

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}

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- All compounds described herein have been characterized spectrally (IR and NMR) and as to composition (mass spectral, elemental analyses).
- ¹³C NMR (CDCl₃): 27.84 (4 C), 40.41 (4 C), and 43.43 ppm (2 C).
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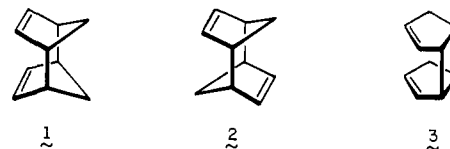
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syn-Tricyclo[4.2.1.1^{2,5}]deca-3,7-diene, the Head-to-Head [4 + 4] Dimer of Cyclopentadiene

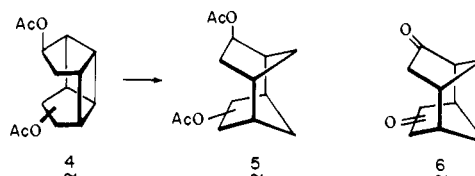
Sir:

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



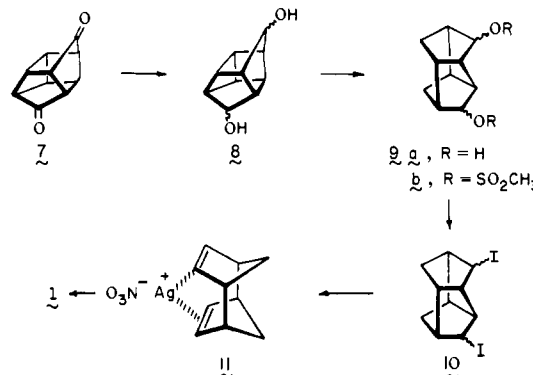
previously been observed,^{2–4} and their successful preparation is clearly dependent upon appropriate improvisation of indirect synthetic methodology. Special interest in these molecules derives not only from the relative proportion of through-space and through-bond electronic interaction which can 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,5b,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 dimesylate **9b** with sodium iodide in anhydrous HMPA at

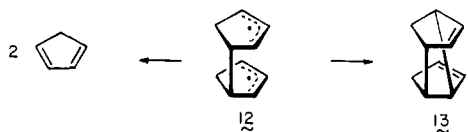


135 °C for 3 days. Although 10–15% unreacted **9b** is routinely recovered, even when the reaction time is extended, the ¹H NMR spectrum of the purified iodides (in CDCl₃) clearly reveals the presence of three epimers on the basis of the distinct methine signals at δ 3.73, 3.83, and 3.95. The isomer of **10** which has the 3.83 peak always predominates (50–70%).

Dehalogenation of **10** (as the epimeric mixture) with excess Na/K alloy (1:1 wt/wt) in ether overnight gave the desired pungent smelling, highly volatile, crystalline diene **1** which, however, could not be purified by preparative VPC. Although **1** can be readily sublimed, this procedure did not adequately remove small amounts of equally volatile byproducts. The preferred method of purification consists in conversion to its stable, colorless, crystalline silver nitrate complex **11** and subsequent liberation by conventional treatment with concentrated ammonium hydroxide solution. The ease with which **1** can be reversibly transformed to **11** contrasts markedly with the stability of its Rh(I) complexes.³ The ¹H NMR spectrum of the title hydrocarbon (C₆D₆, 90 MHz) features an upfield doublet at δ 1.83 (*J* = 9.98 Hz broadened by further small coupling, 2 H), a four-proton singlet at 2.33, a doublet of area 2 centered at 2.71 (*J* = 9.98 Hz), and a downfield singlet at 6.08 (4 H). Again as in its saturated counterpart,⁷ the trans-annular steric strain in **1** is easily detected spectroscopically. Its ¹³C NMR spectrum shows signals at 40.88 (d, ¹*J*_{CH} = 141), 45.59 (t, 133), and 141.71 (d, 165).

