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Photochromism in the Arylaroylaziridine System (1,2,3)

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Photochromism of a number of arylaroylaziridines has been observed in the solid state or in the rigid matrix. The photochromic behavior is dependent on the intensity of the incident radiation, the reaction medium, the wavelength of light used and on the relationship of the substituents on the three-membered ring. From the visible absorption spectra it is clear that cis-arylaroylaziridines give different colored species than do the trans isomers. These results suggest that the coloration is due to an extensive electrical interaction between the bent bonds of the aziridine ring and the π orbitals of the benzoyl and phenyl groups. Attempts to trap the colored species by co-irradiation with substrates containing a multiple bond failed. A reaction has been found to occur upon heating various arylaroylaziridines with dimethylacetylene dicarboxylate in inert solvents.

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 (4, 5). Although these systems have been the subject of valuable and penetrating mechanistic investigations, there are still many gaps in our understanding of this phenomenon (6). The photochromic behavior of small ring carbonyl compounds has received little attention, perhaps because there are relatively few reports of photochromic activity in these systems. In connection with a study of the photochemical transformations of 2-benzoylaziridines (7), we noticed that these compounds developed a slight pink tinge of color on standing in the solid form at room temperature. Since arylaroylaziridines were readily accessible and were the only small ring carbonyl compounds which had been subjected to even a limited study in regard to their color-forming properties, this class of compounds was chosen for the present investigation.

The photoinduced reversible color changes in the arylaroylaziridine system was first described by Cromwell and coworkers (9,10) who reported that exposure of 1-benzyl and 1-cyclohexyl-2-phenyl-3-benzoylaziridine to diffuse daylight resulted in the rapid formation of a deep pink color, and that this pink coloration faded on standing in the dark. Re-investigation of the properties of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (I) confirmed these observations. The red species formed on heating or on ultraviolet irradiation of the solid compound proved to be very sensitive to numerous solvents. Addition of a few drops of solvent immediately discharged the red coloration. All attempts to generate this colored species by carrying out the irradiation

in a mobile solvent failed. Intensely colored solutions could be developed, however, by irradiation of the solid in a frozen glass at 77°K with filtered (310-390 mμ) light from a high pressure mercury arc. The color intensity attained by irradiation proved to be very dependent on both the stereochemistry of the aziridine and on the wavelength of light used. On irradiation in a hydrocarbon glass (1:1-methylcyclohexane-3-methylpentane) at 77°K with 310-390 mμ light, the trans aziridine (I) turned pink and on continued irradiation it became orange. With light of wavelength greater than 345 mμ it turned orange initially. Although the colors faded completely on warming, the orange species seemed to fade slightly slower than the red and became nearly yellow before fading completely. No fading due to visible light (>390 mμ) was observed. cis-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (II) also became colored but at least ten times slower than the trans isomer. In a 1:1-ethanol-ether glass at 77°K the trans-aziridine turned yellow on irradiation with 310-390 mμ light and at a greater rate than in the hydrocarbon glass. On warming, fading again occurred. The cis-isomer also turned yellow in this glass but again at a lower rate. No phosphorescence of either the cis or trans-benzoylaziridine was observed.

The photostationary state concentration of the colored species formed appears to be dependent on the intensity of the incident radiation, the reaction medium, the wavelength of the light used and on the relationship of the substituents on the three-membered ring. Although the physical property of primary concern in this photochromic system is the marked color change, other physical properties of the system may also be altered. In order to identify the colored species produced, attempts were made

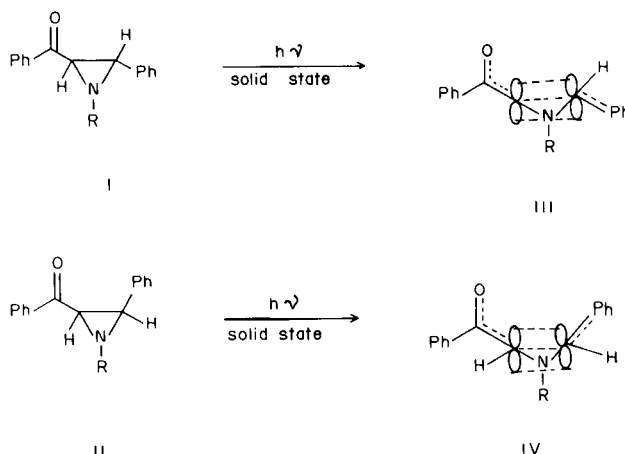to follow its formation by spectroscopic methods.

