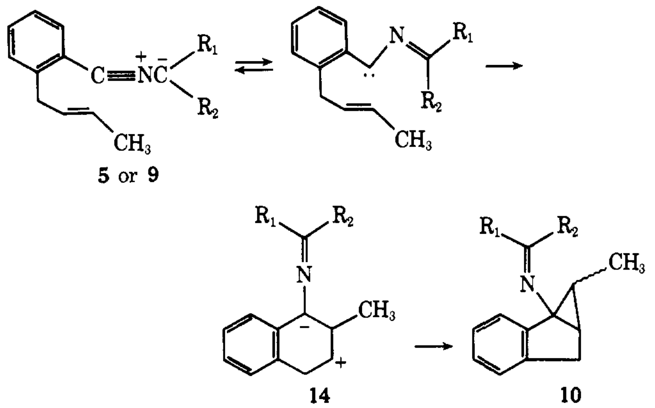
able quantities of the isomeric 1,3-dipolar adduct **13** could be observed in the crude photolysate.

Concerted 1,3-dipolar additions are known to proceed via a "two-plane" orientation complex in which the dipole and dipolarophile approach each other in parallel planes.[2-4] The cycloaddition of nitrile ylides **5** and **9** with added dipolarophiles proceeds in this fashion affording Δ^1-pyrrolines as the primary cycloadducts (e.g., **6** and **12**). Inspection of molecular models of these *o*-allyl substituted nitrile ylides indicates that the normal "two-plane" orientation approach is possible only when the π-orbitals of the aromatic ring are orthogonal to the π-orbitals of the nitrile ylide. This approach is not followed since it involves disruption of phenyl conjugation with the 4π-allyl anion portion of the nitrile ylide. As a result, the normal 1,3-dipolar cycloadduct is not formed. Product formation is possible, however, if the linear nitrile ylide undergoes rehybridization to give a species of bent geometry (carbene form) which subsequently undergoes 1,1-cycloaddition with the neighboring double bond. In an earlier report, we suggested that the most favorable transition state for the 1,1-cycloaddition reaction is one in which the π-orbitals of the nitrile ylide and olefinic double bond are orthogonal.[9] This orthogonality could permit the occurrence of an orbital symmetry-allowed $[\omega_s^2 + \pi_a^2]$ cycloaddition. This unusual mode of addition was postulated in order to account for the complete inversion of stereochemistry that occurred about the π-system.[9] Irradiation of azirine **4b**, however, was found to produce a mixture of stereoisomers. In this case the structure of the major product obtained (80%) corresponds to retention of stereochemistry about the double bond. From this work it is clear that the stereochemistry about the bicyclohexene system is not that predicted by a concerted $[\omega_s^2 + \pi_a^2]$ carbene addition, and, consequently, an alternate explanation for the previous stereochemical results must be sought.[15]

The carbene (bent geometry) form of the nitrile ylide still possesses dipolar character. Attack of the carbene carbon on the terminal position of the neighboring double bond will generate a six-membered ring dipole (i.e., **14**) which contains a secondary carbonium ion as well as an azaallyl anion portion. Collapse of this new 1,3-dipole will result in the formation of the benzobicyclo[3.1.0]hex-2-ene system. In this case, **14** collapses to produce a mixture of the exo and endo substituted bicyclohexenes. The major product obtained corresponds to the thermodynamically more favored exo isomer.[15]

We are continuing to explore the scope and mechanistic details of this novel 1,1-cycloaddition reaction and look forward to determining whether other nitrilium betaines undergo this type of behavior.



Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant PO-37550).

References and Notes

(1) Photochemical Transformations of Small Ring Heterocyclic Compounds. 71. For part 70, see A. Padwa, E. Chen, and A. Ku, *J. Am. Chem. Soc.*, **97,** 6484 (1975).

(2) R. Huisgen, *Angew. Chem., Int. Ed. Engl.,* **2,** 565 (1963); *Ibid.*, **2,** 633 (1963).

