

in the *trans* H-Ir-NCR complexes, the iridium atom can serve as a π donor into antibonding orbitals of the nitrile molecule, leading to the observed decreases in CN frequencies.¹¹ The assignment of the 2080-cm⁻¹ absorption to the Ir-NC mode was confirmed by using deuterium hydrochloride instead of HCl to generate the five-coordinated intermediate **1**. Addition of the nitriles to the deuterated complex **1** gives products with the $\nu_{\text{Ir-N}=\text{C}}$ band (2083 cm⁻¹) unaltered, but with marked diminution of the 2190-cm⁻¹ (Ir-H) band.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This research was also supported by the National Science Foundation through GY-6152 College Science Improvement Program.

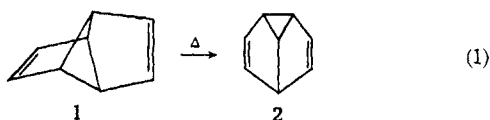
(11) P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968).

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Received January 26, 1970

(CH)₈ Hydrocarbons. Photochemistry of Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene¹

Sir:

The highly strained tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**1**), a valence isomer of cyclooctatetraene, has recently been prepared and characterized.^{2,3} This diene undergoes remarkably facile thermal rearrangement to semibullvalene (**2**),^{2,3} and in further examining its place on the (CH)₈ hydrocarbon energy surface we have explored its photochemistry. We now report the unusual electronic absorption spectrum of **1** as well as its photochemical conversion to cyclooctatetraene and semibullvalene.



The ultraviolet spectrum⁴ of a solution of **1** in isopentane begins to show absorption at about 320 m μ , and the molar extinction at 300 m μ is *ca.* 190. While this absorption seems remarkable for a simple nonconjugated diene, it should be noted that the related monoolefin, tricyclo[3.3.0.0^{2,6}]oct-3-ene,^{5,6} shows a long-wavelength ultraviolet absorption in isooctane with a molar extinction of 150 at 250 m μ . This abnormal electronic spectrum undoubtedly merits further investigation.

(1) The partial support of this research by grants from the National Science Foundation (GP-13085) and the National Institutes of Health (GM-10090) is acknowledged with pleasure.

(2) J. Meinwald and H. Tsuruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969).

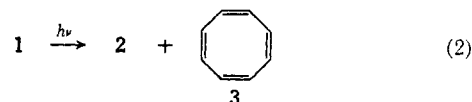
(3) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(4) The sample was a mixture of **1** and **2** (1:2 = 1.4:1) and the measurement was carried out on a Cary Model 14 at 1°. At this temperature the rearrangement of **1** to **2** is quite slow.

(5) J. Meinwald and B. E. Kaplan, *J. Amer. Chem. Soc.*, **89**, 2611 (1967).

(6) M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968).

Solutions of a mixture of **1** and semibullvalene (**2**) (55~60 mg/0.3~0.4 ml of solvent; 1:2 = 0.6~1.2) placed in a Pyrex nmr sample tube were irradiated at -60°, using a 450-W Hanovia medium-pressure lamp through a Vycor immersion well. Under these conditions, the thermal rearrangement of **1** was shown to have a negligible rate. Monitoring the reaction mixtures by means of their nmr spectra showed the appearance of one new component as evidenced by the development of an nmr singlet at τ 4.3; at the same time there was an increase in area of the peaks in the nmr spectrum due to **2**. The new component was identified as cyclooctatetraene (**3**) by infrared and nmr spectral comparisons and by its gas chromatographic retention time. After 80 min of irradiation, the amounts of **2**,



3, and unchanged **1** reached the values shown in Table I. No nmr spectral peaks beyond those accounted for by **1**, **2**, and **3** were observed.

Table I. Results of Low-Temperature Irradiation of Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene^a

Solvent	1, %	2, ^b %	3, %
Toluene	62	12	26
Isopentane	52	19	29
Dimethyl ether	91	~4 ^c	~5 ^c

^a Reaction temperature was maintained at -60° and the reaction time was 80 min. ^b Increase in semibullvalene. ^c The small conversion makes these yields inaccurate.

Since the cyclooctatetraene formed in these experiments might have arisen from photochemical reaction of semibullvalene⁷ in addition to, or even instead of, from the diene (**1**), control experiments were performed as follows. Semibullvalene (**2**) was irradiated as previously described in isopentane and in toluene at -60° and at -20 to -30°. No nmr singlet corresponding to **3** was observed in these experiments, confirming the formation of cyclooctatetraene⁸ (**3**) from tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (**1**) itself.

In the pyrolysis of **1** to **2**, a concerted, suprafacial [1,3] sigmatropic process (observed in the thermal conversion of bicyclo[2.1.1]hexene derivatives to the corresponding bicyclo[3.1.0]hexenes)⁹⁻¹¹ seems unlikely, since the tricyclic structure does not permit inversion of the migrating center.¹² A two-step rearrangement by way of the doubly allylic diradical intermediate **4** seems to provide the best rationalization of this process.

(7) Acetone-sensitized conversion of **2** to **3** is reported: H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

(8) The possible formation of **2** from **3** was also excluded, since irradiation of **3** in isopentane under the same conditions described gave no nmr spectral peaks due to **2**. A slow, sensitized conversion of **3** to **2**, however, has been demonstrated by H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968).

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(12) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).