Synthesis and Reactivity of *trans*-Tricyclo[4.2.0.0^{1,3}]oct-4-ene

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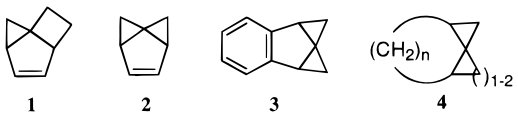
Received February 15, 2000

The first synthesis of *trans*-tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**), an ethenyl bridged spirohexane, was accomplished in four steps starting from Carpino et al. *gem*-dichloro ketone **6**. An X-ray crystal structure of **1** with one substituent was obtained to provide geometry data on this novel ring system and to confirm the stereochemical assignment of the penultimate synthetic intermediate. Tricyclo-[4.2.0.0^{1,3}]oct-4-ene is surprisingly stable. It reacts with glacial acetic acid but only slowly at 145 °C; the products were isolated and identified. A unimolecular rearrangement takes place at elevated temperatures (165 °C and higher), presumably, via a biradical intermediate to afford tricyclo-[4.2.0.0^{1,5}]oct-3-ene (**23**). The structure of this 1,5-bridged bicyclo[2.1.0]pentane derivative was established by NMR and an X-ray crystal structure of its Diels−Alder adduct with isobenzofuran. Tricyclo[4.2.0.0^{1,3}]oct-4-ene equilibrates with **23**, so equilibrium constants and reaction rates were measured over a 20 °C temperature range from 180 °C to 200 °C. The difference in the heats of formation ($\Delta\Delta H°_f$ (**23** − **1**)) is −2.1 kcal/mol, which is in good agreement with ab initio (HF and MP2) calculations using the 6-31G(d) basis set (−1.9 (HF) and −1.4 (MP2) kcal/mol). Computations on *trans*-tricyclo[4.2.0.0^{1,3}]octane and spirohexane also were carried out, and the structures and energies were compared.

Introduction

Structures and properties of small-ring bridged spiro hydrocarbons such as spiropentane and spirohexane have been a topic of interest for many years.[1] These compounds are challenging synthetic targets since they possess a high degree of both torsional and angular strain which often results in unusual rearrangements and new synthetic transformations.[2] *trans*-Tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**)[3] represents a novel structure that contains fused three-, four-, and five-membered rings and a carbon−carbon double bond. Even though a variety of saturated bridged spiropentanes and spirohexanes containing 0−3 methylene groups has been reported (**4**),[1] there is only one known compound, 4,5-benzotricyclo[4.1.0.0^{1,3}]hept-4-ene (**3**), with a two-carbon unsaturated bridge.[2c]



1 **2** **3** **4**

It is thought that introduction of an olefin into the five-membered ring destabilizes the tricyclic system.[1a,g,4] An interaction between the spiro moiety and the double bond may promote rearrangements leading to formation of less-strained and thermodynamically more stable compounds. This interaction should be reflected in the thermal behavior of these tricyclic olefins. Consistent with this notion, 4,5-benzotricyclo[4.1.0.0^{1,3}]hept-4-ene (**3**) dimerizes and rearranges to 2-methylnaphthalene at 30 °C.[2c] It has been suggested that spiro tricycloheptene **2** has eluded isolation because of a facile [$\sigma_{2s} + \pi_{2s} + \sigma_{2s}$] pericyclic rearrangement initially leading to 5-methylene-1,3-cyclohexadiene, which subsequently undergoes a hydrogen shift to afford toluene.[2b,c,4] Tricyclo[4.2.0.0^{1,3}]-oct-4-ene (**1**) contains only an extra methylene group in comparison to tricyclo[4.1.0.0^{4,6}]hept-2-ene (**2**). Thus, in principle, tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) could undergo an analogous pericyclic rearrangement which would thermally destabilize the system and, potentially, lead to the formation of spirobicyclo[5.2]octa-2,4-diene.

Synthesis of bridged spiro hydrocarbons is typically accomplished via intramolecular addition of small ring carbenes (i.e., divalent carbon in three- or four-membered rings) to double bonds.[1,2] Nevertheless, an attempt to synthesize tricyclo[4.2.0.0^{1,3}]octane (**5**), the saturated analogue of compound **1**, by such an approach was not successful primarily due to a competing ring contraction reaction and 1,2-hydrogen migration to give methylenecyclopropane and cyclobutene derivatives, respectively (eq 1).[1a] Therefore, in the synthesis of tricyclo[4.2.0.0^{1,3}]-oct-4-ene (**1**) an intramolecular cyclization sequence originally described by Carpino, Gund, Springer, and Gund[5] in 1981 was used to prepare *gem*-dichloro ketone **6**, which contains the complete tricyclic skeleton. A subsequent reduction scheme led to the preparation of

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(1) (a) Brinker, U. H.; Schrievers, T.; Xu, L. *J. Am. Chem. Soc.* **1990**, *112*, 8609−8611. (b) Miebach, T.; Brinker, U. H. *J. Org. Chem.* **1993**, *58*, 6524−6525. (c) Wiberg, K. B.; McMurdie, N.; McClusky, J. V.; Hadad, C. M. *J. Am. Chem. Soc.* **1993**, *115*, 10653−10657. (d) Wiberg, K. B.; Snoonian, J. R. *Tetrahedron Lett.* **1995**, *37*, 1171−1174. (e) Wiberg, K. B.; Snoonian, J. R.; Lahti, P. M. *Tetrahedron Lett.* **1996**, *37*, 8285−8288. (f) Wiberg, K. B.; Snoonian, J. R. *J. Org. Chem.* **1998**, *63*, 1390−1401. (g) Boese, R.; Blaser, D.; Gomann, K.; Brinker, U. H. *J. Am. Chem. Soc.* **1989**, *111*, 1501−1503.

(2) (a) Skattebol, L. *J. Org. Chem.* **1966**, *31*, 2789−2794. (b) Brinker, U. H.; Fleischhauer, I. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 396−397. (c) Brinker, U. H.; Streu, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 631−632. (d) Brinker, U. H.; Gomann, K.; Zorn, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 869−870. (e) Brinker, U. H.; Wilk, G.; Gomann, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 868−869. (f) Skattebol, L. *Chem. Ind.* (*London*) **1962**, 2146.

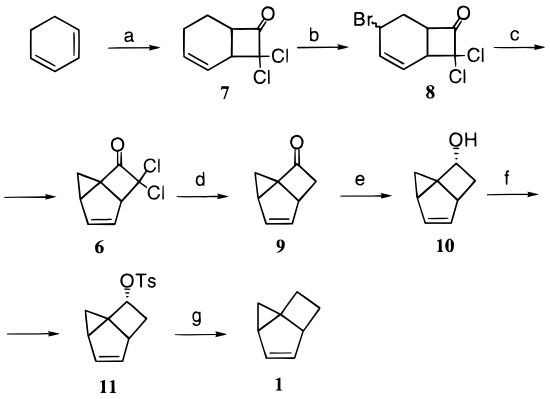
(3) The trans in *trans*-tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) will be omitted for simplicity sake.

(4) (a) Dombrowski, G. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, 1995. (b) Sauer, J.; Sustman, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779−807.

(5) Carpino, L.; Gund, P.; Springer, J., P.; Gund, T. *Tetrahedron Lett.* **1981**, *22*, 371−374.

