74410-90-5; 2,2,2-trifluoroethylamine, 753-90-2; sulfur tetrafluoride, 7783-60-0; 4,5-bis(carbomethoxy)-3-(trifluoromethyl)-1,2-thiazole, 74410-91-6; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; 4-(carbomethoxy)-3-(trifluoromethyl)-1,2-thiazole, 74410-92-7; 5-(carbomethoxy)-3-(trifluoromethyl)-1,2-thiazole, 74410-93-8; *N*-phenyl-3-(trifluoromethyl)-2-isothiazoline-4,5-carboximide, 74410-94-9; *N*-phenylmaleimide, 941-69-5; 3-(trifluoromethyl)-1,2-thiazolo[5,4-*b*][1,4]naphthoquinone, 74410-95-0; naphthoquinone, 130-15-4; 5-hydroxy-3-(trifluoromethyl)-1,2-thiazolo-[5,4-*b*][1,4]naphthoquinone, 74410-96-1; juglone, 481-39-0; (ethylimino)sulfur difluoride, 3880-02-2; 4,5-bis(carbomethoxy)-3-methyl-1,2-thiazole, 49570-33-4; 4-(carbomethoxy)-3-methyl-1,2-thiazole, 74410-97-2; 5-(carbomethoxy)-3-methyl-1,2-thiazole, 15901-54-9; ((phenylmethyl)imino)sulfur difluoride, 56973-71-8; 4-(carbomethoxy)-3-phenyl-1,2-thiazole, 21905-48-6; 5-(carbomethoxy)-3-phenyl-1,2-thiazole, 68438-26-6.

Intramolecular Cycloaddition Reactions of Olefinic Tosylhydrazones

Albert Padwa* and Hao Ku

Department of Chemistry, Emory University, Atlanta, Georgia 30322

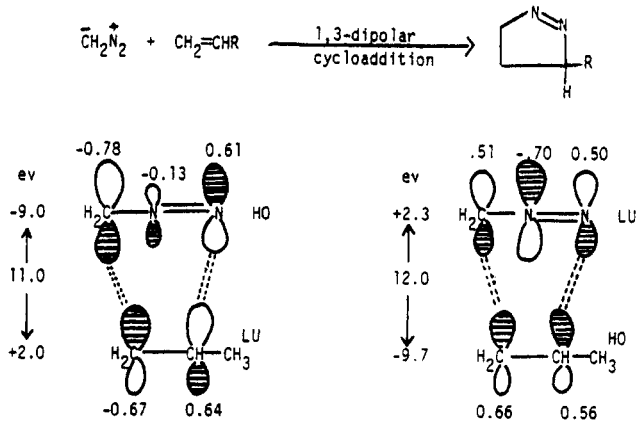
Received April 25, 1980

A series of olefinic tosylhydrazones were prepared, and their base- and acid-induced behavior was investigated. Thermolysis of the sodium salt of the tosylhydrazones generates diazoalkenes which undergo intramolecular 1,3-dipolar cycloaddition reactions. The exclusive formation of the tetrahydroindeno[1,2-*c*]pyrazole ring from thermolysis of *o*-allylbenzaldehyde tosylhydrazones is unusual and cannot be easily accounted for on the basis of frontier molecular orbital theory. Our results indicate that geometrical factors can force the reaction to occur in a manner opposite to that normally encountered. Further heating of several methyl-substituted indeno-[1,2-*c*]pyrazolines indicates that benzobicyclo[3.1.0]hexene formation proceeds with predominant inversion of configuration. The results are consistent with a mechanism involving C–N bond cleavage followed by rotation about the σ bond and back-side displacement of nitrogen. Treatment of the olefinic tosylhydrazones with boron trifluoride etherate resulted in a novel cyclization reaction. The regioselectivity associated with the acid-induced cyclization is the consequence of a carbocation pathway.

Although 1,3-dipolar cycloadditions have been successfully employed by chemists for decades,[1-3] it is only within the last few years that a fundamental understanding of the reactivity, stereoselectivity, and regioselectivity phenomena of the reaction has begun to emerge.[4-6] The additions of diazoalkanes to olefins are among the most thoroughly studied 1,3-dipolar cycloadditions.[1,7] Tosylhydrazones are commonly used as precursors to generate diazoalkanes. The cycloadditions of simple diazoalkanes are HO (1,3-dipole)–LU (dipolarophile) controlled.[5,6] Both conjugating and electron-attracting groups accelerate reactions of dipolarophiles with diazoalkanes as compared to ethylene. With these dipolarophiles, 3-substituted Δ^1-pyrazolines are favored, a result of the union of the larger diazoalkane HO coefficient on carbon with that of the larger dipolarophile LU coefficient on the unsubstituted carbon.[5] Huisgen has recently shown that introduction of a carbomethoxy group into diazomethane shifts the 1,3-dipole to a type II (Sustmann's classification)[8] in methyl diazoacetate and further toward a type III for dimethyl diazomalonate and methyl diazo(phenylsulfonyl)acetate.[9] Electron-releasing substituents in the diazoalkane, on the other hand, raise the HO energy and enhance the cycloaddition rate[10] (see Scheme I).

Simple diazoalkanes and alkylethylenes are rather unreactive as a result of the large energy gap between the frontier molecular orbitals. Surprisingly, the literature

Scheme I



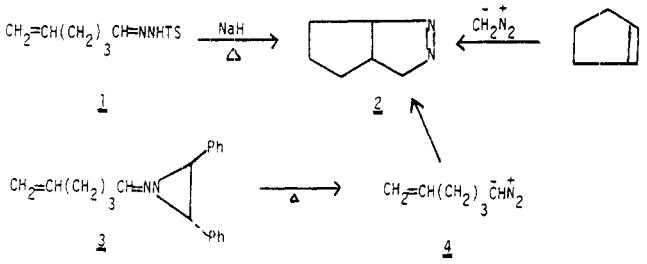
contained very few examples of the regiochemistry of cycloaddition of diazoalkanes with simple monoalkylethylenes when we initiated our studies.[11-15] Very recently, it has been shown that 3-substituted pyrazolines are formed as the major products in the 1,3-dipolar cycloaddition of diazomethane with 1-alkenes.[16,17] With these systems, the difference between the two frontier orbital interactions is quite small, but the nearly equal magnitude of the terminal coefficients in the diazomethane LU suggests that the diazomethane HO determines product regiochemistry.

In spite of the copious literature dealing with bimolecular cycloaddition reactions of diazoalkanes, intramo-

(1) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963).
(2) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes", S. Patai, Ed., Interscience, London, 1964, pp 806-878.
(3) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968); **41**, 403 (1976).
(4) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, New York, 1976.
(5) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, **95**, 7301 (1973).
(6) R. Sustmann, *Tetrahedron Lett.*, 2717 (1971).
(7) G. W. Cowell and A. Ledwith, *Q. Rev., Chem. Soc.*, **24**, 119 (1970).
(8) R. Sustmann, *Tetrahedron Lett.*, 2721 (1971); *Pure Appl. Chem.*, **40**, 569 (1974); J. Geittner, R. Huisgen, and R. Sustmann, *Tetrahedron Lett.*, 881 (1977).
(9) W. Bihlmaier, R. Huisgen, H. U. Reissig, and S. Voss, *Tetrahedron Lett.*, 2621 (1979).
(10) R. Huisgen and J. Geittner, *Heterocycles*, **11**, 105 (1978).
(11) J. M. Stewart, C. Carlisle, K. Kern, and G. Lee, *J. Org. Chem.*, **35**, 2040 (1970).
(12) H. Paul and A. Kausmann, *Chem. Ber.*, **101**, 3700 (1968).
(13) K. Kondo and I. Ojima, *Chem. Lett.*, 771 (1972); *Bull. Chem. Soc. Jpn.*, **46**, 2571 (1973); *J. Chem. Soc., Chem. Commun.*, 63 (1972).
(14) J. Geittner, R. Huisgen, and R. Sustmann, *Tetrahedron Lett.*, 881 (1977).
(15) K. B. Becker and M. K. Hohermuth, *Helv. Chim. Acta*, **62**, 2025 (1979).
(16) R. Huisgen, J. Koszinowski, A. Ohta, and R. Schiffer, *Angew. Chem., Int. Ed. Engl.*, **19**, 202 (1980).
(17) R. A. Firestone, *Tetrahedron Lett.*, 2209 (1980).

0022-3263/80/1945-3756$01.00/0

Scheme II



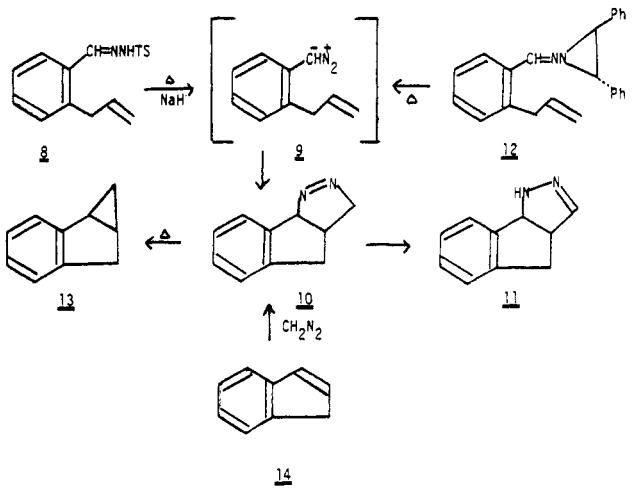
lecular examples have received only a minimum of attention.[18-21] Previous workers have found that the internal dipolar cycloaddition of diazoalkenes 1 generally leads to bicyclo[*n*.3.0] adducts 2 rather than bicyclo[*n*.2.1]azoalkanes.[22,23] Moreover, these reactions require polar[24] or strained alkenes[25] in order to proceed in satisfactory yield.[26] As part of a research program designed to uncover new cycloaddition reactions of diazoalkanes,[27] we initiated a study dealing with the chemistry of diazo compounds containing a π bond in close proximity to the dipole center. In this paper we wish to report on the mechanistic features associated with the intramolecular 1,3-dipolar cycloaddition reaction of diazoalkenes generated from tosylhydrazone precursors.

Results and Discussion

As our first model we chose to investigate the intramolecular dipolar cycloaddition reaction of the tosylhydrazone of 5-hexenal (1). Heating the tosyl salt of 1 in benzene gave rise to a single cycloadduct whose structure was assigned as 3,3a,4,5,6,6a-hexahydrocyclopentapyrazole (2, Scheme II). The structure of the thermal cycloadduct was unambiguously established by comparison with an independently synthesized sample prepared by treating cyclopentene with diazomethane.[28] Cyclopentapyrazole 2 was also formed in good yield by heating a sample of 6-(*trans*-2,3-diphenylaziridinylimino)-1-hexene (3). Eschenmoser and his co-workers[29] have used aziridinyl imines as masked diazo compounds; these have the advantage over other diazoalkane precursors, such as tosylhydrazones, in that they are cleaved thermally without the introduction of an external base, and, being soluble in organic solvents, they allow homogeneous reactions to occur.

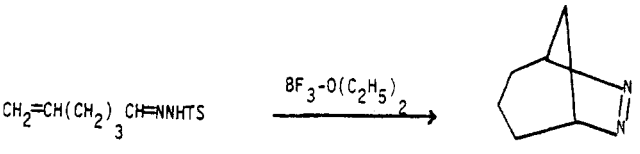
The exclusive formation of 2 is especially intriguing in light of Huisgen's work dealing with the bimolecular cycloaddition of diazoalkanes with monosubstituted olefins.[16] As was mentioned earlier, Huisgen's group was able to show that the regiochemistry of the reaction of diazoalkanes with 1-alkenes gives 3-substituted pyrazolines. Thus,

Scheme III



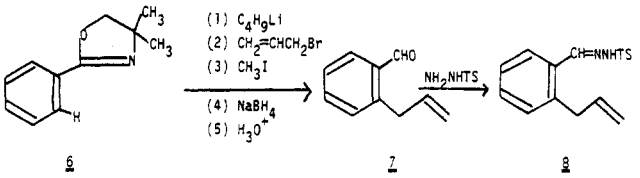
it is very interesting to note that the regioselectivity observed in the reaction of diazoalkene 4 is directly opposite to that encountered by Huisgen. It would seem as though the regioselectivity of the intramolecular cycloaddition of diazoalkene 4 is controlled by steric factors and not by the HO–LU interaction, which generally controls the regioselectivity in bimolecular cycloaddition reactions.

