reactions. Extraneous signals in the η^5-$(CH_3)_5C_5$ region indicate that competing thermolysis of **2**,[17a] which likely involves ring methyl metalation,[4b,13c,17b] is also operative. Interestingly, the reaction of **2** with CD_4 is significantly slower than with CH_4 and a preliminary analysis yields a kinetic isotope effect of 6 ± 2.[18] This result argues that H_3C–H bond breaking is the rate-limiting step in methane activation. That hydrolysis of the CD_4 reaction product produces pentamethylcyclopentadiene with <3% $H(CH_3)_4(CH_2D)C_5$ by GC/MS indicates that CD_4 attack on a ring-metalated species is not a major reaction pathway. That the neopentane produced upon hydrolysis contains ca. 3 ± 1% neopentane-d_2[19] suggests that eq 4 may be reversible.

These results demonstrate that it is possible to design isolable organoactinides of sufficiently high energy content that the stoichiometric (as opposed to catalytic) activation (with some selectivity) of saturated hydrocarbon molecules becomes thermodynamically favorable. Moreover and perhaps most fascinating, such activations are kinetically rather facile.

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(17) (a) Verified by independent thermolysis of **2** in C_6D_{12}. (b) For example, thermolysis of **2** in C_6D_{12} followed by D_2O quenching results in appreciable quantities of $D(CH_3)_4(CH_2D)C_5$.[13c]

(18) A highly accurate measurement is precluded by the considerably greater participation of the side reactions under these conditions.

(19) In addition to the expected neopentane-d_1, substantial quantities of neopentane-d_0 are also detected. Such a result is expected from the competing thermolysis of **2**, which produces a ring-metalated neopentyl compound.[13c,17]

Synthesis of a Stable Cyclopropene Fused by a Six-Membered Ring. A Novel Approach from Fused Thiirene Sulfoxide

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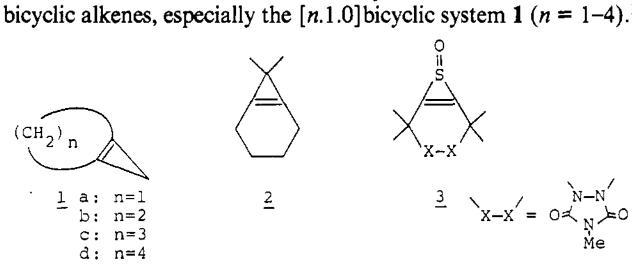
Considerable attention has recently been focused on strained bicyclic alkenes, especially the [*n*.1.0]bicyclic system **1** (*n* = 1–4).[1]



Although olefins should have a planar structure unless geometrical constraints[2a,b] are present or the appropriate symmetry[2c] is lacking, Wagnar[3a] and Pople[3b] have shown by ab initio calculations that

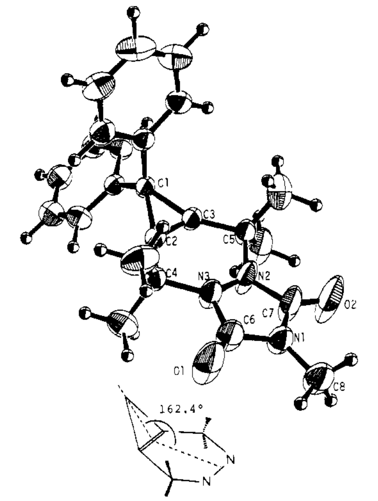
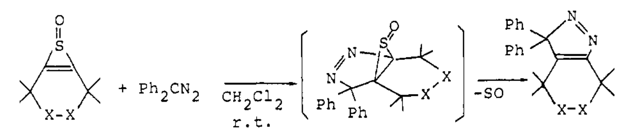


Figure 1. ORTEP drawing of the molecular structure of bicyclo[4.1.0]hex-1(6)-ene **8**. Bond lengths (Å): C_1–C_2 1.521, C_1–C_3 1.526, C_2–C_3 1.286, C_2–C_4 1.491, C_3–C_5 1.478. Bond angles (°): C_2–C_1–C_3 49.92, C_1–C_2–C_3 64.82, C_1–C_3–C_2 65.26, C_2–C_3–C_5 130.23, C_3–C_2–C_4 129.16.

all bicyclic alkenes **1** should have nonplanar structures. Considerably efforts have been directed toward the preparation of bicyclic alkenes.[1,4] Evidence for intermediacy of bicyclo-[4.1.0]alkene[5] **1d**[6,7] as well as **1a**,[8] **1b**,[9] and **1c**,[7] produced by dehydrohalogenation and dehalogenation of the corresponding halides, was presented as trapped Diels–Alder adducts by Gassman[6] and Wiberg.[7] The dimethyl derivative **2** was spectroscopically identified below −35 °C by Closs and Boll.[10] However, experimental structural studies have never been reported for **1** owing to their instability.