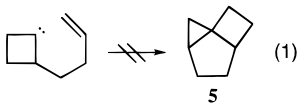
10.1021/jo000215r CCC: $19.00
Published on Web 05/11/2000

Scheme 1[a]



[a] Reagents and conditions: (a) Cl_3CCOCl, Zn(Cu), DME, 71%; (b) CCl_4, NBS, 83%; (c) DBN, Et_2O, 31%; (d) Zn, TMEDA, AcOH, EtOH, 94%; (e) $LiAlH_4$, 95%; (f) TsCl, Py, 74%; (g) $LiBEt_3H$, Et_2O, ~2%.

tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) and enabled us to explore its reactivity and thermal stability.



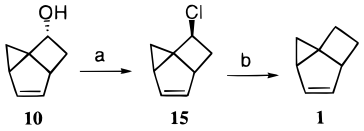
(1)

Results and Discussion

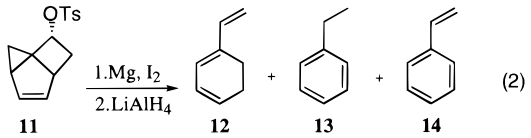
Synthesis of Tricyclo[4.2.0.0^{1,3}]oct-4-ene (1). Tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) was formed via a reduction sequence starting from the known dichloro ketone **6** (Scheme 1). The literature procedure for the preparation of compound **7**,[5] however, was modified. Dichloroketene addition to 1,3-cyclohexadiene followed by radical bromination and subsequent distillation gave a single allylic bromide (**8**, the relative stereochemistry of the bromine was not deduced since it was removed in the next step) in 59% overall yield. Deprotonation of ketone **8** with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in diethyl ether followed by an intramolecular cyclization, as originally described by Carpino et al.,[5] enabled **6** to be obtained in a 48% yield.

Dechlorination of **6** with zinc, tetramethylethylenediamine (TMEDA), and acetic acid afforded ketone **9** in a 67% yield. This compound was found to be relatively unstable and was rapidly carried on. Direct deoxygenation of ketone **9** via its tosylhydrazone was unsuccessful due to the thermal instability of the starting material. Thus, tricyclic ketone **9** was converted into its corresponding alcohol **10** with lithium aluminun hydride ($LiAlH_4$) in a 95% yield. It turned out that only one diastereomer of alcohol **10** formed under these reaction conditions. Attempts to reduce alcohol **10** by either a Barton deoxygenation[6] or by converting it to an iodide or bromide (the latter two derivatives would have an inverted configuration relative to alcohol **10**) with subsequent reduction failed, presumably, because of rapid decomposition of the strained bridged spirohexane system. The tosylate derivative **11** of alcohol **10** was successfully prepared with *p*-toluenesulfonyl chloride and pyridine at 0 °C and was found to be stable at room temperature for several hours. However, all efforts to convert tosylate **11** to the corresponding (inverted) bromide or iodide were unsuccessful. When tosylate **11** was treated with magnesium and iodine in diethyl ether and the resulting product was reduced in situ with lithium aluminum hydride, 1-vinylcyclohexa-1,3-diene (**12**), ethylbenzene (**13**), and styrene (**14**) were isolated in a 4:1.2:1 ratio, respectively (eq 2). Formation of hydrocarbons **12**–**14** suggests that the iodo derivative of alcohol **10** is generated under these reaction conditions, but that it is unstable and rapidly rearranges.

Scheme 2[a]



[a] Reagents and conditions: (a) CCl_4, PPh_3, Et_2O; (b) $LiAlH_4$, Et_2O, 17% overall.



(2)

a. 1. Mg, I_2 ; 2. $LiAlH_4$

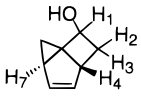
The desired olefin **1** was successfully prepared by reduction of tosylate **11** with lithium triethylborohydride ($LiBHEt_3$, Super Hydride) in diethyl ether. Super Hydride is commercially available as a 1 M solution in tetrahydrofuran; however, it was necessary to switch to a more volatile solvent like diethyl ether for better separation of the volatile hydrocarbon product from the solvent. Purification of the tricyclic olefin was accomplished by preparative gas chromatography. To our disappointment the estimated yield of the final step was only 2%, and it was difficult to generate sufficient amounts of material in this way. Thus, another reduction sequence for the preparation of hydrocarbon **1** was developed. Alcohol **10** was transformed into chloride **15** (with inversion of configuration) using CCl_4 and PPh_3 in Et_2O at 45 °C[7] and reduced in situ with $LiAlH_4$ to give **1** in a 17% overall yield (Scheme 2). Chloride **15** was found to be air and thermally sensitive and could not be isolated from the solvent (Et_2O or CCl_4). Any traces of THF in the reaction mixture led to decomposition of the product. Thus, it was found that inverted chloride **15** is more stable than the corresponding bromide or iodide, but less stable than the tosylate derivative **11**, which has the same configuration as the original alcohol **10**.

Stereochemistry of Alcohol 10. Reduction of ketone **9** with $LiAlH_4$ in the synthesis of tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) yields only one diastereomer of alcohol **10**, thus indicating that one side of the tricyclic skeleton is much more hindered than the other. To determine which epimer is formed and which face is more open to nucleophilic attack, the relative stereochemistry of the hydroxyl group (or hydrogen H1) and the cyclopropyl ring must be determined (Table 1). Upon the basis of molecular models and the X-ray crystal structure of dichloro ketone **6**,[5] the two bridgehead hydrogen atoms H4 and H7 are

(6) Barton, D. H. R.; McCombie, S. W. J. *J. Chem. Soc., Perkin Trans. I* **1975**, *16*, 1574–1585.

(7) Temperature control is critical. Only decomposition products are observed when the reaction is carried out above 45 °C, and the reaction does not take place below 40 °C.

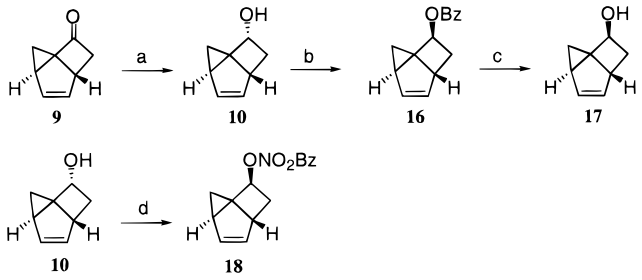
Table 1. Experimental and Calculated Coupling Constants in Hertz[a]



cmpd	$J_{1,2}$	$J_{1,3}$	$J_{2,4}$	$J_{3,4}$
10	7.5 (7.6)	7.5 (7.0)	7.0 (7.1)	7.0 (6.5)
16	1.0 (0.2)	5.5 (6.7)	8.0 (7.1)	7.0 (6.5)
17	3.0 (0.2)	3.0 (6.7)	8.0 (7.1)	8.0 (6.5)

[a] Parenthetical values were obtained using the Karplus equation and the MP2/6-31G(d) geometry for **1**.

