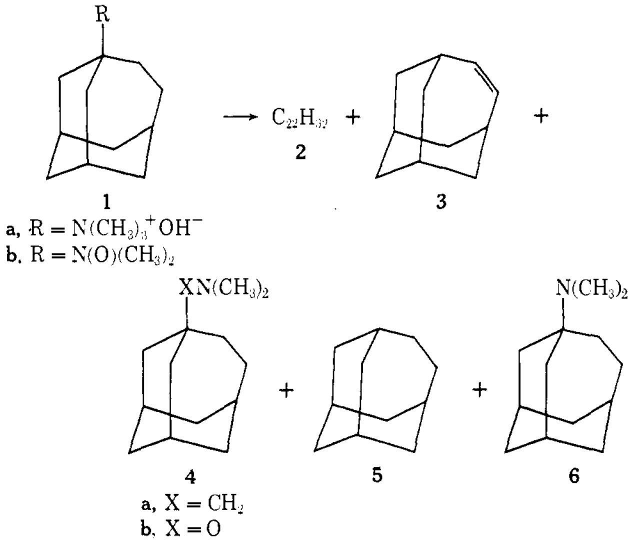
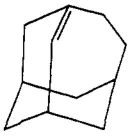
synthetically to yield unrearranged olefins, we decided to investigate this approach with the homoadamantyl system in connection with the question of the limits of Bredt's rule. This report presents evidence for formation of bridgehead homoadamantene, and subsequent dimerization, from pyrolysis of **1a**[3] and **1b**.[3]

Decomposition of **1a** at 140–175° (1 mm) provided a mixture of bridgehead homoadamantene dimers (10%) (**2**), 4-homoadamantene[4] (0.3%) (**3**), *N*,*N*-dimethyl-3-aminomethylhomoadamantane[5] (43%) (**4a**), homoadamantane[4] (5%) (**5**), and *N*,*N*-dimethyl-3-aminohomoadamantane[3] (11%) (**6**).



Under the same conditions, **1b** yielded an identical mixture of dimers (9%) (**2**), 4-homoadamantene (5%) (**3**), *N*,*N*-dimethyl-*O*-(3-homoadamantyl)hydroxylamine[5] (25%) (**4b**), homoadamantane (29%) (**5**), *N*,*N*-dimethyl-3-aminohomoadamantane (12%) (**6**), and unidentified material (about 2% of the product).

The dimer mixture (**2**) (mol wt, vapor pressure method: calcd for $C_{22}H_{32}$, 296.5; found, 298) was isolated as a white solid which had sublimed at the higher temperatures to cooler portions of the pyrolysis flask. Product **2**, from both pyrolyses, was found by glpc to consist of four components, a (29%), b (8%), c (3%), and d (60%). Preparative glpc provided material from the two major peaks (a and d), which gave satisfactory elemental analyses. The presence of a cyclobutane structure is supported by laser Raman spectral data for the solid dimers a and d (cyclobutane deformations at 970–980, 935–940, and 731–735 cm^{-1}, and cyclobutane ring puckering at 221–256 cm^{-1}). The Raman spectra compare favorably to that of adamantene dimer. The two investigated dimers displayed essentially identical Raman spectra and glpc retention times in comparison with the corresponding ones from 1-adamantylcarbene.[6] Both the 2- (**7**) and 3- (**8**) isomers are theoretically possible from these eliminations. Since the carbene route would be expected to provide only **8**, the similarity of the dimer mixtures suggests that reaction in our case occurs preferentially *via* **8** or else that **7** is favorably disposed toward rearrangement to **8**.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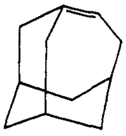
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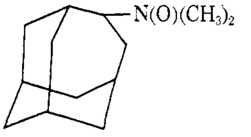

9

4-Homoadamantene (**3**) might be produced in Hofmann elimination by base-catalyzed isomerization or hydride shift,[7] and in the Cope pyrolysis by reverse[8] cycloelimination of **8** to **9** which can act as precursor. Note the tenfold increase in yield of **3** from **1b** *vs.* **1a**.

