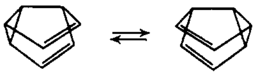
Semibullvalene from Tricyclo[3.3.0.0^{2,6}]octane[1]

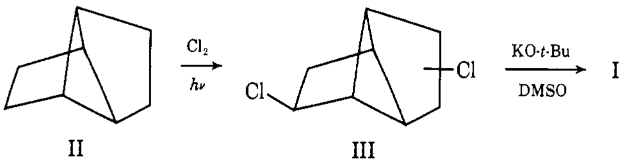
Sir:

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]

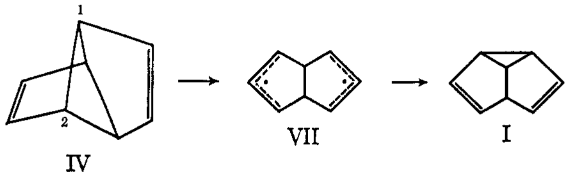


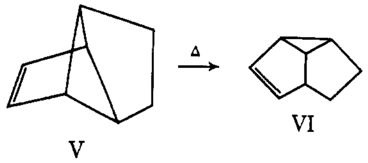
I

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]

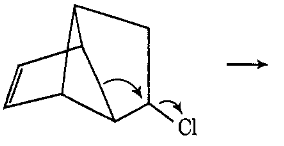


One attractive pathway for this synthesis of semibullvalene would involve initial double dehydrochlorination of III to the highly strained tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (IV), which was, in fact, our original synthetic objective. Subsequent rearrangement of IV to I, in analogy with the pyrolitic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

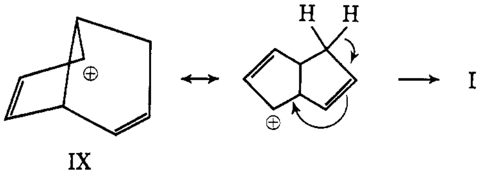




As a second possibility, dehydrochlorination of III to give 3-chlorotricyclo[3.3.0.0^{2,6}]oct-7-ene (VIII) followed by ionization and bond cleavage would give the bicyclo[3.3.0]octadienyl cation IX, which might easily produce I as shown.



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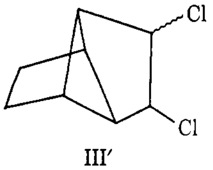
[1] The partial support of this research by grants from the National Institutes of Health (GM-10090) and the National Science Foundation (GP-7013) is acknowledged with pleasure.

[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, 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]



III′

[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.

Jerrold Meinwald, Douglass Schmidt
Department of Chemistry, Cornell University
Ithaca, New York 14850

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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).