(fraction A) (methanol, 23°, c 1.54): $[\alpha]_{360}$ $-3585°$, $[\alpha]_{353}$ $-4030°$ (tr), $[\alpha]_{311}$ $+13{,}950°$ (pk).

Further boiling of the Schiff base with 1 N hydrochloric acid for 0.5 hr and work-up as before yielded 2.3 g of (+)-**3** (fraction B) (methanol, 23°, c 1.74): $[\alpha]_{360}$ $+4020°$, $[\alpha]_{352}$ $+4880°$ (pk), $[\alpha]_{310}$ $-18{,}100°$ (tr).

Optically Active *trans*-2-Phenylcyclopropanecarboxylic Acid (*trans*-2). Racemic trans acid[10] was resolved by fractional crystallization of the brucine salt[14] and work-up to give material having mp 49.5–50° and $[\alpha]^{26}\mathrm{D}$ $-309°$ (c 1, 95% ethanol) (lit.[14] mp 51–52°, $[\alpha]^{22}\mathrm{D}$ 311.7°).

Friedel–Crafts Cyclization of Acid Chloride from Active *trans*-2. The acid chloride was prepared by reaction of *trans*-**2**, $[\alpha]^{25}\mathrm{D}$ $-259°$ (c 8.5×10^{-2}, methanol), with oxalyl chloride. A 1.0-g sample (5.6 mmol) in 10 ml of dichloromethane was added slowly to a stirred suspension of 1.1 g (8.6 mmol) of aluminum chloride in 25 ml of dichloromethane at 0°. The mixture was kept at 0° for 2 hr and worked up; distillation afforded ketone **3** which showed no detectable rotation in the accessible uv–visible region. Isolated acidic material (0.17 g) also was optically inactive; esterification (diazomethane) and vpc analysis (10% QF-1, DMCS on Chromosorb W, 5 ft × $^1/_8$ in. column, 135°) showed a cis–trans ester ratio of 15:85.

Configurational Stability of Acid Chloride from Active *trans*-2. A portion of *trans*-**2** having $[\alpha]^{26}\mathrm{D}$ $-309°$ (c 1.0, 95% ethanol) was converted to acid chloride (as above); hydrolysis back to *trans*-**2** afforded material having $[\alpha]^{26}\mathrm{D}$ $-307°$ (c 0.189, 95% ethanol).

Optically Active *cis*-2-Phenylcyclopropanecarboxylic Acid (*cis*-2). Dehydroabietylamine (1,2,3,4,4a,9,10,10a-octahydro-7-isopropyl-1,-4a-dimethylphenanthrenemethylamine)[6] (25.3 g, 0.089 mol) was dissolved in a boiling mixture of 1200 ml of methanol and 320 ml of water, and 14.3 g (0.088 mol) of racemic *cis*-**2** was added. Slow cooling of the solutions gave, after 24 hr, 22 g of colorless needles, mp 185–187°. Recrystallization from 90% aqueous methanol yielded 12 g of salt, mp 200–201°. Work-up[6] afforded 4.18 g (95.4%) of *cis*-**2**, mp 83–84°, $[\alpha]^{25}\mathrm{D}$ $-28°$ (c 1.023, $CHCl_3$) (lit.[14] mp 78–98°, $[\alpha]^{23}\mathrm{D}$ $-20°$). Resolved *cis*-**2** from another run had $[\alpha]^{23}\mathrm{D}$ $-27.6°$ ($CHCl_3$) and $[\alpha]^{23}\mathrm{D}$ $-22.1°$ (CH_3OH).

Friedel–Crafts Cyclization of Acid Chloride from (+)-*cis*-2. The acid chloride was made from *cis*-**2**, $[\alpha]^{22}\mathrm{D}$ $+16.6°$ (c 1, methanol), by reaction with oxalyl chloride. A 1.4-g sample was cyclized as described for active *trans*-**2**; work-up and distillation afforded optically inactive ketone **3**. Isolated acidic material (0.26 g) also was optically inactive; esterification (diazomethane) and vpc analysis showed a cis–trans ester ratio of 15:85.

Configurational Stability of Ketone 3. A mixture of (−)-**3** (2.0 g from fraction A, above) and an equivalent amount of aluminum chloride in 40 ml of methylene chloride was kept 20 hr at 0–7°. After a duplicate work-up and redistillation, recovered ketone (1.67 g, 83.5%) had the following ORD features (methanol, 24°, c 1.62): $[\alpha]_{360}$ $-3400°$ (tr), $[\alpha]_{353}$ $-3700°$ (tr), $[\alpha]_{311}$ $+14{,}800°$ (pk).

Epimerization of *cis*-2-Phenylcyclopropanecarboxylic Acid Chloride. A benzene solution of 1.4 g of acid chloride (from *cis*-**2**, $[\alpha]^{22}\mathrm{D}$ $+16.6°$) and 1 ml of thionyl chloride was refluxed 4 hr and allowed to stand 20 hr at room temperature. Benzene and thionyl chloride were removed under reduced pressure. The residual red oil was stirred with 25 ml of water for 16 hr and extracted into ether. Washing, drying, and solvent removal afforded soft, brown crystals. These were charcoaled in benzene–hexane to give 450 mg of yellow, waxy solid, which was esterified by diazomethane in ether. Preparative vpc (20% QF-1, DMCS on Chromosorb W, 10 ft × $^1/_8$ in. column, 135°) provided *trans*-**2** methyl ester, $[\alpha]^{22}\mathrm{D}$ $-97°$ (c 1.02, methanol), and *cis*-**2** methyl ester, $[\alpha]^{22}\mathrm{D}$ $+50.5°$ (c 1.11, methanol). Diazomethane esterification of independently prepared *trans*-**2**, $[\alpha]^{22}\mathrm{D}$ $-314°$ (∼99% optical purity assumed),[4a] gave trans ester, $[\alpha]^{22}\mathrm{D}$ $-319°$; similar esterification of *cis*-**2**, $[\alpha]^{21}\mathrm{D}$ $-10.6°$, gave cis ester, $[\alpha]^{22}\mathrm{D}$ $-31°$.

Acknowledgments. Financial support from the Research Corporation (Frederick Gardner Cottrell grant) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[14] H. M. Walborsky and L. Plonsker, *J. Amer. Chem. Soc.*, **83**, 2138 (1961).

The Persistence of Stereoselectivity in the Intramolecular Diels–Alder Reactions of 5-Alkenylcyclohexa-1,3-dienes. A Novel Route to Functionalized Bridged Tricyclic Rings Using a Regenerable Diene[1]

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Contribution from the Department of Chemistry,
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Abstract: Heating 5-(pent-4-enyl)cyclohexa-1,3-diene (**3**) at 210° leads to predominantly tricyclo[5.3.1.0^{3,8}]undec-9-ene (**11**) by direct stereoselective cyclization. Minor amounts of the epimeric tricyclo[5.2.2.0^{1,5}]undec-8-enes (**26** and **27**) are likely formed through a competing sequence involving the intermediate 1-(pent-4-enyl)cyclohexa-1,3-diene (**9**). Ketones corresponding in their skeletal structure to these tricyclic hydrocarbons have been obtained by heating α-pyrone with hepta-1,6-dien-3-one. These reactions are discussed in the context of the intramolecular Diels–Alder reaction.

The identification[1] of molecules **1** with C_s symmetry as the sole tricyclic products of the thermal Diels–Alder[2] reactions of 5-alkenylcyclohexa-1,3-dienes (**2**) (n = 0, 1, 2) prompted the investigation of the thermal behavior of higher homologs of this system.[3] These

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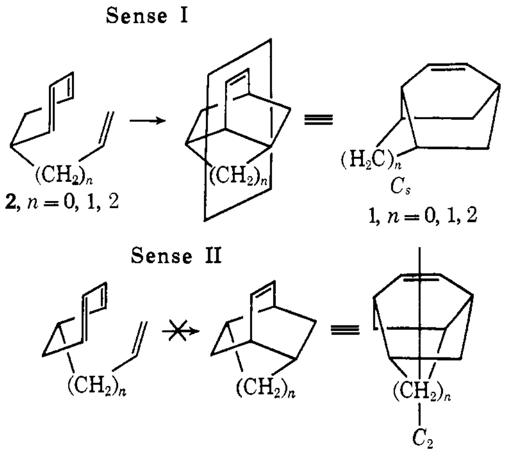
[1] (a) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract ORGN-95. (b) For a preliminary communication, see A. Krantz and C. Y. Lin, *Chem. Commun.*, 1287 (1971).

[2] (a) W. von E. Doering and A. Krantz, to be submitted for publication; (b) A. Krantz, Ph.D. Thesis, Yale University, 1967.

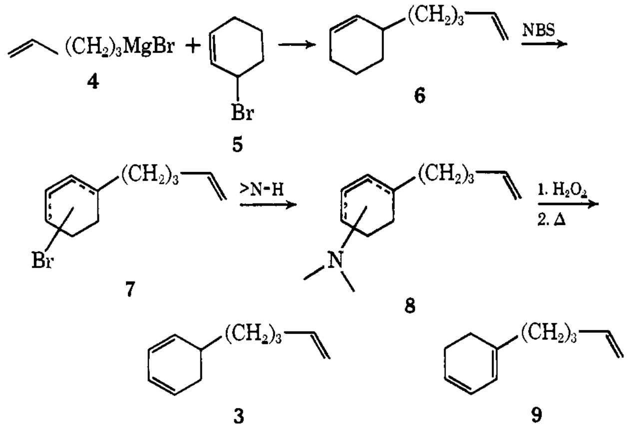
[3] For some general reviews of the Diels–Alder reaction, see (a) M. C. Kloetzel, *Org. React.*, 4, 1 (1948); (b) H. L. Holmes, *ibid.*, **4**, 60 (1948); (c) K. Alder, in "Newer Methods of Preparative Organic Chemistry," Interscience, New York, N. Y., 1948, pp 381–511; (d) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961); (e) A. J. Onishchenko, "Diene Synthesis," Davey, New York, N. Y., 1964; (f) A. Wassermann, "The Diels–Alder Reaction," Elsevier, Amsterdam, 1965;



reactions are of interest because of the incomplete state of knowledge of stereochemical determinants in the Diels–Alder reaction and the dearth of stereospecific routes to doubly bridged tricyclic carbon rings.[4,5] Whereas a number of isolated examples of such systems have been reported, no facile general routes to this class of compounds have been published. The principal objectives of this study were the determination of the course of direct cyclization from 5-(pent-4-enyl)cyclohexa-1,3-diene (**3**) and the development of a ready route to functionalized tricyclic derivatives possessing the bicyclo[2.2.2]octene skeleton.

If the rate of a Diels–Alder reaction is related to the ease with which the dienophile can approach both termini of the diene moiety, then the limited flexibility of the side chain in **2** (n = 0, 1, 2) may have inhibited the vinyl group from bridging the terminal positions of the diene in Sense II, thus resulting in a preference for Sense I addition. From an examination of Dreiding models, the five-membered length of the side chain in **3** would seem to allow bridging of the diene ring by the vinyl group oriented in either Sense I or Sense II without the development of significant angle strain.