Compounds **4a** and **4b** are formed by Stevens[1,9] and Meisenheimer[1,10] rearrangements, respectively. Two similar mechanistic possibilities[9,10] have been advanced for the nature of the migrating group in the two cases, namely carbanion and radical. The radical[10] route appears to be favored in the Meisenheimer rearrangement. These represent unusual rearrangements since we have found no prior examples involving migration of a secondary or tertiary group. Compound **4a** was synthesized *via* an alternate route from 3-homoadamantanecarboxamide[3] by $LiAlH_4$ reduction followed by methylation with formaldehyde–formic acid.

Formation of **5** is analogous to the generation of neopentane as a by-product in the Stevens rearrangement of *N*,*N*,*N*-trimethylneopentylammonium iodide.[11] Apparently, the reactive intermediates can separate to some extent with subsequent abstraction of a proton[11] or a hydrogen atom.

Compound **6** is probably formed from **1a** *via* S_N2 attack by hydroxide ion. Recent evidence[8] indicates that *N*,*N*-dimethylhydroxylamine, formed from elimination, can reduce the amine oxide to the corresponding tertiary amine. This is a plausible rationalization for the formation of **6** from **1b**.

Another approach to bridgehead homoadamantene *via* ester pyrolysis is presented elsewhere.[12]

Acknowledgment. We thank the National Science Foundation for support of this work, Dr. K. L. Watters for assistance with laser Raman spectra, Dr. G. B. Gill and Dr. Z. Majerski for samples of 4-homoadamantene, and G. Karas for molecular weight determinations.

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(5) Satisfactory elemental analysis and spectra were obtained for this compound.

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(9) S. H. Pine, *Org. React.*, **18**, 403 (1970).

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(11) S. H. Pine, B. A. Catto, and F. G. Yamagishi, *J. Org. Chem.*, **35**, 3663 (1970).

(12) B. L. Adams and P. Kovacic, *J. Chem. Soc., Chem. Commun.*, 1310 (1972).

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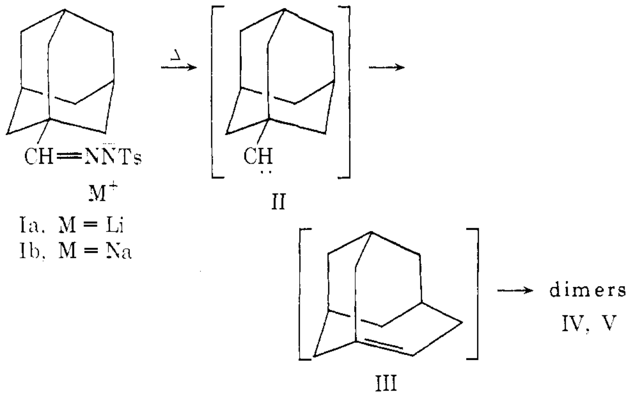
Received July 6, 1973

Fate of 1-Adamantylcarbene. Evidence for the Formation of the Bridgehead Olefin, 3-Homoadamantene

Sir:

We wish to describe a new method involving carbene ring expansion for the generation of "anti-Bredt" olefins[1] in bridged systems. Specifically, the thermal decomposition of the tosylhydrazone salts Ia and Ib, expected to proceed *via* carbene II,[2] gave among the products $C_{22}H_{32}$ isomers which we believe to be dimers of 3-homoadamantene (III).



