in the five-membered chelate rings (see Figure 2B) causes the observed reversal in stability.

Acknowledgment. Thanks are due to Professor K. Vrieze for his stimulating interest.

Registry No. 1a, 56174-66-4; **1b**, 82621-99-6; **2**, 82622-01-3; Ar_2-Li_2·4THF, 82622-00-2; Li, 7439-93-2.

Supplementary Material Available: Listings of positional and thermal parameters for $Li_4[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]_4$ and of bond distances and bond angles (14 pages). Ordering information is given on any current masthead page.

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4-(1-Adamantyl)homoadamant-3-ene: An Extraordinarily Stable Bridgehead Olefin[†,1]

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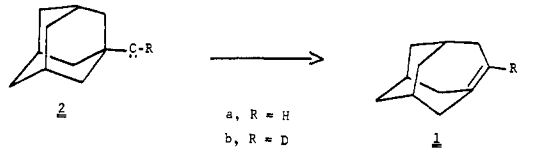
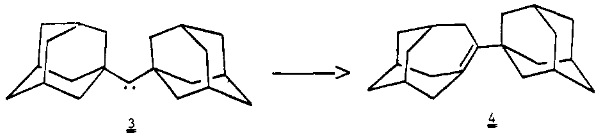
An extensive, recent analysis of experimentally known and calculated bridgehead ("anti-Bredt") olefins[2] confirmed Wiseman's prediction:[3] when a *trans*-cycloheptene unit is present, such alkenes are too reactive to be isolable at room temperature. Homoadamant-3-ene (tricyclo[4.3.1.1^{3,8}]undec-3-ene) (**1**) affords an example. Prepared via carbene **2**, **1** could be characterized by infrared spectroscopy on a NaCl plate at low temperature. Warming to −20 °C resulted in dimerization.[4]

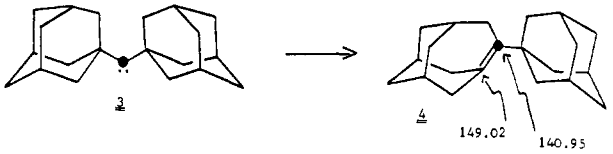


As we have pointed out, replacement of the vinyl hydrogen in trisubstituted bridgehead olefins by a bulky ("R") group should inhibit dimerization or other side reactions and enhance thermal stability, perhaps markedly.[2] This prediction has now been verified. In introducing such an "R" group we would also create the possibility of reactions of the divalent carbon of **2** with the new "R" group. There is, however, a special "R", adamantyl, that avoids all problems. Ring expansion of diadamantylcarbene, **3**, using any one of the six equivalent C–C bonds adjacent to the divalent carbon gives the same product, 4-(1-adamantyl)homoadamant-3-ene (**4**), in which the double bond is guarded by the second adamantane.[5]

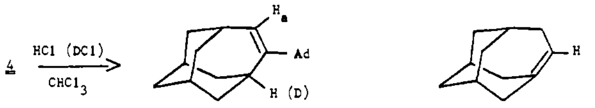


$$\text{1-Ad}^{13}\text{CN} \xrightarrow{\text{Na}} (\text{1-Ad})_2{}^{13}\text{C}{=}\text{NH} \xrightarrow[\text{H}_3\text{O}^+]{\text{N}_2\text{H}_4} (\text{1-Ad})_2{}^{13}\text{C}{=}\text{NNH}_2 \xrightarrow{\text{BaMnO}_4} \underset{\mathbf{5}}{(\text{1-Ad})_2{}^{13}\text{C}{=}\text{N}_2}$$

Diadamantyldiazomethane (**5**) was produced from 1-adamantylcyanide by minor modification of Wynberg's method[6] in which MnO_2 oxidation was replaced by one using $BaMnO_4$.[7] Introduction of ^{13}C at the divalent carbon position was routine. Flash-vacuum pyrolysis of **3** from a flask maintained at 420 °C with rapid trapping at −196 °C[4] led to solid material (>85% conversion, >90% purity) whose ^1H NMR spectrum revealed no vinyl hydrogens. Absorptions in the δ 2.2–3.0 range were indicative of the correct number of allylic protons. The ^{13}C NMR showed two very weak signals in the olefinic region at 140.95 and 149.02. The intensity of the former peak, assigned to C_4 in **4**, was appropriately enhanced in the ^{13}C enriched product. These ^{13}C chemical shifts extend Becker's observation that bridgehead alkene signals in *trans*-cyclooctene systems (at ca. 147 ppm) are not shifted to abnormal values.[8] We conclude that our product **4** contains a tetrasubstituted double bond.



