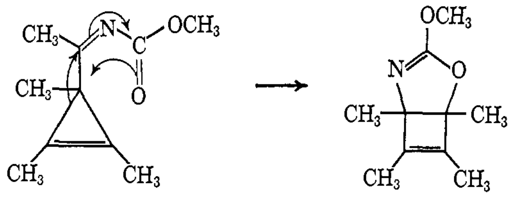
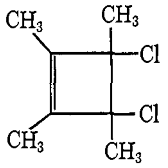
formula to be $C_{10}H_{15}NO_2$. The strong carbonyl absorption of **9** at 5.79 μ is absent in this material, but a strong infrared band at 6.02 μ, attributable to >C=N– stretching, is present. Again only ultraviolet end absorption was observed. The nmr spectrum of B showed two three-proton singlets at τ 8.89 and 8.71, in addition to two unresolved allylic methyl absorptions occurring as a symmetrical multiplet at τ 8.40 and a singlet methoxyl peak at τ 6.28. These data suggest structure **10** for B, the rearrangement of **9** corresponding to the cyclopropenylcarbinyl → cyclobutenyl transformation[11] shown below.

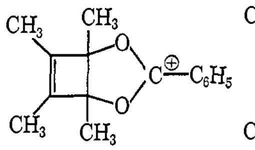


9 **10**

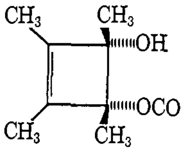
Support for the presence of a cyclobutene ring in B was obtained by an experiment based on some recent results of Wilcox and Nealy.[12] These workers showed that, upon dissolving 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (**11**) and benzoic acid in 97% sulfuric acid, the nmr spectrum of the cation **12** was observed. This cation could be hydrolyzed to give *cis*-1,2,3,4-tetramethylcyclobutene-3,4-diol monobenzoate (**13**). In a similar experiment, we have found that methylurethan (**14**) displaces the chlorine substituents of **11** in sulfuric acid solution to give a cation whose nmr spectrum is identical with that from **10** in the same medium. The sulfuric acid solution from either source could be quenched in methanol to give a mixture of two stereoisomeric methyl ethers, **15**. Structure **15** for these ethers is supported by characteristic infrared and nmr absorptions, by a mass spectrometric parent peak at *m/e* 213, and by an elementary analysis compatible with the molecular formula $C_{11}H_{19}NO_3$.



11



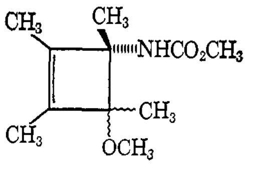
12



13

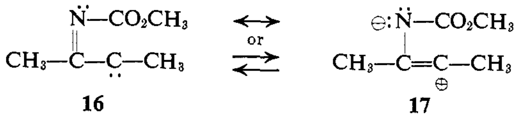
$NH_2CO_2CH_3$

14



15

While these results establish the products of this photochemical azidoformate–alkyne reaction, they leave the pathways leading to these products speculative. As a first step, the addition of singlet[13] **1b** to **5** could lead to an intermediate with predominant carbene (**16**) or carbonium ion (**17**) character, which could then add to a second molecule of **5** to give the observed cyclopropene, **9**. The oxazole **7** could arise from cyclization of the same intermediate, from concerted 1,3-dipolar addition of **1b** to **5**, or even from rearrangement of the intrinsically unstable azirene, **6**. In view of the uncertainties in the electronic and stereochemical nature of the intermediates responsible for the formation of **7** and **9**, we prefer to postpone further discussion of the reaction mechanisms until a more thorough study can be undertaken.



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle \dot{N}{-}CO_2CH_3}{\|}}{C}{-}\underset{\cdot\cdot}{C}{-}CH_3} \quad \overset{\longleftrightarrow}{\underset{\rightleftarrows}{\text{or}}} \quad \mathrm{CH_3{-}\overset{\overset{\displaystyle \ominus\!:\!\dot{N}{-}CO_2CH_3}{|}}{C}{=}\underset{\oplus}{C}{-}CH_3}$$

16 **17**

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[11] *Cf.* R. Breslow, J. Lockhart, and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962).