Ia, M = Li
Ib, M = Na
II
III

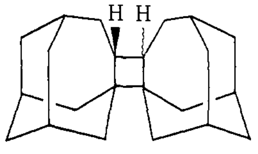
Methyl 1-adamantanecarboxylate was treated with sodium bis(2-methoxyethoxy)aluminum hydride[3] for 9 hr at −67 to −70° in tetrahydrofuran and the crude 1-adamantanecarboxaldehyde was converted into the corresponding tosylhydrazone[4] (70% yield, based on the ester) following a general procedure.[5] The lithium (Ia) and sodium salts (Ib) of the tosylhydrazone were prepared with butyllithium and sodium hydride, respectively, in tetrahydrofuran at −30 to −50° for 1 hr followed by slow warming to room temperature.[6] After evaporation of solvent under vacuum, the salt (Ia or Ib) was ground and dried (75–85° at 0.1 mm).[8] Pyrolysis of either Ia or Ib was conducted in a Pyrex tube at 240–260° (2 mm) under nitrogen, and the products were collected at −195°.[9,10] Chromatography on basic alumina gave a hydrocarbon mixture (*ca.* 30% yield) eluting with pentane, as well as variable amounts (up to 44%) of the azine (VI).[4]

The hydrocarbon mixture was shown (glc and glc–mass spectrum) to consist of 5% adamantane, 10% 1-methyladamantane, 12% homoadamantane (also isolated by preparative glc[4b]), and 73%[12] of five "dimeric" $C_{22}H_{32}$ hydrocarbons (mol wt = 296.250283 by mass spectrometry; calcd 296.250389). No peak with mol wt = 148 corresponding to III or to 3,5-dehydrohomoadamantane (product of carbene insertion into a neighboring C–H bond) was found by glc–mass spectroscopy.

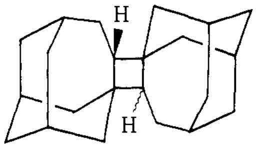
The 60-MHz ^{1}H nmr spectrum of the dimer mixture consists of three rather broad peaks centered at $\delta \sim 1.5$, ~ 1.8, and ~ 2.0 ppm. Olefinic and high field cyclopropane resonances were not observed.

The five $C_{22}H_{32}$ isomers (A:B:C:D:E relative yields 5:7:14:16:58, respectively) were well separated by glc (relative retention times: 0.40:0.50:0.60:0.75:1.00, respectively, on a 1.5 m × 3 mm 5% carbowax 20 M column at 208°). The glc mass spectra of all isomers showed base peaks at m/e 296 ($M\cdot^{+}$) and strong peaks at m/e 239 and 135 with different intensity ratios for different isomers.

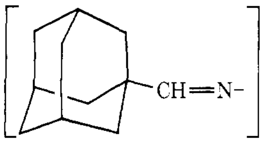
Possible structures for these dimers include IVa and b and Va and b (dimers of III), VII (dimer of II), and VIII (adduct of II and III). The lack of nmr features expected for VII rules out this structure for the major components (C, D, and E) of the dimer mixture, and renders VIII less likely. Additional evidence[13] rules out this structure as well.



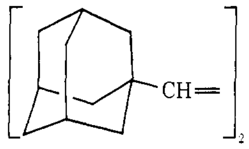
IVa, cis
b, trans



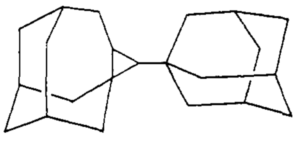
Va, cis
b, trans



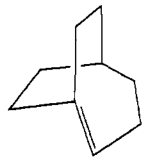
VI



VII



VIII



IX

We were able to isolate small amounts of compounds C, D, and E by preparative glc. Their laser Raman spectra of CCl_4 solution exhibited characteristic cyclobutane deformation bands in the 900–1000-cm^{-1} region:[13] 959 and 975 cm^{-1} (C); 930, 956, and 970 cm^{-1} (D); 933, 950, 964, and 976 cm^{-1} (E). Due to their low concentration in the reaction mixture, the other two $C_{22}H_{32}$ products were not characterized further.

Other highly strained anti-Bredt olefins in bridged systems are known to dimerize readily.[1] Examples include 1-norbornene[14] and adamantene.[15] In 3-

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(1) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973), and references cited therein.

(2) L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, **81**, 5512 (1959).

(3) J. Vit, *Org. Chem. Bull.*, 42, 1 (1970).

