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.

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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).

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

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(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.

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(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.

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(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}.)

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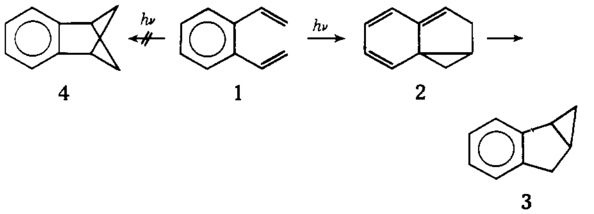
Photochemistry of *o*-Vinylstilbenes. I. A [2 + 2] Cycloaddition of an *o*-Divinylbenzene Derivative

Sir:

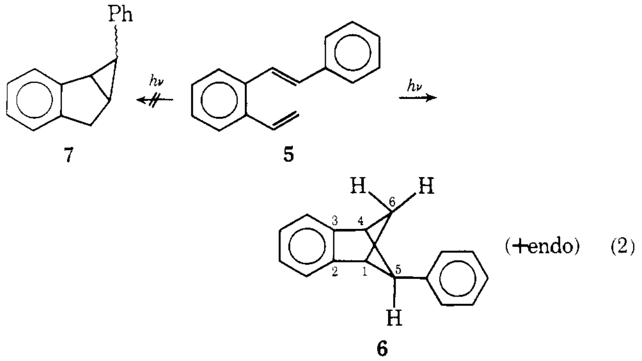
Some years ago Pomerantz[1] and Meinwald[2] reported that irradiation of *o*-divinylbenzene (**1**) yields benzobicyclo[3.1.0]hex-2-ene (**3**) as the main product (30%). They demonstrated that it was formed via a [4 + 2] cycloaddition, followed by a vinylcyclopropane-cyclopentene rearrangement (eq 1). 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)

Later on, Meinwald[4] found that 2,3-divinylnaphthalene, but not the 1,2-isomer, does give a small amount (5%) of the [2 + 2] cycloadduct on irradiation.

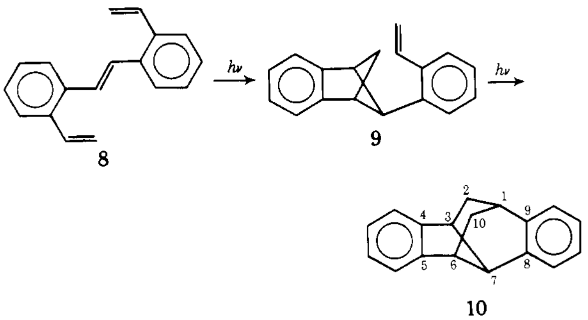
In the course of our investigations on the photochemistry of stilbene-like compounds, we have found that [2 + 2] cycloaddition is the main reaction on photoexcitation of the phenyl substituted divinylbenzene, 2-vinylstilbene[5] (**5**). Irradiation of a 10^{-3} M solution in hexane at 300 nm under nitrogen in a Rayonet reactor followed by column chromatography of the reaction mixture gave, besides 1-vinylphenanthrene[6] (15%), polymeric products (10%) and traces of two unidentified compounds, 70% *exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene (**6**, mp 32-33°) and 2% of the corresponding *endo* isomer (mp 88-90°) (eq 2). The absence of *endo*- and *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-enes (**7**) in the reaction mixture could be demonstrated by an independent synthesis of these compounds.[7] The occurrence of the isomeric *endo*- and *exo*-4-phenylbenzobicyclo[3.1.0]-hex-2-enes was excluded because of the absence of NMR signals due to methylene protons of a cyclopropane ring (δ 0.0-1.0). The [2 + 2] cycloaddition products were identified on the basis of their spectral data: *exo*-isomer (**6**) mass spectrum *m/e* 206 (M^+, 69%), 91 (100); uv λ_{max} (CH_3OH) 274 nm (log ϵ 3.13), 267 (3.15), 260 (3.09), 254 sh (2.99); NMR (Me_4Si, CCl_4) δ 6.6-7.2 (m, 9 aromatic protons), 3.87 (d, H_{5endo}, $J_{5,6endo} = 7.5$ Hz,[8] $J_{5,6exo} = J_{1,5} = J_{4,5} = 0$), 3.31 (d, H_1 and H_4, $J_{1,6exo} = J_{4,6exo} = 2.5$ Hz, $J_{1,5} = J_{4,5} = J_{1,6endo} = J_{4,6endo} = 0$), 3.07 (doublet of triplets, H_{6exo}, $J_{6endo,6exo} = 6.25$ Hz), 2.32 (doublet of doublets, H_{6endo}); *endo*-isomer mass spectrum *m/e* 206 (M^+, 54%), 91 (100); uv λ_{max} (CH_3OH) 275 nm (log ϵ 2.93), 269 (2.98), 262 (2.90), 256 sh (2.77); NMR (Me_4Si, CCl_4) δ 6.6-7.2 (m, 9 aromatic protons), 4.26 (t, H_{5exo}, $J_{1,5} = J_{4,5} = 2.5$ Hz), 3.44 (t, H_1 and H_4, $J_{1,6exo} = J_{4,6exo} = 0$), 2.66 (doublet of triplets, H_{6exo}, $J_{6exo,6endo} = 5.5$ Hz), 2.35 (d, H_{6endo}). Reduction with H_2 on Pd/C of this compound yielded 1-benzylindane as can be expected for **6**. It excludes that the photoproducts are 5-phenylbenzobicyclo[2.2.0]hex-2-enes.



