THE JOURNAL OF Organic Chemistry

VOLUME 44, NUMBER 19

SEPTEMBER 14, 1979

Synthetic Approaches toward the Bi(2*H*-azirine) System

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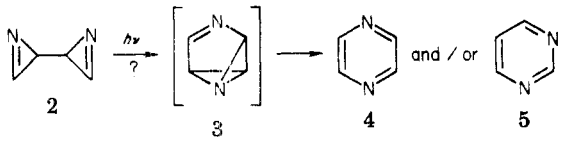
Received March 5, 1979

Three different approaches toward the synthesis of the bi(2*H*-azirine) system (**2**) were investigated. The first route is based on a modified Neber reaction in which the bis(trimethylhydrazonium) salt of 2,3-dimethyl-1,4-diphenyl-1,4-butanedione was treated with base. No indication of any bi(2*H*-azirine) could be detected in this reaction. In a second approach, the reaction of 2-styryl-3-phenyl-2*H*-azirine with iodine azide was investigated. The major product isolated from this reaction was 1-phenyl-5-(1-azidocinnamyl)tetrazole. Subsequent studies with model systems showed that the reaction of iodine azide with 3-phenyl-2-substituted 2*H*-azirines gives azidotetrazoles in moderate yield. The reaction is believed to involve the addition of iodine azide across the C–N double bond followed by ring opening of a transient iodoaziridine. Attack of azide on the incipient carbonium ion followed by electrocyclization of the azidoimine formed readily accommodates the formation of the tetrazole ring. The third approach utilized for the synthesis of the bi(2*H*-azirine) system involved an attempt to dimerize 2-chloro-2*H*-azirines with activated metals or by electrolysis. A sample of 2-chloro-2-methyl-2-phenyl-2*H*-azirine was found to rearrange to the isomeric 2-chloro-3-methyl-2-phenyl-2*H*-azirine in solution. This rearrangement is consistent with the intermediacy of an azacyclopropenyl ion–chloride pair. All attempts at dimerization proved unsuccessful.

Small-ring compounds are particularly interesting species because their high energy content relative to the acyclic isomers often endows them with unusual reactivity patterns.[1] Studies dealing with the chemical reactions of unsaturated three-ring systems have played an important role in the development of our understanding of the mechanism by which carbon–carbon bonds may be broken and re-formed.[2] During the last few years the chemistry of 3,3′-bicyclopropenyls has attracted considerable interest.[3-10] The rearrangement of 3,3′-bicyclopropenyls (**1**) to benzene derivatives is one of the most exothermic unimolecular isomerizations known.[10] The conversion of the isoelectronic bi(2*H*-azirine) system **2** to a substituted nitrogen heteroaromatic represents a more complicated transformation since several different possibilities are available.



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On the basis of the earlier findings with the 3,3′-bicyclopropenyl system we felt that the irradiation of a representative bi(2*H*-azirine) would have important consequences and novel features worthy of investigation. As part of a general study concerned with the photochemistry of 2*H*-azirines[11-13] we developed a need for a synthetic route to **2**. This paper provides the details of our attempts to prepare bi(3-phenyl-2*H*-azirine) derivatives.

Results and Discussion

The first approach we investigated for the synthesis of the bi(2*H*-azirine) system is based on a modified Neber reaction which is commonly used for the synthesis of 2*H*-azirines.[14-16] Unfortunately, all attempts to convert

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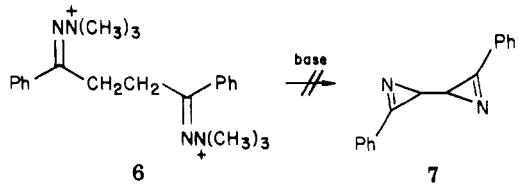
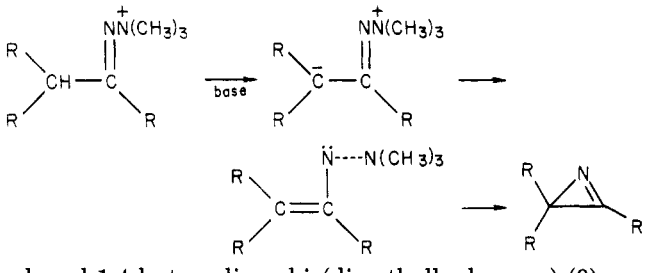
the dimethiodide salt **6** to bi(2*H*-azirine) **7** by the standard methods of elimination[17-20] were unsuccessful.

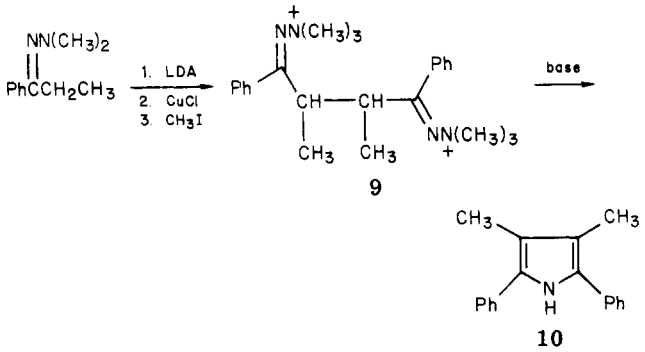


6 **7**

Earlier work in the literature has shown that the synthesis of 2*H*-azirines based on the modified Neber reaction is affected by the type of hydrogen that is available on the α-carbon atom.[21] The reaction generally proceeds in high yield if the α hydrogen is tertiary. This is probably related to the fact that the mechanism of the Neber rearrangement involves the formation of a species resembling a vinylnitrene which undergoes subsequent cyclization.[22] The transition state leading to the azirine ring would be expected to be lower in energy when the double bond is tetrasubstituted. With this in mind, we decided to investigate the base-induced reactions of a series of bis(dimethylhydrazonium) salts of diketones containing tertiary α hydrogens. A sample of 2,3-dimethyl-1,4-di-



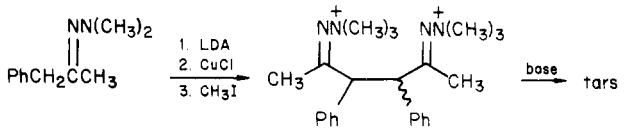
phenyl-1,4-butanedione bis(dimethylhydrazone) (**8**) was obtained by treating the dimethylhydrazine anion of propiophenone with cuprous chloride. This oxidative dimerization reaction was patterned after the work of Kaufmann and Schoenfelder who found that the anions of azines can be readily oxidized to a dimer by cuprous chloride from which the 1,4-diketone can be obtained by hydrolysis.[23] The major diastereomer isolated from this reaction was a crystalline solid, mp 129–130 °C, which was obtained in 84% yield. Treatment of this material with methyl iodide gave the dihydrazonium salt **9** in quanti-



9 **10**

tative yield. When this salt was subjected to basic conditions, the only product that could be isolated from the reaction mixture was 3,4-dimethyl-2,5-diphenylpyrrole (**10**) in 89% yield. The structure of this material was established by comparison with an authentic sample.[24]

