Spiro[5.5]undeca-5,11-(propan-2′-one)-2,8-dione—a Possible Precursor of the Benzo[*d*]naphthalene Cation

Charles F. Wilcox, Jr.,* and G. D. Grantham

Department of Chemistry, Cornell University, Ithaca, New York, 14853

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The synthesis of two stereoisomers of the title compound is described and their stereochemistries assigned using a combination of high-field NMR and lanthanide shift reagents. These results are applied to the stereochemical assignment of the previously synthesized spiro[5.5]undeca-5,11-propano-2,8-dione.

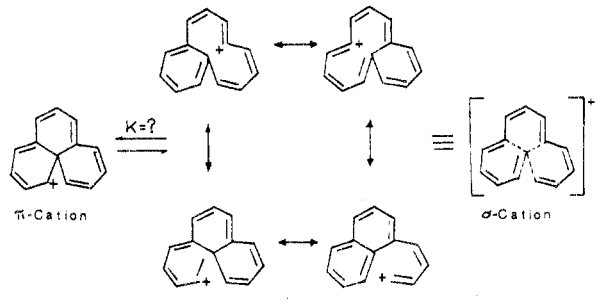
The tetrahedral carbon atom is the cornerstone of organic structural theory, although very few compounds possess pure tetrahedral geometry.[1] The question naturally arises as to how much the tetrahedral geometry may be distorted, the ultimate distortion being represented by a square planar geometry.

Extended Hückel calculations[2] predict that tetrahedral methane is more stable than the planar geometry by 127 kcal/mol, while a CNDO[3] calculation yields 187 kcal/mol for the same quantity. An ab initio calculation using a minimal basis set[4] predicts the energy of planar methane to be 250 kcal/mol greater than that of tetrahedral methane. More recently Wiberg and Ellison[5] found that an ab initio calculation using a larger basis set which included 3d functions on carbon and 2p functions on the hydrogens reduced the total energy of planar methane to 160 kcal/mol; if the bond angle was reduced from 180° (planar) to 140° the total energy using the larger basis set was only 37 kcal/mol above that of tetrahedral methane.

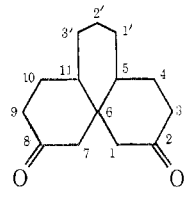
Clearly the energy requirements are high, and in order to be accessible the planar geometry must be stabilized or the tetrahedral geometry destabilized. Recently Hoffmann, Alder, and Wilcox[6] have outlined several ways in which this problem might be solved. One of the more promising approaches for stabilizing the planar geometry involves incorporation of the lone pair of the planar tetracoordinate carbon into an annulene perimeter.

One such possibility is the benzo[*d*]naphthalene cation system (Chart I). In this system the planar σ cation is an aromatic (i.e., $4n + 2$) [14]annulene with a Hückel π energy of 19.3β. The nonplanar π cation (fully conjugated, positive charge in the π network) has a π energy of 15.8β. The 3.5β difference is therefore available to provide the driving force for promotion of a pair of σ electrons into the π system to create the planar σ cation.

Chart I
The Benzo[*d*]naphthalene Cation System



In order to test this approach a suitable precursor having the correct carbon skeleton and with sufficient functionality to permit subsequent introduction of the required unsaturation is necessary. Entry into the desired carbon skeleton can be attained through a novel reaction between 1-(1-pyrrolidino)cyclohexene and methyl vinyl ketone originally discovered by House and coworkers.[7] This paper describes an elaboration of this reaction that provides such an appropriately functionalized precursor. The product of the House reaction, spiro[5.5]undeca-5,11-propano-2,8-dione[8] (**1**), already has appropriate functionality in two of its three



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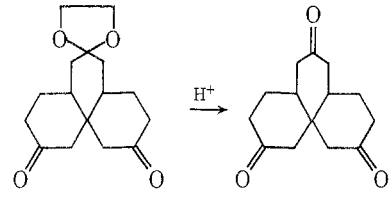
rings. The original plan was to introduce a third carbonyl group at the 2′ position by employing the analogous reaction between the pyrrolidine enamine of 1,4-cyclohexanedione monoethylene ketal[9] and methyl vinyl ketone to afford **2**, which could then be converted to spiro[5.5]undeca-5,11-(propan-2′-one)-2,8-dione (**3**). Unfortunately, **2**



