Enhanced Endo–Exo Selectivity in the Stereochemistry of Ketonization of Enols[1,2]

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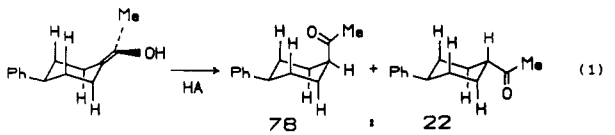
The behavior of enols of 9-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane and 9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane was investigated. The enols were generated by (i) reaction of the bromo ketone with mercaptans, (ii) reaction of the bromo ketone with dilute HI in acetone, or (iii) conversion of the enol acetates to the enolates followed by protonation. The enol of the acetyltricyclic ketone was also generated by photolysis of the enoloxy dimer. The enols proved to be appreciably stable with half-lives ranging from a half hour to more than 24 h, depending on conditions. The presence of the enols could be monitored by reaction with oxygen. The enoloxy dimer was formed when the (α-bromoacetyl)tricyclic was irradiated in isopropyl alcohol in the presence of sodium acetate; this dimer was found to have two enoloxy radicals bonded from the α-carbon of one to the enoloxy oxygen of the second. Base-catalyzed equilibration of the ketones led to the endo and the exo isomers with a product ratio less than 1 to 1000. Enol ketonization occurs with exo attack, affording the endo isomers, being preferred by at least 3300 to 1. The very large kinetic preference for the less stable endo ketone isomers results from steric hindrance by the C-3 and C-5 axial methylene groups blocking the endo approach of proton donors. A MM2 treatment of the stereochemistry of ketonization revealed the expected preference for exo protonation of both the tricyclic enol in the present study and also unsubstituted exocyclic six-ring enols. For the 2-phenyl-1-acetyl system, the axial phenyl conformer of starting material was preferred. However, for the protonation transition state, the equatorial phenyl conformer with exo protonation was lowest in energy. Next was the axial phenyl conformer with axial protonation. Third was the axial phenyl conformer with exo protonation, and least stable was the equatorial phenyl conformer with endo protonation.

Nearly 3 decades ago the concept of steric control of ketonization of enols was advanced.[3] It was suggested[4,5] that the transition state for ketonization of enols of simple ketones was close to sp^2 hybridized and that approach of the proton donor to one of the two lobes of the α-carbon p orbital was controlled by the relative steric hindrance from the two sides of the enol. It was noted that this kinetic preference often led to the less stable of two a priori products. Since a large number of organic reactions proceed via transient enol intermediates, the stereochemistry of ketonization is germane to considerable chemistry.

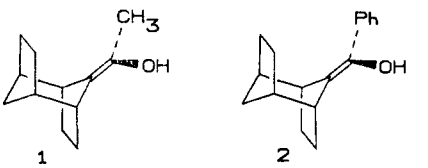
In the special case of six-ring compounds with an exocyclic enolic moiety, it was suggested that the axial hydrogens at C-3 and C-5, relative to the enol function, tended to block access of the proton donor on one side of the molecule. The result suggested was a kinetic preference, again, for the less stable stereoisomer of product (see eq 1).



(1)

Where only C-4 anchor substituents are present,[4b,g,6] the hindered nature of the endo approach to the six-ring is of necessity responsible for the observed stereochemistry which invariably affords the less stable cis stereoisomer of product. Where there is a C-2 anchor substituent, the less stable cis isomer is, again, formed. However, there is some question[7] whether in the transition state this group is equatorial, with an exo approach of the proton donor or axial with an endo approach. We have noted that in any case the stereochemistry will be controlled by the least hindered approach. It is observed[3–6] that less stereoselectivity is encountered where the anchoring substituent is at C-4 than at C-2.[4b]

It was of considerable interest to explore an example where only the C-3 and C-5 interference was involved and where this was larger than a simple pair of hydrogens. For this purpose the acetyl and benzoyl enols **1** and **2** were selected.



1 **2**

Results

Synthesis of the Tricyclic Ketones and Their Enol Precursors. As enol precursors, the corresponding α-bromo ketones **5** and **6** and the enol acetates were synthesized starting from cyclopentadiene and chlorocyclopentanone as outlined in Scheme I. This scheme includes the preparation of the parent ketones **3** and **4**.

The initial, triethylamine-catalyzed condensation of chlorocyclopentanone with cyclopentadiene, to afford tricyclic ketone **7**, has a parallel in the condensation of 2,5-dibromocyclopentanone with cyclopentadiene using diiron nonacarbonyl[8] and the 2-chlorocyclopentanone en-

(1) (a) This is paper 201 of our general series.
(2) (a) For paper 200, see: Zimmerman, H. E.; Carpenter, C. W.; Weber, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 1073–1075.
(3) Zimmerman, H. E. *J. Org. Chem.* **1955**, *20*, 549–557.
(4) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1956**, *78*, 1168–1173. (b) Zimmerman, H. E.; Giallombardo, H. J. *J. Am. Chem. Soc.* **1956**, *78*, 6259–6263. (c) Zimmerman, H. E. *J. Am. Chem. Soc.* **1957**, *79*, 6554–6558. (d) Zimmerman, H. E.; Nevins, T. E. *J. Am. Chem. Soc.* **1957**, *79*, 6559–6561. (e) Zimmerman, H. E.; Cutshall, T. W. *J. Am. Chem. Soc.* **1958**, *80*, 2893–2896. (f) Zimmerman, H. E.; Chang, W. *J. Am. Chem. Soc.* **1959**, *81*, 2086–2091. (g) Zimmerman, H. E.; Mais, A. *J. Am. Chem. Soc.* **1959**, *81*, 3644–3651. (h) Zimmerman, H. E.; Cutshall, T. W. *J. Am. Chem. Soc.* **1959**, *81*, 4305–4308.
(5) Zimmerman, H. E. "Molecular Rearrangements"; DeMayo, P., Ed.; Interscience: New York, 1963; Chapter 6, pp 345–406.
(6) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1968**, *90*, 6091–6096.
(7) (a) Malhotra, S. K.; Johnson, F. *J. Am. Chem. Soc.* **1965**, *87*, 5493–5495. (b) Johnson, F.; Dix, D. T. *J. Am. Chem. Soc.* **1971**, *93*, 5931–5932.
(8) Berson, J. A.; Siemionko, R. K. *J. Am. Chem. Soc.* **1980**, *102*, 3870–3882.

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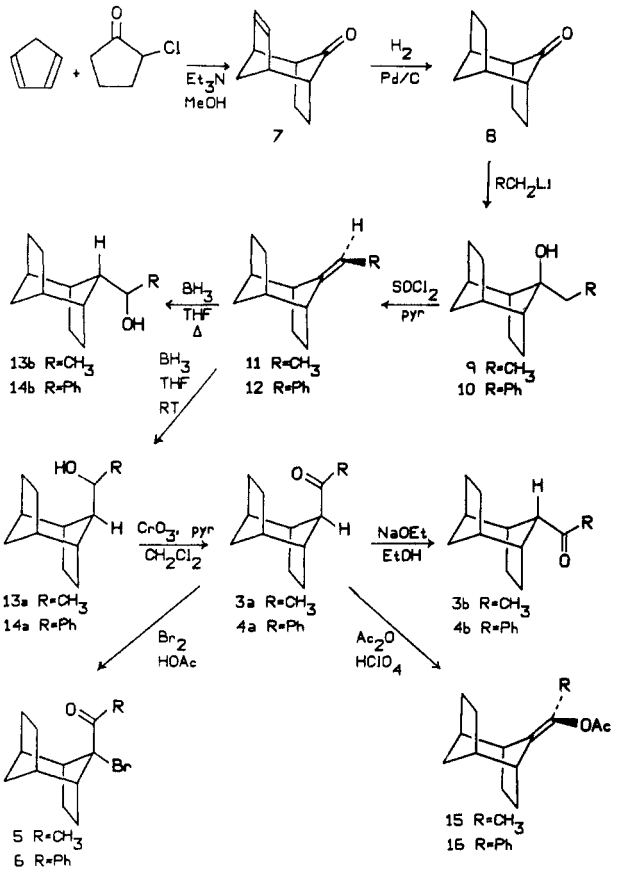
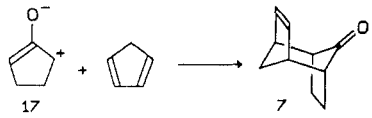
Scheme I. Synthesis of Enol Precursors and Keto Tautomers



amine with the same diene with silver fluoborate.[9] Additionally, it was known[10] that 2-chlorocyclopentanone reacts with furan in similar fashion. The chief advantage of the method developed is the simplicity of the reaction and the reagents employed. The reaction mechanism may be envisaged as the electrocyclic dipolar cycloaddition of the enolate zwitterion **17** with cyclopentadiene as in eq 2.



(2)

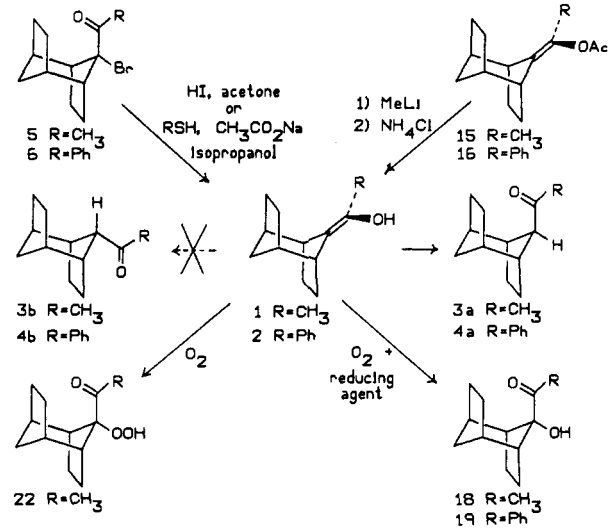
The exo addition of borane to exocyclic tricyclic ketones **11** and **12** led stereoselectively to the endo carbinols **13a** and **14a**. Interestingly, more drastic reaction conditions in the hydroboration resulted in equilibration and led nicely to the exo carbinols **13b** and **14b**.

Use was made of the greater thermodynamic stability of equatorial isomers in the ethoxide-catalyzed conversion of the endo tricyclic ketones **3a** and **4a** to the exo stereoisomers **3b** and **4b**, respectively.