Scheme 3[a]



[a] Reagents and conditions: (a) $LiAlH_4$; (b) DEAD, $PhCO_2H$, PPh_3; (c) $LiAlH_4$; (d) DEAD, NO_2PhCO_2H, PPh_3.

trans to one another in the tricyclic skeleton of **1**. The problem, therefore, comes down to determining the relative configuration of hydrogens H1 and H4. This can be done by establishing their positions relative to hydrogens H2 and H3 via ^{1}H NMR coupling constants. It is well-known that the relative configuration of two vicinal hydrogen atoms can usually be assigned based upon their coupling constants.[8] The most reliable results are obtained if both isomers are available; consequently, alcohol **10** was inverted by the Mitsunobu method[9] to afford the corresponding benzoate (**16**, Scheme 3). Subsequent reduction of **16** with $LiAlH_4$ afforded the inverted alcohol **17**. Vicinal coupling constants for both diastereomers (**10** and **17**) and the benzoate **16** were obtained.

The Karplus equation (eq 3) relates the magnitude of the coupling constant (^3J) to the dihedral angle (θ) between the vicinal hydrogens. The constants J^0 and J^{180} vary with the system but commonly are taken to be 8.5 and 9.5 Hz, respectively.[8]

$$^3J_{ab} = J^0 \cos^2\theta - 0.28 \quad (0° \le \theta \le 90°) \qquad (3a)$$

$$^3J_{ab} = J^{180} \cos^2\theta - 0.28 \quad (90° \le \theta \le 180°) \qquad (3b)$$

All of the vicinal dihedral angles between H1, H2, H3, and H4 for both diastereomers were obtained from the MP2/6-31G(d) geometry of the tricyclic hydrocarbon **1**, and the coupling constants were estimated using eq 3. Our assignments were based on the agreement of the calculated and experimental values, which is excellent in the case of **10** and quite reasonable for **16** and **17**.

To confirm our structural assignment, the inverted *p*-nitrobenzoate **18** was synthesized from **10** via the Mitsunobu reaction (Scheme 3), and an X-ray crystal structure at 173(2) K was obtained. Suitable single crystals of *p*-nitrobenzoate **18** were formed by recrystallization from a 1:1 ethanol/pentane mixture. The resulting crystals are orthorhombic, their space group is *Pbca*, and the unit cell is comprised of eight molecules with the following dimensions: $a = 7.215$ (1) Å, $b = 12.496$ (2) Å, $c = 28.951$ (4) Å, and $\alpha = \beta = \gamma = 90°$. Direct methods were employed to solve the molecular structure and further refinement by full-matrix least-squares methods were carried out to a conventional R-factor of 0.0476 (full details can be found in the Supporting Information). The X-ray data indicate that the stereochemistry of alcohol **10** was deduced correctly via the coupling constants analysis. In the initially formed alcohol **10**, the hydroxyl group is anti to the cyclopropane ring. Therefore, the cyclopropyl side of the four-membered ring is more open to attack by $LiAlH_4$ than the bottom or cyclopentenyl side. It follows that the inverted alcohol **17** has the syn configuration and that the hydroxyl substituent is on the same side as the three-membered ring.

The X-ray crystal structure of ester **18** provides the first geometrical data on this type of strained tricyclic skeleton (preliminary X-ray results were reported for dichloro ketone **6** but no geometry information was provided[5]). Selected bond lengths, bond angles, and dihedral angles are given in the Supporting Information along with the corresponding MP2/6-31G(d) structural parameters for **1**; there is good agreement between the experimental and computed values except for the carbon−carbon (C5−C6) double bond length which is computed to be 1.35 Å and found to be 1.31 Å. As expected, the C2−C1−C8 bond angle is the most distorted one in the molecule and is 138.8° (expt, 139.5° (MP2)), which is about 30° more than an average C−C−C bond angle at an sp^3-hybridized center. The double bond is bent by only 0.2° (expt, 0.3° (MP2)) as indicated by the C4−C5−C6−C7 dihedral angle, and is slightly shorter than an average C−C double bond length of 1.34 Å.[10]

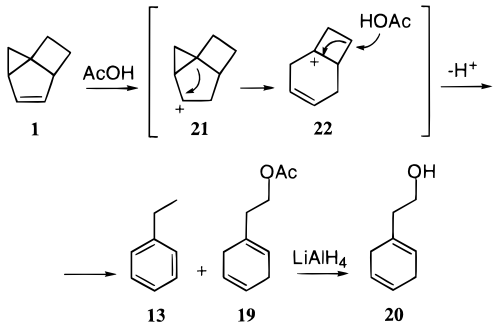
Several inverted (syn) derivatives of alcohol **10** were found to be unstable. For example, anti tosylate **11** was readily isolated whereas several attempts to prepare the analogous syn derivative of the inverted alcohol **17** were unsuccessful presumably because of the rapid decomposition of the product. Chloride **15**, also is quite labile as discussed above, and attempts to invert alcohol **17** by the Mitsunobu method were unsuccessful. These results suggest that inverted syn species are more reactive and less stable due to rapid ring opening of the tricyclic skeleton. This behavior is analogous to that of 2-substituted bicyclo[2.1.0]pentane derivatives[11] in that a disrotatory ring opening of the C1−C7 bond toward the backside of a syn leaving group should be facile whereas the same process for an anti leaving group is structurally retarded.

Rearrangements Studies

Acetolysis. Tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) is an unusual molecule due to the interaction between the spirohexyl moiety and the ethenyl bridge. The thermal rearrangement of this hydrocarbon and its reactivity toward electrophiles are of particular interest. Somewhat sur-

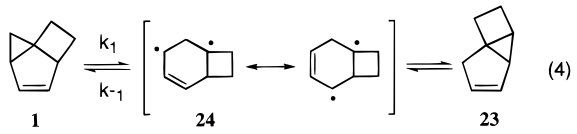
(8) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill: London, 1987; pp 91−101.
(9) Overman, L. E.; Bell, K., L.; Ito, F. *J. Am. Chem. Soc.* **1984**, *106*, 4192−4201.
(10) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275−311.
(11) Wiberg, K. B.; Williams, V. Z., Jr.; Friedrich, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 564−567.

Scheme 4

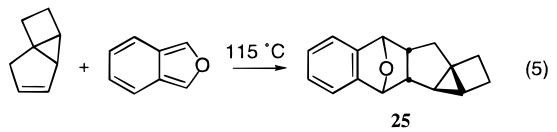


prisingly, **1** is relatively stable under acidic conditions. Glacial acetic acid does not react with it at room temperature and only slowly gives products at 145 °C. Gas chromatography was used to monitor the reaction, and after 8 h (≈1.1 half-lifes) two major products, ethylbenzene (**13**) and acetate **19**, were formed in 5:1 ratio, respectively (Scheme 4). To identify the structure of the isolated acetate, it was reduced with $LiAlH_4$ to afford alcohol **20**. This compound was purified by column chromatography and its ^{1}H NMR spectrum was found to match the literature spectrum for 1-(2-hydroxyethyl)-cyclohexa-1,4-diene.[12] Formation of both products, **13** and **19**, can be explained by protonation of the double bond to afford a tricyclic cyclopropylcarbinyl cation (**21**) which rearranges to bicyclic, homoallylic, tertiary cation **22**.[13] Nucleophilic attack by AcOH with concomitant cleavage of the four-membered ring leads to the observed acetate. Ethylbenzene may arise via the loss of a proton from **22** to afford 1-vinyl-1,4-cyclohexadiene followed by its isomerization/aromatization, but it also maybe a secondary product derived from **19**.

