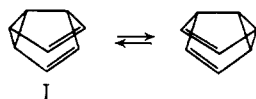


Semibullvalene from Tricyclo[3.3.0.0^{2,6}]octane¹

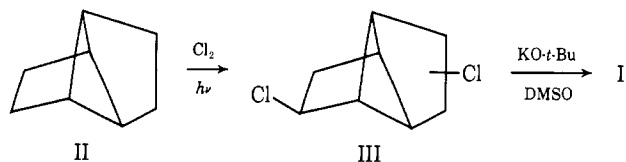
Sir:

Semibullvalene (I), first described by Zimmerman, *et al.*,² has been produced by the sensitized irradiation of barrelene or, at low temperatures, of cyclooctatetraene. It has the unique property of undergoing a degenerate Cope rearrangement more rapidly than any compound previously described. We now wish to report a convenient two-step synthesis of this fascinating



hydrocarbon from tricyclo[3.3.0.0^{2,6}]octane (II),³ by which I can be obtained on a gram scale. This synthesis involves a novel skeletal rearrangement, the mechanism of which is discussed in the accompanying communication.⁴

Tricyclo[3.3.0.0^{2,6}]octane (II), dissolved in benzene, was irradiated at ice-water temperature with a GE sunlamp while chlorine gas (*ca.* 2 equiv) was carefully bubbled through the solution. Work-up furnished 3-chlorotricyclo[3.3.0.0^{2,6}]octane^{3b} (26%), a mixture of isomeric dichlorotricyclo[3.3.0.0^{2,6}]octanes (III) (43%, bp 71° (3 mm)), and a mixture of more highly chlorinated products. The gross structure of III⁵ was established on the basis of its elemental analysis, mass spectrum, and nmr spectrum in CCl₄: τ 5.6 (broad doublet, 2 H), 7.1~8.2 (complex multiplet, 8 H). Without further purification,⁶ III was treated for 3 hr with potassium *t*-butoxide in dimethyl sulfoxide at 70°, giving semibullvalene (I), bp 55–60° (40 mm), as the sole volatile product in 40% yield. The structure of I was



proved by comparison of its nmr and infrared spectra with those reported.²

One attractive pathway for this synthesis of semibullvalene would involve initial double dehydrochlorina-

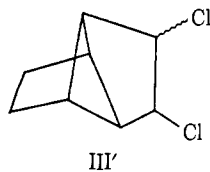
(1) The partial support of this research by grants from the National Institutes of Health (GM-10090) and the National Science Foundation (GP-7013) is acknowledged with pleasure.

(2) (a) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Am. Chem. Soc.*, **91**, 3316 (1969); (b) H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968); (c) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); (d) we are indebted to Dr. Zimmerman for providing us with a copy of the nmr spectrum of semibullvalene.

(3) (a) R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964); (b) J. Meinwald and B. E. Kaplan, *ibid.*, **89**, 2611 (1967).

(4) J. Meinwald and H. Tsuruta, *ibid.*, **91**, 5877 (1969).

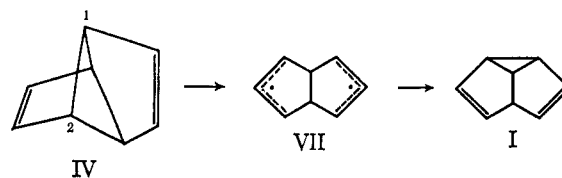
(5) Of the possible isomers, the vicinal one (III') appears unlikely,



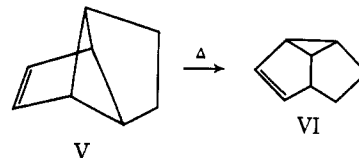
since attempted dechlorination with zinc dust and acetic acid gave only unchanged starting material without formation of tricyclo[3.3.0.0^{2,6}]oct-3-ene (V).^{3b}

(6) Careful spinning-band distillation gave one crystalline dichloro compound, mp 51.5–52.5°, as a minor component; nmr (CCl₄) τ 5.54 (broad doublet, 2 H), 7.16–8.23 (complex multiplet, 8 H).

tion of III to the highly strained tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (IV), which was, in fact, our original synthetic objective. Subsequent rearrangement of IV to I, in