Finally, of interest was the complete failure of the exo tricyclic benzoyl ketone **4b** to brominate.

Stereochemical Studies of Ketonization Using Ground-State Approaches. A number of modes of generation of unstable enols have been tested.[3-6] One very useful method involves treatment of α-bromo ketones with hydriodic acid in acetone. When applied to the tricyclic bromo ketones **5** and **6**, iodine was quickly generated and isolation quantitatively afforded the endo tricyclic ketones

Scheme II. Enol Generation Experiments



4a and **5a** as depicted in Scheme II.

In a second approach to enol generation, the reaction of the bromo ketones with mercaptans was investigated. This reaction has been observed to lead to dehalogenated ketones starting with bromo ketones[11] and iodo ketones.[12] While enol intermediates have been considered[12] in the reaction of iodo ketones, the dehalogenation mechanism seemed uncertain.

In the generation of the acetyl and benzoyl enols **1** and **2** it was observed that ketonization was relatively slow and depended on the reaction conditions. Monitoring of ketonization proved possible, since residual enol reacted rapidly with oxygen with formation of the corresponding hydroperoxy ketones. Enols have long been recognized as reacting avidly with oxygen to form hydroperoxy ketones.[13] With mercaptan present, the hydroperoxy ketones were readily reduced and the corresponding hydroxy ketones **18** and **19** were isolated. Where the enol was generated in isopropyl alcohol alone, as in the photoreaction of the acetyl enol dimer **21**, a stable hydroperoxy ketone **22** could be isolated.

Treatment of the tricyclic bromo ketones with butyl and phenyl mercaptans in isopropyl alcohol, with added sodium acetate, afforded the endo tricyclic ketones **3a** and **4a**. In the reaction of the benzoyltricyclic bromo ketone **6**, premature product isolation led instead to the corresponding α-hydroxy ketone **19** as a consequence of oxygen trapping of the enol. Also, in the dehalogenation of the benzoyltricyclic bromo ketone **6**, it was determined that the half-life of the enol thus generated was of the order of 1 h.

A third approach to the enol utilized the reaction of the enol acetates with methyllithium followed by treatment with ammonium chloride. This, too, is listed in Scheme II. Again the endo tricyclic ketones were found to be formed exclusively. However, the ketonization process was quite slow and exposure to oxygen had to be delayed to afford appreciable ketone.

Stereochemical Studies of Ketonization Using Photochemical Approaches. The photolysis of α-sub-

(9) Ernst, B.; Ganter, C. *Helv. Chim. Acta* **1978**, *61*, 1107–1109.
(10) Föhlisch, B.; Gottstein, W.; Kaiser, R.; Wanner, I. *Tetrahedron Lett.* **1980**, *21*, 3005–3008.
(11) Oki, M.; Funakoshi, W.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 828–832.
(12) Seshadri, R.; Pegg, W. J.; Israel, M. *J. Org. Chem.* **1981**, *46*, 2596–2598.
(13) (a) Kohler, E. P. *J. Am. Chem. Soc.* **1906**, *36*, 177–195. (b) Kohler, E. P. *J. Am. Chem. Soc.* **1932**, *54*, 1594–1600. (c) Kohler, E. P. *J. Am. Chem. Soc.* **1935**, *57*, 2517–2521.

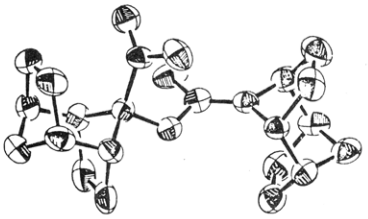
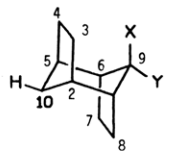


Figure 1. ORTEP drawing of dimer **21**.

stituted ketones is known[14] to result in α-expulsion, with loss of the α substituent either as a radical or anionic species. In the present instance photolysis of the (α-bromoacetyl)tricyclic ketone **5** in unbuffered isopropyl alcohol led to formation of debrominated ketone. However, hydrogen bromide was liberated and only the epimerized exo acetyl ketone stereoisomer **3b** was isolated.

When the same photolysis was carried out with added sodium acetate, the dimeric product **21** ($C_{24}H_{34}O_2$, parent



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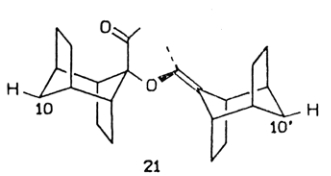


21

MS peak m/e 354.2568), was isolated. The structure of the dimer was suggested by the spectral data. In the proton NMR spectrum two methyl peaks were observed at δ 1.77 and 2.20. In addition, the C-10 exo hydrogen was observed characteristically as a doublet of triplets at an unusually high field for all of the tricyclic derivatives of structure **20**. More cogently, the C-10 exo hydrogens of dimer **21** appeared as two doublets of triplets (note Experimental Section), thus showing the two tricyclic ring structures to be nonequivalent.

The ^{13}C spectrum had a carbonyl peak at 186 ppm and two olefinic absorbances at 120 and 112 ppm, hence suggesting the presence of a O=C—C—O—C=C— moiety. Also, as for most of the compounds studied, the number of ^{13}C peaks were observed to correspond precisely to the number of differently located carbons in the tricyclic derivatives, with the assumption of an effective plane of symmetry through carbons 9 and 10 (note structure **20** for numbering).[15]

An X-ray structure determination confirmed structure **21** as indicated by the ORTEP drawing in Figure 1.[16]

Photolysis of the acetyl dimer **21** led to the acetyltricyclic ketone stereoisomers **3**, thus providing further support for the structural assignment. More importantly, the photolysis of dimer **21** is seen to consist of an α-expulsion reaction which affords two enoloxy radicals which, in isopropyl alcohol, afford the enol of the acetyltricyclic ketone **3** in addition to some tricyclic ketone **3** arising from a route other than ketonization of the enol (vide infra). The ratio of enol to ketone was ca. 1:1.

Enol formation was evidenced by reaction with oxygen to form hydroperoxy ketone **22** which, in turn, was reducible with sodium iodide to hydroxy ketone **18**. The enol was long-lived and tended to survive for days without added acetate.

Table I. Summary of Ketonization Results

mode of generation	product distribution
Acetyl Enol	
HI debromination	>1000:1[a]
dimer photolysis	>100:1[a]
mercaptan debromination	>1000:1[a]
Benzoyl Enol	
HI debromination	>3300:1[b]
mercaptan debromination	>1000:1[a]

[a] NMR analysis. [b] HPLC analysis.

Evidence for direct formation of the acetyltricyclic ketone stereoisomers **3a** and **3b** came from the observation that without added acetate ketone **3** was formed with increasing photolysis time but not with time subsequent to the irradiation. Thus, either the enol is ketonizing photochemically or the dimer irradiation leads to ketone **3** by photochemical mechanisms not involving the enol. A likely possibility is that dimer irradiation affords the enoloxy radical which leads to enol by hydrogen abstraction by oxygen and directly to the tricyclic ketone stereoisomers **3a** and **3b** via abstraction by the α-carbon. Further, the ketone stereochemistry under these conditions varied from 100:1 (endo:exo) at short conversions to 5:1 with longer conversion times. Independent photolysis of the *endo*-acetyltricyclic ketone **3a**, in absence of radical generating species, did not lead to epimerization.

With added acetate, ketonization was complete in 24 hours as evidenced by formation of the acetyltricyclic ketone rather than hydroxy ketone. Acceleration of the ketonization process also occured with addition of acid (note Experimental Section). When the stereochemistry of tricyclic ketone **3** observed under these conditions was corrected for the amount of exo ketone **3b** formed directly, the ratio of endo to exo tricyclic ketone (i.e., **3a** to **3b**) was the same as observed for ketonization via the other approaches described above.

Quantitative Measure of Stereoselectivity and Limits. The ratio of stereoisomer products was obtained by NMR analysis and, in one instance, using HPLC. The results are summarized in Table I. Throughout, the endo stereoisomers were formed to the exclusion of the exo products. A limit of ca. 1/1000 was found by NMR analysis for production of the exo stereoisomer. HPLC analysis, using triphenylmethane as an internal standard, permitted the more stringent limit of 1/3300 to be placed on formation of the exo stereoisomer in the case of ketonization of the benzoyl enol. These limits reflect the analytical methods used. Hence we are provided with a lower limit on stereoselectivity.

Interpretative Discussion

Overall Stereoselectivity of the System. The first item meriting discussion is the exceedingly high stereoselectivity encountered in protonation of the tricyclic enols. The analytical methods available in previous studies provided only limits in those cases where large stereoselectivity resulted. Nevertheless, it is clear that a dramatic enhancement of selectivity is found in the tricyclic system under study compared with the comparable cyclohexane enols having anchoring groups at C-4. A listing of some previously studied systems is presented in Table II.

Secondly, in enols **1** and **2** it is clear that the axial endo ethylene bridge spanning C-3 and C-5 must offer a more stringent impediment to endo approach of the proton donor than is provided by the axial ethylene bridge

(14) (a) Zimmerman, H. E. 17th National Organic Symposium of the American Chemical Society, Bloomington, IN, 1961, pp 31–41. (b) Zimmerman, H. E. *Tetrahedron, Suppl.* **1963**, *19*, 393–401. (c) Zimmerman, H. E. "Advances in Photochemistry"; Noyes, A., Jr., Hammond, G. S., Pitts, J. N., Jr., Eds.; Interscience, New York, 1963; Vol. 1, pp 183–208.

(15) Exceptions were observed where hindrance to rotation about the C-9 to carbonyl bond was increased leading to two non-time-averaged conformers with loss of the effective plane of symmetry. This occurred for the 9-*exo*-bromo-*endo*-benzoyltricyclic ketone **6**.

(16) Structure to be published by K. Haller and L. W. Linder.