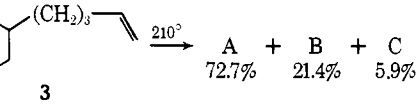
Synthesis of 5-(Pent-4-enyl)cyclohexa-1,3-diene (3). The preparation of 5-(pent-4-enyl)cyclohexa-1,3-diene[6] (**3**) was initiated by coupling the Grignard reagent of 5-bromopentene (**4**) with 3-bromocyclohexene (**5**) to



give 3-(pent-4-enyl)cyclohexene (**6**). Bromination of a fourfold excess of **6** with *N*-bromosuccinimide produced a mixture of allylic bromides **7** which was transformed with dimethylamine in benzene to a mixture of allylic amines **8** that were not characterized. Oxidation of the mixture **8** with 30% hydrogen peroxide, followed by pyrolysis between 105 and 120°, furnished in 68% yield (based on the allylic amines) two isomeric hydrocarbons, **3** and **9**, that were separated by vapor phase chromatography (vpc) and easily characterized from spectral data and by hydrogenation to *n*-pentylcyclohexane (see Experimental Section). In a series of runs the ratio of the products **3**:**9** varied from 1.8 to 2.76:1.[7]

Results

Heating 5-(pent-4-enyl)cyclohexa-1,3-diene (**3**) (>99.9% pure by vpc) in the gas phase at 210° for 21 hr led to three tricyclic products—A, B, and C—in the



ratios of 72.7:21.4:5.9. Each isomer was analyzed for $C_{11}H_{16}$ and possessed a parent peak in the mass spectrum at m/e 148. The major product, A, was a colorless solid (mp 41–43°) which exhibited ir absorption due to unsaturation[5] at ν 3042 and 1611 cm^{-1} and displayed only end absorption (hexane) in the ultraviolet spectrum. The presence of nonidentical allylic protons at δ 1.96 and 2.4 ppm and the symmetrical pattern displayed in the olefinic region of the 300-MHz nmr

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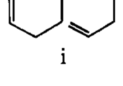
(g) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); **6**, 16 (1967); (h) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968); (i) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), have discussed Diels–Alder reactions in relation to orbital symmetry correlations; (j) H. Wollweber, in "Methoden der Organische Chemie," Houben-Weyl, Vol. 5, Part 3, 1970, p 976; (k) S. Seltzer, *Advan. Alicycl. Chem.*, **2**, 1 (1968).

(4) The doubly bridged tricyclics under discussion are arbitrarily defined herein as systems which possess two nonzero bridges, with each bridge spanning a set of noncontiguous atoms numbered (n, m) and (p, q), respectively, where $n < p < m$.

(5) Representatives of this class have been prepared as follows. (a) By multistep conventional routes, as in H. W. Whitlock, Jr., *J. Amer. Chem. Soc.*, **84**, 3412 (1962); A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1613, 1615 (1965); R. R. Sauers, R. A. Parent, and S. B. Damie, *ibid.*, **88**, 2257 (1966); B. R. Vogt and J. E. Hoover, *Tetrahedron Lett.*, 2841 (1967); B. R. Vogt, *ibid.*, 1575, 1579 (1968); S. A. Monti and S. S. Yuan, *J. Org. Chem.*, 36, 3350 (1971); R. R. Sauers and J. C. Oppelt, *Tetrahedron*, **25**, 613 (1961). (b) For photochemical syntheses, see H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6266 (1971); A. Padwa and W. Eisenberg, *ibid.*, **94**, 5859 (1972); J. Meinwald and B. E. Kaplan, *ibid.*, **89**, 2611 (1967); J. Meinwald and R. A. Schneider, *ibid.*, **87**, 5218 (1965); R. R. Sauers, W. Schinski, M. M. Mason, E. O'Hara, and B. Byrne, *J. Org. Chem.*, **38**, 642 (1973), and references therein; R. Noyori, H. Inoue, and M. Kato, *Chem. Commun.*, 1695 (1970), and references therein; F. S. Lewis and R. A. Ruden, *Tetrahedron Lett.*, 715 (1971). (c) *Via* metal and metal halide promoted rearrangements: J. T. Groves and B. S. Packard, *J. Amer. Chem. Soc.*, **94**, 3252 (1972); P. v. R. Schleyer and M. M. Donaldson, *ibid.*, **82**, 4645 (1960); P. v. R. Schleyer and E. Wiskott, *Tetrahedron Lett.*, 2845 (1970); W. Grimme, *Chem. Ber.*, **100**, 113 (1967). (d) By solvolytic rearrangement: H. W. Whitlock, Jr., and M. W. Siefkin, *J. Amer. Chem. Soc.*, **90**, 4929 (1968); B. E. Ratcliffe and C. H. Heathcock, *J. Org. Chem.*, **37**, 531 (1972); R. R. Sauers, K. W. Kelly, and B. K. Sickles, *ibid.*, **37**, 537 (1972). (e) Thermal routes include: J. N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schröder, *J. Amer. Chem. Soc.*, **89**, 612 (1967); P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 2493 (1968); L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 72, 181 (1972), and references therein.

(6) After the present study was begun, G. Brieger and D. R. Andersen, *J. Org. Chem.*, **36**, 242 (1971), reported a ready synthesis of **3**.

(7) Since both **3** and **9** were required for this study, a route involving **6** was chosen. When 4-(pent-4-enyl)cyclohexene (i) was subjected to



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a procedure essentially identical with that employed for the diene **6**, mixtures of **3** and **9** were obtained in ratios as high as 15:1: A. Krantz, unpublished results.

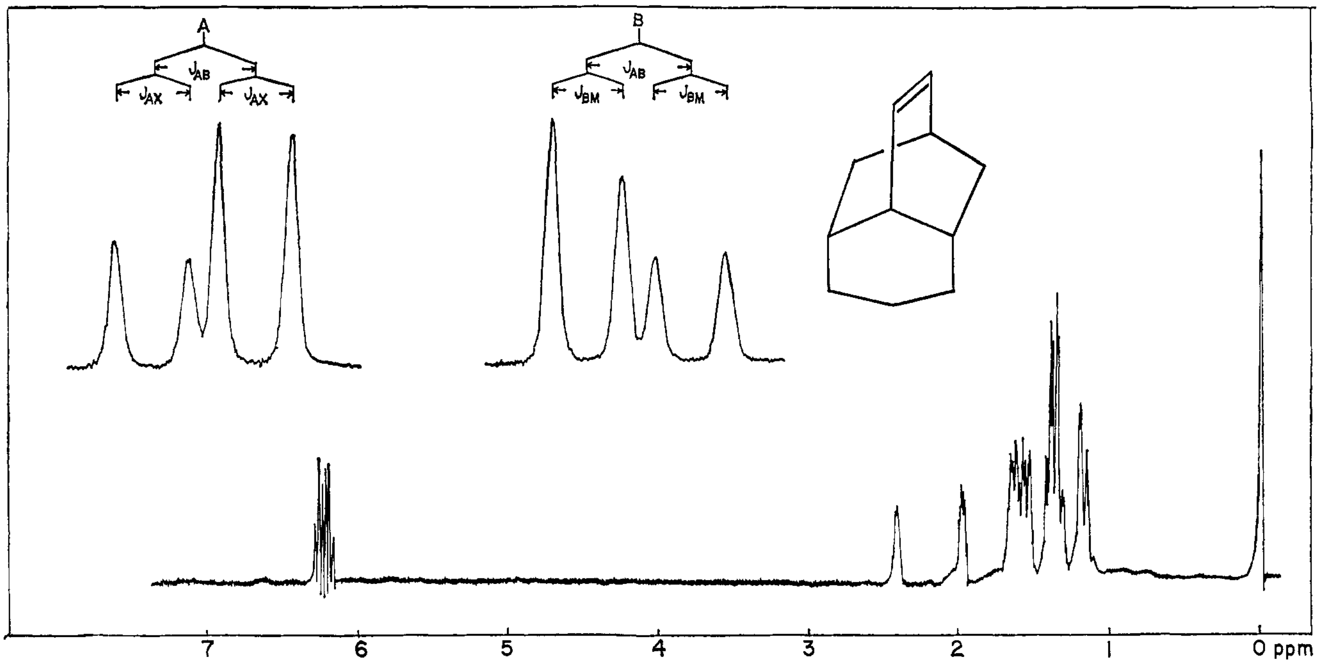
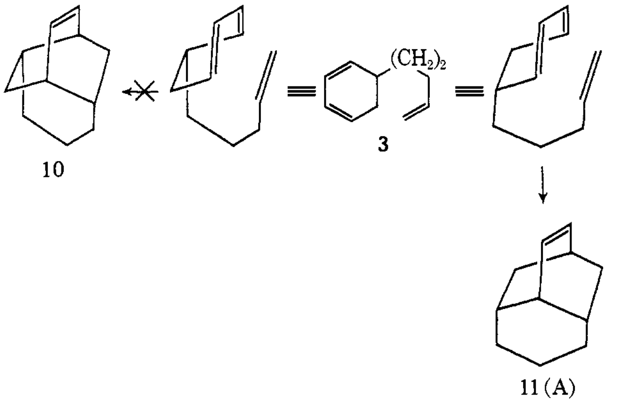


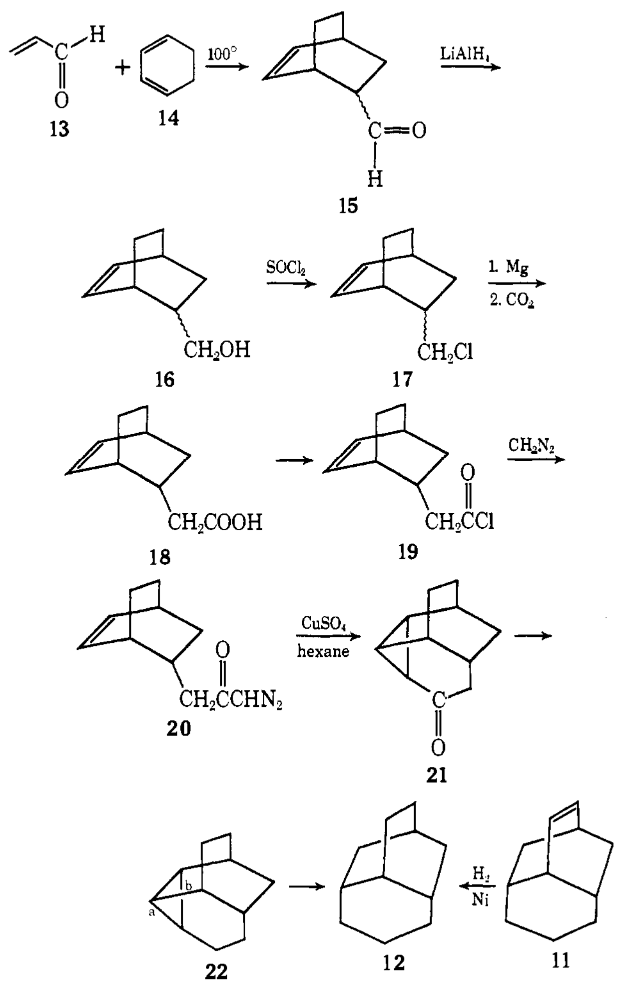
Figure 1. The 300-MHz nmr spectrum of product A (tricyclo[5.4.0.0^{3,9}]undec-8-ene (**11**)) in carbon tetrachloride. The olefinic protons (decoupled from their distal allylic protons) are shown above the full spectrum.

spectrum (Figure 1) are noteworthy features. Field sweep decoupling experiments revealed strong coupling of the high field allylic proton (δ 1.96 ppm, J = 5.8 Hz) to the low field olefinic proton (δ 6.27 ppm) and similar coupling (J = 5.6 Hz) of the low-field allylic proton (δ 2.4 ppm) to the high field (δ 6.16 ppm) olefinic hydrogen. The emergent patterns are shown above the full spectrum in Figure 1, and together clearly indicate the underlying AB character of the olefinic protons (J_{AB} = 8.2 Hz).[8]

Although A cannot be tricyclo[5.4.0.0^{3,9}]undec-8-ene (**10**), which possesses a set of equivalent allylic and a set of equivalent olefinic protons, the data are entirely consistent with tricyclo[5.3.1.0^{3,8}]undec-9-ene (**11**), the



product of Sense I addition.[9] That A indeed possesses



the tricyclo[5.3.1.0^{3,8}]undecane skeleton is confirmed by the independent synthesis of tricyclo[5.3.1.0^{3,8}]decane (**12**) and the identity of its physical properties with those of hydrogenated A.