During the course of our studies with the above system, we found that treatment of 1 with boron trifluoride etherate resulted in an entirely different reaction. The only characterizable product obtained from this reaction corresponded to 6,7-diazabicyclo[3.2.1]oct-6-ene (5). This



unusual reaction provides a synthesis of a previously unaccessible bicyclic azo compound and represents a novel acid-catalyzed reaction of a tosylhydrazone which may be of use in many other synthetic applications.

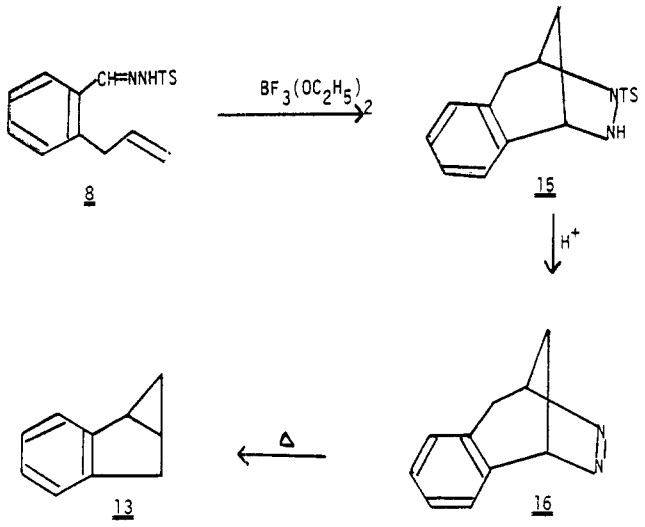
As a result of this observation, we decided to study a number of related systems in order to determine the generality of the reaction. *o*-Allylbenzaldehyde (7) was synthesized from 2-phenyl-4,4-dimethyl-2-oxazoline (6) according to the general procedure of Meyers[30] and Gschwend.[31] This unsaturated aldehyde was converted to tosylhydrazone 8 in high yield by heating with *p*-toluenesulfonylhydrazine.



Thermolysis of the sodium salt of tosylhydrazone 8 at 120 °C gave *cis*-1,3a,4,8b-tetrahydroindeno[1,2-*c*]pyrazole (11) in high yield (Scheme III). The NMR spectrum of 11 showed a doublet of doublets at δ 3.02 (1 H, J = 18, 2.0 Hz), a doublet of doublets at δ 3.26 (1 H, J = 18, 8.0 Hz),

(18) For a recent review on intramolecular 1,3-dipolar cycloadditions, see A. Padwa, "New Synthetic Methods", Vol. 5, Verlag Chemie, New York, 1979, pp 25–69.
(19) W. Kirmse and H. Dietrick, *Chem. Ber.*, **100**, 2710 (1967).
(20) M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).
(21) E. Piers, R. W. Britton, R. J. Keziere, and R. D. Smillie, *Can. J. Chem.*, **49**, 2623 (1971).
(22) W. Kirmse and D. Grassman, *Chem. Ber.*, **99**, 1746 (1966).
(23) R. M. Wilson and J. W. Rekers, *J. Am. Chem. Soc.*, **101**, 4005 (1979).
(24) D. S. Wulfman, G. Linstrumelle, and C. F. Cooper, "The Chemistry of Diazonium and Diazo Groups", S. Patai, Ed., Interscience, New York, 1978, Part 2, p 284.
(25) P. J. Garratt and J. F. White, *J. Org. Chem.*, **42**, 1733 (1977).
(26) For an example of intramolecular dipolar cycloaddition of a diazoalkane across an acetylene bond, see J. P. Mykytka and W. M. Jones, *J. Am. Chem. Soc.*, **97**, 5933 (1975).
(27) A. Padwa and H. Ku, *Tetrahedron Lett.*, 1009 (1980).
(28) H. Paul, I. Lange, and A. Kausmann, *Chem. Ber.*, **95**, 1789 (1965).
(29) D. Felix, R. K. Muller, U. Horn, R. Joos, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **55**, 1276 (1972).
(30) A. I. Meyers, D. L. Temple, D. Haidukewych, and E. D. Mihelich, *J. Org. Chem.*, **39**, 2787 (1974); A. I. Meyers and E. D. Mihelich, *ibid.*, **40**, 3158 (1975).
(31) H. W. Gschwend and A. Hamdan, *J. Org. Chem.*, **40**, 2008 (1975).

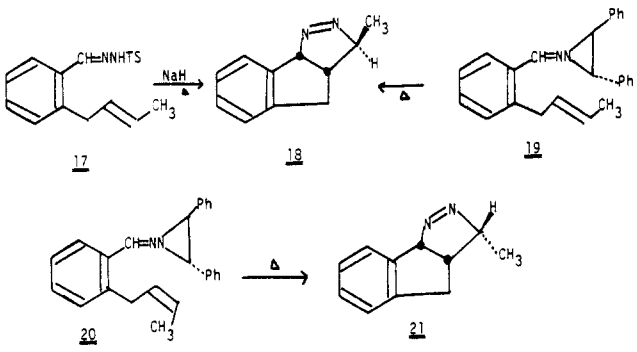
Scheme IV



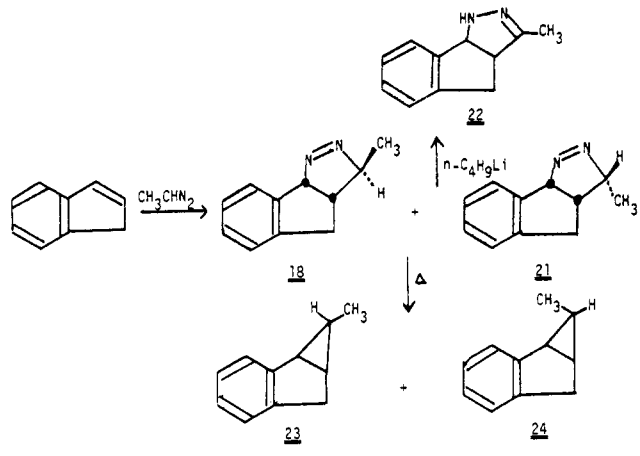
a doublet of triplets at δ 3.85 (1 H, J = 8.0, 2.0 Hz), a broad singlet at δ 4.75 (1 H), a singlet at δ 6.70 (1 H), and a multiplet at δ 7.30 (4 H). Dihydropyrazole **11** is apparently formed by intramolecular dipolar cycloaddition of the initially generated diazoalkene **9** followed by a proton-transfer reaction of the transient cycloadduct **10**. Photolysis of the tosylhydrazone salt of **8** gave benzobicyclohexane **13**, thus supporting the intermediacy of cycloadduct **10**. Further support for the above sequence of reactions was obtained by thermolyzing aziridinamine **12**. Thermolysis of **12** at 80 °C resulted in the isolation of 3,3a,4,8b-tetrahydroindeno[1,2-*c*]pyrazole (**10**) in 75% yield. The NMR spectrum of **10** showed a set of doublet of doublets at δ 2.60 (1 H, J = 15.0, 2.0 Hz), 3.22 (1 H, J = 15.0, 8.0 Hz), 4.30 (1 H, J = 19.0, 4.0, 2.0 Hz), and 4.70 (1 H, J = 19.0, 8.0 Hz), a multiplet at δ 2.70–3.05 (1 H), a doublet at δ 6.20 (1 H, J = 8.0 Hz), and a multiplet at δ 7.0–7.80 (4 H). The structure of cycloadduct **10** was unambiguously established by comparison with an independently synthesized sample prepared by treating indene **14** with diazomethane. In the presence of base, structure **10** was readily converted to the isomeric 1*H*-dihydropyrazole **11** when heated at 100 °C. Upon photolysis or thermolysis, cycloadduct **10** readily loses nitrogen to give benzobicyclohexene **13**. It should be pointed out that the regioselectivity observed in the intramolecular cycloaddition of diazoalkene **9** is identical with that observed with **4** and is directly opposite that predicted by FMO theory.

In contrast to the thermal results, treatment of tosylhydrazone **8** with boron trifluoride etherate followed by silica gel chromatography gave 4,5-dihydro-1,4-methano-1*H*-2,3-benzodiazepine (**16**) as the exclusive product in 97% overall yield (Scheme IV). The NMR spectrum of **16** showed multiplets at δ 1.92 (2 H), 2.80–3.20 (2 H), and 7.0–7.4 (4 H) and broad singlets at δ 5.20 (1 H) and 5.60 (1 H). Addition of $Eu(fod)_3$ to the solution resulted in the separation of the multiplet at δ 1.92 into a doublet at δ 2.84 (1 H, J = 12.0 Hz) and a multiplet at δ 3.10 (1 H). The multiplet at δ 2.80–3.20 separated into a distinct AB pattern at δ 3.60 (dd, 1 H, J = 18.0, 2.0 Hz) and 3.94 (d, 1 H, J = 18.0 Hz). Heating a sample of **16** produced benzobicyclohexene **13** in quantitative yield. Examination of the crude reaction mixture before column chromatography clearly showed the presence of **15** as an isolable intermediate: 90%; NMR δ 1.20 (m, 1 H), 1.66 (d, 1 H, J = 10.0 Hz), 2.40 (s, 3 H), 3.16 (m, 2 H), 4.08 (d, 1 H, J = 5.0 Hz), 4.40 (m, 1 H), 6.8–7.8 (m, 8 H). This material

Scheme V



Scheme VI

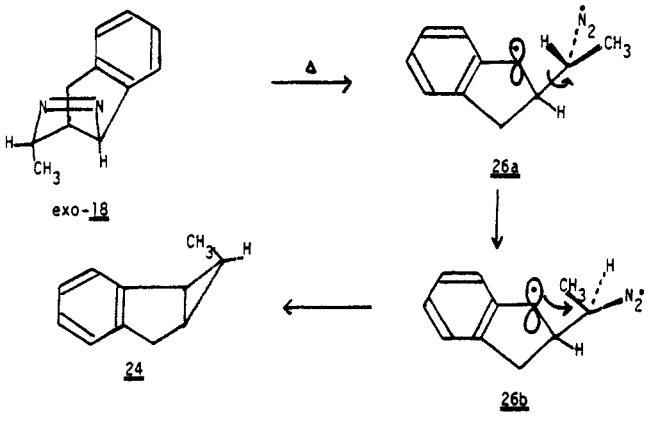


was converted to **16** on treatment with acid. These results clearly show that the mode of internal cycloaddition of tosylhydrazone **8** is markedly dependent on the experimental conditions employed.

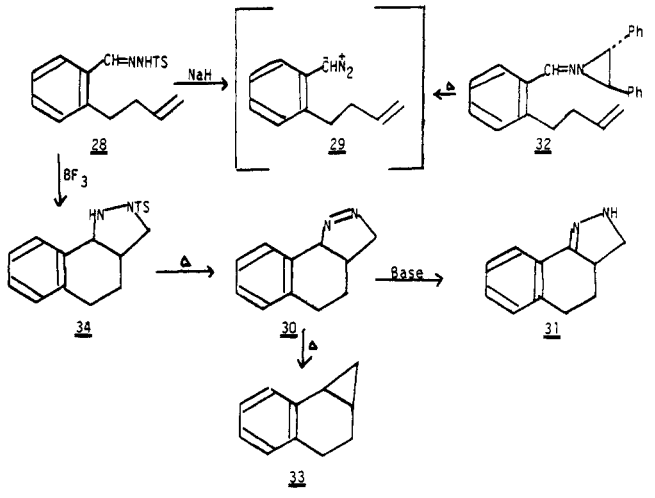
In order to probe the stereochemical aspects of the intramolecular dipolar cycloaddition reaction, we have investigated the thermolysis of the sodium salt of *trans-o*-(2-butenyl)benzaldehyde tosylhydrazone (**17**). When a benzene solution of **17** was heated at reflux for 12 h, a single product was obtained (Scheme V). Assignment of this material as *exo*-3,3a,4,8b-tetrahydro-3-methylindeno[1,2-*c*]pyrazole (**18**) was made on the basis of its straightforward spectral data: NMR ($CDCl_3$, 100 MHz) δ 1.45 (d, 3 H, J = 6.0 Hz), 2.20–2.50 (m, 1 H), 2.60 (dd, 1 H, J = 16.0, 4.0 Hz), 3.15 (dd, 1 H, J = 16.0, 8.0 Hz), 4.30 (ddd, 1 H, J = 6.0, 4.0, 2.0 Hz), 6.10 (d, 1 H, J = 8.0 Hz), 6.90–7.65 (m, 4 H). This same cycloadduct was obtained from the thermolysis of *trans-N*-[[2-[(*E*)-2-butenyl]-phenyl]methylene]-2,3-diphenyl-1-aziridinamine (**19**). A similar reaction occurred when *cis*-aziridinamine **20** was heated at 80 °C. The only product obtained here was the endo-substituted 1,3-dipolar cycloadduct **21**. Further support for the structure of cycloadducts **18** and **21** was obtained by comparison with independently synthesized samples prepared by treating indene with diazoethane.

