Communications to the Editor

The Photochemical Addition of Methyl Azidoformate to 2-Butyne

Sir:

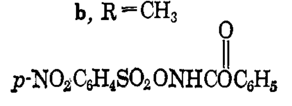
The chemistry of nitrenes has been the subject of intensive investigation in recent years.[1] The generation of carbethoxynitrene (**1a**) by irradiation of ethyl azidoformate (**2a**) or by base cleavage of N-*p*-nitrobenzenesulfonoxyurethan (**3**), and its reaction with cyclohexene, has been studied especially thoroughly by Lwowski and his co-workers.[2] This group has shown that **1a** adds to the double bond of cyclohexene to give the aziridine **4** as the major product, accompanied by lesser amounts of isomeric urethans derived from carbon–hydrogen insertion reactions.[2] We have studied the photochemically induced reaction of methyl azidoformate (**2b**) with 2-butyne (**5**) in the hope of obtaining the theoretically interesting azirene **6**, *via* the formally analogous addition of **1b** to the triple bond of **5**. While **6** has not been isolated or detected in this reaction, we have observed the formation of an isomeric product shown to be the oxazole **7**,[3] along with a larger amount of a product A incorporating two molecules of acetylene and one molecule of nitrene into a structure which rearranges on heating to another 2:1 product, B. The formation of these 2:1 products reveals a novel feature of this type of reaction which is of both synthetic and mechanistic interest.

$:\underset{\cdot\cdot}{N}-CO_2R$

1a, $R=C_2H_5$
b, $R=CH_3$

N_3CO_2R

2a, $R=C_2H_5$
b, $R=CH_3$



$p\text{-}NO_2C_6H_4SO_2ONHCOC_6H_5$

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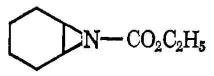

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$CH_3C{\equiv}CCH_3$

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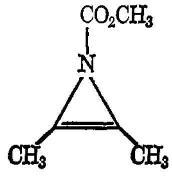

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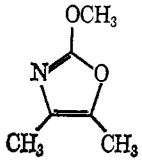

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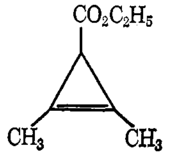
In a typical experiment, irradiation of a 1% solution of **1b** in **5** at 0–5° using a high-pressure 450-w Hanovia mercury lamp with a Vycor filter resulted in the evolution of 90% of the theoretical nitrogen within 5 hr. After removal of excess **5**, unreacted **1b** was recovered in 9% yield by distillation at 0.05 mm. At the same time a higher boiling fraction (bp 65° (20 mm) on redistillation), shown below to be the oxazole **7**,[4] was obtained in 12% yield. The mass spectrum of **7** had a parent peak at *m/e* 127, corresponding to the molecular formula $C_6H_9NO_2$; however, the infrared spectrum lacked carbonyl absorption in the normal urethan range and instead showed a characteristic strong absorption at 6.22 μ.[3,5] The oxazole structure was apparent from the nmr spectrum of this product, which showed two three-proton allylic methyl peaks occurring as two quartets (J = 0.9 cps) at τ 8.10 and 7.91 and a singlet methoxyl absorption at τ 6.08 (three protons).

The residue after removal of **1b**, **5**, and **7** was composed primarily of a thermally labile substance A, which rearranged completely on heating to 115° for 1 hr to a crystalline product B, mp 49–50°. By short-path distillation in base-washed glassware it is possible to isolate A, bp 50–65° (0.05 mm),[8] in *ca.* 30% yield, with less than 15% rearrangement to B.

The infrared spectrum of A has characteristic absorption at 5.25 (weak) (cyclopropene),[9] 5.79 (>C═O), and 6.02 μ (>C═N–). The ultraviolet spectrum shows only end absorption. The nmr spectrum is made up of two three-proton singlets at τ 8.82 and 8.43, a six-proton singlet at τ 7.96, and a singlet methoxyl peak at τ 6.32 (three protons). These data, which find good analogy in those reported for the dimethylcyclopropene **8**,[10] lead to our assigning structure **9** to compound A.