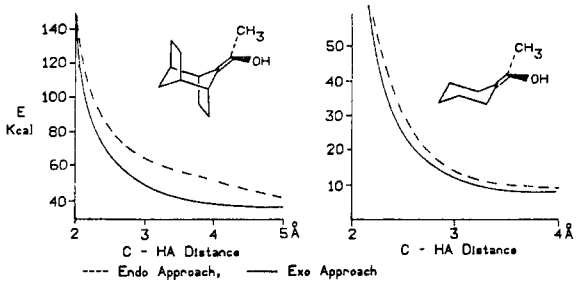
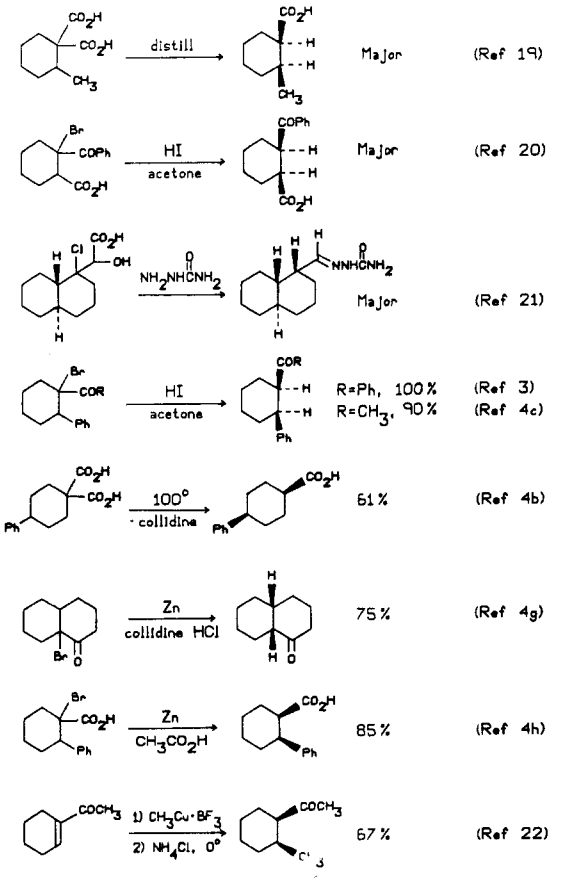


Figure 2. Exo and endo approach of the proton donor for the tricyclic and monocyclic enols.

Table II. Listing of Stereoselectivity in Ketonization



spanning C-2 and C-6. Models confirm this point.

Related to ketonization stereochemistry is enolization. Thus, the striking observation was made that the *exo*-benzoyltricyclic ketone **4b** was completely inert to acid-catalyzed bromination while the *endo*-benzoyltricyclic ketone **4a** brominated readily. This type of behavior has been observed earlier.[3,4a] The unfavorable transition state interposed between exo ketone and enol, as observed in ketonization, is avoided as well when enolization is required for bromination.

Molecular Mechanics Predictions. More convincing than models was a molecular mechanics study making use of MM2[17] as incorporated in a variation of TRIBBLE.[18] A proton donor the size of a bromine atom was brought in toward the enol along both exo and endo perpendicular approaches. The assumption here is a transition state which is still close to sp^2 hydridized as postulated earlier.[3]

(17) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(18) (a) A variation of TRIBBLE[18b] was written to permit more ready construction of three-dimensional molecules. This added a variety of graphic features but used the basic assortment of MM1, MMPI, and MM2 programs in TRIBBLE. (b) Pensak, D. *Ind. Res. Dev.* **1983**, *25*, 74–78.

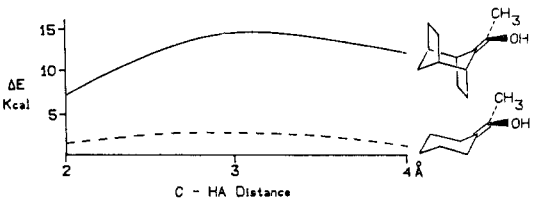


Figure 3. Energy differences between endo and exo approaches as a function of distance.

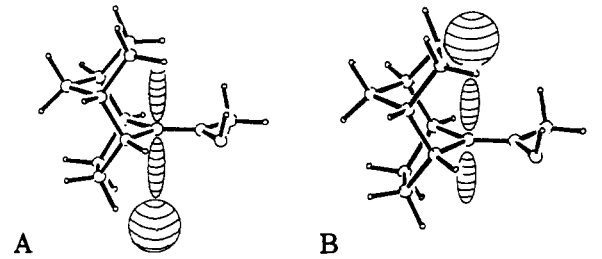


Figure 4. ORTEP drawings for protonation transition state in case of the tricyclic enol: (A) exo approach; (B) endo approach.

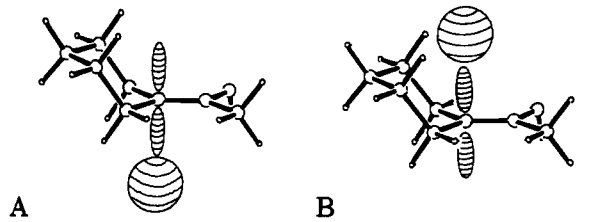


Figure 5. ORTEP drawings for protonation transition state in case of the cyclohexane enol: (A) exo approach; (B) endo approach.

Table III. MM2 Energies of Ketonization Transition State for a 3-Å Approach

enol (geometry[a])	proton donor approach	steric energy, kcal
unsubstituted	exo	11.70
unsubstituted	endo	14.27
2-Ph-equatorial (cis OH)	exo	15.50
2-Ph-axial (cis OH)	endo	16.19
2-Ph-axial (cis OH)	exo	17.89
2-Ph-equatorial (cis OH)	endo	18.02
2-Ph-equatorial (trans OH)	exo	19.31
2-Ph-axial (trans OH)	endo	19.04
2-Ph-axial (trans OH)	exo	21.53
2-Ph-equatorial (trans OH)	endo	28.53
tricyclic	exo	49.11
tricyclic	endo	63.06

[a] Where cis–trans configurations about the enol π-bond exist in the enol of 1-acetyl-2-phenylcyclohexane.

In using MM2 we fixed the distances of the proton donor from the α-carbon and optimized geometry for the remainder of the system. A plot of steric energy was made as a function of distance of the proton donor from the α-carbon. This was carried out for both exo and endo approaches in the tricyclic enol and for both approaches to a simple unsubstituted exocyclic cyclohexane enol. This data is plotted in Figure 2. Figure 3 plots the difference in energies between exo and endo approaches as a function of distance.

Interestingly, while the steric repulsive energies increase with decreasing distance due to van der Waals effect, the differences in repulsive forces reach a broad maximum (note Figure 3) at ca. 3–3.3 Å. This seems to derive from maximum interaction of the proton donor with the axial groups at C-3 and C-5 in the case of the endo approach.

Table III lists the energies obtained for the exo and endo transition states using a 3.0-Å approach.

Table IV. MM2 Steric Energies of Enols

enol	steric energy, kcal
tricyclo[4.2.1.1^{2,5}] enol	39.43
exocyclic cyclohexane enol	9.29
axial-2-Ph cyclohexane enol	12.14
equatorial-2-Ph cyclohexane enol	12.95

ORTEP drawings for exo and endo approaches for the tricyclic and cyclohexane enols are presented in Figures 4 and 5. These clearly show the difficult endo approach hindered by the axial substituents at C-3 and C-5.

A particularly intriguing question derives from the work of Johnson[7] who employed our principle of least hindered approach to discuss the stereochemistry of ketonization of 2-phenyl-substituted cyclohexane enols. However, the discussion made the interesting and reasonable assumption that the preferred transition state would have the phenyl group axial as a result of A^{13} strain. NMR and X-ray study of the enol acetate indicated[7] an axial phenyl group. Also, the MM2 calculations do predict the axial phenyl enol to be lower in energy prior to protonation (note Table IV).

However, there are four possible transition states for protonation of the 2-phenyl exocyclic cyclohexane enols. And it is of interest to consider an application of MM2 to such an example. That of the enol of 2-phenyl-1-acetylcyclohexane was selected as representative. As expected, the importance of A^{13} strain depends on the size of the group cis to the carbon-2 substituent (here Ph). Where the stereoisomer with hydroxyl cis to C-2 is considered, it is seen that the transition states, in order of increasing energy as determined by MM2, are (1) phenyl equatorial–exo protonation, (2) phenyl axial–endo protonation, (3) phenyl axial–exo protonation, and (4) phenyl equatorial–endo protonation. The energies are included in Table III. Conversely, the enols having the enol hydroxyl trans to C-2 show energies slightly favoring the axial 2-phenyl plus endo protonation stereochemistry. To the extent that still larger groups are present cis to C-2 or that there is extensive solvation of the enol oxygen, the axial transition state with endo protonation will be favored, and our MM2 calculations confirm this.

Hence it is clear that two factors control the energy of the transition state for 2-phenyl six-ring enols, namely, A^{13} strain in the substrate portion of the molecule and proton donor steric interaction with the 3,5-axial substituents. We see that in the special case of exocyclic cyclohexane enols substituted at carbon-2 (e.g., with phenyl), either of the two transition states may become preferred depending on molecular details of the particular case.

Both transition states follow our basic hypothesis that protonation occurs from the least hindered approach. Thus, in the 2-phenyl enol case, the lowest energy and next lowest energy transition states both satisfy this criterion.[23] In the absence of a 2-phenyl group, not only the present study but also our earlier work reveals a preferential exo protonation.[6]

Conclusion. Although many concepts in organic chemistry tend to change with time, the stereochemistry of ketonization seems to be one which has remained constant for nearly 3 decades.

Experimental Section[24]

Preparation of *anti*-Tricyclo[4.2.1.1^{2,5}]dec-2-en-9-one. To a stirred solution of 150 mL (123 g, 1.9 mol) of cyclopentadiene, 170 mL of methanol, and 90 mL (65 g, 0.65 mol) of triethylamine was added 36 mL (42 g, 0.36 mol) of 2-chlorocyclopentanone in 50 mL of methanol. The solution was stirred for 14 h, poured into a mixture of 100 mL of 12 M HCl and ice, extracted with hexane (3×), washed with water (3×), and dried over $MgSO_4$, and the solvent was evaporated to afford a pale yellow semisolid which was crystallized from hexane with dry ice cooling for 1 h. The cold precipitate was filtered and recrystallized twice in a similar manner to afford 8.5 g (15%) of *anti*-tricyclo[4.2.1.1^{2,5}]dec-2-en-9-one as a white solid: mp 178–180 °C; IR ($CHCl_3$) 2975, 2900, 1750, 1620, 1480, 1350, 1175, 1040 cm^{-1}; 100-MHz ^{1}H NMR ($CDCl_3$) δ 6.13 (s, 2 H, vinyl), 2.77 (bt, 2 H, bridgeheads), 2.29 (bt, 2 H, bridgeheads), 2.02 (d, 1 H, J = 13 Hz, endo H-C_{10}), 1.66–1.80 (m, 4 H, CH_2), 1.48 (dt, 1 H, exo H-C_{10}); 50-MHz ^{13}C NMR ($CDCl_3$) δ 212.69, 135.7, 48.0, 45.55, 37.05, 22.8; MS, m/e 148.0888 (calcd for $C_{10}H_{12}O$, 148.0888).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.24; H, 8.08.

