1-Phenyl-1-azaspiro[2.2]pentanes. Synthesis and Reactions[1a]

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Phenyl azide adds to methylenecyclopropanes **2a–c** to produce the corresponding triazolines, which are photochemically converted to azaspiropentanes **1a–c**. These novel heterocycles isomerize to imines **5a–c**; the first two add methanol to yield **7a** and **7b**. Azaspiropentane **1a** also adds HCl to generate chloride **6a**, which can be reconverted to **1a** by the DMSO anion. Pyrolysis of **1a** leads to **5a** and *N*-phenylketenimine. The same products are obtained from vapor phase pyrolysis of its triazoline precursor. Benzene-sensitized irradiation of **1a** also gives **5a**. These reactions are discussed in mechanistic terms.

Substantial recent interest has focused on the synthesis and characterization of heterocyclic analogs of various highly strained, small-ring hydrocarbons. Several laboratories have reported upon oxaspiropentanes in recent years[2] and examples of a thiaspiropentane[3] and dioxaspiropentanes[4] are known. The synthesis of 2-phenyl-1-azaspiro[2.2]pent-1-ene is briefly mentioned in the literature,[5] but this novel unsaturated azaspiropentane derivative constitutes the only example of this structural type previously described. The present report details our studies of this heterocyclic system.[6]

The key step of our synthetic approach to **1a–c** exploits the well-known photochemical ring contraction of the appropriate triazolines.[7] The requisite triazolines were obtained from the thermal addition[7] of phenyl azide to methylenecyclopropanes **2a–c**. The adducts were obtained as sharply melting, crystalline solids whose nmr spectra confirmed their homogeneity and gross structure. The tentative assignment of structures **3a–c** is based upon the general observation that the substituent-bearing nitrogen of phenyl azide ordinarily bonds to the olefinic carbon best able to bear positive charge.[7] Nonetheless, alternate structures **4a–c** which would result from the alternate mode of addition cannot be rigorously excluded on the basis of the available data. This ambiguity is of little practical consequence, however, since the photochemical expulsion of nitrogen from either of the triazoline isomers should lead to the desired azaspiropentanes.

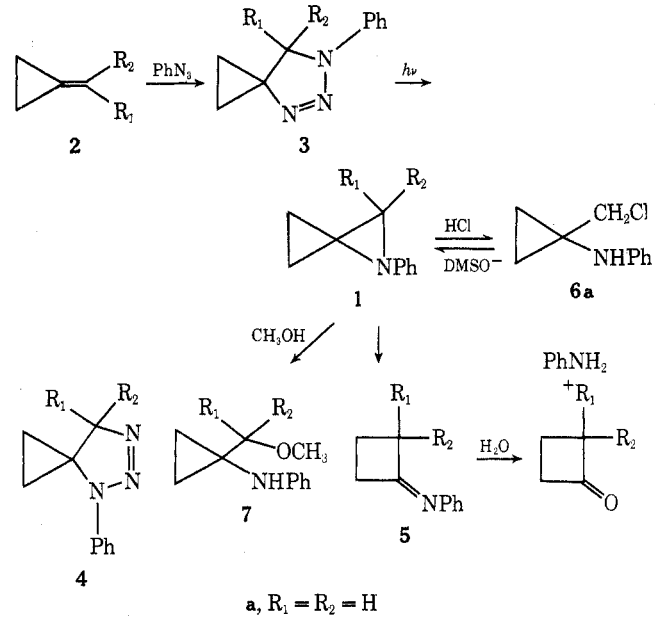
Irradiation of the appropriate triazoline in halocarbon solvents through Pyrex with 3100-Å bulbs gave azaspiropentanes **1a–c** cleanly. However, the photolysis leading to **1c** had to be performed at −78°, since this material underwent facile rearrangement to cyclobutanone anil **5c** upon warming to room temperature. Performing the photolysis of **1c** at room temperature gave only **5c**. The structure of this material was unambiguously established by its spectral data and clean hydrolytic conversion to aniline and 2,2-diphenylcyclobutanone.