Treatment of either the *exo*-methyl-substituted (**18**) or the *endo*-methyl-substituted (**21**) pyrazolines with *n*-butyllithium at −78 °C resulted in a base-induced isomerization to give the isomeric 1*H*-dihydropyrazole **22** (Scheme VI). Upon photolysis or thermolysis, cycloadducts **18** and **21** readily lost nitrogen to give a mixture of *exo*- and *endo*-6-methyl-2,3-benzobicyclo[3.1.0]hex-2-enes (**23** and **24**). The stereochemical assignments for the exo and endo bicyclohexenes were made of the basis of their characteristic NMR spectra. The location of the *endo*-methyl group of compound **24** at higher chemical field (δ 0.55) relative to the exo isomer **23** (δ 1.05) is consistent with the

Scheme VII

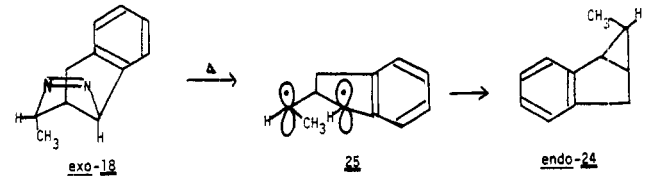


Scheme VIII



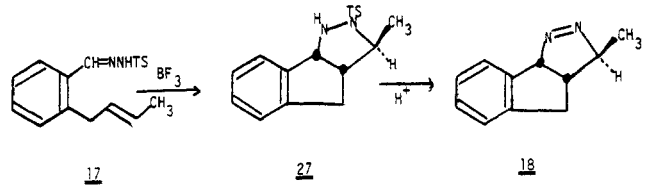
expected anisotropic shielding effect of the neighboring aromatic ring.[32] The structures of both of these compounds were unambiguously established by comparison with authentic samples.[33,34]

It is of interest to note that the thermal decompositions of indeno[1,2-*c*]pyrazolines **18** and **21** proceed with predominant inversion of configuration at the methyl-substituted carbon. In the case of *endo*-methylpyrazoline **21**, the stereoselectivity (**23**/**24**, 3:1) is about the same as that found in the decomposition of *trans*-3,4-dimethylpyrazoline,[35] while *exo*-**18** decomposes with even greater inversion (**23**/**24**, 1:6) than that found in *cis*-3,5-dimethylpyrazoline.[35] The thermolysis of simple alkyl-1-pyrazolines has been suggested to proceed via the formation of a trimethylene intermediate having planar geometry and which undergoes a subsequent conrotatory closure.[36,37] The π-cyclopropane intermediate **25**, which can be suggested to explain the above results, appears to be highly strained because carbon atoms C_1 and C_2 are connected by a short three-carbon bridge. This strain would be expected to decrease the amount of π-cyclopropane which intervenes relative to that observed in the 3,5-dimethylpyrazoline thermolysis,[35] thus lowering the stereoselectivity. Since this decrease in stereoselectivity is not observed, another factor must be responsible for the high degree of inversion observed. One possibility is that only one C–N bond cleaves in the rate-determining step of the reaction producing intermediate **26** (Scheme VII). If free-radical displacement at the methyl-substituted carbon occurs from the back side,[38] then the initial rotamer produced (**26a**) would have to undergo rotation to **26b** before ring closure could occur. This would ultimately produce the inverted benzobicyclohexene as the final product. The above mechanism is closely related to that suggested by Roth and Martin to account for the stereochemistry of pyrazoline decompositions.[39] This hypothesis is also consistent with some earlier experimental findings by Bergman[40] and Crawford[41] which suggest that O,O-diradicals are not involved in the pyrolysis of five-membered-ring azo compounds.



In contrast to the thermal results, photochemical decompositions of **18** and **21** proceed via intermediates which behave more like conventional diradicals. Both of the pyrazoline isomers produce benzobicyclohexenes with slight retention of configuration (i.e., **18** gives 2:1 **23**/**24** and **21** gives 2:3 **23**/**24**) under direct irradiation. Most likely, absorption of a photon provides enough energy to cleave both C–N bonds rapidly. The fact that the benzobicyclohexenes produced from both pyrazolines partially retain the stereochemistry of the starting material parallels the behavior observed in related systems.[42,43]

We have found that treatment of tosylhydrazone **17** with boron trifluoride etherate gave rise to 1,2,3,3a,4,8b-hexahydro-3-methyl-2-[(4-methylphenyl)sulfonyl]indeno[1,2-*c*]pyrazole (**27**) as the exclusive product. The identity of



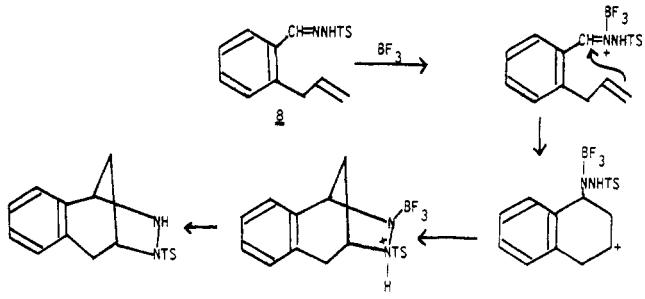
27 was determined by its straightforward spectral properties: NMR (100 MHz) δ 1.38 (d, 3 H, J = 6.0 Hz), 2.28 (s, 3 H), 2.30–2.60 (m, 3 H), 3.90 (q, 1 H, J = 6.0 Hz), 4.50 (d, 1 H, J = 12.0 Hz), 6.8–7.8 (m, 8 H). Thick-layer chromatography of **27** resulted in the loss of *p*-toluenesulfenic acid and gave pyrazoline **18** in high yield. This result clearly establishes that attachment of a methyl substituent on the double bond has a pronounced effect on the regiochemistry of the Lewis acid induced cyclization of the *o*-allyl-substituted tosylhydrazone system.

(32) J. L. Pierre, P. Chantemps, and P. Arnaud, *C. R. Hebd. Seances Acad. Sci.*, **261**, 4025 (1965).
(33) J. Nishimura, J. Furukawa, and N. Kawabata, *Nippon Kagaku Kaishi*, **43**, 2195 (1970).
(34) S. S. Hixson and J. Borossley, *J. Am. Chem. Soc.*, **98**, 2840 (1976).
(35) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).
(36) For some leading references, see R. J. Crawford and M. Ohno, *Can. J. Chem.*, **52**, 3134 (1974).
(37) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).
(38) W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **92**, 2731 (1970), and references cited therein.
(39) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967); *Justus Liebigs Ann. Chem.*, **702**, 1 (1967).
(40) P. B. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971); D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 7931 (1972).
(41) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970).
(42) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968).
(43) K. B. Wiberg and A. deMeijere, *Tetrahedron Lett.*, 59 (1969).

In view of the stringent spatial requirements associated with intramolecular 1,3-dipolar cycloaddition reactions,[18] we thought it worthwhile to consider what effect a variation in the spatial proximity between the dipole and dipolarophile would have on the course of the reaction. To this end we examined the thermolysis of the sodium salt of *o*-(3-butenyl)benzaldehyde tosylhydrazone (**28**). Heating **28** at 80 °C gave dihydropyrazole **31** in high yield (Scheme VIII). Structure **31** can be rationalized in terms of an intramolecular dipolar cycloaddition of the initially generated diazoalkene **29** followed by a proton-transfer reaction of the transient cycloadduct **30**. Support for this sequence was obtained from the thermolysis of aziridinamine **32**. Heating a benzene solution of **32** at 80 °C resulted in the isolation of tetrahydronaphtho[1,2-*c*]pyrazole **30** in 85% yield. The structure of **30** was established by comparison with an authentic sample prepared by treating 1,2-dihydronaphthalene with diazomethane. In the presence of base, cycloadduct **30** was readily isomerized to dihydropyrazole **31**. Thermolysis of a sample of naphtho[1,2-*c*]pyrazoline **30** resulted in the extrusion of nitrogen and the formation of tetrahydrocyclopropanaphthalene **33**. Treatment of tosylhydrazone **28** with boron trifluoride etherate yielded structure **34** in high yield as a crystalline solid, mp 127–128 °C. Heating a sample of **34** produced dihydropyrazole **31** as the major reaction product. Thus, in this case, as in the case of tosylhydrazone **8**, intramolecular cyclization occurs on treatment with a mild Lewis acid. With this system, however, none of the alternate 7,8-diazabenzobicyclo[4.2.1]hexene regioisomer could be detected in the crude reaction mixture.

All of the above thermal reactions can be rationalized in terms of an intramolecular 1,3-dipolar cycloaddition of a diazoalkene. The high degree of regio- and stereospecificity encountered (i.e., **17** gives **18** and **20** gives **21**) is consistent with a single-step, four-center cycloaddition, in which the two new bonds are both partially formed in the transition state, although not necessarily to the same extent.[3] As was mentioned earlier, the HO (dipole)–LU (dipolarophile) interaction controls the rate and regioselectivity of 1,3-dipolar cycloadditions of 1-alkenes with diazoalkanes. Thus, cycloaddition of diazoalkanes with alkyl-substituted ethylenes produces 3-substituted pyrazolines as the predominant regioisomer.[16,17] The exclusive formation of the tetrahydroindeno[1,2-*c*]pyrazole ring with the above systems is unusual and cannot be easily accounted for on the basis of frontier molecular orbital theory. Our results indicate that geometrical factors can force the reaction to occur in a manner opposite to that normally encountered. The inversion of regiospecificity must be related to steric effects which destabilize the transition states for formation of the alternate bridged structures. Similar "orientation inversions" have been reported with a number of other 1,3-dipoles which undergo intramolecular dipolar cycloadditions.[44-47] Another factor which undoubtedly plays an important role in the above cycloadditions is the high degree of order present in the transition state. Bimolecular cycloadditions exhibit large negative entropies of activation,[1-3] since the reactants must be precisely aligned with respect to each other. The facility with which these cycloadditions occur undoubtedly reflects an extremely favorable entropy factor which offsets the unfavorable electronic factor.

Scheme IX



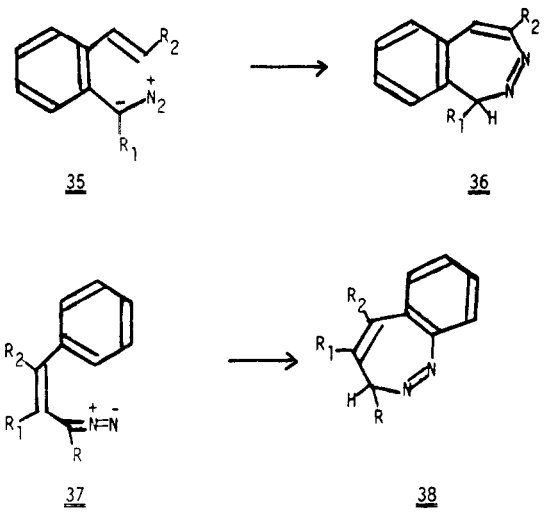
The Lewis acid induced decomposition of unsaturated diazo ketones is a well-known and useful reaction leading to an intramolecular addition to the double bond to form cyclopropyl ketones.[48,49] The reactions of diazoalkanes with common Lewis acids, on the other hand, have not been studied in any detail.[50] Tosylhydrazones are commonly used as precursors to generate diazoalkanes. In view of the extensive work that has been done with tosylhydrazones under basic conditions,[51] we were somewhat surprised to find that so little had been reported in the literature dealing with tosylhydrazone chemistry under acidic conditions.[52-55] Lewis acids hold the potential for activation of tosylhydrazones and, as we have found, can be employed advantageously to effect cyclization reactions. The results that we obtained clearly show that the mode of internal cycloaddition of unsaturated tosylhydrazones depends on the experimental conditions used and on the nature of the substituent groups attached to the double bond.