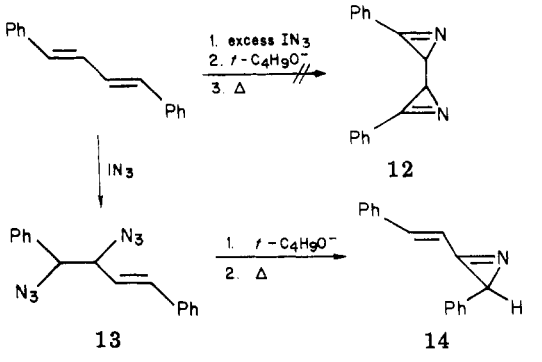
One additional Neber approach was used in an attempt to synthesize a representative bi(2*H*-azirine) system. This involved a study of the base-induced reaction of the isomeric dihydrazonium salt **11**. The coupling reaction



11

of phenylacetone *N*,*N*-dimethylhydrazone anion and cuprous chloride proceeded in high yield to give a mixture of two diastereomers which could readily be separated by recrystallization from ethyl acetate. Both diastereomers could be readily converted into the corresponding hydrazonium salts **11** on treatment with methyl iodide. All attempts to convert **11** into the bi(2*H*-azirine) system were unsuccessful, and this approach was abandoned.

The negative results encountered with dihydrazonium salts **9** and **11** indicate that the modified Neber reaction approach is ineffective in promoting the formation of the bi(2*H*-azirine) system. In a second approach to the synthesis of bi(2*H*-azirines), we decided to try the vinyl azide route developed by Hassner and co-workers.[25-27] Our initial attempts to isolate a bi(2*H*-azirine) (i.e., **12**) from



12 **13** **14**

the reaction of 1,4-diphenyl-1,3-butadiene with excess iodine azide followed by base elimination and thermolysis failed. Instead, reaction of diphenylbutadiene with iodine azide gave the stable diazide **13**, which was converted by HN_3 elimination and pyrolysis to styrylazirine **14**.[28] The diazide **13** apparently results from allylic displacement by azide ion on the initially formed iodine azide adduct.[29]

In order to circumvent this problem, we decided to use *trans*-2-styryl-3-phenyl-2*H*-azirine (**16**) as our starting material for the iodine azide reaction. This azirine was obtained in high yield from the reaction of 2-formyl-3-phenyl-2*H*-azirine (**15**)[30] with (phenylmethylene)triphenylphosphorane in ether at 25 °C.[31] Treatment of **16** with iodine azide afforded a crystalline solid possessing the molecular formula $C_{16}H_{13}N_7$ which corresponds to the

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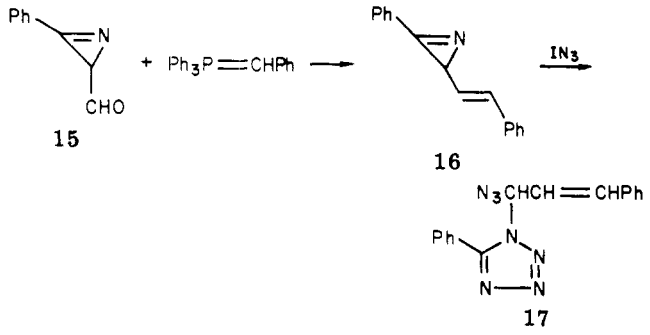
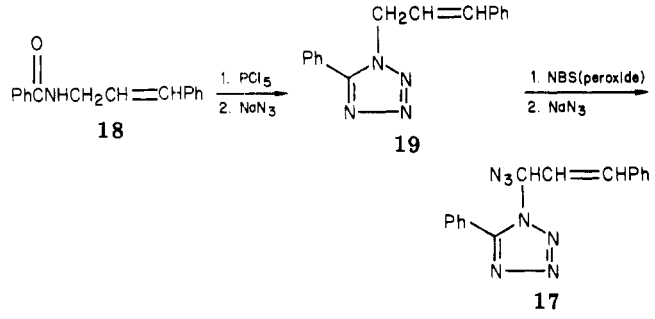
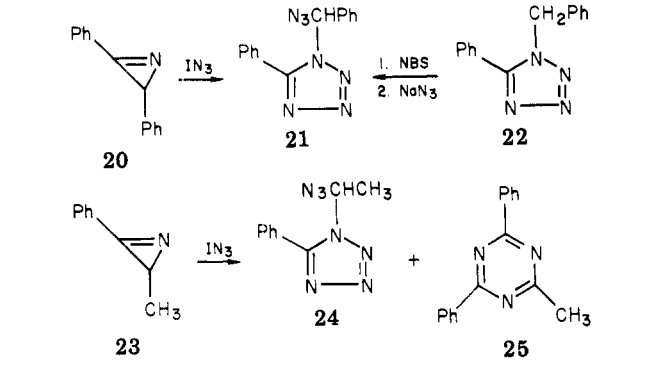


addition of two moles of iodine azide followed by the loss of an iodine molecule. The structure of this material is assigned as 1-phenyl-5-(1-azidocinnamyl)tetrazole (17) on the basis of its spectroscopic properties (see Experimental Section). This structure was further established by an independent synthesis. *N*-Cinnamylbenzamide 18 was



treated with phosphorus pentachloride to give the corresponding imidoyl chloride. Reaction of this material with sodium azide gave tetrazole 19 in 76% yield. Bromination of 19 with NBS in the presence of benzoyl peroxide followed by treatment of the resulting allylic bromide with sodium azide afforded azidotetrazole 17 which was identical with the product obtained from the reaction of azirine 16 with iodine azide.

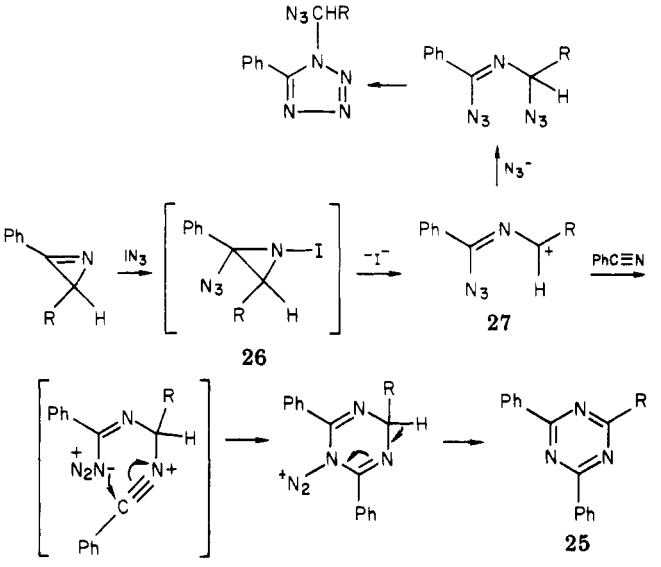
The formation of 17 from the reaction of 16 with iodine azide prompted us to study this reaction in greater detail. We have found that the conversion of 2*H*-azirines to azidotetrazoles is a general reaction. Thus, treatment of 2,3-diphenyl-2*H*-azirine (20) with iodine azide afforded 21



in good yield. The structure of 21 was established by comparison with an independently synthesized sample prepared from tetrazole 22. Similarly, treatment of 2-methyl-3-phenyl-2*H*-azirine (23) with iodine azide afforded azidotetrazole 24 which could be independently synthesized. In this case a minor component (10%), whose structure was established as 2,4-diphenyl-6-methyltriazine (25) by comparison with an authentic sample,[32] was also formed.

