine-8,8*a*(1*H*)-dicarboxylate (11) on the basis of the following data: ir (KBr) 3.43, 5.75, 5.88, 6.98, 7.50, 8.20, 8.60, 8.90, 9.40, 9.70, 11.20, 11.90, 12.40, 13.10, 14.00, and 14.35; uv (methanol) 235 nm (ϵ 3500); *m/e* 445 (parent), 387, 386, 292, and 276 (base); nmr ($CDCl_3$) δ 0.6–2.0 (m, 10 H), 3.16 (s, 3 H), 3.4–3.76 (m, 1 H), 3.8 (s, 3 H), 4.58 (s, 1 H), and 7.0–7.9 (m, 9 H).

Anal. Calcd for $C_{27}H_{27}NO_5$: C, 72.79; H, 6.11; N, 3.40. Found: C, 72.54; H, 6.21; N, 3.40.

The fastest moving band on the thick layer plate contained 100 mg (23%) of a crystalline solid, mp 146–148°, whose structure is assigned as dimethyl 4-phenyl-1-naphthol-2,3-dicarboxylate (10) on the basis of the following data: ir (KBr) 5.73, 6.00, 6.93, 7.13, 7.23, 7.43, 8.03, 9.08, 9.63, 10.16, 12.80, 13.83, and 14.26 μ; uv (methanol) 230 (ϵ 30,400), 240 (36,100) and 345 nm (ϵ 6200); *m/e* 305 (base), 218, and 189; nmr ($CDCl_3$) δ 3.48 (s, 3 H), 3.90 (s, 3 H), 6.8–8.5 (m, 9 H), and 12.18 (s, 1 H).

Anal. Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found: C, 71.26; H, 4.86.

Acid-Induced Rearrangement of Dimethyl 1-cyclohexyl-1a,2-dihydro-2-oxo-7-phenylbenzo[4.5]cyclohept[1,2-*b*]azirine-8,8*a*(1*H*)-dicarboxylate (11). A solution containing 208 mg of 11, 25 ml of a 2 *N* hydrochloric acid solution, and 25 ml of methanol was refluxed for 2 days. After removal of the solvent under reduced pressure, the crude reaction mixture was extracted with ether and washed with water. Removal of the solvent gave 168 mg (84%) of a colorless solid, mp 206–208°, which was assigned as anhydride 12 on the basis of the following data: ir (KBr) 5.60, 5.75, 5.85, 7.03, 8.02, 8.60, 8.72, 9.20, 9.63, 10.10, 10.43, 10.90, 11.13, 13.43, and 14.35 μ; uv (methanol) 273 nm (ϵ 540); *m/e* 431, 400, 387 (base), 350, 262, 250, and 218; nmr ($CDCl_3$) δ 1.0–2.0 (m, 10 H), 3.04 (s, 3 H), 3.76–4.20 (m, 1 H), 4.76 (s, 1 H), 6.25 (s, 1 H), and 6.80–7.60 (m, 9 H).

Anal. Calcd for $C_{26}H_{25}NO_5$: C, 72.37; H, 5.84; N, 3.25. Found: C, 72.08; H, 5.88; N, 3.29.

Thermal Cycloaddition of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Methyl Propiolate. A solution of 0.5 g of 1 and 1.0 g of methyl propiolate was refluxed in 100 ml of xylene for 2 days. The solvent was removed under reduced pressure and the residue was triturated with cold methanol to give 400 mg (67%) of methyl 10-cyclohexyl-8,9-dihydro-9-(cyclohexylimino)-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6-carboxylate (17) on the basis of the following data: mp 147–149°; ir (KBr) 3.43, 3.55, 5.80, 6.10, 7.70, 8.20, 9.10, 10.40, 11.62, 12.70, 12.98, 13.10, 13.40, and 14.20 μ; uv (methanol) 240 nm (ϵ 17,400); nmr ($CDCl_3$) δ 0.6–2.2 (m, 21 H), 3.60 (s, 3 H), 3.60–3.80 (m, 1 H), 5.18 (d, 1 H, J = 2.5 Hz), 6.06 (d, 1 H, J = 2.5 Hz), 7.0–8.20 (m, 9 H); *m/e* 468 (parent), 435, 371, and 359 (base).

Anal. Calcd for $C_{31}H_{32}N_2O_2$: C, 79.45; H, 7.74; N, 5.98. Found: C, 79.25; H, 7.76; N, 5.98.