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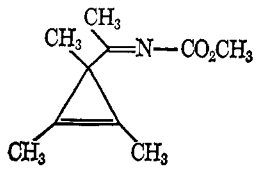

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The crystalline rearrangement product, B, can be formed from **9**, either thermally or by treating with a catalytic amount of *p*-toluenesulfonic acid at room temperature. Low-temperature crystallization gave a sample of B whose elemental analysis and mass spectrometric parent peak at *m/e* 181 show the molecular

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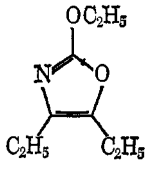
[1] L. Horner and A. Christmann, *Angew. Chem. Intern. Ed. Engl.*, **2**, 599 (1963); R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

[2] W. Lwowski, T. Maricich, and T. W. Mattingly, *J. Am. Chem. Soc.*, **85**, 1200 (1963); W. Lwowski and T. W. Mattingly, *ibid.*, **87**, 1947 (1965); W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965).

[3] While our work was in progress R. Huisgen and H. Blaschke [*Tetrahedron Letters*, 1409 (1964); *Chem. Ber.*, **98**, 2985 (1965)] described the thermal 1,3-dipolar addition of **2a** to conjugated aryl and carboalkoxyl acetylenes to give the corresponding oxazoles in 3–33% yields.

[4] Satisfactory analytical data were obtained for all new compounds.

[5] In a parallel series of experiments using 3-hexyne and **1a**, the analogously produced oxazole i gave similar spectral data, and could be hydrolyzed to the known oxazolone ii.[6,7]



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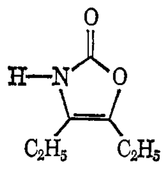

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[6] R. Gompper, *Chem. Ber.*, **89**, 1748 (1956).

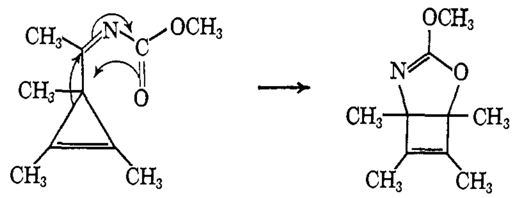
[7] R. Gompper and H. Herlinger, *ibid.*, **89**, 2825 (1956).

[8] No analysis was obtained for A because of its thermal instability.

[9] *Cf.* G. L. Closs and L. E. Gloss, *J. Am. Chem. Soc.*, **83**, 1003 (1961); **85**, 99 (1963); R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

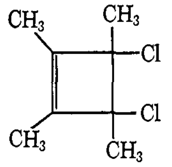
[10] R. Silberman, M.S. Thesis, Cornell University, 1963, reported for this substance a weak infrared absorption at 5.31 μ and an allylic methyl peak at τ 8.07.

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 $C_{11}H_{19}NO_3$.



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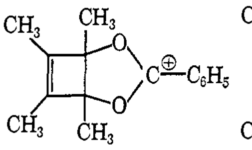

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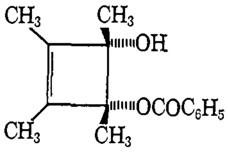

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$NH_2CO_2CH_3$

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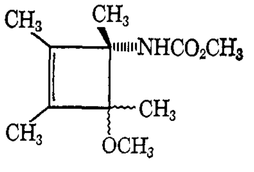

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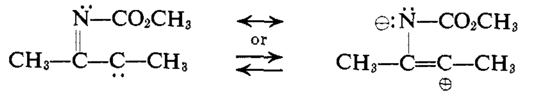
While these results establish the products of this photochemical azidoformate–alkyne reaction, they leave the pathways leading to these products speculative. As a first step, the addition of singlet[13] **1b** to **5** could lead to an intermediate with predominant carbene (**16**) or carbonium ion (**17**) 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-



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

16 **17**

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.

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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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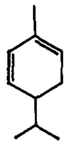
Received April 18, 1966

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



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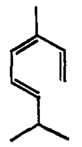

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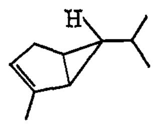
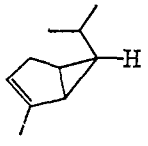


III



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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).

[3] L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 90.

[4] R. J. DeKock, N. G. Minnard, and E. Havinga, *Rec. Trav. Chim.*, **79**, 922 (1960).

[5] K. J. Crowley, *J. Am. Chem. Soc.*, **86**, 5692 (1964).

[6] J. Meinwald, A. Eckell, and K. L. Erickson, *ibid.*, **87**, 3532 (1965).

[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).