[12] C. F. Wilcox and D. L. Nealy, *J. Org. Chem.*, **28**, 3446 (1963); **29**, 3668 (1964).

[13] *Cf.* W. Lwowski and J. S. McConaghy, *J. Am. Chem. Soc.*, **87**, 5490 (1965); W. Lwowski and F. P. Woerner, *ibid.*, **87**, 5491 (1965).

[14] National Science Foundation Cooperative Graduate Fellow, 1963–1966.

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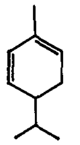
Photochemical Formation of Bicyclo[3.1.0]hex-2-ene and 3-Vinylcyclobutene from 1,3-Cyclohexadiene[1]

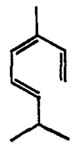
Sir:

The photochemistry of 1,3-cyclohexadienes has been the subject of extensive investigation,[2] and, largely because of its importance in vitamin D syntheses from steroidal 5,7-dienes,[3] it has had the benefit of intense examination long before the current renaissance of organic photochemistry.

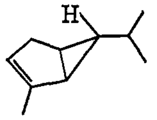
One of the simplest 1,3-cyclohexadienes to be studied photochemically has been α-phellandrene (I), which Havinga and his co-workers have shown undergoes ring opening upon irradiation of an ethereal solution, giving a mixture of acyclic trienes II.[4] We have found that continued irradiation (λ >250 mμ) leads chiefly to two monomeric products, III (*ca.* 50%) and IV (*ca.* 10%).[5–7] While this pattern of reactivity finds analogy in the conversion of vitamin D_2 (V) to suprasterol-II (VI)[8] as well as in several other relatively complex cases, the literature does not describe a comparable ring opening



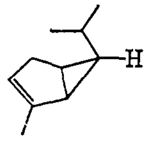
I



II



III



IV

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[1] The partial support of this research by National Science Foundation Grant No. GP-4128 is acknowledged with pleasure.

[2] W. G. Dauben, *Pure Appl. Chem.*, **9**, 539 (1964).

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[7] K. J. Crowley, K. L. Erickson, A. Eckell, and J. Meinwald, manuscript in preparation.

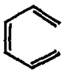
[8] W. G. Dauben, I. Bell, T. W. Hutton, G. F. Laws, A. Rheiner, Jr., and H. Urscheler, *J. Am. Chem. Soc.*, **80**, 4116 (1958); W. G. Dauben and P. Baumann, *Tetrahedron Letters*, 565 (1961); C. P. Saunderson and D. C. Hodgkin, *ibid.*, 573 (1961).

and subsequent cyclization for 1,3-cyclohexadiene (VII) itself. Thus prolonged irradiation of VII in solution has been reported to give only trienes VIII and polymer.[4,9] In the hope of providing some basis for understanding the influence of structural variations on photochemical reaction patterns, we have reexamined the solution photochemistry of this parent compound, with the results described below.

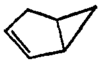
Ethereal solutions (1%) of VII were irradiated with a Hanovia high-pressure mercury lamp through a Vycor filter. Initial ring opening to a mixture of 1,3,5-hexatrienes (VIII) was evidenced by a large increase in ultraviolet absorption (λ 256 mμ) which was paralleled by the appearance of a new glpc peak.

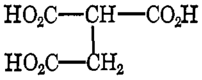
Continued irradiation led to the appearance of two additional glpc peaks, of shorter retention times, whose intensity increased as those of VII and VIII decreased. These new components (*ca.* 12% each as estimated by glpc) could be isolated by fractionation of the reaction mixture and were proven to be bicyclo[3.1.0]hex-2-ene (IX)[10] and 3-vinylcyclobutene (X) on the basis of the following evidence.