(3) R. Huisgen, *J. Org. Chem.*, **33,** 2291 (1968).

(4) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, N.Y., 1964, pp 806–878.

(5) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, **74,** 31 (1962).

(6) K. Burger and J. Fehn, *Chem. Ber.*, **105,** 3814 (1972).

(7) A. Padwa and J. Smolanoff, *J. Am. Chem. Soc.*, **93,** 548 (1971); A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *ibid.*, **94,** 1395 (1972); *ibid.*, **95,** 1945, 1954 (1973); *Pure Appl. Chem.*, **33,** 269 (1973).

(8) N. Gakis, M. Marky, J. H. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55,** 748 (1972); H. Giezendanner, M. Marky, B. Jackson, H. J. Hansen, and H. Schmid, *Ibid.*, **55,** 745 (1972); *Ibid.*, **55,** 919 (1972).

(9) For the first case of 1,1-cycloaddition from a nitrile ylide see A. Padwa and P. H. J. Carlsen, *J. Am. Chem. Soc.*, **97,** 3862 (1975).

(10) R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105,** 1324 (1972), have shown that three-membered rings are not primary products in 1,3-dipolar cycloadditions leading to five-membered heterocycles with both nitrilium and diazonium betaines.

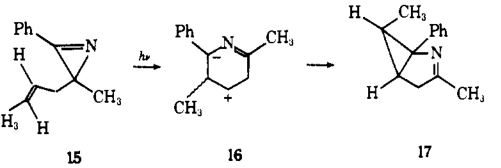
(11) A. I. Meyers, D. L. Temple, D. Haidukewych, and E. D. Mihelich, *J. Org. Chem.*, **39,** 2787 (1974); A. I. Meyers and E. D. Mihelich, *ibid.*, **40,** 3158 (1975).

(12) H. W. Gschwend and A. Hamdan, *J. Org. Chem.*, **40,** 2008 (1975).

(13) Variable quantities of *o*-allyl *N*-(*p*-nitrobenzyl)benzamide were also obtained in this experiment. The formation of this product resulted from the rapid hydrolysis of imidoyl chloride **2**.

(14) The endo bicyclohexene amine **11b** showed the following spectral properties: (60 MHz) τ 9.50 (d, 3 H, J = 6.0 Hz), 8.1–8.7 (m, 2 H), 7.60 (s 2 H, exchanged with D_2O), 7.26 (d, 1 H, J = 17.0 Hz), 6.90 (dd, 1 H, J = 17.0 and 6.0 Hz), 2.6–2.8 (m, 4 H); benzene sulfonamide derivative mp 116–118 °C; exo bicyclohexene amine **11b** (60 MHz) τ 9.42 (dq, 1 H, J = 6.0 and 4.0 Hz), 8.76 (d, 3 H, J = 6.0 Hz), 8.30 (m, 1 H), 7.95 (s, 2 H, exchanged with D_2O), 7.26 (d, 1 H, J = 17.0 Hz), 6.82 (dd, 1 H, J = 17.0 and 6.0 Hz), 2.6–2.8 (m, 4 H); benzene sulfonamide derivative, mp 165–166 °C.

(15) We previously reported that 2-phenyl-3-methyl-3-crotylazirine (**15**) produced 1-phenyl-3-methyl-6-*endo*-methyl-2-azabicyclo[3.1.0]hex-2-ene (**17**) on irradiation.[9] The formation of this product is the result of a complete inversion of stereochemistry about the double bond. The stereochemical results can now be rationalized by assuming that collapse of the initial 1,3 dipole (i.e., **16**) to the thermodynamically more favored exo isomer will result in a severe torsional barrier on closure. Collapse of **16** to the thermodynamically less favored endo isomer (i.e., **17**) moves the phenyl and methyl groups increasingly further apart and accounts for the formation of the less stable product. This type of eclipsing interaction is not present with dipole **14** and consequently closure will favor the thermodynamically more stable isomer (i.e., *exo*-**11b**).