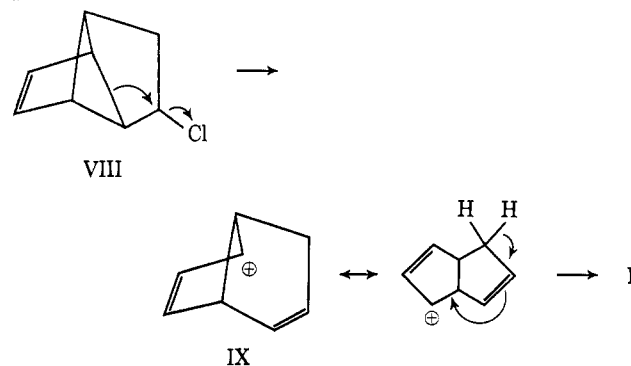


analogy with the pyrolytic rearrangement of tricyclo[3.3.0.0^{2,6}]oct-3-ene (V) to dihydrosemibullvalene (VI), would complete the process.⁷ The higher strain of IV compared to that of V should encourage more rapid bond cleavage between C₁ and C₂, producing the doubly



allylic diradical VII, which might easily form I.⁸

As a second possibility, dehydrochlorination of III to give 3-chlorotricyclo[3.3.0.0^{2,6}]oct-7-ene (VIII) followed by ionization and bond cleavage would give the bicyclo[3.3.0]octadienyl cation IX, which might easily produce I as shown.



In continuing our pursuit of the diene IV, we have been able to provide evidence in support of the first of these two hypotheses.⁴

(7) We find this rearrangement proceeds readily at 150°.

(8) According to a private communication from Professor H. M. Frey, the estimated half-life for the conversion of IV to I might be less than 1 hr at 20°, based on his kinetic study of the isomerization of V to VI.

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Tricyclo[3.3.0.0^{2,6}]octa-3,7-diene¹

Sir:

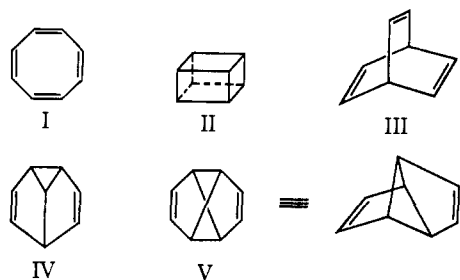
Known compounds corresponding to the molecular formula (CH)₈ include cyclooctatetraene (I), cubane (II),² barrelene (III),³ and semibullvalene (IV).⁴

(1) The partial support of this research by grants from the National Science Foundation (GP-7013) and the National Institutes of Health (GM-10090) is acknowledged with pleasure.

(2) P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 3158 (1964).

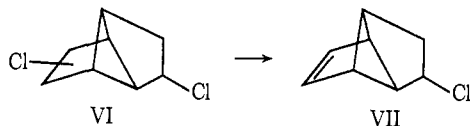
(3) (a) H. E. Zimmerman and R. M. Paufler, *ibid.*, **82**, 1514 (1960); (b) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969).

(4) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).



We have been interested in developing a synthesis of the cyclooctatetraene valence isomer V, tricyclo[3.3.0.0^{2,6}]octa-3,7-diene, in connection with our studies on highly strained ring systems and also in connection with our recently reported (inadvertant) synthesis of semibullvalene from dichlorotricyclo[3.3.0.0^{2,6}]octane.⁵ We now wish to report the successful synthesis and characterization of this (CH)₈ diene.

Dichlorotricyclo[3.3.0.0^{2,6}]octane (VI),⁵ treated with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) at room temperature, was converted into 3-chlorotricyclo[3.3.0.0^{2,6}]oct-7-ene (VII),⁶ bp 64° (18 mm), in 42% yield, accompanied by semibullvalene (13%) and unchanged VI (27%). The characterization of VII is based on its nmr spectrum in CCl₄ (τ 3.63 (multiplet, 2 H), 5.64 (broad doublet, 1 H), 6.24 (quartet, $J = 6.6$, 1.5 cps, 1 H), 6.42 (multiplet, 1 H), 7.78–8.23 (multiplet, 4 H)) and on the result of hydrogenation over 5% Pd-C in ethyl acetate to give the known 3-chlorotricyclo[3.3.0.0^{2,6}]octane.⁷