VI


VIII


X


IX


$$\begin{array}{l} HO_2C-CH-CO_2H \\ \qquad\quad | \\ HO_2C-CH_2 \end{array}$$
XI

The mass spectrum of IX showed its parent peak at *m/e* 80 in accord with the molecular formula C_6H_8. The nmr spectrum showed resonances at τ 4.0, 4.7, 7.65, 8.35, 9.25, and 10.25 as reported recently for authentic IX prepared by the action of bis(iodomethyl)zinc on cyclopentadiene.[10] The infrared spectrum of IX showed maxima at 3100 (s), 2920 (s), 1360 (m), 1020 (s), 910 (s), 800 (s), 780 (m), 765 (s), and 715 cm^{-1} (s).

The mass spectrum of X again had its parent peak at *m/e* 80. In the nmr it showed a typical ABX pattern at τ 6.6, 7.2, and 7.8, a sharp singlet at τ 4.0 (cyclobutene protons), and multiplets at τ 4.2 and 5.0 (vinyl protons). The infrared spectrum showed absorption at 3100 (s), 2940 (s), 1820 (w), 1640 (w), 1440 (w), 990 (s), 910 (s), 770 (s), and 685 cm^{-1} (s). Pyrolysis at 200° gave quantitative conversion to *trans*-1,3,5-hexatriene, in accord with expectations for structure X.[11] Under the pyrolysis conditions chosen, IX was completely unchanged. Chemical support for the assignment of structure X to this product was obtained by ozonolysis followed by an oxidative work-up using hydrogen peroxide. Under the conditions used, succinic acid (identified as its dimethyl ester) was the only isolable product, in accord with the expected facile decarboxylation of the initially formed carboxysuccinic acid XI.

Photochemical formation of IX in this reaction shows that the 1,3-cyclohexadiene → bicyclo[3.1.0]hex-2-ene transformation, which probably proceeds *via* 1,3,5-hexatriene, is an important reaction for the parent compound, as is the case for I and V. The simultaneous formation of a cyclobutene (X) finds its simplest analogy in the observation that 1,3-butadiene itself can yield cyclobutene upon irradiation[11,12] and suggests that analogous vinylcyclobutenes might be found in the more complex cases of 1,3-cyclohexadiene or 1,3,5-hexatriene irradiation if the reaction mixtures were examined closely enough.

The influence of substituents on the preferred course of these reactions, the factors controlling their stereochemistry, the role of the 1,3,5-hexatrienes as intermediates in the production of monocyclic and bicyclic photoproducts, and the nature of the excited states involved in these transformations all remain to be analyzed. We hope to be able to contribute to some of these questions in a continuation of the present work.

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[13] Public Health Service Postdoctoral Fellow, 1965–1967.

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Liquid Phase Photolysis of Simple Alcohols

Sir:

Because of the lack of suitable light sources, photochemical reactions of organic compounds in the liquid phase with light from the vacuum ultraviolet region have not been extensively investigated, especially with respect to detailed product analyses.[1] Although low-pressure mercury discharge lamps emit at 185 mμ as well as at 254 mμ, the former line is strongly absorbed by the impurities in fused quartz. Recently, the quality of fused quartz has been improved to such an extent that light at 185 mμ is transmitted at an appreciable intensity. The current communication deals with photochemistry of simple alcohols in the liquid phases.[1–7]

The reactions were carried out in a fused quartz apparatus as previously described.[8] The apparatus has a volume of 170 ml and an emission surface of approximately 190 cm². External heating is provided by means of a heating tape. The reactions were completely inhibited by a Vycor filter. No attempts were made to isolate the 185-mμ line from other emissions of mercury. The alcohols used were reagent grade, fractionated through a 50-plate column and analyzed by vps before use. The alcohols were flushed with high purity nitrogen and the photolyses were performed at the reflux temperatures of the alcohols to exclude air from the reactions. The reactions were carried out to about 2–3% completion. The gas evolution was fairly rapid at the beginning (150–220 ml/hr) and slowed down to a steady rate (75–100 ml/hr) after the second hour. The gaseous products were analyzed by vpc with a Molecular Sieve 5-A column at 100°, and higher boiling products were analyzed by vpc and fractional distillation. The results of photolyses of methanol, ethanol,

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