homoadamantene (III) the double bond is part of two seven-membered rings; III should be less strained[16] than adamantene in which the double bond is part of two six-membered rings. Perhaps III can be compared in its expected behavior with 1-bicyclo[3.2.2]nonene (IX) which dimerizes slowly (half-life about 25 min at 0°).[17] The strain energies of these bridgehead olefins await experimental determination or accurate molecular mechanics calculation.

Hofmann degradation of *N*,*N*,*N*-trimethyl-3-homoadamantylammonium hydroxide, expected to give rise to 3-homoadamantene (III) or its 2- isomer, gave a mixture of at least three $C_{22}H_{32}$ dimers,[18] which showed identical laser Raman spectra and glc retention times with dimers C, D, and E.

Current investigations in this laboratory show that the carbene ring enlargement method is general for the synthesis of other bridgehead olefins in bridged systems.[19]

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[15] D. Grant, D. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972); D. Lenoir, *Tetrahedron Lett.*, 4049 (1972); J. E. Gano and L. Eizenberg, *J. Amer. Chem. Soc.*, **93**, 972 (1973); A. H. Alberts, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 3047 (1973).

[16] H–D Exchange of the α-bridgehead position of 4-homoadamantanone was not observed under mild basic conditions: P. v. R. Schleyer, E. Funke, and S. H. Liggero, *J. Amer. Chem. Soc.*, **91**, 3965 (1969).

[17] J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, **91**, 7775 (1969).

[18] B. L. Adams and P. Kovacic, *J. Amer. Chem. Soc.*, **95**, 8206 (1973).

[19] A. D. Wolf and M. Jones, Jr., *J. Amer. Chem. Soc.*, **95**, 8209 (1973).

[20] A.B. Thesis, Princeton University, 1970.

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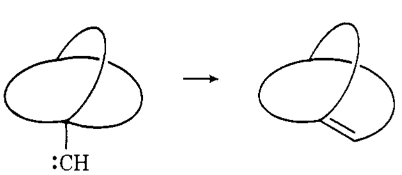
A Carbene Route to Bridgehead Olefins. Bicyclo[2.2.2]oct-1-ene[1]

Sir:

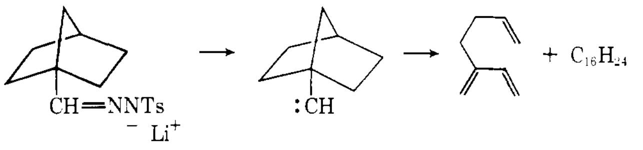
Bredt's rule[2] which proscribes formation of a double bond at the bridgehead of polycyclic molecules has succumbed to violation in small systems only recently.[3] We describe here a new route to anti-Bredt molecules which promises great versatility. It is applied here to the synthesis of bicyclo[2.2.2]oct-1-ene.

We hoped that gas-phase generation of a molecule containing a carbene attached to the bridgehead position



of a small bicyclic system would lead to ring expansion and formation of a bridgehead olefin. This approach had been tried in solution some years ago by Wilt and his collaborators[4] but even under conditions thought to be aprotic, products of apparent ionic reactions appeared. When the conditions were made truly aprotic no volatile compounds could be isolated. It seemed to us impossible that bridgehead olefins could have survived the reaction conditions.

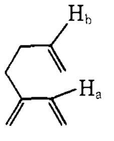
We decomposed tosylhydrazone salt **1** in a flash pyrolysis apparatus at 330° thus generating carbene **2** in the gas phase. We isolated 3-methylenehepta-1,6-diene (**3**, 31% yield) as well as compounds of the formula



1 **2** **3**

$C_{16}H_{24}$ (12% yield). At lower temperatures the relative yield of the latter compounds increased. The dimeric compounds showed no resonances for vinyl hydrogens in their nmr spectra and a center cut of the largely unresolved series of peaks on the gas chromatograph showed a parent mass of 216.187114 (calcd for $C_{16}H_{24}$, 216.187792). These properties are entirely consistent with cyclobutanes formed by dimerization of a bridgehead olefin and serve to exclude the product of formal dimerization of **2**.[5]