Preparation of *anti*-Tricyclo[4.2.1.1^{2,5}]decan-9-one. To a 125-mL Parr bottle was added 4.0 g (22 mmol) of *exo*-tricyclo[4.2.1.1^{2,5}]dec-2-en-9-one, 50 mL of methyl acetate, and 50 mg of 10% palladium on carbon. This mixture was hydrogenated on the Parr apparatus at 45 psi for 2 h. The mixture was filtered and concentrated in vacuo to afford 4.0 g (98%) of *anti*-tricyclo[4.2.1.1^{2,5}]decan-9-one as a white solid: mp 120–125 °C; IR ($CHCl_3$) 2950, 2875, 1760, 1750, 1550, 1260, 1225, 1010 cm^{-1}; 100-MHz ^{1}H NMR ($CDCl_3$) δ 2.38 (m, 2 H, bridgeheads α to carbonyl), 2.20 (m, 2 H, bridgehead protons), 1.2–2.0 (m, 10 H, CH_2).

Preparation of 9-*exo*-Benzyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a 250-mL round-bottomed flask was added 13.3 g (1.90 mol) of lithium metal cut into small pieces and 90 mL of anhydrous THF. To the stirred suspension at ambient temperature was added 15.45 g (127 mmol) of benzyl methyl ether in 45 mL of ether at a rate of about 30 drops per min. When the reaction mixture turned green, the mixture was cooled with a carbon tetrachloride/dry ice bath. After the addition was complete, the mixture was stirred an additional hour, and 9.5 g (63.3 mmol) of *anti*-tricyclo[4.2.1.1^{2,5}]decan-9-one was added in 30 mL of ether. The mixture was warmed to ambient temperature, stirred for 0.5 h, added to saturated ammonium chloride, ether extracted, and dried over $MgSO_4$, and the solvent was evaporated to afford 16.0 g (105%) of a pale yellow oil which crystallized after evacuation. Recrystallization from hexane with dry ice cooling afforded 11.9 g (78%) of 9-*exo*-benzyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid: mp 82–83 °C; IR ($CHCl_3$) 3560, 2900, 1600, 1500, 1095 cm^{-1}; 100-MHz ^{1}H NMR ($CDCl_3$) δ 7.20 (m, 5 H, aromatic), 2.80 (s, 2 H, -CH_2-), 1.2–2.4 (mm, 14 H, aliphatic and hydroxyl), 0.92 (dt, 1 H, J_1 = 12 Hz, J_2 = 3 Hz, endo H-C_{10}); MS, m/e 242.1672 (calcd for $C_{17}H_{22}O$, 242.1671).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25, H, 9.15. Found: C, 85.03, H, 9.12.

Preparation of 9-Benzylidene-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a solution of 15.24 g (128 mmol) of thionyl chloride

(19) Goodwin, W.; Perkin, W. H. *J. Chem. Soc.* **1895**, 119–128.
(20) Jansen, Ph. D. Thesis, Harvard University, 1937.
(21) Dauben, W. G.; Teit, R. C.; Mannerskantz, C. *J. Am. Chem. Soc.* **1954**, *76*, 4420–4426.
(22) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem.* **1982**, *47*, 119–126.
(23) (a) The model chosen has the acetyl methyl trans to the ring carbon bearing the C-2 phenyl group and MM2 assumes that we are dealing with an unsolvated enolic oxygen. If the oxygen is strongly solvated, then that atom does become effectively larger and the axial phenyl transition state does become lower in energy. The values given in Table III are intended to show that in the simplest approximation hindrance to approach of the proton donor becomes the dominant factor. (b) Hence there is no basic disagreement between the work of Johnson et al.[7] and our basic theory.

(24) Melting points were determined by using a calibrated hot-stage apparatus or, in cases where sublimation occurred, in sealed tubes. Elemental analyses were performed by Galbraith Laboratory, Inc., Knoxville, TN. All reactions were run under an atmosphere of dry nitrogen unless otherwise specified. Column chromatography was performed on silica gel (Matheson, Coleman and Bell, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into quartz columns such that band elution could be monitored by a hand-held UV lamp. All exploratory irradiations were performed on a 450-W medium-pressure mercury lamp immersion apparatus fitted with a Corex glass filter sleeve and cooled directly with regulated tap water. All runs were purged with purified nitrogen for at least 1 h before photolysis.

in 125 mL of anhydrous pyridine cooled in an ice bath was added 15.5 g (64 mmol) of 9-*exo*-benzyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 50 mL of pyridine dropwise over 15 min. The mixture was stirred in the ice bath for 1 h, added to 50% concentrated HCl–ice, and ether extracted. The combined ether layers were water washed, and dried over $MgSO_4$, and the solvent was evaporated to afford 11 g (77%) of 9-benzylidene-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a pale yellow oil: IR (thin film) 2890, 1660, 1590, 1480, 1440, 900, 840, 730, 690 cm^{-1}; 100-MHz ^{1}H NMR ($CDCl_3$) δ 7.2 (m, 5 H, phenyl), 6.04 (s, 1 H, vinyl), 0.9–2.4 (m, 14 H, aliphatic); MS, *m/e* 224.1565 (calcd for $C_{17}H_{20}$, 224.1565).

Anal. Calcd for $C_{17}H_{20}$: C, 91.01, H, 8.99. Found: C, 90.83, H, 9.21.

Preparation of 9-*endo*-(Phenylhydroxymethyl)-*anti*-tricyclo[4.2.1.1^{2,5}]decane. A solution of 2.69 g (12 mmol) of 9-benzylidene-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 37 mL of 0.97 M borane in THF was stirred at ambient temperature for 20 h. The mixture was cooled with an ice bath, 95% ethanol was added to quench the remaining borane, a solution of 3 g of NaOH in 25 mL of 30% hydrogen peroxide was added, and the mixture was heated at reflux for 1 h. The mixture was then cooled to ambient temperature, added to water, ether extracted, and dried over $MgSO_4$, and the solvent was evaporated to afford 2.84 g of a clear oil. Crystallization from hexane affored 1.61 g (59%) of 9-*endo*-(phenylhydroxymethyl)-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid (mp 95–96 °C): IR ($CHCl_3$) 3360, 2925, 2880, 1600, 1490, 1475, 1460, 1450 cm^{-1}; 100-MHz ^{1}H NMR ($CDCl_3$) δ 7.19 (m, 5 H, aromatic), 5.30 (d, 1 H, J = 12 Hz, -CHOH-), 1.1–2.4 (mm, aliphatic + hydroxy); 50-MHz ^{13}C NMR ($CDCl_3$) δ 145.562, 128.334, 127.370, 126.465, 74.810, 58.487, 40.734, 40.296, 39.186, 38.076, 35.127, 30.893, 30.835, 30.150, 28.908; MS, *m/e* 242.1671 (calcd for $C_{17}H_{22}O$, 242.1671).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25, H, 9.15. Found: C, 84.25, H, 8.90.

A similar run which was refluxed for 5 h prior to the same workup gave an approximately 1:1 mixture of 9-*endo*- and 9-*exo*-(phenylhydroxymethyl)-*anti*-tricyclo[4.2.1.1^{2,5}]decanes as evidenced by the appearance of a doublet (J = 11 Hz) at δ 4.18 (R_2CHOH). Oxidation of this material with CrO_3–pyridine resulted in the formation of a 1:1 mixture of 9-*endo*- and 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decanes.

Preparation of 9-*endo*-Benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]-decane. To a stirred solution of 24 mL (298 mmol) of anhydrous pyridine in 250 mL of methylene chloride was added 14.9 g (149 mmol) of chromium trioxide. After 5 min of stirring, 6.0 g (24.8 mmol) of 9-*endo*-(phenylhydroxymethyl)-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 25 mL of methylene chloride was added, and the mixture was stirred for 15 min. To the now brown mixture was added 10 mL of 2-propanol and stirring was continued for another 15 min. The mixture was then filtered and the solvent evaporated, the residue was refluxed in hexane and filtered, and the solvent was evaporated and crystallized from hexane to afford 4.79 g (80%) of 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid: mp 137–138 °C; IR (CCl_4) 2950, 2880, 1680, 1603, 1585, 1495, 1480, 1450, 1370, 1320, 1290, 1245, 1218, 1180, 1975, 1030, 1000, 985, 875, 853 cm^{-1}; 100-MHz ^{1}H NMR ($CDCl_3$) δ 7.60 (m, 2 H, aromatic), 7.30 (m, 3 H, aromatic), 2.77 (bs, 3 H, bridgehead + CHC=O), 2.03 (m, 3 H, bridgehead + endo H-C_{10}), 1.1–1.85 (m, 8 H, aliphatic), 0.90 (dt, 1 H, J_1 = 11.7 Hz, J_2 = 3.8 Hz, exo H-C_{10}); MS, *m/e* 240.1514 (calcd for $C_{17}H_{20}O$, 240.1514).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.24; H, 8.36.