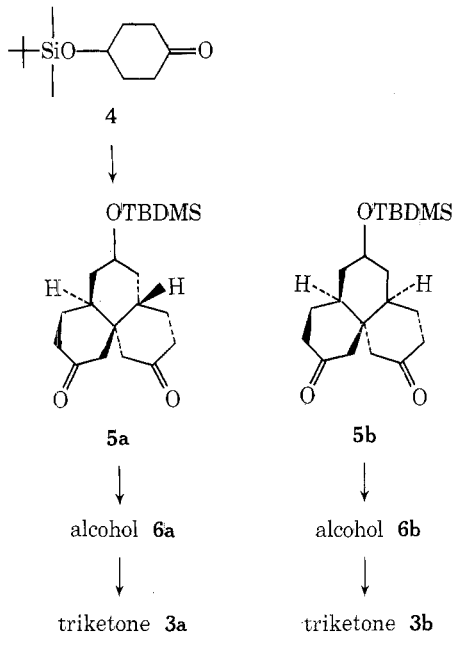
2 **3**

could be obtained in only 1.4% yield. This low yield is presumably due to the acid lability of the ketal protecting group, which fails to survive under the conditions necessary to hydrolyze the intermediate enamine. As a result, an alternate approach utilizing a protected hydroxyl function (Scheme I) was employed. Corey's[10] work utilizing *tert*-butyldimethylchlorosilane as a hydroxyl protecting group suggested that this silyl ether would survive a mild acid hydrolysis yet be removable under conditions which would not affect the integrity of the ring system.

4-*tert*-Butyldimethylsiloxycyclohexanone (**4**, Scheme I) could be prepared in high yield using Corey's[10] imidazole-catalyzed procedure. The enamine was prepared using standard[9] procedures and reacted with methyl vinyl ketone. Work-up of this reaction followed by column chromatography afforded a white, amorphous powder, **5**, in 16% yield based on **4** together with a viscous resin which NMR indicated consisted primarily of a mixture of 6-*tert*-butyldimethylsiloxy-$\Delta^{1,9}$- and -$\Delta^{9,10}$-octal-2-one epimers. Careful examination of this amorphous powder by thin layer chromatography revealed the presence of two components. The two compounds, later identified as isomers **5a** and **5b** (vide infra), were separated as outlined below.

Isomer **5a** could be obtained in pure form (mp 113.5–114.4°) by careful column chromatography on alumina

Scheme I



using chloroform as the eluent. Once isolated in pure form it was easily hydrolyzed to the alcohol **6a** (mp 163.5–164.5°), which in turn was converted in high yield to the triketone **3a** (mp 155–157°) via Jones oxidation. Unfortunately, isomer **5b** could not be freed entirely of isomer **5a** by column chromatography. However, in the course of hydrolyzing a mixture of isomers **5a** and **5b** it was observed that **5b** hydrolyzed much more slowly than isomer **5a.** By exploiting this observation it was possible to obtain isomer **5b** in pure form (mp 129–130°) by subjecting the mixture to a short hydrolysis followed by column chromatography to separate **5b** from the mixture of isomeric alcohols **6a** and **6b.** Isomer **5b** was then converted to the alcohol **6b** (mp 182–184°), which in turn was oxidized to the triketone **3b** (mp 215–218°).

Stereochemistry of Isomers 3a and 3b. There are three possible geometrical arrangements for the triketone **3.** Isomer **3a,** in which there are two cis ring fusions, is a very flexible configuration. In the all-chair conformation **3a** is unsymmetrical; however, a slight distortion of the all-chair conformation would result in a potential twofold rotational axis (Chart II). Isomer **3b,** in which there is one cis and one

Chart II
Stereoisomer of Triketone 3

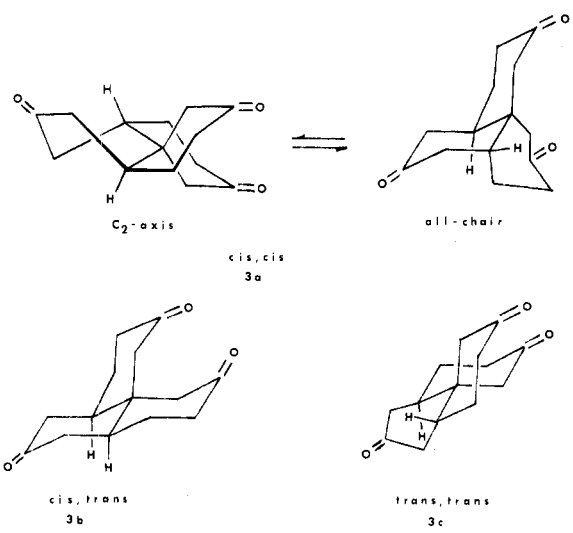


Table I
Chemical Shifts and Coupling Constants for Isomer 3a[a]