The skeleton of triene **3** was established by hydrogenation to 3-methylheptane which was identified by comparison of infrared spectra with authentic material.[6] Examination of the uv (λ_{max}^{EtOH} 224.0 nm, log ϵ 4.1; myrcene:[7] λ_{max}^{EtOH} 224.5 nm, log ϵ 4.2; α-myrcene:[8] $\lambda_{max}^{isooctane}$ 224.5 nm, log ϵ 4.3) and nmr [τ 3.71 (1 H, doublet of doublets), 4.24 (1 H, multiplet), 4.79–5.24 (6 H, multiplet) and 7.88 (4 H, multiplet)] spectra leaves no doubt as to the positions of the three double bonds. It is important to note that the nmr spectrum is also unequivocal as to the chemical shifts of H_a and H_b. H_a appears as an archetypal four-line "A" portion of an



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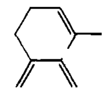
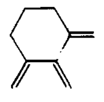


myrcene



α-myrcene

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[1] Support for this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (GP-30797X) is gratefully acknowledged.

[2] J. Bredt, H. Thovet, and J. Schmit, *Justus Liebigs Ann. Chem.*, **437**, 1 (1924).

[3] For a review see G. Köbrich, *Angew. Chem.*, **85**, 494 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973).

[4] J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kramer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966). See also J. O. Reed and W. Lwowski, *ibid.*, **36**, 2864 (1971), for work on the related nitrene.

[5] W. Kirmse has observed the formation of a dimer on photolysis of 7,7-dimethylbicyclo[2.2.1]hept-1-yl diazomethane in solution. We thank Professor Kirmse for communication of this result.

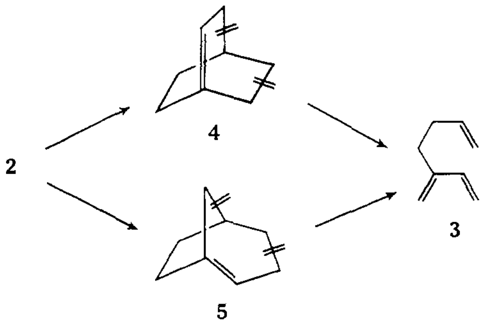
[6] Sadtler infrared spectrum No. 11833.

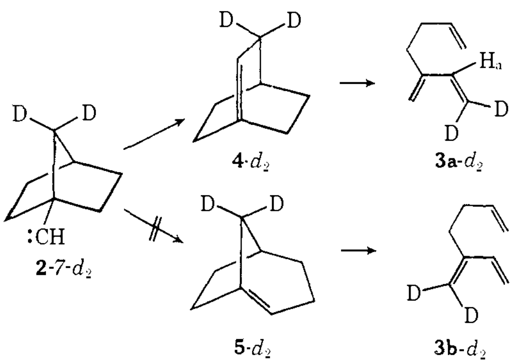
[7] H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).

[8] B. M. Mitzner, E. T. Theimer, L. Steinbach, and J. Wolt, *J. Org. Chem.*, **30**, 646 (1965). See also L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, **87**, 4506 (1965), for the uv and nmr spectra of 3-methylenehexa-1,5-diene.

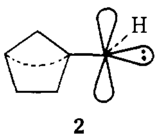
ABC spectrum[9] at τ 3.71 (myrcene shows a similar pattern at τ 3.70).[8] H_b is a multiplet at higher field and is clearly coupled to the methylene protons. Myrcene has no analogous resonance in its spectrum[8] as here H_b is no longer part of a vinyl group and appears at higher field.

