tion[11] which competes with the 1,3-dipolar cycloaddition of *cis*-II with III. It was indeed shown that *cis*-I in dioxane (without III) was isomerized to 18% *trans*-I after 7 min of irradiation. On the other hand, *trans*-I in dioxane is slowly converted by irradiation to a mixture of diastereomeric dimers;[2] *cis*-I could not be detected. It may be justified to suppose that the photolysis of *cis*-I to *cis*-II is the eighth stereospecific process in the scheme, and that a secondary photoisomerization of *cis*-II becomes the more disturbing the lower the concentration of the dipolarophile III is.

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(11) In the thermal reaction of *trans*-I with a 7.8% solution of III in boiling dioxane (24 hr), no lack of stereospecificity in the adduct formation was observed, although the same intermediate *cis*-II is involved. Nmr analysis disclosed 21% *trans*-I and 61% *cis*-IV, but no *trans*-IV. This rules out the possibility that the *thermal* isomerization *trans*-I → *cis*-I or *cis*-II → *trans*-II, respectively, is the cause of the nonstereospecificity of adduct formation in the photochemical reaction of *cis*-I.

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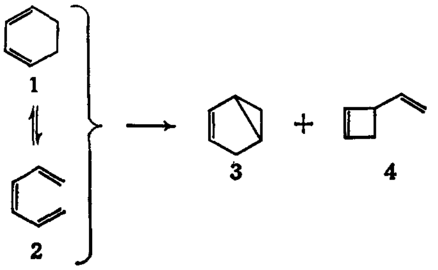
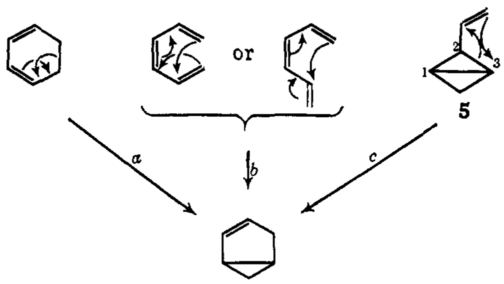
Studies on the Photochemistry of 1,3,5-Hexatrienes[1]

Sir:

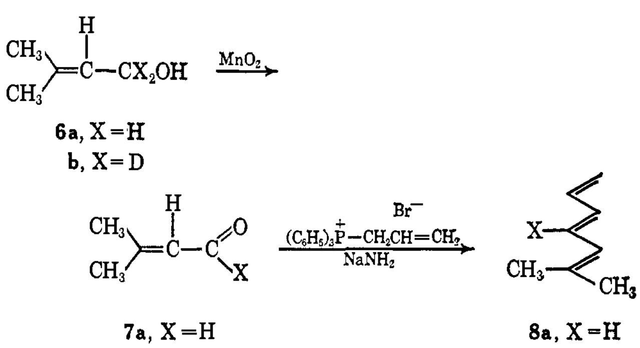
Recently we reported that ultraviolet irradiation of 1,3-cyclohexadiene (**1**) leads initially to the formation of 1,3,5-hexatriene (**2**) and that extended irradiation yields a mixture (1:1) of bicyclo[3.1.0]hex-2-ene (**3**) and 3-vinylcyclobutene (**4**).[2] Many analogous photochemical bicyclo[3.1.0]hexene forming reactions have been reported.[3] These reactions have been discussed in terms of at least three mechanistic pathways: (1) a bond-switching process for cyclohexadiene (path a);[4] (2) an electrocyclic reaction of the hexatriene, formally analogous to an intramolecular Diels–Alder reaction (path b);[5] and (3) a vinylcyclopropane–cyclopentene rearrangement[6] of the hypothetical intermediate, 2-vinylbicyclo[1.1.0]butane (**5**) (path c).[5,7]



We wish to report the results of a tracer experiment which excludes the vinylbicyclo[1.1.0]butane hypothesis.



Our mechanistic study utilizes the fact that **5** has a plane of symmetry,[8] making C_1 and C_3 (*i.e.*, C_2 and C_3 of the original hexatriene) equivalent. Since this equivalence does not occur in paths a or b, photoisomerization of an appropriately labeled triene can provide mechanistic information. The triene chosen for this study was 6-methyl-1,3,5-heptatriene (**8**), prepared and characterized as described below.



6a, X=H
b, X=D

7a, X=H
b, X=D

8a, X=H
b, X=D

Reduction of methyl β-methylcrotonate with lithium aluminum hydride afforded 3-methyl-2-buten-1-ol[9] (**6a**), bp 77–79° (65 mm), in 73% yield.