The nmr spectrum of azaspiropentane **1a** is temperature dependent. Under ambient conditions there are only three signals for the aliphatic methylene groups at δ 0.77 (m), 1.07 (m), and 2.48 (s). However, at −50° each of these signals is split into a pair. This behavior is in accord with a relatively slow inversion at the nitrogen center at −50°, whereas a time-averaged spectrum is observed at the normal probe temperature where inversion is more rapid.

Prolonged irradiation of azaspiropentane **1a** in CH_2Cl_2 resulted in its conversion into chloride **6a**. This material is thought to result from the nonphotochemical addition of HCl to **1a**. The HCl apparently arises from a photochemically initiated decomposition of the solvent. Dry HCl in ether also transformed **1a** into **6a**. Performing this reaction at −20° allowed the isolation of a white, crystalline solid (tentatively identified as the hydrochloride of **1a**) which could be kept at this temperature in the solid state, but which was converted into **6a** by warming or more simply by dissolving it in $CDCl_3$ at −50°. On the other hand, azaspiropentane **1b** was transformed to cyclobutanone anil **5b** in high yield by HCl in benzene. Compound **5b** hydrolyzed to aniline and 2-phenylcyclobutanone as expected. Prolonged photolyses of **1b** in CH_2Cl_2 also gave **5b**, perhaps by HCl formation and acid-catalyzed rearrangement (*vide infra*).

Chloride **6a** was reconverted to azaspiropentane **1a** in good yield upon reaction with the sodium salt of DMSO. This process constitutes a second synthetic pathway to the subject heterocyclic system which may be employed in future synthetic approaches to azaspiropentanes.

Azaspiropentane **1a** reacted remarkably easily with methanol which added to the heterocyclic ring yielding **7a**. A similar process occurred with **1b** which gave **7b**. In this case it was demonstrated that performing the reaction in the presence of $NaHCO_3$ retarded the reaction slightly, whereas the addition of minute quantities of acetic acid accelerated the conversion substantially. An attempt to add methanol to **1c** by carrying out the photolysis of **3c** in methanol was unsuccessful; the previously indicated rearrangement to **5c** was observed instead.

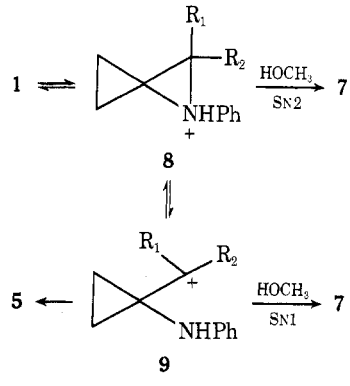


a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = Ph$
c, $R_1 = R_2 = Ph$

Interestingly, azaspiropentane **1a** was not reactive toward strong bases such as KO-*t*-Bu or $LiNEt_2$. A provocative, but obscure, transformation resulted in the formation of acetone and aniline in modest yields upon prolonged treatment with the sodium salt of DMSO.

In general, the azaspiropentanes obtained in this study undergo two types of reactions under protonic conditions:

ring expansion to the cyclobutyl isomer **5** and addition of methanol (or HCl) to the peripheral C–N bond of the heterocyclic ring. The former reaction appears to be more efficient with an increase in the number of phenyl groups on the carbon adjacent to the heteroatom. The second reaction type apparently displays an opposite response to this substitution change, since no **7c** was obtained from **1c** in methanol. The ring-expansion process is at least formally analogous to both the spiropentane–methylenecyclobutane[8] and oxaspiropentane–cyclobutanone[2] rearrangements. This isomerization of **1** is probably catalyzed by acid which transforms the nitrogen into a better leaving group as indicated in structure **8**. Ring opening leads to cyclopropylcarbinyl cation **9**, which then undergoes a 1,2-



