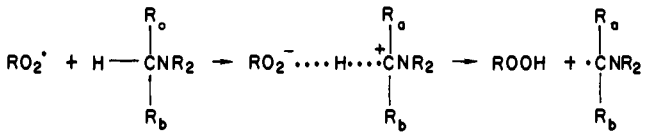
we have assumed that if $HO_2\cdot$ is the major rate-controlling peroxyl for Et_3N and i-Pr_3N the values of k_{11}, k_{13}, and k_{14} should be the same for the two amines. The value of k_{10} is, therefore, a little larger than the value that can be calculated from $k_p/(2k_t)^{1/2}$.

Conclusions

Low concentrations of tertiary amines inhibit the liquid-phase autoxidation of cumene by a mechanism which is similar to the one proposed by Russell for inhibition of cumene by tetralin.[8] Thus they possess the two criteria, high reactivity toward propagation *and* termination, required by the Russell mechanism. They are extremely reactive in propagation because the transition state for abstraction of an α-hydrogen atom has substantial charge separation and because α-(dialkylamino)alkyls have remarkably high stabilization energies.[17,25]



Furthermore the peroxyls derived from tertiary amines have very large overall termination rate constants. In some cases this is because $HO_2\cdot$ is the major rate-controlling chain-carrying radical.

Although homo- and cross-propagation and -termination rate constants can be derived from rates of co-oxidation by a curve-fitting procedure these rate constants should not be construed as absolute values but should only be taken as giving some indication of the magnitude of these rate constants.

Finally, a number of years ago Hammond, Boozer, Hamilton, and Sen[32] reported that *N*,*N*-dimethylaniline and *N*,*N*′-tetramethyl-*p*-phenylenediamine are inhibitors of hydrocarbon autoxidation "despite the absence of labile hydrogens". This was held as evidence for an inhibition mechanism in which the first step was the rate-controlling reversible formation of a loose molecular complex between inhibitor and $RO_2\cdot$. Clearly these tertiary amines do contain quite labile hydrogens and inhibition is adequately explained by the Russell mechanism.

Acknowledgment. The authors are grateful to Dr. K. F. Preston for writing the computer program to solve eq 15. We also thank Dr. D. Griller and Dr. J. C. Scaiano for helpful discussions.

(32) G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, 77, 3238 (1955).

Electronic Control of Stereoselectivity. 8. The Stereochemical Course of Electrophilic Additions to Aryl-Substituted 9-Isopropylidenebenzonorbornenes[1]

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Abstract: A series of aryl-substituted 9-isopropylidenebenzonorbornenes (**1–4**) and the parent 7-isopropylidenenorbornene (**5**) have been synthesized, and the stereochemistry of addition of numerous electrophiles to their exocyclic double bond has been determined. For assistance in interpreting the results, photoelectron spectroscopic investigations and extensive ZDO and MINDO/3 calculations were also undertaken. When weak electrophilic reagents such as singlet oxygen, *m*-chloroperbenzoic acid, *N*-bromosuccinimide, *N*-methyltriazolinedione, and *tert*-butyl hypochlorite were studied, all gave product distributions which greatly favored anti addition when the aryl ring was unsubstituted or substituted by a pair of methoxyl groups. The placement of chlorine or fluorine groups on the aromatic ring was accompanied by a substantial enhancement in the relative amount of syn product. For strong electrophiles such as protonated *tert*-butyl hypochlorite, dichlorocarbene, the acetylium cation, and protonated formaldehyde, syn attack was greatly favored or dominated exclusively. These marked crossovers in syn/anti stereoselection, which serve as a convenient tool with which to assess relative electrophilicity, may be explained in terms of the involvement of bridged or open ion pathways. Where bridged ions develop (weak electrophiles), long-range homoaromatic charge delocalization to the aromatic ring develops, with the result that anti attack becomes kinetically dominant. When powerfully electrophilic species are involved, this phenomenon is not important and transient aryl complex formation appears controlling.

Numerous kinetic and product studies of electrophilic reactions have been carried out in an attempt to describe the structural features of transition states and activated complexes. Despite considerable success in this area,[3] essentially no attention has been paid to the possible control of electrophilic stereoselection by remote electronic influences. In our view, such electronic control of stereoselectivity is considered a potentially rich source of information concerning several important aspects of electrophilic processes. These include the following: (a) knowledge of pivotal transition-state orbital interactions which often go unappreciated, since they now will be determinative of product stereochemistry; (b) added reliability in gaining pertinent information concerning the nature of the transient species, in particular whether an open or bridged cation is involved; and (c) development of a stereochemical method for the qualitative assessment of relative electrophilicity.

It is widely recognized that linear free-energy relationships such as the Hammett and Taft correlations, as well as more recent multiple parameter versions, are of limited use because a single set of substituent steric and polar parameters is inadequate for

(1) Part 7: Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4922.

(2) (a) The Ohio State University. (b) Universität Heidelberg. (c) Chemistry Division, D-200 Argonne National Laboratory, Argonne, Illinois 60439.

(3) Review: Freeman, F. *Chem. Rev.* **1975**, *75*, 439.

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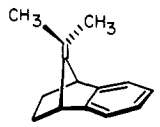
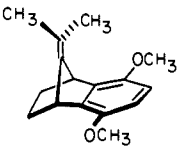
both open and bridged-ion pathways. An obvious solution to this dilemma is the acqusition of a substrate, or group of substrates, which would give rise to stereochemically different products under these two sets of mechanistic circumstances. In this way, it should prove possible to establish if the rate-determining step for a particular electrophilic process involves substantial π-bond distortion, as usually required by weak electrophiles, or more closely resembles the highly polarized open ion situation commonly characteristic of more powerful electrophilic reagents.

In this paper, we report on the product distributions which arise upon addition of a host of electrophilic reagents to the four 9-isopropylidenebenzonorbornenes **1–4** and to the parent alicyclic



1



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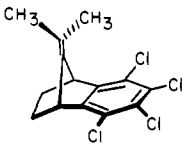

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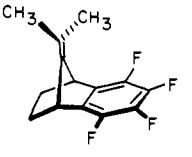

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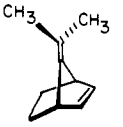
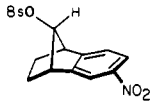


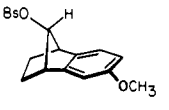
5

diene **5**.[4,5] This choice was predicated upon several key considerations. Whereas Bartlett and Giddings showed that *anti*-9-benzonorbornenyl brosylate solvolyzes 10^5 times more rapidly than the 7-norbornyl derivative,[6] Tanida and his co-workers elegantly demonstrated the pronounced susceptibility of the solvolysis rate to the nature and extent of aromatic substitution.[7] For example, the relative rates for the series **6–8** vary by a factor of greater



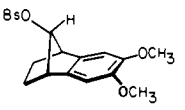
6

k_{rel} (77.6°C) 10^{-4}



7

54

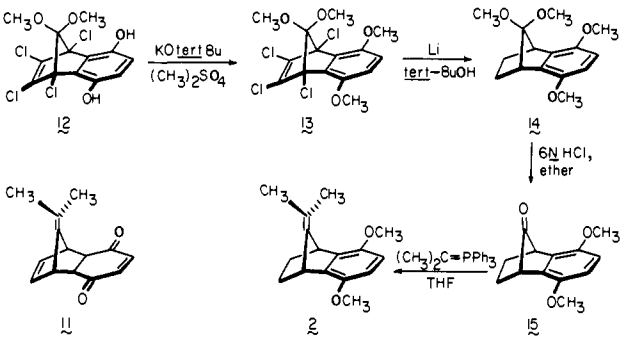


8

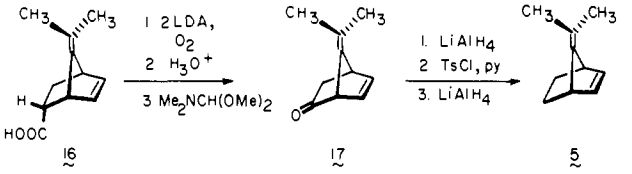
3,000

than 10^7 (k_{rel} for the unsubstituted benzo derivative is assigned as 1). Thus, the solvolytic transition state is not only anchimerically assisted, but all indications also point to the involvement of a symmetrical species where possible. In another context, the photoelectron spectra of **5**[8] and 9-isopropylidenebenzonorbornadiene[9] have been measured and the extents of orbital splitting arising from interaction of the exocyclic and endocyclic double bonds have been estimated. Additionally, Hoffmann and Kurz have established by ^{13}C NMR spectroscopy that the exocyclic double bond in 7-methylenenorbornene is polarized, the unsubstituted trigonal carbon being somewhat more shielded than normal due to homoconjugation.[10] Similar effects were expected to prevail in **1–5**, although to varying degrees. Of added relevance is the fact that recourse to such a series of closely related molecules obviates the often encountered complications of steric and conformational variability, while allowing extensive electronic alteration to be implemented.

Scheme I

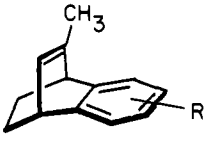


Scheme II

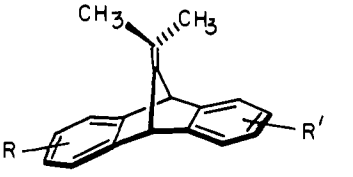


At the time when this work was initiated several years ago,[5] no reports had yet appeared describing the *stereochemical* consequences of long-range electronic interactions. Since then, however, considerable interest has developed in this field. Interested parties are urged to consult the nicely complementary contributions of Mukai dealing with **1**, **5**, and related molecules,[11] Hoffmann in the area of bicyclofulvenes[12] and 8-methylene-*endo*-tricyclo[3.2.1.$0^{2,4}$]octanes,[13] and Malpass concerning stereoselectivity in the chlorination of 9-azabenzonorbornenes and 9-azabenzonorbornadienes.[14]

In ensuing papers, the stereochemical preferences of electrophilic additions to aryl substituted derivatives of **9** and **10** are detailed.



9



10

In case of **9**, movement of the double bond from an exocyclic to an endocyclic environment is found to exert a fundamental change in product ratios as compared to **1–4**.[15] In **10**, the two faces of the exocyclic double bond differ not from steric shielding (now essentially comparable) but only from π-orbital distortions which are generated by homoconjugation with the aromatic rings which are in direct competition.[16]

Results

Synthesis. Compounds **1**, **3**, and **4**, available by cycloaddition of the appropriate benzyne with 6,6-dimethylfulvene and subsequent regiospecific diimide reduction, have been previously reported.[17,18] The dehydro form of dimethoxy derivative **2** could

(4) For two preliminary reports describing portions of this work, see: (a) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. *J. Am. Chem. Soc.* **1978**, *100*, 6510. (b) Hertel, L. W.; Paquette, L. A. *Ibid.* **1979**, *101*, 7620.
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(9) Haselbach, E.; Rossi, M. *Helv. Chim. Acta* **1976**, *59*, 278. See also: Pfaendler, H. R.; Tanida, H.; Haselbach, E. *Ibid.* **1974**, *57*, 383.
(10) Hoffmann, R. W.; Kurz, H. *Chem. Ber.* **1975**, *108*, 119. See also: Paquette, L. A.; Oku, M.; Farnham, W. B.; Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 700.
(11) (a) Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 6509. (b) Okada, K.; Mukai, T. *Tetrahedron Lett.* **1979**, 3429.
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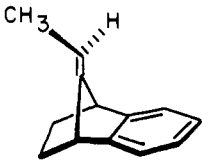
(14) Malpass, J. R.; Walker, M. P. *J. Chem. Soc., Chem. Commun.* **1979**, 585.
(15) Paquette, L. A.; Bellamy, F.; Wells, G.; Böhm, M. C.; Gleiter, R., following paper in this issue.
(16) Paquette, L. A.; Klinger, F. M.; Hertel, L. W. *J. Org. Chem.* **1981**, *46*, 4403.
(17) Muneyuki, R.; Tanida, H. *J. Org. Chem.* **1966**, *31*, 1988.
(18) Hankinson, B.; Heaney, H.; Price, A. P.; Sharma, R. P. *J. Chem. Soc. Perkin Trans. 1* **1973**, 2569.