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[8] This value is consistent with the coupling constants of a number of bicyclo[2.2.2]octene derivatives and appears to be characteristic of the bicyclo[2.2.2]octene framework. M. A. Cooper and S. L. Manatt, *J. Org. Mag. Res.*, 2, 511 (1970), have furnished accurate data in support of the claim that cis vicinal proton–proton coupling constants in cycloalkenes are dependent on ring size.

[9] The intermolecular Diels–Alder reaction of a monosubstituted olefin with a 5-alkylcyclohexa-1,3-diene could lead to as many as four adducts. In the case of thermally reorganized **3**, the structures of adducts which contain a trimethylene bridge trans-fused to the C_2 and C_6 positions of a bicyclooctene unit are excluded from consideration because of prohibitive strain.

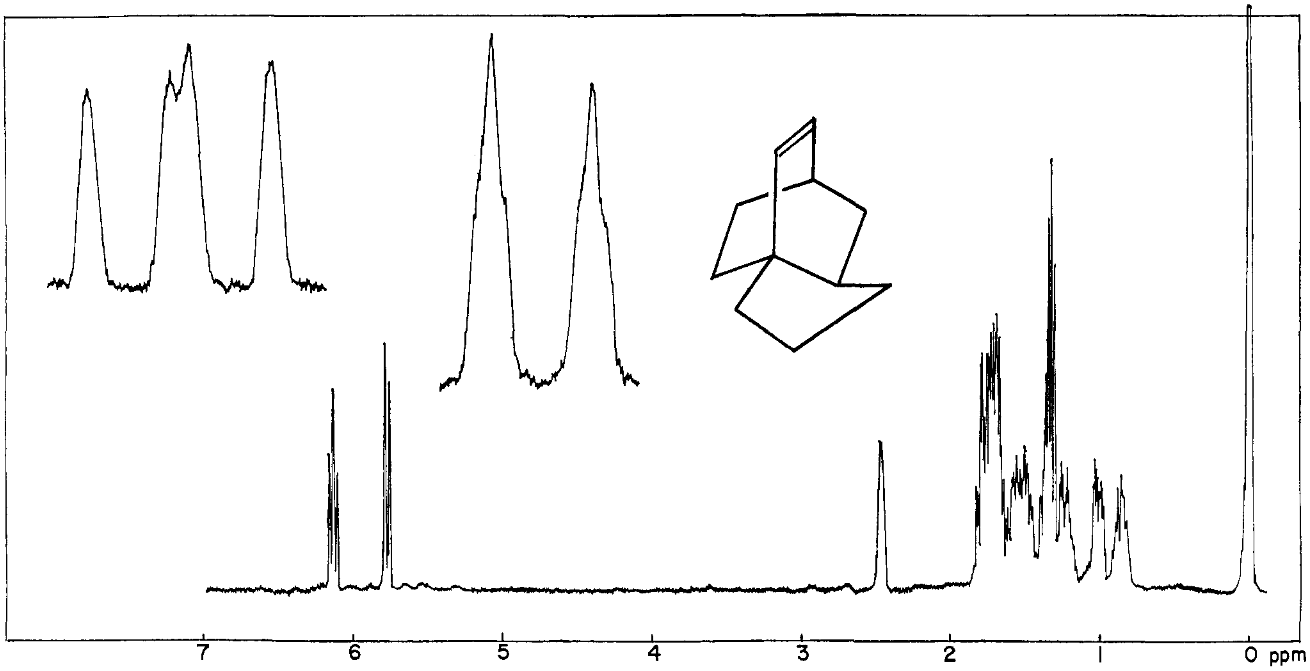
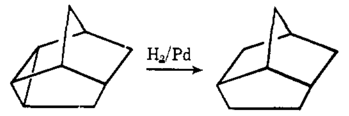


Figure 2. The 300-MHz nmr spectrum of product B (*endo*-tricyclo[5.2.2.0^{1,5}]undec-8-ene (**26**)) with signals due to olefinic protons expanded above the full spectrum.

Hydrocarbon **12** was synthesized by a path commencing with the condensation of acrolein (**13**) with cyclohexa-1,3-diene (**14**),[10] and is detailed in the Experimental Section. Interestingly, nickel-catalyzed hydrogenation of **22** produced a substance which was homogeneous on several vpc columns, identical[11] with hydrogenated A, and which was formulated as tricyclo[5.3.1.0^{3,8}]decane (**12**). It should be noted that while the specificity of hydrogenation is unusual, it is not unprecedented. Nickon[12] and coworkers and Krantz and Doering[2] have observed selective catalytic hydrogenation in the structurally related systems **24** and **25**, respectively.



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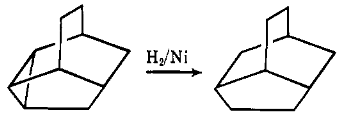

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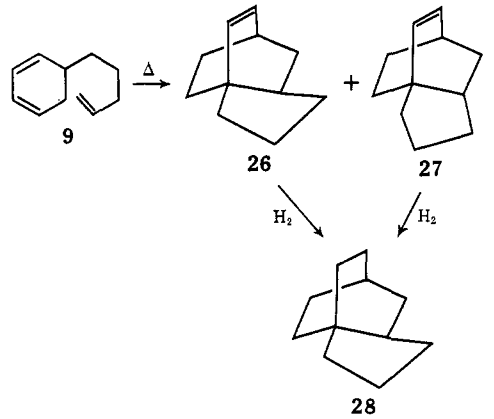
Proof of the structures B and C was more problematical. The most revealing features of the 300-MHz nmr spectrum of B (pictured in Figure 2) were absorption by a single allylic proton at δ 2.49 ppm (1) and signals in the olefinic region at δ 5.79 (d, 1, J_{AB} = 8.2 Hz)[8] and 6.15 ppm (dd, 1, J_{AX} = 6.2, J_{AB} = 8.2 Hz).[8] The 60-MHz nmr spectrum of C displayed absorption at δ 0.77–1.93 (m, 13) and 2.41 ppm (br singlet, 1, allylic), and an essentially reversed pattern from that of B in the olefinic region at 6.03 (dd, 1, J_{BX} = 6.2, J_{AB} = 8.2 Hz) and 6.25 ppm (d, 1, J_{AB} = 8.2 Hz). The value of J_{AB} = 8.2 Hz for the olefinic coupling in both B and C is commonly observed for bicyclooctenes and differs quite significantly from the reported values for norbornene (5.68 Hz), bicyclo[3.2.1]oct-2-ene (9.5 Hz), bicyclo[3.2.1]oct-6-ene (5.8 Hz), and their derivatives.[8,13]

Based on the nmr spectra, speculation centers about the structures *endo*- and *exo*-tricyclo[5.2.2.0^{1,5}]undec-8-ene (**26** and **27**, respectively) which fit the data for B and C. This hypothesis is mechanistically plausible since **26** and **27** can formally be derived from Diels–Alder reactions of **9**, which in turn can be the result of a [1,5] shift of hydrogen from **3**. Indeed, thermal reorganization of **9** at 208° afforded only B and C in a ratio essentially identical with that observed from heating **3** under said conditions. That B and C were endowed with the same carbon skeleton was substantiated by hydrogenation of either olefin to a common saturated tricyclic hydrocarbon **28**.



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(10) O. Diels, K. Alder, E. Petersen, and F. Queberitz, *Justus Liebigs Ann. Chem.*, **478**, 137 (1930).

(11) The criteria of superimposability of ir and nmr spectra, identity of melting points, and identity of retention times on several vpc columns were employed and this rules out tricyclo[5.4.0.0^{3,9}]undecane (**23**), the product of hydrogenation of bond a in **22**.

(12) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Amer. Chem. Soc.*, **87**, 1615 (1965).

(13) R. V. Moen and H. S. Makowski, *Anal. Chem.*, **39**, 1860 (1967).