Recently, Pitts has demonstrated the feasibility of qualitative and quantitative studies of solid-state chemical reactions in pressed alkali halide disks of the type customarily used for infrared analysis (10,11). Since the photochromic activity of the arylaroylaziridine appeared to be important only in the solid state or in a frozen glass, it seemed that the "pellet" technique would be a simple and convenient method for qualitative study of the structure of the colored species produced on irradiation. When a typical potassium bromide pellet containing 0.18 mole % of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (I) was exposed to light at 3650 Å, the pellet turned deep pink. The pink coloration faded on standing in the dark for several hours. The infrared spectrum of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine was insignificantly affected by irradiation, a result which suggests that the photostationary state concentration of the colored species is too small to be detected by infrared spectroscopy. Similarly, no detectable changes in the infrared spectrum of the cis isomer (II) were observed on irradiation in a potassium bromide pellet, even though a marked coloration of the pellet occurred.

Since infrared spectroscopy was not sensitive enough to detect the extremely low steady state concentration of the colored material, an attempt was made to record the transient absorption spectrum of this species in the visible region. Brief irradiation (3-5 minutes) of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine in a frozen glass at 77°K produced the colored species which displayed a single absorption maximum in the visible spectrum at 475 mμ. Since the preparation of solutions of known concentrations of the colored species was not feasible, it was necessary to determine its concentration by indirect means. The extinction coefficient of the colored material was estimated by irradiation of the arylaroylaziridine in the glass, rapidly scanning the spectrum in both the ultraviolet and visible region and noting the decrease in the optical density of the arylaroylaziridine in the ultraviolet range (12). On the assumption that the decrease in concentration of the arylaroylaziridine was equal to the increase in concentration of the colored form it was possible to estimate its extinction coefficient. The resulting absorption maxima and extinction coefficients for a number of different arylaroylaziridines are summarized in Table I.
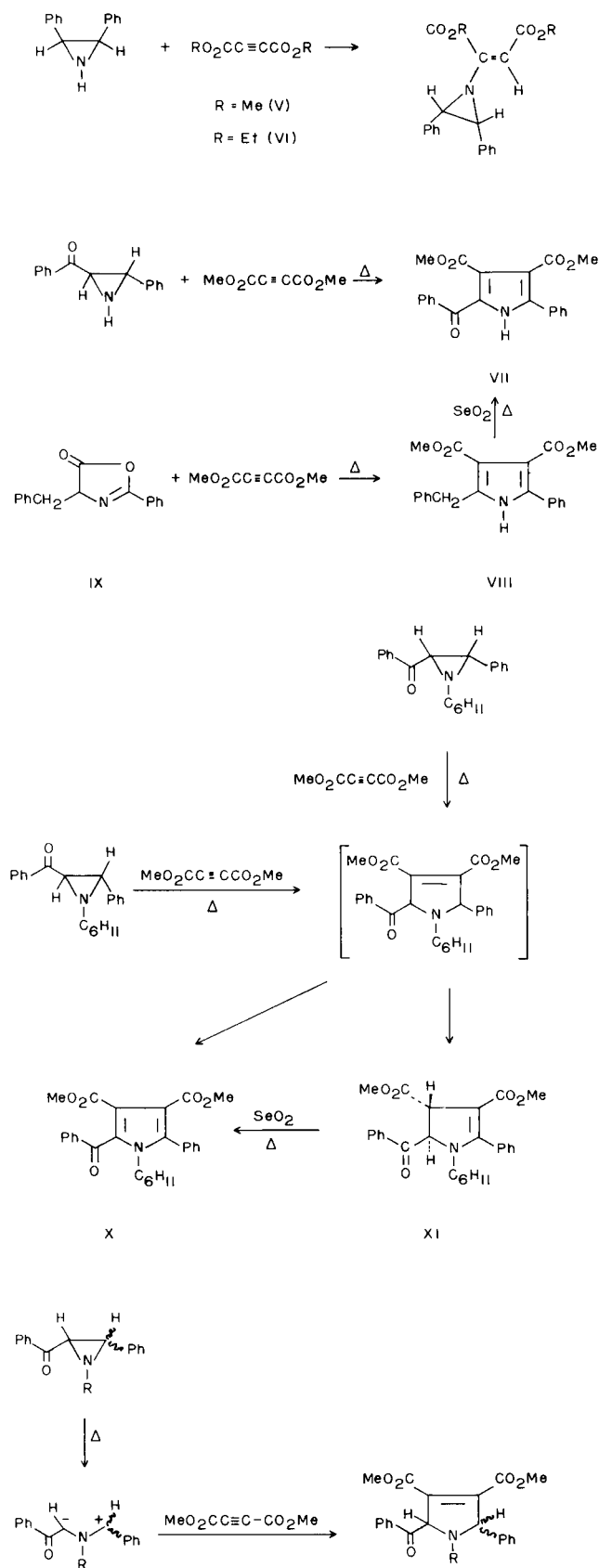
It is obvious from the absorption spectra that the cis compounds give different colored species than do the trans-compounds. The colored material formed from irradiation of the cis-isomers absorb at a somewhat lower wavelength and with less intensity than do the trans-compounds. There is only a small solvent effect on the spectra of the colored species compared to what might be expected if the transitions had very large moments (e.g. charge transfer transitions). On changing to the more polar glass the absorption band in the cis series moved to longer wavelengths while that in the trans series moved to shorter wavelengths. The rates of formation and disappearance of the colored species in both series were different. Also, the rate of formation of the colored form for both isomers was unchanged in a glass containing 40% isoprene. This indicates that either the triplet state of the arylaroylaziridine is not involved or that it rearranges within about 10-11 seconds (13).