Chemical shifts (Hz from external Me_4Si)		Coupling constants, Hz	
H_8, H_9	869.0[b], 1040.6[b]	$J_{1,2} = -7.56$	$J_{4,6} = 6.65$
		$J_{1,3} = 7.68$	$J_{4,7} = 7.46$
H_1, H_2	963.3, 962.7	$J_{2,3} = 4.50$	$J_{5,6} = 6.40$
		$J_{3,4} = 7.09$	$J_{5,7} = 7.97$
H_6, H_7	846.1, 841.8	$J_{3,5} = 4.63$	$J_{6,7} = -13.68$
H_3	814.8	$J_{4,5} = -14.42$	$J_{8,9} = -14.0$[b]
H_5	732.8		
H_4	657.1		

[a] The chemical shifts and coupling constants were extracted from the 220-MHz Eu(thd)$_3$-shifted spectrum of **3a** (Figure 1) using a LAOCOON III computer program on an IBM 370/168 computer. [b] H_8 and H_9 were not included in the LAOCOON III calculation; these values were measured directly from the spectrum.

trans ring fusion, is a relatively rigid all-chair conformation in which there is no C_2 axis. Isomer **3c,** in which there are two trans ring fusions, is locked into a conformation which requires a C_2 axis.

The usual 60-MHz proton NMR spectra were of little use in assigning the structures of isomers **3a** and **3b:** both spectra consist of a broad envelope in which there are no recognizable structural features. However, more stereochemical information could be obtained with the use of high field strength 220-MHz instrumentation in conjunction with the lanthanide shift reagent Eu(thd)$_3$.

Upon addition of successive increments of Eu(thd)$_3$ to a solution of **3a** in deuteriochloroform several resonances are progressively shifted downfield until at saturation the 220-MHz spectrum appears as in Figure 1. Most strongly affected was a two-proton doublet which was shown by double resonance to be one half of an isolated four-proton AB system (δ_{Eu} 4.73, 3.95, $J \simeq 14$ Hz).[11] The observation that this system was not coupled to any other protons in the spectrum permitted the assignment of these resonances to the methylene protons isolated between the quaternary carbon and the adjacent carbonyl groups (H_8 and H_9 in Figure 1). Somewhat less strongly affected was a four-proton doublet (δ_{Eu} 4.38) which was shown to be coupled ($J \simeq 7$ Hz) solely to H_3 by irradiation of the latter signal. This observation permitted the assignment of this resonance to H_1 and H_2. A four-proton triplet (actually a pair of overlapping doublets, δ_{Eu} 3.85, 3.83) was shown to be coupled to H_4 and H_5 by irradiation of the latter two signals and can therefore be assigned to H_6 and H_7. The four coupling constants in this system are all approximately 7 Hz. Finally, protons H_4 and H_5 were shown to be coupled to H_3 as well as to H_6 and H_7. The measured coupling constants and chemical shifts were then used as input for an iterative LAOCOON III calculation which gave the refined values in Table I. The bottom portion of Figure 1 is a computer simulation of the NMR spectrum of **3a** using these calculated values.

The proton NMR results clearly demand a C_2 axis (either static or dynamic) for the lower melting triketone isomer (**3a**). Consistent with this requirement, the ^{13}C NMR spectrum of this isomer (without shift reagent) shows only eight absorptions, whereas the precursor alcohol (**6a**) in which the C_2 axis is destroyed shows all 14 individual carbon resonances. The requirement of a C_2 axis is sufficient to eliminate isomer **3b** from consideration as the correct stereochemistry for the lower melting triketone isomer.

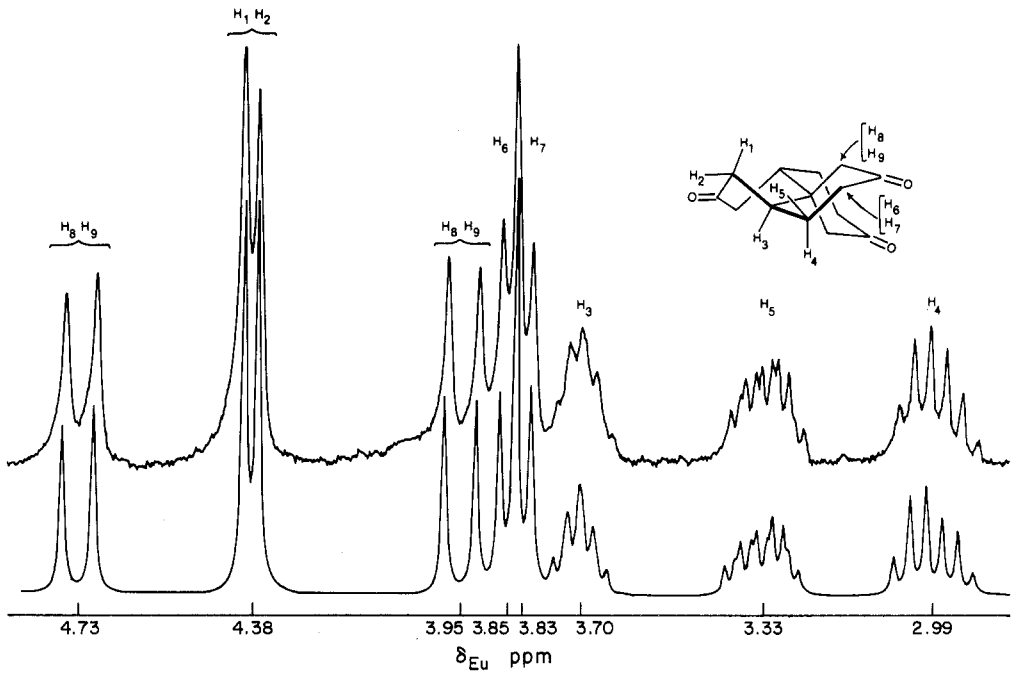
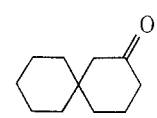