Oxidation of **6a** with a 15:1 excess of manganese dioxide[10] gave β-methylcrotonaldehyde (**7a**), bp 72–76° (100 mm), in 52% yield. The infrared spectrum of **7a** showed maxima at 2900 (w), 2720 (w), 1670 (s), 1630 (w), 1440 (m), 1190 (m), 1120 (m), and 1040 (m) cm^{-1}. The nmr spectrum showed resonances at τ 8.29 and 8.09 (allylic methyl doublets, J = 1.5 cps), 4.5 (complex olefinic proton doublet), and 0.75 (aldehyde proton doublet, J = 7 cps). The mass spectrum showed its parent peak at m/e 84 with a strong peak at 83.[11]

Treatment of **7a** with the Wittig reagent prepared from allyltriphenylphosphonium bromide and sodamide afforded **8a** in 40% yield. The infrared spectrum of **8a** showed maxima at 2910 (m), 1800 (w), 1640 (w), 1620 (m), 1580 (w), 1440 (m), 1000 (s), 945 (m), and 895 (s) cm^{-1}. The nmr spectrum showed a broad methyl singlet at τ 8.25 and olefinic protons from 3.1 to 5.1 in the expected ratio of 1:1. The ultraviolet spectrum was typical of 1,3,5-hexatrienes,[12] showing $\lambda_{\max}^{\mathrm{Et_2O}}$ 261 mμ (ε 22,400), 269 (28,000), and 280 (25,000). The mass spectrum showed its parent peak at m/e 108.

Irradiation of **8a** gave a 27% yield of the expected 6,6-dimethylbicyclo[3.1.0]hex-2-ene (**9**) as the only important monomeric product. The structural assign-

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(1) The partial support of this research by the National Science Foundation is acknowledged with pleasure.

(2) J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **88**, 2850 (1966).

(3) For example, see R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

(4) R. J. Theis and R. E. Dessy, *J. Org. Chem.*, **31**, 4248 (1966).

(5) H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965).

(6) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963), and references cited therein.

(7) For examples of the photochemical conversion of conjugated dienes to bicyclo[1.1.0]butanes, see W. G. Dauben, *Pure Appl. Chem.*, **9**, 539 (1964), and references cited therein.

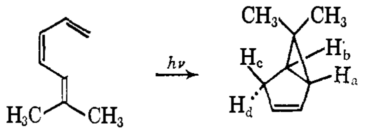
(8) Only the *exo* isomer is shown. The same argument would apply to the *endo* isomer.

(9) H. Eggerer, *Chem. Ber.*, **94**, 174 (1961).

(10) R. J. Britter and T. J. Wallace, *J. Org. Chem.*, **24**, 1051 (1959).

(11) High voltage mass spectrum; ionizing potential = 70 v.

(12) G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **70**, 3394 (1948).



8a **9**

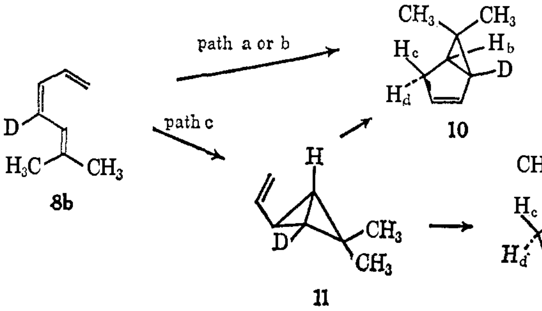
ment was based on analogy with previously studied cyclization reactions and the following physical evidence.

The infrared spectrum of **9** showed maxima at 3020 (m), 2910 (s), 1440 (m), 1370 (m), and 940 (m) cm^{-1}. The mass spectrum showed its parent peak at *m/e* 108, and the ultraviolet spectrum showed $\lambda_{\max}^{\text{cyclohexane}}$ 211 mμ (ϵ 4030). The 100-Mc nmr spectrum of **9**[13] allowed the identification of *endo*- and *exo*-methyl groups at τ 9.3 and 9.0, respectively, H_b as a triplet ($J_{ab} = J_{bd} = 7$ cps) at 8.86, H_a as an unresolved multiplet at 8.45, H_c as a doublet ($J_{cd} = 18$ cps, $J_{bc} = 0$ cps) at 8.1, H_d as a doublet of doublets ($J_{cd} = 18$ cps, $J_{bd} = 7$ cps) centered at 7.60, and the olefinic protons as an unresolved multiplet at 4.55. Thus, a good, unidirectional example of the desired photocyclization was available for the key labeling experiment.

The synthesis of **8b** was carried out in a manner analogous to that of **8a**. Reduction of methyl β-methylcrotonate with lithium aluminum deuteride afforded **6b**. Manganese dioxide oxidation of **6b** gave **7b**, whose infrared spectrum showed pertinent maxima at 2100 (m) and 1670 (s) cm^{-1}. The nmr spectrum had resonances at τ 8.30 and 8.10 (allylic methyl doublets) and a broad singlet at 4.50 (olefinic proton). The aldehydic proton signal, at τ 0.75 in **7a**, was absent. The mass spectrum showed its parent peak at *m/e* 85 with a strong peak at 83.[11,14]

Treatment of **7b** with the appropriate Wittig reagent afforded **8b**. The infrared spectrum showed pertinent maxima at 2250 (w), 2200 (w), and 2100 (w) cm^{-1}. The nmr spectrum showed a broad allylic methyl signal at τ 8.25 and olefinic protons from 3.1 to 5.1. The mass spectrum had its parent peak at *m/e* 109.[14]

Photoisomerization of **8b** *via* paths a or b should now lead to **10**, while preliminary cyclization to **11** should lead to equivalent amounts of **10** and **12** (neglecting small kinetic isotope effects).