Albert Padwa,* Audrey Ku
Arthur Mazzu, Stanley I. Wetmore, Jr.
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

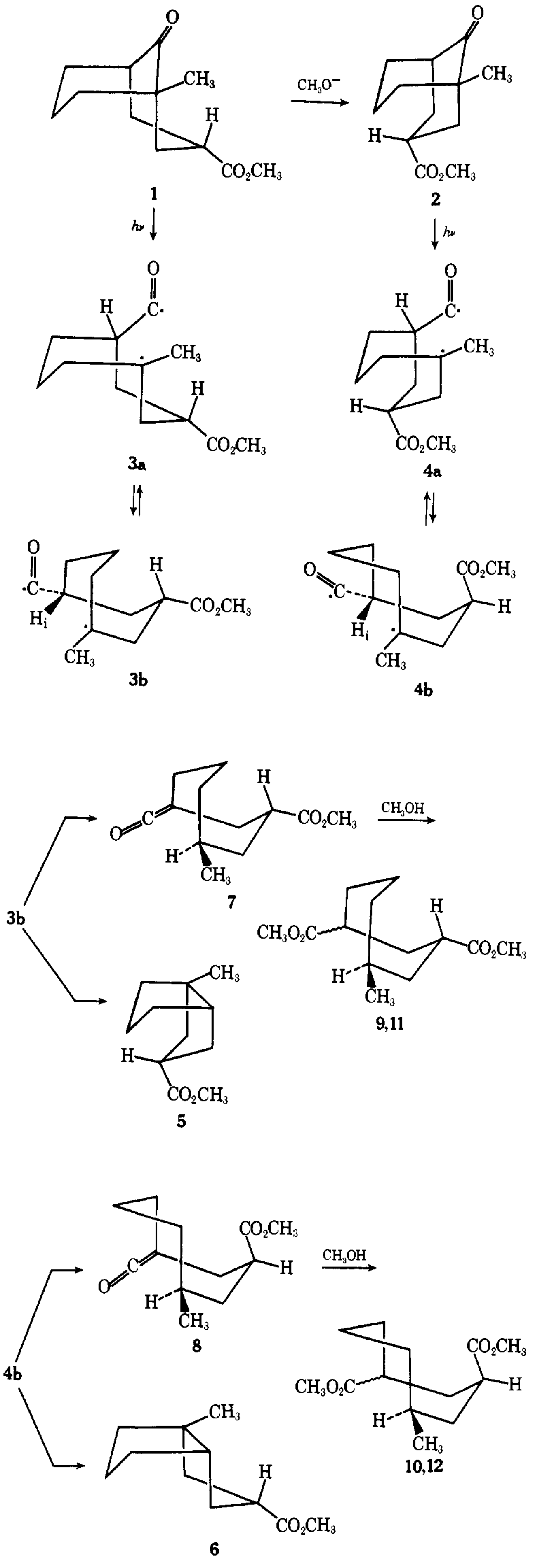
Received November 10, 1975

Photochemistry of Methyl 1-Methylbicyclo[3.3.1]nonan-9-one-3-carboxylates

Sir:

Photolysis[1] of a dioxane solution of methyl 1-methylbicyclo[3.3.1]nonan-9-one-3-*endo*-carboxylate (**1**) affords a single volatile product identified as the *cis*-methyl bicyclo[3.3.0]octane ester **5** while irradiation of the epimeric bicyclononanone exo ester **2** gives a single volatile product identified as cis fused endo ester **6**.[2] Significantly, there is no product crossover in either experiment.[3] Though decarbonylation has been previously documented for other cyclic and bicyclic ketones,[4] these examples provide the first dem-

Scheme I



onstration that a photodecarbonylation reaction can be stereospecific.