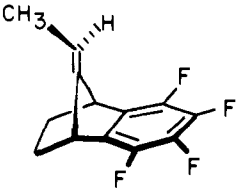
be obtained by O-methylation of **11**, but only in very low yield (7%) because of ready retrograde Diels–Alder fragmentation under either acidic or basic conditions. A more rewarding route to **2** is outlined in Scheme I. Heating *p*-benzoquinone and tetrachlorocyclopentadienone dimethyl ketal at 170 °C as described by Rakoff and Miles[19a] gave **12** directly. This product could be O-methylated and reductively dechlorinated with reasonable efficiency to furnish **14**. Hydrolysis of this ketal gave **15** which when subjected to appropriate Wittig condensation delivered the desired **2** in 17% overall yield.

Access to **5** was gained by oxidative decarboxylation[20] of **16** to give ketone **17**[21] followed by implementation of Martin and Forster's stepwise reduction procedure (Scheme II).[22]

As the study progressed, stereoselectivity comparisons between tri- and tetra-substituted olefinic systems appeared desirable in the case of certain weakly electrophilic reagents. For this purpose, **1** and **4** were sequentially ozonized and condensed with ethylidenetriphenylphosphorane to provide **18** and **19**. The



18

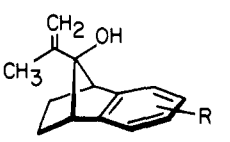


19

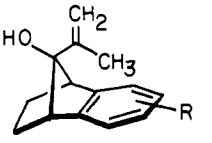
substitution plans in **1–5** were tailored to two requirements: (a) the presence of a plane of symmetry which passes through the double bond and includes both of the trigonally hybridized carbon atoms, and (b) allowance for the operation of ene reactions at the reactive π bond. The first of these criteria is obviously not met by **18** and **19**; nonetheless, the electronic control of stereoselection appears little affected by a structural change of this type.

Singlet Oxygenation. The mechanism of the ene reaction of $^1O_2$ with olefins which forms allylic hydroperoxides continues to be controversial despite several decades of experimental and theoretical attention.[23] The process is recognized to be stereospecific (suprafacial relative to the ene component),[24] to exhibit small deuterium isotope effects whose magnitudes are dependent on the relative position of the isotopic center,[24c,25,26] and to favor hydrogen abstraction from the more hindered side of an olefin.[23a,27] At the center of the controversy lies the question whether such reactions proceed by a concerted ene pathway,[28] involve transient polar intermediates such as perepoxides[29] or open zwitterions,[30] follow a free radical mechanism,[31] or lead via π or charge-transfer complexes to products.[32] Although the electrophilic nature of singlet oxygen suggests that HOMO-olefin LUMO-oxygen interaction should be controlling,[33] the general applicability of frontier molecular orbital analysis remains unclear in this instance.[34] One of our goals was to gain *comparative information* between the stereoselectivities exhibited by singlet oxygen and those shown by other electrophilic reagents whose transition-state behavior are thought to be more well understood.

The customary dye sensitization technique (rose bengal) was employed herein. The initially formed allylic hydroperoxides were not examined but directly reduced with sodium borohydride to the allylic alcohols for characterization. When solutions of **1** in methanol were treated in this manner, both possible products (**20a** and **21a**) were formed in unequal amounts, as determined by direct



20



21

	20	**21**
a, R = H	24(20)%	76(80)%
b, R = 5,8-$(OCH_3)_2$	17(21)	83(79)
c, R = 5,6,7,8-$(Cl)_4$	59(52)	41(48)
d, R = 5,6,7,8-$(F)_4$	56(54)	44(46)

integration of the adequately separated vinyl proton signals in the ^1H NMR spectra of the unpurified reactions mixtures. *This latter technique was employed throughout the entire investigation; the percentages cited represent the average values determined from at least two independent experiments.* A change in solvent from methanol to dichloromethane altered the stereochemical results very little (the CH_2Cl_2 values are given in parentheses).

The stereochemistries of the purified allylic alcohols were assigned on the basis of (a) the higher field position of the methyl signal in **21a**, a circumstance attributable to shielding by the underlying aromatic ring,[35] (b) upfield shifting of the exo protons on the ethano bridge in **20a** as a result of the anisotropy of the isopropenyl group,[36] and (c) lanthanide shifting with $Eu(fod)_3$.

Absolute rate constants for the reaction of $^1O_2$ with **1–4** were obtained at the Center for Fast Kinetic Research, Austin, TX, through the courtesy of Dr. M. A. J. Rodgers. In these experiments, a laser flash was used to generate anthracene triplets in aerated dichloromethane solutions containing diphenylisobenzofuran (DPIBF). The quenching of such triplets by O_2 ($^3\Sigma_g^-$) produced the $^1\Delta_g$ species, the reactivity of which was determined by time-resolved observation of DPIBF bleaching. Upon addition

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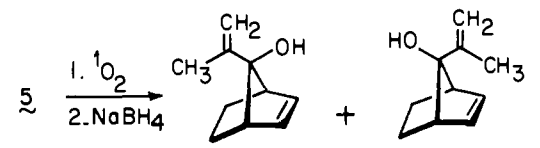
(34) (a) Kretschmer, G.; Paquette, L. A. *Heterocycles* **1978**, *11*, 359. (b) Adam, W.; Carballeira, N.; Cheng, C.-C.; Sakanishi, K.; Gleiter, R. *J. Org. Chem.* **1979**, *44*, 851. (c) Ensley, H. E.; Carr, R. V. C.; Martin, R. S.; Pierce, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 2836.
(35) Feiner, N. F.; Abrams, G. D.; Yates, P. *Can. J. Chem.* **1976**, *54*, 3955.
(36) Berson, J. A.; Miyashi, T.; Jones, G. III *J. Am. Chem. Soc.* **1974**, *96*, 3468.

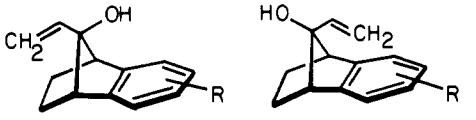
of the four 9-isopropylidenebenzonorbornenes to such reaction mixtures, the respective absolute rate constants (k_s) were determined to be the following: **1**, 1.36×10^5; **2**, 4.28×10^6; **3**, 9.63×10^4; **4**, 5.24×10^4 L mol^{-1} s^{-1}.

When **5** was exposed to singlet oxygen, there was obtained a



22 (14%) **23** (86%)

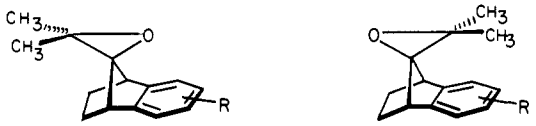
14:86 ratio of **22** and **23**. Comparable treatment of 9-ethylidene compounds **18** and **19** saw little change in the allylic alcohol isomer ratios (**24** vs. **25**) relative to the respective isopropylidene counterparts.



24 **25**

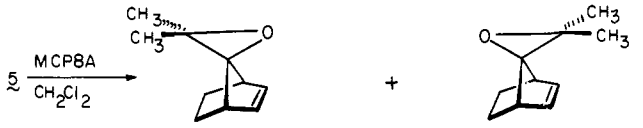
a, R = H	15%	85%
b, R = 5,6,7,8-(F)$_4$	53	47

Epoxidation. Although the peracid oxidation of olefins is an electrophilic process, it is known[37] to exert less tendency for charge buildup in the activated complex than other reactions of this type. Since this useful calibration point was available, **1–4** were treated with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane at 25 °C. In every instance, high yield conversion was observed to mixtures of epoxides **26** and **27** enriched in the anti isomer.



26 **27**

a, R = H	17%	83%
b, R = 5,8-(OCH$_3$)$_2$	11	89
c, R = 5,6,7,8-(Cl)$_4$	31	69
d, R = 5,6,7,8-(F)$_4$	37	63



28 (34%) **29** (66%)

Stereochemical sssignments were made on the basis of the higher field position of the methyl signals in the anti isomer and substantiated by base-promoted opening to allylic alcohols **20** or **21** of previously established structure. From epoxidation of diene **5**, a 34:66 distribution of **28** and **29** was realized.

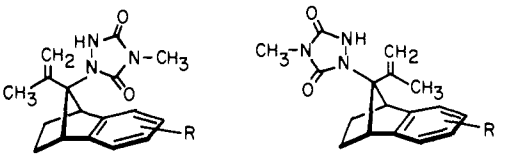
Bromination. Despite extensive investigation of the electrophilic halogenation of alkenes,[38] some vagueness persists in the detailed characterization of the transition states of these reactions, particularly where unsymmetrical olefins are concerned. Complexities arise chiefly because of difficulties encountered in amalgamating kinetic and product data coherently. However, the recent work of Dubois and Chrêtien on the correlation of charge distribution with regio- and chemiselectivity in bromonium ions makes substantial inroads into the satisfactory clarification of this matter.[39] *N*-Bromosuccinimide (NBS) in 10% aqueous glyme (25 °C) was utilized herein, since these conditions were found to lead directly to the allylic bromides **30** and **31**. The ^{1}H NMR spectra of these

30 **31**

a, R = H	19%	81%
b, R = 5,8-(OCH$_3$)$_2$	14	86
c, R = 5,6,7,8-(Cl)$_4$	58	42
d, R = 5,6,7,8-(F)$_4$	55	45

products were closely similar to those of **20** and **21**. Stereochemical assignments and isomer ratios were determined on the basis of preceding criteria. Interestingly, the relative proportions of **30** and **31** in each instance proved identical within experimental error to those realized for $^1O_2$.

***N*-Methyltriazolinedione Addition.** The ability of *N*-methyltriazolinedione (MTAD) to enter into ene reactions involving highly dipolar intermediates is well recognized.[40] Due to the structural features of **1–5**, the buildup of positive charge was expected to materialize ultimately on the newly substituted carbon center. The nature of the transition state leading to such zwitterions has not been heretofore examined because the question is difficultly amenable to kinetic analysis (if at all). However, the present methodology offered the possibility of defining certain characteristics of the activated complex, at least in a qualitative sense. Watson and Warrener[41] have previously demonstrated that 9-isopropylidenebenzonorbornadiene readily forms a single ene-addition product of stereochemically undefined structure with *N*-phenyltriazolinedione in chloroform at room temperature. In the present study, dichloromethane solutions of the reagents were employed at 25 °C. As can be seen from the product distributions of **32** and **33**, the stereoelectronic demands of MTAD show little



32 **33**

a, R = H	19%	81%
b, R = 5,8-(OCH$_3$)$_2$	16	84
c, R = 5,6,7,8-(Cl)$_4$	59	41
d, R = 5,6,7,8-(F)$_4$	57	43

deviation from those previously determined for $^1O_2$ and NBS. Where the electron-deficient tetrachloro (**3**) and tetrafluoro (**4**) examples are concerned, these values differ notably from those

(37) (a) Bartlett, P. D. *Rec. Chem. Progr.* **1957**, *18*, 111. (b) Waters, W. A. "Mechanism of Oxidation of Organic Compounds"; Wiley: New York, 1965. (c) Hanzlik, R. P.; Schearer, G. O. *J. Am. Chem. Soc.* **1975**, *97*, 5231. (d) Kwart, H.; Starcher, P. S.; Tinsley, S. W. *Chem. Commun.* **1967**, 335. (e) Plesnicar, B.; Tasewski, M.; Azman, A. *J. Am. Chem. Soc.* **1978**, *100*, 743.

(38) (a) Fahey, R. C. *Top. Stereochem.* **1968**, *3*, 237. (b) Schmid, G. H.; Modro, A.; Yates, K. *J. Org. Chem.* **1977**, *42*, 871. (c) Ruasse, M. F.; Dubois, J.-E. *Ibid.* **1977**, *42*, 2689.

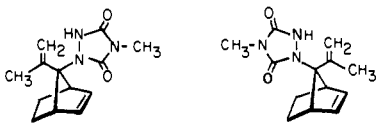
(39) Dubois, J.-E.; Chrêtien, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 3506.