The photoelectron spectrum¹² of **1** is characterized by broad bands at low energies having a first IP at 8.65 ± 0.1 eV and the second at 8.90 ± 0.07 eV. The structural features of this diene are therefore conducive to very intimate coupling of its σ and π orbitals as judged, in particular, by the extreme broadness of the bands. Effective through-bond coupling of exceptionally high lying σ levels is precedented,¹³ although examples of preferred through-space overlap also do exist.¹⁴

Warming a solution of **1** in C₆D₆ brings about exceptionally clean Cope rearrangement to **3**. The progress of reaction was monitored by integration of magnetic resonance signals of key protons in both **1** (disappearance) and **3** (appearance) against the singlet absorption peak of internal dioxane standard. The skeletal isomerization conforms nicely to first-order kinetics with rate constants *k*_{58.5°} = 1.64 × 10⁻⁵ s⁻¹, *k*_{68.5°} = 5.68 × 10⁻⁵, and *k*_{79.5°} = 18.41 × 10⁻⁵. The corresponding activation parameters are Δ*H*[‡] = 26.1 kcal/mol and Δ*S*[‡] = -1.98 eu. After numerous half-lives, no spectroscopically detectable quantities of cyclopentadiene, *endo*-dicyclopentadiene, or *exo*-dicyclopentadiene (**13**) were seen. It would appear therefore that the prescribed conditions are not conducive to the generation of biradical **12** which might be expected either to fragment or reclose with formation of **13**.



Structural assignment to **3** as the syn,*cis* [2 + 2] cyclopentadiene dimer follows from its spectral properties: ¹H NMR (C₆D₆) δ 2.25 (m, 4 H), 2.89 (m, 2 H), 3.42 (m, 2 H), 5.44 (m, 2 H), and 5.77–5.83 (br m, 2 H). Double resonance studies revealed that independent saturation of the δ 2.89 and 5.44 signals causes the downfield olefinic peak to become a doublet (*J* = 5.1 Hz) and triplet (*J* = 4.0 Hz), respectively.

Mechanistically instructive is the overwhelming adherence by **1** to the synchronous six-electron rearrangement rather than to a stepwise homolytic pathway with initial generation of a pair of allyl radicals (cf. **12**). The observed reaction course delivers **3** whose strain, although less than that of its precursor (the **1** → **3** conversion is thermally irreversible), remains significant. The exclusion of more thermodynamically favored

products (e.g., **13**) can be regarded as an exploitable benefit of orbital symmetry. In the present instance, the synthetic implications are that **3**, as well as **1**, now becomes directly available for further experimental scrutiny.¹⁵

References and Notes

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- (3) A Rh(I) complex of **1** has been prepared independently by Professor P. E. Eaton, private communication.
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Use of Phenyl Vinyl Sulfoxide as an Acetylene Equivalent in Diels–Alder Cycloadditions

Sir:

As a consequence of the unreactive nature of acetylene in [4 + 2] cycloadditions¹ and the safety hazards associated with its handling at elevated temperatures and pressures, there has been sustained interest in the development of a reliable acetylene Diels–Alder synthon. A number of specialized and limited procedures have been developed, but all are multistep processes requiring the isolation of intermediates followed by functional group manipulation, and suffer from modest overall yields and/or undesirable side reactions. Some of the more frequently reported methods include (a) dehydrobromination of vinyl bromide adducts;² (b) zinc-induced dechlorination of *cis*-dichloroethylene-derived substrates;³ (c) thermal extrusion of cyclopentadiene from norbornadiene adducts;⁴ (d) cycloaddition of 2-thiono-1,3-dioxol-4-ene with reactive dienes^{5,6} followed by treatment with trimethyl phosphite,⁷ [Ni(COD)₂],⁸ or Fe(CO)₅;⁶ (e) comparable use of 2-phenyl-1,3-dioxol-4-ene;^{5,9} (f) diene addition to dimethyl acetylenedicarboxylate, hydrolysis, and decarboxylation, either by direct methods^{3c} or involving prior chromous ion reduction;¹⁰ and (g) formation of maleic anhydride adducts, hydrolysis, and oxidative decarboxylation by one of several techniques.¹¹ We now report the development of a high-yield, single-step alternative which exploits the dienophilicity of phenyl vinyl sulfoxide (**1**)