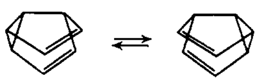
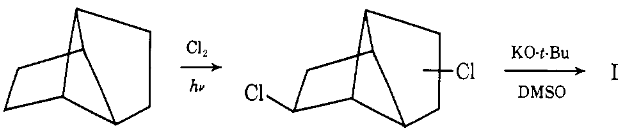
Semibullvalene from Tricyclo[3.3.0.0^{2,6}]octane[1]

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]

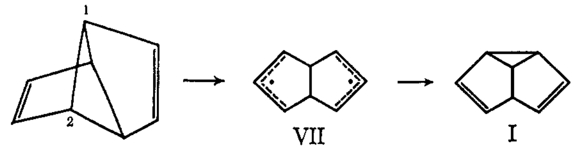

I

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 III[5] was established on the basis of its elemental analysis, mass spectrum, and nmr spectrum in CCl_4: 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]

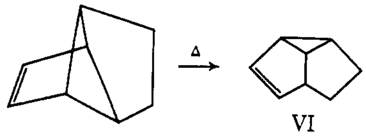


II III

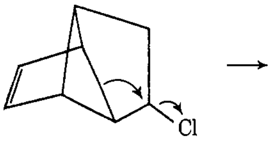
One attractive pathway for this synthesis of semibullvalene would involve initial double dehydrochlorination of III to the highly strained tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (IV), which was, in fact, our original synthetic objective. Subsequent rearrangement of IV to I, in analogy with the pyrolitic 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 C_1 and C_2, producing the doubly allylic diradical VII, which might easily form I.[8]



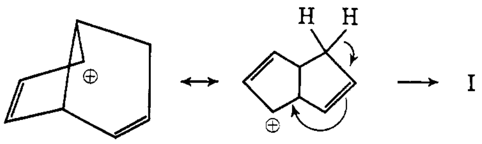
IV VII I


V VI

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.



VIII



IX

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]

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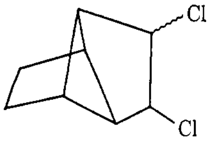
[1] The partial support of this research by grants from the National Institutes of Health (GM-10090) and the National Science Foundation (GP-7013) is acknowledged with pleasure.

[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,



III′

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 (CCl_4) τ 5.54 (broad doublet, 2 H), 7.16–8.23 (complex multiplet, 8 H).

[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-diene[1]

Sir:

Known compounds corresponding to the molecular formula $(CH)_8$ include cyclooctatetraene (I), cubane (II),[2] barrelene (III),[3] and semibullvalene (IV).[4]

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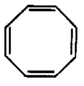
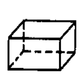
[1] The partial support of this research by grants from the National Science Foundation (GP-7013) and the National Institutes of Health (GM-10090) is acknowledged with pleasure.

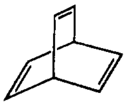
[2] P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 3158 (1964).

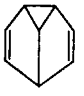
[3] (a) H. E. Zimmerman and R. M. Paufler, *ibid.*, **82**, 1514 (1960); (b) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969).

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


I


II

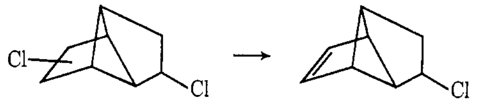

III


IV


V

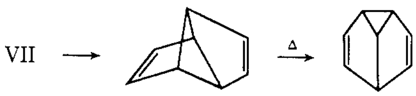
We have been interested in developing a synthesis of the cyclooctatetraene valence isomer V, tricyclo[3.3.0.$0^{2,6}$]octa-3,7-diene, in connection with our studies on highly strained ring systems and also in connection with our recently reported (inadvertant) synthesis of semibullvalene from dichlorotricyclo[3.3.0.$0^{2,6}$]octane.[5] 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 CCl_4 (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]



VI VII

In order to generate the potentially unstable diene under the mildest possible conditions, VII was treated with potassium *t*-butoxide in DMSO at ~25° 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 CCl_4 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; 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 cyclooctatraene-related compounds. In 1964, Stiles and Burckhardt called attention to a possibility of this sort,[9] and subsequent work of both Criegee[10] and Jones[11] would be compatible with labile intermediates closely related to V. Further exploration of the chemistry of this intriguing diene is in progress.

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(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.

(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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C_8H_8 Interconversions. An Unusual Rearrangement Providing a New Route to Semibullvalene

Sir:

We wish to report an unusual rearrangement leading to semibullvalene[1] (**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 cyclooctatetraene[6] 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]

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(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.