Figure 1. Top: observed Eu(thd)$_3$-shifted 220-MHz proton NMR spectrum of **3a**. Bottom: computer-simulated NMR spectrum using the chemical shifts and coupling constants in Table I.

However, the presence of a C_2 axis does not distinguish between **3a** and **3c**. In order to distinguish between these two possibilities one must be able to detect the presence of either cis or trans ring fusions. Crucial to this distinction are the magnitudes of the coupling constants $J_{3,4}$ and $J_{3,5}$ between the methine proton (H_3) and the adjacent methylene protons (H_4 and H_5). In the isomer having two trans fusions (**3c**) one would expect one trans diaxial interaction (typically J = 8–10 Hz) and one axial–equatorial interaction (typically J = 2–3 Hz). In the isomer having two cis ring fusions (**3a**) the relationship between the methine and methylene protons is nearly gauche and there should therefore be a tendency for the coupling constants to equalize. Since **3a** is conformationally mobile, the observed coupling constants will be a weighted average of the coupling constants over all the conformations of the molecule. Examination of models suggests that these coupling constants should fall in the range $J_{3,4}$ = 6–7 and $J_{3,5}$ = 3–4 Hz. Thus, the observed values, $J_{3,4}$ = 7.09 and $J_{3,5}$ = 4.63 Hz, are suggestive of cis ring fusions in the lower melting ketone isomer. However, since the vicinal coupling constant–dihedral angle correlation is approximate at best, these results do not rigorously exclude isomer **3c**. It may be argued that the fact that the triketones are formed under relatively mild conditions via a series of presumably reversible reactions mitigates against the formation of the trans,trans isomer (**3c**) in which the two trans fusions introduce a substantial amount of strain.[7] While we cannot rigorously exclude isomer **3c**, we feel that this argument, coupled with the foregoing NMR evidence, makes the cis,cis geometry (**3a**) most probable for the lower melting ketone isomer.

The foregoing discussion leaves **3b** as the only possible stereochemistry for the higher melting triketone isomer. The required absence of a C_2 axis is confirmed by the ^{13}C NMR spectrum, in which 12 separate carbon resonances appear. Unfortunately, this isomer proved too insoluble in deuteriochloroform to obtain high-field continuous wave lanthanide shifted proton NMR spectra. However, we were able to obtain a pulsed Fourier transform proton NMR (90 MHz) in the presence of Eu(fod)$_3$.[13] It seems reasonable to assume that the protons in this isomer shift in the same order that was observed for **3a**. The extra splitting which would be expected based on the absence of a C_2 axis and the presence of both a cis and a trans ring fusion is readily apparent in this spectrum. The NMR results are therefore consistent with the required assignment of stereochemistry **3b** to the higher melting triketone isomer.

In the course of isolating **3a** and **3b**, we obtained the mass spectra of these isomers. Weringa[14] has extensively studied the mass spectra of spiroalkanones with five- and six-membered rings. In particular, he has found that two of the principal peaks in the mass spectrum of spiro[5.5]undecan-2-one (**7**) arise from the loss of C_3H_6O (P − 58, rel intensity 92) and C_3H_5O (P −57, rel intensity 23) fragments. As might be expected, these two modes of decomposition are also important in the triketone isomers **3a** and **3b**. More interesting, however, are the marked differences in the relative amounts of the two decomposition modes observed for these isomers. In the cis,cis isomer (**3a**) the relative intensity of the peak resulting from the loss of C_3H_6O (*m/e* 176) is nearly four times the relative intensity of the peak resulting from the loss of C_3H_5O (*m/e* 177), whereas in isomer **3b** the relative intensities of the peaks resulting from these two modes of decomposition are nearly equal.