The cycloaddition occurs in the singlet excited state of **5**, since the triplet sensitizer benzophenone does not convert **5** into **6**. *cis*- and *trans*-**5** give nearly the same product ratio. In both cases the sterically more favorable *exo* product **6** strongly predominates over the *endo* isomer.

The remarkable difference in photochemical behavior between **1** and **5** may be ascribed, at least in part to conformational differences. In the rather rigid stilbene moiety of **5** the vinyl substituted phenyl group has been twisted out of a planar conformation by about 30°.[9] Due to this the olefinic bonds may be nearly perpendicular to each other at least in the *cis* isomer, according to models. However, it is not yet known if the reaction is a concerted process and to what extent the electronic properties of the phenyl substituent may be of influence. It is improbable, however, that the different photoreactivity is caused by differences in bond order of the central bond in the relevant hexatriene moieties of *o*-divinyl aromatics as has previously been suggested.[1b] A further study of the influence of conformational factors on the photochemistry of this type of molecules is in progress.

The [2 + 2] cycloaddition observed for **5** could be used for the synthesis of a new tricyclic $C_{10}H_{12}$ system (**10**). Brief irradiation of 2,2′-divinylstilbene (**8**) gave a [2 + 2] cycloadduct (**9**) similar to **5**. On further irradiation it underwent a $\pi 2 + \sigma 2$ cyclization giving dibenzotricyclo-[4.3.1.$0^{3,7}$]deca-4,8-diene (**10**, mp 157-158°) in 70% yield (eq 3). The structure given is based on the following spectral data: mass spectrum *m/e* 232 (M^+, 100%); uv λ_{max} (CH_3OH) 264 nm (log ϵ, 4.19), 258 (4.29), 251 (4.19), 246 sh (4.00), 239 sh (3.75); NMR (Me_4Si, CCl_4) δ 6.98-7.35 (symmetrical multiplet, 8 aromatic protons), 3.72 (t, H_7, $J_{6,7}$, $J_{3,7} = 4.5$ Hz), 3.14 (q, H_1, $J_{1,2} = J_{1,2'} = J_{1,10} = J_{1,10'} = 2.9$ Hz), 2.82 (m, H_3 and H_6, $J_{2,3} = J_{61,0} = 1.5$ Hz, $J_{2',3} = J_{6,10'} = 9.0$ Hz), 1.95-1.40 (m, H_2, $H_{2'}$, H_{10}, $H_{10'}$, $J_{2,2'} = J_{10,10'} = 12$ Hz).



(3)

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(5) *trans*-2-Vinylstilbene (**5**) was synthesized by a Wittig synthesis using the triphenylphosponium salt of 2-bromomethylstilbene and formaldehyde.

(6) 1-Vinylphenanthrene was identified by an independent synthesis starting from 1-methylphenanthrene.

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On the "Utilization of Excited State pK's to Initiate a Ground State Chemical Reaction"

Sir:

A recent communication by Saeva and Olin[1] concludes by stating that "we have demonstrated an excited state acid catalyzed bimolecular reaction." The authors claim to have demonstrated the first photochemical reaction that takes advantage of the increased acidity of phenols in the lowest excited singlet state, one of many important discoveries of