We wish to report an attractive route to a thermally stable bicyclo[4.1.0]hept-1(6)-ene derivative via [2 + 3] cycloaddition of fused thiirene sulfoxide **3** with diphenyldiazomethane and its X-ray crystal analysis.

Fused thiirene sulfoxide **3**, recently prepared in our laboratory, was shown to be quite reactive.[11] It was treated with a 5-fold amount of diphenyldiazomethane in CH_2Cl_2 at room temperature. After standing for several hours, 3*H*-pyrazole **5** (54%)[12,13] was obtained by chromatographic purification.



3 4 5

Photolysis (≥365 nm)[14] of **5** in benzene at room temperature

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(12) Spectral and elemental analysis data of **5**: mp 142.0–143.0 °C from hexane–benzene; ^{1}H NMR δ ($CDCl_3$) 1.34 (s, 6 H), 2.08 (s, 6 H), 3.10 (s, 3 H), 7.64–7.35 (m, 10 H); ^{13}C NMR δ ($CDCl_3$) 157.4, 153.7, 153.4, 150.2, 133.3, 129.0, 128.3, 107.2, 62.4, 59.1, 25.1, 25.0, 23.6; UV (nm, hexane) λ_{max} 356 (ε 203) (N=N); MS, *m/e* 415 (M^+). Anal. Calcd for $C_{25}H_{25}N_5O_2$: C, 69.40; H, 6.02; N, 16.87. Found: C, 69.22; H, 6.15; N, 16.79.

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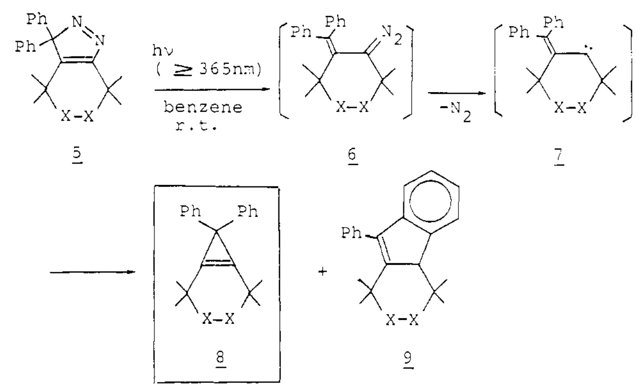
resulted in the quantitative release of nitrogen and gave a 63% yield of the fused cyclopropene **8**[15] in addition to a 37% yield of the indene **9**.[16,17]



The desired product **8** was separated by recrystallization from hexane–benzene at room temperature. Surprisingly, the fused cyclopropene **8** is a stable colorless crystalline compound (mp 143.5–144.0 °C). Weak absorption, presumably due to C–C double bond of the cyclopropene ring, appeared at 1805 cm^{-1} (shoulder).[15] The structure of **8** was determined by X-ray crystal structure analysis (Figure 1).[18]

Inspection of the X-ray crystal analysis data revealed the nonplanar structure of **8**, and the angle between the two rings was 162.4°, which is 7.4° larger than that estimated for **1c**.[3a,19] The bond angles of C_3–C_2–C_4 and C_2–C_3–C_5 (129.2° and 130.2°, respectively) are ca. 20° smaller than those in nonfused cyclopropene (149.9°),[20] as expected. The ^1H NMR spectrum[11] of **5** shows resonances at 1.75 (s, $CH_3 \times 4$), 3.03 (s, NCH_3), and 7.24 ppm (s, Ph) characteristic of its C_2 symmetry. The ^{13}C NMR spectrum indicates that the olefinic carbon resonance appears at 155.5 ppm.[15] Surprisingly, this value is ca. 30 ppm lower than those found for tetramethyl- (118.9 ppm) and 3,3-dimethylcyclopropenes (125.0 ppm) etc.[21] This large downfield shift should be due to the highly strained framework of **8** by ring fusion, as found in the case of the thiirene sulfoxide **3**.[11a]

The stability of **8** is clearly dependent on the α-subtitution of tetramethyl groups, which might fix the bicyclic ring system. Above all, the nonplanar structure of bicyclo[4.1.0]alkene suggested by the calculations is confirmed by the present result.