In chloroform containing HCl isomerization occurs to give a trisubstituted double-bond isomer, 4-(1-adamantyl)homoadamant-4-ene (**6**). Column chromatography (silica gel/hexane) gave pure **6** (mp 167–170 °C), which was identified by ^1H and ^{13}C NMR spectroscopy including a variety of decoupling experiments. The vinyl hydrogen (H_a in **6**) appears as a doublet of doublets (J = 8.8, 1.8 Hz) and, when DCl is used in place of HCl, collapses to a single doublet (J = 8.8 Hz).



Of prime interest is the position of the C=C double bond stretch in the infrared spectrum. In **1a**, as we reported earlier,[4] a shift from the "expected" value of 1673 cm^{-1} (*cis*-1-methylcycloheptene)[9] to 1610 cm^{-1} occurs. The double bond in **4** is tetrasubstituted and thus harder to observe. Moreover, we have been unable to achieve greater than ca. 90% purity (estimated by NMR) despite substantial effort. Compound **4** does not survive gas or column chromatography, and liquid chromatography has

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[†] Dedicated to Professor Dr. H. Stetter, Aachen, a pioneer in adamantane chemistry, on the occasion of his 65th birthday.

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(9) Lord, R. C.; Walker, R. W. *J. Am. Chem. Soc.* **1954**, *76*, 2518.

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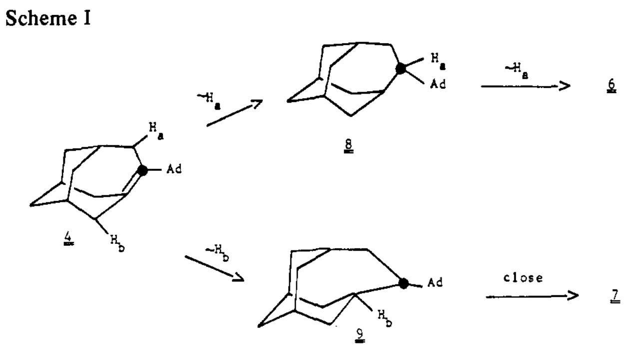
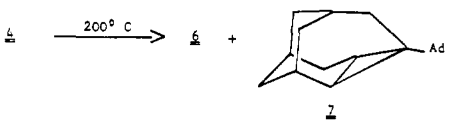
Scheme I



been ineffective in our hands. Although the purity of **4** suffices for NMR and chemical observations, it complicates the determination of the C═C double-bond stretching frequency. A number of weak bands appear in the infrared between 1600 and 1550 cm^{-1}, and there is a weak band in the Raman[10] spectrum at 1577 cm^{-1}. Any assignment must remain tentative for the moment.

Compound **4** is extraordinarily stable thermally. Heating in benzene-d_6 or toluene-d_8 results in no change over 24 h at 185 °C! Only at 200 °C does reaction begin. Two isomeric products are found (80–90% conversion) in approximately equal amounts, **6** and a compound assigned the structure of the cyclopropane **7**.