(40) (a) Evnin, A. B.; Miller, R. D.; Evanega, G. R. *Tetrahedron Lett.* **1968**, 5863. (b) Huisgen, R.; Konz, W. E.; Gream, G. E. *J. Am. Chem. Soc.* **1970**, *92*, 4105. (c) Huisgen, R.; Konz, W. E. Schnegg, U. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 715. (d) Paquette, L. A.; James, D. R.; Birnberg, G. H. *J. Am. Chem. Soc.* **1974**, *96*, 7454. (e) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (f) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.

(41) Watson, P. L.; Warrener, R. N. *Aust. J. Chem.* **1973**, *26*, 1725.

obtained with MCPBA. The ^{1}H NMR spectra of **32** and **33** show the expected close similarities to the earlier ene products.

The highly favored status of **35** (95%) as produced from **5**



34 **35** **36**

argues in favor of domination by the endocyclic double bond in 9-isopropylidenebenzonorbornadiene. We would therefore reverse Watson and Warrener's assignment to that illustrated by **36**; however, this point has not been established by chemical interconversion.

Ene Chlorinations with *tert*-Butyl Hypochlorite. In the preceding examples, it was possible to show that the choice between the two bonding approaches to the exocyclic p orbital could be varied by manipulation of the electronic character of the aromatic ring. When *tert*-butyl hypochlorite[42] was allowed to react in the dark with **1**, **2**, and **4**, pairs of allylic chlorides (**37** and **38**) were

	37	**38**
a, R=H	15%	85%
$HCOCH_3$ (12 eq HCOH)	42	58
$HCOCH_3$: HCOH (1:1)	80	20
b, R=5,8-$(OCH_3)_2$	24	76
$HCOCH_3$ (12 eq HCOH)	53	47
$HCOCH_3$: HCOH (1:1)	67	33
c, R=5,6,7,8-$(F)_4$	47	53
$HCOCH_3$ (12 eq HCOH)	58	42
$HCOCH_3$: HCOH (1:1)	91	9

similarly formed. This reagent differs from those employed earlier in that it now becomes possible to modify its electrophilic characteristics by the addition of incremental amounts of formic acid to the methyl formate solvent system.[43] Under these circumstances, progressively higher levels of O-protonation materialize and electrophilicity is enhanced. As a consequence, the stereochemical response of these bridged systems to increasingly more electrophilic conditions could be examined while the aromatic ring substitution plan was kept constant.

The reaction of **1** with *tert*-butyl hypochlorite in methyl formate solution gave rise to a 15:85 mixture of **37a** and **38a**. Admixture of 12 equiv of formic acid increased the amount of syn isomer produced to 42%. Further adjustment of the solvent system to methyl formate–formic acid (1:1) led to additional enhancement in the level of **37a** formed (80%). Entirely similar trends were encountered with the dimethoxy and tetrafluoro derivatives, although the overall changes were somewhat narrower in breadth because of the nature of the aryl substitution. Certainly, the effect of solvent change cannot be disregarded here. Nonetheless, the observed stereochemical crossovers suggested that 9-isopropylidenebenzonorbornenes are appreciably responsive to reagent electrophilicity.

Dichlorocarbene Addition. The foregoing developments led us to examine next the behavior of the electron-deficient carbene $:CCl_2$ as an electrophilic probe of stereoselectivity.[44,45] When

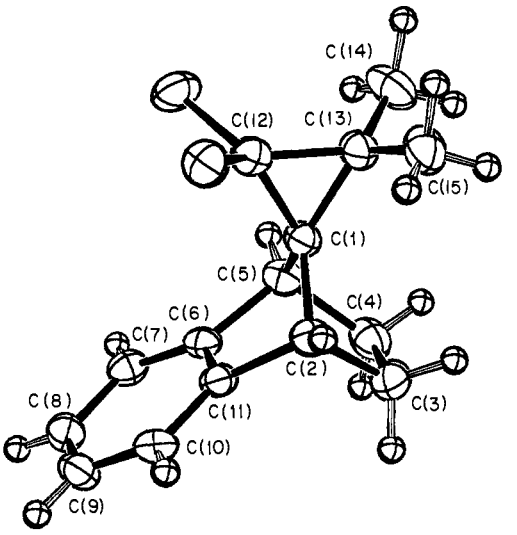
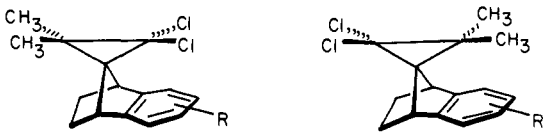


Figure 1. A computer generated perspective drawing of the final X-ray model of dichlorocyclopropane **39a**.

1, **2**, and **4** were heated with sodium trichloroacetate in glyme solution, two dichlorocyclopropane adducts (**39** and **40**) were



	39	**40**
a, R = H	65%	35%
b, R = 5,8-$(OCH_3)_2$	80	20
c, R = 5,6,7,8-$(F)_4$	87	13

obtained in each case, with one isomer predominating significantly. ^{1}H NMR spectral comparisons clearly showed the methyl signals of one set of isomers (**40a–c**) to reside at a higher field position than those in **39a–c**. Also, the peaks due to the exo hydrogens on the ethano bridge within **40** appeared at lower field than those in **39**. Although these features can be attributed to benzenoid ring anisotropy and chlorine deshielding effects, respectively, they were not considered adequately confirmatory of structure and an X-ray crystal analysis of **39a** was therefore undertaken.

The final X-ray model is depicted in Figure 1 which also indicates the particular numbering scheme used in the study. Table I lists pertinent bond distances and angles. The molecule possesses noncrystallographic mirror symmetry within the error of measurement. The cyclopropane moiety is substituted in such a way that the methyl groups are exo and the chloro groups are endo with respect to the fused phenyl moiety. The asymmetry of the cyclopropane ring reflects the different kinds of substituent groups. Presumably, the cyclopropane C–C bond trans to the methyl substituents is shorter than the bond trans to the spiro-linked norbornyl grouping because of the angle strain imposed on C(2)–C(1)–C(5) and the consequent rehybridization of C(1). Halogen substituents have been presumed to lead to overall cyclopropane C–C bond lengthening,[46] but it would appear from this structure and other evidence[47] that methyl substitution yields a stronger trans-directed lengthening. The external compression

(42) Cooper, R. D. G. *Tetrahedron Lett.* **1980**, 781. We thank Dr. Cooper for informing us of his results prior to publication.
(43) Offermann, W.; Vogtle, F. *Synthesis* **1977**, 272.
(44) Dichlorocarbene additions to 8-methylene-*endo*-tricyclo[3.2.1.$0^{2,4}$]-octane[13] and to 9-isopropylidenebenzonorbornadiene have been reported: Gheorghiu, M. D.; Parvulescu, L.; Draghici, C. *Rev. Roum. Chim.* **1979**, *24*, 1005.
(45) Professor Mukai has kindly informed us that Dr. Keiji Okada has examined the addition of $:CCl_2$ to **1** in his laboratory (Oct 18, 1979).
(46) Jason, M. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6012.
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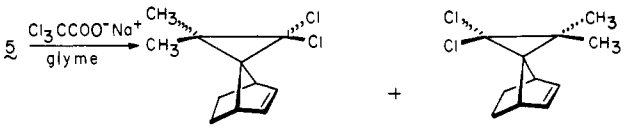
Table I. Bond Distances and Angles for 39a

atoms	dist, Å	atoms	angle, deg	atoms	angle, deg
C(13)-Cl(1)	1.758 (3)	Cl(1)-C(13)-Cl(2)	110.8 (1)	C(4)-C(5)-C(1)	100.0 (3)
C(13)-Cl(2)	1.752 (3)	Cl(1)-C(13)-C(1)	119.1 (2)	C(6)-C(5)-C(1)	98.8 (3)
C(1)-C(2)	1.534 (4)	Cl(1)-C(13)-C(12)	119.4 (2)	C(2)-C(1)-C(5)	95.8 (3)
C(1)-C(5)	1.530 (4)	Cl(2)-C(13)-C(1)	119.2 (2)	C(5)-C(6)-C(11)	106.6 (3)
C(1)-C(12)	1.521 (4)	Cl(2)-C(13)-C(12)	119.7 (2)	C(2)-C(11)-C(6)	107.1 (3)
C(1)-C(13)	1.485 (4)	C(1)-C(13)-C(12)	60.6 (3)	C(5)-C(6)-C(7)	132.4 (3)
C(2)-C(3)	1.555 (4)	C(13)-C(12)-C(1)	58.3 (3)	C(2)-C(11)-C(10)	132.6 (3)
C(2)-C(11)	1.506 (4)	C(12)-C(1)-C(13)	61.0 (3)	C(11)-C(6)-C(7)	121.0 (3)
C(3)-C(4)	1.550 (4)	C(13)-C(1)-C(2)	123.7 (3)	C(6)-C(7)-C(8)	118.2 (3)
C(4)-C(5)	1.551 (4)	C(13)-C(1)-C(5)	123.9 (3)	C(11)-C(10)-C(9)	118.6 (3)
C(5)-C(6)	1.521 (4)	C(12)-C(1)-C(2)	126.2 (3)	C(7)-C(8)-C(9)	120.6 (3)
C(6)-C(7)	1.374 (4)	C(12)-C(1)-C(5)	127.0 (3)	C(10)-C(9)-C(8)	121.3 (3)
C(6)-C(11)	1.398 (4)	C(13)-C(12)-C(14)	117.8 (4)	C(14)-C(12)-C(15)	113.1 (5)
C(7)-C(8)	1.394 (4)	C(13)-C(12)-C(15)	118.2 (4)	av C-H dist	0.96 Å
C(8)-C(9)	1.376 (4)	C(1)-C(12)-C(14)	119.6 (4)		
C(9)-C(10)	1.377 (4)	C(1)-C(12)-C(15)	119.4 (4)		
C(10)-C(11)	1.378 (4)	C(1)-C(2)-C(3)	99.7 (3)		
C(12)-C(13)	1.527 (4)	C(1)-C(2)-C(11)	99.1 (3)		
C(12)-C(14)	1.509 (5)	C(2)-C(3)-C(4)	103.3 (3)		
C(12)-C(15)	1.494 (5)	C(3)-C(4)-C(5)	103.7 (3)		

of the C(2)–C(1)–C(5) angle, however, seems to have effectively diminished this effect for the bond trans to C(1). Interestingly, the value of this angle at C(1) is not significantly different than the corresponding angle in norbornene,[48] but the C(1)–C(2) and C(1)–C(5) distances at 1.534 (4) and 1.530 (4) Å are much shorter than the 1.566 (5) Å for the corresponding bonds in norbornene and 1.57 (1) Å in norbornadiene.[48] These bonds in several norbornane derivatives average 1.52 (1) Å (in camphene-8-carboxylic acid)[49] and 1.536 (7) Å (in *exo-N*-(2-norbornyl)benzamide).[50] The remaining bond distances and angles in the structure are unremarkable.

Where **5** was concerned, a 12:88 distribution of **41** and **42** was

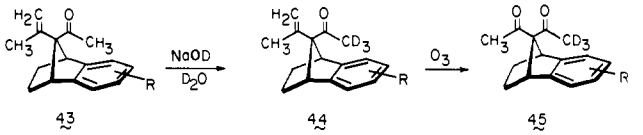


41 (88%) **42** (12%)

obtained. The structural assignments follow by analogy and are based on the upfield position of the methyl signal in **41** relative to that which characterizes **42** and the relative shifts of the vinyl and ethano protons in the two isomers (see Experimental Section).