The regioselectivity encountered on treatment of tosylhydrazones **1** and **8** with boron trifluoride etherate cannot be easily accounted for in terms of a 1,3-dipolar cycloaddition path. It should be noted that Wilson and co-workers[55] have also found that tosylhydrazones of olefinic ketones undergo a cyclization reaction similar to that reported here. These workers were able to discount a path involving the prior loss of a proton followed by a 1,3-dipolar cycloaddition of the resulting azomethine imine. The most likely mechanism to account for the Lewis acid induced cyclization involves a stepwise carbocation addition to the olefin followed by the loss of a proton as shown in Scheme IX.

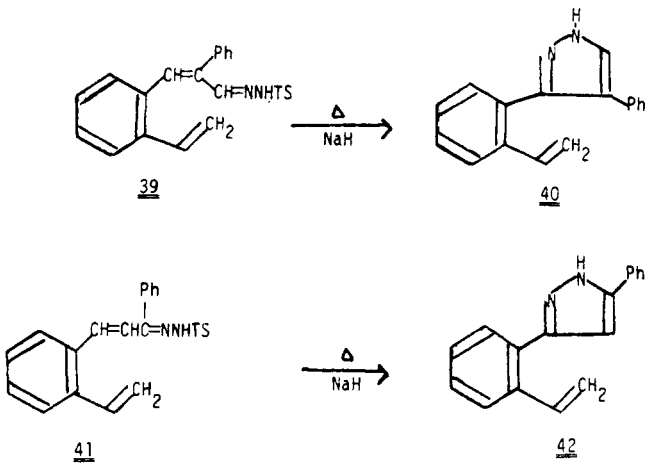
Our results with tosylhydrazones **1** and **8** indicate that the boron trifluoride induced rearrangement proceeds in a completely regiospecific manner to yield the products expected of a carbocation cyclization. Most interestingly, the orientation observed is different from that obtained under basic conditions. The acid-mediated condensation potentially provides for a versatile new type of carbon–carbon bond-forming reaction which may complement the extensive work that has been done with tosylhydrazones under basic conditions.[51] It should be noted that the Lewis acid induced reactions of **17** and **28** gave rise to the same ring system as that obtained from the thermolysis of the

(44) A. Padwa and N. Kamigata, *J. Am. Chem. Soc.*, **99**, 1871 (1977).
(45) A. Padwa, H. Ku, and A. Mazzu, *J. Org. Chem.*, **43**, 381 (1978).
(46) R. Fusco, L. Garanti, and G. Zecchi, *Chim. Ind. (Milan)*, **57**, 15 (1975).
(47) L. Garanti, A. Sala, and G. Zecchi, *J. Org. Chem.*, **40**, 2403 (1975).
(48) G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961).
(49) C. V. Scanio and D. L. Lickei, *Tetrahedron Lett.*, 1363 (1972).
(50) The reactions of diazoalkanes with Lewis acids have been reported to be extremely rapid and generally result in insertion or polymerization; see M. F. Lappert and J. S. Poland, *Adv. Organomet. Chem.*, **9**, 397 (1970).
(51) R. H. Shapiro, *Org. React.*, **23**, 405 (1976).
(52) L. Caglioti, *Tetrahedron*, **22**, 487 (1966).
(53) S. Cacchi, L. Caglioti, and G. Paolucci, *Bull. Chem. Soc. Jpn.*, **47**, 2323 (1974).
(54) R. O. Hutchins and N. R. Natale, *J. Org. Chem.*, **43**, 2299 (1978).
(55) R. M. Wilson, J. W. Rekers, A. B. Packard, and R. C. Elder, *J. Am. Chem. Soc.*, **102**, 1633 (1980).

Scheme X



Scheme XI



corresponding sodium salt. The regioselectivity associated with the cyclization of tosylhydrazone **17** may be ascribed to an entropically favored five-membered-ring closure as compared with six-membered-ring formation. With this system a secondary carbonium ion is formed by cyclization in either direction. An analogous argument (preferred cyclization to a six- rather than a seven-membered ring) may also serve to rationalize the boron trifluoride induced cyclization of **28** to **34**.

The final system that we examined involved the base-induced thermolysis of several α,β-unsaturated tosylhydrazones. α,β-Unsaturated diazoalkenes generated from the thermal decomposition of tosylhydrazone salts react by two major pathways.[56,57] These involve the loss of nitrogen to give carbene-derived products or ring closure to give pyrazoles. Brewbaker and Hart have examined the mechanism of pyrazole formation and concluded that ring closure occurs via an intramolecular 1,3-dipolar cycloaddition.[58] More recently, Sharp and co-workers have shown that diazo compounds with α,β-aromatic and γ,δ-olefinic unsaturation undergo 1,7 ring closure to give 2,3-benzodiazepines.[59] These workers also found that certain β-aryl α,β-unsaturated diazoalkenes, e.g., **37**, in which the aryl group is cis to the diazo function, undergo 1,7 ring closure to give 3*H*-1,2-benzodiazepines **38**[60] (Scheme X).

We have studied the reactions of tosylhydrazones **39** and **41** in order to test whether it would be possible to induce these systems to undergo an intramolecular 1,3-dipolar cycloaddition across the vinyl group. Thermolysis of the sodium salt of **39** resulted in 1,5-electrocyclization to give pyrazole **40** in quantitative yield (Scheme XI). A similar reaction occurred when tosylhydrazone **41** was heated in the presence of sodium hydride. The formation of the pyrazole ring involves a 6-π-electron disrotatory closure of an initially formed diazoalkene. The 3*H*-pyrazole ring, which is the initial cyclization product, undergoes a subsequent hydrogen migration[61] to give the more stable 1*H*-pyrazole system. This two-step process occurs at a faster rate than 1,3-dipolar cycloaddition across the neighboring vinyl group.

In conclusion, the results reported here clearly show that *o*-alkenylphenyl-substituted tosylhydrazones and aziridinamines undergo novel cyclization reactions. The most useful of these is the intramolecular cycloaddition to form bicycloazoalkanes. The factors which govern the regioselectivity of cycloaddition under basic conditions are still unclear. The regioselectivity encountered under acidic conditions, on the other hand, is probably the consequence of the carbocation pathway involved in the cycloaddition. The intramolecular addition of tosylhydrazones to olefins under acidic conditions potentially provides for a versatile new type of carbon–carbon bond-forming reaction which may complement the extensive work that has been done with tosylhydrazones under basic conditions.

Experimental Section[62]

Thermolysis of the Sodium Salt of 5-Hexenal Tosylhydrazone (1). To a 2.5-g sample of 5-hexenal[63] in 50 mL of pentane was added 1.05 equiv of tosylhydrazine at 0 °C. After the mixture was stirred at 0 °C for 8 h, the resulting solid was collected by filtration, washed with pentane, and dried under vacuum to give 5-hexenal tosylhydrazone (1): 70% yield; mp 57–58 °C; IR (KBr) 3.19, 6.12, 6.26, 7.36, 8.56 μm; NMR ($CDCl_3$, 60 MHz) δ 1.1–2.42 (m, 6 H), 2.42 (s, 3 H), 4.81–5.06 (m, 2 H), 5.34–6.13 (m, 1 H), 7.02–8.06 (m, 6 H).

Anal. Calcd for $C_{13}H_{18}SO_2N_2$: C, 58.63; H, 6.81; N, 10.52. Found: C, 58.72; H, 6.74; N, 10.46.

To a solution containing 200 mg of tosylhydrazone 1 in 5 mL of dry tetrahydrofuran was added 30 mg of an oil dispersion of sodium hydride under a nitrogen atmosphere. After the mixture was stirred for 1 h at room temperature, 50 mL of pentane was added, and the resulting precipitate was filtered as a white solid which was used immediately in the next step. A 190-mg sample of the above salt in 10 mL of benzene was heated under a nitrogen atmosphere at reflux for 10 h. Removal of the solvent left a clear oil whose structure was shown to be 3,3a,4,5,6,6a-hexahydrocyclopentapyrazole (2): NMR ($CDCl_3$, 100 MHz) δ 0.75–2.70 (m, 7 H), 4.22 (dt, 1 H, J = 18.0, 3.0 Hz), 4.50 (ddd, 1 H, J = 18.0, 8.0, 2.0 Hz), 4.98 (td, 1 H, J = 8.0, 2.0 Hz). The structure of **2** was established by comparison with an independently synthesized sample prepared according to the method of Paul, Lange, and Kausmann.[64] To a solution containing 10.0 g of cyclopentene

(56) G. L. Closs, L. E. Closs, and W. A. Boll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); G. L. Closs and W. A. Boll, *Angew. Chem., Int. Ed. Engl.*, **2**, 399 (1963).
(57) J. T. Sharp, R. H. Findlay, and P. B. Thorogood, *J. Chem. Soc., Perkin Trans. 1*, 102 (1975).
(58) J. L. Brewbaker and H. Hart, *J. Am. Chem. Soc.*, **91**, 711 (1969).
(59) A. A. Reid, J. T. Sharp, H. R. Sood, and P. B. Thorogood, *J. Chem. Soc., Perkin Trans. 1*, 2543 (1973).
(60) K. M. Stanley, J. Dingwall, J. T. Sharp, and T. W. Naisby, *J. Chem. Soc., Perkin Trans. 1*, 1433 (1979); C. D. Anderson, J. T. Sharp, and R. S. Strathdee, *ibid.*, 2209 (1979).
(61) A. Ledwith and D. Parry, *J. Chem. Soc. B*, 41 (1967).
(62) All melting points are corrected, and boiling points are uncorrected. Elemental analyses were performed by the Atlantic Microanalytical Laboratory. 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 resonance spectra were determined at 60 MHz with a Varian T-60 spectrometer and at 100 MHz with a Varian XL-100 spectrometer.
(63) A. Viola, *J. Am. Chem. Soc.*, **87**, 1150 (1965).

in 10 mL of ether was added 3.0 g of diazomethane. After the mixture was stirred at room temperature for 7 days, the solvent was removed under reduced pressure, and the residual oil was distilled at 40 °C (3 mm) to give 1.30 g of hexahydrocyclopentapyrazole **2** which was identical in every detail with a sample prepared from the thermolysis of the sodium salt of hydrazone 1.

Treatment of 5-Hexenal Tosylhydrazone (1) with Boron Trifluoride Etherate. To a solution containing 1.2 g of 5-hexenal tosylhydrazone (1) in 40 mL of methylene chloride at 0 °C was added 980 mg of boron trifluoride etherate. The mixture was allowed to warm to room temperature and was stirred for an additional 24 h. The solution was then washed with a saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Removal of the solvent left a yellow oil which was purified by Kugelrohr distillation to give 110 mg of 6,7-diazobicyclo-[3.2.1]oct-6-ene (**5**) as a crystalline solid:[55] mp 140 °C; IR (KBr) 6.62 μm; NMR ($CDCl_3$, 60 MHz) δ 0.71–1.94 (m, 8 H), 4.83 (br t, 2 H, J = 5.0 Hz); UV (cyclohexane) 347 nm (ε 320).

Anal. Calcd for $C_6H_{10}N_2$: C, 65.42; H, 9.15. Found: C, 65.38; H, 9.04.

Thermolysis of 6-(*trans*-2,3-Diphenylaziridin-1-ylimino)-1-hexene (3). To a solution containing 980 mg of 5-hexenal in 30 mL of ether was added 2.30 g of 1-amino-*trans*-2,3-diphenylaziridine.[29] The mixture was allowed to stir for 20 h at 5 °C, and then the solvent was removed under reduced pressure. The residual oil that remained was subject to Florisil column chromatography using a 10% ether–pentane mixture as the eluent. The product material isolated from the column contained 810 mg of a clear oil whose structure was assigned as 6-(*trans*-2,3-diphenylaziridin-1-ylimino)-1-hexene (**3**): IR (neat) 3.50, 6.14, 6.24, 6.70, 6.93, 10.98, 13.40, 14.44 μm; NMR ($CDCl_3$, 100 MHz) δ 1.24 (p, 2 H, J = 7.0 Hz), 1.75 (q, 2 H, J = 7.0 Hz), 1.98 (q, 2 H, J = 7.0 Hz), 3.42–3.62 (br s, 2 H), 4.64–4.95 (m, 2 H), 5.35–5.78 (m, 1 H), 6.80–7.50 (m, 11 H); UV (methanol) 298 nm (ε 7950); mass spectrum, m/e 180, 164, 114, 113, 82, 81, 80, 76.

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.58; H, 7.67; N, 9.61.

