

Communications to the Editor

syn-Tricyclo[4.2.1.1^{2,5}]decane. Comparison with *anti*-Tricyclo[4.2.1.1^{2,5}]decane

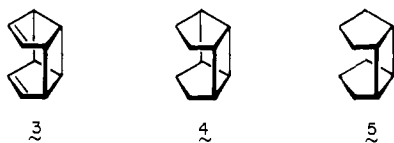
Sir:

From among the many tricyclic C₁₀H₁₆ isomers which are possible, two have special topological appeal. The first is *syn*-tricyclo[4.2.1.1^{2,5}]decane (**1**), assessed to be a rather highly

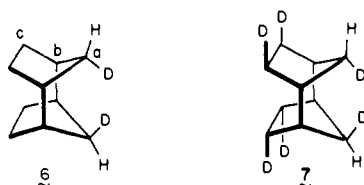


strained isomer of adamantane by molecular mechanics calculations,¹ which arises by 1,3 bonding of two fully eclipsed cyclopentane rings in "head-to-head" fashion. Its interior methylene hydrogens clearly are subject to severe nonbonded interaction. In the corresponding *anti* isomer (**2**) where a "head-to-tail" orientation is adopted, such steric strain is lessened owing to the staggered arrangement of the rings. Therefore, this pair of isomers could provide an estimate of the steric forces which gain importance as one five-membered ring is rotated by $\pi/5$ radians above a second while being maintained within bonding proximity. Also, the Lewis acid catalyzed isomerizations of **1** and **2** are anticipated to hold considerable mechanistic interest.^{2,3} We report here a most direct synthesis of **1** which affords the hydrocarbon free of any side products and describe, in addition, rearrangement reactions of derivatives of **1** which provide convenient access to **2**.

Our approach is based on the relatively recent discovery that strained cyclobutane rings are subject to hydrogenolysis under mild conditions, the observed reactivity order generally paralleling the level of stress at a particular C-C bond.⁴ Thus, catalytic hydrogenation of hypostrophene (**3**)⁵ over 5% Pd/C

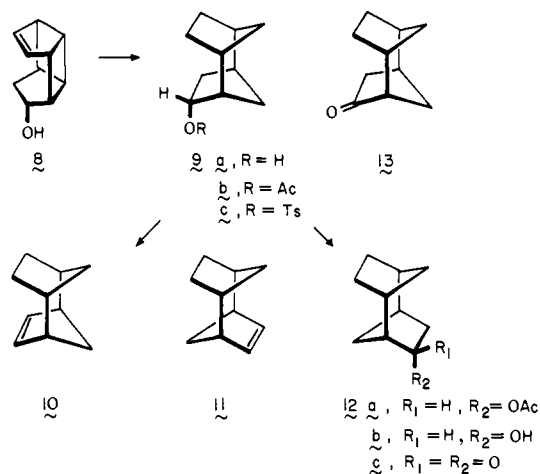


at atmospheric pressure in hexane solution for several hours led quantitatively to **1** (mp 148–150 °C, 75% isolated)⁶ which clearly differed from **4**, available by diimide reduction of **3**,⁷ and **5**, available in low yield from Cu(I)-catalyzed photodimerization of cyclopentene.⁸ The C_{2v} symmetry of **1** is particularly evident in its ¹³C NMR spectrum (CDCl₃) which is comprised of three peaks at 25.79 (t, ¹J_{CH} = 132 Hz), 29.57 (t, 131), and 36.04 ppm (d, 133). That the opposed methylene hydrogens in **1** are highly compressed is apparent from the ¹H NMR spectrum which is characterized by five multiplets at δ 0.45 (2 H), 1.19 (4 H), 1.65–1.74 (4 H), 1.75 (2 H), and 2.27 (4 H). Given the spectrum of **6** (prepared by catalytic deu-



teration of **4**),⁹ which lacks the two proton signal centered at δ 1.75 and has the normal upfield doublet at 0.45 supplanted by a broad singlet, we see that the H_a endo protons are substantially deshielded.¹⁰ Hydrocarbon **7**, available from reduction of **3** with D₂ over Pd/C, shows only three singlets at δ 0.43 (2 H), 1.65 (4 H), and 2.26 (4 H) attributable to H_a exo, H_c endo, and H_b, respectively. Thus, compression effects at positions c are not reflected in equally dramatic chemical shift differences ($\Delta\delta$ = 0.46), as expected. In the infrared, **1** exhibits C-H stretching frequencies at 3025 (sh), 3000 (sh), and 2975 cm⁻¹.¹¹

A hypothetical scheme for effecting rearrangement of **1** to **2** involves Wagner–Meerwein shift of an interconnective bond. This was considered impractical with the hydrocarbon itself because of probable rapid cascade past 2⁺ to thermodynamically more stable carbocations upon exposure to strong Lewis acids,^{2,3} but proved quite feasible under more controlled conditions. For example, catalytic hydrogenation of alcohol **8**^{5c} over 5% Pd/C in hexane furnished **9a** (98%, mp 137–138 °C),



the acetate of which (**9b**) underwent gas-phase pyrolysis (600 °C) to give olefins **10** and **11** (ratio 1.4:1) in addition to a minor unidentified substance. A more favorable product distribution (1:2) and improved yields have been realized through dehydration of **9a** with POCl₃ in pyridine. In yet a different approach, buffered acetolysis of **9c** (mp 73–73.5 °C) afforded **11** and **12a** (3:7). The identity of the latter was established spectroscopically and by conversion (LiAlH₄; CrO₃·2 py) to **12c**, the translocated isomer of **13** available by Collins' oxidation of **9a**.