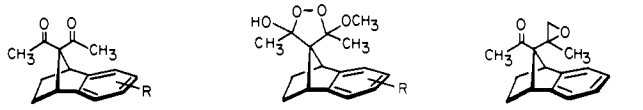
Friedel–Crafts Acylation. The contrasting stereochemical response of these bridged systems to dichlorocarbene prompted our assessment of the stereoselectivity which would result with still more electrophilic reagents. The acetyl chloride–$AlCl_3$ combination has frequently been used for the Friedel–Crafts acylation of olefins,[51,52] and there is general agreement based on kinetic evidence[53] that acetylium ions may be involved, although the direct role of a 1:1 donor–acceptor complex cannot be ruled out.[54] The 9-isopropylidenebenzonorbornenes **1**, **2**, and **4** are highly reactive toward this reagent combination. Consequently, the acetylations had to be conducted for short periods of time at −10 °C in dichloromethane solution. Because these conditions constituted a rather significant departure from those utilized in the earlier segments of this investigation, acetylations were also performed in acetic anhydride with zinc chloride catalysis at room temperature.[55,56] The two reagent systems led to identical results. That is, the *syn*-9-acetyl derivatives **43** were produced exclusively in high yield.

The exclusivety of syn attack in these examples was established in the following manner. Of the two methyl peaks in the ^1H NMR spectrum of **43a** (δ ($CDCl_3$) 1.97 (s) and 1.75 (m, $v_{1/2}$ = 3 Hz)),



43 **44** **45**

a, R = H ; **b**, R = 5,8-$(OCH_3)_2$; **c**, R = 5,6,7,8-$(F)_4$



46 **47** **48**

a, R = H ; **b**, R = 5,6,7,8-$(F)_4$

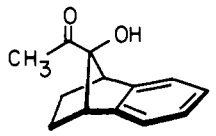
only the upfield isopropenyl signal remained after suitable hydrogen–deuterium exchange provided **44a**. Upon ozonolysis, both **43a** and **44a** were converted to their diacetyl derivatives (**44a** and **46a**, respectively). Whereas, **46a** shows a pair of methyl singlets at δ 2.19 and 1.91 (in $CDCl_3$), the spectrum of **44a** is characterized by a lone absorption at 2.19. Since the more shielded methyl group in **46a** resides above the benzene ring, structural assignment to **43a** is secured. The stereochemistry of **43c** was established in analogous fashion.

The ozonolysis of **43a** was somewhat complicated by the formation of two secondary products. The identity of peroxide **47a** was determined by spectral and combustion analysis. Its conversion to **46a** could be achieved by acidic hydrolysis or catalytic hydrogenation. Expoxy ketone **48**, characterized initially on the

(48) Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356.
(49) Moews, P. C.; Knox, J. R.; Vaughn, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 260.
(50) Newton, M. G.; Pantaleo, N. S.; Kirbawy, S.; Allinger, N. L. *J. Am. Chem. Soc.* **1978**, *100*, 2176.
(51) (a) Nenitzescu, C. D.; Balaban, A. T. "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed.; Wiley: New York, 1964; Vol. III, pp 1033–1052. (b) Groves, J. K. *Chem. Soc. Rev.* **1972**, *1*, 73.
(52) The acetylation of **1** under these conditions had been earlier investigated.[35]
(53) (a) Corriu, R.; Dore, M.; Thomassin, R. *Tetrahedron* **1971**, *27*, 5819 and pertinent references cited therein. (b) Muneyuki, R.; Tanida, H. *Yuki Gosei Kagaku Kyokaishi* **1978**, *36*, 454.
(54) (a) LeCarpentier, J. M.; Weiss, R. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1421. (b) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 7072 and earlier work by this group. (c) Wilinski, J.; Kurland, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 2233.
(55) (a) Deno, N. C.; Chafetz, H. *J. Am. Chem. Soc.* **1952**, *74*, 3940. (b) Groves, J. K.; Jones, N. *J. Chem. Soc. C* **1968**, 2215, 2354, 2898; **1969**, 608. (c) Meerwein, H. *Justus Liebigs Ann. Chem.* **1927**, *455*, 227; (d) Dilthey, W. *Chem. Ber.* **1938**, *71*, 1350. (e) Dubois, M.; Cazaux, M. *Bull. Soc. Chim. Fr.* **1975**, *1-2*, 265, 269. (f) See also Hoffmann, H. M. R.; Tsushima, T. *J. Am. Chem. Soc.* **1977**, *99*, 6008.
(56) Beak, P.; Berger, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 3848. We thank Professor Beak for informing us of his results prior to publication.

basis of its spectra, was independently synthesized by peracid epoxidation of **43a**. The ozonolysis of **43c** produced **46b** as well as **47b**.

Internal consistency throughout the series was shown by ozonolysis of the syn and anti allylic alcohols **20a** and **21a** which gave rise to the epimeric α-hydroxy ketones **49** and **50**, respectively.



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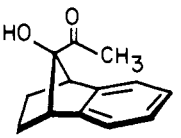
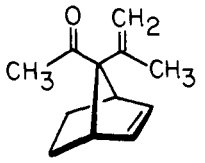


50

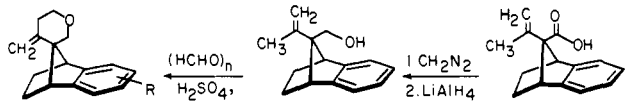
The methyl singlet in the ^{1}H NMR spectrum of **50** appears at δ 1.7, while that in **49** is seen at δ 2.25, a circumstance again attributable to shielding by the underlying aromatic ring.

The exclusivety of syn attack on **5** to give **51** was established by controlled diimide reduction to achieve selective saturation of the norbornene double bond. This chemical change was accompanied by a downfield shift of the acetyl singlet (δ 2.03 → 2.13) while the isopropenyl methyl signal (δ 1.75) remained unaltered.



51

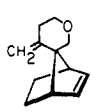
Hydroxymethylation. The response of **1**, **3**, and **4** to the Prins reaction proved entirely comparable. The stereochemical features of the lone products (**52**) obtained by reaction with formaldehyde and sulfuric acid (10 equiv) in dioxane at 25 °C were elucidated by the independent synthesis of **52a**. Thus, haloform degradation



52 a, R = H; b, R = 5,8-$(OCH_3)_2$; c, R = 5,6,7,8-$(F)_4$ — **54** — **53**

of **43a** gave carboxylic acid **53** which was esterified with diazomethane and reduced with lithium aluminum hydride. When **54** was independently submitted to the Prins conditions, **52a** was formed exclusively. In order to establish that **54** was not subject to acid-catalyzed elimination of formaldehyde and readdition in the opposite sense, we subjected the alcohol to the Prins reactions in the absence of formaldehyde. Only **54** was recovered.

The cyclic ether **55** obtained uniquely from **5** exhibits a methylene proton absorption (δ 4.82 (2 H) differing little in chemical shift from that of **52** ($\sim\delta$ 4.94). This internal consistency comprises the reference point for this stereochemical assignment.



55

Photoelectron Spectroscopic Investigations. The He I photoelectron spectrum of **1** is shown in Figure 2. Below 10 eV, two peaks are encountered. The ratio of the areas of the two peaks is approximately 1:2, suggesting that these peaks are due to the removal of electrons from three molecular orbitals (MO's). From past investigations involving the substituted benzenes **56** and **57**,[57] 7-isopropylidenenorbornane (**58**),[8] and 9-isopropylidenebenzonorbornadiene (**59**),[9] it is evident that these three MO's are π

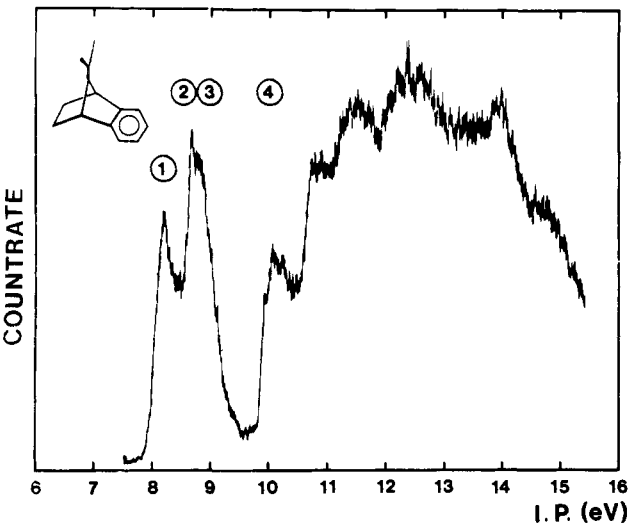
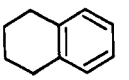


Figure 2. Photoelectron spectrum of **1**.

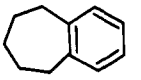
MO's. Two of these are localized mainly on the aromatic ring while the third arises from the exocyclic double bond.



56

IP_1 = 8.44 eV

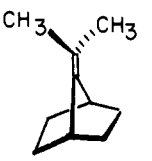
IP_2 = 8.96 eV



57

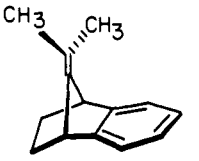
IP_1 = 8.44 eV

IP_2 = 8.96 eV



58

IP_1 = 8.49 eV



59

IP_1 = 8.34 eV

IP_2 = 9.05 eV

IP_3 = 9.34 eV

For interpretation of bands 1-3 in the PE spectrum of **1**, use is made of Koopmans' theorem ($-\epsilon_J = I_{V,J}$)[58] which allows for comparison to be made between the calculated orbital energies (ϵ_J) and the measured vertical ionization potentials ($I_{V,J}$). Derivations of the π MO's of **1** by the ZDO technique and by the MINDO/3 method[59] follow.

(a) ZDO Model. Application of this procedure requires knowledge of the basic orbital energies of the exocyclic methylene group and the benzene fragment. The wave functions of the unperturbed fragments are taken, their orbital energies being derived in the manner previously accomplished for **59**.[9] The following values are obtained: $A(\pi_{exocyclic})$ = −8.49 − 0.15 (eV) = −8.64 eV; $A(\pi_{benzene}^{S})$ = −8.44 + 0.05 (eV) = −8.39 eV; $A(\pi_{benzene}^{A})$ = −8.96 + 0.02 (eV) = −8.94 eV. For the off-diagonal element B, which relates to the through-space interaction between the exocyclic double bond and the benzene ring, a value of −0.318

(57) Brogli, F.; Giovannini, E.; Heilbronner, E.; Schuster, R. *Chem. Ber.* **1973**, *106*, 961.

(58) Koopmans, T. *Physica (Utrecht)* **1934**, *1*, 104.

(59) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

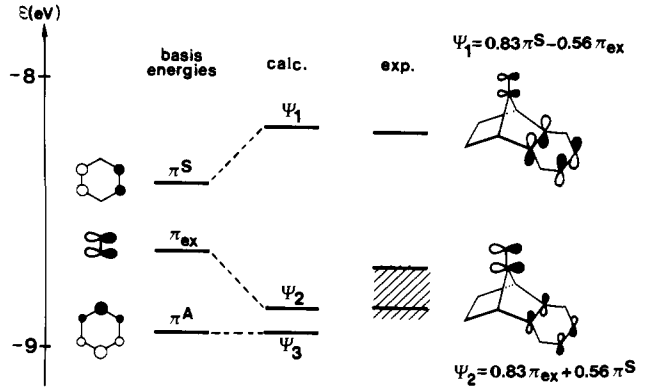


Figure 3. Comparison between theoretical and experimental orbital energies of **1**. The ZDO wave functions of **1** are indicated at the right.

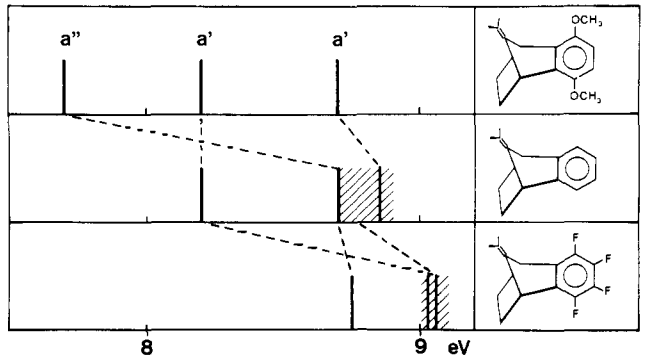


Figure 4. Correlation of the first three bands in the PE spectra of **1**, **2**, and **4**.