Thermolysis. Investigation of the thermal rearrangement of tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) led to the isolation of a bridged bicyclo[2.1.0]pentane derivative (**23**, eq 4).



The structural assignment for this hydrocarbon was initially based upon ^{1}H NMR data. We subsequently were able to prepare the Diels−Alder adduct with isobenzofuran at 115 °C (**25**, eq 5), but not with the sterically more encumbered 1,3-diphenylisobenzofuran; under these forcing conditions the diene undergoes competitive dimerization. Suitable, but less than optimal, single crystals



of **25** were obtained for X-ray crystallography by recrystallization from a 1:1 acetonitrile/pentane mixture. The resulting crystals are monoclinic, their space group is *C*2/*c*, and the unit cell is comprised of 16 molecules with the following dimensions: a = 37.761(9) Å, b = 6.284(2) Å, c = 26.651(7) Å, and $\alpha = \gamma = 90°$, β = 130.392(3)°. The asymmetric unit contains two molecules (the same stereoisomers), and one of them is involved in an intermolecular hydrogen bond (i.e., the C22−H26···O2′ distance is 2.56 Å; see the Supporting Information for full details). Direct methods were employed to solve the molecular structure, and further refinement by full-matrix least-squares methods were carried out to a conventional R-factor of 0.0656. The X-ray data indicates that the product is the *endo* isomer as expected and provides the first geometrical data for this type of strained tricyclic skeleton (a bridged 1,5-bicyclo-[2.1.0]pentane). Selected experimental and calculated bond lengths, bond angles, and dihedral angles are given in the Supporting Information. As expected, the C2−C1−C8 bond angle is the most distorted one in the molecule and is 132.3° in one structure and 132.6° in the other (expt, 133.9° MP2/6-31G(d)). Both angles are about 23° more than a typical value at an sp^3-hybridized center. This angle, however, is less distorted than the C2−C1−C8 bond angle in **1**.

Table 2. Kinetic and Equilibrium Data for the Conversion of 1 to 23

T (°C)	k_1 (h^{-1})	k_{-1} (h^{-1})	K	$t_{1/2}$ (h)[a]
180	0.053	0.0035	15.2 ± 0.3	12
190	0.1	0.0070	14.6 ± 0.4	6
200	0.23	0.015	15.0 ± 0.1	3

[a] The half-life time for achieving equilibrium in the **1** to **23** direction.

The thermolysis of tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) originally was carried out in toluene and then in xylene-d_{10}, and to our surprise it is stable up to 165 °C. No deuterium incorporation was detected, and since the same product and approximate reactivity also was observed in decalin, we chose to use this solvent for making quantitative measurements. Spirohexane **1** and bicyclo[2.1.0]pentane derivative **23** interconvert at elevated temperatures so equilibrium data and rate constants were measured over a 20 °C range from 180 °C to 200 °C (Table 2). The resulting equilibrium constants are the same within experimental error indicating that ΔS for the reaction must be small (i.e., around zero). In accord with this, we estimate that ΔS_{190} = 0.9 cal/mol K by using standard statistical mechanics expressions[14] and MP2/6-31G(d) structures and scaled vibrational frequencies (0.9427)[15] for **1** and **23**. The free energy difference for this reaction (ΔG_{190}) is −2.5 kcal/mol, which leads to a difference in the heats of formation ($\Delta\Delta H_f$(**23** − **1**) of −2.1 kcal/mol. This is in a good accord with the HF/6-31G(d) and MP2/6-31G(d) energy differences of −1.9 and −1.4 kcal/mol, respectively. Rate constants for the forward reaction also were measured, and the Arrhenius plot is linear and leads to a rearrangement barrier (E_a) of 31 kcal/mol.[16]

Most likely the isomerization of **1** to **23** proceeds via cleavage of the C1−C7 cyclopropane bond to afford

(12) Engel, P. S.; Allgren, R. L.; Chae, W.-K.; Leckonby, R. A.; Marron, N. A. *J. Org. Chem*. **1979**, *44*, 4233−4239.

(13) Cation **22** has previously been invoked. For additional details, see: Wiberg, K. B.; Olli, L. K.; Golembeski, N.; Adams, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 7467−7475.

(14) Herzberg, G. H. *Molecular Spectra and Molecular Structure: Infrared and Raman Spectra of Poliatomic Molecules*; D. Van Nostrand: Princeton, NJ, 1945; Vol. 2, p 510.

(15) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem*. **1993**, *33*, 345−350.

(16) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981. The A factor is $10^{13.8}$ s^{-1}, but given the limited temperature range and the fact that the rate constants were measured only once, this value should not be over interrupted.

Table 3. Calculated Heats of Formation and Strain Energies[a]

cmpd	Method	Energy	ΔH_f	SE
 **26**	HF/6-31G(d)	-232.96551	29.2	53.4
	MP2/6-31G(d)	-232.60126	33.5	57.7
 **5**	HF/6-31G(d)	-309.86564	33.5	59.9
	MP2/6-31G(d)	-310.90657	36.2	62.6
 **1**	HF/6-31G(d)	-308.67753	59.6	57.0
	MP2/6-31G(d)	-309.70785	62.0	59.4
 **23**	HF/6-31G(d)	-308.53182	57.7	55.1
	MP2/6-31G(d)	-309.55568	60.6	58.0

[a] Computed energies are in hartrees, all other values in kcal/mol.

biradical intermediate **24**, which can re-close at the other end of the allylic system to give the observed bicyclo-[2.1.0]pentane derivative. Ample literature precedents exist for this pathway.[17] For example, Frey and Roth[18] proposed that the interconversion of *cis*- and *trans*-2-methylvinylcyclopropanes occurs by way of a biradical intermediate. The reported activation energy (E_a = 48.6 kcal/mol) is 17 kcal/mol larger than in our case, but this difference can readily be explained by the difference in stability of the two biradicals; **24** has a tertiary radical center compared to a primary one in Frey and Roth's compound, and in our case the C−C bond cleavage relieves more strain.

Calculations

Full geometry optimizations and vibrational frequencies for tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**), its saturated analogue *trans*-tricyclo[4.2.0.0^{1,3}]octane (**5**), bicyclo[2.1.0]-pentane derivative **23**, and spirohexane (**26**) were computed at the HF and MP2 levels using the 6-31G(d) basis set (Table 3). Calculated heats of formation (ΔH_f) were obtained using Wiberg's group equivalent approach.[1f,19] Strain energies (SE) for these compounds also were computed using the calculated heats of formation and Franklin group equivalents for the energies of corresponding unstrained models.[20] The MP2/6-31G(d) structures of tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) and bicyclo[2.1.0]-pentane derivative **23** are shown in Figure 1, and in both cases there is good agreement with the related X-ray crystal data.