From these results we conclude that the magnitude of the molar absorptivity and the position of the absorption maximum of the colored species is dependent on the initial disposition of the carbonyl group and the three-membered ring. The position of the absorption maximum in the visible region suggests that there is an extensive electrical interaction between the bent bonds of the aziridine ring and the π orbitals of the benzoyl and phenyl groups. It is difficult, however, to describe clearly by structural formulas the nature of this electronic interaction which ultimately leads to the formation of the colored material. The modified Lewis structures shown below are used to describe pictorially the resonance representations of such electronic interactions.

[chemical scheme: structure I (Ph-CO-aziridine with H, Ph, H, N-R substituents) → hν, solid state → structure III; structure II → hν, solid state → structure IV]

I   III

II   IV

The above representations (i.e., III and IV) differ in their spatial arrangement which in turn affects the degree of orbital overlap of the bent bonds of the small ring with the π orbitals of the attached groups. The differences in the spectra observed may be rationalized in a manner similar to that suggested by Cromwell (14,15) and Padwa (16) to account for the ultraviolet absorption spectra of the two stereoisomers in the arylaroylaziridine system. The variation in color and absorption maximum is probably associated with the electrical vibrations and resonance in an excited state of the entire small ring system which, in the cis isomer, has increased difficulty in obtaining orbital overlap and delocalization (14). The trans arrangement

$$\text{(aziridine)} + RO_2CC \equiv CCO_2R \longrightarrow \text{(product)}$$

R = Me (V)
R = Et (VI)

$$\text{(ketoaziridine)} + MeO_2CC \equiv CCO_2Me \xrightarrow{\Delta} \text{VII}$$

$$\text{VII} \xleftarrow{SeO_2 \uparrow \Delta}$$

$$\text{IX} + MeO_2CC \equiv CCO_2Me \xrightarrow{\Delta} \text{VIII}$$

$$MeO_2CC \equiv CCO_2Me \downarrow \Delta$$

$$\xrightarrow{MeO_2CC \equiv CCO_2Me} \xrightarrow{\Delta}$$

X $\xleftarrow{SeO_2 \; \Delta}$ XI

$$\downarrow \Delta$$

$$\xrightarrow{MeO_2CC \equiv C-CO_2Me}$$

provides for a more extensive polycentric molecular orbital than is possible with the more sterically hindered cis isomer and accounts for the larger molar absorptivity and longer wavelength of the colored species in this series.