The conversion of **9b** to **11** may proceed by an ion-pair mechanism of the type proposed by others to account for charge effects observable in such acetate eliminations¹² or by the surface-catalyzed carbonium ion pathway advanced recently by Wertz and Allinger.¹³ Irrespective of the mechanistic question, the driving force behind the entire range of rearrangements examined by us is undoubtedly steric strain relief since they involve passage of a boat cyclohexane conformation to a chain form (also see below).

Efficient access to **2** was gained by reduction of **11**. The ¹H NMR spectrum (90 MHz) of **2** in CDCl₃ is composed of a two-proton upfield multiplet centered at δ 0.89 and companion

Table I. Calculated Heats of Formation and Strain Energies^a

C ₁₀ H ₁₆ isomer	ΔH_f° (gas, 25 °C)		Strain energy (gas, 25 °C)	
	E	A	E	A
1	0.96	-1.48	40.38	38.28
2	-8.76	-12.70	30.66	27.06
Adamantane	-32.50	-33.82	6.87	5.94

^a Kilocalories/mole.¹

multiplets at 1.58 (8 H), 1.78 (2 H), and 1.95 (4 H). The ¹³C NMR spectrum attests to the inherent C_{2h} symmetry of the molecule: 29.28 (t, ¹J_{CH} = 132 Hz), 33.69 (t, 130), and 39.66 ppm (d, 143). The variability in the observed ¹³C-H coupling constants (compare **1**) is noteworthy.

The heats of formation and strain energies of **1** and **2** as calculated using the Engler (E)¹ and Allinger (A)¹⁴ force fields (Table I) conform to our ability at the experimental level to transform derivatives of **1** to **2**, but not the reverse. The 8–11-kcal/mol greater stability of **2** is rather sizable and suggests that pathways for conversion to **1** will be energetically inhibited even when dihedral angles associated with possible migrating bonds are favorably aligned. Finally, we note that the chemical transformations described herein proved capable of arresting molecular rearrangement after a single Wagner–Meerwein shift and prior to entry into the intricate entanglements of “adamantaneland”^{2,15,16}

References and Notes

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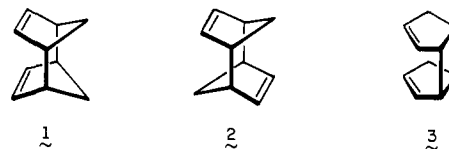
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syn-Tricyclo[4.2.1.1^{2,5}]deca-3,7-diene, the Head-to-Head [4 + 4] Dimer of Cyclopentadiene

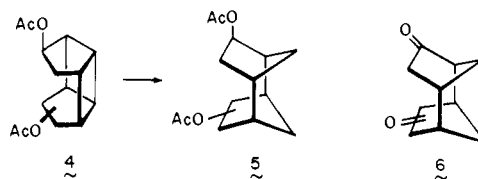
Sir:

Many of the possible dimerization reactions of cyclopentadiene are either forbidden by orbital symmetry or disfavored by entropic factors. The rates of thermal association are therefore such that conversion to *endo*-dicyclopentadiene by [4 + 2] π bonding is overwhelmingly favored. Photochemical activation leads only to intramolecular electronic reorganization.¹ The interesting tricyclic hydrocarbons **1–3** have not



previously been observed,^{2–4} and their successful preparation is clearly dependent upon appropriate improvisation of indirect synthetic methodology. Special interest in these molecules derives not only from the relative proportion of through-space and through-bond electronic interaction which can operate, but also from their anticipated reluctance to undergo fragmentation, the magnitude of which could provide quantitative measure of the “forbiddenness” to [4 + 4] and [2 + 2] cycloreversion. We here describe a convenient directed synthesis of **1**, the most highly strained member of this C₁₀H₁₂ subset, and detail its sigmatropic behavior upon thermal activation.

The key step in each of two approaches we have examined is the unmasking of the pair of double bonds in the final step. The first route consisted in exhaustive hydroboration of hypostrophene⁵ and conversion of the two diols so produced to diacetate **4**.⁶ Catalytic hydrogenation⁷ of **4** led efficiently to



5 which, however, did not undergo thermal extrusion of acetic acid below 550 °C. Although a small amount of olefinic material could be isolated at this temperature and above, it proved not to be **1** and remains uncharacterized. Nor was the action of lithium 2,2,6,6-tetramethylpiperidide on the bistosylhydrazone of **6** successful.⁸

The following scheme avoids all of these difficulties. The readily available bishomocubaneone **7**^{2a,b,9} was treated with lithium aluminum hydride and the resulting mixture of epimeric diols **8** was catalytically reduced over 10% Pd/C in ethyl acetate solution^{7,10} at 40–50 psi (2 days) to give **9a** (mp 232–238.5 °C). Sulfenylation¹¹ of **9a** was followed by reaction of dimethylsilylate **9b** with sodium iodide in anhydrous HMPA at