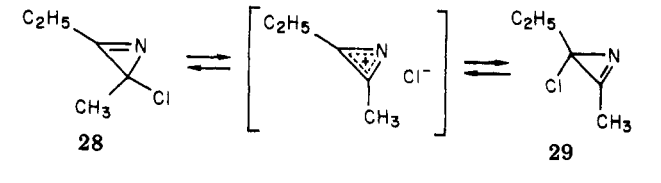
(32) Yanagiya, K.; Yasumoto, M.; Kurabayashi, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2809.

The conversion of 2*H*-azirines to azidotetrazoles on treatment with iodine azide represents a novel reaction and merits some comment. In simplest valence-bond terms, this transformation can be rationalized by assuming initial addition of azide across the C–N double bond followed by rapid ring opening to give 27 as a transient species. Attack



of azide ion at the terminal position followed by electrocyclization of the resulting azido imine nicely accommodates the formation of product. The formation of 25 can be postulated to arise by attack of benzonitrile on the carbonium center of 27 followed by internal cyclization and aromatization. In fact, the yield of 25 could be significantly enhanced when benzonitrile was added to the reaction mixture. It should be noted that Gassman and coworkers[33] have reported on a ring opening related to that proposed with structure 26. These workers have found that *N*-chloroaziridines undergo conversion to carbonyl compounds via a disrotatory ring opening of an electron-deficient nitrenium ion.[34]

In view of our lack of success in preparing a representative bi(2*H*-azirine) via the iodine azide route, an alternate approach was used in an attempt to reach our ultimate goal. Breslow and co-workers had previously described the synthesis of various 3,3′-bicyclopropenyls by both metal[35] and electrochemical[36] reduction of cyclopropenyl cations. On the basis of these findings, we decided to investigate the reduction of the isoelectronic azirinium cation with the hope that this species could be used to prepare the desired bi(2*H*-azirine) system. 2-Halo-substituted 2*H*-azirines not only are potential precursors to the theoretically interesting 2π-electron azacyclopropenyl ion but can also be used as an attractive starting material for the synthesis of the bi(2*H*-azirine) system. Ciabattoni and Cabell had previously found that the azacyclopropenyl cation functions as an intermediate in the interconversion of 2-chloro-2*H*-azirines 28 and 29.[37]



(33) Gassman, P. G.; Dygoa, D. K. *J. Am. Chem. Soc.* **1969**, *91*, 1543.
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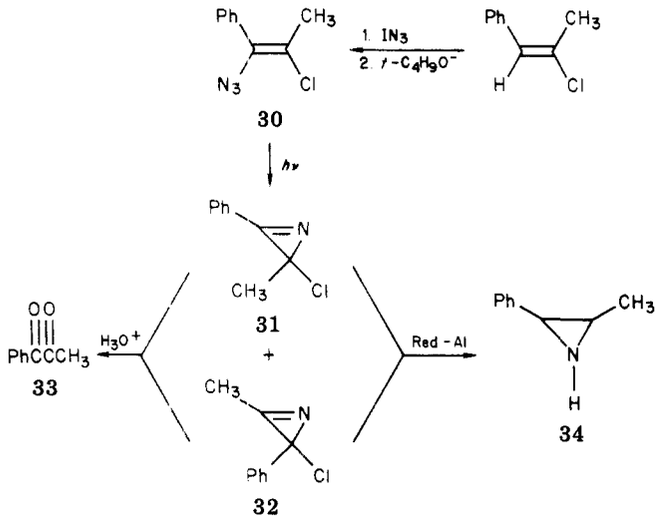
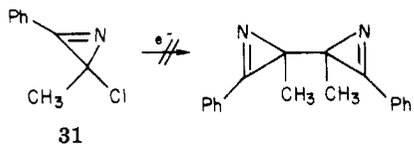
(37) Ciabattoni, J.; Cabell, M., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 1482.

With this in mind we decided to synthesize a sample of 2-chloro-2-methyl-3-phenyl-2*H*-azirine (**31**) with the expectation that this substrate might undergo a subsequent dimerization reaction. Addition of iodine azide to 1-phenyl-2-chloro-1-propene followed by the elimination of hydrogen iodide with potassium *tert*-butoxide yielded a mixture of *cis*- and *trans*-1-azido-2-chloro-1-phenyl-1-propene (**30**). Photolysis at 3500 Å afforded a 5:1 mixture of **31** and 2-chloro-3-methyl-2-phenyl-2*H*-azirine (**32**) as a pale yellow liquid. Chemical evidence was provided by aqueous hydrolysis of the mixture to 1-phenyl-1,2-propanedione (**33**) and by Red-Al reduction to 2-methyl-3-phenylaziridine (**34**). The relative ratio of the two isomeric chloroazirines was found to depend on the nature of the solvent system employed. In carbon tetrachloride the ratio of **31** to **32** was 5:1 while in CD_3CN it was 3.3:1. The thermal nature of the isomerization of azirines **31** and **32** was revealed by conducting the photolysis at low temperatures. Irradiation of **30** at −40 °C afforded exclusively azirine **31** which was detected by NMR. Warming the solution of pure **31** in the NMR probe resulted in the appearance and growth of a new methyl peak corresponding to azirine **32**. As expected, chromatography of the mixture resulted in the formation of dione **33**. The conversion of **31** to **32** is consistent with the intermediacy of an azacyclopropenyl ion–chloride pair although an alternative mechanism involving a polar, bridged transition state cannot be excluded.



Numerous attempts at dimerization of **31** proved unsuccessful. Activated zinc,[38] precipitated zinc,[39] precipitated magnesium,[39] lithium metal, nickel tetracarbonyl[40] and nickel dicyclooctadiene[41] all failed to give a dimer. Similar results were obtained with the corresponding 2-bromo-2-methyl-3-phenyl-2*H*-azirine (**35**). In every case, 1-phenyl-1,2-propanedione (**33**) was the only product obtained. The failure of these metal-induced dimerization reactions was not able to be easily rationalized. On the possibility that the metal might be complexing with the azirine nitrogen, large excesses of metal were used. However, this was also ineffective. In an extreme test, refluxing **31** with an excess of highly precipitated zinc[39] failed to promote the dimerization reaction.



We also undertook a study of the electrolysis of these systems in order to determine whether chemical behavior similar to the cyclopropenyl system could be observed. The half-wave potential of **31** was measured polographically in 0.1 N tetra-*n*-butylammonium perchlorate in anhydrous acetonitrile at a dropping mercury electrode. A wave was observed at −1.70 V which by cyclic voltametry was found to be irreversible. Preparative electrochemical reduction of **31** or **35** gave only dione **33** in low yield. This was presumably due to capture of the azirinium ion with trace amounts of water present in the system.

In summary, three independent routes to the bi(2*H*-azirine) system have been explored and have been shown to be unsuccessful for a variety of reasons. We are continuing to seek additional methods for the construction of this interesting small-ring heterocyclic system.