Preparation of 9-*exo*-Benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a stirred solution of sodium ethoxide prepared from 100 mg (4.35 mmol) of sodium and 45 mL of anhydrous ethanol was added 400 mg of 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane, and the solution was stirred for 12 h at ambient temperature. The mixture was then poured into water, ether extracted, and dried, and the solvent evaporated to afford 395 mg of a pale yellow oil which was crystallized from hexane to afford 300 mg (75%) of 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid: mp 54–57 °C (Further recrystallization from 95% ethanol raised the melting point to 58.5–59 °C.); IR (CCl_4) 2950, 2880, 1690, 1605, 1590, 1475, 1450, 1240, 990, 710, 700, 645 cm^{-1}; 270-MHz ^{1}H NMR ($CDCl_3$) δ 7.87 (m, 2 H), 7.42 (m, 3 H), 3.55 (bs, 1 H), 2.40 (bs, 2 H), 2.15 (bs, 2 H), 1.92 (d, 1 H, J = 4.3 Hz), 1.6–1.8 (m, 8 H), 0.95 (dt, 1 H, J_1 = 11.6 Hz, J_2 = 3.8 Hz); 50-MHz ^{13}C NMR ($CDCl_3$) δ 202.88, 136.39, 132.16, 128.42, 128.27, 51.71, 42.51, 39.65, 32.29, 29.35, 27.16; UV (cyclohexane) 240 (12,200), 276 (807), 288 (sh, 600); MS, *m/e* 240.1514 (calcd for $C_{17}H_{20}O$, 240.1514).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96, H, 8.39. Found: C, 84.95, H, 8.31.

Preparation of 9-*endo*-Benzoyl-9-bromo-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a stirred 0 °C solution of 200 mg (0.83 mmol) of 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 15 mL of glacial acetic acid and 10 mL of chloroform was added 0.050 mL of bromine via syringe. The solution was then added to 0.1 N sodium thiosulfate solution, extracted with ether, and dried, and the solvent was evaporated to afford 250 mg of a pale yellow solid, mp 127–130 °C. Recrystallization from hexane afforded 200 mg (75%) of 9-*endo*-benzoyl-9-bromo-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid, mp 137–140 °C. Two further recrystallizations afforded ultrapure material: mp 139–140 °C); IR (CCl_4) 3050, 3000, 2960, 2920, 2880, 1670, 1600, 1580, 1490, 1475, 1460, 1450, 1315, 1290, 1280, 1250, 1210, 1190, 1180, 1160, 1055, 1030, 975, 875, 850, 700, 690, 665, 615 cm^{-1}; 100-MHz ^{1}H NMR ($CDCl_3$) δ 8.08 (m, 2 H), 7.36 (m, 2 H), 3.08 (m, 2 H), 1.6–2.8 (m, 9 H), 0.98 (dt, 1 H, J_1 = 11.7 Hz, J_2 = 3.8 Hz); 50-MHz ^{13}C NMR δ 189.80, 136.92, 131.81, 129.97, 128.27, 90.31, 48.24, 47.25, 44.12, 41.96, 34.43, 31.51, 28.99, 28.65, 26.05; MS, *m/e* 318.0620 (calcd for $C_{17}H_{19}BrO$, 318.0619).

Anal. Calcd for $C_{17}H_{19}BrO$: C, 63.97; H, 5.96. Found: C, 64.29; H, 6.09.

Preparation of the Enol Acetate of 9-*endo*-Benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a stirred solution of 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane (4.17 mmol) in 50 mL of ethyl acetate at ambient temperature was added a solution of 9.6 mL of acetic anhydride (10.2 mmol) and 0.10 mL of 60% perchloric acid in 40 mL of ethyl acetate. The solution was stirred for 10 min and added to saturated $NaHCO_3$ and pentane, and the phases were separated. The organic phase was washed several times with saturated $NaHCO_3$ until CO_2 evolution ceased and dried over Na_2SO_4, and the solvent was evaporated to afford 1.16 g (93%) of the enol acetate as a pale yellow oil which darkened and deposited a dark solid unless used promptly.

The spectral data were as follows: IR (thin film) 2950, 2860, 1745, 1370, 1220, 1050, 1030, 790, 760 cm^{-1}; 100-MHz ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H, aromatic), 2.70 (bs, 2 H), 2.16 (s, 3 H, CH_3), 2.04 (m, 2 H), 1.8–1.0 (m, 10 H).

Preparation of 9-*exo*-Ethyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a stirred 0 °C solution of 0.5 g (3.33 mmol) of 9-oxo-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 10 mL of anhydrous ether at ambient temperature was added 26 mL (5.0 mmol) of 0.19 M ethyllithium in ether via syringe. The resulting solution was warmed to ambient temperature, added to saturated NH_4Cl solution, ether extracted, and dried over $MgSO_4$, and the solvent was evaporated to afford 0.50 g (83%) of 9-*exo*-ethyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a clear oil: IR (thin film) 3600, 3500, 2920, 1500, 1300, 1200, 1140, 1020 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 3.86 (bs, 1 H, R_2CHO-), 2.34 (m, 2 H, C3 + C4), 2.10 (d, 1 H, J = 11.8 Hz, endo H-C_{10}), 2.05 (bs, 2 H, C1 + C6 H's), 1.86 (bs, 3 H, C2 + C4-H's + OH), 1.52 (s, 6 H, aliphatic), 1.10 (bd, 1 H, J = 11.8 Hz, exo H-C_{10}); MS, *m/e* 180.1514 (calcd for $C_{12}H_{20}O$, 180.1514).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.08. Found: C, 79.89; H, 11.00.

Preparation of 9-Ethylidene-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a stirred solution of 5.6 g (31 mmol) of 9-*exo*-ethyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 100 mL of anhydrous pyridine at 0 °C was added 4.5 mL (7.4 g, 62 mmol) of thionyl chloride. After being stirred for 1 h at 0 °C, the mixture was added to 250 mL of cold 15% HCl, ether extracted, and dried over $MgSO_4$, and the solvent was evaporated to afford 4.46 g (89%) of 9-ethylidene-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a pale yellow oil: IR (thin film) 2920, 2840, 1470, 1390, 1120, 1220, 1150, 1000, 840 cm^{-1}; 200-MHz ^{1}H NMR δ 5.02 (q, 1 H, J = 6.6 Hz, vinyl), 2.59 (m, 1 H, C-H), 2.05 (m, 4 H, C-H), 1.68 (d, 1 H, J = 12 Hz, endo H-C_{10}), 1.60 (d, 3 H, J = 6.6 Hz, CH_3), 1.42 (m, 7 H, C-H), 1.10 (dt, 1 H, J_1 = 12 Hz, J_2 = 3.8 Hz, exo H-C_{10}); MS, *m/e* 162.1409 (calcd for $C_{12}H_{18}$, 162.1409).

Preparation of 9-*endo*-(1-Hydroxyethyl)-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a flask containing 0.5 g (3.1 mmol) of

9-ethylidene-*anti*-tricyclo[4.2.1.1^{2,5}]decane was added 9.3 mL (9.3 mmol) of 1 M borane in THF and the resulting solution stirred at ambient temperature for 19 h. Excess borane was then quenched with 95% ethanol, the solution was cooled to 0 °C, and a solution of 0.66 g of sodium hydroxide in 6.5 mL of hydrogen peroxide was added. The mixture was then refluxed for 1 h, cooled, added to water, ether extracted, and dried over $MgSO_4$, and the solvent was evaporated to afford 0.5 g (90%) of 9-*endo*-(1-hydroxyethyl)-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid: mp 83–87 °C (Recrystallization from pentane afforded 0.45 g, mp 93–94 °C.); IR ($CHCl_3$) 3600, 3440, 2940, 1470, 1450, 1370, 1240, 1115, 1060, 1010, 980, 950, 870 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 4.5 (dq, 1 H, J_1 = 15 Hz, J_2 = 7.5 Hz, R_2CHOR), 2.0 (m, 7 H, aliphatic + OH?), 1.55 (m, 7 H, aliphatic), 1.30 (m, 1 H, aliphatic), 1.20 (d, 3 H, J = 7.5 Hz, CH_3), 0.95 (dt, 1 H, J_1 = 11.7 Hz, J_2 = 3.8 Hz, exo H-C_{10}); MS, m/e 180.1514 (calcd for $C_{12}H_{20}O$, 180.1514).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94, H, 11.08. Found: C, 79.44, H, 11.16.

A similar run which was refluxed for 1 h in THF gave a 1:1 mixture of 9-*endo*- and 9-*exo*-(1-hydroxyethyl)-*anti*-tricyclo-[4.2.1.1^{2,5}]decanes as evidenced by the appearance of a doublet (J = 7 Hz) at δ 1.12 (CH_3) in the ^{1}H NMR spectrum. Oxidation of this material with CrO_3–pyridine gave a 1:1 mixture of 9-*endo*- and 9-*exo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decanes.

Preparation of 9-*endo*-Acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a stirred solution of 4.3 g (17 mmol) of chromium trioxide–pyridine complex in 25 mL of methylene chloride at ambient temperature was added 0.5 g (2.8 mmol) of 9-*endo*-(1-hydroxyethyl)-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 5 mL of methylene chloride, and the mixture was stirred for 15 min. To the now brown mixture was added 1.0 mL of 2-propanol, and stirring was continued for another 15 min. The mixture was then filtered, the solvent evaporated, the residue refluxed in hexane and filtered, and the solvent evaporated to afford 0.32 g (65%) of 9-*endo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane as an oily solid, mp 30–60 °C, which was pure by NMR. Two recrystallizations from pentane (–78 °C) afforded an analytical sample, mp 78–79 °C: IR ($CHCl_3$) 2940, 2860, 1700, 1470, 1450, 1150, 1230, 1195, 1175, 1160 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 2.56 (bs, 2 H, C1 + C6-H), 2.30 (s, 3 H, CH_3), 2.02 (m, 4 H, CH), 1.62 (m, 8 H, CH), 0.95 (m, 1 H, exo H-C_{10}); MS, m/e 178.1358 (calcd for $C_{12}H_{20}O$, 178.1358).

Anal. Calcd for $C_{12}H_{20}O$: C, 80.85, H, 10.18. Found: C, 80.45, H, 10.56.