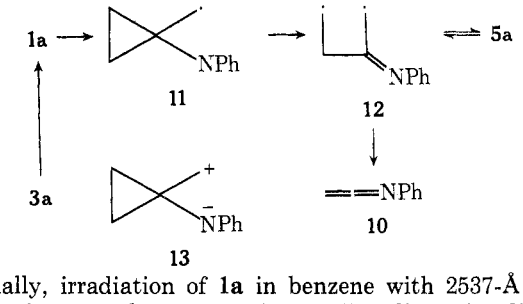
alkyl migration to the electron-deficient center and subsequently deprotonates to produce **5**. Concerted and uncatalyzed variants of this mechanism are also possible. The competing reaction, involving the acid-catalyzed addition of methanol, may occur either by nucleophilic displacement on **8** (SN2) or by nucleophilic capture of cation **9** (SN1). In the first case the substituent effect of the phenyls could result from their steric retardation of SN2 attack on **8** coupled with the simultaneous enhancement of the bond-breaking process leading to **9**. On the other hand, if the competition is simply between rearrangement of **9** leading to **5** and nucleophilic attack giving **7**, the phenyl substituents should serve to stabilize **9** and thereby decrease both rearrangement and methanol attack. If the latter is affected to a much greater degree than the former, the results are understandable. It is not clear, however, that this should be the case, and consequently the first description is tentatively preferred.

The thermal chemistry of **1a** was also examined in some detail. This azaspiropentane can be vacuum transferred through a tube heated to 250° without change. However, raising the temperature to 275° gives a mixture of starting material, cyclobutanone anil (**5a**), and *N*-phenylketenimine[9] (**10**) in a 56:18:16 ratio. At 400° complete conversion of **1a** to a 50:50 mixture of **5a** and **10** occurred. Upon increasing the temperature further there was a decrease in the ratio of **5a** to **10**. This is accountable by a secondary pyrolysis of **5a** to **10** and, presumably, ethylene. This reaction was demonstrated by the independent pyrolysis of **5a** to **10** at temperatures above 400°. However, the presence of the ketenimine in the pyrolysates from **1a** at lower temperature indicates that some of this material is formed directly. Interestingly, refluxing a benzene solution of **1a** for 48 hr gave 20% conversion of **1a** to a 50:50 mixture of **5a** and **10**. Under comparable conditions product **10** was stable.

The most straightforward explanation of these thermal reactions invokes homolytic rupture of the peripheral C–N bond of **1a**, yielding biradical **11**. Ring opening of this species generates new biradical **12**, which can lead to **5a** by bond formation and to ketenimine **10** by bond fission of the 1,4-biradical moiety. The pyrolytic transformation of **5a** to **10** undoubtedly results from the reversible formation of **12**. It is remarkable that the fragmentation of **12** leading to **10** is competitive with rearrangement to **5a** even in refluxing benzene. Dipolar species **13** could be considered as an alternate intermediate in the thermal **1a** to **5a** conversion, but it is not an attractive precursor of **10**.

Azaspiropentane **1b** was isomerized to **5b** by heating a $CDCl_3$ solution to 100° and, as indicated previously, **1c** undergoes spontaneous transformation to **5c** below room temperature. These reactions may be related to the thermal conversion of **1a** just described, but acid-catalyzed processes appear to be equally likely.

The vacuum transfer of triazoline **3a** through a heated chamber at 550° also produced **5a** and **10** in a 34:66 ratio. The similarity of this product mixture with that from **1a** under these conditions suggests strongly that the former process intersects the pathway of the latter somewhere along the way from **1a** to **5a** and **10**. The thermolysis of **3a** probably leads initially to either **1a** itself or to the derived biradical **11**.



Finally, irradiation of **1a** in benzene with 2537-Å light results in very slow conversion to **5a**; direct irradiation with light of this wavelength was ineffective. It appears that energy is transferred from excited benzene to **1a**, resulting in the formation of a species capable of giving **5a**. The most likely candidate for this important intermediate is the triplet state of **11**.