A 300-mg sample of aziridinylimine **3** in 50 mL of benzene was heated at reflux under a nitrogen atmosphere for 24 h. Removal of the solvent under reduced pressure left an oily solid which was chromatographed on a thick-layer plate. In addition to *trans*-stilbene, the major component isolated from the plate contained 105 mg of a clear oil whose structure was assigned as 3,3a,4,5,6,6a-hexahydrocyclopentapyrazole (**2**). The structure of this material was verified by comparison with an authentic sample.[64]

Preparation of *o*-Allylbenzaldehyde Tosylhydrazone (8). To a solution containing 1.38 g of tosylhydrazine in 6 mL of methanol was added 1.02 g of *o*-allylbenzaldehyde.[65] The mixture was allowed to stir for 30 min at 40 °C, and then 2 mL of water was added. The resulting solid was collected and recrystallized from methanol–water to give 2.08 g (95%) of *o*-allylbenzaldehyde tosylhydrazone (**8**) as a white solid: mp 120–121 °C; IR (KBr) 3.25, 6.30, 6.97, 7.48, 7.60, 8.60, 9.20, 9.60, 10.65, 12.35, 12.98, 14.35 μm; NMR ($CDCl_3$, 100 MHz) δ 2.40 (s, 3 H), 3.40 (d, 2 H, J = 6.0 Hz), 4.92 (m, 2 H), 5.60–6.00 (m, 1 H), 7.0–7.32 (m, 4 H), 7.60–8.04 (m, 4 H), 8.50 (s, 1 H); UV (methanol) 278 nm (ε 16300); mass spectrum, m/e 130 (base), 129, 128, 127, 115, 91.

Anal. Calcd for $C_{17}H_{18}N_2O_2S$: C, 64.91; H, 5.79; N, 8.92; S, 10.20. Found: C, 64.80; H, 5.80; N, 8.84; S, 10.12.

Thermolysis of the Sodium Salt of *o*-Allylbenzaldehyde Tosylhydrazone (8). To a solution containing 200 mg of tosylhydrazone **8** in 5 mL of dry tetrahydrofuran was added 36 mg of an oil dispersion of sodium hydride under a nitrogen atmosphere. After the mixture was stirred for 1 h at room temperature, 50 mL of pentane was added, and the resulting precipitate was filtered and dried under vacuum to give 190 mg (85%) of the sodium salt as a white solid which was used immediately in the next step. A 230-mg sample of the above salt in 20 mL of benzene was heated under a nitrogen atmosphere at reflux for 12 h. The precipitate that formed was filtered, and the solvent was removed under reduced pressure. The residual yellow oil was purified by silica gel chromatography using a 3:1 methylene chloride–ethyl acetate mixture as the eluent. The major fraction obtained (46 mg, 51%) was a white solid (mp 60–62 °C) whose structure was assigned as *cis*-1,3a,4,8b-tetrahydroindeno[1,2-*c*]pyrazole (**11**) on the basis of its spectroscopic properties: IR (KBr) 3.05, 3.48, 6.30, 6.80, 6.90, 13.35 μm; UV (methanol) 272 nm (ε 1670), 265 (1950); NMR ($CDCl_3$, 100 MHz) δ 3.02 (dd, 1 H, J = 18.0, 2.0 Hz), 3.26 (dd, 1 H, J = 18.0, 8.0 Hz), 3.85 (dt, 1 H, J = 8.0, 2.0 Hz), 4.75 (br s, 1 H, exchanged with D_2O), 5.12 (d, 1 H, J = 8.0 Hz), 6.70 (s, 1 H), 7.30 (s, 4 H); mass spectrum, m/e 158 (M^+), 157, 132, 131, 130, 129, 117, 116.

Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.87; H, 6.36; N, 17.71.

The structure of **11** was further established by comparison with an independently synthesized sample prepared by treating **10** with sodium hydride. To a solution containing 80 mg of **10** in 5 mL of benzene was added 25 mg of sodium hydride. The mixture was heated in a sealed tube at 120 °C for 10 min. The excess sodium hydride was decomposed by the addition of water, and the organic layer was washed with a 5% sodium bicarbonate solution followed by water. After the organic layer was dried over sodium sulfate, the solvent was removed under reduced pressure to give 65 mg (80%) of a crystalline solid whose spectral characteristics were identical with those of the material obtained from the thermolysis of the sodium salt of *o*-allylbenzaldehyde tosylhydrazone.

Treatment of *o*-Allylbenzaldehyde Tosylhydrazone with Boron Trifluoride Etherate. To a solution containing 800 mg of hydrazone in 40 mL of benzene was added 0.4 mL of boron trifluoride etherate. The mixture was allowed to stir at room temperature for 6 h and was then washed with a saturated sodium bicarbonate solution followed by water. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The resulting yellow oil was subjected to silica gel chromatography using a 1:1 ether–pentane mixture as the eluent. The major fraction isolated contained 360 mg (97%) of a colorless oil whose structure was assigned as 4,5-dihydro-1,4-methano-1*H*-2,3-benzodiazepine (**16**) on the basis of the following spectral data: IR (neat) 3.40, 6.77, 6.89, 7.60, 7.74, 8.50, 13.32, 14.00 μm; UV (methanol) 340 nm (ε 100), 276 (400), 267 (500); NMR ($CDCl_3$, 100 MHz) δ 1.92 (m, 2 H), 2.80–3.20 (m, 2 H), 5.20 (br s, 1 H), 5.60 (br s, 1 H), 7.0–7.4 (m, 4 H). Addition of $Eu(fod)_3$ to the solution caused the signal at δ 1.92 to separate into a doublet at δ 2.84 (1 H, J = 12 Hz) and a multiplet at δ 3.10 (1 H). In addition, the multiplet at δ 2.80–3.20 separated into a distinct AB pattern at δ 3.60 (dd, 1 H, J = 18.0, 2.0 Hz) and 3.94 (d, 1 H, J = 18.0 Hz). The multiplet at δ 5.20 now appeared as a broad triplet (1 H, J = 4.0 Hz) at δ 6.80 and the signal at δ 5.60 appeared as a doublet (J = 4.0 Hz) at δ 7.12. The mass spectrum is as follows: m/e 130 (base), 129, 128, 127, 115.

Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.95; H, 6.37; N, 17.71. Found: C, 75.63; H, 6.41; N, 17.61.

Examination of the crude reaction mixture before column chromatography showed that only a small quantity (ca. 10%) of **16** was present in the crude reaction mixture. Instead, a series of peaks associated with 2,3,4,5-tetrahydro-3-[(4-methylphenyl)sulfonyl]-1,4-methano-1*H*-2,3-benzodiazepine (**15**) was found in the NMR spectrum: ($CDCl_3$, 100 MHz) δ 1.20 (m, 1 H), 1.66 (d, 1 H, J = 10.0 Hz), 2.40 (s, 3 H), 3.16 (m, 2 H), 4.08 (d, 1 H, J = 5.0 Hz), 4.40 (m, 1 H), 6.8–7.8 (m, 8 H). When the crude reaction mixture was stirred with some silica gel, the signals associated with **15** disappeared, and a new set of peaks which correspond to structure **16** appeared in the NMR spectrum.

The structure of compound **16** was further verified by conversion to benzobicyclo[3.1.0]hex-2-ene (**13**) on heating. A 158-mg sample of **16** in 5 mL of benzene was heated at 130 °C in a sealed tube for 5 h. Removal of the solvent under reduced pressure afforded 128 mg (98%) of benzobicyclo[3.1.0]hex-2-ene (**13**) as a colorless oil whose spectral properties were identical in every detail with an authentic sample.[66]

Preparation of *trans*-*N*-[(2-Allylphenyl)methylene]-2,3-diphenyl-1-aziridinamine (12). To a solution containing 1.46

(64) H. Paul, I. Lange, and A. Kausmann, *Chem. Ber.*, **95**, 1789 (1965).
(65) A. Padwa and A. Ku, *J. Am. Chem. Soc.*, **100**, 2181 (1978).
(66) M. Pomerantz, *J. Am. Chem. Soc.*, **89**, 694 (1967).

g of *o*-allylbenzaldehyde in 30 mL of ether was added 2.31 g of *N*-amino-*trans*-2,3-diphenylaziridine.[29] The mixture was allowed to stir for 20 h at 8 °C. Removal of the solvent under reduced pressure left 3.77 g of aziridinamine **12** as a pale yellow oil: IR (neat) 3.30, 6.24, 6.68, 6.90, 9.67, 10.00, 10.32, 10.88, 13.25, 14.37 μm; UV (methanol) 293 nm (ε 14 100); NMR ($CDCl_3$, 100 MHz) δ 3.05–3.20 (m, 2 H), 3.75 (br s, 2 H), 4.65–5.05 (m, 2 H), 5.30–5.90 (m, 1 H), 6.95–7.80 (m, 14 H), 8.30 (s, 1 H); mass spectrum, *m/e* 180, 179, 178, 130, 129 (base), 115.

Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.03; H, 6.92; N, 7.92.

Thermolysis of *trans*-*N*-[(2-Allylphenyl)methylene]-2,3-diphenyl-1-aziridinamine (12). A 676-mg sample of aziridinamine **12** in 40 mL of benzene was heated at reflux under a nitrogen atmosphere for 5 h. Removal of the solvent under reduced pressure left an oily solid which was subjected to silica gel chromatography using a 1:1 ether–pentane mixture as the eluent. The first component isolated from the column contained 350 mg of *trans*-stilbene. The second component eluted from the column contained 230 mg (73%) of a clear oil which was sublimed at 30 °C (0.05 mm) to give 3,3a,4,8b-tetrahydroindeno[1,2-*c*]-pyrazole (**10**) as a crystalline solid: mp 36–37 °C; IR (KBr) 3.37, 6.42, 6.72, 6.81, 6.87, 8.65, 10.18, 13.20 μm; UV (methanol) 327 nm (ε 430), 227 (1460), 266 (1360); NMR ($CDCl_3$, 100 MHz) δ 2.60 (dd, 1 H, *J* = 15.0, 2.0 Hz), 2.76–3.04 (m, 1 H), 3.22 (dd, 1 H, *J* = 15.0, 8.0 Hz), 4.30 (ddd, 1 H, *J* = 19.0, 4.0, 2.0 Hz), 4.70 (dd, 1 H, *J* = 19.0, 8.0 Hz), 6.20 (d, 1 H, *J* = 8.0 Hz), 7.00–7.38 (m, 3 H), 7.50–7.78 (m, 1 H); mass spectrum, *m/e* 130 (base), 129, 128, 127, 115.

Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.95; H, 6.37; N, 17.71. Found: C, 75.61; H, 6.46; N, 17.37.

The structure of **10** was established by comparison with an independently synthesized sample. To a solution containing 5.80 g of indene in 20 mL of ether was added a solution of 3.0 g of diazomethane in 20 mL of ether. The mixture was allowed to stand at room temperature for 7 days. At the end of this time the solvent was removed under reduced pressure, and the yellow residue was subjected to silica gel chromatography using a 1:1 ether–pentane mixture as the eluent. The first fraction collected contained 4.6 g of indene. The second component isolated from the column contained 1.20 g of 3,3a,4,8b-tetrahydroindeno[1,2-*c*]pyrazole (**10**) as a white solid (mp 36–37 °C) which was identical in every detail with a sample of **10** prepared from the thermolysis of aziridinamine **12**.

Thermolysis of a sample of indeno[1,2-*c*]pyrazole **10** resulted in the extrusion of nitrogen and formation of benzobicyclo-[3.1.0]hex-2-ene (**13**). Thus, a 158-mg sample of **10** in 5 mL of benzene was heated in a sealed tube at 130 °C for 5 h. Removal of the solvent under reduced pressure left 125 mg (96%) of **13** as a colorless oil: NMR ($CDCl_3$, 100 MHz) δ 0.08 (m, 1 H), 1.08 (m, 1 H), 1.70–2.00 (m, 1 H), 2.20–2.48 (m, 1 H), 2.90 (d, 1 H, *J* = 18.0 Hz), 3.18 (dd, 1 H, *J* = 18.0, 6.0 Hz), 7.0–7.4 (m, 4 H). The structure of benzobicyclo[3.1.0]hex-2-ene (**13**) was verified by comparison with an authentic sample.[66]

Irradiation of a 329-mg sample of aziridinamine **12** in 200 mL of benzene for 30 min under an argon atmosphere with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve afforded a mixture of **10**, **13**, and *trans*-stilbene. Further irradiation of the mixture for an additional 3 h resulted in the isolation of *cis*-stilbene and benzobicyclohexene **13** as the major photoproducts. When a pure sample of **10** was subjected to similar irradiation conditions, the only product that was isolated (96%) was benzobicyclohexene **13**.

