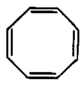
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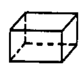
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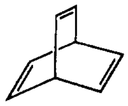
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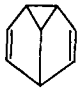
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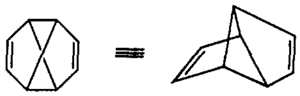
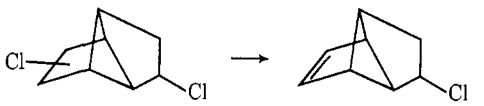

V

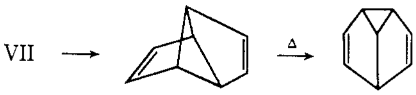
We have been interested in developing a synthesis of the cyclooctatetraene valence isomer V, tricyclo[3.3.0.0^{2,6}]octa-3,7-diene, in connection with our studies on highly strained ring systems and also in connection with our recently reported (inadvertant) synthesis of semibullvalene from dichlorotricyclo[3.3.0.0^{2,6}]octane.[5] 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$_8$H$_8$ 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).

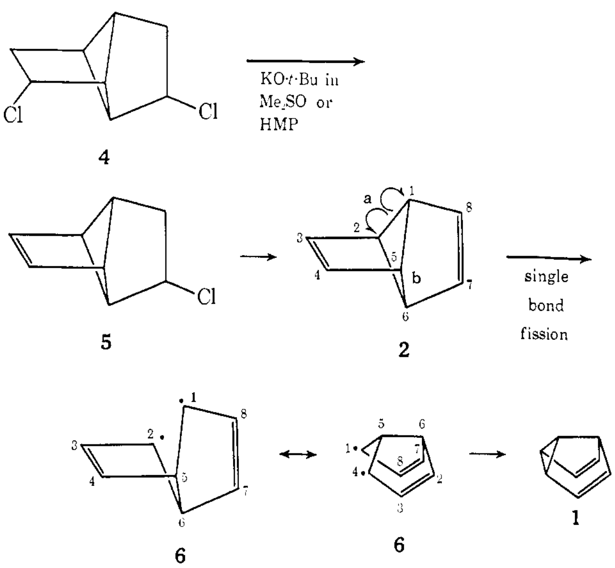
(8) R. Srinivasan, *ibid.*, **86**, 3318 (1964).

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

Treatment of dichlorotricyclooctane **4** with 6 equiv of potassium *t*-butoxide in dimethyl sulfoxide (0.8 *M*) at room temperature for times ranging from 24 to 48 hr or with potassium *t*-butoxide in hexamethylphosphoramide (HMP) under otherwise similar conditions led[9] to 3-chlorotricyclo[3.3.0.0^{2,6}]-7-octene (**5**) in *ca.* 17% yield and semibullvalene (**1**). Nmr and vpc analyses showed the semibullvalene to be formed in 31–44% yields. This product was isolated by preparative vpc (Ucon polar) and identified by comparison with authentic material.[9] Assignment of structure to **5** was based on the nmr spectrum, mode of formation, and reactivity. It was found that under the reaction conditions the chlorotricycloolefin **5** did proceed onward to semibullvalene. Throughout these runs no cyclooctatetraene was observed.

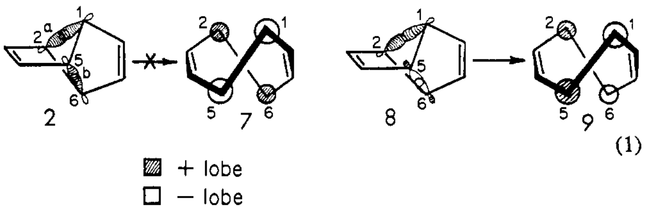
When the reaction was run in hexamethylphosphoramide under vacuum (15 mm) with a Dry Ice cooled receiver, the nmr of the distillate showed semibullvalene and new peaks at τ 3.95 and 6.22 along with absorption due to by-product. The absorptions at τ 3.95 and 6.22 disappeared (and semibullvalene increased) with time and are ascribed to an intermediate but unstable tricyclic diene **2**. The reactions are summarized in Chart I.