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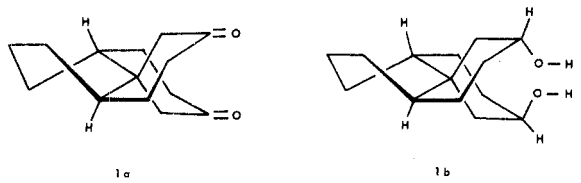
The same three stereochemical arrangements are of course possible for the diketone **1**. House et al.[7] eliminated the trans,trans diketone from consideration on the grounds that the formation of the strained trans,trans ring fusions was unlikely in a series of reversible reactions. Furthermore, the all-chair conformation for the cis,cis isomer was assumed. The diketone was assigned the cis,trans structure on the grounds that the diol resulting from reduction of the diketone with sodium borohydride showed evidence of an *intramolecular* hydrogen bond in its infrared spectrum; the formation of an intramolecular hydrogen bond in the diol which would result from reduction of the all-chair form of cis,cis diketone being deemed impossible since the oxygens would be too far apart. Our results, however, indicate

that the possibility of the stereochemistry **1a** cannot be ignored (this stereochemistry being accessible in triketone **3a**). Examination of models indicates that if the diketone were to assume this conformation the distance between the carbonyl groups would be precisely the same as that in cis,trans isomer. Furthermore, even if the diketone itself did not prefer the stereochemistry **1a**, it could be argued that the formation of an intramolecular hydrogen bond might provide the impetus for a change in this conformation in the corresponding diol (**1b**). Thus, the formation of such a



1a 1b

hydrogen bond does not itself provide enough evidence to distinguish between the cis,cis isomer and the cis,trans isomer. In an effort to clarify this point we obtained ^{13}C and lanthanide-shifted 60-MHz proton NMR spectra of diketone **1**. Fourteen individual carbon resonances are visible in the ^{13}C spectrum of diketone **1**, indicating the absence of a C_2 axis. This absence of a C_2 axis is consistent with either the all-chair cis,cis stereochemistry or the cis,trans stereochemistry and indicates that if the diketone prepared by House et al.[7] is the cis,cis isomer, the conformation **1a** is not accessible under the same conditions as it was for the corresponding triketone conformer **3a**. The ^{13}C NMR spectrum therefore does not offer a means of distinguishing between these two possibilities; it does, however, exclude the trans,trans stereochemistry.

Efforts to assign either the cis,cis or the cis,trans stereochemistry on the basis of coupling constants between the methine proton and the adjacent methylene protons were thwarted because the methine resonances could not be shifted out of the broad envelope of resonances arising from the saturated three-carbon bridge in **1**. One piece of evidence in favor of the cis,trans stereochemistry is provided by the mass spectrum, which resembles the mass spectrum of triketone isomer **3b** in that the loss of C_3H_6O (P − 58) is not the major fragmentation mode. Thus, while we are unable to offer any positive evidence for the assignment of the cis,trans stereochemistry to the diketone prepared by House and coworkers,[7] failure to observe a C_2 axis, particularly in the light of the findings for the triketone isomers, constitutes strong presumptive evidence that the diketone **1** has the cis,trans stereochemistry.

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The continuous wave 60-MHz proton NMR spectra were obtained on a Varian A-60A spectrometer in the solvent indicated using tetramethylsilane as an internal reference. ^{13}C NMR spectra were obtained at 22.6 MHz in $CDCl_3$ on a Bruker HFX-90 spectrometer equipped with a Digilab Fourier transform accessory; chemical shifts are reported in parts per million relative to internal tetramethylsilane. Mass spectra were obtained on an AEI MS902 spectrometer at 70 eV. Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Spiro[5.5]undeca-5,11-propano-2,8-dione (1) was prepared as described by House et al.:[7] mp 159–160° (lit.[7] mp 161–162°); ^{13}C NMR 25.7, 26.3, 26.5, 27.4, 27.9, 36.7, 40.0, 41.2, 41.6, 43.4, 44.7, 50.9, 208.0, 208.8 ppm; MS m/e (rel intensity) 221 (16), 220 (100), 163 (45), 162 (26), 156 (68), 149 (61), 141 (61).

4-Hydroxycyclohexanone was first prepared by the method of Jones and Sondheimer,[15] and later by a shorter route developed by Radlick and Crawford.[16]

Preparation of 4-*tert*-Butyldimethylsiloxycyclohexanone (4). A solution of 4-hydroxycyclohexanone (6.13 g, 0.053 mol), *tert*-butyldimethylchlorosilane (9.70 g, 0.064 mol, Willowbrook Labs), and imidazole (9.00 g, 0.132 mol, Aldrich) in 13 ml of dry (distilled from CaH_2) dimethylformamide was stirred for 48 hr at room temperature under a silica gel drying tube.[12] The mixture was then poured into water and extracted several times with diethyl ether. The ether extracts were back extracted with distilled water, dried over anhydrous Na_2SO_4, and concentrated under vacuum to afford 12.6 g of the crude silyl ether. Distillation afforded 10.01 g (84%) of 4-*tert*-butyldimethylsiloxycyclohexanone as a clear, viscous liquid: bp 71–72° (0.45 Torr); ir (neat) 1710, 1260, 1110, and 1050 cm^{-1}; NMR ($CDCl_3$) δ 4.15 (multiplet, 1 H), 3.0–1.7 (complex multiplet, 8 H), 0.95 (singlet, 9 H), 0.15 (singlet, 6 H).