Preparation of *o*-(*trans*-2-Butenyl)benzaldehyde Tosylhydrazone (17). To a solution containing 2.0 g of tosylhydrazine in 6 mL of methanol was added 1.6 g of *o*-(*trans*-2-butenyl)-benzaldehyde. The resulting mixture was allowed to stir for 30 min at 40 °C. At the end of this time 2 mL of water was added, and the precipitated solid was collected and recrystallized from methanol–water to give 2.85 g (87%) of *o*-(*trans*-2-butenyl)-benzaldehyde tosylhydrazone (**17**) as a crystalline solid: mp 104–105 °C; IR (KBr) 3.19, 6.24, 6.95, 7.56, 8.61, 9.58, 10.59, 12.28, 12.87, 14.18 μm; UV (methanol) 278 nm (ε 16 200); NMR ($CDCl_3$, 100 MHz) δ 1.55 (d, 3 H, *J* = 6.0 Hz), 2.32 (s, 3 H), 3.30 (m, 2 H), 5.30 (m, 2 H), 6.90–7.30 (m, 4 H), 7.50–8.0 (m, 4 H), 8.48 (s, 1 H); mass spectrum, *m/e* 180, 179, 145, 129 (base), 115, 91.

Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.81; H, 6.15; N, 8.53; S, 9.77. Found: C, 65.80; H, 6.14; N, 8.49; S, 9.72.

Thermolysis of the Sodium Salt of *o*-(*trans*-2-Butenyl)-benzaldehyde Tosylhydrazone (17). To a solution containing 430 mg of hydrazone **17** in 10 mL of anhydrous tetrahydrofuran was added 78 mg of a 50% oil dispersion of sodium hydride under a nitrogen atmosphere. The mixture was allowed to stir for 1 h, and then 100 mL of pentane was added, and the resulting precipitate was filtered and dried under vacuum to give 405 mg (88%) of a white solid which was immediately used in the next step. A 200-mg sample of the above salt in 20 mL of dry benzene under a nitrogen atmosphere was heated at reflux for 12 h. The precipitate that formed was removed by filtration, and the solvent was removed from the mother liquor to give 65 mg (67%) of a pale yellow oil. This material was sublimed at 35 °C (0.05 mm) to give 55 mg of a white crystalline solid (mp 40–41 °C) whose structure is assigned as *exo*-(3α,3aα,8bβ)-3,3a,4,8b-tetrahydro-3-methylindeno[1,2-*c*]pyrazole (**18**) on the basis of the following spectral data: IR (KBr) 3.45, 6.50, 6.81, 6.91, 10.47, 11.01, 13.36 μm; UV (methanol) 333 nm (ε 260), 276 (1310), 267 (1280); NMR ($CDCl_3$, 100 MHz) δ 1.45 (d, 3 H, *J* = 6.0 Hz), 2.20–2.40 (m, 1 H), 2.60 (dd, 1 H, *J* = 16.0, 4.0 Hz), 3.15 (dd, 1 H, *J* = 16.0, 8.0 Hz), 4.30 (m, 1 H), 6.10 (d, 1 H, *J* = 8.0 Hz), 6.90–7.20 (m, 3 H), 7.40–7.60 (m, 1 H); mass spectrum, *m/e* 144, 130, 129 (base), 115.

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.65; H, 7.06; N, 16.25.

Treatment of dihydropyrazole **18** with base resulted in the formation of *cis*-1,3a,4,8b-tetrahydro-3-methylindeno[1,2-*c*]-pyrazole (**22**). To a solution containing 172 mg of **18** in 20 mL of ether was added 0.6 mL of a 1.6 M *n*-butyllithium solution in hexane at −78 °C. The mixture was allowed to stir at this temperature for 30 min and was then warmed to room temperature. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick-layer chromatography using a 1:1:1 ethyl acetate–chloroform–hexane mixture as the eluent. The major component isolated from the thick-layer plate was identified as [1,2-*c*]pyrazole **22** on the basis of its spectral properties: IR (neat) 3.48, 6.81, 6.92, 7.04, 7.30, 7.60, 13.38 μm; UV (methanol) 272 nm (ε 1800), 265 (2000); NMR ($CDCl_3$, 100 MHz) δ 1.92 (s, 3 H), 2.95 (dd, 1 H, *J* = 16.0, 6.0 Hz), 3.17 (dd, 1 H, *J* = 16.0, 8.0 Hz), 3.40–3.90 (m, 1 H), 4.72 (d, 1 H, *J* = 8.0 Hz), 7.0–7.4 (m, 4 H); mass spectrum, *m/e* 144, 130, 129 (base), 115.

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.65; H, 7.13; N, 16.21.

Preparation and Thermolysis of *trans*-*N*-[[2-[(*E*)-2-Butenyl]phenyl]methylene]-2,3-diphenyl-1-aziridinamine (19). To a solution containing 1.60 g of *o*-(*trans*-2-butenyl)benzaldehyde in 30 mL of ether was added 2.31 g of *N*-amino-*trans*-2,3-diphenylaziridine.[29] The mixture was allowed to stir for 20 h at 8 °C and then the solvent was removed under reduced pressure to give 3.8 g (100%) of *trans*-*N*-[[2-[(*E*)-2-butenyl]phenyl]-methylene]-2,3-diphenyl-1-aziridinamine (**19**) as a colorless oil: IR (neat) 3.48, 6.24, 6.92, 10.31, 13.21, 14.41 μm; UV (methanol) 295 nm (ε 10 200); NMR ($CDCl_3$, 100 MHz) δ 1.57 (d, 3 H, *J* = 6.0 Hz), 3.0–3.25 (m, 2 H), 3.75 (m, 2 H), 5.20–5.50 (m, 2 H), 7.05–7.85 (m, 14 H), 8.40 (s, 1 H); mass spectrum, *m/e* 180, 179, 178, 144, 130, 129 (base), 115.

Anal. Calcd for $C_{25}H_{24}N_2$: C, 85.19; H, 6.86; N, 7.95. Found: C, 85.15; H, 6.87; N, 7.95.

A 704-mg sample of aziridinamine **19** in 40 mL of benzene was heated at reflux under a nitrogen atmosphere for 5 h. Removal of the solvent under reduced pressure left an oily solid which was subjected to silica gel column chromatography using a 1:1 ether–pentane mixture as the eluent. The first component isolated from the column contained 340 mg of *trans*-stilbene. The second fraction eluted from the column contained 165 mg of a solid which was sublimed at 35 °C (0.05 mm) to give 145 mg (43%) of *exo*-3-methylindeno[1,2-*c*]pyrazole **18**.

Further support for the structure of **18** was derived from a thermolysis experiment. A 172-mg sample of *exo*-**18** in 5 mL of benzene was heated at 125 °C in a sealed tube for 6 h. Removal of the solvent under reduced pressure left a yellow oil whose NMR spectrum indicated a 1:6 mixture of *exo*- and *endo*-6-methyl-2,3-benzobicyclo[3.1.0]hex-2-enes (**23** and **24**) as determined by analysis of the methyl doublets (*J* = 6.0 Hz) at δ 0.55 and 1.08.

Photolysis of **18** in benzene for 2 h with a Hanovia 450-W mercury lamp afforded a 2:1 mixture of the *exo*- and *endo*-methylbicyclohexenes **23** and **24**.

Independent Synthesis of 3,3a,4,8b-Tetrahydro-3-methylindeno[1,2-*c*]pyrazoles 18 and 21. To a solution containing 5.80 g of indene in 20 mL of benzene was added 3.0 g of diazoethane in 10 mL of ether. The mixture was allowed to stir at room temperature for 2 days. At the end of this time the solvent was removed under reduced pressure, and the residual yellow oil was subjected to silica gel chromatography using a 1:1 ether–pentane mixture as the eluent. The first fraction obtained corresponded to unreacted indene (5.0 g). The second component isolated from the column contained 600 mg of exo isomer **18** (mp 40–41 °C) which was identical in every detail with the sample obtained from the thermolysis of **19**. The last component isolated from the column contained 80 mg of endo isomer **21** which was identical in every detail with the minor component isolated from the thermolysis of **20**.

Irradiation of *trans*-*N*-[[2-[(*E*)-2-Butenyl]phenyl]-methylene]-2,3-diphenyl-1-aziridinamine (19). A 200-mg sample of **19** in 150 mL of benzene was irradiated under an argon atmosphere with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 35 min. Removal of the solvent under reduced pressure left a yellow oil whose NMR spectrum indicated it to contain a mixture of starting material and diaza compound **18** (3:1 ratio). When the irradiation of **19** was carried out for 3.5 h, the NMR spectrum showed the presence of *cis*-stilbene and a 2:1 mixture of *exo*- and *endo*-methylbenzobicyclohexenes **23** and **24**. The structures of the *exo*- and *endo*-methylbenzobicyclohexenes were established by comparison with authentic samples which were independently synthesized. A modification of the procedure of Kawabata and co-workers[33] was used to prepare *endo*-6-methyl-2,3-benzobicyclo[3.1.0]hex-2-ene. To a solution containing 5.8 g of indene in 30 mL of *n*-heptane was added 40 mL of a 25% diethylzinc solution. To this mixture was added 31 g of ethylidene iodide over a 30-min interval. The resulting mixture was allowed to stir at 80 °C for 12 h and then quenched by being poured into 50 mL of a 10% hydrochloric acid solution. The aqueous layer was extracted with ether, and the ethereal extracts were washed with water and a 5% sodium bicarbonate solution. The organic solution was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residual brown oil was fractionally distilled to give 1.90 g of *endo*-methylbicyclohexene **24**: bp 64–65 °C (3.0 mm); IR (neat) 3.36, 3.50, 6.81, 6.90, 9.80, 12.34, 13.20, 13.92 μm; NMR ($CDCl_3$, 100 MHz) δ 0.55 (d, 3 H, J = 6.0 Hz), 1.02–1.28 (m, 1 H), 1.75 (q, 1 H, J = 7.0 Hz), 2.40 (dt, 1 H, J = 6.0, 2.0 Hz), 2.65 (dd, 1 H, J = 16.0, 2.0 Hz), 3.05 (dd, 1 H, J = 16.0, 7.0 Hz), 6.80–7.40 (m, 4 H); UV (methanol) 279 nm (ε 1700), 272 (1630); mass spectrum, m/e 144 (M^+), 130, 129 (base), 128, 127, 115. The spectral properties of this material were identical in every detail with a sample of *endo*-methylbicyclohexene **24** isolated from the photolysis and thermolysis of aziridinamine **19** and indeno[1,2-*c*]pyrazole **18** or **21**.

An authentic sample of *exo*-6-methyl-2,3-benzobicyclo[3.1.0]-hexene (**23**) was prepared by the Wolff–Kishner reduction of *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxaldehyde.[34] To a solution containing 1.0 g of the above aldehyde in 20 mL of toluene was added 1.0 mL of anhydrous hydrazine. The mixture was allowed to stir at room temperature for 20 min, and then 0.5 g of potassium *tert*-butoxide was added. The reaction mixture was heated at reflux for 10 h. At the end of this time 5 mL of water was added, and the mixture was extracted with ether and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick-layer chromatography using hexane as the eluent. The major component isolated from the thick-layer plate contained 130 mg of a clear oil whose structure was assigned as *exo*-6-methylbenzobicyclohexene **23** on the basis of its NMR spectrum: ($CDCl_3$, 100 MHz) δ 0.40 (m, 1 H), 1.08 (d, 3 H, J = 6.0 Hz), 1.50 (m, 1 H), 2.04 (dd, 1 H, J = 7.0, 2.0 Hz), 2.90 (d, 1 H, J = 16.0 Hz), 3.12 (dd, 1 H, J = 16.0, 7.0 Hz), 3.0–3.4 (m, 4 H). This material was identical in every detail with the sample of *exo*-6-methylbicyclohexene **23** isolated from the photolysis of **18** or the thermolysis of **17** or **18**.

Preparation and Thermolysis of *trans*-*N*-[[2-[(*Z*)-2-Butenyl]phenyl]methylene]-2,3-diphenyl-1-aziridinamine (20). To a solution containing 1.30 g of *o*-(*cis*-2-butenyl)benzaldehyde in 25 mL of ether was added 2.16 g of *N*-amino-*trans*-2,3-diphenylaziridine.[29] The mixture was allowed to stir for 48 h at 10 °C, and then the solvent was removed under reduced pressure to give 3.5 g (100%) of *trans*-*N*-[[2-[(*Z*)-2-butenyl]phenyl]-methylene]-2,3-diphenyl-1-aziridinamine (**20**) as a colorless oil: IR (neat) 3.46, 6.18, 6.90, 10.42, 13.26, 14.40 μm; UV (methanol) 293 nm (ε 9800); NMR ($CDCl_3$, 100 MHz) δ 1.49 (d, 3 H, J = 6.0 Hz), 3.0–3.25 (m, 2 H), 3.75 (m, 2 H), 5.1–5.40 (m, 2 H), 7.0–7.90 (m, 14 H), 8.36 (s, 1 H); mass spectrum, m/e 180, 129 (base), 115.