Chart I. Semibullvalene Formation from Dehydrochlorination of 3,7-Dichlorotricyclo[3.3.0.0^{2,6}]octane



Two intriguing points are noted. First, one might inquire why the tricyclic diene **2** does not afford cyclooctatetraene, since fission of bonds a and b in **2** (note Chart I) would lead directly to this product. Furthermore, such a process occurs in the fascinating example presented by Stiles,[10] which is just a dibenzo analog. Secondly, the observed reaction involves fission of bond 1,2 (bond a) and formation of bond 1,4 and thus is a 1,3-suprafacial sigmatropic rearrangement,[11] a reaction which should be thermally forbidden.[12]

Actually the two points are related. The absence of cyclooctatetraene formation seems most likely to derive from the high energy required for the thermally forbidden retro-2 + 2 cycloaddition depicted in eq 1. Thus this reaction would lead to the chiral form of *cis,-trans,cis,trans*-cyclooctatetraene (**7**) *via* a transition state in which four orbitals (*i.e.*, 1, 2, 5, and 6) are in a cyclic array with zero, two, or four sign inversions between orbitals. Such transition states have been shown to have two nonbonding MO's (*i.e.*, a degeneracy), showing that one bonding MO of the reactant is becoming antibonding in the product, and *vice versa* (*i.e.*, a crossing point).



(1)

Inspection of the bonding MO $\sigma_a - \sigma_b$ (**8**) shows that this MO becomes antibonding (*i.e.*, product MO **9**) since, as product forms, nodes are developing between π-bonded carbons 1 and 5 as well as 2 and 6. This can be seen by consideration of the coefficients of the Hückel cyclobutadienoid transition state as well as qualitatively.

Hence with retrocycloaddition forbidden, the observed single bond (*i.e.*, a) fission becomes preferred. In the dibenzocyclooctatetraene example[10] such a process leading to a semibullvalene would demand loss of aromaticity of one ring. Regarding the 1,3-sigmatropic shift, it seems more likely that a discrete allylic biradical (**6**) is formed and that a forbidden process is not encountered.

The present evidence permits but does not require the tricyclic diene **2** to be an intermediate in the cyclooctatetraene to semibullvalene conversion.[7] Thus the low-temperature photolysis could give chiral *cis,trans,-cis,trans*-cyclooctatetraene (**7**) which then in a photochemically allowed process affords tricyclic diene **2**; this, in turn, would thermally give semibullvalene. However, formation of only one of the bonds (*e.g.*, a) in the reaction could lead directly to the allylic biradical **6** and thence to semibullvalene (**1**). Hence the tricyclic diene **2** may be an actual intermediate or just a closely related species on the same potential energy surface. The same is true for the formation of semibullvalenes by other routes, although in the special case of the barrelene photolysis this surface seems not to be utilized.[14]

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[10] (a) M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, **86**, 3396 (1964); (b) M. Stiles, 19th National Organic Symposium, June 1965, p 62, has presented evidence for a doubly allylic biradical as **6** in the thermal rearrangement of dibenzocyclooctatetraenes.

[11] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

[12] An equivalent approach[13] pictures a concerted rearrangement using a cyclic array of four orbitals—one each at carbons 1, 2, 3, and 4—with zero or an even number of sign inversions between orbitals, the exact number depending on choice of orientation for the basis set of orbitals. Reactions with zero or an even number of sign inversions between contiguous orbitals have been termed Hückel and are ground-state forbidden with 4*N* electrons present.[13]

[13] H. E. Zimmerman, *Angew. Chem.*, **81**, 45 (1969); *Angew. Chem. Intern. Ed. Engl.*, **8**, 1 (1969); *J. Amer. Chem. Soc.*, **88**, 1564 (1966).

[14] H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

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