Table II. Measured Vertical Ionization Potentials and Calculated Orbital Energies of 1 (All Values in eV)

band	$I_{V,J}$	assignt	ZDO	MINDO/3	SPINDO
1	8.20	a'(π)	8.18 (a')	8.58 (a')	9.09 (a')
2	8.70	a"(π)	8.85 (a')	8.95 (a")	9.36 (a")
3	8.85	a'(π)	8.94 (a")	8.98 (a')	9.71 (a')

eV is adopted.[9] With these parameters, we obtain the orbital energies and wave functions shown in Figure 3. The agreement between experiment and calculation is excellent, predicting an MO with large coefficients at the benzene ring to be the HOMO.

(b) MINDO/3 Results. The orbital sequence derived from our ZDO model is confirmed by a MINDO/3 calculation. The latter procedure also predicts ψ_1 to be the HOMO and ψ_3 to be slightly above ψ_2. Whereas the ZDO model considered through-space interaction only, MINDO/3 predicts considerable mixing of π and σ orbitals. The experimental data obtained for **1** are compared with the calculated values in Table II.

In Figure 4, the first bands of the PE spectra of **1**, **2**, and **4** are compared. The assignments made in Table II are seen to be nicely corroborated there. Thus, the methoxy groups in **2** shift the a" orbital strongly and leave the other two essentially unchanged. Fluorine substitution as in **4** shifts the first band toward higher energy. These observations are uniquely consistent with the assignments given in Tables II and III.

Discussion

A certain level of steric bias is present in the bridged olefins **1–5**. Syn attack generates the lesser steric inhibition since the electrophile approaches above a planar aromatic ring or double bond. In contrast, anti attack is inhibited to some degree by the presence of exo hydrogens on the ethano bridge. Consequently, the formation of an anti product must be viewed as a contrathermodynamic phenomenon whose origins are necessarily electronic. Clearly, the variable stereoselectivity which we have observed within a particular reaction type cannot be dictated by steric effects.

Table III. Measured Vertical Ionization Potentials and Calculated Orbital Energies for 2 and 4

compd	band	$I_{V,J}$	assignt	MINDO/3
2	1	7.70	a"(π)	7.69 (a")
	2	8.20	a'(π)	8.66 (a')
	3	8.70	a'(π)	8.93 (a')
4	1	8.75	a"(π)	9.14 (a")
	2	9.03	a'(π)	9.23 (a')
	3		a'(π)	9.54 (a')

Table IV. Crystal Data for 29a

$C_{15}H_{16}Cl_2$	ρ_{calcd} = 1.367 g cm^{-3}
M_r = 267.20	λ(Mo Kα) = 0.710 69 Å
F_{000} = 140 e$^-$	μ(Mo Kα) = 3.52 cm^{-1}
space group $P2_1/c$ (C_{2h}^5, No. 14)	$A_{max} = e^{-\mu r}_{min}$ = 0.952
cell constants (T = −76 (1) °C)	$A_{min} = e^{-\mu r}_{max}$ = 0.846
a = 16.530 (2) Å	no. of unique data = 3807
b = 6.774 (1) Å	no. of data with $I >$
c = 12.460 (2) Å	$3\sigma(I)$ = 1646
β = 111.44 (1)°	
V = 1298.5 (3) Å^3	

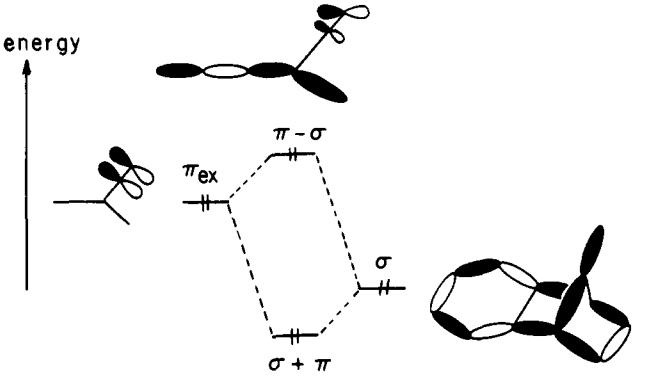


Figure 5. Interaction diagram between the exocyclic π orbital and a high-lying σ orbital to visualize the distortion of the resulting linear combination.

Certain variations in solvent were understandably necessary to accommodate the range of reagents studied. In other instances, the influence of solvent changes was examined purposefully. As an example, the product ratios determined for singlet oxygen were essentially unchanged in methanol, dichloromethane, or acetonitrile.[11a] The bromination of **1** with NBS in either 10% aqueous glyme or methyl formate–formic acid (1:1) gave identical results within experimental error. This was, of course, not the situation with *tert*-butyl hypochlorite where increased levels of formic acid served to protonate this reagent on oxygen and increase its electrophilicity. The latter chemistry reflects a gradual change from weak to strong electrophilic character, a distinction which we employ below to permit the best contrasts to be made.

Weak Electrophiles. The experimental facts are that **1**, **2**, and **5** are attacked by singlet oxygen, NBS, *N*-methyltriazolinedione, and *tert*-butyl hypochlorite (under neutral conditions) predominantly from the anti direction and that appreciable reversal of this stereoselectivity occurs with **3** and **4**. With *m*-chloroperbenzoic acid, smooth oxidation to produce mixtures enriched in the anti isomer was seen in every instance, although again in decreased amounts when **3** and **4** were involved. The observed switch in the syn/anti ratios suggest the possible operation of several effects. The predominant anti addition in the case of **1**, **2**, and **5** may be explained in terms of the shape of ψ_2, the wave function which has a large coefficient at the exocyclic double bond. The considerable mixing of this π orbital with a high lying σ orbital causes a distortion to materialize in such a way that overlap with an orbital approaching from the anti side is favored (Figure 5). According to this interpretation, the HOMO ($\pi_s - \pi_{ex}$) could not be responsible for the observed reactions. This conclusion is derived from the fact that **1** and **2** give rise to very similar syn/anti ratios although their HOMO's are different (Figure 4).

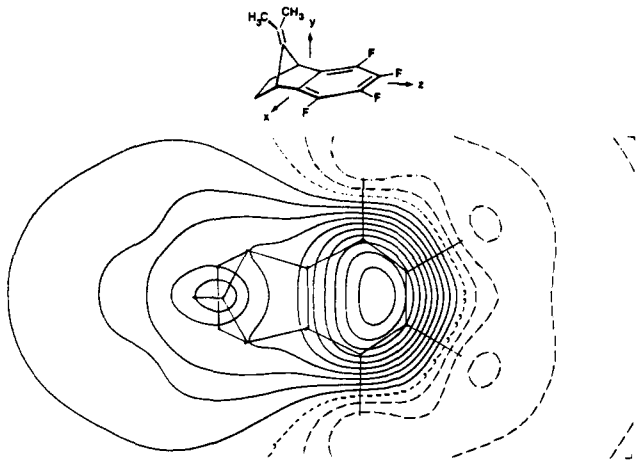


Figure 6. Contour diagram of the calculated electrostatic potentials of **4**. The map is drawn parallel to the x,z plane 1.5 Å above the benzene ring. The gap between the contours is 5 kcal/mol. Positive potentials are indicated by solid lines, negative one with broken lines. Nodes are indicated by short dashes.

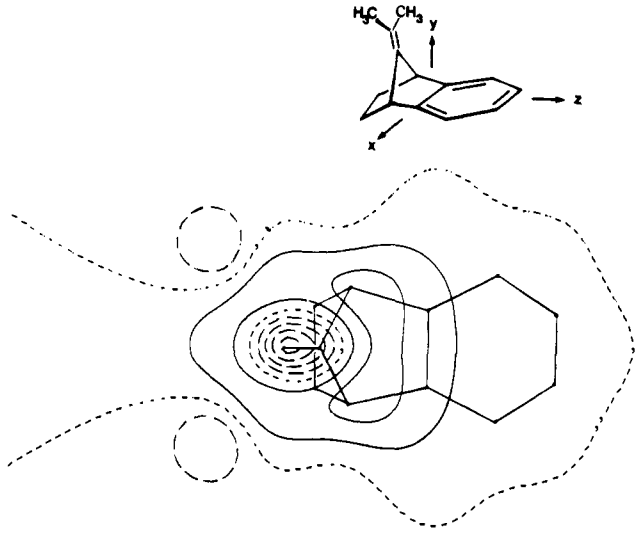


Figure 7. Contour diagram of the calculated electrostatic potentials of **1**. See comments below Figure 6.

Notwithstanding the attractiveness of this argument, we believe this effect to be too small to generate stereoselectivity of the magnitude that is observed (substantively contrasteric in many instances). Certainly, it is unlikely to be at the root of the variable stereoselectivity caused by the different aromatic substitution plans. This is not to say that orbital distortion is not important in the ground states of these molecules. In actual fact, various spectroscopic techniques provide clear indication that this is so (vide infra). But the stereoselectivity factors gain their importance in the various transition states and these need not necessarily reflect ground-state phenomena, although the trends could, of course, parallel each other.

When electron-withdrawing substituents are located on the benzene ring, a second stereoselectivity determining factor can gain importance. Such groups as fluoro and chloro effectively reduce the electron density above and below the aromatic ring, as dramatically illustrated by contour diagram plots of the calculated electrostatic potential fields (EPF).[60] For example, the plot for **4** (Figure 6) is seen to display an intensely positive region

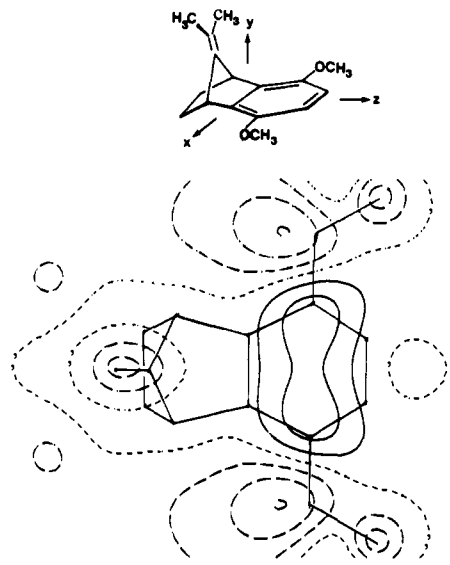
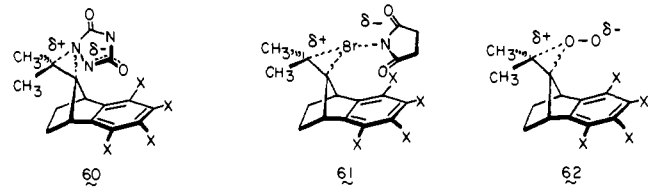


Figure 8. Contour diagram of the calculated electrostatic potentials of **2**. See comments below Figure 6.

above and below the benzene ring, while those for **1** (Figure 7) and **2** (Figure 8) reflect the absence of meaningful long-range electrostatic interaction. Accordingly, transition states for uniparticulate electrophilic additions[61] and those for biparticulate electrophilic processes where closely trailing δ^- fragments are involved can receive added stabilization when the attacking reagent is positioned above the electron-deficient benzenoid portions of **3** and **4**. The transition states which develop during syn attack by NMTAD[40] (**60**) and NBS[62] (**61**) are representative of our



60 **61** **62**

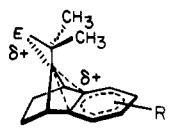
thinking. Since peracid oxidations do not proceed by way of similar charge-separated activated complexes,[36] they are not necessarily affected similarly. Since the stereoselectivity of $^1O_2$ attack very closely parallels that of the first two of these model reactions, it appears plausible that a perepoxide transition state such as **62** is involved.

