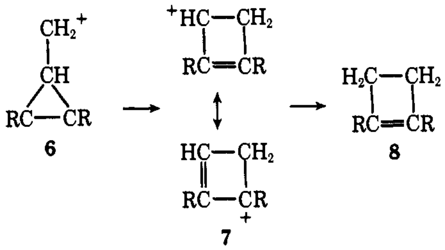
ester or ketone function by action of the reagent pair[14] to the alcohol stage. Thereafter, development of electron deficiency at the external carbon (*cf.* **6**) would



lead to a Wagner–Meerwein rearrangement with ring expansion to the cyclobutene cation (*cf.* **7**). Delivery of hydride ion would complete the processes and form the cyclobutene product (*cf.* **8**). The **6**–**7** ring expansion has been reported before,[15] though without trapping the four-membered ring system as we have done here. Questions about the nature of the ionic intermediates[15] and why only product **3** and none of **4** or **5** is obtained will be reserved for a more detailed treatment.

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[14] According to E. C. Ashby and B. Cooke (*J. Amer. Chem. Soc.*, 90, 1625 (1968)), E. C. Ashby and J. Prather (*ibid.*, **88**, 729 (1966)), and E. L. Eliel (*Rec. Chem. Progr.*, **22**, 129 (1961)), a 1:1 mixture of lithium aluminum hydride and aluminum chloride may be regarded as monochloroaluminum dihydride (H$_2$AlCl), which is an effective reducing agent as well as a strong Lewis acid.

[15] R. Breslow and M. Battiste, *J. Amer. Chem. Soc.*, **82**, 3626 (1960); R. Breslow, J. Lockhart, and A. Small, *ibid.*, **84**, 2793 (1962).

[16] NASA Predoctoral Trainee, 1967–1970.

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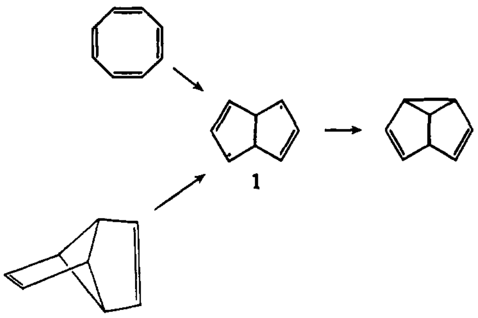
Synthesis and Thermal Reorganization of 1,2,5,6-Tetramethyl-3,4,7,8-tetramethylenecyclooctadiene

Sir:

The diradical **1** has recently been implicated in a number of thermal reorganizations. It is a probable intermediate in both the thermal rearrangement of octamethylcyclooctatetraene to octamethylsemibullvalene[1,2] and of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene to semibullvalene.[3,4]

If **1** is indeed a common intermediate in these two rearrangements leading to semibullvalene, it ought to prove possible to observe the equilibration *via* **1** of an appropriate cyclooctatetraene derivative with the corresponding tricyclo[3.3.0.0^{2,6}]octadiene, provided that the exit to semibullvalene is blocked. Indeed, Stiles has postulated just such an equilibration to account for the thermal isomerization of 5,6- to 5,11-substituted dibenzocyclooctatetraenes.[5] In these benzocyclooctatetraenes the incorporation of the radical stabilizing double bonds of **1** into benzene rings renders unfavorable the conversion to semibullvalene, which would necessitate destruction of the aromaticity of one of the benzene rings.



Another mode of foiling the conversion of the diradical to semibullvalene would be to position the stabilizing double bonds exocyclic to the bicyclo[3.3.0]ring system. This should allow equilibration of a dimethylene-substituted cyclooctadiene with the corresponding tricyclo[3.3.0.0^{2,6}]cyclooctane, while making semibullvalene formation inpossible. We herein report the experimental realization of this expectation in the thermal reorganization of 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenecyclooctadiene (**3**) to 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (**4**).