Experimental Section

General. All nmr spectra were recorded on a Varian HR-220 spectrometer. Mass spectra were obtained on MS-9 and CH-4 spectrometers. Infrared spectra were obtained on a Perkin-Elmer IR-37. Analyses were performed by Midwest Microanalytical Laboratories. Anhydrous $MgSO_4$ was routinely used as drying agent.

Addition of Phenyl Azide to Methylenecyclopropane. A mixture of 1 g of methylenecyclopropane[10] and 3 g of phenyl azide[11] was refluxed for 72 hr under nitrogen using a Dry Ice–acetone condenser. After the addition of 50 ml of pentane, the solution was cooled to 0° and filtered to give 1.8 g (56%) of light yellow crystals: mp 108–110°; ir (CCl_4) 6.25, 6.70, 6.75, 9.05, 9.2, 9.4, 10.8 μ; nmr δ 1.01 (m, 2), 1.52 (m, 2), 3.50 (s, 2), 6.90 (t, 1, J = 6 Hz), 2.08 (d, 2, J = 6 Hz), and 7.20 (t, 2, J = 6 Hz).

Anal. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26. Found: C, 69.4; H, 6.3; N, 24.1.

A 1-g sample of methylenecyclopropane and 3 g of phenyl azide were placed in a 100-ml glass tube, cooled in liquid N_2, and sealed under vacuum. The tube was heated to 50° for 24 hr, cooled in liquid N_2, and opened to give a yellow slurry which was diluted with pentane. The solid was collected by filtration to give 2.6 g (80%) of product. Several other reaction mixtures heated for 48 hr under identical conditions resulted in shattering of the tube.

1-Phenyl-1-azaspiro[2.2]pentane (1a). A 100-mg sample of triazoline in 10 ml of CH_2Cl_2 in a Pyrex flask was irradiated for 2 hr with 3100-Å bulbs in a Rayonet reactor. Removal of the solvent under vacuum gave 75 mg (90%) of **1a** as a dark yellow oil: ir (CCl_4) 6.25, 6.85, 7.9, 9.9, 11.2 μ; nmr δ 0.77 (m, 2), 1.07 (m, 2), 2.48 (s, 2), 6.66 (d, 2, J = 7 Hz), 6.82 (t, 1, J = 7 Hz), and 7.08 (t, 2, J = 7 Hz). A sample was purified by column chromatography on basic alumina for analysis.

Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.8; H, 7.6; N, 9.5.

A 25-mg sample of **1a** in acetone-d_6 was cooled to −50°: nmr δ 0.74 (m, 1), 0.88 (m, 1), 1.09 (m, 1), 1.13 (m, 1), 2.48 (s, 1), 2.66 (s, 1), 6.60 (d, 2, J = 6 Hz), 6.91 (t, 1, J = 6 Hz), and 7.15 (t, 2, J

= 6 Hz). The singlets at δ 2.48 and 2.66 broadened and merged into one peak at δ 2.48 upon warming the sample. The coalescence temperature for this process was −22°. The complex multiplets at δ 0.74 and 0.88 and those at δ 1.09 and 1.13 also merged into single signals at δ 0.77 and 1.11, respectively.

A 5% impurity in the sample from photolysis in CH_2Cl_2 continued to increase upon prolonged irradiation as **1a** decreased. After 4 hr of irradiation the sample was quantitatively converted to **6a:** ir (CCl_4) 2.93, 6.25, 6.70, 6.75, 8.0, 9.7, 13.9, and 14.5 μ; nmr δ 0.91 (m, 2), 1.02 (m, 2), 3.59 (s, 2), 4.36 (broad s, 1), 6.5–7.5 (m, 5); mass spectrum *m/e* (rel intensity) 183 (8), 181 (21), 146 (100), 132 (58), 119 (14), 118 (30), 117 (29), 104 (71), 91 (33), 77 (83).

Photolysis of the triazoline in ether solution under the same conditions gave only **1a** after 5 hr.

Reaction of 1a with HCl. A 100-mg sample of **1a** in 10 ml of ether was cooled to 0° and HCl gas was bubbled into the solution. A white solid formed which turned into a brown oil upon filtration. Extraction of the oil into $CDCl_3$ and examination by nmr revealed the formation of **6a**, pure by nmr.