Endo keto ester **1** (yield 67%) was synthesized from the pyrrolidine enamine of 2-methylcyclohexanone and β,β'-dibromoisobutyric ester.[5] Epimerization with sodium methoxide in methanol afforded exo ester **2** (yield 100%).[5] Irradiation of **1** or **2** in dioxane was conveniently monitored, and the single volatile product **5** or **6** isolated by gas chromatography.[1] Mass spectroscopic (parent at *m/e* 182) and elemental analysis indicated that **5** and **6** resulted from decarbonylation of the starting keto esters. This was confirmed by examination of the ir spectra which showed ester as the only functional group. Absorption: **5** (2942, 2855, 1735 cm^{-1}); **6** (2940, 2858, 1732 cm^{-1}). The NMR spectra were also similar but distinctly not identical: **5** δ 1.11 (3 H, s (CH_3), 1.3-2.2 (11 H, m), 2.81 (1 H, m (CHC=O), 3.69 (3 H, s (OCH_3)); **6** δ 1.04 (3 H, s (CH_3)), 1.2-2.2 (11 H, m), 2.70 (1 H, m (CHC=O)), 3.65 (3 H, s (OCH_3)). The presence of singlet methyl resonances and the absence of any vinyl absorption in the NMR spectra indicated bicyclic structures for these compounds. A bicyclo[3.3.0]octane skeleton was suggested from the origin of the compound and subsequently confirmed (vide infra). That **5** and **6** were epimers was shown by conversion of either into a mixture of both, approximately 67:33 on treatment with sodium methoxide in methanol.[6] To further define the stereochemical relationships of **5** and **6**, each was reduced by lithium aluminum hydride to a primary alcohol which was subjected to 100-MHz NMR analysis in deuteriochloroform with stepwise additions of $Eu(fod)_3$ to aid in analysis. The alcohols obtained also have very similar but not identical NMR spectra. With the aid of $Eu(fod)_3$[7] it was possible to determine that the methyl group in the alcohol derived from **5** was definitely closer to the hydroxyl oxygen than the methyl of **6**.[8] The combined data permit assignment of exo ester stereochemistry to **5** and endo ester stereochemistry to **6** but the stereochemistry of ring fusion (assumed to be cis) was demonstrated by another sequence.

5 was irradiated at 200 °C in methanol-benzene (1:1).[9] After irradiation, **5** and **6** were both observed and isolated as a 67:33 mixture.[6] In addition, a new longer retention time product was obtained which was related to but different from **5** and **6** (ir 2940, 2860, 1735 cm^{-1}; NMR δ 0.77 (3 H, broad singlet (CH_3)), 1.2-2.2 (11 H, m); 3.32 (1 H, m); 3.63 (3 H, s (OCH_3))). The broadened high field methyl resonance indicated that this product was also a mixture of epimers. When this mixture was treated with 10% Pd-C[10] at 200° for 80 h, gas chromatographic analysis indicated quantitative isomerization to **5** and/or **6**.[11] On the basis of this result, we assign to **5** and **6** the thermodynamically more stable *cis*-[3.3.0]bicyclooctane structure and to the high temperature product we assign the isomeric trans ring fusion.

In all of the chemical and spectral examinations of **5** and **6** described above, no evidence for product crossover in the room temperature irradiations of **1** and **2** were detected. Thus, this is the first demonstration of a completely[3] stereospecific photodecarbonylation.

Irradiation of **1** in methanol or benzene-methanol[12] resulted in the formation of two new products **9** and **11** in addition to **5**. Irradiation of **2** under similar conditions also gave two new products, **10** and **12**, which were similar but not identical with the products from **1**. Mass spectral (parent at *m/e* 242) and elemental analysis of all four products indicated that methanol addition had taken place. The ir spectra were all very similar with ester absorption at 1720 cm^{-1} and suggest the formation of cyclooctane diesters **9–12** derived from the anticipated ketenes. We are not able to assign stereochemistry on the basis of this evidence, but it is apparent that cyclooctane diester formation occurs from **1** and **2** with complete stereospecificity.