On the assumption that III and IV represent the correct structures for the colored material, attempts were made to trap them. Since these structures are closely related to 1,3-dipolar intermediates, it seemed reasonable to trap them with an unsaturated system. It was felt that, since the preparation of five-ring heterocycles by 1,3-dipolar additions to multiple bonds is a general reaction for a large number of 1,3-dipolarophiles (17,18), this would provide additional evidence for the intermediacy of III and IV. Experiments designed to trap the colored species at low temperatures in the presence of dimethylacetylene dicarboxylate, 2,5-diphenyl-3,4-isobenzofuran, cyclohexene or with substituted butadienes were unsuccessful. Failure to detect a reaction under these conditions, however, does not necessarily reject III or IV as the structure of the colored material. The lack of reaction may be due to partial 1,3-bonding which markedly retards the reactions at the low temperatures employed.

Detailed clarification of the structure of the colored species produced upon irradiation or arylaroylaziridines has proved to be difficult because of the low steady state concentration and apparent unreactivity at the low temperatures employed. With these difficulties in mind, we considered it desirable to carry out the trapping experiments at higher temperatures. At the time we began this study there were no reports in the literature which described the thermal reaction of aziridines with various alkenes and alkynes (3). Since the commencement of this work, other aziridines were subsequently reported to form adducts with various multiple bonds by carbon-carbon cleavage of the aziridine ring (3,19,20).

The reaction initially examined was the treatment of cis-2,3-diphenylaziridine with dimethylacetylene dicarboxylate in refluxing benzene. At the time, it was hoped that the reaction would serve as a suitable model for comparison with the arylaroylaziridines to be used. Refluxing equimolar ratios of cis-2,3-diphenylaziridine and dimethylacetylene dicarboxylate in benzene for 12 hours results in the formation of an adduct (V) in 85% yield. The structure of V was assigned as dimethyl 2-[1-(2,3-diphenylaziridyl)] maleate on the basis of the analytical and spectral data. Diphenylaziridine also forms an analogous adduct VI with diethylacetylene dicarboxylate. The stereochemistry of the reaction product obtained has been assigned as the cis-diester by analogy with Dolfini's results (21). In the presence of a nonprotic solvent, the initially formed zwitterion would be expected to undergo stereospecific collapse via intramolecular protonation, leading to the cis-disposition of the ester functions.

The reaction course followed by refluxing *trans*-2-phenyl-3-benzoylaziridine with dimethylacetylene dicarboxylate in xylene for 18 hours proved to be dramatically different. The reaction product obtained in this case (80%) was identified as 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (VII). The structure of VII was elucidated by elemental analysis, infrared, ultraviolet, n.m.r., and independent synthesis. An authentic sample of 2-benzyl-3,4-dicarbomethoxy-5-phenylpyrrole (VIII), prepared by heating 2-phenyl-4-benzyl-5-oxazolone (IX) (22) with dimethylacetylene dicarboxylate followed by selenium dioxide oxidation, was identical to VII with respect to the infrared spectrum and melting point.

The mechanistic nature of the transformation was further elucidated by examination of the reaction of dimethylacetylene dicarboxylate with *cis* and *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridine. In this case, dimethylacetylene dicarboxylate was observed to react with either *cis* or *trans* aziridine to form two products in high yield. These adducts are assigned structures X (m.p., 140-141°) and XI (m.p., 155-156°). The assignments are supported by elemental analysis, n.m.r. data, and analogy with other aziridine reactions, and they are consonant with the observed ultraviolet data.