Synthesis of a 1,2,5,6-tetramethylenecyclooctadiene was of interest to us as an extension of our studies of the chemistry of 1,2,5,6-tetramethylenecyclooctane.[6] Employing an approach to a member of the former class of compounds which had proven successful in our synthesis of the latter,[7] we carried out the benzophenone-sensitized irradiation of 1,2-dimethyl-3,4-dimethylenecyclobutene. From the crude photolysate a single photodimer[8] was obtained in 50% yield. The nmr spectrum of this material showed three sharp singlets at (CDCl$_3$) δ 1.05, 4.70, and 5.27 in the ratio 3:1:1, indicating the gross structure **2** for the product.[9,10] The anti stereochemistry of **2** was established by reduction to the octamethyltricyclooctadiene,[9] either catalytically[11] or using lithium in ammonia–tetrahydrofuran–*tert*-butyl alcohol. The nmr spectrum of the product was similar to but distinguishable from that of authentic *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene[12] and the melting point was in acceptable agreement with that reported for the anti compound.[13]

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[1] R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **7**, 537 (1968).

[2] Diradical **1** has also been proposed as an intermediate in the rearrangement of cyclooctatetraene to dihydropentalene; M. Jones, Jr., and L. O. Schwab, *J. Amer. Chem. Soc.*, 90, 6549 (1968).

[3] (a) J. Meinwald, D. Schmidt, and H. Tsuruta, *ibid.*, **91**, 5877 (1969); (b) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

[4] Photochemical interconversion of (CH)$_8$ isomers has also been studied: (a) H. E. Zimmerman and G. L. Grunwald, *ibid.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) H. E. Zimmerman and H. Iwamura, *ibid.*, 90, 4763 (1968); (d) J. Meinwald and H. Tsuruta, *ibid.*, **92**, 2579 (1970).

[5] (a) M. Stiles and U. Burckhardt, *ibid.*, **86**, 3396 (1964); (b) M. Stiles (19th National Organic Symposium, Tempe, Ariz., June 1965, p 62) has also presented strong evidence for the intermediacy of the biradical in these reactions.

[6] W. T. Borden, I. L. Reich, L. A. Sharpe, and H. Reich, *J. Amer. Chem. Soc.*, **92**, 3808 (1970).

[7] W. T. Borden, L. A. Sharpe, and I. L. Reich, *Chem. Commun.*, 461 (1970).

[8] The crystalline photodimer decomposes rapidly unless stored at Dry Ice temperature.

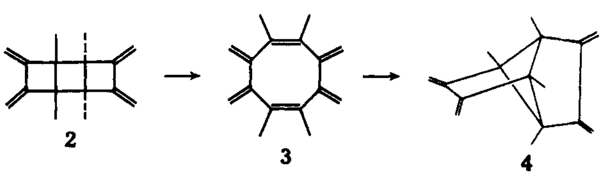
[9] Spectral and analytical data were in accord with this proposed structure.

[10] It is of some interest that the photodimerization takes place exclusively at what is the most sterically hindered double bond.

[11] 1,2-Dimethylenecyclobutanes generally add hydrogen 1,4 when a 5% palladium on carbon catalyst is used; R. Stafford, Ph.D. Thesis, Harvard, 1971.

[12] Prepared by the procedure of R. Criegee and G. Louis, *Chem. Ber.*, 90, 417 (1957).

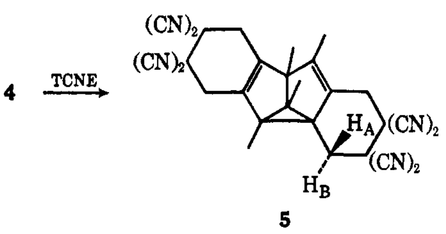
On pyrolysis in a flow system at 240°, **2** underwent smooth conversion to **3**:[9] nmr ($CDCl_3$) δ 1.80 (s), 4.80 (d, J = 1.5 Hz), and 5.10 (d, J = 1.5 Hz); ratio 3:1:1. At higher temperatures, however, another compound was observed, which was the only identifiable product at 380°. At this temperature **3** was also converted to the new isomer, whose nmr was very much like that of **2**, δ 0.70, 4.83, and 5.48, ratio 3:1:1, except for the shift of the methyl signal to higher field. Two structures are consistent with the spectral and analytical data for this compound—the syn isomer of **2** and **4**. The former structure seemed highly unlikely because of the demonstrated greater thermodynamic stability of **3** compared to **2**, whereas chemical analogy[1-5] supported the latter. Moreover, the upfield shift of the methyl resonance is readily explicable in terms of structure **4**, since such shielding of equatorial methyl groups on puckered cyclobutane rings is well documented.[14]