Anal. Calcd for $C_{25}H_{24}N_2$: C, 85.19; H, 6.86; N, 7.95. Found: C, 85.31; H, 6.92; N, 7.86.

A 400-mg sample of aziridinamine **20** in 25 mL of benzene was heated at reflux under a nitrogen atmosphere for 5 h. Removal of the solvent under reduced pressure left an oily solid which was subjected to silica gel column chromatography using a 1:1 ether–pentane mixture as the eluent. The first component isolated from the column contained 197 mg of *trans*-stilbene. The second fraction eluted from the silica gel chromatography column contained 93 mg of a colorless oil whose structure was assigned as *endo*-(3α,3aβ,8bβ)-3,3a,4,8b-tetrahydro-3-methylindeno[1,2-*c*]-pyrazole (**21**) on the basis of the following spectral data: IR (neat) 3.42, 6.48, 6.78, 6.85, 9.98, 13.30 μm; UV (methanol) 333 nm (ε 280), 276 (1600), 267 (1400); NMR ($CDCl_3$, 100 MHz) δ 1.48 (d, 3 H, J = 6.0 Hz), 2.70–3.20 (m, 3 H), 4.60 (t, 1 H, J = 8.0 Hz), 5.90 (br d, 1 H, J = 8.0 Hz), 7.10–7.40 (m, 3 H), 7.60–7.80 (m, 1 H). Addition of $Eu(fod)_3$ shift reagent to the NMR sample separated the multiplet at δ 2.70–3.20 into three distinct signals. The upfield proton at δ 3.80 consisted of a doublet of doublets (1 H, J = 18.0, 10.0 Hz). The signal at δ 3.94 consisted of a doublet of doublets (1 H, J = 18.0, 5.0 Hz), and the downfield proton at δ 4.30 was a multiplet (1 H). The mass spectrum was as follows: m/e 144, 130, 129 (base), 218, 127, 115.

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.74; H, 7.18; N, 15.92.

This material was identical in every detail with one of the cycloadducts obtained from the reaction of indene with diazoethane. Thermolysis of **21** afforded a mixture of *exo*- and *endo*-methylbicyclohexenes **23** and **24** in a 3:1 ratio.

Treatment of *o*-(*trans*-2-Butenyl)benzaldehyde Tosylhydrazone (17) with Boron Trifluoride Etherate. To a solution containing 328 mg of hydrazone **17** in 30 mL of benzene was added 0.3 mL of boron trifluoride etherate. The mixture was allowed to stir at room temperature for 5 min, was washed with a saturated sodium bicarbonate solution, and was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick-layer chromatography using a 1:1 ether–pentane mixture as the eluent. The major component isolated from the thick-layer plate contained 120 mg (70%) of **18** which was identical in every detail with a sample obtained from the thermolysis of **17**. Examination of the crude reaction product before thick-layer chromatography showed that only a small quantity (15%) of **18** was present in the crude reaction mixture. Instead, a series of peaks associated with (3α,3aα,8bα)-1,2,3,3a,4,8b-hexahydro-3-methyl-2-[(4-methylphenyl)sulfonyl]indeno[1,2-*c*]pyrazole (**27**) was found in the NMR spectrum: ($CDCl_3$, 100 MHz) δ 1.38 (d, 3 H, J = 6.0 Hz), 2.28 (s, 3 H), 2.30–2.60 (m, 3 H), 3.90 (q, 1 H, J = 6.0 Hz), 4.50 (d, 1 H, J = 12.0 Hz), 6.8–7.8 (m, 8 H). When the crude reaction mixture was allowed to stand at room temperature, the signals associated with **27** disappeared, and a new set of peaks which correspond to structure **18** appeared in the NMR spectrum.

Preparation of *trans*-*N*-[[2-(3-Butenyl)phenyl]-methylene]-2,3-diphenyl-1-aziridinamine (32). To a solution containing 1.60 g of *o*-(3-butenyl)benzaldehyde[65] in 30 mL of ether was added 2.30 g of *N*-amino-*trans*-2,3-diphenylaziridine.[29] The mixture was allowed to stir for 20 h at 8 °C. Removal of the solvent under reduced pressure left 3.80 g of aziridinamine **32** as a pale yellow oil: IR (neat) 3.26, 6.17, 6.24, 6.74, 6.86, 10.02, 10.86, 13.12, 14.32 μm; UV (methanol) 290 nm (ε 10 400); NMR ($CDCl_3$, 100 MHz) δ 1.85–2.20 (m, 2 H), 2.35–2.70 (m, 2 H), 3.80 (br s, 2 H), 4.80–5.20 (m, 2 H), 5.50–5.95 (m, 1 H), 7.0–7.8 (m, 14 H), 8.40 (s, 1 H); mass spectrum, m/e 180, 179, 178, 144, 130, 129 (base), 128, 127, 115.

Anal. Calcd for $C_{25}H_{29}N_4$: C, 85.19; H, 6.86; N, 7.95. Found: C, 85.08; H, 6.86; N, 7.91.

Thermolysis of *trans*-*N*-[[2-(3-Butenyl)phenyl]-methylene]-2,3-diphenylaziridinamine (32). A 704-mg sample of aziridinamine **32** in 40 mL of benzene was heated at reflux under a nitrogen atmosphere for 5 h. Removal of the solvent under reduced pressure left a yellow solid which was subjected to silica gel chromatography using a 1:1 ether–pentane mixture as the eluent. The first component isolated from the column contained 335 mg of *trans*-stilbene. The second component eluted from the column contained 230 mg of a yellow solid which was sublimed at 30 °C (0.05 mm) to give 200 mg (85%) of a white solid (mp 40–41 °C) whose structure was assigned as 3,3a,4,5-tetrahydronaphtho[1,2-*c*]pyrazole (**30**) on the basis of its spectral properties: IR (KBr) 3.48, 6.50, 6.74, 6.92, 7.02, 8.04, 10.48, 13.40 μm; NMR ($CDCl_3$, 100 MHz) δ 0.80–1.20 (*m*, 1 H), 1.50–1.85 (m, 1 H), 2.20–2.70 (m, 3 H), 4.25 (ddd, 1 H, *J* = 18.0, 8.0, 4.0 Hz), 4.60 (td, 1 H, *J* = 18.0, 2.0 Hz), 4.90 (br d, 1 H, *J* = 8.0 Hz), 6.90–7.40 (m, 3 H), 7.90 (d, 1 H, *J* = 6.0 Hz); mass spectrum, *m/e* 144, 129 (base), 115.

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.66; H, 7.02; N, 16.25.

The structure of **30** was unequivocally established by comparison with an independently synthesized sample. To a solution containing 3.50 g of 1,2-dihydronaphthalene in 10 mL of ether was added a solution of 3.0 g of diazomethane in 20 mL of ether. The mixture was allowed to stand at room temperature for 7 days. At the end of this time the solvent was removed under reduced pressure, and the yellow residue was subjected to silica gel chromatography using a 1:1 ether–pentane mixture as the eluent. The first fraction contained 2.5 g of recovered starting material. The second component isolated from the column contained 1.35 g of 3,3a,4,5-tetrahydronaphtho[1,2-*c*]pyrazole (**30**) which was identical in every detail with a sample obtained from the thermolysis of **32**.

Thermolysis of a sample of naphtho[1,2-*c*]pyrazole **30** resulted in the extrusion of nitrogen and the formation of tetrahydrocyclopropanaphthalene **33**. Thus, a 172-mg sample of **30** in 5 mL of benzene was heated at 125 °C in a sealed tube for 3 h. Removal of the solvent under reduced pressure gave a clear colorless oil (140 mg, 97%) whose structure was shown to be tetrahydrocyclopropanaphthalene **33** by comparison with an authentic sample:[67] NMR ($CDCl_3$, 100 MHz) δ 0.75–0.95 (m, 2 H), 1.40–2.58 (m, 6 H), 6.85–7.35 (m, 4 H).

Preparation of *o*-(3-Butenyl)benzaldehyde Tosylhydrazone (28). To a solution containing 2.0 g of tosylhydrazine in 6 mL of methanol was added 1.60 g of *o*-(3-butenyl)benzaldehyde. The mixture was allowed to stir at 40 °C for 30 min, 10 mL of water was added, and the resulting solid was collected and recrystallized from methanol–water to give 3.15 g (96%) of *o*-(3-butenyl)benzaldehyde tosylhydrazone (**28**) as a crystalline solid: mp 105–106 °C; IR (KBr) 3.24, 6.15, 6.32, 7.01, 7.41, 7.52, 8.46, 8.60, 9.22, 10.55, 10.85, 12.27, 13.00, 14.30 μm; UV (methanol) 278 nm (ε 17 200); NMR ($CDCl_3$, 100 MHz) δ 2.0–2.35 (m, 2 H), 2.36 (s, 3 H), 2.60–2.85 (m, 2 H), 4.80–5.00 (m, 2 H), 5.50–5.90 (m, 1 H), 6.95–7.32 (m, 5 H), 7.50–7.68 (m, 1 H), 7.85 (d, 2 H, *J* = 8.0 Hz), 8.00 (s, 1 H), 8.45 (s, 1 H); mass spectrum, *m/e* 181, 180, 166, 145, 130 (base), 129, 115, and 91.

Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.80; H, 6.15; N, 8.53; S, 9.77. Found: C, 65.74; H, 6.15; N, 8.54; S, 9.76.

Thermolysis of the Sodium Salt of *o*-(3-Butenyl)benzaldehyde Tosylhydrazone (28). To a solution containing 600 mg of tosylhydrazone **28** in 15 mL of dry tetrahydrofuran was added 108 mg of an oil dispersion of sodium hydride under a nitrogen atmosphere. After the mixture was stirred for 1 h at room temperature, 150 mL of pentane was added, and the resulting precipitate was filtered and dried under vacuum to give 500 mg of a white solid which was used immediately in the next step. A 400-mg sample of the above salt in 40 mL of benzene was heated under a nitrogen atmosphere at reflux for 12 h. The precipitate that formed was filtered, and the solvent was removed under reduced pressure. The residual yellow oil was subjected to thick-layer chromatography using a 1:1 chloroform–ethyl acetate mixture as the eluent. The major band isolated from the thick-layer plate contained 108 mg (55%) of a pale yellow oil whose structure was assigned 2,3a,4,5-tetrahydronaphtho[1,2-*c*]pyrazole (**31**) on the basis of the following data: IR (neat) 2.95, 3.44, 5.95, 6.24, 6.87, 8.14, 9.10, 13.44 μm; UV (methanol) 292 nm (ε 1750), 247 (10 700); NMR ($CDCl_3$, 100 MHz) δ 1.80–2.40 (m, 2 H), 2.50–3.30 (m, 3 H), 3.80 (dd, 1 H, *J* = 12.0, 4.0 Hz), 3.92 (dd, 1 H, *J* = 12.0, 8.0 Hz), 7.10–7.60 (m, 4 H), 8.02 (d, 1 H, *J* = 8.0 Hz); mass spectrum, *m/e* 172 (M^+), 158 (base), 146, 131, 130, 129, 128, 127, 120, 119, 116, 91, 90, 89.

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.76; H, 7.03; N, 16.24.

The structure of **31** was further established by comparison with an independently synthesized sample prepared by treating **30** with potassium *tert*-butoxide. To a solution containing 200 mg of **30** in 30 mL of ether was added 95 mg of potassium *tert*-butoxide at −78 °C. The mixture was allowed to stir at −78 °C for 20 min, and then 2 mL of water was added. The mixture was warmed to 25 °C, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting yellow oil was subjected to thick-layer chromatography using a 1:1 ethyl acetate–chloroform mixture as the eluent. The major band isolated from the thick-layer plate was identical in every detail with the sample obtained from the thermolysis of the sodium salt of tosylhydrazone **28**.