Preparation of 9-*exo*-Acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To 40 mL of anhydrous ethanol was added 100 mg (4.35 mmol) of sodium metal, and the mixture was stirred until ethoxide formation was complete. A solution of 324 mg (1.82 mmol) of 9-*endo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 10 mL of ethanol was added, the solution was stirred for 16 h, added to water, pentane extracted, washed with water (2×), and dried over sodium sulfate, and the solvent was evaporated to afford 306 mg (94%) of 9-*exo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a clear oil: IR (thin film) 2940, 2870, 1705, 1470, 1360, 1210, 1160 cm^{-1}; NMR ($CDCl_3$) δ 2.66 (s, 1 H, α-CO), 2.39 (bs, 2 H, bridgehead), 2.08 (s, 3 H, CH_3), 2.08 (bs, 2 H, bridgehead), 1.86 (d, 1 H, 11.7 Hz, endo H-C_{10}), 1.58 (m, 8 H, CH_2), 0.91 (dt, 1 H, J = 11.7, 3.7 Hz, exo H-C_{10}); MS, m/e 178.1358 (calcd for $C_{12}H_{20}$, 178.1358).

Anal. Calcd for $C_{18}H_{20}O$: C, 80.85; H, 10.18. Found: C, 80.36; H, 10.14.

Preparation of 9-*endo*-Acetyl-9-bromo-*anti*-tricyclo-[4.2.1.1^{2,5}]decane. To a solution of 5.23 g (29.4 mmol) of 9-*endo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 50 mL of glacial acetic acid and 50 mL of chloroform at 0 °C was added 1.66 mL of bromine dropwise. Each drop was decolorized instantly except for the last drop or two. The solution was added to 0.1 N sodium thiosulfate solution and extracted with pentane (2×), the combined extracts were washed with 1 M sodium acetate solution (3×) and dried over sodium sulfate, and the solvent was evaporated to afford 7.28 g of a pale yellow oil which was crystallized from pentane with dry ice cooling to afford 4.67 g (62%) of 9-*endo*-acetyl-9-bromo-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid, mp 80–95 °C. Recrystallization from pentane afforded 3.91 g (52%) of material: mp 134–135 °C; IR (thin film) 2940, 2880, 1700, 1470, 1450, 1350, 1270, 1230, 1170 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 2.82 (m, 1 H, CH), 2.65 (s, 3 H, CH_3), 2.24 (m, 5 H, CH), 1.94 (m, 2 H, CH), 1.64 (m, 2 H, CH), 1.41 (m, 2 H, CH), 1.04 (dt, 1 H, J = 11.9, 3.4 Hz, exo H-C_{10}).

Anal. Calcd for $C_{12}H_{17}OBr$: C, 56.05; H, 6.66. Found: C, 56.49; H, 6.85.

Preparation of the Enol Acetate of 9-*endo*-Acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a stirred solution of 0.325 g (1.83 mmol) of 9-*endo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 5 mL of ethyl acetate was added a solution prepared from 50 mL of ethyl acetate, 0.050 mL of 60% perchloric acid, and 4.8 mL of acetic anhydride. The resulting solution was stirred at ambient temperature for 5 min, added to saturated $NaHCO_3$ solution, extracted with pentane, washed with $NaHCO_3$ solution until CO_2 evolution ceased, and dried over Na_2SO_4, and the solvent was evaporated to afford 0.401 g (93%) of the desired enol acetate as a pale yellow oil: IR (neat) 2940, 2860, 1750, 1370, 1250, 1240, 1210, 1200, 1190, 1140, 1060, 1020 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 2.49 (m, 2 H, bridgehead), 2.115 (3 H, s, CH_3), 2.00 (m, 4 H), 1.878 (s, 3 H, CH_3), 1.55 (m, 7 H), 1.02 (1 H, dt, J_1 = 11.9 Hz, J_2 = 3.8 Hz, endo H-C_{10}).

Generation of the Enol from the Enolate of 9-Benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. Synthesis of 9-*endo*-Benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To 15 mL of anhydrous DME at 0 °C was added 2.19 mL (1.84 mmol) of 0.84 M methyllithium in ether, and a white precipitate was formed. The enol acetate of 9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane (0.216 g, 0.766 mmol) was added via syringe in 10 mL of anhydrous DME, and the mixture was stirred for 1 min. The mixture was then added to saturated NH_4Cl solution in a separatory funnel, extracted with pentane, washed with water, and dried over anhydrous sodium sulfate while oxygen was bubbled into the solution for 5 min. The solvent was evaporated carefully without heating to afford 184 mg of a white solid. This material was dissolved in 10 mL of $CHCl_3$ and treated with 10 mL of acetic acid and 5 mL of a saturated aqueous solution of sodium iodide. A strong iodine-colored solution resulted, and the mixture was diluted with pentane, washed with 0.1 N sodium thiosulfate, 2 M sodium acetate (3×), and dried over sodium sulfate, and the solvent was evaporated to afford 159 mg (81%) of 9-*endo*-benzoyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a pale pink solid, mp 140–150 °C. Recrystallization from hexane gave 124 g (63%) of white solid, mp 154–155 °C.

A similar run in which the enolate was transfered via cannula to a stirred mixture of saturated aqueous NH_4Cl and pentane, stirred under nitrogen for 48 h, and worked up in the same fashion gave a 5:1 ratio of hydroxybenzoyl to endo benzoyl ketone by ^{1}H NMR. No *exo* benzoyltricyclic could be detected.

The spectral data for the hydroxybenzyltricyclic were as follows: IR ($CHCl_3$) 3560, 3400, 2930, 2880, 1660, 1590, 1470, 1440, 1260, 1180, 1010, 950, 860, 850 cm^{-1}; 200-MHz ^{1}H NMR δ 8.01 (m, 2 H, aromatic), 7.38 (m, 3 H, aromatic), 2.73 (m, 1 H), 2.53 (m, 1 H), 2.2–2.0 (variable) (s, 1 H, OH), 1.27 (m, 3 H), 0.82 (dt, 1 H, J_1 = 11.6 Hz, J_2 = 3.3 Hz).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.63; H, 7.86.

Generation of the Enol from the Enolate of 9-Acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. Preparation of 9-*endo*-Acetyl-9-hydroperoxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To 15 mL of anhydrous DME at 0 °C was added 1.38 mL (1.16 mmol) 0.84 M methyllithium in ether, and a white precipitate was formed. The enol acetate of 9-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane (0.106 g, 0.482 mmol) was added via syringe in 10 mL of anhydrous DME, and the mixture was stirred for 1 min. The mixture was then added to saturated NH_4Cl solution in a separatory funnel, extracted with pentane, washed with water, and dried over anhydrous sodium sulfate while oxygen was bubbled into the solution for 5 min. The solvent was evaporated carefully without heating to afford 63 mg (62%) of 9-*endo*-acetyl-9-hydroperoxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid. Recrystallization from hexane/CH_2Cl_2 by partial evaporation of solvent under a stream of nitrogen afforded 49 mg (48%) of the hydroperoxide as a white solid: IR ($CHCl_3$) 3540, 3320, 2940, 1715, 1485, 1470, 1370, 1160 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 7.7 (bs, 1 H, OOH), 2.75 (bs, 1 H), 2.419 (s, 3 H, acetyl), 2.3–1.2 (13 H, m), 0.9 (dt, 1 H, J_1 = 11.6 Hz, J_2 = 3.4 Hz, exo H-C_{10}).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 67.90; H, 8.59.

Reduction of 9-*endo*-Acetyl-9-hydroperoxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Sodium Iodide. Synthesis of 9-*endo*-Acetyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane. A solution of 49 mg (0.23 mmol) of 9-*endo*-acetyl-9-hydroperoxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 3.0 mL of chloroform and 3.0 mL of acetic acid was treated with 1.0 mL of a saturated solution of sodium iodide. Iodine was liberated immediately, the mixture was extracted with pentane, washed with sodium thiosulfate and pH 7.0 buffer, and dried over $MgSO_4$, and the solvent was evaporated. Crystallization from cold pentane afforded 38 mg (84%) of 9-*endo*-acetyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid: mp (sealed tube) 117–118 °C; IR (CCl_4) 3570, 3540, 2920, 1705, 1475, 1460, 1160, 1290, 1250, 1180, 1150, 950 cm^{-1}; 200-MHz ^{1}H NMR δ 2.44 (s, 3 H, acetyl), 2.3–0.9 (mm, 15 H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.22; H, 8.99.

Debromination of 9-*exo*-Bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Hydriodic Acid. Run A: In Acetone at 0 °C. To a solution of 25 mg (0.078 mmol) of 9-*exo*-bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 3 mL of acetone at 0 °C was added 0.050 mL of 57% hydriodic acid. The solution turned red-brown immediately and was added to 0.1 N sodium thiosulfate solution, extracted with methylene chloride, dried over $MgSO_4$, and the solvent was evaporated to afford 19.3 mg (102%), of a clear oil. The 200-MHz ^{1}H NMR of this material was identical in all respects with that of 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. No 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane could be detected, and a detectability limit of 0.1% for 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane was established by independent sampling of a similar sample prepared from pure materials. Attempted analysis by HPLC was complicated by interference of compounds other than the 9-benzoyl ketones. A control experiment in which acetone alone was treated with hydriodic acid under identical conditions showed the same peaks when analyzed by HPLC.

Run B: In Tetrahydrofuran at 0 °C. To a solution of 25 mg (0.078 mmol) of 9-*exo*-bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 3 mL of tetrahydrofuran at 0 °C was added 0.050 mL of 57% hydriodic acid. The solution turned red-brown immediately and was added to 0.1 N sodium thiosulfate solution, extracted with methylene chloride, and dried over $MgSO_4$, and the solvent was evaporated to afford 18.3 mg (97%) of a clear oil. The 200-MHz NMR of this material was identical in all respects with that of 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. No 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane could be detected, and a detectability limit of 0.1% of 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane was established by independent sampling of a similar sample prepared from pure materials. Analysis by HPLC established the more stringent limit of less than 0.03% 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. More stringent limits could not be set due to interfering peaks.

Run C: In Acetone for 4 h. To a stirred solution of 50 mg (0.157 mmol) of 9-*exo*-bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]-decane in 3.0 mL purified acetone at ambient temperature was added 0.100 mL of 57% hydriodic acid, and the resulting red solution was stirred for 4 h. The mixture was added to 0.1 N sodium thiosulfate solution, extracted with methylene chloride, and dried over magnesium sulfate, and the solvent was evaporated to afford 37.9 mg (100%) of a white solid. Analysis by 200-MHz ^{1}H NMR showed the mixture to be 29% 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane and 71% 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane.