When the HCl was added at −20°, the white solid could be collected and was stable at −20°. The solid was dissolved in $CDCl_3$ at −50°; examination of the nmr indicated only **6a.**

A 10-mg sample of azaspiropentane **1a** was dissolved in 1.0 ml of acetone-d_6 and 0.5 equiv of gaseous HCl was added. Analysis by nmr revealed **6a** (45%) and **1a** (55%).

Reaction of 1a with Methanol. A mixture of 100 mg of **1a** and 1 ml of methanol was stirred at 130° for 24 hr. Removal of methanol under vacuum and vacuum transfer (0.01 mm) gave 100 mg (82%) of **7a:** ir 3.0, 6.3, 6.75, 9.1, and 9.8 μ; nmr (100 MHz) δ 0.78 (m, 4), 3.18 (s, 3), 3.32 (s, 2), 3.8 (br s, 1), and 6.8 (m, 5); mass spectrum *m/e* (rel intensity) 177 (61), 176 (26), 146 (24), 144 (45), 132 (100), 130 (27), 118 (24), 117 (45), 93 (100), 91 (68), 86 (92), 84 (100), 77 (73), 51 (81), 49 (100); exact mass, 177.116 (calcd for $C_{11}H_{15}ON$, 177.115).

Treatment of 6a with Base. A 1-g sample of **6a** was dissolved in 50 ml of DMSO and 4 equiv of NaH was added at 0° under nitrogen. The solution was stirred at 0° for 30 min and the reaction was quenched by the addition of 100 ml of water. The solution was extracted twice with ether and the ether extract was washed with water and dried. Solvent removal gave 750 mg (~100%) of crude **1a.** A similar reaction run for 15 min gave 85% conversion to **1a.**

Treatment of 1a with Base. A 100-mg sample of **1a** in 50 ml of ether was treated with 4 equiv of lithium diethylamide at 20° for 72 hr. The addition of water, separation of the ether layer, drying, and solvent removal gave a sample whose nmr indicated a mixture of diethylamine and **1a.**

A 100-mg sample of **1a** in 50 ml of ether was refluxed with 5 equiv of *t*-BuOK for 72 hr. The addition of 10 ml of water, separation of the ether layer, and solvent removal gave a sample whose nmr showed only *tert*-butyl alcohol and **1a.**

Treatment of 1a with DMSO Anion. A 100-mg sample of **1a** in 50 ml of DMSO was stirred at 0° while 4 equiv of NaH was added. The reaction was stirred for 72 hr at 30°. The addition of 10 ml of water followed by vacuum transfer (20 mm) of the volatile material into a Dry Ice trap gave 10 mg (25%) of acetone. Addition of 100 ml of water to the reaction mixture, extraction with ether, drying, and solvent removal gave a sample whose nmr indicated aniline and **1a** in a 1:5 ratio. Column chromatography of this mixture gave 50 mg of **1a** and 10 mg of aniline (15%).

Pyrolysis of 1a. Seven 25-mg samples of **1a** were transferred under vacuum (0.1 mm) through a chamber filled with quartz chips and heated to the temperature indicated. Only two products were observed by nmr analysis of the crude pyrolysate: *N*-phenylketenimine (**10**) and **5a** (Table I).

A sample of **5a,** isolated by column chromatography, was subjected to the pyrolysis conditions above. No reaction was observed below 400°; at 400°, <5% of **10** was formed; at 550°, 10% of **10** was observed; at 600°, 20% was observed.

A 25-mg sample of **1a** was refluxed in benzene for 48 hr. Solvent removal by vacuum (20 mm) and nmr analysis indicated **1a, 10,** and **5a** in a 80:10:10 ratio. Refluxing a solution of **5a** in benzene for 72 hr gave no **10.**

Vacuum transfer (0.001 mm) of 1.0 g of **1a** through a 600° chamber filled with quartz required 72 hr and gave 0.50 g (54%) of **10** pure by nmr.