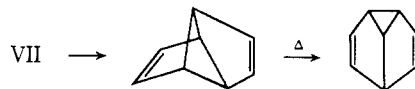
In order to generate the potentially unstable diene under the mildest possible conditions, VII was treated with potassium *t*-butoxide in DMSO at $\sim 25^\circ$ in a cold room maintained at 0° , during which time the reaction surface was slowly purged with dry nitrogen, sweeping products out into an isopropyl alcohol-Dry Ice cooled trap. In this way, a mixture of unchanged VII, IV, and a new product proven to be the desired tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (V) was collected.⁸ Careful distillation of the trapped mixture at 0° under reduced pressure (3–5 mm) furnished a mixture of only two components, whose nmr spectrum in CCl₄ showed a pair of apparent triplets of equal areas at τ 4.0 ($J = 2.0$ cps) and 6.24 ($J = 2.0$ cps), superimposed on the peaks due to IV. The chemical shifts for the protons in V are in good agreement with those of the olefinic (τ 3.93) and bridgehead protons (τ 6.53) in tricyclo[3.3.0.0^{2,6}]oct-3-ene.⁷ It was noted that the pair of peaks due to V rapidly decreased in intensity at room temperature while the peaks due to IV increased correspondingly, indicating facile rearrangement of V to IV.⁵ Catalytic reduction of a mixture of IV and V (2:1) over Adams catalyst at -1° gave the known tricyclo[3.3.0.0^{2,6}]octane in 34% yield;

(5) J. Meinwald and D. Schmidt, *J. Am. Chem. Soc.*, **91**, 5877 (1969).

(6) Satisfactory elemental analyses were obtained for all new compounds.

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

(8) The ratio of these three compounds changes slightly depending on experimental conditions. A typical ratio of IV:V:VII is 3:2:4.



this transformation establishes the structure of V unequivocally.

The instability of V with respect to semibullvalene (IV) supports its possible intermediacy in the previously described synthesis of IV.⁵ It is also interesting to note that V or its derivatives may well play a role in the chemistry of many cyclooctatetraene-related compounds. In 1964, Stiles and Burckhardt called attention to a possibility of this sort,⁹ and subsequent work of both Criegee¹⁰ and Jones¹¹ would be compatible with labile intermediates closely related to V. Further exploration of the chemistry of this intriguing diene is in progress.

(9) M. Stiles and U. Burckhardt, *J. Am. Chem. Soc.*, **86**, 3396 (1964); M. Stiles, Abstracts, Nineteenth National Organic Chemistry Symposium, Tempe, Ariz., June 13–17, 1965, pp 57–62.

(10) R. Criegee and R. Askani, *Angew. Chem. Intern. Ed. Engl.*, **7**, 537 (1968).

(11) M. Jones, Jr., and L. O. Schwab, *J. Am. Chem. Soc.*, **90**, 6549 (1968).

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C₈H₈ Interconversions. An Unusual Rearrangement Providing a New Route to Semibullvalene

Sir:

We wish to report an unusual rearrangement leading to semibullvalene¹ (1). The reaction is of both synthetic and mechanistic significance.

Our original goal in the present research was the synthesis of tricyclo[3.3.0.0^{2,6}]-3,7-octadiene (2, "tricyclic diene" for brevity). This compound was of interest to us partially because it would be the seventh member of the (CH)₈ series; barrelene,² semibullvalene,¹ cubane,³ bicyclo[4.2.0]-2,4,7-octatriene,⁴ tricyclo[4.2.0.-0^{2,5}]-3,7-octadiene,⁵ and cyclooctatetraene⁶ were already known. Additionally, the tricyclic diene 2 seemed to be a possible intermediate in the photochemical formation of semibullvalene (1) from cyclooctatetraene as reported by us recently,⁷ and knowledge of the behavior of independently prepared tricyclic diene 2 promised to be mechanistically helpful.

Irradiation of tricyclo[3.3.0.0^{2,6}]octane (3)⁸ in benzene with (3:1 excess) chlorine using a 100-W GE H100A4 lamp through Pyrex afforded as the major product ca. 20% of the 3,7-dichlorotricyclo[3.3.0.0^{2,6}]octane stereoisomers (4).⁹

(1) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966).

(2) H. E. Zimmerman and R. M. Paufler, *ibid.*, **82**, 1514 (1960); H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969).

(3) P. E. Eaton and T. W. Cole, *ibid.*, **86**, 3157 (1964).

(4) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

(5) M. Avram, I. Dinulescu, E. Marcia, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Ber.*, **97**, 382 (1964).

(6) R. Willstätter and E. Waser, *ibid.*, **44**, 3423 (1911).

(7) H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, **90**, 4763 (1968).

(8) R. Srinivasan, *ibid.*, **86**, 3318 (1964).

(9) Complete spectral, analytic, and synthetic details will be given in our full paper.