According to the MP2 calculations, introduction of an ethanyl bridge into spirohexane increases the strain energy by only 5 kcal/mol. Tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) has about the same strain energy as its saturated analogue, indicating that the double bond does not increase the SE of the tricyclic system. In fact, it lowers the strain energy at the HF and MP2 levels by 2.9 and 3.2 kcal/mol, respectively. This negative olefin strain energy[21] presumably is due to relief of hydrogen−hydrogen eclipsing interactions in **5**. Given these modest energetic changes, it is not surprising that the bend (180° − ∠ a1b; see Figure 1 for the labeling scheme) and twist (90° and −90° − 8ab2 and 7ab4) angles in **1** (20.8° and 6.8−7.0°, respectively) and **5** (19.7° and 6.6−11.0°, respectively) are similar and relatively small.[22]

Conclusions

Synthesis of the novel bridged spiro hydrocarbon **1** was accomplished in four steps starting from the previously reported tricyclic dichloro ketone **6**. *trans*-Tricyclo[4.2.0.0^{1,3}]-oct-4-ene (**1**) was found to be relatively stable toward electrophiles only reacting with glacial acetic acid at 145 °C. 1-(2-Acetoxyethyl)cyclohexa-1,4-diene (**19**) and ethylbenzene **13** were obtained in a 1:5 ratio, respectively. Thermolysis of **1**, contrary to our expectations, requires temperatures of 165 °C or higher and leads to the formation of tricyclo[4.2.0.0^{1,5}]oct-3-ene (**23**). Equilibrium and rate constants were measured at various temperatures and E_a = 31 kcal/mol and $\Delta\Delta H_f$(**23** − **1**) = −2.1 kcal/mol. The latter quantity was computed at the HF and MP2 levels with the 6-31G(d) basis set (−1.9 (HF) and −1.4 (MP2) kcal/mol), and both values are in good

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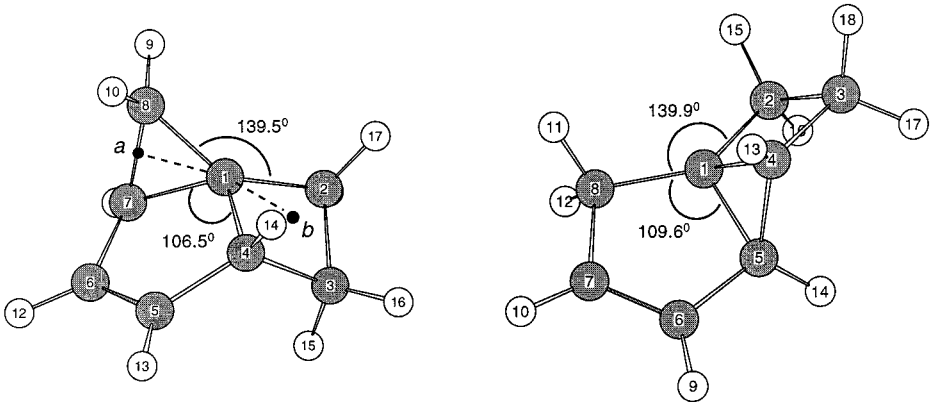
(22) The corresponding bend and twist angles in spirohexane (**26**) are 6.0° and 0°, respectively.



1 **23**

Figure 1. MP2/6-31G(d) calculated structures of tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) and tricyclo[4.2.0.0^{1,5}]oct-3-ene (**23**). Points a and b are at the C7−C8 and C2−C4 midpoints and lie in the C1−C7−C8 and C1−C2−C4 planes.

agreement with experiment. Strain energies (SE) for tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) and its saturated analogue also were calculated and are very similar.

X-ray crystal structures of the Diels−Alder adduct between **23** and isobenzofuran and the *p*-nitrobenzoate of **10** were obtained. These structures provide the first geometrical data on these tricyclic systems and confirm our spectroscopic assignments.

Experimental Section

General Methods. All reactions were carried out using anhydrous solvents under an inert atomosphere of N_2 in flame-dried flasks. Ether and THF were distilled from sodium/benzophenone ketyl prior to use. Dichloromethane was distilled from calcium hydride. All reagents were of commercial grade and were either distilled or recrystallized prior to use. Merck silica gel (230−400) mesh was used for flash chromatography.

8,8-Dichlorobicyclo[4.2.0]oct-2-en-7-one (7). To a mixture of 9.8 g (0.15 mol) of Zn(Cu)[23] couple and 4.4 g (0.05 mol) of 1,3-cyclohexadiene in 90 mL of Et_2O was added 20 g (0.11 mol) of trichloroacetyl chloride in 35 mL of DME over a 1 h period. After 20 h at room temperature the resulting brown mixture was filtered and the solid was washed with hexanes. The filtrate was washed with ice cold 0.5 N HCl and 5% NaOH. The organic layer was washed further with saturated NaCl and then filtered through charcoal and a plug of silica gel. The resulting solution was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Distillation at 0.9 mm (bp 55−67 °C) afforded 6.8 g (70.8%) of a colorless oil. The proton NMR was as previously described.[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.06 (m, 1H), 5.85 (m, 1H), 4.10 (m, 1H), 3.43 (m, 1H), 2.03 (m, 3H), 1.71 (m, 1H).

4-Bromo-8,8-dichlorobicyclo[4.2.0]oct-2-en-7-one (8).[5,24] A solution of 3.5 g (0.019 mol) of NBS, 3.45 g (0.018 mol) of 8,8-dichlorobicyclo[4.2.0]oct-2-en-7-one (**7**), and a catalytic amount of AIBN in 60 mL of dry CCl_4 was refluxed and irradiated with a 60 W table lamp until a white precipitate formed (1 h). The reaction mixture was left in a refrigerator overnight so that all of the succinimide would crystallize out of the solution. The cold carbon tetrachloride solution was filtered, and the precipitate was washed with additional cold CCl_4. The filtrate was concentrated under reduced pressure to yield 4.8 g (100%) of a yellow oil. Distillation at 1.1 mm (bp 115 °C) afforded 3.3 g (83%) of the product **8** as a single stereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (ddd, J = 1.8, 3.9, and 10.2 Hz, 1H), 5.98 (dd, J = 3.9 and 10.2 Hz, 1H), 4.6 (m, 1H), 4.15 (dt, J = 6.9 and 9.9 Hz, 1H), 3.58 (ddt, J = 1.2, 3.0, and 9.6 Hz, 1H), 2.55 (m, 1H), 2.27 (q, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 134.0, 124.8, 86.5, 51.9, 43.3, 39.9, 29.9.

3,3-Dichlorotricyclo[5.1.0.0^{1,4}]oct-5-en-2-one (6).[5,24] A solution of DBN (3.47 mL, 0.028 mol) in 50 mL of Et_2O was added over a 1 h period to 7.5 g (0.028 mol) of bromide **7** in 70 mL of Et_2O at −65 °C (dry ice/ethanol). The resulting brown reaction mixture was stirred for an additional 30 min and poured into 300 mL of an ice cold 1:1 H_2O/Et_2O mixture. The cold aqueous layer was extracted with Et_2O, and the combined organic material was washed with ice cold H_2O, 1 N HCl (until the pH was < 7), sat. $NaHCO_3$ and sat. NaCl. The resulting solution was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Distillation at 0.25 mm (bp 65−75 °C) afforded 1.6 g (31%) of white crystalline product. Alternatively, **6** can be purified by column chromatography (R_f value = 0.34 in 7% EtOAc/ hexanes). ^{1}H NMR (300 MHz, $CDCl_3$)[24] δ 6.24 (d, J = 4.8 Hz, 1H), 5.83 (d, J = 4.8, 1H), 3.8 (m, 1H), 3.02 (td, J = 2.8 and 6.0 Hz, 1H), 2.16 (dd, J = 5.8 and 6.0 Hz, 1H), 1.31 (t, J = 5.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 137.5, 132.3, 98.2, 61.3, 47.3, 45.3, 23.0.