Experimental Section[42]

Preparation of 1,4-Diphenylbutane-1,4-dione Bis(*N*,*N*-dimethylhydrazone) (6). To a stirred suspension containing potassium amide in 200 mL of liquid ammonia (prepared by dissolving 800 mg of potasium in liquid ammonia with a catalytic amount of ferric nitrate) was added 3.2 g of an ethereal solution of acetophenone dimethylhydrazone. The mixture was allowed to stir for 1 h and then 2.4 g of 2,3-dibromo-2,3-dimethylbutane[43] in 50 mL of ether was added according to the procedure of Henoch.[44] The liquid ammonia was allowed to evaporate, and the resulting solution was washed with water and dried. Removal of the solvent left a red oil which was distilled under reduced pressure. The fraction (2.2 g) boiling at 75–80 °C (0.5 mmHg) was unreacted acetophenone dimethylhydrazone. The second fraction contained 1.0 g of a yellow oil (bp 160–170 °C (0.2 mmHg)) which solidified on standing. Recrystallization of this material from pentane gave 440 mg of yellow needles, mp 89–90 °C, whose structure was assigned as 1,4-diphenyl-1,4-butanedione *N*,*N*-bis(dimethylhydrazone) (**6**) on the basis of the following data: IR (KBr) 3.50, 6.22, 6.36, 6.90, 7.62, 9.80, 10.40, 12.95, 14.45 μm; UV (methanol) 233 nm (ε 22 400), 306 (2860); NMR ($CDCl_3$, 60 MHz) τ 7.50 (s, 12 H), 6.98 (s, 4 H), 2.1–2.8 (m, 10 H); *m*/*e* 322 (M^+), 278, 248, 233, 220, 219 (base), 144, 115, 104, 103. Anal. Calcd for $C_{20}H_{26}N_4$: C, 74.49; H, 8.13; N, 17.38. Found: C, 74.41; H, 8.23; N, 17.40.

A mixture containing 500 mg of the above dimethylhydrazone, 1.2 g of iodomethane, and 10 mL of ether was heated in a sealed tube at 65 °C for 36 h. Removal of the solvent left a thick oil which failed to crystallize. All attempts to obtain a sample of bi(2*H*-azirine) by treating this material with a variety of bases failed. Further efforts with this system were discontinued.

Synthesis of 2,3-Dimethyl-1,4-diphenyl-1,4-butanedione Bis(*N*,*N*-dimethylhydrazone) (8). A mixture containing 26.8 g of propiophenone, 24 g of *unsym*-dimethylhydrazine, 4 g of sodium acetate, and 4 drops of glacial acetic acid was heated at reflux for 17 h. The reaction mixture was diluted with ether, and

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(40) Corey, E. J.; Wat, E. D. W. *J. Am. Chem. Soc.* **1967**, *89*, 2757.
(41) Semmelhack, M. F.; Helquist, P. M.; Garzynski, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 9234.
(42) All melting points are corrected, and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 100 MHz with a Varian XL-100 spectrometer and at 60 MHz with a Varian T-60 spectrometer. All NMR spectra were recorded with deuteriochloroform as the solvent unless otherwise stated.
(43) Grosse, A. V.; Ipatieff, V. N. *J. Org. Chem.* **1943**, *8*, 438.
(44) Henoch, F. E.; Hampton, K. G.; Hauser, C. R. *J. Am. Chem. Soc.* **1969**, *91*, 676.

the organic layer was washed with water and dried over sodium sulfate. Removal of the solvent followed by distillation of the residue at 92–94 °C (3 mmHg) gave 32.6 g (93%) of propiophenone dimethylhydrazone as a yellow oil: IR (neat) 3.45, 3.52, 6.80, 6.90, 9.71, 10.26, 10.53, 12.90, 14.39 μm; NMR ($CDCl_3$, 60 MHz) τ 8.95 (t, 3 H, J = 7.0 Hz), 7.67 and 7.48 (s, 6 H), 7.12 (q, 2 H, J = 7.0 Hz), 2.61–2.82 (m, 3 H), 2.29–2.53 (m, 2 H).

In a flame-dried, nitrogen-flushed, three-necked flask fitted with a reflux condenser and a dropping funnel and cooled in an ice bath were placed 21 mL of diisopropylamine and 125 mL of dry tetrahydrofuran. To this solution was added 62.5 mL of a 2 M solution of *n*-butyllithium, and the mixture was stirred at 0 °C for 15 min. The resulting solution of lithium diisopropylamide was then cooled to −78 °C, and a solution of propiophenone dimethylhydrazone (17.6 g) in 100 mL of dry tetrahydrofuran was added over 30 min. The mixture was allowed to warm to room temperature and was then stirred at 25 °C for 30 min. At the end of this time the solution was cooled to −78 °C, and 19.8 g of anhydrous cuprous chloride was added. The mixture was allowed to warm to room temperature and was heated at reflux for 15 min. At the end of this time the mixture was poured into a solution containing 250 g of potassium cyanide and 37.5 g of potassium hydroxide in 1 L of water. The solution was vigorously stirred until a clear aqueous phase was obtained. The mixture was extracted with ether and dried over magnesium sulfate, and the solvent was removed under reduced pressure. Trituration of the yellow oil (17 g) with pentane gave 11.5 g (84%) of 2,3-dimethyl-1,4-diphenyl-1,4-butanedione bis(*N*,*N*-dimethylhydrazone) (**8**) as a pale yellow solid: mp 129–130 °C; IR (KBr) 6.21, 6.83, 6.90, 7.35, 8.30, 8.66, 9.52, 9.80, 10.26, 10.42, 12.82, 14.18 μm; NMR ($CDCl_3$, 60 MHz) τ 8.55–8.98 (m, 6 H), 7.63 (s, 12 H), 6.90–7.24 (m, 2 H), 2.71 (m, 10 H); mass spectrum, *m/e* 306, 290, 275, 247 (base), 246, 231, 230, 172, 128, 118, 115, 100, 103. Anal. Calcd for $C_{22}H_{30}N_4$: C, 75.39; H, 8.63; N, 15.99. Found: C, 75.47; H, 8.71; N, 15.90.

Preparation and Base-Induced Reactions of 2,3-Dimethyl-1,4-diphenyl-1,4-butanedione Bis(*N*,*N*,*N*-trimethylhydrazonium iodide) (9). A solution containing 188 mg of dihydrazone **8** in 10 mL of iodomethane was stirred at room temperature for 5 days. Filtration of the mixture gave 298 mg (88%) of the bis(trimethylhydrazonium iodide) **9** as a white solid: mp 196–197 °C; IR (KBr) 3.02, 3.40, 6.23, 6.73, 6.95, 7.30, 8.00, 8.23, 9.30, 9.63, 10.45, 10.64, 10.82, 12.13, 12.99, 14.10 μm; NMR (100 MHz, dimethyl-d_6 sulfoxide) τ 8.61 (d, 6 H, J = 6.0 Hz), 6.68 (s, 18 H), 6.30 (s, 2 H), 2.2–2.6 (m, 10 H).

