peak at m/e 84, clearly demonstrating that I readily absorbs three moles of hydrogen.

The infrared spectrum of a dilute solution of I in carbon tetrachloride shows intense absorption at 881 cm^{-1}, which is near the characteristic region for the hydrogen out-of-plane deformations in terminal disubstituted olefins.[8] Other characteristic bands in the infrared spectrum of I appear at 910, 928, 992, 1026, and 2950 cm^{-1}. It is noteworthy that the infrared spectrum of III[3] shows strong absorption at 880 cm^{-1}.

trans-1,2,3-Triiodomethylcyclopropane (IId) was prepared from *trans*-1,2,3-tricarbomethoxycyclopropane.[6] The latter compound was reduced with lithium aluminum hydride in ether. Several attempts to convert the resulting triol IIf directly to the desired triiodide with phosphorus triiodide gave only unpromising oils. Consequently the alcohol was first converted to the corresponding tritosylate IIg (mp 101–102.5°) with *p*-toluenesulfonyl chloride in pyridine at −5°. The nmr spectrum of IIg exhibits resonance peaks (in addition to peaks for the aromatic protons) at τ 6.10 (CH_2O), 7.56 ($ArCH_3$), and 7.91 (cyclopropyl CH), whose areas are in the anticipated ratio of 2:3:1. Treatment of IIg with sodium iodide in acetone under reflux gave the unstable triiodide IId, mp 80–81.5°, which can be stored indefinitely at 0° in an opaque container. The nmr spectrum of IId shows two multiplets at τ 8.92 (1) and 8.42 (2) assigned to the cyclopropyl hydrogens, and signals centered at τ 6.88 for the methylene protons. When IId is subjected to treatment with sodium ethoxide in ethanol under nitrogen within a few hours the characteristic ultraviolet spectrum of I appears. The product readily codistils with ethanol, and the distinct absorption bands disappear overnight and are replaced by intense absorption over a broad region of the spectrum.

Other studies on the physical and chemical properties of I, including its reaction with dienophiles, are in progress.

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[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 31.

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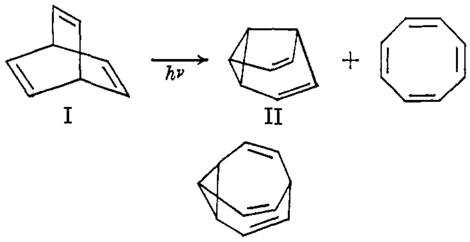
The Chemistry of Barrelene. III. A Unique Photoisomerization to Semibullvalene

Sir:

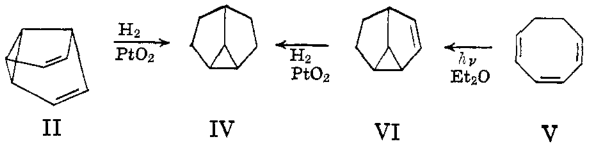
Previously we have reported the synthesis and some ground-state chemistry of barrelene[1] (I). We now communicate a most intriguing photochemical isomerization of barrelene to afford cyclooctatetraene and a C_8H_8 isomer whose structure is shown to be that of II, a compound reminiscent of bullvalene (III)[2,3] but lacking one of bullvalene's three ethylenic bridges. We term II "semibullvalene."



(1)

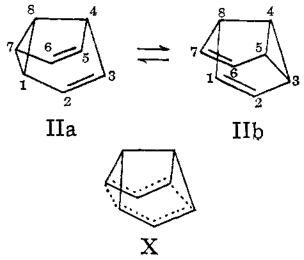
Thus, photolysis[4] of 1–2% isopentane solutions of barrelene containing 3–8% acetone as a photosensitizer afforded 25–40% yields of semibullvalene (II) and 1–2% of cyclooctatetraene, all based on 55–70% unrecovered barrelene. Barrelene, cyclooctatetraene, and semibullvalene were separated by Apiezon vpc and 25% silver nitrate–ether liquid–liquid partition chromatography.[5]