Whereas electrostatic potential field effects may be responsible for the increased levels of syn attack on **3** and **4**, the *general preference* for anti attack cannot be attributed to such influences. However, if the π electrons of the exocyclic double bond experience partial rehybridization as they come under the influence of the approaching electrophile, stabilizing bishomoconjugative interaction can develop, particularly when the benzene ring is unsubstituted or endowed with electron-donating groups. Anti attack is then highly favored. This effect would be negated somewhat by the presence of electron-withdrawing aryl substituents, as solvolytic studies on *anti*-7-benzonorbornenylsulfonates have so convincingly demonstrated.[6,7] The relative rates of singlet oxygenation of **1**–**4** are also nicely accommodated by this hypothesis. The kinetically determining factor is the ability of the aromatic ring to delocalize charge as in **63**. In benzonorbornadiene derivatives, the isolated double bond is better able to delocalize charge than the benzene ring (see **64**) and stereoselectivity is dictated accordingly.[11] The same argument applies to the 2,3-dicarbomethoxynorbornadiene example (see **65**).[11]

(60) (a) Scrocco, E.; Tomasi, J. *Fortschr Chem. Forsch.* **1973**, *42*, 95. (b) Klopman, G.; Hudson, R. F. *Theor. Chem. Acta* **1967**, *8*, 165. (c) Hudson, R. F.; Klopman, G. *Tetrahedron Lett.* **1967**, 1103. (d) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223. (e) Almlof, J.; Henriksson-Enflo, A.; Kowalewski, J.; Sundbom, M. *Chem. Phys. Lett.* **1973**, *21*, 560. (f) Almlof, J.; Haselbach, E.; Jachimowicz, F.; Kowalewski, J. *Helv. Chim. Acta* **1975**, *58*, 2304.

(61) Paquette, L. A.; Allen, G. R., Jr.; Broadhurst, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 4503.

(62) Bellucci, G.; Berti, G.; Ferretti, M.; Ingrosso, G.; Mastroilli, E. *J. Org. Chem.* **1978**, *43*, 422 and references cited therein.



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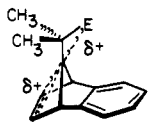

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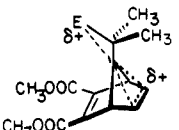
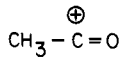


65

Our conclusions are that π-orbital effects do not prevail in these systems as in some cycloaddition reactions. The polarization component,[63] which is herein an expression of the latent homoaromatic delocalization available between the aromatic ring and C_9, is simply too overwhelming. Okada and Mukai[11,64] have proposed that secondary orbital interactions contribute significantly to the stereoselectivity of singlet oxygen capture in these systems. Although such influences appear to gain considerable importance in other situations, we are of the opinion that they are too weak to be significant in **1–5** because of their unique electronic character. This point is discussed in more detail below for the dichlorocarbene example. Attention is also directed to the ensuing paper dealing with benzobicyclo[2.2.2]octadienes[15] where homoaromatic stabilization no longer can operate efficiently and the weaker electronic effects discussed above become influential.

Strong Electrophiles. The Friedel–Crafts and Prins reactions afford syn products exclusively. The electrophiles which are believed to intervene in these processes are **66** and **67**, respectively.



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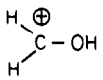

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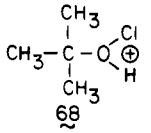

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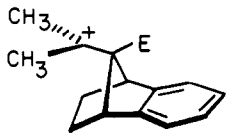
Both species carry a high proportion of electron deficiency at the attacking site. The significant stereochemical determinant would appear to be whether or not the attacking reagent requires assistance from the π bond to become adequately polarized (uniparticulate cases, e.g., **60** and **62**) or disengaged from its anionic component (biparticulate cases, e.g., **61**). When such π-bond assistance is unnecessary as with **66** and **67**, then the reagent is expected to become *less* discriminant and to afford a mixture of products. However, the exclusive formation of syn stereoisomers via **69** and **70** is seen. A likely contributing influence could be



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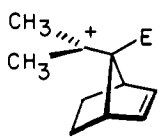
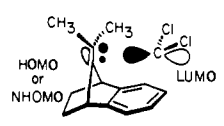


70

prior coordination of the stronger electrophiles to the benzo ring or norbornene double bond with ensuing intramolecular delivery to the syn surface of the double bond. This facet of the problem is discussed in detail in ensuing papers.[15,16]

The levels of syn attack by protonated *tert*-butyl hypochlorite (**68**) does not attain 100%, presumably because the positive charge is associated chiefly with the oxygen atom *adjacent to* the attacking chlorine atom. Accordingly, the degree of electrophilicity is somewhat diminished.

Carbenes have high electrophilicity and formally neutral charge character. The extent of polarization which develops in the transition state is said to be dependent upon the angle of attack and the reactivity of the olefin involved.[65] For dichlorocarbene, the stereoselectivity for capture by the various 9-isopropylidenebenzonorbornenes and 7-isopropylidenenorbornene (**5**) is decidely syn, in agreement with the concept of aryl interaction. In fact, the most important orbital interaction involving **1** and $:CCl_2$ appears to be **71**. However, secondary effects must also be



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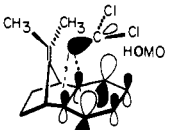

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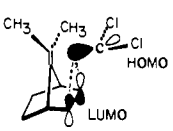
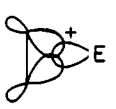


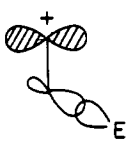
73

considered, since the carbene HOMO becomes positioned above the benzene ring where the low-lying LUMO or NLUMO of the substrate should be heavily localized. The role played by **72** is to direct syn stereoselectivity as well, in agreement with our results. Significantly, however, the LUMO of **5**, which is predomdinantly localized at the endocyclic double bond, is antisymmetric and cannot interact favorably with the carbene HOMO (see **73**). Consequently, syn attack by the carbene should be electronically disfavored, in direct contradiction to our findings.

Summary. We have demonstrated that electrophilic additions to **1–5** proceed with variable stereoselectivity. When weak electrophiles are involved, syn attack occurs preferentially. However, this reaction course can be reversed in large measure by the placement of electron-deficient substituents on the aromatic ring. In the addition of strong electrophiles, syn stereoselection dominates heavily or is exclusive irrespective of the aryl substitution plan. In essence, a stereochemical method for qualitatively assessing the relative electrophilicity of various electron-deficient species has been developed. This new tool appears to derive its success from the ability of the substrate molecules to distinguish stereochemically between pathways **74** and **75**. In the bridged



74



75

ion situations which are generally required for weak electrophiles, homoaromatic charge delocalization is called into action and contrasteric anti attack is kinetically favored. The more powerful reagents which react via open ions such as **75** are not dependent upon the development of long-range stabilization and entry from the syn direction is observed chiefly because of transient complex formation.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian T-60 and EM-360 spectrometers, and apparent splittings are given in all cases. Mass spectra were measured with an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Microanalytical determinations were made at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

5,8-Dimethoxy-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene. A solution of *p*-benzoquinone (10.8 g, 0.1 mol) in anhydrous ether (100 mL) was treated with 6,6-dimethylfulvene (10.6 g, 0.1 mol) in ether (20 mL) at 0 °C. After 1 h at 0 °C, chloroform (3 mL) was added and the solution was stirred at room temperature for 12 h. After removal of solvent, the residue was mixed with 10% sodium hydroxide solution (120 mL) and cooled to 0 °C. Dimethyl sulfate (40 g, 0.32 mol) was added, and the stirred solution was allowed to warm to room temperature for 5 h. Sodium hydroxide (6 g in 15 mL of water) was added to the reaction mixture along with dimethyl sulfate (20 g, 0.15 mol), and stirring was continued for an additional 3 h. More sodium hydroxide (3 g in 10 mL of water) was added, and stirring was continued for 10 h. The reaction mixture was acidified with 5% hydrochloric acid solution and extracted with ether. The ether extracts were dried and evaporated under reduced pressure. The resulting black residue was chromatographed on alumina (benzene elution), and the product was purified by recrystallization from ethanol: 1.66 g (7%), mp 137–137.5 °C; ^1H NMR ($CDCl_3$) δ 6.85 (m, 2 H), 6.42 (s, 2 H), 4.6 (m, 2 H), 3.8 (s, 6 H), 1.55 (s, 6 H).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.31; H, 7.61.

5,8-Dimethoxy-9-benzonorbornenone Dimethyl Ketal (14). To a stirred solution of **13**[19b] (1 g, 2.5 mmol), *tert*-butyl alcohol (2.04 g, 26.9 mmol), and tetrahydrofuran (15 mL) under a nitrogen atmosphere was added freshly cut lithium metal (0.48 g, 68.9 mol). The mixture was stirred at the reflux temperature for 15 h. The reaction mixture was

(63) Fijimoto, H.; Inagaki, S. *J. Am. Chem. Soc.* **1977**, *99*, 7424.
(64) We thank Professor Mukai and Dr. Okada for several informative exchanges of information.
(65) (a) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. (b) Skell, P. S.; Cholod, M. S. *Ibid.* **1969**, *91*, 7131.

cooled in an ice bath, and excess lithium was destroyed by the slow addition of methanol. After dilution with water, the organic layer was separated. The aqueous layer was reextracted with ether, and the combined organic layers were washed with water and brine prior to drying. After solvent removal, the residue was purified by chromatography on silica gel (petroleum ether elution): 0.45 g (70%); mp 122.5–123.5 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 6.62 (s, 2 H), 3.82 (s, 6 H), 3.57 (m, 2 H), 3.35 (s, 3 H), 3.12 (s, 3 H), 2.1 (m, 2 H), 1.15 (m, 2 H).

5,8-Dimethoxy-9-benzonorbornenone (15). A solution of **14** (2.43 g, 9.3 mmol) in ether (75 mL) was stirred for 12 h at room temperature with 6 N hydrochloric acid solution (50 mL). The ether phase was separated and evaporated under reduced pressure. The resulting residue was purified by recrystallization from ethanol to give 1.8 g (90%) of **15**: mp 107.5–108.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.7 (s, 2 H), 3.82 (s, 6 H), 3.53 (m, 2 H), 2.17 (m, 2 H), 1.37 (m, 2 H); ν_{max}^{Nujol} 1782 and 1770 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.35; H, 6.49.

5,8-Dimethoxy-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (2). To a solution of isopropyltriphenylphosphonium bromide (9.9 g, 25.7 mmol) in anhydrous tetrahydrofuran (250 mL) cooled to 0 °C was added 20 mL of 1.29 N *n*-butyllithium (25.7 mmol) in hexane. After 1.5 h at 0 °C, a solution of **15** (5 g, 23.4 mmol) in tetrahydrofuran (40 mL) was added dropwise. After 1 h at 0 °C, the reaction mixture was allowed to warm to room temperature and heated at reflux for 16 h. The cooled reaction mixture was filtered through a pad of Celite, and the filtrate was diluted with water. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with saturated sodium bicarbonate solution, water, and brine prior to drying. After solvent removal, the residue was purified by chromatography on silica gel (benzene elution) to give 3.66 g (65%) of **2**: mp 129–130 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 6.57 (s, 2 H), 4.0 (m, 2 H), 3.82 (s, 6 H), 1.87 (m, 2 H), 1.64 (s, 6 H), 1.24 (m, 2 H).

7-Isopropylidenenorbornene (5). A solution of 6,6-dimethylfulvene (29.7 g, 0.28 mol) and acrylic acid (20.2 g, 0.28 mol) in tetrahydrofuran (50 mL) was heated at the reflux temperature for 19 h. The cooled reaction mixture was diluted with ether and extracted with 10% sodium hydroxide solution. The alkaline aqueous layer was extracted with ether and slowly acidified with 6 N hydrochloric acid. The acidic solution was extracted three times with ether. The combined ether layers were dried and evaporated under reduced pressure to yield 32.2 g (65%) of **16** as an oil. The product was carried on to the next step without further purification: ^{1}H NMR ($CDCl_3$) δ 11.93 (s, 1 H), 6.35–6.03 (m, 2 H), 3.65–3.47 (m, 1 H), 3.35–3.17 (m, 1 H), 3.05–2.7 (m, 1 H), 2.4–1.66 (m, 2 H), 1.55 (s, 6 H).