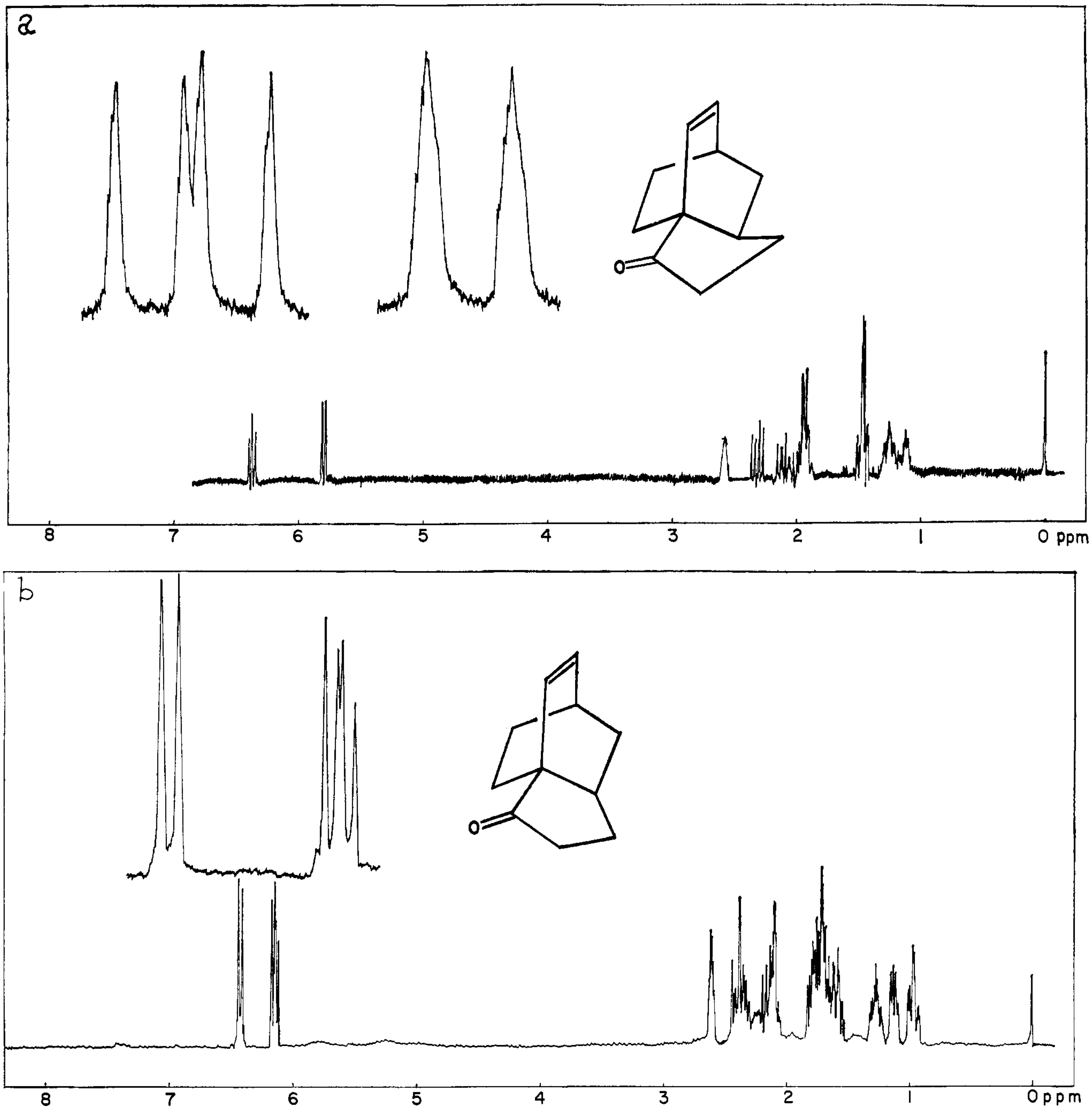
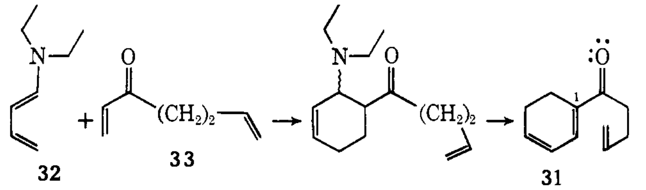


Figure 3. a. The 300-MHz nmr spectrum of *endo*-tricyclo[5.2.2.0^{1,5}]undec-8-en-2-one (**29**) with signals due to olefinic protons, expanded and shown above the full spectrum. b. The 300-MHz nmr spectrum of *exo*-tricyclo[5.2.2.0^{1,5}]undec-8-en-2-one (**30**) with signals due to olefinic protons, expanded and shown above the full spectrum.

To confirm the presence of a five-membered ring in B and C, a route to the *endo*-tricyclo[5.2.2.0^{1,5}]undec-8-en-2-one (**29**) and its exo epimer **30** was devised.



Synthesis of 1-(cyclohexa-1,3-dien-1-yl)pent-4-en-1-one (**31**) in 42.7% overall yield was effected by condensing 1-diethylaminobutadiene[14] (**32**) with hepta-1,6-dien-3-one[15] (**33**), followed by treatment of the intermediate amino ketones with acid.

At 227° in the gas phase **31** was quantitatively converted to a mixture of isomeric tricyclic ketones which were separated by vpc using a 5% FFAP column (5 ft × 0.25 in.). The faster moving component was designated as *endo*-tricyclo[5.2.2.0^{1,5}]undec-8-en-2-one (**29**, 79%), while the minor product (21%) was assigned the structure of the exo epimer **30** (*vide infra*). Nmr spectra of these isomers are portrayed in Figure 3.

Each isomer showed nmr resonances due to a single allylic proton and had carbonyl absorption characteristics of five-membered ring ketones in the vicinity of

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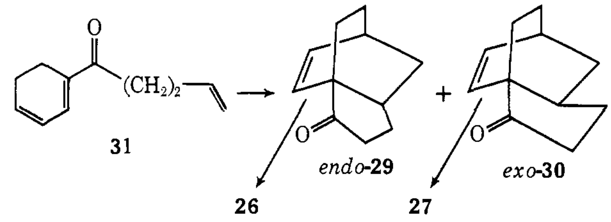
[14] This method is an adaptation of a general synthesis of 1-substituted cyclohexa-1,3-dienes developed by S. Hunig and H. Kahanek, *Chem. Ber.*, **90**, 243 (1957).

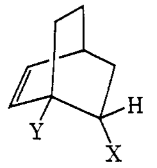
[15] B. S. Kupin, A. A. Petrov, and D. A. Koptev, *Zh. Obshch. Khim.*, **32**, 1758 (1962).



ν 1740 cm^{-1}.[5] The 300-MHz nmr spectrum (Figure 3a) of the major product **29** exhibited peaks in the olefinic region at δ 5.82 (d, 1, J_{AB} = 8.2 Hz) and 6.38 ppm (dd, 1, J_{AB} = 8.2, J_{BX} = 6.5 Hz). An essentially reversed pattern of absorption (Figure 3b) was displayed by the minor component in the olefinic region at δ 6.15 (dd, 1, J_{AB} = 8.2 Hz, J_{BX} = 6.2) and 6.43 ppm (d, 1, J_{AB} = 8.2 Hz).

A strikingly similar example of reciprocity between olefinic spectral patterns was noted above for the isomeric hydrocarbons **26** and **27**. Not surprisingly, the major product **29** from heating **31** could be related to B and **30** could be converted to C by Wolff–Kishner reductions. These relations thus substantiate the presence of a five-membered ring in B and C and, with the previously described data, impose a common structural framework necessarily that of the carbon skeleton of tricyclo[5.2.2.0^{1,5}]undecane on both pairs of epimers.

The assignment of structure **26** to product B is provisionally based on examination of the nmr spectra of certain epimeric 5-substituted derivatives of bicyclo[2.2.2]oct-2-ene. Ouellette[16] has noted that the difference in chemical shift of the two vinyl hydrogens is larger for the endo isomer than for the exo isomer in the cases of the carbomethoxy (**34a–35a**) and nitrobicyclooctenes (**34b–35b**). The spectra of the endo epimers **34c–e** are also broader in the olefinic region than the corresponding exo compounds.[17]



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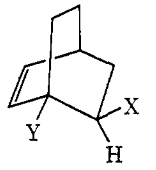
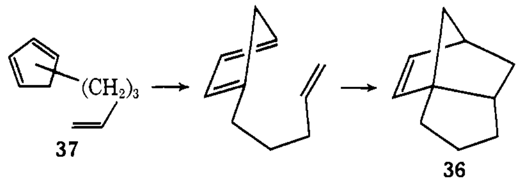


35

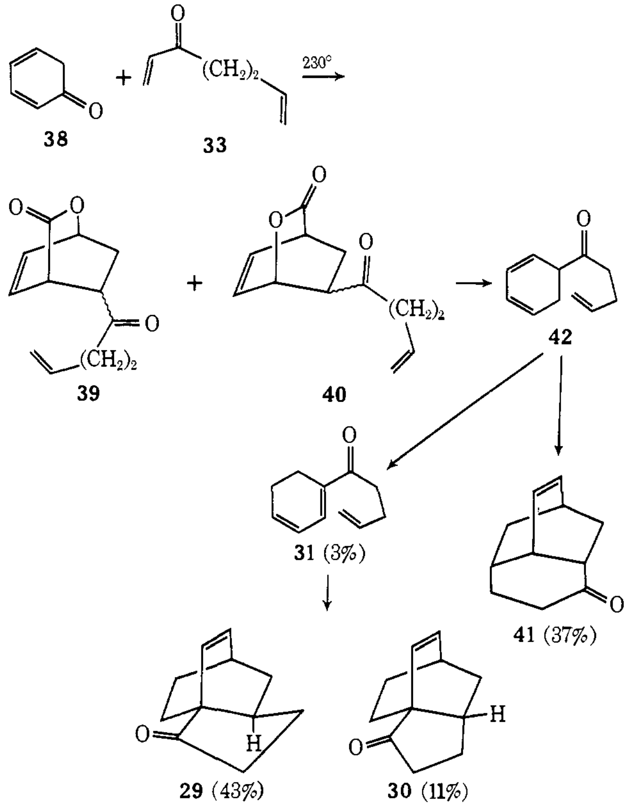
a, X = CO_2CH_3; Y = H
b, X = NO_2; Y = H
c, X = OH; Y = CH_3
d, X = OAc; Y = CH_3
e, X = OTs; Y = CH_3

A similar phenomenon has been observed in the norbornene system in which the chemical shift difference between olefinic protons of a wide range of compounds was 10–15 Hz for the endo isomer and was much less for the exo compound.[13,18] The exo and endo structural assignments for **26** and **27** are also in line with the notion that repulsive interactions between the protons of the incipient five-membered ring and the atoms of the developing bicyclooctene ring are greater in the activated complex leading to **27** than in that from which **26** arises.[19]

Finally, our attribution of structure **26** to the major product of thermally reorganized **9** parallels Corey's[20] assignment of **36** to the only product reported from heating (pent-4-enyl)cyclopenta-1,3-diene bond isomers (**37**).



A Novel Route to Bridged Tricycloundecenones. Ready entry into the tricyclic ring systems of **11**, **26**, and **27** was achieved by heating α-pyrone **38** with 1,6-heptadien-3-one (**33**). The novel feature of this synthetic method involves generating from two reactive components a substituted cyclohexa-1,3-diene which can rapidly undergo intramolecular condensation with a suitably disposed double bond. In the case of α-pyrone, the thermal lability of intermediates of the type **39** and **40** is exploited.[21,22] Analogous routes to bridged tricyclic rings can be formulated using the "ene" synthesis of cyclohexa-1,4-diene[23] or Diels–Alder reactions of either cyclopentadienones[24] or of



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[16] R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, 30, 423 (1965).

[17] We thank Professor J. A. Berson of Yale University for making available unpublished spectra of these compounds for our examination.

[18] The assignments to B and C are, of course, tentative, as the effect of alkyl substituents X on the olefinic region has not been studied.

[19] In noting the preference of a substituent for the endo position in bicyclooctenes, R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, 31, 3065 (1966), suggested that "the preference was undoubtedly a reflection of the unfavorable interaction between a substituent in the exo position and the syn-7 proton."

[20] E. J. Corey and R. S. Glass, *J. Amer. Chem. Soc.*, **89**, 2600 (1967).

[21] Reference 3e, Chapter VII, p 572.

[22] For a recent example of a double diene synthesis with a pyrone, see T. Imagawa, M. Kawanisi, and K. Sisido, *Chem. Commun.*, 1292 (1971).

[23] K. Alder, F. Brochhagen, C. Kaiser, and W. R. Roth, *Justus Liebigs Ann. Chem.*, **593**, 1 (1955); (b) L. Dorfman, E. Donoghue, C. F. Huebner, F. A. Stuber, N. Danielli, and E. Wenkert, *Tetrahedron Lett.*, 1185 (1966).