Photochemical Cycloaddition of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with Methyl Propiolate. A solution containing 500 mg of 1 and 2 ml of methyl propiolate in 500 ml of benzene was irradiated through a Corex filter sleeve for 4 hr. The solvent was removed under reduced pressure and the crude product was chromatographed over 30 g of neutral alumina. The column was eluted with 100 ml of dry hexane followed by a mixture of 5% ethyl acetate–benzene. The first 100-ml fraction contained 100 mg of methyl 10-cyclohexyl-8,9-dihydro-9-(cyclohexylimino)-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6-carboxylate (17), mp 147–149°. The later fractions contained 50 mg (9%) of a solid material, mp 164–166°, whose structure is assigned as methyl 2-cyclohexyl-1,2-dihydro-1-(cyclohexylimino)-6-phenyl-2-benzazocine-5-carboxylate (18) on the basis of the following data: ir (KBr) 3.50, 3.55, 5.85, 6.15, 6.96, 9.15, 11.22, 13.40, and 14.30 μ; uv (methanol) 235 nm (ϵ 22,200); nmr ($CDCl_3$) δ 0.8–2.10 (m, 20 H), 2.4–2.7 (m, 1 H), 3.44 (s, 3 H), 4.16–4.50 (m, 1 H), 5.52 (d, 1 H, J = 8.0 Hz), 6.0 (d, 1 H, J = 8.0 Hz), 6.70–7.30 (m, 9 H); *m/e* 468 (parent), 359 (base), 284, 245, and 217.

Anal. Calcd for $C_{31}H_{31}N_2O_2$: C, 79.45; H, 7.74; N, 5.98. Found: C, 79.41; H, 7.86; N, 6.00.

This same product could be obtained in high yield (62%) from the irradiation of 17 in benzene for 1.5 hr using a 450-W Hanovia lamp equipped with a Corex filter sleeve.

Reaction of Methyl 10-Cyclohexyl-8,9-dihydro-9-(cyclohexylimino)-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6-carboxylate with Sodium Methoxide. A solution containing 218 mg of 17 and 100 mg of sodium in 20 ml of anhydrous methanol was stirred at room temperature for 17 hr. The solvent was removed under reduced pressure and the residue was dissolved in ether and washed with water. Removal of the ethereal layer followed by trituration of the residue with pentane gave 154 mg (66%) of a white crystalline solid, mp 136–138°, whose structure is assigned as the Michael adduct 19: ir (KBr) 5.80, 6.10, 6.90, 7.50, 10.80, 11.20, 12.70, 13.23, 14.15 μ; uv (cyclohexane) 247 nm (ϵ 17,300); nmr ($CDCl_3$) δ 0.6–2.40 (m, 21 H), 3.30 (s, 3 H), 3.36 (s, 3 H), 3.88 (d, 1 H, J = 4.0 Hz), 4.22 (d, 1 H, J = 4.0 Hz), 3.6–4.0 (m, 1 H), 4.68 (s, 1 H), and 6.44–8.24 (m, 9 H); *m/e* 468, 372, 302, 116, and 85 (base).

Anal. Calcd for $C_{32}H_{40}N_2O_3$: C, 76.76; H, 8.05; N, 5.60. Found: C, 76.63; H, 8.03; N, 5.65.

Acid Hydrolysis of Methyl 10-Cyclohexyl-8,9-dihydro-9-(cyclohexylimino)-5-phenyl-5H-benzocyclohept-5,8-imine-6-carboxylate. A solution containing 312 mg of 17 in 2 ml of benzene was chromatographed through a column containing 30 g of

alumina (acid-washed Merck) using benzene as the eluent. The main fraction contained 200 mg (78%) of methyl 10-cyclohexyl-8,9-dihydro-9-oxo-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6-carboxylate (**20**) as white needles: mp 129–131°; ir (KBr) 3.45, 3.53, 5.80, 5.88, 6.20, 6.92, 7.75, 8.03, 8.28, and 9.12 μ; uv (methanol) 235 nm (ϵ 14,500); nmr ($CDCl_3$) δ 0.6–2.0 (m, 11 H), 3.64 (s, 3 H), 4.56 (d, 1 H, J = 2.5 Hz), 7.08 (d, 1 H, J = 2.5 Hz), and 7.10–8.0 (m, 9 H); *m/e* 387 (parent), 328, 305, 278, and 246 (base).

Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.62. Found: C, 77.40; H, 6.56; N, 3.59.