Reaction of 1-(1-Pyrrolidino)-4-*tert*-butyldimethylsiloxycyclohexene with Methyl Vinyl Ketone (Preparation of 5). The pyrrolidine enamine of 4-*tert*-butyldimethylsiloxycyclohexanone was prepared by refluxing a solution of the ketone (22.80 g, 0.10 mol) and pyrrolidine (16.1 ml, 0.20 mol, Aldrich) in 150 ml of benzene under a Dean-Stark trap until water ceased to separate (about 8 hr). The benzene and excess pyrrolidine were removed under vacuum on a rotary evaporator. The crude enamine was used without further purification (the crude material gave spectra consistent with the desired product): ir (neat) 1640, 1260, and 1110 cm^{-1}; NMR ($CDCl_3$) δ 4.2–3.5 (multiplet, 2 H), 3.2–1.5 (complex multiplet, 6 H), 0.95 (singlet, 9 H), 0.15 (singlet, 6 H).

The crude enamine was placed under a nitrogen atmosphere and dissolved in 35 ml of absolute ethanol (dried over 3-Å molecular sieves). Freshly distilled methyl vinyl ketone (18.0 g, 0.30 mol, Aldrich) was added (exothermic reaction!) with stirring at a rate sufficient to maintain a gentle reflux. After the addition of methyl vinyl ketone was complete the solution was refluxed for 4 hr. Acetate buffer solution (15 ml, prepared by dissolving 12.5 g of sodium acetate in 25.0 ml of distilled water and 25.0 ml of glacial acetic acid) was added, and the solution was refluxed for an additional 2 hr. The reaction mixture was cooled, most of the solvent was removed under vacuum on the rotary evaporator, and the residue was taken up in CH_2Cl_2 and washed with several portions of water. The organic extracts were filtered through a 2 × 5.5 cm column of Woelm Activity Grade I alumina (100–200 mesh) to afford 44.1 g of an orange resin.

The products were isolated by chromatography on 1200 g of Woelm Dry Column Grade alumina (100–200 mesh). The fractions eluted with anhydrous ether afforded 22.0 g of a reddish liquid which NMR indicates is predominantly a mixture of 6-*tert*-butyldimethylsiloxy-$\Delta^{1,9}$-octal-2-one and 6-*tert*-butyldimethylsiloxy-$\Delta^{9,10}$-octal-2-one: NMR ($CDCl_3$) δ 5.85 (singlet), 4.25 (broad multiplet), 3.0–1.2 (complex multiplet), 0.95 (singlet), 0.15 (singlet). When the eluent was changed to 50:50 (v/v) ethyl acetate–diethyl ether, the desired products were obtained as a yellow, resinous material which crystallized on trituration with pentane to afford 5.78 g (16%) of the mixed isomers **15** as a white, amorphous powder: mp 90–110°; ir (Nujol) 1705, 1110, and 1080 cm^{-1}; NMR ($CDCl_3$) δ 4.15 (broad multiplet, 1 H), 3.2–1.5 (complex multiplet, 18 H), 0.95 (singlet, 9 H), 0.15 (singlet, 6 H).

In several runs of this reaction on a similar scale yields ranged from 8–20% of the theoretical (based on 4-*tert*-butyldimethylsiloxycyclohexanone). The remainder of the starting material was always accounted for in the yield of 6-*tert*-butyldimethylsiloxy-$\Delta^{1,9}$- and -$\Delta^{9,10}$-octal-2-one epimers.

Separation of *cis,cis*-Spiro[5.5]undeca-5,11-(2'-*tert*-butyldimethylsiloxypropane)-2,8-dione (5a). In a typical separation 1.38 g of the mixed isomers **15** was chromatographed on 500 g of Woelm Dry Column Grade alumina (100–200 mesh) using chloroform as the eluent. Forty 25-ml fractions were collected. Fractions 1–5 gave 106 mg of the cis,cis isomer (**5a**), mp 113–114°. Fractions 6–19 gave 840 mg of mixed isomers, mp 90–110°. Fractions 20–40 afforded 357 mg of mixed isomers, mp 104–108°. The middle fractions could be rechromatographed to yield additional pure cis,cis isomer. Treatment of 5.00 g of the mixed isomers in this manner followed by crystallization from Fisher "hexanes" gave 1.38 g of the cis,cis isomer (**5a**), mp 113.5–114.5°, ir (KBr) 2850, 1690, 1440, 1240, 1050, 865, 830, and 770 cm^{-1}, NMR ($CDCl_3$) δ 4.15 (broad multiplet, 1 H), 3.2–1.6 (complex multiplet, 18 H), 0.95 (singlet, 9 H), 0.15 (singlet, 6 H), and 2.75 g of the mixed isomers, mp 104–107°. Attempts to improve the melting point of this latter mixture by further chromatography were not successful.