A solution containing 38 mg of sodium hydride in 10 mL of dry 2-propanol was added to a solution containing 0.5 g of the above trimethylhydrazonium iodide in 10 mL of 2-propanol. The mixture was stirred for 1 h and was taken up in ether. The ethereal layer was washed with water and dried over magnesium sulfate. Removal of the solvent left 0.16 g (89%) of a crystalline solid, mp 133–135 °C, whose structure was established as 3,4-dimethyl-2,5-diphenylpyrrole (**10**) on the basis of its spectral data and by comparison with an authentic sample:[24] IR (KBr) 2.95, 3.45, 6.24, 6.74, 6.95, 7.23, 7.91, 8.49, 9.32, 9.70, 9.91, 10.94, 13.12, 14.40 μm; UV (95% ethanol) 321 nm (ε 25 700), 203 (23 450); NMR ($CDCl_3$, 60 MHz) τ 7.80 (s, 6 H), 2.45–2.80 (m, 10 H). Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.28; H, 6.82; N, 5.64.

Synthesis of 3,4-Diphenyl-2,5-hexanedione Bis(*N*,*N*-dimethylhydrazone). A solution containing 10.5 mL of diisopropylamine in 100 mL of tetrahydrofuran was cooled to −78 °C, and 40 mL of a 1.6 M *n*-butyllithium solution was added. The reaction mixture was allowed to warm to 0 °C and stirred at this temperature for 15 min. At the end of this time the solution was cooled to −78 °C, and a solution containing 8.8 g of phenylacetone *N*,*N*-dimethylhydrazone in 200 mL of tetrahydrofuran was added over a 30-min interval. The reaction mixture was allowed to warm to room temperature and was stirred at 25 °C for an additional 30 min. The mixture was cooled to −78 °C, 10.9 g of anhydrous cuprous chloride was added in one portion, and the mixture was stirred at room temperature for 12 h. The reaction mixture was then poured into a stirred solution containing 95 g of sodium cyanide in 500 mL of water. After the mixture was stirred for 2 h, the organic layer was separated, dried over magnesium sulfate, and concentrated under reduced pressure. The crude solid obtained was recrystallized from ethyl acetate to give both diastereomers. The major product (3.5 g (40%)), mp 135–136 °C, showed the following spectroscopic properties: IR (KBr) 3.40, 3.50, 6.12, 6.25, 6.69, 6.80, 6.90, 7.20, 7.41, 7.79, 8.13, 8.30, 8.44, 8.67, 9.02, 9.31, 9.66, 10.05, 10.24, 10.90, 11.29, 12.12, 13.20, 14.33 μm; NMR (CCl_4, 100 MHz) τ 8.40 (s, 6 H), 7.92 (s, 12 H), 5.76 (s, 2 H), 2.60–3.00 (m, 10 H); mass spectrum, *m/e* 290 (base), 275, 249, 205, 172, 165, 128, 115, 91, 77. Anal. Calcd for $C_{22}H_{30}N_4$: C, 75.39; H, 8.63; N, 15.99. Found: C, 75.35; H, 8.60; N, 15.89.

The minor component contained 2.6 g (30%) and was recrystallized from hexane: mp 104–105 °C; IR (KBr) 3.40, 3.51, 6.09, 6.21, 6.70, 6.80, 6.90, 7.21, 7.40, 8.02, 8.76, 9.15, 9.30, 9.75, 10.00, 10.62, 11.01, 12.29, 13.10, 14.30 μm; NMR (CCl_4, 100 MHz) τ 8.16 (s, 6 H), 7.66 (s, 12 H), 5.90 (s, 2 H) and 3.10 (s, 10 H); mass spectrum *m/e* 290, 275, 220, 207, 205, 190, 172, 129, 115, 105, 103, 91 (base), 77. Anal. Calcd for $C_{22}H_{30}N_4$: C, 75.39; H, 8.63; N, 15.99. Found: C, 75.55; H, 8.68; N, 16.02.

Preparation and Base-Induced Reactions of 3,4-Diphenyl-2,5-hexanedione Bis(*N*,*N*,*N*-trimethylhydrazonium iodide) (11). A solution containing 240 mg of the major diastereomer of the above hydrazone in 2 mL of methyl iodide was stirred at room temperature for 6 h. Removal of the solvent gave 395 mg of the bis(trimethylhydrazonium iodide) **11** as a white solid: mp 195–196 °C; IR (KBr) 3.30, 3.40, 6.06, 6.75, 6.85, 7.20, 8.34, 10.52, 12.30, 13.02, 14.01 μm; NMR (Me_2SO-d_6, 100 MHz) τ 7.80 (s, 6 H), 6.90 (s, 18 H), 5.34 (s, 2 H), 2.3–2.8 (m, 10 H). Anal. Calcd for $C_{24}H_{36}N_4I_2$: C, 45.43; H, 5.72; N, 8.83. Found: C, 45.53; H, 5.63; N, 8.69.

The dihydrazonium iodide salt from the minor diastereomer was prepared in a similar fashion from 310 mg of the above hydrazone and 3 mL of methyl iodide. The crystalline solid obtained (451 mg (80%)), mp 193–194 °C, exhibited the following spectroscopic properties: IR (KBr) 3.30, 3.41, 6.08, 6.76, 6.86, 7.21, 8.30, 9.26, 10.46, 12.31, 13.02, 14.25 μm; NMR (Me_2SO-d_6, 100 MHz) τ 7.60 (s, 6 H), 6.40 (s, 18 H), 5.49 (s, 2 H), 2.82 (s, 10 H). Anal. Calcd for $C_{24}H_{36}N_4I_2$: C, 45.43; H, 5.72; N, 8.83. Found: C, 45.78; H, 5.68; N, 9.01.

All attempts to obtain bi(2*H*-azirine) by treatment of the above hydrazonium iodides with various bases failed. Further work along these lines was discontinued.

Reaction of *trans*-2-Styryl-3-phenyl-2*H*-azirine (16) with Iodine Azide. To a solution of 1.83 g of sodium azide in 25 mL of acetonitrile cooled in a methanol–ice bath was added a solution of 1.5 g of iodine monochloride in 20 mL of acetonitrile. The mixture was allowed to stir for an additional 30 min while the temperature was kept at 0 °C. To this solution was added 1.8 g of *trans*-2-styryl-3-phenyl-2*H*-azirine (**16**)[31] in 30 mL of acetonitrile at −10 °C. The mixture was kept at 0–5 °C for 12 h and then allowed to warm to room temperature. The resultant orange slurry was added to water and extracted with ether. The ether extracts were washed with a 5% sodium thiosulfate solution and were dried over magnesium sulfate. Removal of the solvent left a crude oil which solidified on standing. The crystalline material obtained was recrystallized from ether to give 780 mg of 1-phenyl-5-(1-azidocinnamyl)tetrazole (**17**) as a white solid: mp 87–88 °C; IR (KBr) 4.68, 4.76, 6.90, 8.20, 10.85, 11.85, 12.86, 13.62, 14.28 μm; UV (methanol) 237 nm (ε 21 500); NMR ($CDCl_3$, 60 MHz) τ 3.4–3.8 (m, 2 H), 2.41–3.05 (m, 11 H). Anal. Calcd for $C_{16}H_{13}N_7$: C, 63.35; H, 4.32; N, 32.33. Found: C, 63.28; H, 4.45; N, 32.49.