This same product could also be formed by treating **17** with aqueous hydrochloric acid in methanol.

Reaction of Methyl 10-Cyclohexyl-8,9-dihydro-9-oxo-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6-carboxylate with Sodium Methoxide. A solution containing 178 mg of **20** and 60 mg of sodium in 100 ml of anhydrous methanol was stirred at room temperature for 4.5 hr. The solution was diluted with water and extracted with ether. After removal of the dried ethereal solution, the residue was triturated with pentane to give 137 mg (71%) of a yellow crystalline solid, mp 123–125°, whose structure is assigned as Michael adduct **23** on the basis of the following data: ir (KBr) 5.75, 5.85, 6.25, 7.95, 8.50, 9.90, 10.40, 12.55, and 14.10 μ; uv (methanol) 245 (ϵ 13,400) and 290 nm (ϵ 200); nmr ($CDCl_3$) δ 0.64–1.68 (m, 10 H), 2.04–2.24 (m, 1 H), 3.32 (s, 3H), 3.36 (s, 3 H), 3.92 (d, 1 H, J = 5.0 Hz), 4.08 (s, 1 H), 4.27 (d, 1 H, J = 5.0 Hz) and 6.52–8.04 (m, 9 H); *m/e* 116, 101, 87, and 85.

Anal. Calcd for $C_{26}H_{29}NO_4$: C, 74.44; H, 6.97; N, 3.34. Found: C, 74.24; H, 6.96; N, 3.29.

Thermal Rearrangement of Methyl 10-Cyclohexyl-8,9-dihydro-9-oxo-5-phenyl-5*H*-benzocyclohepten-5,8-imine-6-carboxylate. A solution containing 170 mg of **20** in 40 ml of toluene was refluxed for 3.5 hr. The solvent was removed under reduced pressure and the residue was triturated with pentane to give a nearly quantitative yield of methyl 2-cyclohexyl-1,2-dihydro-1-oxo-6-phenyl-2-benzazocine-5-carboxylate (**21**): mp 146–149°; ir (KBr) 5.85, 6.10, 6.95, 7.10, 7.55, 8.65, 9.20, 11.15, 13.32, and 14.15 μ; uv (95% ethanol) 275 nm (ϵ 8500); nmr ($CDCl_3$) δ 0.7–2.00 (m, 10 H), 3.44 (s, 3 H), 4.3–4.6 (m, 1 H), 6.0–6.2 (AB q, 2 H, J = 8.0 Hz), and 7.0–7.3 (m, 9 H); *m/e* 387, 328, 305, 278, 250, and 246 (base).

Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.62. Found: C, 77.62; H, 6.56; N, 3.45.

This same product was also formed in high yield (73%) by irradiating a benzene solution of **20** through a Pyrex filter sleeve with a 450-W Hanovia lamp.

Irradiation of Methyl 2-Cyclohexyl-1,2-dihydro-1-oxo-6-phenyl-2-benzazocine-5-carboxylate. A solution containing 95 mg of **21** in 120 ml of benzene was irradiated through a Corex filter using a 450-W Hanovia lamp for 1.5 hr. The solvent was removed under reduced pressure and the residue was subjected to thick layer chromatography. The plate was developed using a 1:1 mixture of pentane and ether. The slowest moving band on the thick layer plate was extracted with ether to give 57 mg (61%) of a white crystalline solid, mp 161–163°. The structure of this material is assigned as methyl 1-cyclohexyl-1*a*,2-dihydro-2-oxo-7-phenylbenzo[4.5]cyclohept[1,2-*b*]azirine-8(1*H*)-carboxylate (**22**) on the basis of the following information: ir (KBr) 3.40, 5.73, 5.93, 6.90, 7.12, 8.05, 9.80, 10.65, 12.55, 12.85, 13.12, and 14.25; uv (methanol) 275 nm (ϵ 570); nmr ($CDCl_3$) δ 0.6–2.0 (m, 10 H), 3.24 (s, 3 H), 3.40–3.76 (m, 1 H), 3.42 (d, 1 H, J = 6.0 Hz), 3.98 (d, 1 H, J = 6.0 Hz), 6.8–7.6 (m, 9 H); *m/e* 387 (parent), 328, 262 (base), and 250.

Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.62. Found: C, 77.19; H, 6.58; N, 3.65.

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Supplementary Material Available. The positional and thermal parameters obtained from the least-squares refinement (Tables I and II) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 m, 24× reduction; negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-75-175.

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