The usual mechanisms involved in cyclic ketone photochemistry begin with α-cleavage, Norrish type I, as the primary photoprocess.[13] Our quenching and sensitization experiments[14] do not distinguish whether the observed reactions come from singlet and/or triplet excited states.

A complete picture of the reaction mechanism which explains stereospecific cyclooctane diester formation is given in Scheme I.[2] From the diradical conformations **3b** and **4b**, abstraction of H$_i$ by the acyl radical would yield ketenes **7** and **8** stereospecifically. Reaction of the ketenes with alcohol can occur from either face leading to the observed diester pairs. The structures of **9–12** were not investigated further because ketene formation has been extensively investigated and the observed stereospecificity is actually not exceptional but forced on the molecule by structural and conformational features.[15]

The mechanism of the photodecarbonylation is more interesting since stereospecific inversion is observed. [3.3.0]Bicyclooctane product formation could occur in several possible ways. Loss of carbon monoxide from **3a, 3b** or **4a, 4b** would give cyclooctane biradicals which could close to **5** and **6**. A direct decarbonylation leading to the same cyclooctane biradicals cannot be ruled out. In either case, we might expect nonstereospecific product formation to result as is observed in the high temperature photochemistry of **5**.

A plausible explanation for the observed stereospecificity is preferential closure from conformations **3b** and **4b** or the cyclooctane diradicals derived from them by loss of carbon monoxide. However, examination of models of these diradical species fails to indicate any definitive basis for such conformational preferences. We propose as a possible rationale for the observed preferences in these molecules that a backside alkyl radical assisted loss of carbon monoxide occurs to form the bicyclo[3.3.0]octane. Mechanisms involving radical assisted loss of nitrogen have been proposed to account for the stereochemistry of product formation in the reactions of certain azo compounds,[16] and the occurrence of a similar process in photodecarbonylation seems reasonable. In addition, it is known that loss of carbon monoxide from an acyl radical is an activated process[17] and the proposed mechanism offers a reasonable means of overcoming this barrier.

In conclusion, previous work on photodecarbonylation had led to the generalization that molecules with radical stabilizating substituents and/or structural features which prevent competing secondary reactions of the acyl-alkyl biradical formed on α-cleavage are prone to photodecarbonylation. We would now like to propose that a structural feature or conformation which allows backside assistance by the alkyl radical formed on α-cleavage may also be a general but heretofore unrecognized mechanistic component in the photodecarbonylation reactions of cycloalkanones.

Acknowledgment. M.H. acknowledges graduate fellowships from the Dow Chemical, Eastman Kodak, and General Electric Corporations. D.S.W. acknowledges financial support from the University of Michigan, College of Literature, Sciences and the Arts, and the Horace H. Rackham School of Graduate Studies.

References and Notes

(1) Preparative photolyses were carried out through Pyrex in a Rayonet reactor equipped with 3000 Å lamps and the products isolated by preparative gas chromatography, 6 ft × .25 in. OV-101. All new compounds were consistent with spectral data and gave satisfactory combustion analyses (±0.2%).

(2) Racemic materials were used throughout, only one enantiomer is shown in Scheme I. Conformations depicted in Scheme I are idealized and a and b represent different conformations of the same molecule.

(3) Within the limits of detection by gas chromatography and NMR spectroscopy.

(4) (a) C. D. Gutsche and J. W. Baum, *J. Am. Chem. Soc.*, **90,** 5862 (1968); (b) H. Kato, N. Miyamoto, M. Hawanishi, and H. Nozaki, *Tetrahedron*, **26,** 2975 (1970); (c) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc. C*, **473** (1967); (d) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31,** 1393 (1966); (e) G. Quinkert, J. Palmowski, H. Lorenz, W. Wiersdorf, and M. Finke, *Angew. Chem., Int. Ed. Engl.*, **10,** 198 (1971); (f) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966).

(5) J. M. McEuen, R. P. Nelson, and R. G. Lawton, *J. Org. Chem.*, **35,** 690 (1970).

(6) Determined by integration of the NMR methyl resonances at δ 1.11 for **5** and δ 1.04 for **6**.