Photolysis of 1a. A 100-mg sample of **1a** in 100 ml of ether was irradiated through quartz using 2537-Å bulbs in a Rayonet reactor for 72 hr. Solvent removal gave 97 mg of recovered starting material. A similar experiment with benzene as the solvent gave 10% conversion to **5a** with 85% recovery of **1a.**

Table I

Temp, °C	1a, %	5a, %	10, %
200	100		
250	100		
275	66	18	16
300	42	36	22
400		50	50
550		46	54
600		25	75

Pyrolysis of 3a. A 100-mg sample of **3a** was transferred under vacuum through a chamber filled with quartz chips at 550°. The material collected was shown by nmr and ir to be a 66:34 ratio of **10** and **5a.** *N*-Phenylketenimine[9] gave ir 4.93 and 11.0 μ; nmr δ 3.41 (s, 2), 7.0–7.3 (m, 5). Imine **5a** gave ir 5.89 μ; nmr δ 1.97 (quintet, 2, *J* = 7 Hz), 2.83 (t, 2, *J* = 7 Hz), 3.04 (t, 2, *J* = 7 Hz), 6.68 (d, 2, *J* = 7 Hz), 6.91 (t, 1, *J* = 7 Hz), and 7.15 (t, 2, *J* = 7 Hz).

The crude reaction mixture was hydrolyzed with 10% HCl. The reaction mixture was extracted with ether and the extract was concentrated and purified by glpc to give 5 mg (40%) of cyclobutanone and 38 mg (75%) of acetanilide. The water layer was neutralized with $NaHCO_3$ and an ether extract was shown to contain 30 mg (74%) of aniline.

Addition of Phenyl Azide to Benzylidenecyclopropane[12] (2b). A mixture of 2 g of **2b** and 2 g of phenyl azide was heated on a steam bath for 24 hr. The addition of pentane caused 1.5 g (38%) of **3b** to precipitate as tan crystals, mp 136–140°. Recrystallization from cyclohexane gave a pure sample: mp 147–148° (gas evolution at 180–185°); ir ($CHCl_3$) 3.29, 3.48, 6.25, 6.75, 6.92, 7.42, 9.03, 9.3, 9.4, and 9.71 μ; nmr δ 0.55 (m, 1), 1.00 (m, 1), 1.29 (m, 1), 1.70 (m, 1), 4.79 (s, 1), and 7.0–7.3 (m, 10).

Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.1; H, 6.3; N, 16.8.

Photolysis of 3b. A solution of 100 mg of **3b** in 10 ml of CH_2Cl_2 was irradiated at 0° through a Pyrex test tube in a Rayonet reactor using 3100-Å bulbs until gas evolution ceased (~4 hr). Removal of the solvent gave 92 mg (99%) of a brown liquid identified as 1,2-diphenyl-1-azaspiro[2.2]pentane (**1b**) which could not be further purified without decomposition. This crude sample gave ir 6.25, 6.70, 6.89, 7.16, 8.0, 9.0, and 9.7 μ; nmr δ 0.82 (m, 1), 0.91 (m, 1), 1.14 (m, 1), 1.38 (m, 1), 3.57 (s, 1), and 6.9–7.5 (m, 10). No change in the nmr was observed after storage of a pure sample of **1b** for 1 year at 0°. Photolysis in cyclohexane or chloroform did not proceed as rapidly or give as pure a product.

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.9; H, 6.8; N, 6.4.

Pyrolysis of 1b. A solution of 20 mg of **1b** in 1 ml of $CDCl_3$ was sealed in an nmr tube. The sample was heated to 100° and its spectrum was recorded at 15-min intervals. Conversion to one product in 55% yield was complete in 100 min as judged by nmr integration. Solvent removal and purification of the residue by column chromatography under a nitrogen atmosphere using basic alumina which had been pretreated by elution with 400 ml of anhydrous ether gave 7 mg of **5b:** ir ($CHCl_3$) 3.3, 5.9, 6.28, 6.74 μ; nmr δ 2.10 (m, 1), 2.65 (m, 1), 2.86 (m, 2), 4.45 (t, 1, *J* = 7 Hz), and 6.8–7.2 (m, 10).