Tricyclo[5.1.0.0^{1,4}]oct-5-en-2-one (9). To a mixture of 2 g of Zn dust and 4.5 mL of TMEDA (0.029 mol) in 10 mL of absolute EtOH at 0 °C was added 1.9 mL (0.033 mol) of AcOH over a 10 min period. The reaction mixture was maintained at 0 °C while a solution of 1 g (5.3 mmol) of compound **6** in 2 mL of EtOH was added over a 10 min period. After an additional 15 min at 0 °C the reaction mixture was allowed to warm to room temperature and stir for 2 h. The resulting gray mixture was filtered, and the solid was washed with a 1:1 pentane/Et_2O solution. The filtrate was extracted with ice cold 1 N HCl, H_2O, sat. $NaHCO_3$, and sat. NaCl. The resulting material was dried over $MgSO_4$ and concentrated under reduced pressure to afford 0.6 g (94%) of ketone **9** which was of sufficient purity for subsequent transformations. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99 (ddd, J = 1.2, 2.1, and 5.4 Hz, 1H), 5.86 (dt, J = 1.5 and 5.4 Hz, 1H), 3.12 (m, 1H), 3.09 (ddt, J = 0.6, 7.8, and 15.0 Hz, 1H), 2.71 (dd, J = 4.2 and 15.0 Hz, 1H), 2.68 (m, 1H), 1.96 (dddd, J = 0.6, 1.5, 5.7, and 8.1 Hz, 1H), 1.1 (t, J = 5.7, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 133.3, 53.2, 50.0, 42.7, 39.0, 21.6 (carbonyl resonance missing); IR (neat) 1758 (CO) cm^{-1}; HRMS-EI M$^+$ calcd for C_8H_8O 120.0575, found 120.0571.

***anti*-Tricyclo[5.1.0.0^{1,4}]oct-5-en-2-ol (10).** To a 0 °C solution of 0.6 g (5.0 mmol) of ketone **9** in 10 mL of THF was added 3 mL of a 1 M solution of $LiAlH_4$ in THF. The reaction mixture was allowed to warm to room temperature and stir for an additional 2 h. Ice cold Et_2O (10 mL) was slowly added to the reaction mixture followed by 5 mL of sat. NH_4Cl. The organic layer was washed with sat. NaCl and dried over $MgSO_4$. Concentration under reduced pressure afforded 0.58 g (95%)

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of alcohol **10** which was of sufficient purity for subsequent reactions. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 (dt, J = 1.5, and 5.0 Hz, 1H), 5.64 (dt, J = 2.0, and 5.0 Hz, 1H), 4.80 (dd, J = 1.0 and 7.5 Hz, 1H), 2.72 (dt, J = 7.5 and 11.0 Hz, 1H), 2.55 (dd, J = 1.0 and 7.5 Hz, 1H), 1.96 (m, 1H), 1.70 (dt, J = 7.5 and 11.0 Hz, 2H), 1.03 (ddtt, J = 0.5, 1.0, 5.0, and 8.0 Hz, 1H) 0.43 (t, J = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 136.1, 70.1, 43.0, 40.3, 38.5, 24.7, 16.0; IR (neat) 3587, 3411, 1430, 1419, 1397, 1074, 1019 cm^{-1}. HRMS-EI M^+ calcd for $C_8H_{10}O$ 122.0731, found 122.0741.

Tricyclo[5.1.0.0^{1,4}]oct-5-en-2-ol Tosylate (11). Alcohol **10** (0.24 g, 2 mmol) was dissolved in 2 mL of dry pyridine at 0 °C. A catalytic amount of DMAP and *p*-TsCl (0.45 g, 2.4 mmol) were added sequentially, and the reaction mixture was stirred for 96 h at 0 °C. Saturated NH_4Cl and water were added to obtain a homogeneous solution that was extracted with ether. The combined ether layers were washed with 1 N HCl (until the pH was <7), H_2O, sat. $NaHCO_3$, and sat. NaCl and then dried over $MgSO_4$ at 0 °C. Concentration under reduced pressure afforded 0.4 g (74%) of tosylate **11** that was of sufficient purity for subsequent reactions. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 5.93(dt, J = 4.8 and 2.4 Hz, 1H), 5.56 (dt, J = 4.8 and 1.5 Hz, 1H), 5.32 (t, J = 7.2 Hz, 1H), 2.57 (m, 2H), 2.44 (s, 3H), 2.1 (m, 1H), 2.0 (m, 1H), 0.83 (ddd, J = 1.0, 4.7, and 7.8 Hz, 1H), 0.34 (t, J = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 136.9, 135.1, 133.8, 129.8, 127.8, 77.3, 41.1, 39.2, 35.4, 27.4, 21.7, 15.7; HRMS-CI (isobutane) $(M + H)^+$ calcd for $C_{15}H_{16}SO_3$ 227.0898, found 227.0893.

Reaction of Tricyclo[5.1.0.0^{1,4}]oct-5-en-2-ol Tosylate (11) with Mg, I_2, and $LiAlH_4$. A solution of I_2 (45 mg, 0.17 mmol) in 0.5 mL of Et_2O was added over a period of 10 min to a mixture of tosylate **11** (0.05 g, 0.19 mmol) and activated Mg (15 mg, 0.63 mmol) in 1 mL of Et_2O at 0 °C. The reaction mixture was allowed to warm to room temperature and stir for an additional 30 m. The resulting solution was cannulated to a different reaction vessel and cooled to 0 °C. A 1 M solution of $LiAlH_4$ (0.3 mL, 0.3 mmol) in THF was slowly added, and the reaction mixture was allowed to warm to room temperature and stir overnight. An ice-cold saturated solution of NH_4Cl (0.5 mL) was added to the reaction mixture, and the organic layer was washed with H_2O and then dried over $MgSO_4$. The resulting solution was analyzed by GC-MS, and the products were purified via preparative gas chromatography (12 ft × 0.2 in. 20% Squalane on Chrom W column at 90 °C). 1-Vinylcyclohexa-1,3-diene (**12**), ethylbenzene (**13**), and styrene (**14**) were isolated in 4:1.2:1 ratio, respectively. 1-Vinylcyclohexa-1,3-diene (**12**):[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (dd, J = 11.0 and 17.4 Hz, 1H), 5.95 (m, 1H), 5.85 (m, 2H), 5.21 (d, J = 17.4 Hz, 1H), 5.03 (d, J = 11.0 Hz, 1H), 2.34 (m, 2H), 2.25 (m, 2H); ethylbenzene (**13**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 5H), 3.48 (q, 2H), 1.2 (t, 3H); styrene (**13**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25−7.45 (m, 5H), 6.7 (dd, J = 10.8 and 17.5 Hz, 1H), 5.75 (d, J = 17.5 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H).