Preparation of *cis,cis*-Spiro[5.5]undeca-5,11-(propan-2'-ol)-2,8-dione (6a). A solution of 710 mg of *cis,cis*-spiro[5.5]undeca-5,11-(2'-*tert*-butyldimethylsiloxypropane)-2,8-dione (**5a**) in 15 ml of 3:1:1 acetic acid–tetrahydrofuran–water was stirred at

room temperature for 24 hr. The reaction mixture was then diluted to 100 ml with distilled water and most of the acetic acid was neutralized by addition of solid $NaHCO_3$. The resulting solution was extracted twice with 25-ml portions of $CHCl_3$, and the aqueous layer was saturated with NaCl and then reextracted with a total of 100 ml of $CHCl_3$. The combined organic extracts were dried over anhydrous K_2CO_3 and concentrated under vacuum to afford an oily residue. Trituration with pentane and filtration afforded 400 mg (84%) of the alcohol **6a** as a white powder, mp 163–164°. Crystallization from ethyl acetate gave white plates: mp 163.5–164.5°; ir (KBr) 3350, 2900, 1690, 1420, 1315, 1290, 1140, 1080, 1040, and 1010 cm^{-1}; NMR ($CDCl_3$) δ 4.05 (broad multiplet, 1 H) 3.15–170 (complex multiplet, 19 H).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.54; O, 20.31. Found: C, 71.17; H, 8.51; O, 20.32.

Preparation of *cis,cis*-Spiro[5.5]undeca-5,11-(propan-2′-one)-2,8-dione (3a). A solution of 313 mg of *cis,cis*-spiro[5.5]undeca-5,11-(propan-2′-ol)-2,8-dione (**6a**) in 25 ml of acetone (Mallinkrodt, reagent grade) was titrated at room temperature with a total of 0.67 ml of Jones reagent (prepared by dissolving 100.00 g of CrO_3 in 84 ml of concentrated H_2SO_4 and diluting to 500 ml with water). After addition was complete, the reaction mixture was stirred for 15 min at room temperature and a few drops of ethanol were added to destroy any excess reagent. The precipitated chromium salts were filtered off and washed with acetone. The combined acetone fractions were concentrated and the residue was taken up in $CHCl_3$ and washed with water to remove a faint green tinge. The $CHCl_3$ solution was dried over K_2CO_3 and concentrated. Crystallization of the residue from 50:50 ethyl acetate–cyclohexane gave 250 mg (90%) of *cis,cis*-spiro[5.5]undeca-5,11-(propan-2′-one)-2,8-dione as fine, white needles: mp 155–157°; ir (KBr) 2900, 1690, 1430, 1310, and 1220 cm^{-1}; NMR ($CDCl_3$) δ 3.0–1.5 (complex multiplet), see also Figure 1 and Table I; ^{13}C NMR 27.9, 37.8, 38.3, 42.6, 45.4, 49.1, 209.3, 209.6 ppm; MS m/e (rel intensity) 235 (13.0), 234 (75.8), 177 (16.3), 176 (63.0), 163 (13.6), 149 (8.9).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74; O, 20.49. Found: C, 71.68; H, 7.52; O, 20.80.

Separation of *cis,trans*-Spiro[5.5]undeca-5,11-(2′-*tert*-butyldimethylsiloxypropane)-2,8-dione (5b). The cis,trans isomer (**5b**) could be obtained in pure form by exploiting the faster rate of hydrolysis of the cis,cis isomer (**5a**). In a typical separation 5.56 g of the mixed isomers (mp 104–108° obtained from the chromatography described above) was hydrolyzed in 120 ml of a 3:1:1 mixture of acetic acid–tetrahydrofuran–water at room temperature. After 24 hr the reaction mixture was diluted with water and most of the acetic acid was neutralized by addition of solid $NaHCO_3$. The resulting solution was extracted several times with $CHCl_3$, and the aqueous layer was saturated with NaCl and reextracted with $CHCl_3$. The combined organic extracts were dried over anhydrous K_2CO_3 and concentrated to afford 4.78 g of waxy semisolid material which was chromatographed on 200 g of Woelm Dry Column Grade alumina (100–200 mesh) using $CHCl_3$ as the eluent. A total of 13 125-ml fractions was collected. Fractions 3–9 gave 2.24 g of the pure *cis,trans*-spiro[5.5]undeca-5,11-(2′-*tert*-butyldimethylsiloxypropane)-2,8-dione: mp 129–130°; ir (KBr) 2850, 1710, 1460, 1420, 1240, 1050, 880, 840, and 770 cm^{-1}; NMR ($CDCl_3$) δ 4.25 (broad multiplet, 1 H), 2.7–1.3 (complex multiplet, 18 H), 0.95 (singlet, 9 H), 0.15 (singlet, 6 H).