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 87.0; H, 6.8; N, 6.1.

Hydrolysis of 5b. A 34-mg sample of **5b** was stirred with 5 ml of 10% HCl for 6 hr. The solution was extracted with ether, the extract was dried, and the solvent was removed to give 20 mg (89%) of 2-phenylcyclobutanone which was purified by glpc: ir 3.41, 5.62, 6.72, 6.93, 13.3, and 14.4 μ; nmr δ 2.2 (m, 1), 2.5 (m, 1), 3.0 (m, 1), 3.1 (m, 1), 4.44 (t, 1, *J* = 7 Hz), and 7.19 (m, 5).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.4; H, 6.7.

The acid solution was neutralized with $NaHCO_3$ and extracted with ether. Solvent removal after drying gave 12 mg (84%) of aniline.

Photolysis of 1b. A 100-mg sample of **1b** in 3 ml of CH_2Cl_2 was irradiated through Pyrex with 3100-Å bulbs in a Rayonet reactor for 24 hr. Solvent removal gave a brown liquid whose nmr was identical with that of **5b** except for an excess of absorption in the aromatic region. Purification by column chromatography as described above gave 48 mg (48%) of **5b.** Hydrolysis as described above gave 25 mg (89%) of 2-phenylcyclobutanone and 18 mg (82%) of aniline.

Reaction of 1b with HCl. An 80-mg sample of **1b** in 10 ml of benzene was stirred at 0° while 1 drop of a saturated solution of

dry HCl in benzene was added. The benzene was removed under vacuum to give 73 mg of **5b** (90%).

Reaction of 1b with Methanol. An 80-mg sample of **1b** in 0.3 ml of methanol was stirred at 25° for 6 hr. Solvent removal gave 81 mg (93%) of **7b**: ir 2.95, 3.34, 6.25, 6.70, 9.15, 13.3, 14.3 μ; nmr δ 0.57 (m, 1), 0.75 (m, 2), 1.02 (m, 1), 3.15 (s, 3), 3.97 (broad s, 1), 4.48 (s, 1), 6.60 (d, 3, J = 7 Hz), 7.03 (t, 2, J = 7 Hz), and 7.18 (m, 5) purified by column chromatography.

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.3; H, 7.8; N, 5.4.

An 80-mg sample of **1b** was dissolved in 0.3 ml of CD_3OD and its disappearance was followed by nmr at 15° to determine its approximate half-life. For CD_3OD stirred over solid $NaHCO_3$, $\tau_{1/2}$ was ~58 min; for neutral CD_3OD, $\tau_{1/2}$ was ~42 min; and for 0.01% AcOD in CD_3OD, $\tau_{1/2}$ was ~4 min. The reaction was over in 1% AcOD in CD_3OD before a spectrum could be recorded.

Reaction of Diphenylmethylenecyclopropane[12] (2c) with Phenyl Azide. A 1.0-g sample of **2c** and 1.0 g (1.7 equiv) of phenyl azide were heated on a steam bath for 48 hr, after which time **2c** had completely reacted upon nmr examination. Addition of 100 ml of pentane gave 0.1 g of a dark brown solid whose nmr had only aromatic absorption. Removal of this solid by filtration, concentration of the pentane solution to 25 ml, and cooling to −20° gave 0.8 g (51%) of solid **3c** (mp 145–147°, gas evolution at 180°): ir 3.3, 6.25, 6.80, 6.90, 7.5, and 9.4 μ; nmr δ 0.55 (m, 2), 1.50 (m, 2), and 6.6–7.2 (m, 15); mass spectrum m/e (rel intensity) 325 (<1), 297 (19), 296 (38), 282 (11), 269 (46), 170 (100), and 165 (23).