(7) (a) A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73,** 553 (1973); (b) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Am. Chem. Soc.*, **92,** 5735 (1970).

(8) Determined by extrapolation of a plot of log ΔEu vs. log *R* (Å),[7b] least-squares correlation coefficient 0.97. A molar ratio of Eu(fod)$_3$ to alcohol of 0.29 was chosen for reference. A distance, hydroxyl oxygen to methyl hydrogen, of 7.8 Å for **5** and 9.1 Å for **6** was determined.

(9) Epimerization of **5** to **6** was not observed.

(10) N. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **82,** 2553 (1960).

(11) No isomerization took place in the absence of catalyst.

(12) The yields of **5** and **6** were essentially unchanged in the alcoholic solvent irradiations.

(13) (a)N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautola, D. Morton, M. Niemczyk, and N. Shore, *Acc. Chem. Res.*, **5,** 92 (1972); (b) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Am. Chem.,Soc.*, **93,** 7213 (1971).

(14) (a) **1** was found to have a fluorescence intensity in hexane solution approximately six times that of cyclohexanone under the same conditions. We thank Professor J. C. Dalton, University of Rochester, for this determination. (b) Solutions of **1** in a mixture of benzene, cyclohexane and methanol, 1:1:1, (tetradecane internal standard) containing up to 0.72 M *trans*-1,3-pentadiene were degassed (four freeze-pump-thaw cycles) and irradiated on a merry-go-round apparatus using a Hanovia 450-W mercury lamp with a basic potassium chromate filter solution (transmission maximum at 313 nm). Irradiation was carried out to less than 2% conversion, and the solutions were analyzed by gas chromatography (flame ionization detector) on a 6 ft OV-101 column at 120 °C. Quenching was slight and for unknown reasons nonlinear. (Stern-Volmer slope between 0.2 and 0.8 M^{-1}.)

(15) (a) W. C. Agosta and S. Wolff, *J. Am. Chem. Soc.*, **97,** 456 (1975); (b) W. C. Agosta and W. L. Schreiber, *ibid.*, **93,** 3947 (1971); (c) N. C. Yang and R. H.-K. Chen, *ibid.*, **93,** 530 (1971).

(16) (a) W. R. Roth and M. Martin, *Tetrahedron Lett.*, **4695** (1967); (b) *Justus Liebigs Ann. Chem.*, **702,** 1 (1967); (c) D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, **94,** 7931 (1972).

(17) D. R. Morton and N. J. Turro, *Adv. Photochem.*, **1,** 197 (1974).

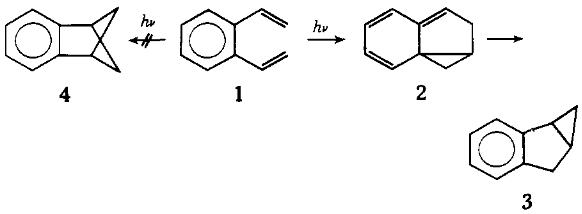
David S. Weiss,* Martin Haslanger, Richard G. Lawton
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

Received September 16, 1975

Photochemistry of *o*-Vinylstilbenes. I. A [2 + 2] Cycloaddition of an *o*-Divinylbenzene Derivative

Sir:

Some years ago Pomerantz[1] and Meinwald[2] reported that irradiation of *o*-divinylbenzene (**1**) yields benzobicyclo[3.1.0]hex-2-ene (**3**) as the main product (30%). They demonstrated that it was formed via a [4 + 2] cycloaddition, followed by a vinylcyclopropane-cyclopentene rearrangement (eq 1). Traces of tetralin, dihydronaphthalene, and naphthalene, formed via an electrocyclic reaction, were found as side-products. A [2 + 2] cycloaddition product (viz., **4**) which usually arises from 1,5-hexadienes could not be detected. Several derivatives of **1** having alkyl substituents at one or both vinyl groups gave quite similar results.[3]



(1)