The stereochemistry of XI was determined from the n.m.r. spectrum. The coupling constants are consistent with the Karplus correlation (23) and the observed values are in good agreement with those calculated by applying the Karplus equation to the dihedral angles measured on Dreiding models (24). The n.m.r. of a substituted 3-pyrroline would not have had as large a coupling constant as that observed (26). Interestingly, adduct XI is markedly resistant to further oxidation. Heating XI with iodine in toluene or with palladium on charcoal in *p*-cymene resulted in recovered starting material. Only when XI was heated with selenium dioxide at 200° in a sealed tube was oxidation achieved. The stability of this adduct and the n.m.r. data are the major reasons for our current preference for the postulation of a *trans* relationship of the hydrogens as opposed to a *cis* relationship. It is easier to account for the fact that the oxidation of a *trans* species is more formidable than that of the *cis*, as the geometry of the *cis* isomer would appear to be more conducive for elimination of molecular hydrogen.

The formation of the 2-pyrroline in high yield is of interest since in the related reaction of triarylaziridines with dimethylacetylene dicarboxylate only 3-pyrrolines were isolated. The data therefore suggest that X is not derived from XI but rather results from the initially-formed 3-pyrroline. Under the reaction conditions, the initial adduct may either rearrange to XI or lose hydrogen to give the substituted pyrrole. The formation of the transient 3-pyrroline can be rationalized by the assumption

that the initial step in the reaction involves cleavage of the carbon-carbon bond of the aziridine ring and the formation of a 1,3-dipolar intermediate (XII) which subsequently adds to the unsaturated substrate. This is consistent with the finding that *cis*-2,3-diphenylaziridine undergoes Michael addition as opposed to carbon-carbon cleavage. In this case the formation of a 1,3-dipolar intermediate would be expected to be difficult as the developing carbanion is not stabilized to the same degree as is possible in the arylaroylaziridine case.

On the basis of our studies it seems reasonable to conclude that 1,3-dipolar intermediates are involved in the addition of arylaroylaziridines to dimethylacetylene dicarboxylate (27). Since it seems necessary to invoke a similar species to explain the photochromic activity of these small rings, one can assume that more than one kind of 1,3-dipolarophile is involved. The main difference between dipolarophile XII and dipolarophile III (or IV) is a matter of the degree of overlap of the carbon atoms of the three-membered ring. Dipolarophile III is stabilized by overlap of the developing carbanion adjacent to the benzoyl group with the similarly developing carbonium ion adjacent to the phenyl ring. This interaction allows for an extensive polycentric molecular orbital that exhibits a pronounced coloration but which is relatively unreactive in the matrix. Dipolarophile XII on the other hand, is essentially devoid of this overlap and is expected to have a lower 1,3-bond order thereby accounting for its enhanced reactivity. Alternatively, it may be argued that at the higher temperatures the ionized state of the entire small-ring system is capable of addition to the multiple bond whereas this is not possible in the matrix at low temperatures and instead, an increase in the steady state concentration of the dipolarophile is observed.

TABLE I

Visible Absorption Spectral Maxima For Colored Species Produced Upon Irradiation of Arylaroylaziridines at 77°K (a,b)

Compound	Glass	λ max, mμ	ε
cis-1-Cyclohexyl-2-phenyl 3-benzoylaziridine	EA (c)	475	1 x 10³
	3MP (d)	463	1 x 10³
trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine	EA	493	1.4 x 10⁴
	3MP	498	1.4 x 10⁴
cis-1-benzyl-2-phenyl-3-benzoylaziridine	EA	475	1 x 10³
trans-1-benzyl-2-phenyl-3-benzoylaziridine	EA	485	1 x 10⁴
cis-1-benzyl-2-phenyl-3-*p*-toluylaziridine	EA	475	1 x 10³
trans-1-benzyl-2-phenyl-3-*p*-toluylaziridine	EA	486	1.4 x 10⁴

(a) Irradiation of the rigid matrix at 77°K was carried out with filtered light (3130 A°) from a high pressure mercury arc. (b) Aziridine concentration was approximately 10^{-3} M. (d) 1:1 Ethanol-ether glass. (d) 3-Methylpentane glass.