Irradiation of **8b** followed by glpc isolation of the product afforded labeled 6,6-dimethylbicyclo[3.1.0]hex-2-ene whose mass spectrum showed its parent peak at *m/e* 109.[14] The product was shown to be **10** rather than a mixture of **10** and **12** on the basis of its 100-Mc nmr spectrum. The nmr spectrum of **10** showed, as expected, H_b as a doublet ($J_{bd} = 7$ cps) at τ 8.86, H_c as a doublet ($J_{cd} = 18$ cps, $J_{bc} = 0$ cps) at 8.1, and H_d as a doublet of doublets ($J_{cd} = 18$ cps, $J_{bd} = 7$ cps) at 7.60. There was no resonance at τ 8.45 corresponding to H_a in **9**.

The theoretical spectrum for a path c product mixture would show H_b as a doublet ($J_{bd} = 7$ cps) at τ 8.86 (from **10**), H_a as a diffuse singlet at 8.45 (from **12**), and H_d as a doublet ($J_{cd} = 18$ cps) at 7.60 superimposed on a doublet of doublets ($J_{cd} = 18$ cps, $J_{bd} = 7$ cps) from both **10** and **12**.

These data suggest that, at least in simple cases, 2-vinylbicyclo[1.1.0]butanes are not intermediates in the photoisomerization of 1,3,5-hexatrienes or 1,3-cyclohexadienes to bicyclo[3.1.0]hexenes.[15]

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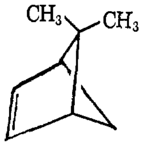
[13] For data on the nmr spectra of bicyclo[3.1.0]hexenes see: W. G. Dauben, *Pure Appl. Chem.*, **9**, 539 (1964); H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965); K. J. Crowley, *Tetrahedron Letters*, 2863 (1965).

[14] A low-voltage mass spectrum indicated that this product was >95% d_1.

[15] By similar arguments it can also be shown that the bicyclo[2.1.1]hexene (i) is not an intermediate in this transformation.



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[16] National Institutes of Health Postdoctoral Fellow, 1965–1967.

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Received February 10, 1967

Stereochemistry of Asymmetric Silicon. Optically Active Functionally Substituted Disilanes[1]

Sir:

We wish to report the resolution of the first optically active functionally substituted disilanes[2] and the first stereospecific reactions of asymmetric silicon in a disilane in which the silicon–silicon bond remains intact.[3]

Diastereomeric phenylmethyl-(−)-menthoxychlorosilanes, bp 110° (0.1 torr), prepared from phenylmethyldichlorosilane and (−)-menthol,[4] were allowed to couple with triphenylsilyllithium,[5] yielding (±)-1,2,2,2-

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[1] Preliminary studies carried out at The Pennsylvania State University.

[2] For previous work with optically inactive functionally substituted disilanes see: (a) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 355–356; (b) V. Bazant and V. Chavalovsky, "Organosilicon Compounds," Vol. 1, Academic Press Inc., New York, N. Y., 1965, pp 152–162; (c) A. D. Petrov, B. F. Mironov, V. A. Ponomarenko, and E. A. Chernyshev, "Synthesis of Organosilicon Monomers," Consultants Bureau, New York, N. Y., 1965, pp 292–293, 374, 483; (d) H. Gilman and R. A. Tomasi, *Chem. Ind.* (London), 954 (1963); (e) H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **26**, 254 (1961); (f) J. V. Urenovitch and A. G. MacDiarmid, *J. Chem. Soc.*, 1091 (1963); (g) U. Stolberg, *Ber.*, **96**, 2798 (1963); (h) J. E. Drake and J. Simpson, *Inorg. Nucl. Chem. Letters*, **2**, 219 (1966); (i) U. Wannagat, G. Schreiner, O. Brandstaetter, and M. Peach, *Monatsh. Chem.*, **96**, 1902 (1965); (j) J. V. Urenovitch and R. West, *J. Organometal. Chem.* (Amsterdam), 3, 138 (1965); (k) M. Kumada and M. Ishikawa, *ibid.*, 1, 153 (1963); (l) M. Kumada, K. Naka, and M. Ishikawa, *ibid.*, **2**, 136 (1964); (m) M. Kumada, M. Ishikawa, and S. Maedo, *ibid.*, **2**, 478 (1964).

[3] A nonfunctionally substituted optically active disilane and the stereochemistry of the lithium cleavage of its silicon–silicon bond have been reported previously: L. H. Sommer and R. Mason, *J. Am. Chem. Soc.*, **87**, 1619 (1965).

[4] For a discussion of the partial alcoholysis of polyhalogen silanes, see ref 2a, p 288.

[5] Prepared *via* the modified procedure of H. Gilman, *et al.* See H. Gilman and H. J. S. Winkler "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.