[24] G. I. Fray and A. W. Oppenheimer, *Chem. Commun.*, 599 (1967).

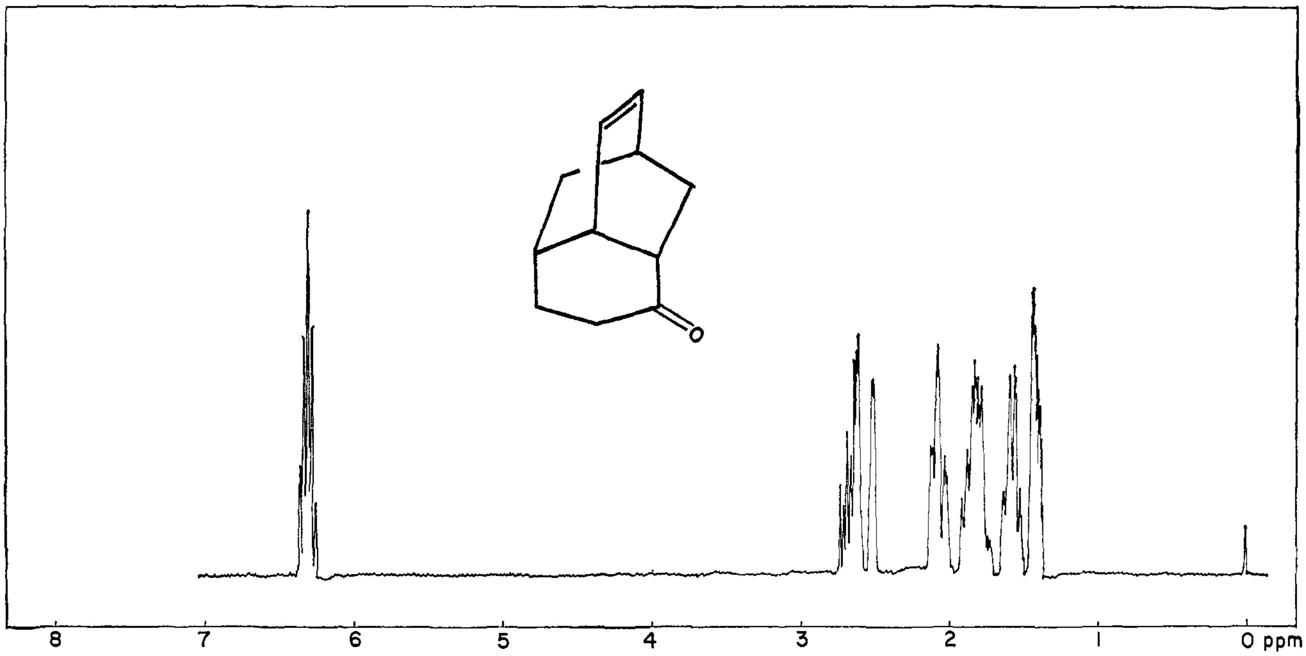


Figure 4. The 300-MHz nmr spectrum of tricyclo[5.3.1.0^{3,8}]undec-9-en-4-one (**41**).

thiophene dioxides[25] with appropriately substituted bis dienophiles.

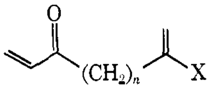
Heating α-pyrone **38** with **33** at 227–232° produced a mixture of three isomeric tricyclic ketones, along with 3% of the conjugated ketone **31**. The first two substances to elute from a 15% Carbowax 20M column proved to be *endo*-tricyclo[5.2.2.0^{1,5}]undec-8-ene (**29**, 43%) and the exo epimer **30** (11%).

The structure of the slowest moving component was established as tricyclo[5.3.1.0^{3,8}]undec-9-en-4-one (**41**, 37%) based on its conversion to **11** by Wolff–Kishner reduction and the following spectral considerations.

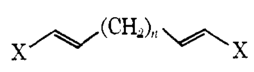
The uv spectrum of **41** with low intensity absorption at $\lambda_{\max}^{\mathrm{EtOH}}$ 284.5 nm (ϵ 90.6) and the ir spectrum with bands at ν (CCl_4) 3064, 1708, and 1665 cm^{-1} (w) indicated an unconjugated carbonyl in a ring larger than five members.[26] The fact that **41** can be related to **11** and possesses an nmr spectrum (Figure 4) indicating three acetonyl and two allyl protons is uniquely consistent with the tricyclo[5.3.1.0^{3,8}]undec-9-en-4-one structure.

Whereas the formation of **41** indicates that the bis-dienophilic starting material need not contain more than one activated double bond to achieve a double diene synthesis, it should be noted that the intramolecular Diels–Alder reaction of the likely intermediate **42** is not rapid enough to prevent formation of ketones **29** and **30** through a pathway mediated by **31**. Because of an increasingly unfavorable entropy factor for cyclization of higher homologs of **42**, complicating side reactions resulting from [1,5] hydrogen shifts[27] would be expected to seriously weaken this method as a general route to Diels–Alder adducts of 5-substituted cyclohexa-1,3-dienes.[28] Thus, thermal reorganizations of higher homologs of **42** (and **3**) should resemble reactions in the cyclopentadiene series[29–31] in which intramolecular diene syntheses are preceded by [1,5] hydrogen shifts, a situation which results in a competition for tricyclic product among the various bond isomers. The prospect of a high yield route to tricyclic adducts from higher homologous 5-alkenylcyclohexa-1,3-dienes is undermined by an unfavorable entropy factor which frustrates direct cyclization and allows the intervention of equilibrating hydrogen shifts.

This difficulty may be overcome by appropriate modification of the dienophile since it is well known that activation of an olefin by a strong electron-withdrawing substituent causes a substantial increase in the rate of its reactions with electron-rich dienes.[3e–g] The final, internal cyclization in the double diene synthesis should proceed much more rapidly using species **43** or **44** than using their mono-activated analogs, whereas the rate of competing ring hydrogen shifts should be essentially unaffected by these modifications to the side chain. Depending on the extent of activation of the bis dienophile (and the value of n in **43** and **44**) bridged tricyclic rings may be derived from either 1- or 5-substituted cyclohexa-1,3-dienes.



43



44

X = CN, COR, COOR...

Some support for this analysis is drawn from the results of heating α-pyrone with methyl vinyl ketone.[32]

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[25] H. Bluestone, R. Bimber, R. Berkey, and Z. Mandel, *J. Org. Chem.*, 26, 346 (1961).

[26] G. Berthier and J. Serre, in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Vol. 1, Wiley-Interscience, New York, N. Y., 1966, pp 17–28.

[27] D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966).

[28] In the lower homologs this complication from the competing Diels–Alder reaction of the 1-isomer is vitiated because of prohibitive strain in the tricyclic adducts.

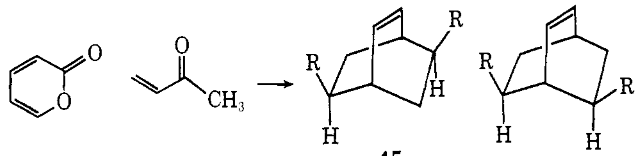
[29] S. McLean and P. Haynes, *Tetrahedron Lett.*, 2385 (1964).

[30] G. Brieger, *J. Amer. Chem. Soc.*, 85, 3783 (1963).

[31] G. Brieger and D. R. Andersen, *J. Org. Chem.*, 36, 243 (1971).

[32] H. E. Zimmerman and R. M. Paufler, *J. Amer. Chem. Soc.*, 82, 1514 (1960).

The fact that 5,7- and 5,8-diacetylbicyclo[2.2.2]-2-octenes (**45** and **46**, respectively) are formed in good yield suggests that even intermolecular capture of 5-substituted cyclohexa-1,3-dienes can compete favorably with internal hydrogen shifts. Hence, the potential of this method for generating derivatives of alkenylcyclohexa-1,3-dienes for the synthesis of bridged tricyclic rings can be exploited by a judicious choice of binary dienophiles with regenerable dienes.



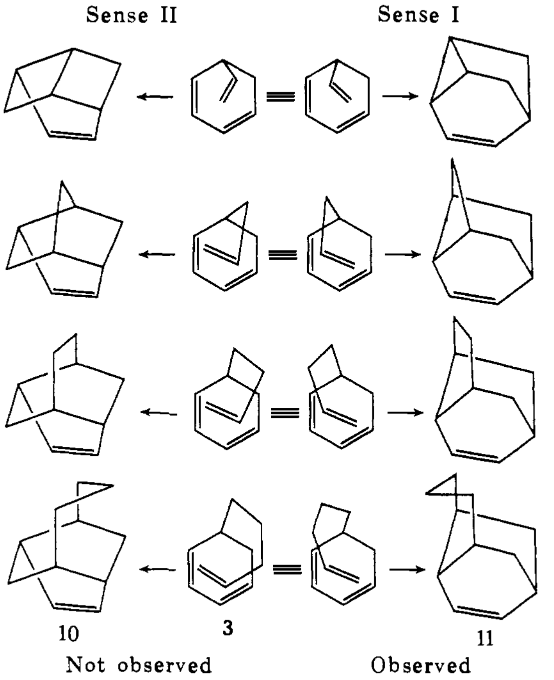
45 **46**

R = COCH$_3$

Discussion

The identification of tricyclo[5.3.1.0^{3,8}]undec-9-ene (**11**) as the sole tricyclic product[33] of direct cyclization of 5-(pent-4-enyl)cyclohexa-1,3-diene (**3**) strengthens the conclusion drawn from the previous observations with the lower homologs that only tricyclic products from Diels–Alder addition in Sense I are obtained. This remarkable expression of stereoselectivity is summarized in Scheme I.

Scheme I



Studies of intramolecular reactions[23,34] in other cyclic dienes have been complicated by competing sigmatropic shifts of hydrogen,[20,30,31,35] which ultimately lead to mixtures of tricyclic products in the cycloheptadiene series and to stereoselective formation of products derived either from the 1[20,30] or the 5 isomer[31] in thermal reorganizations of cyclopentadienes challenged by a vinyl group.

The most obvious distinction between the isomers **10** and **11** is the seven- and six-membered rings formally derived from alternative modes of connecting the trimethylene unit to opposing ethano bridges of the bicyclooctene framework. The reaction of **3** to give either **10** or **11** would be very exothermic.[36]

Since **11** is stable to 370°, the unknown olefin **10** must undoubtedly be stable to the much less severe conditions (170–210°) used to reorganize **3**. Consequently, the formation of **11** must be the result of a kinetically controlled reaction. If 1% of **10** had gone undetected in the reaction mixture, then the free energy of activation must favor **11** over **10** by a minimum of 3.7 kcal/mol ($-RT \ln k_2/k_1$, where $T = 170° + 273.2 = 443$°K and $k_2/k_1 = 72.7/1$).

Although this minimum difference of 3.7 kcal/mol is substantial, the results of Schmid indicate that the preference for Sense I addition can be abolished by appropriate modification of the basic alkenyl cyclohexadiene framework. Thus, Schmid[40] observes that the mesityl ether **46** rearranges at 180° to two tricyclic ketones in a ratio of 1:1 presumably *via* alternative Diels–Alder reactions of the unisolated ortho diene **47**.