EXPERIMENTAL

Dimethyl 2-[1-(2,3-Diphenylaziridyl)] Maleate (V).

A solution of 0.15 g. of cis-diphenylaziridine (28) and 0.08 g. of dimethylacetylene dicarboxylate in 10 ml. of benzene was refluxed for 12 hours. The solvent was removed in vacuo to give a yellow oil which was chromatographed on a 1.5 x 40 cm. alumina (Woelm, neutral, grade 3) column. The column was eluted with 500 ml. of 30% benzene-hexane. The eluent, in 50 ml. fractions, was concentrated and dried in vacuo. Fractions 5-10 contained 117 mg. of a white solid, m.p. 90-95°. Recrystallization from methanol afforded pure dimethyl 2-[1-(2,3-diphenylazirdyl)] maleate (V), m.p. 94-95°.

Anal. Calcd. for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.11; H, 5.85; N, 4.32.

The infrared spectrum shows two strong carbonyl bands at 5.70 and 5.80 μ and a series of sharp bands at 6.18, 6.86, 6.95, 7.06, 7.27, 7.37, 8.90, 9.56 and 11.62 μ. The ultraviolet spectrum in 95% ethanol exhibited a maximum λ max at 262 mμ (ε, 21,800). The n.m.r. spectrum is in excellent agreement with the structure. There is a multiplet centered at τ 2.85, a singlet at 4.45, a singlet at 6.20, a singlet at 6.29, and a singlet at 6.33. The peak areas are in the ratio of 10:1:3:2:3.

Diethyl 2-[1-(2,3-Diphenylaziridyl)] Maleate (VI).

cis-2,3-Diphenylaziridine (492 mg.) and diethylacetylene dicarboxylate (453 mg.) were dissolved in 25 ml. of benzene and the solution was refluxed for 12 hours. After cooling, the solution was evaporated to dryness to give an orange oil. The crude residue was chromatographed on a 1.5 x 50 cm. alumina (Woelm, neutral, grade 3) column. After elution of small amounts of material with 500 mg. of 10% benzene-hexane, 857 mg. (88%) of a colorless oil was eluted with 350 ml. of 90% benzene-hexane. The oil solidified on standing and recrystallization from methanol gave white, crystalline material, m.p. 71-72°.

Anal. Calcd. for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.22; H, 6.19; N, 4.01.

The infrared spectrum of this material showed intense absorption at 5.80, 6.18, 8.00, 8.35, 8.65, 9.00, and 9.60 μ. The ultraviolet spectrum (95% ethanol) has λ max 265 mμ (ε, 19,700). The n.m.r. spectrum in carbon tetrachloride shows a multiplet at τ 2.86, a singlet at 4.47, a quartet centered at 5.79, a singlet at 6.29 and a triplet centered at 8.83. The peak areas are in the ratio of 10:1:4:2:6.

2-Benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (VII).

A mixture of 223 mg. of trans-2-phenyl-3-benzoylaziridine (29) and 142 mg. of dimethylacetylene dicarboxylate in 25 ml. of xylene was heated to reflux for 18 hours. Evaporation of the solvent left 374 mg. of a yellow oil which was chromatographed on a column of florisil. The first fractions obtained with 3% ethyl acetate-benzene gave 290 mg. (80%) of a white solid, m.p. 153-160°. Recrystallization from hexane-benzene afforded a crystalline solid, m.p. 159-160°. The structure of this adduct was determined to be 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (VII) on the basis of the following data.

Anal. Calcd. for $C_{21}H_{17}NO_5$: C, 69.41; H, 4.72; N, 3.86. Found: C, 69.18; H, 4.82; N, 3.86.

The infrared spectrum had bands at 3.03, 5.81, 6.14, 7.93, 8.10, 12.69, 13.06, 13.57, 14.36 μ. The ultraviolet spectrum in 95% ethanol had maxima at 246 mμ (ε, 17,000) and 312 mμ (ε, 11,700).