In principle, carbene **2** could undergo ring expansion in two ways to give **4** and/or **5**. Either or both of these could give the observed triene **3** through a retro Diels–Alder reaction. Both **4**[10] and **5**[11] have been trapped previously, but neither has been isolated. We have resolved the structural problem by noting that pyrolysis of **1**-7-d_2 (1.5 deuterium/molecule at the 7 position[12]) gave a triene whose 100-MHz nmr spectrum differed from that of **3** in two important ways. First the signal for the terminal methylene protons at τ 4.79–5.21 was reduced by 1.5 protons. Second, and most importantly, the 4-line signal for H_a was collapsed to a broad singlet. Only **3a**-d_2, the product of decomposition of **4**-d_2, can explain this spectrum and thus ring expansion must have taken place through the short bridge.[13]





Such an event is not unexpected, even though **4** contains a trans double bond in a six-membered ring and **5** a trans double bond in a seven-membered ring. One would expect ring expansion to begin by interaction of the empty p orbital with a pair of electrons in an adjacent bond, and thus carbonium ion **6** appears to be a good model for the carbene **2**. Ions such as **6** are known to undergo ring expansion to bridgehead species, and expansion through the short bridge is the normal route.[14]



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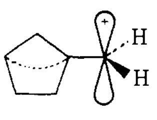

6

We are hopeful of extending this method to even smaller systems[15] and think that prospects for eventual isolation of **4** and similar bridgehead olefins are bright.

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[9] For analyses of ABC spectra and diene systems see: R. T. Hobgood, Jr. and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964), A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3445 (1965), and C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

[10] H. H. Grootveld, C. Blomberg, and F. Bickelhaupt, *J. Chem. Soc., Chem. Commun.*, 542 (1973). We thank Professor Bickelhaupt for communication of results prior to publication and for stimulating conversations.

[11] J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, **94**, 8627 (1972).

[12] Checked by examination of Eu(dpm)$_3$ shifted spectra in the related alcohol.

[13] We cannot exclude small amounts of ring expansion through the long bridge. An upper limit of *ca.* 15% could have gone undetected.

[14] R. C. Fort, Jr., "Carbonium Ions," Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1973, p 1783.

[15] This method has been applied to a synthesis of 3-homoadamantene, M. Fărcaşiu, D. Fărcaşiu, R. T. Conlin, M. Jones, Jr., and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8207 (1973).

[16] Petroleum Research Fund Postdoctoral Fellow, 1972–1973.

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Received August 30, 1973

A Photochemical 1,3-Sigmatropic Vinyl Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1]

Sir:

In our earlier studies[2] we have reported the occurrence of the di-π-methane rearrangement of acyclic 1,4-dienes *via* the singlet excited state and have noted that it is one of the more ubiquitous photochemical processes. For a majority of these molecules the triplet is too rapidly deactivated to give observable photochemistry.

One di-π-methane reactant whose singlet photochemistry we have previously described is 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene (**1**).[2b] We now (1) report a relatively efficient rearrangement of the triplet of triphenylpentadiene **1**,[2d] (2) note that this rearrangement formally involves a 1,3-vinyl migration, (3) provide evidence favoring one of the two potential routes, (4) comment on the failure of a potential free rotor to inhibit triplet reactivity, and (5) describe an unusual selectivity controlling the steady state between reactant and product.

Preparative irradiation of 500 mg of triphenylpentadiene **1** in *tert*-butyl alcohol, using a 450-W medium pressure lamp with Pyrex filter and acetophenone sensitizer,[3] afforded 242 mg of 1,1,4-triphenyl-5-methyl-1,4-hexadiene (**2**) along with 139 mg of recovered reactant **1**.

The structure of triphenylhexadiene **2** was suggested by its spectrum which contained a vinyl triplet at τ 4.03 (J = 7.0 Hz, 1 H), a methylene doublet at 6.82 (J = 7.0 Hz, 2 H), and two methyl singlets at 8.31 and 8.48. This assignment was confirmed by synthesis from methyl 4-phenyl-5-methyl-4-hexenoate (**3**) using phenylmagnesium bromide followed by thionyl chloride–pyridine elimination of the resulting carbinol.

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[1] (a) This is paper LXXXII of the series. (b) For the previous publication note H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, **95**, 4606 (1973).

[2] (a) See H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969) as a leading reference; (b) H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971); (c) note S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 73, 531 (1973); (d) the previous report[2b] of the lack of triplet reactivity of pentadiene **1** was in error.

[3] Complete experimental detail will be given in our full paper; all compounds analyzed satisfactorily.