(4) Satisfactory (a) elemental analysis and (b) spectra were obtained for this compound.

(5) T. Jacobson, *Acta Chem. Scand.*, **21**, 2235 (1967).

(6) Treatment of the tosylhydrazone with butyllithium at 20°, instead of below −20°, results in formation (after pyrolysis) of 1-pentyladamantane[4] (48% yield). Under the same conditions, 2-pentyladamantane[4] (*ca.* 35% yield) was obtained from 2-adamantanecarboxaldehyde tosyldrazone and butyllithium followed by pyrolysis.[7] The product proved to be identical with a sample prepared from adamantanone *via* 2-pentyl-2-adamantanol,[4] mp 38.2–40° (treatment with *n*-pentyllithium 98% yield), 2-(*n*-pentylidene)adamantane[4b] (dehydration, 87% yield), and catalytic hydrogenation (PtO_2, 4 atm, 82% yield).

(7) The decomposition of 2-adamantanecarboxyaldehyde tosylhydrazone lithium salt involves mainly a 1,2-hydrogen migration to give 2-methyleneadamantane (48% yield).

(8) J. H. Wieringa and H. Wynberg, personal communication; D. Fărcașiu and P. v. R. Schleyer, *Tetrahedron Lett.*, 3835 (1972).

(9) W. M. Jones, R. C. Joines, J. A. Meyers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *J. Amer. Chem. Soc.*, **95**, 826 (1973).

(10) Decomposition of Ib on a solid support (Chromosorb W) as described[9] gave homoadamantane (50% yield) as the main product. While the formation of homoadamantane can be rationalized by a carbocationic mechanism (with hydride abstraction), it is remarkable that such a "protic medium mechanism"[11] takes place on a support usually considered inert, with both the support and the salt (Ib) carefully dried.[8,9]

(11) A. Nickon and H. H. Werstiuk, *J. Amer. Chem. Soc.*, **94**, 7081 (1972).

(12) The total yield of $C_{22}H_{32}$ isomers was 22% based on the initial quantity of tosylhydrazone.

(13) M. Avram and G. Mateescu, "Infrared Spectroscopy," Wiley-Interscience, New York, N.Y., 1972, p 159.

(14) R. Keese and E. P. Krebs, *Angew. Chem.*, **83**, 254 (1971); *Angew. Chem., Int. Ed. Engl.*, 10, 262 (1971); **11**, 518 (1972).

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]

Acknowledgments. This work was supported by grants from the National Institutes of Health (GM-19134), the National Science Foundation (GP-30797X and GP-29078X), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Hoffmann-La Roche, Nutley, N. J. The glc-mass spectrometry facility was made available by a grant from the National Science Foundation to the Chemistry Department of Princeton University (GP-32826).

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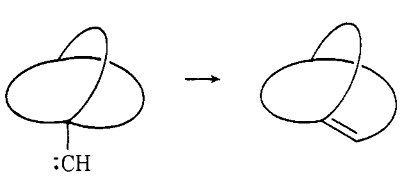
A Carbene Route to Bridgehead Olefins. Bicyclo[2.2.2]oct-1-ene[1]

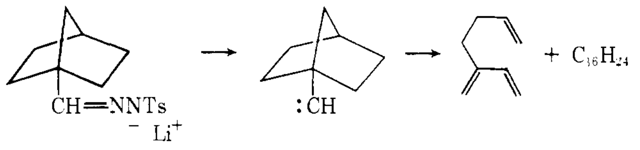
Sir:

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.



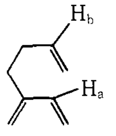
We decomposed tosylhydrazone salt **1** in a flash pyrolysis apparatus at 330° thus generating carbene **2** in the gas phase. We isolated 3-methylenehepta-1,6-diene (**3**, 31% yield) as well as compounds of the formula



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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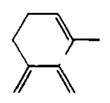
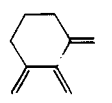


myrcene



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.