Elution with ethyl acetate afforded 1.36 g of mixed *cis,cis*- and *cis,trans*-spiro[5.5]undeca-5,11-(propan-2′-ol)-2,8-dione isomers, mp 140–170°.

Preparation of *cis,trans*-Spiro[5.5]undeca-5,11-(propan-2′-ol)-2,8-dione (6b). A solution of 2.00 g of *cis,trans*-spiro[5.5]undeca-5,11-(2′-*tert*-butyldimethylsiloxypropane)-2,8-dione in 50 ml of 3:1:1 acetic acid–tetrahydrofuran–water was stirred at room temperature for 142 hr. Distilled water (100 ml) was added to the reaction mixture and the solution was neutralized by addition of solid Na_2CO_3. The resulting solution was extracted with a total of 200 ml of ethyl acetate. The organic extracts were given a preliminary drying with anhydrous Na_2SO_4 followed by final drying with anhydrous $MgSO_4$. Concentration under vacuum gave a residue which was crystallized from ethyl acetate to afford 1.04 g (74%) of the alcohol **6b:** mp 182–184°C; ir (KBr) 3400, 2850, 1690, 1410, 1240, and 1030 cm^{-1}; NMR ($CDCl_3$) δ 4.30 (broad multiplet, 1 H), 2.70–1.20 (complex multiplet, 19 H).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.54; O, 20.31. Found: C, 71.08; H, 8.63; O, 20.29.

Preparation of *cis,trans*-Spiro[5.5]undeca-5,11-(propan-2′-one)-2,8-dione (3b). A solution of 504 mg (2.13 mmol) of *cis,trans*-spiro[5.5]undeca-5,11-(propan-2′-ol)-2,8-dione (**6b**) in 50 ml of acetone (Mallinkrodt, reagent grade) was titrated with a total of 1.07 ml of Jones reagent (prepared by dissolving 100.00 g of CrO_3 in 84 ml of concentrated H_2SO_4 and diluting to 500 ml with H_2O). After addition was complete, the solution was stirred for approximately 15 min at room temperature and then a few drops of ethanol were added to destroy any excess reagent. The insoluble chromium salts were filtered off and washed with acetone. The combined acetone fractions were concentrated under vacuum and the residue was taken up in CH_2Cl_2 and washed with water to remove a faint green coloration. The CH_2Cl_2 was dried over K_2CO_3 and concentrated under vacuum to afford a white, crystalline residue. One crystallization from ethyl acetate gave 444 mg (89%) of *cis,trans*-spiro[5.5]undeca-5,11-(propan-2′-one)-2,8-dione as small, white crystals: mp 215–218°; ir (KBr) 2900, 1690, 1450, 1420, 1310, and 1210 cm^{-1}; NMR ($CDCl_3$) δ 2.9–1.5 (complex multiplet); ^{13}C NMR 25.8, 27.4, 35.9, 39.6, 40.6, 42.0, 43.9, 48.6, 50.0, 204.8, 206.7, 207.2; MS m/e (rel intensity) 235 (6.9), 234 (54.4), 177 (11.4), 176 (10.8), 163 (1.5), 149 (15.2).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74; O, 20.49. Found: C, 71.74; H, 7.87; O, 20.39.

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Registry No.—**1,** 3284-28-4; **3a,** 55176-82-4; **3b,** 55145-53-4; **4,** 55145-45-4; **5a,** 55145-46-5; **6a,** 55145-47-6; 4-hydroxycyclohexanone, 13482-22-9; *tert*-butyldimethylchlorosilane, 18162-48-6; 1-(1-pyrrolidino)-4-*tert*-butyldimethylsiloxycyclohexene, 55145-48-7; methyl vinyl ketone, 107-25-5; 6-*tert*-butyldimethylsiloxy-$\Delta^{1,9}$-octal-2-one, 55145-49-8; 6-*tert*-butyldimethylsiloxy-$\Delta^{9,10}$-octal-2-one, 55145-50-1; benzo[*d*]napthalene cation, 55145-43-2.

References and Notes

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