The structure of semibullvalene was established by elemental analysis, mass spectral molecular weight determination (parent ion 104), hydrogenation, and nmr. Hydrogenation of semibullvalene with PtO_2 in ether yielded as the major product the known tricyclo[5.1.0.0^{4,8}]octane (IV)[6–8] which we synthesized for comparison by photolysis[6,7,9] of 1,3,5-cyclooctatriene (V) to VI followed by PtO_2 hydrogenation. Tetrahydrosemibullvalene (IV) from photolysis of barrelene followed by hydrogenation proved identical (nmr, infrared, vpc) with IV prepared from the literature routes, and the spectral data agreed with that reported.[6,8]



(2)

As the name implies, semibullvalene is in rapid equilibrium with its degenerate valence tautomer (IIa ⇌ IIb), more rapid in fact than any of the previously reported degenerate Cope interconversions. The nmr (note Table I) showed only three varieties of hydrogens in a ratio of 2:4:2. Thus hydrogens 1, 3, 5, and 7 become equivalent, as do 4 and 8, while the set 2 and 6 remain unchanged but equivalent. Despite the nmr similarity in chemical shift of semibullvalene with the related compounds barbaralone (VII)[2a,10] and di-



(3)

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[1] (a) For paper I describing the synthesis of barrelene (bicyclo[2.2.2]-2,5,7-octatriene) *cf.* H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960); (b) paper II: H. E. Zimmerman and G. L. Grunewald, *ibid.*, **86**, 1434 (1964).

[2] (a) W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); (b) *Tetrahedron*, **19**, 715 (1963).

[3] G. Schröder, *Chem. Ber.*, **97**, 3140, 3150 (1964).

[4] Photolysis in Vycor tubes external to a 450-w Hanovia medium pressure lamp for 45–80 min.

[5] Lack of $AgNO_3$ and vpc isomerization was established by nmr.

[6] J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

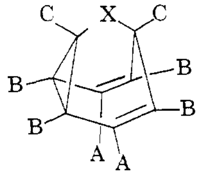
[7] O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Am. Chem. Soc.*, **86**, 2660 (1964).

[8] M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, 30, 2425 (1965).

[9] W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964).

[10] J. B. Lambert, *Tetrahedron Letters*, 1901 (1963).

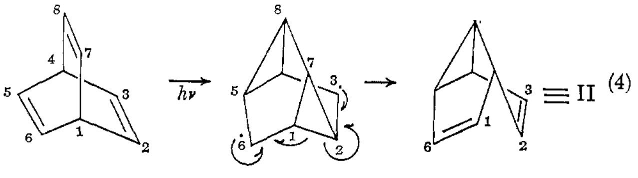
Table I. Nuclear Magnetic Resonance Data

Type H	Compd	τ^a	Ref	
A	II	4.92	Presently[b]	
	VII	4.3	2a	
	VIII	4.37	3[c]	
B	II	5.83	Presently[b]	II, X = zero carbon bridge
	VII	5.8	2a	VII, X = carbonyl bridge
	VIII	6.32	3[c]	VIII, X = $-CH_2CH_2-$ bridge
C	II	7.03	Presently[b]	
	VII	7.3	10[d]	
	VIII	8.1	3[c]	

[a] Multiplets in each case. [b] CCl_4. [c] CS_2. [d] Acetone-d_6.

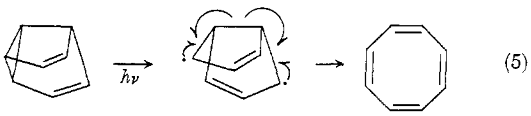
hydrobullvalene (VIII),[3] semibullvalene exhibited no nmr change to −110°. This contrasts with VII and VIII, where valence tautomerism is inhibited. The exciting possibility that IIa and IIb might instead be resonance contributors to a symmetrical species X seems ruled out by the ultraviolet spectrum (shoulder at 225–235 mμ (ϵ 2450)), which is quite similar to that reported[3] for dihydrobullvalene, and by the normal nmr.