The structure of the above tetrazole was established by comparison with an independently synthesized sample. A mixture containing 30.5 g of cinnamyl chloride, 37 g of potassium phthalimide, and 300 mL of dimethyl sulfoxide was heated on a steam bath for 3 h. The mixture was then poured into water, and the resulting phthalimide which precipitated was collected and dried under vacuum. To a solution containing 6.5 mL of hydrazine hydrate in 200 mL of methanol was added 13.75 g of the above phthalimide. The mixture was heated at reflux for 1 h, cooled, and treated with 50 mL of concentrated hydrochloric acid. After 15 min, the precipitate which formed was filtered and washed with water. The filtrates were combined, and a 20% potassium hydroxide solution was added until the mixture became slightly alkaline. The aqueous solution was extracted with benzene, washed with water, and dried over magnesium sulfate. To the above solution was added 8 mL of triethylamine followed

by 6 mL of benzoyl chloride in 100 mL of benzene. After the solution was stirred for 12 h at room temperature, the precipitated trimethylamine hydrochloride was filtered, and the benzene was removed under reduced pressure to give 8.85 g (72%) of *N*-cinnamylbenzamide (**18**) as a white solid: mp 88–90 °C (lit.[45] mp 94–95 °C); NMR ($CDCl_3$, 100 MHz) τ 5.82 (dd, 2 H, J = 7.0 and 5.5 Hz), 3.4–3.9 (m, 2 H), 3.1–3.3 (m, 1 H), 2.5–2.9 (m, 8 H), 2.1–2.4 (m, 2 H).

To a solution containing 2.37 g of the above amide in 50 mL of benzene was added 2.30 g of phosphorus pentachloride. The mixture was stirred for 4.5 h at 25 °C, and the benzene was removed under reduced pressure to give the corresponding imidoyl chloride: NMR ($CDCl_3$, 100 MHz) τ 5.54 (d, 2 H, J = 5.5 Hz), 3.2–3.8 (m, 2 H), 2.4–2.9 (m, 8 H), 1.8–2.1 (m, 2 H). This material was dissolved in 25 mL of dimethylformamide, and the resulting solution was added to a slurry containing 1.95 g of sodium azide in 25 mL of dimethylformamide at 0 °C. The mixture was stirred for 12 h and then poured into 40 mL of water. The mixture was extracted with methylene chloride, and the organic layer was washed with a 5% sodium bicarbonate solution, followed by water. The solution was then dried over sodium sulfate, and the solvent was removed under reduced pressure to give 1.99 g (76%) of 1-phenyl-5-cinnamyltetrazole (**19**): mp 93–95 °C; IR (KBr) 3.3, 6.14, 6.53, 6.83, 7.16, 7.27, 8.80, 9.07, 9.31, 10.30, 12.80, 13.15, 13.63, 14.50 μm; NMR ($CDCl_3$, 100 MHz) τ 4.81 (d, 2 H, J = 5.0 Hz), 3.5–3.9 (m, 2 H), 2.6–2.9 (m, 4 H), 2.4–2.6 (m, 4 H), 2.2–2.4 (m, 2 H).

A 0.75-g sample of the above tetrazole and 0.81 g of *N*-bromosuccinimide together with 0.1 g of benzoyl peroxide were heated at reflux in 50 mL of carbon tetrachloride for 36 h. The mixture was filtered, and the solvent was removed under reduced pressure. The residual oil was dissolved in acetonitrile and filtered. The resulting solution was added to a slurry containing 0.80 g of sodium azide in 25 mL of acetonitrile at 25 °C. After stirring for 50 h at 35 °C, the mixture was poured into water and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The white solid which remained (36%) was identical in every detail with a sample of **17** prepared by the reaction of iodine azide with azirine **16**.

Reaction of 2,3-Diphenyl-2*H*-azirine (20) with Iodine Azide. To a stirred slurry containing 0.75 g of sodium azide in 30 mL of acetonitrile at 0 °C was added 0.92 g of iodine monochloride. The resulting red solution was stirred for 25 min at 0 °C, and then 0.985 g of 2,3-diphenyl-2*H*-azirine (**20**)[46] was added, and the mixture was allowed to stir for 16 h at room temperature. The mixture was then poured into 50 mL of water and extracted with ether. The ethereal solution was washed with a 5% sodium thiosulfate solution followed by water and a saturated salt solution. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The oily residue was chromatographed on a silica gel dry column with a 1:1 ether–pentane mixture as the eluent. The major component contained 0.51 g (36%) of a white solid, mp 74–75 °C, whose structure was assigned as 1-phenyl-5-(1-azidobenzyl)tetrazole (**21**) on the basis of the following data: IR (KBr) 4.52, 4.68, 6.16, 6.47, 6.65, 6.76, 6.86, 7.15, 7.46, 7.57, 7.87, 8.12, 8.87, 9.02, 10.26, 13.11, 12.36, 13.60, 14.50 μm; NMR ($CDCl_3$, 60 MHz) τ 3.20 (s, 1 H), 2.4–2.80 (m, 10 H); mass spectrum, m/e 221, 220, 105, 104, 103 (base), 77. Anal. Calcd for $C_{14}H_{11}N_7$: C, 60.64; H, 4.00; N, 35.36. Found: C, 60.59; H, 4.05; N, 35.31.

The structure of this material was verified by comparison with an independently synthesized sample. A mixture containing 8.44 g of *N*-benzylbenzamide and 120 mL of thionyl chloride was heated at reflux for 30 min. The excess thionyl chloride was removed by distillation, and the resulting residue was taken up in 125 mL of *N*,*N*-dimethylformamide. The above solution was added to a stirred slurry containing 7.8 g of sodium azide in 75 mL of dry dimethylformamide at 0 °C. The mixture was stirred at 0 °C for 9 h and was then poured into 100 mL of water and extracted with methylene chloride. The organic layer was washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The resulting yellow solid (7.46 g, 79%) was crystallized from methanol to give 5-benzyl-1-phenyltetrazole (**22**): mp 90–91 °C; IR (KBr) 3.30, 6.90, 7.17, 7.32, 8.81, 9.03, 9.30, 10.80, 11.95, 12.70, 12.89, 13.80, 14.40 μm; NMR ($CDCl_3$, 60 MHz) τ 4.39 (s, 2 H), 2.3–3.0 (m, 10 H).

A 1.18-g sample of the above tetrazole and 1.78 g of *N*-bromosuccinimide together with 0.1 g of benzoyl peroxide were heated at reflux in 50 mL of carbon tetrachloride for 10 h. The mixture was filtered, and the solvent was removed under reduced pressure. The residual oil was dissolved in acetonitrile and filtered to remove the excess succinimide. The resulting solution was added to a slurry containing 0.98 g of sodium azide in 50 mL of acetonitrile at 0 °C. After stirring for 20 h at room temperature, the mixture was poured in 75 mL of water and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The white solid which remained (0.55 g, 40%) was idential in every detail with the sample of 1-phenyl-5-(1-azidobenzyl)tetrazole (**21**) obtained from the reaction of iodine azide with 2,3-diphenyl-2*H*-azirine (**20**).