Tricyclo[4.2.0.0^{1,3}]oct-4-ene (1). Method 1. A 1 M solution of $LiEt_3BH$ (3.2 mL, 3.2 mmol) in THF was concentrated with a mechanical vacuum pump for 2 h and of 0.18 g of tosylate **11** (0.65 mmol) in 2 mL of Et_2O was added at 0 °C. The reaction mixture was stirred for 6 h at room temperature and 10 mL of an ice-cold 10% NaOH solution was slowly added. The resulting slurry was stirred for an additional 10 min at 0 °C and extracted with Et_2O. The organic phase was dried over $MgSO_4$, and the solvent was slowly distilled at atmospheric pressure. The residue was bulb to bulb transferred and the distillate was purified via preparative gas chromatography to afford small amounts of compound **1**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (d, J = 4.8 Hz, 1H), 5.57 (dt, J = 1.8, and 4.8 Hz, 1H), 3.07 (t, J = 7.2 Hz, 1H), 2.72 (m, 1H), 2.28 (dddd, J = 4.2, 8.1, 8.4, and 12.3 Hz, 1H), 2.03 (m, 2H), 1.59 (m, 1H), 0.84 (ddt, J = 0.6, 5.0, and 7.8 Hz, 1H), 0.18 (t, J = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 135.6, 49.9, 31.4, 30.1, 29.6, 29.4, 16.7; HRMS-CI (self) M^+ calcd for C_8H_{11} 107.0861, found 107.0861.

Method 2. A solution of 0.85 g (6.9 mmol) of alcohol **10**, 1.0 mL (10 mmol) of CCl_4, and 2.21 g (8 mmol) of PPh_3 in 6 mL of CH_2Cl_2 was stirred under reflux (40−45 °C bath) for a period of 6 h. The resulting yellow solution was cooled to room temperature, and 0.62 g of decalin in 8 mL of Et_2O was added. The resulting slurry was refrigerated overnight, and the liquid was pipetted away from the precipitated triphenylphosphine oxide (filtration leads to decomposition of the product). The residue was washed with Et_2O, and the combined organic solutions were concentrated under vacuum (100 mm) without an external heat source. The resulting decalin solution contained the desired chloride (**15**) and some residual PPh_3O and was promptly carried on to the next step. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (dt, J = 1.2 and 5.1 Hz, 1H), 5.65 (dt, J = 1.8, and 5.1 Hz, 1H), 4.63 (ddd, J = 0.9, 2.7, and 3.9 Hz, 1H), 3.52 (m, 1H), 2.57 (dd, J = 1.2 and 7.5 Hz, 1H), 2.56 (d, J = 7.5 Hz, 1H), 2.02 (dddd, J = 1.8, 3.0, 4.2, and 8.4 Hz, 1H), 1.19 (dddd, J = 0.6, 1.5, 5.4, and 8.4 Hz, 1H), 0.5 (dd, J = 4.2 and 5.4 Hz, 1H).

The decalin solution containing **15** was cooled to 0 °C, and 4 mL of 1 M $LiAlH_4$ in diethyl ether was added. The resulting mixture was refluxed for 10 h (35−40 °C bath) until the formation of a white precipitate was observed. The reaction mixture was then cooled to 0 °C, and the liquid was pipetted away from the precipitate. Ice cold H_2O was slowly added to the ether solution, and the aqueous layer was extracted with Et_2O. The combined organic extracts were dried overnight over Na_2SO_4 at 0 °C. The liquid was pipetted away from the drying agent and concentrated at atmospheric pressure to afford a 5:1 mixture of decalin and tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) as determined by GC, in a 17% overall yield. The final product was purified by preparative gas chromatography (12 ft × 0.25 in. 20% Squalane on Chrom W column at 90 °C).

Thermolysis of Tricyclo[4.2.0.0^{1,3}]oct-4-ene (1). Thermolyses were done at various temperatures using a Brinkman K6 Lauda constant-temperature bath with temperature control of ±0.05 °C. Dilute solutions (ca. 0.4 mM) of **1** in decalin were sealed under vacuum in 0.1 mL portions in 0.5 mL thick-walled ampules. The tubes were heated for fixed times, and the rearrangement was monitored by ^{1}H NMR spectroscopy and gas chromatography. Tricyclo[4.2.0.0^{1,5}]oct-3-ene (**23**) was purified via preparative gas chromatography (12 ft × 25 in. 20% Squalane on Chrom W column at 90 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (dddt, J = 1.2, 1.2, 2.1, and 5.7 Hz, 1H), 5.43 (dt, J = 2.1 and 5.7 Hz, 1H), 2.40 (br s, 2H), 2.25 (td, J = 3.9 and 10.8 Hz, 1H), 2.11 (tt, J = 3.6 and 10.8 Hz, 1H), 1.82 (m, 1H), 1.7 (dddd, J = 3.6, 4.2, 5.4, and 10.8 Hz, 1H), 1.37 (dddq, J = 0.9, 3.6, 5.4, and 10.8 Hz, 1H), 1.11 (ddt, J = 0.9, 2.1, and 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.4, 129.2, 38.0, 35.0, 31.4, 27.3, 23.3, 23.0. HRMS-CI $(M + H)^+$ calcd for C_8H_{11} 107.0861, found 107.0862.

Reaction of Tricyclo[4.2.0.0^{1,3}]oct-4-ene (1) with AcOH. A thick-walled glass tube containing 1 mL of a 0.02 M solution of tricyclo[4.2.0.0^{1,3}]oct-4-ene (**1**) in AcOH was sealed under vacuum and heated to 145 °C in a constant-temperature bath for 8 h. The ampule was allowed to cool to room temperature before being cracked open, and 2 mL of diethyl ether was added. The resulting solution was extracted twice with H_2O and once with saturated NaCl. GC-MS analysis showed the presence of starting material and two products, a hydrocarbon and acetate derivative, in a 5:5:1 ratio, respectively. One-half of the solution was purified via preparative gas chromatography (12 ft × 25 in. 20% Squalane on Chrom W column at 100 °C), and one of the two products was collected directly in to a trap containing $CDCl_3$. This compound was identified by its ^{1}H NMR spectrum as ethylbenzene (**13**). Its mass spectrum is consistent with this assignment, and an authentic sample was found to have the same GC retention time. The second half of the ether solution was treated at 0 °C with 0.3 mL of 1 M $LiAlH_4$ (0.3 mmol) in Et_2O, and the reaction mixture was refluxed for 2 h. It was subsequently cooled to 0 °C and quenched by slowly adding ice-cold H_2O. The aqueous layer was extracted with Et_2O, and the combined ethereal solution

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was concentrated under reduced pressure. Purification of the residue by column chromatography (30% EtOAc/hexanes) afforded 1 mg of alcohol **20**. The structural assignment was made based upon the ^{1}H NMR spectrum, which is the same as previously reported for 1-(2-hydroxyethyl)cyclohexa-1,4-diene (**20**).[12] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (br s, 2H), 5.56 (br s, 1H), 3.7 (t, J = 6.3 Hz, 2H), 2.7 (m, 4H), 2.25 (t, J = 6.3 Hz, 2H), 1.6 (br s, 1H).