In order to confirm the structure of **4**, it was subjected to Li reduction in NH_3–THF–*tert*-BuOH.[15] Instead of octamethylsemibullvalene, formed by rearrangement[3] of the octamethyltricyclo[3.3.0.$0^{2,6}$]octa-3,7-diene, which might be expected to be the initial reduction product, the material isolated was a complex mixture of isomeric octamethylbicyclo[3.3.0]octadienes.[9] However, when octamethylsemibullvalene[1] was itself subjected to the reduction conditions, the nmr and glc traces obtained from the product were superimposable on those from the product of the reduction of **4**.

The structure of **4** was further established by its reaction with 2 mol of tetracyanoethylene to give a crystalline adduct. Consistent with its formulation as **5**,[9] the adduct had a uv spectrum very similar to that of authentic octamethylsemibullvalene[1] and an nmr spectrum in which the effective C_2 symmetry of the molecule, caused by its fluxional character, was evident. The two types of methyl groups appeared at (acetone-d_6) δ 1.20 and 1.80 and four methylene protons at δ 3.28 as a somewhat broadened singlet. The remaining two sets of methylene protons appeared at δ 2.76 and 3.88 as an AB quartet with a geminal coupling constant of $|J|$ = 17 Hz. These resonances presumably come from H_A and H_B, the difference in chemical shift being ascribed to the anisotropy of the adjacent carbon.

We are currently studying other cycloaddition reactions of **3** and **4** as well as their photochemistry.



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(13) R. Criegee, G. Schroder, G. Maier, and H. G. Fischer, *Chem. Ber.*, **93**, 1553 (1960).

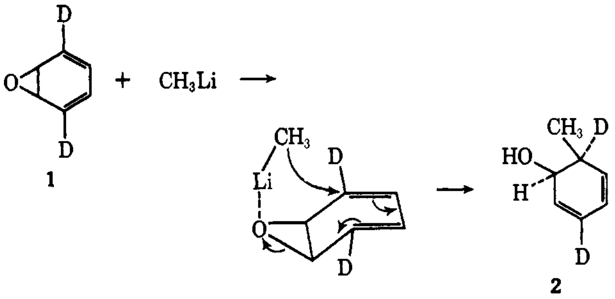
(14) A. Suzuki and M. Itoh, *Tetrahedron Lett.*, 1003 (1967).

(15) Catalytic hydrogenation gave 1,2 rather than 1,4 reduction of the diene. This provides some chemical evidence that the diene moiety is not contained in a cyclobutane ring.[11]

Cis-1,6 Addition of Methyllithium to Oxepin–Benzene Oxide

Sir:

Vogel[1] has reported that oxepin–benzene oxide reacts with methyllithium to give a mixture of *cis*- and *trans*-6-methylcyclohexa-2,4-dien-1-ols in which the cis–trans ratio is higher than 90:10. In our hands the reaction gave only the cis dienol. The absence of any trans isomer in our study may be due to the absence of any halide ion in the CH_3Li solution. The stereochemistry of the cis dienol product was established by reduction (H_2, Pd/C in ethyl acetate) to the known *cis*-2-methylcyclohexanol.[2] Epimerization is not expected during the reduction since it does not occur during the reduction of chorismic acid under similar conditions.[3] We have established that formation of the cis product occurs by a 1,6 addition of methyllithium to **1**. Cyclohexa-1,4-diene-*3,3,6,6-d*$_4$ was prepared from butadiene-*1,1,4,4-d*$_4$[4] as previously described,[5] and the diene was converted to **1** by Vogel's



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(1) E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

(2) E. L. Eliel and C. A. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957).

(3) J. M. Edwards and L. M. Jackman, *Aust. J. Chem.*, **18**, 1227 (1965).

(4) A. C. Cope, G. A. Berchtold, and D. L. Ross, *J. Amer. Chem. Soc.*, **83**, 3859 (1961). The butadiene consisted of 96.2% d_4 and 3.8% d_3 species. The retention of labeling throughout the experimental sequence was established by spectral data.

(5) W. P. Norris, *J. Org. Chem.*, **33**, 4540 (1968).