Addition of Iodine Azide to 2-Methyl-3-phenyl-2*H*-azirine (23). To a stirred slurry containing 1.5 g of sodium azide in 50 mL of acetonitrile at 0 °C was added 1.84 g of iodine monochloride. The resulting red solution was stirred for 25 min at 0 °C, and then 1.31 g of 2-methyl-3-phenyl-2*H*-azirine (**23**)[47] in 100 mL of acetonitrile was added, and the mixture was allowed to stir for 9 h at room temperature. The mixture was poured into water and extracted with ether. The ethereal layer was washed with a 5% sodium thiosulfate solution followed by water and was then dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil. This material was chromatographed on a silica gel dry column with a 1:1 ether–pentane mixture as the eluent. The fastest moving component contained 0.13 g of a white solid, mp 107–108 °C, whose structure was assigned as 2,4-diphenyl-6-methyltriazine (**25**) by comparison with an authentic sample prepared by the procedure of Yanagiya, Yasumoto, and Kurabayashi.[32] The slower moving material (0.62 g, 28%) was a white solid, mp 45–46 °C, whose structure was assigned as 1-phenyl-5-(1-azidoethyl)tetrazole (**24**) on the basis of the following data: IR (KBr) 4.71, 6.89, 7.24, 8.15, 8.62, 9.17, 11.80, 12.82, 13.30, 14.40 μm; NMR ($CDCl_3$, 100 MHz) τ 7.95 (d, 3 H, J = 7.0 Hz), 4.36 (q, 1 H, J = 7.0 Hz), 2.2–2.6 (m, 5 H); mass spectra m/e 159, 119, 118, 105, 104, 103 (base). Anal. Calcd for $C_9H_9N_7$: C, 50.22; H, 4.22; N, 45.56. Found: C, 50.19; H, 4.25; N, 45.52.

The structure of this material was verified by comparison with an independently synthesized sample. A mixture containing *N*-ethylbenzamide and thionyl chloride was heated at reflux for 3 h. The excess thionyl chloride was removed by distillation, and the resulting residue was added to a stirred slurry of sodium azide in dimethylformamide. After stirring for 9 h the mixture was added to water, extracted with ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting solid was recrystallized from ether–pentane to give 5-ethyl-1-phenyltetrazole as a white solid: mp 67–68 °C; IR (KBr) 3.20, 6.20, 6.54, 6.85, 7.10, 8.51, 8.96, 9.27, 12.81, 13.56, 14.40 μm; NMR ($CDCl_3$, 60 MHz) τ 8.45 (t, 3 H, J = 7.0 Hz), 5.53 (q, 2 H, J = 7.0 Hz), 2.2–2.6 (m, 5 H).

The above tetrazole was heated in the presence of *N*-bromosuccinimide and benzoyl peroxide in carbon tetrachloride for 10 h. The solvent was removed under reduced pressure, and the residue was added to a slurry of sodium azide in acetonitrile. After stirring for 20 h, the mixture was added to water, extracted with ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 1-phenyl-5-(1-azidoethyl)tetrazole (**24**) in 53% yield. The material prepared in this fashion was identical with the major component obtained from the reaction of 2-methyl-3-phenyl-2*H*-azirine (**23**) with iodine azide.

Preparation of 2-Chloro-2-methyl-3-phenyl-2*H*-azirine (31). To a solution of iodoazide in acetonitrile (prepared from 6.0 g of sodium azide and 8.8 g of iodine monochloride in 105 mL of acetonitrile) was added 4.0 g of 1-phenyl-2-chloro-1-propene.

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(46) Fowler, F. W.; Hassner, A.; Levy, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 2077.
(47) Hassner, A.; Fowler, F. *J. Am. Chem. Soc.* **1968**, *90*, 2869.

The resulting solution was stirred at room temperature for 22 h. The solution was then extracted with ether, and the ether solution was washed with a 5% sodium thiosulfate solution, water, and a saturated salt solution. The ethereal layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 1-azido-2-chloro-2-iodo-1-phenylpropane as a yellow oil: NMR (CCl_4, 100 MHz) τ 7.64 and 7.60 (s, 3 H), 5.33 and 5.20 (s, 1 H), 2.6–2.9 (m, 5 H); IR (neat) 4.70 μm.

A 5.0-g sample of the above compound was dissolved in 200 mL of dry ether. The solution was cooled to −20 °C, and then 5.0 g of potassium *tert*-butoxide was added in one portion. The resulting slurry was stirred for 12 h, the temperature being kept between −5 and −10 °C. At the end of this time water was added, and the mixture was extracted with ether, dried over magnesium sulfate, and concentrated under reduced pressure to give 1.82 g of a mixture of *cis*- and *trans*-1-azido-2-chloro-1-phenyl-1-propene (**30**). The crude mixture was chromatographed over a silica gel column with hexane as the eluent. The faster moving component contained 0.65 g of a clear oil: NMR (CCl_4, 100 MHz) τ 7.82 (s, 3 H), 2.70 (br s, 5 H); IR (neat) 4.72 μm. The slower moving isomer contained 0.51 g of a clear oil: NMR (CCl_4, 100 MHz) τ 8.04 (s, 3 H), 2.52–2.88 (m, 5 H); IR (neat) 4.73 μm.

A degassed solution containing 350 mg of a mixture of the above vinyl azides in 50 mL of carbon tetrachloride was irradiated for 1.5 h with a 450-W Hanovia lamp equipped with a uranium-glass filter sleeve. Removal of the solvent left a 5:1 mixture of 2-chloro-2-methyl-3-phenyl-2*H*-azirine (**31**) and 2-chloro-3-methyl-2-phenyl-2*H*-azirine (**32**) as a yellow oil: IR (neat) 3.30, 3.41, 5.75, 6.24, 6.65, 6.86, 8.32, 8.45, 9.25, 12.90, 14.50; NMR (CCl_4, 100 MHz) τ 7.98 (s, 3 H), 2.36–2.56 (m, 3 H), 2.0–2.2 (m, 2 H) for the major isomer and τ 7.42 (s, 3 H), 2.76 (br s, 5 H) for the minor isomer. The relative ratio of the two isomeric chlorides was found to be dependent on the nature of the solvent system. In acetonitrile-d_3 the ratio of **31** to **32** was 3.33:1.0. All attempts to separate the two isomers by chromatography resulted in the formation of 1-phenyl-1,2-propanedione (**33**): IR (neat) 3.42, 5.86, 5.98, 6.29, 6.90, 7.03, 7.39, 7.57, 7.75, 8.60, 11.10, 12.71, 14.30 μm; NMR (CCl_4, 100 MHz) τ 7.56 (s, 3 H), 2.4–2.7 (m, 3 H), 1.97–2.08 (m, 2 H).