Anal. Calcd for $C_{22}H_{19}N_3$: C, 81.20; H, 5.89; N, 12.91. Found: C, 81.0; H, 5.8; N, 12.6.

Photolysis of 3c. A 100-mg sample of **3c** in 1 ml of CH_2Cl_2 was irradiated with a medium-pressure Hanovia system through Pyrex. Observation by nmr indicated a reaction time of 60 min. Solvent removal gave a dark brown oil identified as **5c**: ir 5.90, 6.27, 6.82, 6.93, 7.91, 9.0, 9.8 μ; nmr δ 2.83 (m, 4), 6.8–7.8 (m, 15). Purification by column chromatography on basic alumina gave 80 mg (91%) of a light yellow oil.

Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 89.0; H, 6.3; N, 4.5.

Photolysis of **3c** in $CDCl_3$ under the same conditions as above at −78° gave 90% conversion of **3c** to **1c** as observed by low-temperature nmr: δ 1.11 (m, 2), 1.55 (m, 2), and 6.4–7.4 (m, 15). This sample of **1c** was stable up to −30° for periods up to 6 hr. Rapid warming to 20° gave quantitative conversion to **5c** in 10 min as monitored by nmr.

Photolysis of 3c in Methanol. A 100-mg sample of **3c** in 5 ml of MeOH was irradiated with 3100-Å bulbs in a Rayonet reactor for 3 hr. Removal of the MeOH under vacuum gave 82 mg (92%) of **5c**, pure by nmr.

Hydrolysis of 5c. A 100-mg sample of **5c** was stirred with 100 ml of a 5% HCl solution for 2 hr. The HCl solution was extracted with ether, the ether was dried, and the solvent was removed under vacuum to give 70 mg (93%) of 2,2-diphenylcyclobutanone: ir 5.61 μ; nmr δ 2.76 (t, 2, J = 8.5 Hz), 3.08 (t, 2, J = 8.5 Hz), 7–7.8 (m, 10).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 5.92. Found: C, 86.4; H, 5.9.

The HCl aqueous layer was neutralized with $NaHCO_3$ and extracted with ether. Drying and solvent removal gave 25 mg (80%) of aniline.

Registry No. **1a**, 42540-58-9; **1b**, 40323-60-2; **1c**, 42540-60-3; **2a**, 6142-73-0; **2b**, 7555-67-1; **2c**, 7632-57-7; **3a**, 42540-63-6; **3b**, 40323-62-4; **3c**, 42540-65-8; **5a**, 42540-66-9; **5b**, 40323-63-5; **5c**, 42540-68-1; **6a**, 42540-69-2; **7a**, 42540-70-5; **7b**, 40323-64-6; **10**, 42540-72-7; phenyl azide, 622-37-7; 2-phenylcyclobutanone, 42436-86-2; 2,2-diphenylcyclobutanone, 24104-20-9.

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Octahydrophenanthreneaziridines. *syn*- and *anti*-9,10-Imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene

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Preparation of *anti*-9,10-imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (2) is reported. A comparison of the results of ring opening reactions of these syn and anti aziridines (1 and 2) is made. Both isomers are converted to β-chloro amides when treated with benzoyl chloride and subsequently converted to the isomeric oxazolines. Acid-catalyzed ring opening produces amino alcohols in both cases with 1 affording a 57:43 ratio of cis and trans products, 22 and 23. Opening of 2 afforded a 10:90 mixture of cis and trans amino alcohols, 24 and 25.

Current studies required finding suitable methods for the preparation of the isomeric aziridines 1 and 2. Obtention of these aziridines provided a convenient system for study of the stereochemistry of the ring opening process. These compounds offer advantages similar to steroidal aziridines, with the additional quality of the regioselectivity of opening being somewhat predetermined because of the adjacent phenyl group; thus C–N bond breaking would occur primarily at the benzylic position. In previous studies, products of both carbonium ion opening and displacement mechanisms had been reported from styrylaziridines and aziridinium ions.[1-3]