Debromination of 9-*exo*-Bromo-9-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Hydriodic Acid in Acetone at 0 °C. To a solution of 25 mg (0.097 mmol) of 9-*exo*-bromo-9-*endo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 3 mL of acetone at 0 °C was added 0.050 mL of 57% hydriodic acid. The solution turned red-brown immediately, was added to 0.1 N sodium thiosulfate solution, extracted with methylene chloride, dried over $MgSO_4$, and the solvent evaporated to afford 16.9 mg (98%) of 9-*endo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a clear oil. The 200-MHz NMR of this material was identical in all respects with that of 9-*endo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. None of the exo isomer could be detected, and a detectability limit 0.1% of 9-*exo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane was established by independent sampling of a similar sample prepared from pure materials.

Debromination of 9-*exo*-Bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Thiophenol and Sodium Acetate. Isolation of Products. A mixture of 0.100 g (0.313 mmol) of 9-*exo*-bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane, 0.200 g (2.44 mmol) of sodium acetate, and 15 mL (127 mmol) of thiophenol in 135 mL of isopropyl alcohol and was stirred for 0.5 h at ambient temperature. The mixture was added to water and pentane extracted, the combined pentane extracts were washed with water (2×), 5% sodium hydroxide (2×), and water (2×) and dried over Na_2SO_4, and the solvent was evaporated to afford 0.264 g of a pale yellow oil. Chromatography on a 2 × 15 cm silica gel column slurry packed in hexane gave the following results: 75 mL of hexane, nil; 75 mL of hexane, 128 mg of diphenyl disulfide; 150 mL of hexane, nil; 150 mL of 25% CH_2Cl_2/hexane, 18 mg (24%), shown by ^{1}H NMR to be a 4 to 1 mixture of 9-*endo*- and 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decanes; 125 mL of CH_2Cl_2/hexane, 15 mg, unidentified aromatic compound; 150 mL of CH_2Cl_2, 54 mg (67%) of white solid, mp 135–143 °C, identified as 9-*endo*-benzoyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane. Crystallization of the last fraction from hexane afforded 41 mg (51%) of the hydroxybenzoyl tricyclic as a white solid, mp 150–153 °C.

The spectral data for 9-*endo*-benzoyl-9-hydroxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane were as follows: IR ($CHCl_3$) 3560, 3400, 2930, 2880, 1660, 1590, 1470, 1440, 1260, 1180, 1010, 950, 860, 850 cm^{-1}; 200-MHz ^{1}H NMR δ 8.01 (m, 2 H, aromatic), 7.38 (m, 3 H, aromatic), 2.73 (m, 1 H), 2.53 (m, 1 H), 2.2–2.0 (variable) (s, 1 H, OH), 1.27 (m, 3 H), 0.82 (dt, 1 H, J_1 = 11.6 Hz, J_2 = 3.3 Hz).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65, H, 7.86. Found: C, 79.63, H, 7.86.

Reaction of 9-*exo*-Bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane with 1-Butanethiol and Sodium Acetate. A mixture of 0.100 g (0.389 mmol) of 9-*exo*-bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane, 0.200 g (2.44 mmol) of sodium acetate, and 15 mL of 1-butanethiol in 135 mL of isopropyl alcohol was stirred for 1 h at ambient temperature. The mixture was evaporated at aspirator pressure on a bulb-to-bulb apparatus overnight. The solid residue was extracted with carbon tetrachloride, filtered, and evaporated. Analysis by 100-MHz ^{1}H NMR revealed it to be only 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane and di-*n*-butyl disulfide.

Reaction of 9-*exo*-Bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane with *n*-Butyl Mercaptan and Sodium Acetate in Isopropyl Alcohol in the Absence of a Base Workup. A solution of 100 mg (0.313 mmol) of 9-*exo*-bromo-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane, 15 mL of *n*-butyl mercaptan, and 200 mg of sodium acetate in 135 mL of isopropyl alcohol was stirred at ambient temperature for 0.5 h, and the solvent was evaporated on a wide bore bulb-to-bulb apparatus with oil bath heating used to maintain a bath temperature of 25–30 °C at a pressure of approximately 1 torr. Evaporation took 45 min, after which time the oil bath was removed and evacuation was maintained until the distillation flask warmed to ambient temperature. It was then promptly opened to the air, taken up in pentane, added to ice-cold water, washed with water (3×), and dried over sodium sulfate, and the solvent was evaporated. Analysis by 200-MHz ^{1}H NMR gave 69% 9-*exo*-hydroxy-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane, 29% 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane, and 2% 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane. A similar run in which the residue after evaporation was taken up in pentane and methylene chloride and washed with 10% sodium hydroxide gave 58% 9-*exo*-hydroxy-9-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane, 26% 9-*endo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane, and 16% 9-*exo*-benzoyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane.

Reaction of 9-*endo*-Acetyl-9-bromo-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Thiophenol and Sodium Acetate. A mixture of 0.100 g (0.389 mmol) of 9-*endo*-acetyl-9-bromo-*anti*-tricyclo[4.2.1.1^{2,5}]decane, 0.200 g (2.44 mmol) of sodium acetate, and 15 mL (127 mmol) of thiophenol in 135 mL of isopropyl alcohol was stirred at ambient temperature for 1 h. The mixture was added to water and pentane extracted, the combined pentane extracts were washed with water (2×), 5% sodium hydroxide (2×), and water (2×) and dried over Na_2SO_4, and the solvent was evaporated to afford 0.315 g of a pale yellow oil which was analyzed

by 270-MHz ^{1}H NMR and found to be 9-*endo*-acetyl-*anti*-tricyclo[4.2.1.1^{2,5}]decane and diphenyl disulfide. Separation by chromatography on a 2 × 20 cm silica gel column by elution with hexane followed by methylene chloride afforded 64 mg (92%) of the pure endo ketone.

Exploratory Photolysis of 9-*endo*-Acetyl-9-bromo-*anti*-tricyclo[4.2.1.1^{2,5}]decane. Preparation of the Enoloxy Dimer 9-*endo*-Acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1$^{2',5'}$]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane. To a solution of 0.912 g (3.55 mmol) of 9-*endo*-acetyl-9-bromo-*anti*-tricyclo-[4.2.1.1^{2,5}]decane in 150 mL of isopropyl alcohol was added 2.00 g (24.4 mmol) of anhydrous sodium acetate, and the mixture was irradiated at 5–10 °C for 15 min. The photolysate was evaporated, extracted with methylene chloride, and evaporated to afford 0.843 g of a clear oil which was chromatographed on a 2 × 30 cm silica gel column. Elution with 150 mL of 50% methylene chloride–hexane gave 0.679 g of white solid which was recrystallized from methanol to afford 0.491 g (78%) of the enoloxy dimer, mp 126–128 °C. Elution with 100 mL of methylene chloride afforded 0.116 g of an oily solid which was analyzed by 100-MHz ^{1}H NMR to consist of a 2:1:1 mixture of dimer, hydroperoxyacetyltricyclic, and *endo*-acetyltricyclic compounds.

The spectral data were as follows: IR (CCl_4) 2950, 2880, 1705, 1475, 1460, 1380, 1230, 1150, 970, 940 cm^{-1}; 200-MHz ^{1}H NMR ($CDCl_3$) δ 2.79 (m, 2 H, bridgehead), 2.46 (s, 1 H), 2.36 (m, 2 H, bridgehead), 2.20 (s, 3 H, CH_3), 2.13–1.85 (m, 8 H, aliphatic), 1.77 (s, 3 H, CH_3), 1.69–1.27 (m, 13 H, aliphatic), 0.96 (dt, 1 H, J_1 = 11.5 Hz, J_2 = 3.6 Hz, exo H-C_{10}), 0.86 (dt, J_1 = 11.0 Hz, J_2 = 3.2 Hz, exo H-C_{10}); 50-MHz ^{13}C ($CDCl_3$) δ 186.23, 119.69, 112.36, 77.58, 30.75, 26.25, 25.81, 25.26, 25.05, 24.61, 24.03, 22.34, 16.06, 12.50, 12.35, 12.12, 11.91, 11.42, 10.66, 10.37; MS, *m/e* 354.2568 (calcd for $C_{24}H_{34}O_2$, 354.2559).

Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31, H, 9.67. Found: C, 81.27, H, 9.81.

Single-Crystal X-ray Structure of 9-*endo*-Acetyl-9-*exo*-[1-(9′-*anti*-tricyclo[4.2.1.1$^{2',5'}$]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane.[16] Crystals of the dimer suitable for analysis were prepared by slow crystallization from methanol. They were orthorhombic, space group *P*(*CAB*), with a = 12.730 (5) Å, b = 16.521 (10) Å, c = 18.690 (12) Å, and d_{calcd} = 1.198 g cm^{-3} for Z = 8 ($C_{24}H_{34}O_2$, M_r 354). Preliminary examinations and collection of the diffraction data were carried out on a Syntex-Nicolet P3f diffractometer equipped with a graphite monochromated Mo Kα radiation source. The size of the crystal used for data collection was 0.12 × 0.30 × 0.55 mm. A total of 4515 independent reflections were measured for 3.0° < 2θ < 55°, of which 1376 were considered to be observed [$F_o > 3\sigma(F_o)$]. Structure amplitudes and their standard deviations were calculated from the intensity data by procedures similar to those described previously.[25] The structures were solved by direct methods using the MULTAN80[26] package and refined by full matrix least-squares refinement. The final cycles of the least-squares refinement[27] assumed the non-hydrogen atoms to vibrate anisotropically and the hydrogen atoms to vibrate isotropically. Final electron density difference maps showed no significant features. The final discrepancy indices are R = 0.058 and R_w = 0.059.

Exploratory Photolysis of 9-*endo*-Acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane. A solution of 25 mg (0.071 mmol) of 9-*endo*-acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane in 150 mL of isopropyl alcohol containing 0.30 g of lithium acetate was irradiated for 1.0 h at 0–5 °C, added to 500 mL of pH 7.0 buffer, pentane extracted, washed with water and pH 7.0 buffer solution, and dried over $MgSO_4$, and the solvent was evaporated. Analysis by 200-MHz ^{1}H NMR showed conversion to be approximately 30%. Addition of pentane to the residue after evaporation afforded 6 mg (20%) of 9-*endo*-acetyl-9-hydroperoxy-*anti*-tricyclo[4.2.1.1^{2,5}]decane as a white solid. Analysis of the pentane-soluble material by GC with an SE-30 column at 140 °C gave the following relative percentages of volatile products: 61% *endo*-acetyltricyclic, 12% *exo*-acetyltricyclic, 11% hydroxyacetyltricyclic, and an estimated 16% of other unknowns.