The reduction of the chloroazirine mixture with Red-Al was also carried out. To a solution containing 85 mg of **31** and **32** in 150 mL of anhydrous benzene was added 5 mL of a 70% solution of Red-Al in benzene. The solution was stirred for 1 h, and then 5 mL of water was added followed by 5 mL of a 30% sodium hydroxide solution and 25 mL of water. The benzene layer was separated, dried over magnesium sulfate, and concentrated under reduced pressure to give 78 mg of 2-methyl-3-phenylaziridine (**34**). The structure of the aziridine was established by comparison with an authentic sample.[48]

Attempts to Dimerize 2-Chloro-2-methyl-3-phenyl-2*H*-azirine (31). All attempts to obtain a bi(2*H*-azirine) by treatment of chloroazirine **31** with metals failed. Some of the metals tried included zinc dust, magnesium, lithium, nickel tetracarbonyl, and nickel dicyclooctatetraene. Further work along these lines was discontinued, and instead the electrolysis of chloroazirine **31** was studied. A 1.05×10^{-3} M solution of **31** in acetonitrile which was also 0.1 M in tetrabutylammonium perchlorate was prepared. Prior to use, the acetonitrile was filtered through an activated alumina column, and the tetrabutylammonium perchlorate was recrystallized from ethyl acetate. The voltamogram was obtained by using a three-electrode electrolytic cell equipped with a dropping mercury electrode and a SCE reference electrode. A wave was observed at −1.70 V which by cyclic voltametry was found to be irreversible.

Preparative electrolysis experiments were also carried out. A solution containing 315 mg of freshly prepared chloroazirine **31** in 110 mL of acetonitrile and 17 g of tetrabutylammonium perchlorate was placed in an electrolysis cell. The solution was purged with an argon stream and then electrolyzed at −1.80 V until 99% conversion. The reaction mixture was then evaporated almost to dryness and extracted with hexane. The hexane layer was evaporated under reduced pressure, leaving a dark oil whose IR and NMR spectra indicated the absence of the azirine ring. The only product obtained in 13% yield on chromatography was 1-phenyl-1,2-propanedione (**33**). Further studies with this system were abandoned.

Preparation and Photolysis of 1-Azido-2-bromo-1-phenyl-1-propene. To a solution containing 50 g of α-methylcinnammic acid in 250 mL of carbon disulfide was added 54.5 g of bromine. The solution was exposed to an intense visible light for 30 min after the addition was complete. At the end of this time the solvent and excess bromine were removed under reduced pressure, and the resulting solid was collected. A hot solution containing 75 g of sodium carbonate in 250 mL of water was slowly added to the solid, and the mixture was allowed to stir for 8 h. The mixture was then subjected to steam distillation, and the resulting oil was taken up in ether. The ethereal solution was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 27.5 g (45%) of 2-bromo-1-phenyl-1-propene as a yellow oil: NMR ($CDCl_3$, 100 MHz) τ 7.55 (s, 3 H), 3.32 (s, 1 H), 2.4–2.9 (m, 5 H).

To a mixture containing 0.97 g of iodine azide and 0.85 g of sodium azide in 25 mL of acetonitrile was added 0.985 g of the above olefin at 0 °C. The reaction mixture was allowed to stir for 20 h and was then diluted with water, extracted with ether, washed with a 5% sodium thiosulfate solution, dried over magnesium sulfate, and concentrated under reduced pressure to give 0.65 g (36%) of 1-azido-2-bromo-2-iodo-1-phenylpropane as an orange oil: NMR ($CDCl_3$, 100 MHz) τ 7.43 (s, 3 H), 7.39 (s, 3 H), 5.33 (s, 1 H), 5.08 (s, 1 H), 2.4–2.8 (m, 10 H).

The above mixture of diastereomers was taken up in 50 mL of ether and 0.11 g of potassium *tert*-butoxide was added at −15 °C. The mixture was stirred at 0 °C for 18 h and was quenched with water. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting residue was chromatographed on a thick-layer plate with hexane as the eluent to give 1-azido-2-bromo-1-phenyl-1-propene as a mixture (2:1) of the *E* and *Z* isomers: IR (neat) 3.42, 4.75, 6.06, 6.73, 6.94, 7.73, 8.09, 9.03, 9.95, 10.09, 12.81, 14.20 μm; NMR ($CDCl_3$, 100 MHz) τ 7.86 (s, 3 H, *Z* isomer), 7.67 (s, 3 H, *E* isomer), 2.4–2.7 (m, 5 H); UV (cyclohexane) 257 nm (ϵ 12000). Photolysis of the above azide in pentane resulted in a deep black solution which resisted purification. All attempts to isolate a 2*H*-azirine failed, and further study with this system was abandoned.

Acknowledgment. We gratefully acknowledge the National Cancer Institute, DHEW (Grant CA-21471), for generous support of this work (A.P.). Aid in the purchase of the NMR spectrometer (XL-100) used in this work was provided by the NSF via an equipment grant. We also thank Dr. Jerald Rasmussen for some experimental assistance in the early phase of the project.

Registry No. **6**, 71001-17-7; **8**, 71001-18-8; **9**, 71001-19-9; **10**, 17799-61-0; **11** isomer 1, 71001-20-2; **11** isomer 2, 71001-21-3; **16**, 52179-56-3; **17**, 71001-22-4; **18**, 63163-63-3; **19**, 71001-23-5; **20**, 16483-98-0; **21**, 71001-24-6; **22**, 28386-90-5; **23**, 16205-14-4; **24**, 71001-25-7; **25**, 3599-62-0; *cis*-**30**, 71001-26-8; *trans*-**30**, 71001-27-9; **31**, 71001-28-0; **32**, 71001-29-1; **33**, 579-07-7; **34**, 7763-71-5; potassium amide, 17242-52-3; acetophenone dimethylhydrazone, 13466-32-5; 2,3-dibromo-2,3-dimethylbutane, 594-81-0; propiophenone, 93-55-0; 1,1-dimethylhydrazine, 57-14-7; propiophenone dimethylhydrazone, 19679-59-5; phenylacetone dimethylhydrazone, 4836-61-7; 3,4-diphenyl-2,5-hexanedione bis(*N*,*N*-dimethylhydrazone) isomer 1, 71001-30-4; 3,4-diphenyl-2,5-hexanedione bis(*N*,*N*-dimethylhydrazone) isomer 2, 71001-31-5; cinnamyl chloride, 2687-12-9; potassium phthalimide, 1074-82-4; *N*-(α-chlorobenzylidene)-3-amino-1-phenylpropene, 63122-42-9; sodium azide, 26628-22-8; *N*-ethylbenzamide, 614-17-5; 5-ethyl-1-phenyltetrazole, 46165-47-3; 1-azido-2-chloro-2-iodo-1-phenylpropane, 71001-32-6; (*E*)-1-azido-2-bromo-1-phenylpropene, 71001-33-7; (*Z*)-1-azido-2-bromo-1-phenylpropene, 71001-34-8; α-methylcinnamic acid, 1199-77-5; 2-bromo-1-phenylpropene, 71001-35-9; 1-azido-2-bromo-2-iodo-1-phenylpropane isomer 1, 71001-36-0; 1-azido-2-bromo-2-iodo-1-phenylpropane isomer 2, 71001-37-1; *N*-benzylbenzamide, 1485-70-7.

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