Structure VII was further confirmed by its unequivocal synthesis from 2-phenyl-4-benzyl-5-oxazolone and dimethylacetylene dicarboxylate. 2-Phenyl-4-benzyl-5-oxazolone (IX) was prepared by the method of Mohr and Stroschein (29). A solution containing 13.8 g. of d,l-benzoyl phenylalanine in 130 ml. of acetic anhydride was heated at 100° for 1 hour. Concentration of the solution left an oil which was crystallized from 100 ml. of hexane to give 11.5 g. (90%) of a crystalline solid, m.p. 69-70° (lit. (29) m.p. 69-70°).

A mixture of the above 2-phenyl-4-benzyl-5-oxazolone (500 mg.) and dimethylacetylene dicarboxylate (284 mg.) was heated in a sealed tube at 160° for 5 hours. The impure material dissolved in benzene, was chromatographed on a 2.5 x 91 cm. column of florisil slurry packed in benzene. The column was eluted with 1 l. of 1% ethyl acetate-benzene, 500 ml. of 2% ethyl acetate-benzene, and 750 ml. of 3% ethyl acetate-benzene. The eluent, in 50 ml. fractions, was concentrated and dried in vacuo. The crystalline solid from elution with 3% ethyl acetate-benzene (0.71 g., 93%) was identified as 2-benzyl-3,4-dicarbomethoxy-5-phenylpyrrole (VIII) on the basis of the following data. Recrystallization of the crude solid from ethanol

afforded crystals, m.p. 132-133°.

Anal. Calcd. for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.11; H, 5.56; N, 4.15.

The infrared spectrum showed intense absorption bands at 3.10, 5.85, 8.15, 9.13, 12.80, 12.95, and 14.30 μ. The ultraviolet spectrum in 95% ethanol had a maximum at 278 mμ (ε, 14,800).

A mixture of 150 mg. of the above pyrrole (VIII) and 90 mg. of selenium dioxide was heated in a sealed tube at 200° for 20 minutes. The crude residue was recrystallized from hexane-benzene to give 140 mg. (90%) of 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole (VII), m.p. 159-160°. The infrared, ultraviolet, and n.m.r. spectra of this material were identical in every detail with those of 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole prepared from the thermal reaction of trans-2-phenyl-3-benzoylaziridine and dimethylacetylene dicarboxylate. The mixture melting point of these two materials was undepressed at 159-160°.

1-Benzyl-2-o-toluyl-3,4-dicarbomethoxy-5-phenylpyrrole.

A solution containing 327 mg. of cis-1-benzyl-2-p-toluyl-3-phenylaziridine (30) and 142 mg. of dimethyl acetylenedicarboxylate in 25 ml. of benzene was refluxed for 17 hours. The solvent was removed in vacuo to give a yellow oil which was chromatographed on a 1.5 x 40 cm. florisil column. The column was eluted with 650 ml. of 2% ethyl acetate-benzene. The eluent, in 50 ml. fractions, was concentrated and dried in vacuo. Fractions 6-11 contained 400 mg. (84%) of a white solid, m.p. 126-130°. Recrystallization from methanol afforded pure 1-benzyl-2-p-toluyl-3,4-dicarbomethoxy-5-phenylpyrrole, m.p. 130-131°.

Anal. Calcd. for $C_{29}H_{25}NO_3$: C, 74.50; H, 5.39; N, 3.00. Found: C, 74.54; H, 5.42; N, 3.08.

The infrared spectrum showed strong absorption at 5.78, 6.09, 8.25, 10.80, 12.10, 13.30, and 14.40 μ. The ultraviolet spectrum (95% ethanol) has maxima at 260 mμ (ε, 16,700) and at 305 mμ (ε, 11,300). The n.m.r. spectrum (deuteriochloroform) of the adduct shows a multiplet centered at τ 2.65, a singlet at 4.72, a singlet at 6.42, a singlet at 6.78, and a singlet at 7.67. The peak areas are in the ratio of 14:2:3:3:3.