Treatment of *o*-(3-Butenyl)benzaldehyde Tosylhydrazone (28) with Boron Trifluoride Etherate. To a solution containing 600 mg of tosylhydrazone **28** in 60 mL of benzene was added 1.2 mL of boron trifluoride etherate. The mixture was allowed to stir at room temperature for 48 h, was washed with a saturated sodium bicarbonate solution, and was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick-layer chromatography. The major fraction contained 230 mg of a crystalline solid (mp 127–128 °C) whose structure was assigned as 1,2,3,3a,4,9b-hexahydro-2-(4-methylphenylsulfonyl)naphtho[1,2-*c*]pyrazole (**34**) on the basis of the following spectral data: IR (KBr) 2.94, 3.06, 3.47, 6.29, 6.94, 7.25, 7.52, 8.62, 9.26, 9.90, 11.05, 12.50, 13.51, 15.62 μm; NMR ($CDCl_3$, 100 MHz) δ 1.10–2.20 (m, 3 H), 2.35 (s, 3 H), 2.60–3.00 (m, 4 H), 3.80 (dd, 1 H, *J* = 10.0, 6.0 Hz), 4.25 (d, 1 H, *J* = 12.0 Hz), 7.0–7.4 (m, 6 H), 7.90 (d, 2 H, *J* = 8.0 Hz); UV (methanol) 218 nm (ε 13 300).

Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.80; H, 6.15; N, 8.53; S, 9.77. Found: C, 65.66; H, 6.09; N, 8.47; S, 9.83.

The second component isolated from the thick-layer plate contained 45 mg of 2,3a,4,5-tetrahydronaphtho[1,2-*c*]pyrazole (**31**). This material was identical with that obtained from the thermolysis of the sodium salt of *o*-(3-butenyl)benzaldehyde tosylhydrazone. Structure **34** could readily be converted to pyrazole **31** by being stirred with a trace of base in benzene solution.

Thermolysis of the Sodium Salt of 2-Phenyl-3-(*o*-vinylphenyl)propen-1-al Tosylhydrazone (39). To a solution containing 5 mL of a 3.0 N aqueous sodium hydroxide solution and 3 mL of 95% ethanol was added 3.9 g of *o*-vinylbenzaldehyde.[68] The mixture was cooled to 0 °C, and 3.15 g of phenylacetaldehyde in 3 mL of ethanol was added dropwise. The reaction mixture was allowed to stir at 25 °C for 24 h, was poured into 200 mL of water, and was extracted with ether. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting yellow oil was distilled at 125 °C (0.1 mm) to give 0.9 g of 2-phenyl-3-(*o*-vinylphenyl)propen-1-al as a colorless oil: IR (neat) 5.95, 6.42, 6.94, 7.30, 13.51, 14.70 μm; UV (methanol) 254 nm (ε 16 800), 320 (15 800); NMR ($CDCl_3$, 100 MHz) δ 5.30 (d, 1 H, *J* = 10.0 Hz), 5.56 (d, 1 H, *J* = 16.0 Hz), 6.65–7.40 (m, 10 H), 7.53 (s, 1 H), 9.66 (s, 1 H).

To a solution containing 1.10 g of the above aldehyde in 6 mL of methanol was added 960 mg of tosylhydrazine. The mixture was allowed to stir for 30 min at 40 °C, was poured into 30 mL of water, and was extracted with ether. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give the tosylhydrazone of 2-phenyl-3-(*o*-vinylphenyl)propen-1-al (**39**) as a clear oil: NMR ($CDCl_3$, 100

(67) A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

(68) F. G. Baddar, A. El-habashi, and A. K. Fateen, *J. Am. Chem. Soc.*, **87**, 3342 (1965).

MHz) δ 2.30 (s, 3 H), 5.20 (d, 1 H, J = 12.0 Hz), 5.50 (d, 1 H, J = 16.0 Hz), 6.80–8.60 (m, 17 H). This material was immediately used in the next step.

To a solution containing 1.0 g of the above oil in 10 mL of dry tetrahydrofuran was added 150 mg of sodium hydride. The mixture was allowed to stir at 25 °C for 20 min, and then 100 mL of pentane was added. The resulting precipitate was filtered and dried under vacuum to give 680 mg of a solid. This material was heated in 20 mL of dry benzene at 80 °C for 4 h. The precipitate that formed was filtered, and the resulting oil was subjected to thick-layer chromatography using a 1:1 ether–pentane mixture as the solvent. The major component isolated from the thick-layer plate contained 195 mg of 3-(*o*-vinylphenyl)-4-phenylpyrazole (**40**) as a clear oil: IR (neat) 3.28, 6.90, 8.55, 10.31, 12.19, 13.16, 14.70 μm; NMR ($CDCl_3$, 100 MHz) δ 5.05 (d, 1 H, J = 12.0 Hz), 5.60 (d, 1 H, J = 16.0 Hz), 6.65 (dd, 1 H, J = 16.0, 12.0 Hz), 6.90–7.80 (m, 11 H).

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.68; H, 5.81; N, 11.29.

Thermolysis of the Sodium Salt of 1-Phenyl-3-(*o*-vinylphenyl)-2-propen-1-one Tosylhydrazone (41). To a solution containing 5 mL of 3.0 N aqueous sodium hydroxide solution and 3 mL of 95% ethanol was added 1.2 g of acetophenone. The mixture was cooled to 0 °C, and 1.32 g of *o*-vinylbenzaldehyde[68] in 2 mL of ethanol was added dropwise. After being stirred for 48 h at 25 °C, the mixture was poured into 20 mL of water and extracted with ether. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting oil solidified on standing to give 2.15 g (88%) of 1-phenyl-3-(*o*-vinylphenyl)-2-propen-1-one: mp 27–28 °C; IR (KBr) 6.02, 6.25, 6.80, 6.94, 7.25, 7.58, 8.26, 9.90, 10.31, 10.99, 13.51, 14.71 μm; NMR ($CDCl_3$, 100 MHz) δ 5.35 (d, 1 H, J = 12.0 Hz), 5.56 (d, 1 H, J = 16.0 Hz), 6.85–8.15 (m, 12 H); UV (methanol) 252 nm (ε 15900), 310 (15000).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.12; H. 6.06.

To a solution containing 1.17 g of the above ketone in 5 mL of ethanol was added 1.03 g of tosylhydrazine. The mixture was heated at reflux for 8 h and was then concentrated under reduced pressure. The resulting oil was crystallized from ethanol to give 1.15 g (56%) of the tosylhydrazone derivative **41**: mp 91–92 °C; IR (KBr) 2.92, 6.29, 7.25, 8.62, 12.50, 13.16, 14.38 μm; NMR ($CDCl_3$, 100 MHz) δ 2.36 (s, 3 H), 5.20 (d, 1 H, J = 10.0 Hz), 5.45 (d, 1 H, J = 16.0 Hz), 6.50–7.60 (m, 17 H), 7.80 (d, 2 H, J = 8.0 Hz), 8.10 (br s, 1 H).

To a solution containing 804 mg of the above compound in 10 mL of tetrahydrofuran was added 144 mg of sodium hydride under a nitrogen atmosphere. The mixture was stirred at room temperature for 20 min, and then 70 mL of pentane was added. The resulting precipitate was filtered and dried under vacuum to give 690 mg of a white solid. This material was heated in 30 mL of dry benzene for 4 h. The remaining solid was filtered, and the solvent was removed under reduced pressure. The resulting oil was crystallized from hexane to give 235 mg (81%) of 3-(*o*-vinylphenyl)-5-phenylpyrazole (**42**) as a white crystalline solid: mp 88–89 °C; IR (KBr) 3.11, 6.17, 6.25, 6.33, 6.92, 7.25, 10.42, 11.24, 12.66, 13.42, 14.71 μm; NMR ($CDCl_3$, 100 MHz) δ 5.08 (d, 1 H, J = 12.0 Hz), 5.50 (d, 1 H, J = 16.0 Hz), 6.50 (s, 1 H), 6.70–7.70 (m, 11 H); UV (methanol) 353 nm (ε 33000), 238 (32100); mass spectrum, *m/e* 246 (M^+), 215, 169, 143, 130, 118, 77.

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.79; H, 5.77; N, 11.35.

Acknowledgment. We gratefully acknowledge the National Cancer Institute for generous support of this research.

Registry No. 1, 71312-47-5; 1·Na, 74346-37-5; 2, 2387-34-0; 3, 74346-38-6; 5, 71312-53-3; 7, 62708-42-3; 8, 73774-60-4; 8·Na, 73774-54-6; 10, 73774-58-0; 11, 74346-39-7; 12, 73774-57-9; 13, 15677-15-3; 14, 95-13-6; 15, 73774-56-8; 16, 73774-59-1; 17, 74346-40-0; 17·Na, 74346-41-1; 18, 74346-42-2; 19, 74346-43-3; 20, 74365-62-1; 21, 74365-63-2; 22, 74346-44-4; 23, 63949-51-9; 24, 30021-35-3; 27, 74346-45-5; 28, 74346-46-6; 28·Na, 74346-47-7; 30, 74346-48-8; 31, 74346-49-9; 32, 74346-50-2; 33, 25033-22-1; 34, 74346-51-3; 39, 74346-52-4; 39·Na, 74346-53-5; 40, 74346-54-6; 41, 74346-55-7; 41·Na, 74346-56-8; 42, 74346-57-9; 5-hexenal, 764-59-0; tosylhydrazine, 1576-35-8; cyclopentene, 142-29-0; diazomethane, 334-88-3; 1-amino-*trans*-2,3-diphenylaziridine, 28161-60-6; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; *o*-(*trans*-2-butenyl)benzaldehyde, 74346-58-0; diazoethane, 1117-96-0; *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxaldehyde, 74346-59-1; *o*-(*cis*-2-butenyl)benzaldehyde, 74346-60-4; *o*-(3-butenyl)benzaldehyde, 70576-29-3; 1,2-dihydronaphthalene, 447-53-0; *o*-vinylbenzaldehyde, 28272-96-0; phenylacetaldehyde, 122-78-1; 2-phenyl-3-(*o*-vinylphenyl)propen-1-al, 74346-61-5; acetophenone, 98-86-2; 1-phenyl-3-(*o*-vinylphenyl)-2-propen-1-one, 74346-62-6.

Selectivity in Ketenimine–Thioketone Cycloadditions. 1. 1,4- and 1,2-Addition Pathways and the Synthesis of 4*H*-3,1-Benzothiazines, 2-Iminothietanes, and Thioacrylamides[1]

Alessandro Dondoni,*[2a] Arturo Battaglia,*[2b] and Patrizia Giorgianni[2b]

Laboratorio di Chimica Organica, Facoltà di Scienze, Università, 44100 Ferrara, Italy, and Laboratorio dei Composti del Carbonio contenenti Eteroatomi, Consiglio Nazionale delle Ricerche, Ozzano Emilia, Italy

Received January 21, 1980

The cycloadditions of thiobenzophenones to ketenimines take place at different sites of the cumulene depending on the extent of substitution and the nature of the substituents. C,C-Disubstituted ketenimines whose nitrogen bears an alkyl or an ortho,ortho'-disubstituted aryl undergo 1,2-cycloaddition by the C=S bond of the thione across the cumulene C=C bond to give four-membered 1:1 adducts, viz., 2-iminothietanes. An identical cycloaddition takes place from C-monosubstituted ketenimines irrespective of the nature of the N substituent. 2-Iminothietanes formed in these cases are unstable and rearrange to thioacrylamides. On the other hand, C,C-disubstituted ketenimines whose nitrogen is flanked by a phenyl or a meta- or para-substituted phenyl undergo 1,4-cycloaddition by the C=S bond of the thione across the formal heterodiene system formed by the C=N bond of the cumulene and one of the C=C bonds of the *N*-aryl group to yield as final products six-membered ring adducts, viz., 4*H*-3,1-benzothiazines. Evidence for the formation of an intermediate is provided by NMR and IR spectroscopy and, indirectly, by the isolation of a diadduct from 2 mol of thione and 1 mol of ketenimine. *N*-Phenylmethylketenimine, however, reacts with thiobenzophenone according to both the 1,2- and 1,4-cycloaddition modes to give the corresponding 2-iminothietane and 4*H*-3,1-benzothiazine in almost equal amounts. The product distribution, as monitored by following the reaction at intervals by NMR spectroscopy, is under kinetic control.

There is ample documentation on the participation of ketenimines[3] as 2-π-electron components in cycloaddition reactions with 2-π- and 4-π-electron (1,3-dipole) systems to give four- and five-membered 1:1 adducts, respectively.

0022-3263/80/1945-3766$01.00/0