The photochemical formation of semibullvalene from barrelene seems to involve three molecular processes: (i) 2,7 plus 5,8 bonding in barrelene; (ii) 1,2 bond fission; and (iii) triplet–singlet spin inversion. The extent to which the first two are concerted and the stage at which spin inversion occurs will be discussed later;[11] however, for simple presentation these are depicted as separate.



I XI

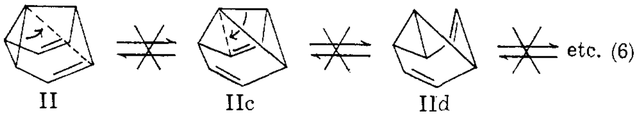
Photolysis of semibullvalene (II) itself was found to afford cyclooctatetraene but no barrelene. This may be pictured as[12]



II XII

where XII may have no real existence.

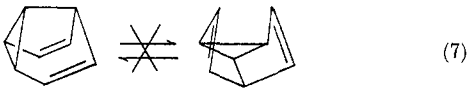
There are two further types of valence tautomerism which II might be envisioned as undergoing but does not. First is the vinylcyclopropane valence tautomerism considered by Viehe.[13] This would lead to a single nmr line as a result of the tautomerism of eq 6 and that of eq 3. However, the valence tautomerism of



II IIc IId

eq 6 involves a four-center, four-electron "cyclobutadienoid" transition state (all front lobes overlapping) and should be energetically unfavorable.

The last type of valence tautomerism in eq 7 is considered, since as far as the atomic nuclei are concerned the top and bottom of semibullvalene are nearly equivalent. Such tautomerism would lead in the extreme to two nmr peaks. The close approximation of the



II IIe

three nmr bands of II to models (Table I) coupled with the low-temperature nmr rules out this exciting potentiality.

Future publications will deal with the chemistry of semibullvalene and the mechanistic aspects of the interconversions described presently.

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(11) It seems likely that spin interconversion and 1,2-bond fission precede completion of the 2,7 and 5,8 bonding, so that the biradical species XI does not fully develop.

(12) Alternative mechanisms may be written and will be discussed subsequently. As in the barrelene reaction, there is an intriguing reaction coordinate–MO correlation.

(13) H. G. Viehe, *Angew. Chem.*, **77**, 768 (1965); the structure II was cited as of interest and the name "octavalene" suggested.

Manganese–Hydrogen Bond Distance in $HMn(CO)_5$

Sir:

We wish to report the measurement of the manganese hydrogen bond distance (1.28 ± 0.01 A) in manganese pentacarbonyl hydride, $HMn(CO)_5$. This measurement is of particular significance in view of the recent interest and speculation concerning transition metal hydrides. Although it is now generally accepted that the hydrogen is directly bonded to the metal, there is a paucity of direct experimental evidence about metal–hydrogen (M–H) bond distances in molecules of this type. Values for the M–H bond distance ranging from 1.0–1.2[1–6] to 1.4–2.0 A[7–11] have been suggested. Manganese carbonyl hydride is especially amenable to a broad-line proton nmr study since manganese-55 has a large spin quantum number and a large magnetogyric ratio and is 100% abundant. The situation is

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(1) F. A. Cotton and G. Wilkinson, *Chem. Ind.* (London), 1305 (1956).

(2) F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958).

(3) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).

(4) E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards, and G. Wilkinson, *ibid.*, 2484 (1959).

(5) A. D. Buckingham and P. J. Stephens, *ibid.*, 2747 (1964).

(6) M. Gerlock and R. Mason, *ibid.*, 296 (1965).

(7) L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964).

(8) W. F. Edgell, C. Magee, and G. Gallup, *J. Am. Chem. Soc.*, **78**, 4185 (1956); W. F. Edgell and G. Gallup, *ibid.*, **78**, 4188 (1956).

(9) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1495 (1964).

(10) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3502 (1963).

(11) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).