Similarly[41] reorganization of the cyclohexadienone **50** in hot benzene produces a mixture of the homotwistanone derivative **51** and its isomer **52**.

The formation of Sense II product in these examples

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(33) The possibility that significant amounts of 10 were formed from 3 is unlikely based on the appearance of the spectra of individual products and their homogeneity on numerous vpc columns.

(34) (a) H. O. House and T. H. Cronin, *J. Org. Chem.*, 30, 1061 (1965), have compiled a listing of some early examples of internal Diels–Alder reactions in their study of the thermal behavior of nona- and decatrienoates. (b) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, 92, 3118 (1970), and references therein, have invoked internal Diels–Alder reactions in the thermal and photochemical transformations of the isomeric (CH)$_{10}$'s. (c) For examples in the cyclophane series, see H. H. Wasserman and A. R. Doumaux, *J. Amer. Chem. Soc.*, 84, 4611 (1962); H. H. Wasserman, A. R. Doumaux, and R. E. Davis, *ibid.*, 88, 4517 (1966); H. H. Wasserman and P. M. Keehn, *ibid.*, 88, 4522 (1966); H. H. Wasserman and R. Kitzing, *Tetrahedron Lett.*, 3343 (1969); D. J. Cram, C. S. Montgomery, and G. R. Knox, *J. Amer. Chem. Soc.*, 88, 515 (1966). (d) L. H. Klemm, D. R. Olson, and D. V. White, *J. Org. Chem.*, 36, 3740 (1971), and references therein, have reported internal Diels–Alder reactions in aromatic diene systems. (e) For the 5-vinylcyclohexa-1,3-diene–tricyclo[3.2.1.0^{3,7}]oct-3-ene transformation: W. von E. Doering and W. R. Roth, *Tetrahedron*, 19, 715 (1963); W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, 685, 56 (1965); P. Heimbach, K. L. Ploner, and F. Thömel, *Angew. Chem., Int. Ed. Engl.*, 10, 276 (1971); T. Imagawa, M. Kawanishi, and K. Sisido, *Chem. Commun.*, 1292 (1971); H. E. Zimmerman and G. L. Grunwald, *J. Amer. Chem. Soc.*, 86, 1434 (1964). (f) Internal Diels–Alder reactions of 6-alkenylcyclohexa-2,4-dienones have been invoked in studies of the anomalous Claisen reaction by J. Zsindely and H. Schmid, *Helv. Chim. Acta*, 51, 1510 (1968). (g) See N. Fukayama, M. Kato, and A. Yoshikoshi, *Chem. Commun.*, 1120 (1971), for a diene synthesis of a derivative of 3. (h) For photochemical Diels–Alder reactions: R. A. Schneider and J. Meinwald, *J. Amer. Chem. Soc.*, 89, 2023 (1967), but see W. G. Dauben and M. S. Kellogg, *ibid.*, 94, 8951 (1972), for a comment.

(35) (a) C. A. Cupas, W. Schumann, and W. E. Heyd, *J. Amer. Chem. Soc.*, 92, 3237 (1970). (b) C. A. Cupas, M. A. Kong, M. Mullens, and W. E. Heyd, *Tetrahedron Lett.*, 3157 (1971). (c) C. A. Cupas, W. E. Heyd, and M. S. Kong, *J. Amer. Chem. Soc.*, 93, 4623 (1971). (d) But see L. Hodakowski and C. A. Cupas, *Tetrahedron Lett.*, 1009 (1973).

(36) From thermochemical data the heat of the reaction of cyclohexa-1,3-diene (+25.38)[37] with ethylene[37] (+12.45) to give bicyclooctene[38] (+4.88) is calculated to be −33.0 kcal/mol. The reaction of 3 to give 10 would be expected to be not much less exothermic than −33.0 minus the strain of cycloheptane[39] (7 kcal/mol) or −26 kcal/mol.

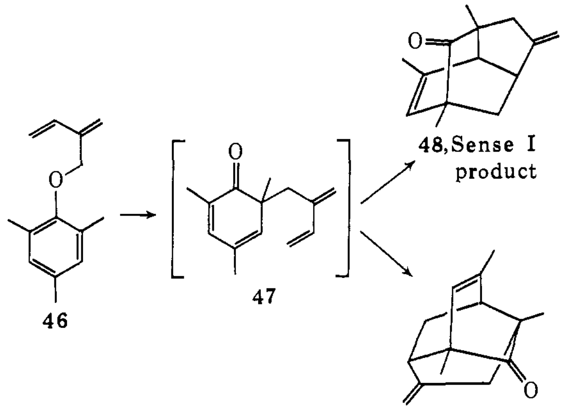
(37) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, p 142.

(38) S. S. Wong and E. F. Westrum, Jr., *J. Amer. Chem. Soc.*, 93, 5317 (1971).

(39) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(40) H. Schmid, J. Zsindely, and H. J. Hansen in "XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., 1971, Special Lectures," Vol. 1, Butterworths, London.

(41) H. Greuter, G. Frater, and H. Schmid, *Helv. Chim. Acta*, 55, 526 (1972).

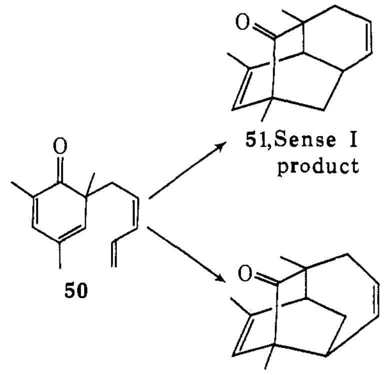


46

47

48,Sense I product

49,Sense II product



50

51,Sense I product

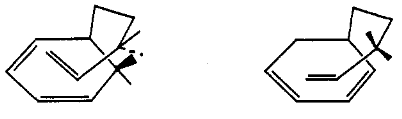
52,Sense II product

is not unexpected in light of experience with diene condensations between asymmetric dienes and dienophiles, which are *almost always* structurally directed.[42] Although theoretical interpretation of the nature of the structural specificity is still at issue, very often the reaction course can be rationalized by assuming a two-step process involving a diradical intermediate compelled to preserve the stereochemical integrity of the starting materials. One can then correlate the substitutive pattern in the product with the most highly stabilized "diradicals." In the cases of **46** and **50**, diradicals related to the products of Sense II addition enjoy an allylic[43] and an oxapentadienylic stabilization,[44] whereas (in this formal representation) the products **48** and **51** must be formed from diradicals experiencing the lesser benefit of only allylic stabilizations.

The most popular model adopted for the geometry of approach of diene and dienophile in the Diels–Alder reaction assumes the molecules are oriented in two parallel planes.[3d–k] If the rate of formation of product is a function of the components' ability to achieve this orientation, then the marked preference for addition in Sense I in 5-alkenylcyclohexa-1,3-dienes is interpretable on the basis of conformational factors. Inspection of molecular models of **3** indicates that diene and dienophilic moieties can most easily be brought into close approximation for maximum overlap when aligned in sense I. In the Sense II orientation, repulsive interactions between an allylic proton of the side chain and the proximate hydrogen attached to C_5 of the ring

Sense II orientation

Sense I orientation



inhibit the parallel plane arrangements of the reactive components. Additional factors which may be stereochemical determinants are van der Waals and torsional interactions between protons of the incipient trimethylene bridge and those of the developing bicyclooctene unit. These interactions may be more severe in the activated complex leading to **10** than in that leading to **11**. The preference for **11** may also be related to the observation that six-membered rings are formed more readily than seven,[45] or perhaps to some more subtle[46] factor. In a general sense, the same factors which stabilize six-membered rings more than seven (and probably **11** more than **10**) could be operative along the reaction path leading from **3** to tricyclic product and be responsible for the observed kinetic preference for **11**.

It is in a sense futile to speculate on the stereochemical factors which determine orientation, rate, and specificity in the intramolecular Diels–Alder reaction without knowledge of the nature of the mechanism(s) involved. Clearly the antarafacial and/or suprafacial nature of the addition to the dienophilic component in alkenylcyclohexa-1,3-dienes must be established and is currently being pursued. In the absence of this vital piece of information, speculation seems premature.

Experimental Section

General. Melting points and boiling points are uncorrected. Nmr spectra were recorded on Varian Associates A-60 and HR-300 spectrometers. Carbon tetrachloride was used as the solvent; chemical shifts are reported as δ values in parts per million downfield from tetramethylsilane. Ir spectra were obtained with Perkin-Elmer Model 257 or 521 spectrophotometers using carbon tetrachloride as solvent. Vpc was performed on Aerograph A-90P and Varian Aerograph Model 90P instruments using the indicated columns. Mass spectra were taken on an Hitachi Perkin-Elmer RMU 7 mass spectrometer operating at 70 eV. Ultraviolet spectra were measured with a Cary 14 recording spectrometer. Anhydrous sodium sulfate was used as a drying agent. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Thermal Reactions of 3, 9, and 31 in Sealed Tubes. General Procedures. Open-end Pyrex tubes ranging between 50 and 250 ml were washed with acetone and water, rinsed with dilute ammonium hydroxide solution, and then dried in an oven at 500°. The tubes were attached to a vacuum system and degassed samples of the reactant were transferred to the tubes at $-196°$ by bulb-to-bulb distillation using a vacuum system evacuated to 5×10^{-4} mm. The tubes were then sealed with a torch and placed in an oven at the indicated temperatures. To isolate products, the small ends of the tubes were cooled in liquid nitrogen, broken open, and analyzed as reported below.

Catalytic Hydrogenations. Catalytic hydrogenations of hydrocarbons were effected on a nickel column using a procedure developed by Doering and Roth.[34e] To prepare the nickel catalyst, 33 g of 60–80 mesh Chromosorb W was mixed with a solution of 16 g of nickel nitrate hexahydrate in 120 ml of water and then treated with 30% aqueous sodium carbonate at 70° with stirring. After being filtered, washed thoroughly with water, and dried at 100°, the catalyst was packed into a column 3 ft × 0.25 in. and was reduced by being passed through hydrogen gas at 250° for 2 hr. For hydrogenations the column was operated at 75° with a flow of 30 ml/min.

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(42) See ref 3e, p 72.

(43) D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3196 (1966).

(44) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381 (1970).

(45) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 198.

(46) For example, R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Amer. Chem. Soc.*, **95**, 631 (1973).

3-(Pent-4-enyl)cyclohexene (6). To 4.7 g (0.196 g-atom) of magnesium turnings in 20 ml of ether was added dropwise a solution of 30.2 g (0.190 mol) of freshly distilled 5-bromopentene (**4**) in 60 ml of ether. After the reaction had subsided, an additional 75 ml of ether was added. The mixture was then heated at reflux for 1 hr, cooled to 10°, and cautiously treated with 30.6 g (0.190 mol) of 3-bromocyclohexene (**5**). After standing at room temperature overnight, the supernatant liquid was separated from the solid magnesium salts which had precipitated and was neutralized with 2 *N* hydrochloric acid. The ethereal layer was separated, washed with 50 ml of 10% aqueous sodium carbonate and 50 ml of saturated aqueous sodium chloride, and then dried. Distillation afforded 21.0 g (0.140 mol, 74%) of **6**: bp 40° (0.5 mm); ν_{max} 3080, 990, and 910 cm^{-1} (HC=CH$_2$); δ 1.08–2.45 (m, 13, allyl and alkyl), 4.96 (m, 2, =CH$_2$), and 5.62 ppm (m, 3, HC= and cyclohexenyl).