On the surface, **6** is the result of a 1,3-hydrogen shift. It takes but a cursory examination of the alignment of the orbitals involved to convince one that a direct 1,3-shift is unlikely on steric grounds.[11] Yet isomerization in deuteriotoluene proceeds at qualitatively the same rate as in deuteriobenzene, and both reactions yield undeuterated **6** and **7**. The reaction does not go by hydrogen abstraction from solvent followed by hydrogen loss or by any other intermolecular route. Alternate routes to **6** and **7** involve 1,2-hydrogen shifts from the two possible allylic positions in **4** (H_a and H_b). Migration of H_a gives **6**, as closure of **8** would yield a badly strained cyclopropane (see Scheme I). Migration of H_b gives **9**, which has no easy further 1,2-shift available but is presented with a relatively simple closure to **7**, in a formal reverse of the usual cyclopropane-to-propene thermal rearrangement. This mechanism predicts that the ^{13}C label must appear in the quaternary cyclopropyl carbon of **7**, and an off-resonance ^{13}C NMR experiment confirms this expectation. Cyclopropane **7** is the same compound as is formed by low-temperature photolysis of **5**.[12] Although the initial 1,2-shifts from **4** to **8** and **9** are symmetry forbidden,[13] the reaction is known to be intramolecular, and the economy of a process leading to both **6** and **7** is attractive.[14] Reverse processes, in which cyclopropanes are converted to propenes in closely related systems, have ample precedent.[15]

Thus the replacement of the vinyl hydrogen in **1** by adamantyl confers exceptional kinetic stability on **4** and effectively stifles dimerization. It does not reduce the strain inherent in such *trans*-cycloheptene bridgehead olefin systems, and the thermodynamic instability of **4** opens the way for otherwise unfavorable reactions.[16] The potential of 1-adamantyl or similar groups to stabilize other, inherently even more reactive bridgehead olefin systems is obvious.

Registry No. 4, 82665-12-1; **5**, 54821-20-4; **6**, 82665-13-2; **7**, 82665-14-3.

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[10] We thank Professor T. G. Spiro and G. Woolery for this measurement.

[11] Although the direct 1,3-shift is also symmetry forbidden, the application of the Woodward–Hoffmann rules to reactions in which poor orbital connectivity is obligatory is not obvious.

[12] Gano, J. E., private communication.

[13] Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7469.

[14] Another explanation for **6** involves delivery of hydrogen by the adamantyl group to the 3-position of **4**, followed by rotation and abstraction of H_a. Coleman, B., Shell Research, Amsterdam, private suggestion. This mechanism, though attractive, fails to account for the presence of **7**.

[15] Baldwin, J. E.; Grayston, M. W. *J. Am. Chem. Soc.* **1974**, *96*, 1629–1630.

[16] Two groups[17,18] have provided theoretical results that bear on this point. Compound **4** is calculated (MM2) to have 9.2 kcal/mol *greater* olefin strain[2] than **1a**.[17] The effect of the adamantyl group is to produce a greater dihedral angle (42.3° vs. 26.0°; CFF)[18] between the orbitals making up the "double" bond and thus to decrease the thermodynamic stability. These calculations make the kinetic stability conferred by the adamantyl group even more remarkable.[2]

[17] Kos, A. J., Erlangen, private communication.

[18] Ermer, O., Bochum, private communication.

Carbon-14 and Deuterium Isotope Effects in the Borderline Solvolysis of Isopropyl β-Naphthalenesulfonate

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In spite of the increasing use of carbon isotope effects in the study of organic reaction mechanisms in recent years,[1] there is a considerable shortage of basic knowledge and experimental data. The carbon isotope effect at the reaction center of aliphatic nucleophilic substitution is believed to be large in S_N2 and small in S_N1. However, the experimental data are mostly limited to primary substrates for the former and a tertiary one for the latter;[1,2] no systematic study with a simple secondary substrate has been reported.[3] In addition, secondary carbon isotope effects are assumed without sufficient investigation to be very small.[4-6] We herein report carbon-14 and deuterium isotope effects at the α and β positions of isopropyl β-naphthalenesulfonate (**1**) in the solvolysis in ethanol–2,2,2-trifluoroethanol (EtOH–TFE). In this solvent system the mechanism of the solvolysis of simple secondary substrate is considered to vary from S_N2-like to S_N1-like.[7,8] Thus, this is the first systematic study of the kinetic isotope effects of all the atoms constructing the isopropyl moiety in a single substrate solvolyzing within a broad spectrum of the borderline mechanism.

Solvolysis of **1** in EtOH, 20% EtOH–80% TFE (20E–80T, v/v), and TFE at 65 °C was followed spectrophotometrically. Carbon-14 kinetic isotope effects were determined according to the procedures described before.[9] Results are summarized in Table I.[10]

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