Exploratory Photolysis of the Dimer 9-*endo*-Acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Acidic Workup. A solution of 25 mg (0.071 mmol) of dimer, 9-*endo*-acetyl-9-[1-(9′-anti-tricyclo-[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane, in 150 mL of isopropyl alcohol containing 0.30 g of lithium acetate was irradiated for 1.0 h. To the stirred photolysate under nitrogen was added 1.0 mL of concentrated HCl, the mixture was added to water, pentane extracted, washed with water and pH 7.0 buffer solution, and dried over $MgSO_4$, and the solvent was evaporated. Analysis by 200-MHz ^{1}H NMR showed conversion to be approximately 50%. Analysis of the material by GC with an SE-30 column at 140 °C gave the following relative percentages: 82% *endo*-acetyltricyclic, 11% *exo*-acetyltricyclic, and an estimated 7% of unknown material.

Exploratory Photolysis of the Dimer 9-*endo*-Acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Delayed Workup. A solution of 25 mg (0.071 mmol) of dimer, 9-*endo*-acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane, in 150 mL of isopropyl alcohol containing 0.30 g of lithium acetate was irradiated for 0.5 h and then left in the well under nitrogen at ambient temperature for 48 h. The mixture was then added to water, pentane extracted, washed with water (2×), and dried over $MgSO_4$, and the solvent was evaporated. The entire product was pentane soluble, and analysis by GC with an SE-30 column at 140 °C gave the following relative percentages: 74% *endo*-acetyltricyclic, 10% *exo*-acetyltricyclic, and 5% hydroxyacetyltricyclic.

Exploratory Photolysis of the Dimer 9-*endo*-Acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Delayed Workup. A solution of 20 mg (0.057 mmol) of dimer, 9-*endo*-acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane, in 150 mL of isopropyl alcohol containing 1.5 mL of cyclohexane, was irradiated for 1.0 h and then left in the well under nitrogen at ambient temperature for 20 h. The solvent was evaporated and the residue was dissolved in a mixture of 3.0 mL of chloroform and 3.0 mL of glacial acetic acid in a separatory funnel. To the solution was added 1.0 mL of saturated aqueous sodium iodide and iodine was liberated immediately. The mixture was extracted with pentane, washed with sodium thiosulfate and saturated sodium acetate solution, and dried over sodium sulfate, and the solvent was evaporated. The product was analyzed by GC with an SE-30 column at 180 °C and gave the following relative percentages: 42% hydroxyacetyltricyclic, 38% *endo*-acetyltricyclic, 10% *exo*-acetyltricyclic, and an estimated 11% of unknown.

Exploratory Photolysis of the Dimer 9-*endo*-Acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane with Oxygen Workup. A solution of 20 mg (0.057 mmol) of dimer, 9-*endo*-acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane, in 150 mL of isopropyl alcohol containing 1.5 mL of cyclohexane, was irradiated for 1.0 h, the lamp turned off, and oxygen bubbled through the solution for 15 min. The solvent was evaporated and the residue was dissolved in a mixture of 3.0 mL of chloroform and 3.0 mL of glacial acetic acid in a separatory funnel. To the solution was added 1.0 mL of saturated aqueous sodium iodide and iodine was liberated immediately. The mixture was extracted with pentane, washed with sodium thiosulfate and saturated sodium acetate solution, and dried over sodium sulfate, and the solvent was evaporated. Analysis by 200-MHz ^{1}H NMR showed conversion to be 50%. The product was analyzed by GC with an SE-30 column at 180 °C and gave the following relative percentages of volatile products: 40% hydroxyacetyltricyclic, 32% *endo*-acetyltricyclic, 15% *exo*-acetyltricyclic, and an estimated 13% of unknown.

Exploratory Low Conversion Photolysis of the Dimer 9-*endo*-Acetyl-9-[1-(9′-*anti*-tricyclo[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane. A solution of 20

(25) Haller, K. J.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3552–3558.
(26) Germain, G.; Main, P.; Woolfson, M. M. *Acta. Crystallogr., Sect. A* **1971**, *27*, 368–376.
(27) (a) Atomic form factors were from Cromer, D. T.; Mann, J. B. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, Table 2.B. (b) The atomic form factor for hydrogen was from Stewart, R. F.; Davidson, E. R.; Simpsin, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table V. MM2 Energies of Ketonization Transition States[a]

proton donor distance, Å	tricyclic enol exo energy	tricyclic enol endo energy	cyclohexane enol exo energy	cyclohexane enol endo energy
2.0	142.33	148.99	101.27	102.69
2.2	101.24	110.45	60.99	62.75
2.4	77.11	88.45	37.41	39.48
2.6	62.74	75.28	23.79	26.11
2.8	54.26	67.77	16.03	18.52
3.0	49.11	63.06	11.70	14.27
3.2	45.87	59.97	9.38	11.91
3.4	43.70	57.69	8.24	10.58
3.6	42.17	55.80	7.76	9.80
3.8	41.02	54.06	7.66	9.29
4.0	40.13	52.36	7.75	8.92
5.0	38.37	43.29		

[a] Energy units are kcal.

mg (0.057 mmol) of dimer, 9-*endo*-acetyl-9-[1-(9'-*anti*-tricyclo-[4.2.1.1^{2,5}]decanylidene)ethoxy]-*anti*-tricyclo[4.2.1.1^{2,5}]decane, in 150 mL of isopropyl alcohol containing 1.5 mL of cyclohexane, was irradiated for 10 min. Analysis by NMR showed conversion to be about 4%. Analysis by GC gave an *endo*-acetyl- to *exo*-acetyltricyclic ratio of 91:1.

Molecular Mechanics Calculations. MM2 calculations were carried out by using MM2[16] as incorporated in a variation of TRIBBLE.[17] Optimized geometries for the tricyclic, cyclohexane, and 2-phenylcyclohexane exocyclic enols were calculated and are tabulated in Table IV. A proton donor was simulated by a bromine atom with a +1 charge, and a series of calculations were carried out in which the position of the proton donor was brought toward the enol along both exo and endo perpendicular approaches. The positions of the proton donor and the two sp^2 hybridized carbons of the enol were fixed, and the geometry was optimized for the rest of the system. The results of these calculations for the tricyclic and cyclohexyl exo enols are summarized in Table V. Due to excessive computational time, the transition-state energies of the 2-phenylcyclohexane exo enols were only calculatred at a single (3.0 Å) distance of the proton donor to the α-carbon. This was the distance that showed the largest endo–exo difference in the other cases studied.

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Registry No. 1, 95693-86-0; 2, 95693-87-1; 2 (lithium enolate), 95693-99-5; 3a, 95693-84-8; 3b, 95782-18-6; 4a, 95693-85-9; 4b, 95782-16-4; 5, 95694-02-3; 6, 95693-91-7; 7, 66953-28-4; 8, 66953-29-5; 9, 95693-93-9; 10, 95693-88-2; 11, 95693-94-0; 12, 95693-89-3; 13a, 95693-95-1; 13b, 95782-17-5; 14a, 95693-90-6; 14b, 95782-15-3; 15, 95693-96-2; 16, 95693-92-8; 18, 95694-01-2; 19, 95693-98-4; 21, 95723-87-8; 22, 95694-00-1; 22 (R = Ph), 95693-97-3; O_2, 7782-44-7; $PhCH_2OCH_3$, 538-86-3; cyclopentadiene, 542-92-7; 2-chlorocyclopentanone, 694-28-0; acetylcyclohexane enol, 95694-03-4; 1-acetyl-2-phenylcyclohexane *cis*-enol, 95694-04-5; 1-acetyl-2-phenylcyclohexane *trans*-enol, 95694-05-6.

Metal-Catalyzed Organic Photoreactions. Iron(III) Chloride Catalyzed Photooxidation of Cyclic Olefins and Its Application to the Synthesis of *exo*-Brevicomin

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Photooxidation of 1,ω-disubstituted cyclic olefins gave α,ω-dichloro ketones or α-chloro 1,ω-diketones, depending upon the reaction conditions. The reaction was applied to the synthesis of the pheromone *exo*-brevicomin in three steps. Starting from 1-ethyl-6-methylcyclohexene, the synthesis was achieved in an overall yield of 51%.

We reported in our previous papers that iron(III) chloride exhibited a characteristic effect on the photooxidation of olefin 1 in pyridine and induced the production of either α-chloro ketone 3 (type A), ω,ω-dichloro ketone 4 (type B), or α,ω-dichloro ketone 5 (type C) as shown in Scheme I.[1] It has been assumed, and in some cases confirmed, that the primary product of the photooxidation is a β-chloro hydroperoxide, 2. We have illustrated the formation of the β-chloro hydroperoxide as involving a photoinduced interligand electron transfer from the chlorine ligand to molecular oxygen through the metal ion and olefin molecule, for which we proposed the term "long-range electron transfer" (Scheme II). The reaction type is dependent on the substitution pattern of the starting olefins: olefins in which R^2 and R^3 are hydrogen undergo the type A reaction through dehydration of the intermediate secondary hydroperoxides, while olefins in which R^2 is alkyl undergo the ring cleavage at either the a- or b-position to afford the type B or type C reaction products, respectively. The position of the bond cleavage was also dependent on the substitution pattern, the cleavage occurring always on the bond to the carbon atom carrying the alkyl group (R^1 or R^3 in Scheme I). Both type B and type C reactions are characteristic in that they afford a chain compound of any length having two functionalities on both ends of the chain by starting from a cyclic olefin having appropriate substituents and ring size. In our previous paper,[1] we demonstrated the utility of the type B reaction as a synthetic method by applying the reaction to the synthesis of some natural products. In the present study, we will demonstrate the synthetic utility of the type C reaction.

(1) A. Kohda, K. Nagayoshi, K. Maemoto, and T. Sato, *J. Org. Chem.*, 48, 425 (1983).

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