Anal. Calcd for $C_{11}H_{18}$: C, 87.94; H, 12.06. Found: C, 87.90; H, 12.09.

Hydrogenation of 5-μl samples of **6** in 15 μl of pentane using a nickel column operated at 75° with 30 ml/min flow of He produced *n*-pentylcyclohexane. This product was identified by comparison of the ir spectrum of hydrogenated **6** with the published spectrum of *n*-pentylcyclohexane.[47a]

Formation of 3 and 9. A mixture of 15.0 g (0.100 mol) of **6**, 4.45 g (0.025 mol) of recrystallized *N*-bromosuccinimide, 120 ml of carbon tetrachloride, and a trace of benzoyl peroxide was heated at reflux for 2 hr, cooled, and filtered. After solvent and excess diene were removed *in vacuo*, the residue was distilled evaporatively in a molecular still to give 5.21 g (22.7 mmol, 91%) of **7**.

A 4.0-g (17.5 mmol) sample of the monobromides **8** was combined with 3.14 g (69.8 mmol) of anhydrous dimethylamine in 10 ml of benzene and heated for 3 hr at 100° in a 50-ml Carius tube. The resulting mixture was cooled, neutralized with 2 *N* sodium hydroxide, and extracted with ether. The ethereal solution was dried over potassium hydroxide, filtered, and concentrated under reduced pressure. The residue was distilled to give 2.63 g (13.6 mmol, 78%) of monoamines **8**, bp 84° (1 mm). Without further purification a 2.0-g (10.4 mmol) sample of **8** in 5 ml of methanol was treated with 4.0 g of 30% hydrogen peroxide and allowed to stand at room temperature for 36 hr. After excess peroxide was decomposed with platinum black, the mixture was filtered and concentrated and the resulting oil was pyrolyzed between 105 and 120° (1 mm). The distillate was collected in a round-bottomed flask cooled in Dry Ice–acetone, extracted with pentane, washed twice with water, and then dried. After removal of solvent, distillation provided 1.04 g (7.03 mmol, 68% based on amine precursors) of a pair of hydrocarbons, bp 47° (2 mm). The hydrocarbons were separated by vpc on a 6 ft × 0.25 in. column containing 10% 1,2,3-tris(cyanoethoxy)-propane on 60–80 mesh Chromosorb W operated at 64° and 17 psi helium pressure. There was isolated **3** (73.4%) with a retention time of 40.1 min: ν_{max} 3079, 1640, 988, and 910 cm^{-1}; δ 1.21–1.7 (m, 4, methylene), 1.8–2.58 (m, 5, allyl), 4.98 (m, 2, =CH$_2$), and 5.75 ppm (m, 5, olefinic); λ_{max}^{hexane} 259.5 nm (ϵ 4311); *m/e* 148.

Anal. Calcd for $C_{11}H_{16}$: C, 89.14; H, 10.86. Found: C, 89.30; H, 11.02.

Also collected was **9** with a retention time of 46 min: ν_{max} 3079, 1638, 987, and 909 cm^{-1}; δ 1.58 (m, 2, methylene), 1.84–2.33 (br singlet, 8, allyl), 4.94 (m, 2, =CH$_2$), and 5.63 ppm (m, 4, olefinic); λ_{max}^{hexane} 263 nm (ϵ 6332); *m/e* 148.

Anal. Calcd for $C_{11}H_{16}$: C, 89.14; H, 10.86. Found: C, 89.2; H, 10.99.

Hydrogenation of 5-μl samples of **3** or **9** in 15 ml of pentane on the nickel column gave only *n*-pentylcyclohexane.

Thermal Reorganization of 5-(Pent-4-enyl)cyclohexa-1,3-diene (3). In each of three 250-ml tubes was sealed in 60–90 μl of **3**. Heating of the tubes in an air oven at approximately 208° for 21 hr resulted in quantitative conversion of **3** to a mixture of hydrocarbons. The mixture was separated and analyzed on a 3.9 ft × 0.25 in. column containing 20% β,β-oxydipropionitrile on 60–80 mesh Chromosorb P operated at 62° and 120 ml/min flow. There was isolated 21.4% of **26** with a retention time of 15.1 min: ν_{max} 3035, 1624, 1608, 1460, and 1450 cm^{-1}; nmr (300 MHz) δ 0.883 (m, 1), 1.04 (m, 1), 1.25 (m, 1), 1.36 (m, 3), 1.54 (m, 2), 1.75 (m, 5), 2.49 (br singlet, 1, allyl), 5.79 (d, 1, J_{AB} = 8.2 Hz, olefinic), and 6.15 ppm (dd, 1, ABX system, J_{AB} = 8.2 Hz, J_{AX} = 6.6 Hz); *m/e* 148.

Anal. Calcd for $C_{11}H_{16}$: C, 89.14; H, 10.86. Found: C, 89.20; H, 11.01.

Also collected was 5.9% of **27** with a retention time of 18.5 min: nmr (60 MHz) δ 0.77–1.93 (m, 13, alkyl), 2.41 (br singlet, 1, allyl), 6.03 (m, 1, olefinic), and 6.25 ppm (d, 1, J = 8.2 Hz, olefinic); *m/e* 148.

Anal. Calcd for $C_{11}H_{16}$: C, 89.14; H, 10.86. Found: C, 89.41; H, 11.02.

The major product was **11** (72.7%) with a retention of 27.4 min: mp 41–43°; ν_{max} 3042, 1611, 1467, 1448, 1439 cm^{-1}; nmr (300 MHz) 1.17 ppm (sl split d, 2, endo), 1.36 (m, 5, alkyl), 1.59 (m, 5, alkyl), 1.96 (br singlet, 1, allyl), 2.4 (br singlet, 1, allyl), and 6.19 ppm (sextet, 2, irradiation of allyl protons revealed an AB pattern, J_{AB} = 8.2 Hz, J_{AX} = 5.8 Hz, J_{AM} = 1.4 Hz, J_{BM} = 5.6 Hz, J_{BX} = 1.2 Hz); *m/e* 148.

Anal. Calcd for $C_{11}H_{16}$: C, 89.14; H, 10.86. Found: C, 89.14; H, 10.96.

Hydrogenation of 11. Samples of 5 μl of **11** in 15 ml of pentane were injected into the nickel column and the effluent was collected as a colorless solid, tricyclo[5.3.1.0^{3,8}]undecane **12**: mp 57–59°; ν_{max} 2920, 2882, 1470, 1458, 1445, and 1438 cm^{-1}. The nmr spectrum showed complex absorption between δ 0.8–1.88 ppm, with the bulk of absorption in the form of a broad singlet at 1.38 ppm.

Anal. Calcd for $C_{11}H_{18}$: C, 87.94; H, 12.06. Found: C, 87.88; H, 12.14.

Hydrogenation of 26 and 27. Hydrogenation of either **26** or **27** in the predescribed manner led to the colorless liquid tricyclo-[5.2.2.0^{1,6}]undecane (**28**): ν_{max} 2942, 2868, 1461, and 1454 cm^{-1}; δ 0.8–1.9 ppm (complex absorption); *m/e* 150.

Anal. Calcd for $C_{11}H_{18}$: C, 87.94; H, 12.06. Found: C, 87.90; H, 12.13.

Thermal Reorganization of 1-(Pent-4-enyl)cyclohexa-1,3-diene (9). Quantitative conversion of **9** into 78.9% of **26** and 21.1% of **27** resulted from heating a 100-mg sample at 208° for 21 hr in the manner predescribed for **3**. The spectra of these products were identical with those of **26** and **27** obtained from **3**.

***endo*- and *exo*-Bicyclo[2.2.2]oct-5-ene-2-carboxaldehyde (15).** A mixture of 25.0 g (0.313 mol) of cyclohexa-1,3-diene (**14**), 20.0 g (0.357 mol) of acrolein (**13**), and 0.2 g of hydroquinone was heated for 8 hr at 100° in a sealed 200-ml Pyrex ampoule. The reaction mixture was distilled to afford 35.4 g (0.260 mol, 80%) of a 90:10 mixture of *endo*- and *exo*-bicyclo[2.2.2]oct-5-ene-2-carboxaldehyde (**15**): bp 63° (2 mm) [lit.[10] bp 84–85° (12 mm)].

***endo*- and *exo*-5-Hydroxymethylbicyclo[2.2.2]oct-2-ene (16).** To a slurry of 3.67 g (96.6 mmol) of lithium aluminum hydride in 125 ml of ether cooled to 0° under a nitrogen atmosphere was added dropwise a solution of 33.0 g (243 mmol) of **15** in 40 ml of the same solvent. The stirred reaction mixture was heated at reflux for 1 hr and then treated with a saturated solution of magnesium sulfate until a precipitate stopped the stirring. After being filtered, the ethereal solution was dried and then concentrated Distillation of the residue afforded 29.6 g (214 mmol, 88%) of **16**: bp 84° (0.5 mm) [lit.[47b] bp 111° (12 mm)].

***endo*-Bicyclo[2.2.2]oct-2-ene-5-carboxylic Acid (18).** To an ice-cooled solution of 30.0 g (217.4 mmol) of **16** in 100 ml of benzene containing 0.5 ml of pyridine was slowly added 55.5 g (466 mmol) of thionyl chloride. After being refluxed for 3 hr, benzene and excess thionyl chloride were removed and the residue was distilled to give 24.1 g (154 mmol, 71%) of **17**, bp 44° (1 mm). To a mixture of 2.24 g (0.093 g-atom) of magnesium and a crystal of iodine was added 10 ml of a solution made from 12.95 g (83 mmol) of **17** and 30 ml of freshly distilled anhydrous tetrahydrofuran. After the reaction was initiated, 50 ml of the same solvent was added to the mechanically stirred mixture, followed by the dropwise addition of the remaining solution of **17**. The resulting brown mixture was heated at reflux for 1 hr, cooled, and then cautiously added to 30 g of coarsely ground Dry Ice. The slurry thus obtained was stirred for 1 hr at room temperature, cooled, and acidified with 50 ml of 6 *M* sulfuric acid. The water layer was extracted with petroleum ether (3 × 30 ml) and discarded. The combined organic solutions were washed twice with saturated sodium chloride solution, dried, and evaporated. There was obtained after recrystallization from a tenfold amount of 10% aqueous methanol 7.0 g (42.1 mmol, 51%) of **18** as a white solid acid, mp 37–39° (lit.[48] mp 39–40.8°).