Preparation of *syn*-Tricyclo[5.1.0.0^{1,4}]oct-5-en-2-ol Benzoate (16). To a room temperature mixture of alcohol **10** (0.04 g, 0.32 mmol), PPh_3 (0.1 g, 0.39 mmol), and benzoic acid (0.047 g, 0.39 mmol) in 1.5 mL of THF was added DEAD (0.062 mL, 0.39 mmol) over a 5 min period. Stirring was continued overnight, and then the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (5% EtOAc/hexanes) to afford 0.058 g (80%) of compound **16**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.1−8.16 (m, 2H), 7.56 (m, 1H), 7.49 (m, 2H), 5.98 (dt, J = 1.5 and 5.1 Hz, 1H), 5.69 (dt, J = 1.5, and 5.1 Hz, 1H), 5.42 (dt, J = 1.0, and 5.4 Hz, 1H), 3.41 (ddd, J = 1.5, 7.0, and 8.0 Hz, 1H), 2.50 (ddd, J = 1.0, 8.0, and 12.5 Hz, 1H), 2.43 (ddd, J = 6.0, 7.0, and 12.0 Hz, 1H), 2.06 (m, 1H), 1.29 (ddd, J = 1.5, 4.5, and 8.4 Hz, 1H), 0.41 (t, J = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 135.9, 135.8, 133.0, 130.9, 129.8, 128.5, 80.4, 47.3, 39.0, 34.1, 30.6, 16.9; HRMS-EI M^+ calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0993.

Preparation of *syn*-Tricyclo[5.1.0.0^{1,4}]oct-5-en-2-ol (17). To a 0 °C solution of 0.056 g (0.24 mmol) of compound **16** in 2 mL of Et_2O was added 0.25 mL of a 1 M solution of $LiAlH_4$ in THF. The reaction mixture was stirred overnight at room temperature, and then Et_2O and sat. NH_4Cl solution were added. The resulting slurry was extracted with Et_2O, and the organic phase was dried over $MgSO_4$. Concentration under reduced pressure followed by column chromatography (30% EtOAc/hexanes) afforded 0.021 g (72%) of the inverted alcohol **17**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (dt, J = 1.5 and 5.0 Hz, 1H), 5.66 (dt, J = 1.5 and 5.0 Hz, 1H), 4.50 (t, J = 3.0 Hz, 1H), 3.40 (ddd J = 1.5, 3.5, and 8.0 Hz, 1H), 2.24 (dd, J = 3.0 and 8.0 Hz, 2H), 2.20 (br s, 1H), 1.83 (dddd, J = 2.0, 3.0, 4.5, and 8.5 Hz, 1H), 1.12 (ddd, J = 1.0, 4.5, and 8.5 Hz, 1H), 0.32 (t, J = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 135.4, 77.0, 47.2, 42.0, 35.6, 30.2, 15.4; HRMS-EI M^+ calcd for $C_8H_{10}O$ 122.0732, found 122.0732.

Preparation of *syn*-Tricyclo[5.1.0.0^{1,4}]oct-5-en-2-ol *p*-Nitrobenzoate (18). To a room temperature mixture of alcohol **10** (0.04 g, 0.49 mmol), PPh_3 (0.15 g, 0.58 mmol), and *p*-nitrobenzoic acid (0.1 g, 0.59 mmol) in 3 mL of THF was added DEAD (0.09 mL, 0.59 mmol) over a 5 min period. The reaction mixture was stirred overnight, and then it was concentrated under reduced pressure. Column chromatography of the residue afforded 0.12 g (82%) of *p*-nitrobenzoate **18** (mp 82−84 °C). Recrystallization from a 1:1 mixture of EtOH and pentane afforded crystals suitable for X-ray crystallography. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (m, 4H), 5.98 (dt, J = 1.0 and 5.1 Hz, 1H), 5.69 (dt, J = 2.1 and 5.1 Hz, 1H), 5.44 (d, J = 5.4 Hz, 1H), 3.43 (t, J = 7.2 Hz, 1H), 2.56 (ddd, J = 1.2, 7.4, and 12.9 Hz, 1H), 2.45 (ddd, J = 5.4, 7.2, and 12.9 Hz, 1H), 2.08 (dddd, J = 1.8, 2.1, 4.5, and 9.0 Hz, 1H), 1.29 (dddd, J = 1.0, 1.6, 4.8, and 9.0 Hz, 1H), 0.43 (t, J = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 150.7, 135.9, 136.2, 135.8, 131.0, 123.7, 81.7, 47.3, 39.0, 34.0, 30.8, 16.9; HRMS-CI $(M + H)^+$ calcd for $C_{15}H_{14}NO_4$ 272.0923, found 272.0919.

Diels−Alder Reaction of Tricyclo[4.2.0.0^{1,5}]oct-3-ene (23) with Isobenzofuran. A mixture of tricyclo[4.2.0.0^{1,5}]oct-3-ene (**23**) (3 mg, 0.028 mmol) in 0.5 mL of decalin and freshly prepared isobenzofuran[26] (0.77 g, 0.66 mmol) in 4.5 mL of benzene was sealed under argon in a thick-walled glass tube. The reaction vessel was immersed in a 115 °C constant temperature oil bath and was heated for 20 h. The ampule was allowed to cool to room temperature before being opened, and the contents were analyzed by GC-MS. Concentration under reduced pressure and purification by column chromatography (5% EtOAc/hexanes) afforded 0.05 g (79%) of compound **25**. Recrystallization from a 1:1 mixture of CH_3CN and pentane afforded useable crystals for X-ray crystallography. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 1H), 7.29−7.14 (m, 3H), 5.30 (d, J = 5.1 Hz, 1H), 5.18 (d, J = 5.4 Hz, 1H), 2.77 (tdd, J = 4.2, 5.4, and 9.0 Hz, 1H), 2.66 (dd, J = 5.1 and 9.0 Hz, 1H), 2.32 (m, 1H), 1.84 (tt, J = 4.2 and 10.8 Hz, 1H), 1.72 (dd, J = 9.0 and 13.4 Hz, 1H), 1.65 (dd, J = 4.2 and 10.8 Hz, 1H), 1.27 (d, J = 4.2 Hz, 1H), 1.06 (quintet, J = 5.4 Hz, 1H), 0.91 (dd, J = 4.2 and 13.4 Hz, 1H), 0.84 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 143.2, 126.5, 126.3, 121.5, 120.9, 83.2, 82.4, 47.8, 46.9, 34.1, 28.6, 28.0, 23.9, 21.7 [one quaternary carbon assignment is absent]; HRMS−FAB M^+ calcd for $C_{16}H_{16}O$ 224.1201, found 224.1194; $(M + Na)^+$ calcd for $C_{16}H_{16}NaO$ 247.1098, found 247.1104.

Acknowledgment. We thank Dr. Gary Dombrowski for bringing this molecule (**1**) to our attention, Drs. Maren Pink and Victor G. Young, Jr. of the X-ray Crystallographic Laboratory at the University of Minnesota for solving the structures of **18** and **25**, and Mr. Dana Reed for assistance in obtaining mass spectrometry data. Support from the National Science Foundation, the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, the Minnesota Supercomputer Institute, and the University of Minnesota-IBM Shared Research Project also are gratefully acknowledged.

Supporting Information Available: X-ray data for **18** and **25**, calculated MP2 structures (*xyz* coordinates) and energies for all of the computed species in this work, and ^{1}H NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO000215R

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