Supplementary Material Available: Listings of atomic positional and thermal parameters, bond lengths, and bond angles for compound **8** (18 pages). Ordering information is given on any current masthead page.

(13) Compound **3** reacted with ethyl diazoacetate to afford 2*H*-pyrazole, via an additional 1,3-H shift, as reported in the reaction of diphenyl thiirene sulfoxide with phenyldiazomethane: Carpino, L. A.; Chen, H.-W. *J. Am. Chem. Soc.* **1979**, *101*, 390.

(14) A methanol solution of phenanthrene (5 g/L) was used as a filtered solution (path length 1 cm).

(15) **8**: colorless crystals, mp 143.5–144.0 °C from hexane–benzene; ^1H NMR δ ($CDCl_3$) 7.24 (brs, 10 H), 3.03 (s, 3 H), 1.75 (s, 12 H); ^{13}C NMR δ ($CDCl_3$) 153.0, 144.2, 135.4, 128.2, 128.0 126.6, 63.3, 58.4, 24.6, 24.3; IR (cm^{-1}, KBr) 1805 ($\nu_{C=C}$); MS, *m/e* 387 (M^+). Anal. Calcd for $C_{25}H_{25}N_3O_2$: C, 74.39; H, 6.50; N, 10.84. Found: C, 74.31; H, 6.44; N, 10.92.

(16) **9**: oil, ^1H NMR δ ($CDCl_3$) 7.28–7.66 (s, 9 H), 3.98 (s, 1 H), 3.06 (s, 3 H), 1.99 (s, 3 H), 1.93 (s, 3 H), 1.28 (s, 3 H), 1.09 (s, 3 H); ^{13}C NMR δ ($CDCl_3$) 155.3, 152.7, 148.4, 145.9, 139.9, 138.7, 134.9, 129.7, 128.6, 127.8, 127.7, 125.3, 123.5, 120.8, 77.3, 65.3, 62.7, 56.2, 28.1, 24.9, 21.2, 21.0; MS, *m/e* 387 (M^+).

(17) The formation of **8** and **9** is explained by the common intermediate, vinyl carbene **7**, derived from the diazo compound **6**. During the photoirradiation the reaction solution initially became light red, which corresponded to **6**, and then N_2 gas was evolved. Indene **9** may be produced from **8** via the known photoequilibrium between **7** and **8**: Halton, B.; Kulig, M.; Battiste, M. A.; Perreten, J.; Gibson, D. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 2327.

(18) The crystal has monoclinic space group $p2_1/c$ with a = 10.381 (2) Å, b = 8.719 (1) Å, c = 23.717 (5) Å, and β = 98.30 (2)° with Z = 4. Intensity data were collected on a four circle diffractometer with graphite monochromated Cu Kα radiation (3° < θ < 120°). 3712 unique reflections measured of which 2670 had intensities greater than $3\sigma |F_0|$ and were used for structure analysis. The structure was refined to a value of 0.086. For the detailed crystallographic data, supplementary material is available.

(19) Unfortunately, the angle for **1d** is not calculated,[3a] but is considered to be slightly larger than 155° given for **1c**.[3a]

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Fourier Transform Infrared Photoacoustic Spectroscopy: A Novel Conformational Probe. Demonstration of α-Helical Conformation of Poly(γ-benzyl glutamate)

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Fourier transform infrared photoacoustic spectroscopy (FT-IR PAS) has emerged as a novel technique for studying a wide range of problems in chemistry and biology.[1] The determination of secondary structures of biopolymers from observed vibrational frequencies is one of the long-range goals of molecular spectroscopy.[2] Biopolymers, in general, have been difficult to be investigated by conventional infrared spectroscopy due to difficulties in uniformly dispersing them into an alkali halide matrix. Incorporation into alkali halide matrix may result in structural alterations during the pelleting process[3] and hydration of the sample as well. FT-IR PAS offers an alternative method to investigate biopolymers per se in less than milligram quantities by totally eliminating artifactual effects introduced by incorporation into alkali halide matrix. FT-IR PAS represents a major advance in infrared spectroscopy which has not been extensively utilized in chemistry and biology. In this communication, the first report in the literature of an application of FT-IR PAS to the determination of molecular conformations, we are presenting the results of the application of this novel conformational probe to poly(γ-benzyl glutamate). Poly(γ-benzyl glutamate) has been shown to prefer α-helical structure in its higher molecular weight fractions by X-ray diffraction,[4] conventional IR,[5] and Raman[6] spectroscopic methods. Abe and Krimm[7] and Nevskaya and

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