***endo*-Bicyclo[2.2.2]oct-5-ene-2-acetyl Chloride (19).** A solution of 6.7 g (40.3 mmol) of **18** and 6.8 g (57.1 mmol) of thionyl chloride in 105 ml of ether containing 0.1 ml of pyridine was heated at reflux for 3 hr under a nitrogen atmosphere and then cooled. After

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(47) (a) "Sadtler Standard," Infrared Spectrum No. 12051, Vol. 12, Philadelphia, Pa. (b) K. Alder, S. Hartung, and O. Netz, *Chem. Ber.*, 90, 1 (1957).

(48) H. Whitlock, Jr., and M. W. Siefkin, *J. Amer. Chem. Soc.*, 90, 4929 (1968).

the solvent had been evaporated, the residue was distilled to afford 5.2 g (28.2 mmol, 70.0%) of **19**, bp 63–65° (1 mm).

Tetracyclo[5.4.0.0.^{3,9}.0^{6,8}]undecan-5-one (21). An ethereal solution of diazomethane (generated from 32.3 g of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, 52 ml of 2-(2-ethoxyethoxy)ethanol, 30 ml of ether, and aqueous potassium hydroxide (9 g in 15 ml of water) solution and dried over potassium hydroxide pellets) was treated overnight with 5.0 g (27.1 mmol) of **19**. The reaction mixture was concentrated under reduced pressure to a brownish yellow solid diazo ketone **20**, ν_{max} 2100 and 1645 cm^{-1}.[49] Without further purification a solution of the diazo ketone in 16 ml of hexane was added to a boiling solution of 80 ml of hexane containing 10.0 g of anhydrous cupric sulfate. After being stirred and boiled under reflux for 1 hr, the solution was filtered and concentrated. Evaporative distillation produced 2.5 g (15.4 mmol, 56.8%) of **21**: ν_{max} 3015 (cyclopropane CH str), 1690 (C=O), and 1032 cm^{-1} (w);[49] δ 0.9–2.4 with overlapping peaks at 2.03, 1.65, and 1.5 ppm; *m/e* 162; semicarbazone mp 216–218° (from EtOH).

Anal. Calcd for $C_{12}H_{17}N_3O$: C, 65.73; H, 7.81; N, 19.16. Found: C, 65.56; H, 7.96; N, 19.07.

Tetracyclo[5.4.0.0^{3,9}.0^{6,8}]undecane (22). A mixture of 0.35 g (7.0 mmol) of hydrazine hydrate and 0.180 g (1.11 mmol) of **21** in 1.2 ml of diethylene glycol was heated at reflux for 30 min. After being cooled, 0.12 g of potassium hydroxide pellets was added to the mixture, which was then heated between 190 and 215° for 16 hr. The product condensed on the distillation apparatus as a white solid. The residue and distillate were each extracted with 20 ml of pentane and the extracts were combined with a 40-ml solution of the product obtained from washing down the glass surface of the distillation apparatus with (2 × 20 ml) pentane. The product (102 mg, 0.69 mmol, 62.2%), which was purified by vpc on a 7-ft TCEP column operated at 73° with a flow of 90 ml/min, had a retention time of 28.6 min: mp 40–42°; ν_{max} 3015 and 1033 cm^{-1} (cyclopropyl); δ 0.74 (br singlet, 3, cyclopropyl) and 1.1–2.2 ppm (m, 13, alkyl); *m/e* 148.

Anal. Calcd for $C_{11}H_{16}$: C, 89.14; H, 10.86. Found: C, 89.30; H, 11.02.

Nickel-catalyzed reduction of **22** in the predescribed manner gave the white solid **12** quantitatively. This product was identical in the details of its ir and nmr spectra and melting point with those of hydrogenated **11**.

Hepta-1,6-dien-3-one (33). A solution of 54.0 g (0.40 mol) of freshly distilled 4-bromobutene in 100 ml of anhydrous ether was added dropwise under nitrogen to 10.2 g (0.43 g-atom) of magnesium turnings. The mixture was diluted with 200 ml of ether, boiled under reflux for 30 min, and then ice cooled. A solution of 22.6 g (0.40 mol) of acrolein (**13**) in 60 ml of ether was slowly added to the dark brown Grignard preparation. After 30 min at reflux, the resulting yellow mixture was cooled and then neutralized with 300 ml of 2 *N* hydrochloric acid. The aqueous layer was extracted with ether (2 × 100 ml). Combined ethereal layers were washed with 5% sodium bicarbonate (2 × 50 ml) and a saturated sodium chloride solution (2 × 50 ml) and dried. After evaporation of the solvent, distillation of the residue gave 17.84 g (0.159 mol, 39.8%) of hepta-1,6-dien-3-ol, bp 21–25° (2 mm) [lit. bp[16] 51° (10 mm)].

A solution of the Jones' reagent (prepared by mixing 12.4 g (0.124 mol) of chromic anhydride in 16 ml of water and 10 ml of concentrated sulfuric acid in 26 ml of water) was slowly added to a solution of hepta-1,6-dien-3-ol in 91 ml of acetone maintained below 10°. The reaction mixture was stirred for 3 hr between 10–28°. The aqueous layer was partitioned with petroleum ether (2 × 40 ml). The combined organic solutions were washed with saturated sodium chloride (2 × 25 ml) and 5% sodium bicarbonate (2 × 15 ml) and dried over magnesium sulfate. After the solvent was removed *in vacuo*, distillation provided 10.32 g (0.094 mol, 58.8%) of **33**, bp 16–18° (1 mm) [lit. bp[16] 82–82.5° (85 mm)].

1-(Cyclohexa-1,3-dienyl)pent-4-en-1-one (31). A solution of 3.75 g (0.030 mol) of 1-diethylaminobuta-1,3-diene was added dropwise to an ice-cold magnetically stirred solution of 4.7 g (0.043 mol) of **33** in 5 ml of benzene. After standing for 26 hr at 8°, 15 ml of 2 *N* hydrochloric acid was added to the rapidly stirred ice-cooled solution. The resulting heterogenous mixture was stirred for 4 hr at 0° and allowed to stand at 8° for an additional 12 hr. The aqueous layer was then extracted with petroleum ether (2 × 25 ml). The organic solutions were combined, dried, and then concentrated. Distillation of the residual oil provided 2.07 g (12.8 mmol, 42.7%) of **31**: bp 60–64° (1 mm), retention time of 9.8 min; ν_{max} 3090 (w), 3053, 1665, 1640, and 990 cm^{-1}; λ_{max}^{EtOH} 300 nm (ϵ 1.11 × 10^4);[50] δ 1.9–2.8 (m, 8), 4.9 (m, 2, =CH_2), 5.8 (d, 2), 5.2–5.7 (m, 1), and 6.5–6.7 ppm (m, 1). Final purification of **31** was accomplished with a 5 ft × 0.25 in. column packed with 15% Carbowax 20M operated at 100° with a flow of 120 ml/min.

Thermal Reorganization of 31. Sealed 30-ml Pyrex ampoules, each containing 40 mg of **31**, were heated at 227° for 21 hr. The reaction mixture was subjected to preparative scale vpc (5 ft × 0.25 in. column packed with 5% FFAP on 60–80 mesh Chromosorb W) operated at 102° with a flow rate of 120 ml/min. There was isolated 79% of **29** with a retention time of 22 min: ν_{max} 3048 (olefinic), 1740 (C=O), and 1665 cm^{-1} (C=C); λ_{max}^{EtOH} 289.5 (ϵ 160); nmr (300 MHz) 1.12 (m, 1), 1.26 (m, 2), 1.47 (m, 3), 1.94 (m, 3), 2.09 (m, 1, acetonyl), 2.32 (m, 1, acetonyl), 2.58 (br singlet, 1, allyl), 5.82 (d, 1, J = 8.2 Hz, olefinic), and 6.38 ppm (dd, 1, J = 8.2 and 6.5 Hz); semicarbazone mp 235–236° (dec) (from EtOH).

Anal. Calcd for $C_{12}H_{17}N_3$: C, 65.73; H, 7.81; N, 19.16. Found: C, 65.51; H, 8.00; N, 19.29.

Also collected was 21% of **30** with a retention time of 27 min: ν_{max} 3050, 1737, and 1660 cm^{-1}; nmr (300 MHz) 0.97 (m, 1), 1.13 (m, 1), 1.28 (m, 1), complex absorption from 1.5–2.5 (8), 2.61 (m, 1, allyl), 6.15 (dd, 1, J = 6.2 and 8.2 Hz), and 6.43 ppm (d, 1, J = 8.2 Hz); λ_{max}^{EtOH} 295 nm (ϵ 124); semicarbazone mp 229.5° (dec) (from sealed capillaries).

Anal. Calcd for $C_{12}H_{17}N_{13}$: C, 65.73; H, 7.81; N, 19.16. Found: C, 65.54; H, 7.90; N, 18.98.

Thermal Reaction of α-Pyrone and Hepta-1,6-dien-3-one (33). A mixture of 0.539 g of **33** (4.9 mmol), 1.094 g (11.4 mol) of α-pyrone, and 0.025 g of hydroquinone was placed in a 5-ml volume of 10-cm tubing attached to the bottom of a 5-l. round-bottomed flask and cooled in liquid nitrogen. The flask was attached to a vacuum system and evacuated to 5 × 10^{-4} mm, and then sealed. After being heated for 50 hr at 230°, a total of 1.43 g (90%) of thermolysate was isolated. Use of an external standard indicated that 92% of the dienone had been consumed. Excess α-pyrone **38** and **33** was separated from the yellow mixture by bulb to bulb distillation and the residual oil was analyzed and collected on a 5 ft × 0.25 in. column containing 15% Carbowax 20M on 60–80 mesh Chromosorb W operated at 140° with a flow of 150 ml/min. The first component (43%), which proved to be **29**, had a retention time of 11.8 min. The second peak (14.2 min) proved to be a mixture of **30** (11%) and **31** sh (3%), which was further resolved on the TCEP column. With longer reaction times (70 hr) **31** could be completely converted to products. The third peak (2%) was found to be an unresolvable mixture of 1-phenyl-4-penten-1-one[51] and what appeared to be disproportionation products of[52] **31**. The slowest moving component (37%), with a retention time of 23.0 min, was characterized as **41**: ν_{max} 3064, 1708, 1665 cm^{-1} (w); λ_{max}^{EtOH} 284.5 nm (ϵ 90.6); δ (300 MHz) 1.42 (m, 2), 1.59 (m, 2), 1.83 (m, 3), 2.08 (m, 2), 2.52 (br singlet, 1, allyl), 2.62 (m, 1, allyl), 2.7 (m, 1, acetonyl), and 6.32 ppm (quintet 2, olefinic). Irradiation of the allylic protons indicated an AB pattern (J = 8.2 Hz); semicarbazone mp 215–216° (from EtOH).

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(49) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, 21, 25 (1965).

(50) The uv spectrum is consistent with the structure of a cyclohexa-1,3-dienyl ketone. For instance, 1-acetylcyclohexa-1,3-diene shows uv absorption at λ_{max}^{EtOH} 301 nm (7380); ref 14, p 239.

(51) A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, **91**, 456 (1969).

(52) It should be noted that the concentrations of the factors are critical to the success of the double diene synthesis and to minimizing the disproportionation reaction.