A solution of lithium diisopropylamide (0.44 mol) in tetrahydrofuran (175 mL) and HMPA (35 mL) at 0 °C was added dropwise with stirring to a solution of **16** (31.3 g, 0.176 mol) in tetrahydrofuran (175 mL). After 3 h, the dianion solution was cooled to −78 °C and transferred via syringe to a reaction well containing ether (500 mL) cooled to −78 °C into which dry oxygen was continuously bubbled. After addition of the dianion, oxygen was bubbled through the solution at −78 °C for an additional 30 min. The reaction mixture was concentrated in vacuo to 200–250 mL, diluted with ether, and poured into cold aqueous 10% hydrochloric acid (250 mL). The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether layers were dried, and an exchange of solvent was accomplished by removal of ether in vacuo and addition of methylene chloride to maintain a volume of 200–250 mL. To this solution at −78 °C under nitrogen was added dropwise a solution of dimethylformamide dimethylacetal (50 g, 0.42 mol) in methylene chloride (175 mL), and the reaction mixture was allowed to warm slowly to room temperature. Stirring was continued until the starch–iodide test for peroxides was negative. The solvent was removed, and the residue was diluted with saturated sodium chloride solution and ether. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether layers were dried and evaporated under reduced pressure. The resulting residue was distilled to yield 5.47 g (21%) of **17** as a yellowish oil: bp 46 °C (0.3 mm) (lit.[21] bp 46 °C (0.3 mm)); ^{1}H NMR, ($CDCl_3$) δ 6.74–6.52 (m, 1 H), 6.3–6.08 (m, 1 H), 3.74–3.43 (m, 2 H), 2.1–1.96 (m, 2 H), 1.69 (s, 3 H), 1.59 (s, 3 H).

The conversion of **17** to **5** was achieved according to Martin and Forster.[22]

1,2,3,4-Tetrahydro-9-ethylidene-1,4-methanonaphthalene (18). A stream of ozone was bubbled for 30 min through a solution of **1** (3 g, 16.3 mmol) in methylene chloride (55 mL) with cooling from a ice–salt bath. Oxygen was then bubbled through the solution to remove excess dissolved ozone. In order to destroy the ozonide, acetic acid (8.4 mL) was introduced slowly to the cold solution with stirring. Zinc powder (2.8 g) and water (2.8 mL) were added alternately portionwise, and the solution was allowed to stir at room temperature. The reaction mixture was extracted three times with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water prior to drying. Removal of the solvent yielded 2.21 g (86%) of **3** as an oil (lit.[17] bp 100–103 °C (7 mm)): ^{1}H NMR ($CDCl_3$) δ 7.15 (m, 4 H), 3.25 (m, 2 H), 2.1 (m, 2 H), 1.3 (m, 2 H); ν_{max}^{Nujol} 1806 and 1792 cm^{-1}.

To a solution of ethyltriphenylphosphonium bromide (1.25 g, 3 mmol) in anhydrous tetrahydrofuran (25 mL) at 0 °C was added 3.8 mL (3 mmol) of 0.79 M *n*-butyllithium in hexane. After 15 min of stirring at 0 °C, the preceding ketone (0.47 g, 3 mmol) in tetrahydrofuran (5 mL) was added dropwise. After 1 h at 0 °C, the reaction mixture was allowed to warm to room temperature and heated at the reflux temperature for 2 h. The cooled reaction mixture was filtered through a pad of Celite and the filtrate was diluted with water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with saturated sodium bicarbonate, water, and brine prior to drying. After solvent removal, the residue was purified by chromatography on silica gel (petroleum ether elution) to give 0.4 g (78%) of **18** as an oil: ^{1}H NMR ($CDCl_3$) δ 7.1 (br s, 4 H), 4.88 (q, J = 7 Hz, 1 H), 3.8 (m, 1 H), 3.45 (m, 1 H), 2.04–1.78 (m, 2 H), 1.6 (d, J = 7 Hz, 3 H), 1.35–1.1 (2 H, m). The analytical sample was prepared by preparative VPC (12 ft × 0.25 in. 5% SF96 on Chromosorb G, 140 °C).

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.67; H, 8.37.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-ethylidene-1,4-methanonaphthalene (19). A solution of **4** (3.0 g, 11.7 mmol) in methylene chloride (55 mL) was ozonized in the predescribed manner. The residue was purified by recrystallization from petroleum ether to afford 1.82 g (67.4%) of tetrafluoro ketone: mp 82–86 °C (lit.[18] mp 96–97 °C); ^{1}H NMR ($CDCl_3$) δ 3.79–3.56 (m, 2 H), 2.54–2.09 (m, 2 H), 1.7–1.27 (m, 2 H); ν_{max}^{Nujol} 1795 cm^{-1}.

Reaction of the preceding ketone (1 g, 4.35 mmol) with ethyltriphenylphosphonium bromide (1.82 g, 4.35 mmol) as before and chromatographic purification on silica gel (petroleum ether elution) gave 0.67 g (64%) of **19** as an oil ^{1}H NMR ($CDCl_3$) δ 4.98 (q, J = 7 Hz, 1 H), 4.15 (m, 1 H), 3.77 (m, 1 H), 2.12–1.8 (m, 2 H), 1.66 (d, J = 7 Hz, 3 H), 1.47–1.19 (m, 2 H). The analytical sample was prepared by preparative VPC (12 ft × 0.25 in. 5% SF96 on Chromosorb G, 140 °C).

Anal. Calcd for $C_{13}H_{10}F_4$: C, 64.46; H, 4.16. Found: C, 64.45; H, 4.20.

Prototypical Photooxygenation Procedure. A solution of **1** (72.5 mg, 0.394 mmol) and rose bengal (1 mg/mL) in methanol was irradiated with a 500-W tungsten filament projector bulb while oxygen was bubbled through the solution, which was being cooled by an ice water bath. The irradiation was carried out for 6 h, at which time the reaction mixture was treated with sodium borohydride (149 mg, 3.94 mmol) and stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the resulting residue was dissolved in ether and water. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with 5% sodium hydroxide solution and water prior to drying. After the removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). For product data see Table V.

Prototypical Epoxidation Procedure. A solution of **1** (1 g, 5.43 mmol) in methylene chloride was reacted with *m*-chloroperbenzoic acid (1.03 g, 5.97 mmol) for 12 h at room temperature. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with saturated sodium sulfite solution, saturated sodium bicarbonate solution, and brine prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution). For product data see Table V.

7-Isopropylidenenorbornene *syn*(*anti*)-Oxide (28 and 29). A solution of **5** (100 mg, 0.75 mmol) in methylene chloride cooled to −23 °C was reacted with *m*-chloroperbenzoic acid (129 mg, 0.75 mmol) for 2 h at −23 °C and then for 12 h at room temperature. Water was added, the organic layer was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic layers were washed with saturated sodium sulfite solution, saturated sodium bicarbonate solution, and brine prior to drying. After removal of solvent, the residue was analyzed by ^{1}H NMR spectroscopy and carried on, without purification, to the allylic alcohols by base-promoted opening.

Base-Promoted Opening of 26a–27a. Prototypical Procedure. To an ice cold solution of lithium diethylamide (4.2 mmol), prepared from diethylamine (0.31 g, 4.2 mmol) and 2.62 mL (4.2 mmol) of 1.6 *M* *n*-butyllithium, was added a sample of the **26a–27a** mixture (0.84 g, 2.5 mmol) dissolved in anhydrous ether (50 mL). After the addition, the solution was allowed to warm to room temperature where it was stirred

for 12 h. Water was added, the organic layer was separated, and the aqueous phase was extracted twice with ether. The combined organic layers were washed with 10% ammonium chloride solution, saturated sodium bicarbonate solution, and water prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene elution): syn isomer **20a**, 80.6 mg (9.6%); anti isomer **21a**, 565 mg (67%).

Prototypical Bromination Procedure. A solution of **1** (430 mg, 2.34 mmol) (2.69 mmol) for 4 h at room temperature. The reaction mixture was treated with 10% sodium bisulfite solution and stirred for 15 min, at which time most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted three times with chloroform. The combined organic layers were washed with saturated sodium chloride solution prior to drying. After removal of solvent, the residue was purified and the isomers were separated by preparative layer chromatography on silica gel (benzene–petroleum ether (1:4) elution). For product data see Table V.

Prototypical Ene Reaction with *N*-Methyltriazolinedione. A solution of **1** (46.5 mg, 0.253 mmol) in anhydrous ether (10 mL) was treated with 4-methyl-1,2,4-triazoline-3,5-dione (28.5 mg, 0.253 mmol) in anhydrous methylene chloride (10 mL) at room temperature. After 4 h, the solvent was removed and the residue was recrystallized from hot methanol–acetic acid (1:1) to yield 46 mg (61%) of anti isomer **33a**. From the mother liquor was isolated syn isomer **32**. For product data see Table V.

***syn*(*anti*)-9-Chloro-*anti*(*syn*)-9-isopropenyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene (37a and 38a).** **A.** To a solution of **1** (150 mg, 0.82 mmol) in freshly distilled methyl formate (3 mL) was added *tert*-butyl hypochlorite (88.5 mg, 0.82 mmol). The solution was stirred at room temperature in the dark for 9 h. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (benzene–petroleum ether (1:4)). syn isomer **37a**: 19.1 mg (10.8%); mp 152.5–154 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 7.13 (br s, 4 H), 5.18–4.96 (m, 2 H), 3.62–3.52 (distorted t, J = 2 Hz, 2 H), 2.18–1.87 (m, a distinct 3 H m at 1.95, 5 H), 1.34–1.04 (m, 2 H).

Anal. Calcd for $C_{14}H_{15}Cl$: C, 76.88; H, 6.91. Found: C, 76.75; H, 6.93.

Anti isomer **38a**: 133.7 mg (76.7%); mp 83–86 °C (preparative VPC (6 ft × 0.25 in. 5% SE 30 on Chromosorb G, 180 °C)); ^{1}H NMR ($CDCl_3$) δ 7.0 (br s, 4 H), 4.69–4.56 (m, 2 H), 3.5–3.39 (distorted t, J = 2 Hz, 2 H), 2.48–2.16 (m, 2 H), 1.65 (m, 3 H), 1.33–1.05 (m, 2 H).

Anal. Calcd for $C_{14}H_{15}Cl$: C, 76.88; H, 6.91. Found: C, 76.54; H, 6.86.

B. To a solution of **1** (100 mg, 0.54 mmol) in methyl formate (1.5 mL) and formic acid (0.25 mL, 6.6 mmol) was added *tert*-butyl hypochlorite (58.6 mg, 0.54 mmol). The solution was stirred at room temperature in the dark for 1.5 h, the solvent was evaporated, and the isomers were separated as above to give 39.2 mg (33.2%) of **37a** and 54.3 mg (46%) of **38a**.

C. To a solution of **1** (150 mg, 0.815 mmol) in methyl formate (6 mL) and formic acid (6 mL) was added *tert*-butyl hypochlorite (88.4 mg, 0.815 mmol). The solution was stirred at room temperature in the dark for 8 h, the solvent was evaporated, and the isomers were separated as above to give 80.2 mg (45%) of **37a** and 14.8 mg (8.3%) of **38a**.

***syn*(*anti*)-9-Chloro-*anti*(*syn*)-9-isopropenyl-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (37b and 38b).** **A.** To a solution of **2** (100 mg, 0.41 mmol) in freshly distilled methyl formate (2 mL) was added *tert*-butyl hypochlorite (44.5 mg, 0.41 mmol). The solution was stirred at room temperature in the dark for 6 h. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (benzene–petroleum ether (1:4)). Syn isomer **37b**: 11.2 mg (18.7% based on recovered **2**), mp 158–160 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 6.6 (s, 2 H), 5.2–5.1 (m, 1 H), 5.02–4.9 (m, 1 H), 3.87–3.67 (m, a distinct s at 3.75, 8 H), 2.2–1.81 (m, a distinct 3 H m at 1.95, 5 H), 1.33–1.02 (m, 2 H).

Anal. Calcd for $C_{16}H_{19}ClO_2$: C, 68.94; H, 6.87. Found: C, 68.67; H, 6.91.

Anti isomer **38b**: 34.3 mg (57.4% based on recovered **2**), mp 126.5–127 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 6.52 (s, 2 H), 4.9–4.8 (m, 1 H), 4.7–4.6 (m, 1 H), 3.75 (s, 6 H), 3.48–3.35 (distorted t, J = 2 Hz, 2 H), 2.43–2.15 (m, 2 H), 1.72 (m, 3 H), 1.3–1.05 (m, 2 H).