Reaction of cis and trans 1-Cyclohexyl-2-benzoyl-3-phenylaziridine with Dimethylacetylene Dicarboxylate.

trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (31) (300 mg.) and dimethylacetylene dicarboxylate (142 mg.) were dissolved in 50 ml. of benzene and the solution was refluxed for 12 hours. After cooling, the solution was evaporated to dryness to give an orange oil. The crude residue was chromatographed on a 2.5 x 91 cm. florisil column (32). The column was eluted with 1 liter of 1% ethyl acetate-benzene, 500 ml. of 2% ethyl acetate-benzene, and 600 ml. of 3% ethyl acetate-benzene. The eluent, in 50 ml. fractions, was concentrated and dried in vacuo. The crystalline solid from elution with 2% ethyl acetate-benzene amounted to 320 mg., m.p. 134-140°. Recrystallization from hexane-benzene afforded white, crystalline material, m.p. 140-141°.

Anal. Calcd. for $C_{27}H_{27}NO_5$: C, 72.79; H, 6.11; N, 3.14. Found: C, 72.73; H, 6.14; N, 3.10.

The infrared spectrum (potassium bromide) of this material showed strong absorption at 5.78, 6.05, 8.02, 8.25 and 8.62 μ. The ultraviolet spectrum (95% ethanol) had λ max at 252 mμ (ε, 21,900) and λ max at 302 mμ (ε, 5,500). The n.m.r. spectrum (deuteriochloroform) shows a multiplet at τ 2.33, a singlet at 6.42, a singlet at 6.70, and a multiplet centered at 8.67. The peak areas are in the ratio of 10:3:3:11. The spectral evidence indicates that this compound is 1-cyclohexyl-2-phenyl-3,4-dicarbomethoxy-5-benzoylpyrrole (X).

On further elution with 3% ethyl acetate-benzene, 120 mg. of a yellow crystalline solid, m.p. 155-156°, was obtained. This material was assigned structure XI, 1-cyclohexyl-2-phenyl-3,4-dicarbomethoxy-5-benzoyl-2-pyrroline on the basis of physical and chemical data cited below.

Anal. Calcd. for $C_{27}H_{29}NO_5$: C, 72.46; H, 6.53; N, 3.13. Found: C, 72.27; H, 6.52; N, 2.95.

The infrared spectrum shows two strong carbonyl bands at 5.78 and 6.05 μ and a series of sharp bands at 6.37, 7.91, 8.23, 8.45, and 8.57 μ. The ultraviolet spectrum (95% ethanol) has maxima at 255 mμ (ε, 15,600) and 303 mμ (ε, 16,350). The n.m.r. spectrum (chloroform) shows the aromatic hydrogens as a multiplet centered at τ 2.55, the methyl protons as singlets at 6.18 and 6.63, the methine protons as a pair of doublets at 5.15 and 6.42 (J = 4 cps) and the cyclohexyl protons as a complex multiplet centered at 8.67. The peak areas are in the ratio of 10:3:3:1:1:11.

A mixture of 200 mg. of the above 2-pyrroline (XI) and 100 mg. of selenium dioxide was heated in a sealed tube at 200° for 20 minutes.

The crude residue was recrystallized from hexane-benzene to give 168 mg. (84%) of 1-cyclohexyl-2-phenyl-3,4-dicarbomethoxy-5-benzoyl-pyrrole (X). The infrared spectrum of this material was identical in every detail with that of a sample of X. The mixture melting point of these two materials was undepressed at 139-140°.

Attempted Trapping of the Colored Species Formed by Irradiation of an Arylaroylaziridine.

Attempts to trap the hypothetical 1,3-dipolarophile by co-irradiation of the arylaroylaziridine with acetylene, dienes and olefins were unsuccessful. In a typical experiment, a clear pyrex plate (4 x 8 x 1/16") was thoroughly sprayed with a methylene chloride solution containing the arylaroylaziridine and dimethylacetylene dicarboxylate. Evaporation of the solvent left a thin layer of both compounds on the plate. The resulting plate was exposed to a high pressure mercury arc (Hanovia, Type L-450 watts) for 10 minutes. After irradiation, the initial colorless layer had turned deep pink. Chromatography of the mixture on a florisil column gave a 93% yield of recovered aziridine.

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