Anal. Calcd for $C_{16}H_{19}O_2Cl$: C, 68.94; H, 6.87. Found: C, 68.48; H, 6.95.

B. To a solution of **2** (250 mg, 1.03 mmol) in methyl formate (5 mL) and formic acid (0.48 mL, 12.60 mmol) was added *tert*-butyl hypochlorite (112 mg, 1.03 mmol). The solution was stirred at room temperature in the dark for 4.5 h, the solvent was evaporated, and the isomers were separated as above to give 123.1 mg (42.9%) of **37b** and 98.5 mg (34.3%) of **38b**.

C. To a solution of **2** (50 mg, 0.207 mmol) in methyl formate (2 mL) and formic acid (2 mL) was added *tert*-butyl hypochlorite (22.4 mg, 0.207 mmol). The solution was stirred at room temperature in the dark for 20 h, the solvent was evaporated, and the isomers were separated as above to give 22.8 mg (39.5%) of **37b** and 12 mg (20%) of **38b**.

***syn*(*anti*)-9-Chloro-*anti*(*syn*)-9-isopropenyl-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (37c and 38c).** **A.** To a solution of **4** (100 mg, 0.39 mmol) in freshly distilled methyl formate (4 mL) was added *tert*-butyl hypochlorite (42.3 mg, 0.39 mmol). The solution was stirred at room temperature in the dark for 16 h. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (benzene–petroleum ether (1:4)). Syn isomer **37c**: 42.5 mg (37.4%); mp 82–84 °C (preparative VPC (6 ft × 0.25 in. 5% SE30 on Chromosorb G, 180 °C)); ^{1}H NMR ($CDCl_3$) δ 5.2–5.0 (m, 2 H), 3.95–3.77 (m, 2 H), 2.22–1.85 (m, a distinct 3 H m at 1.95, 5 H), 1.44–1.1 (m, 2 H).

Anal. Calcd for $C_{14}H_{11}ClF_4$: C, 57.85; H, 3.81. Found: C, 57.74; H, 3.83.

Anti isomer **38c**: 50.5 mg (44.5%); mp 130.5–131.5 °C (preparative VPC (6 ft × 0.25 in. 5% SE30 on Chromosorb G, 180 °C)); ^{1}H NMR ($CDCl_3$) δ 4.9–4.7 (m, 2 H), 3.9–3.7 (m, 2 H), 2.68–2.34 (m, 2 H), 1.75 (m, 3 H), 1.53–1.19 (m, 2 H).

Anal. Calcd for $C_{14}H_{11}ClF_4$: C, 57.85; H, 3.81. Found: C, 57.65; H, 3.89.

B. To a solution of **4** (50 mg, 0.195 mmol) in methyl formate (2 mL) and formic acid (110 mg, 2.39 mmol) was added *tert*-butyl hypochlorite (21.2 mg, 0.195 mmol). The solution was stirred at room temperature in the dark for 16 h, the solvent was evaporated, and the isomers were separated as above to give 20 mg (35.3%) of **37c** and 18.7 mg (33%) of **38c**.

C. To a solution of **4** (50 mg, 0.195 mmol) in methyl formate (1 mL) and formic acid (1 mL) was added *tert*-butyl hypochlorite (21.2 mg, 0.195 mmol). The solution was stirred at room temperature in the dark for 18 h, the solvent was evaporated, and the isomers were separated as above to give 31.5 mg (55.6%) of **37c** and 3.4 mg (6%) of **38c**.

Prototypical Dichlorocyclopropanation Procedure. A solution of **1** (250 mg, 1.36 mmol) and sodium trichloroacetate (5 g, 27 mmol) in 50 mL of tetrachloroethylene–glyme (1:1) was heated at the reflux temperature for 18 h, diluted with water, and extracted three times with ether. The combined organic layers were washed with saturated sodium bicarbonate, 10% ammonium chloride, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (petroleum ether elution). For product data see Table V.

X-ray Analysis of 29a. The data crystal, a colorless prism about 0.37 mm × 0.25 mm × 0.10 mm with prominent faces [010], [101], and [001], was mounted along the longest dimension, coincident with the b axis, sealed with a thin coating of epoxy cement, and attached to the goniometer in a cold stream of dry nitrogen gas. The crystal temperature was reduced to −78 °C and was maintained at this level throughout the determination of the cell constants and the data collection. The cell constants were determined by a least-squares fit of the optimized diffractometer setting angles for 75 medium intensity reflections having $12.05° \leq 2\theta \leq 31.01°$, these values appear in Table IV along with other pertinent crystal data. Excluding check reflections (ten were collected after every 100 reflections), a total of 4605 intensities were measured on a Syntex P$\bar{1}$ automated four-circle diffractometer by the ω–2θ scan technique by using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. The scan rate ranged from 2.0°/min to 8.0°/min, depending upon the reflection intensity estimated by a 2-s preliminary count at the calculated peak center. Step scans were begun for each reflection 1.0° (2θ) below calculated peak center for Kα_1 and ended 1.15° above calculated peak center for Kα_2 to compensate for $\alpha_1 - \alpha_2$ splitting. Backgrounds were collected at each end of each scan for a total of half the step scan time. All reflections in the quadrant $0 \leq h \leq 23$, $0 \leq k \leq 9$, $-16 \leq l \leq 17$ having $4.0° < 2\theta \leq 60.0°$ were collected in this manner. After averaging of multiply measured reflections and deletion of systematic absences, 3807 unique intensities remained. The R factors for multiply measured intensities, principally those in the $0kl$ and $h0l$ zones which were recollected at the conclusion of the data collection, and the check reflections were R_1 v 0.016 and R_2 = 0.029.[66] All 3807 reflections were used in the subsequent analysis. The systematic absences apparent in the intensity data ($h0l$ absent for $l = 2n + 1$, $0k0$ absent for $k = 2n + 1$) and the intensity statistics unambiguously fixed the space group as $P2_1/c$. ψ scans for five reflections with different reciprocal lattice directions showed intensity variations of ±5%. On the basis of this and the predicted range of transmission coefficients (Table II) calculated using the worst case μr values ($\mu r_{max} = 0.165$; $\mu r_{min} = 0.035$), we concluded that the expense of

(66) $R_1 = \sum_i\sum_j n_i(||F_{av_i}| - |F_{j_i}||)/\sum_i\sum_j F_{av_i}$ and $R_2 = [\sum_i\sum_j n_i w_i(F_{av_i}^2 - F_{j_i}^2)^2/\sum_i\sum_j w_i F_{av_i}^4]^{1/2}$, where w_i is the weight for the weight for the ith reflection based on $F_{av_i}^2$.

Table V. Product Data

starting material (mg)	product(s)	mg isolated (yield, %)	mp, °C	^{1}H NMR data (δ, $CDCl_3$)	M$^+$ *m/e* calcd (found)	combustion data
				A. Photooxygenation		
1 (72.5)	20a	7.8 (9.9)	83–83.5	7.23 (br s, 4 H), 5.16 (m, 1 H), 5.06 (m, 1 H), 3.35 (distorted t, J = 2 Hz, 2 H), 2.27–1.94 (m, 2 H), 1.94 (m, 3 H), 1.65 (s, 1 H), 1.30–1.0 (m, 2 H)		calcd: C, 83.96; H, 8.05 found: C, 84.03; H, 8.04
	21a	29.5 (37.4)	128.5–129	7.08 (s, 4 H), 4.8 (m, 1 H), 4.7 (m, 1 H), 3.2 (m, 2 H), 2.45–2.1 (m, 2 H), 1.72 (m, 4 H), 1.3–1.0 (m, 2 H)	200.1201 (200.1204)	
2 (100)	20b	15.6 (14.6)	123–125	6.7 (br s, 2 H), 5.17 (m, 1 H), 5.05 (m, 1 H), 3.80 (s, 6 H), 3.55 (m, 2 H), 1.88 (br s, 3 H), 2.0–1.7 (m, 2 H), 1.67 (br s, 1 H) 1.3–1.0 (m, 2 H)	260.1412 (260.1417)	
	21b	41.8 (39)	127–128	6.57 (s, 2 H), 4.88 (m, 1 H), 4.7 (m, 1 H), 3.78 (s, 6 H), 3.46 (distorted t, J = 2 Hz, 2 H), 2.5–2.15 (m, 2 H), 1.72 (m, 4 H), 1.4–1.1 (m, 2 H)		calcd: C, 73.82; H, 7.74 found: C, 73.87; H. 7.73
3 (100)	20c	21.8 (21)	143.5–144.5	5.20–5.02 (m, 2 H), 3.63 (distorted t, J = 2 H), 2.2–1.9 (m, 2 H), 1.9 (m, 3 H), 1.50 (br s, 1 H), 1.3–1.0 (m, 2 H)		calcd: C, 49.74; H, 3.58 found: C, 49.89; H, 3.76
	21c	17.1 (16.5)	118–119.5	4.83 (m, 1 H), 4.72 (m, 1 H), 3.54 (m, 2 H), 2.53–2.27 (m, 2 H), 1.70 (m, 4 H), 1.37–1.15 (m, 2 H)	355.9642 (355.9650)	
4 (100)	20d	32.5 (30)	130–130.5	5.15–5.0 (m, 2 H), 3.62 (m, 2 H), 2.2–1.92 (m, 2 H), 1.92 (m, 3 H), 1.45 (br s, 1 H), 1.3–1.07 (m, 2 H)		calcd: C, 61.77; H, 4.44 found: C, 61.23; H, 4.55
	21d	20.2 (19)	86–88.5	4.90–4.72 (m, 2 H), 3.55 (m, 2 H), 2.5–2.25 (m, 2 H), 1.72 (m, 4 H), 1.43–1.15 (m, 2 H)	272.0824 (272.0833)	
5 (50)	22[a]	5 (9)		6.08 (t, J = 2 Hz, 2 H), 4.98 (m, 2 H), 2.82 (m, 2 H), 1.8 (m, 3 H), 2.15–0.08 (series of m, 5 H)		
	23[a]	18 (32)		5.92 (t, J = 2 Hz, 2 H), 4.86 (m, 2 H), 2.7 (m, 2 H), 1.78 (m, 3 H), 2.2–0.82 (series of m, 5 H)		
18 (100)	24[a]	7.6 (7)	57.5–58.5	7.21 (m, 4 H), 6.5–6.0 (series of m, 1 H), 5.73–5.17 (series of m, 2 H), 3.12 (distorted t, J = 2 Hz, 2 H), 2.28–1.92 (m, 2 H), 1.76 (s, 1 H), 1.4–1.04 (m, 2 H)	186.1044 (186.1048)	
	25a	30.5 (28)	86–87	7.03 (s, 4 H), 6.05–5.55 (series of m, 1 H), 5.42–4.84 (series of m, 2 H), 3.03 (t, J = 2 Hz, 2 H), 2.5–2.17 (m, 2 H), 1.86 (s, 1 H), 1.4–1.1 (m, 2 H)		calcd: C, 83.83; H, 7.58 found: C, 83.47; H, 7.49
19 (82)	24b	23.2 (26.6)	71–74	6.48–5.95 (series of m, 1 H), 5.69–5.18 (series of m, 2 H), 3.44 (m, 2 H), 2.32–1.83 (m, 2 H), 1.58 (br s, 1 H), 1.37–1.0 (m, 2 H)		calcd: C, 60.47; H, 3.90 found: C, 60.60; H, 4.12
	25b	18.6 (21.4)	55.5–57	6.08–5.58 (series of m, 1 H), 5.45–4.93 (series of m, 2 H), 3.37 (m, 2 H), 2.54–2.26 (m, 2 H), 1.84 (s, 1 H), 1.42–1.08 (m, 2 H)	258.0667 (258.0673)	
				B. Epoxidation		
1 (1000)	26a	50 (4.6)	96–115	7.15 (br s, 4 H), 3.0 (m, 2 H), 2.15–1.83 (m, 2 H), 1.4 (s, 6 H), 1.48–1.05 (m, 2 H)	200.1201 (200.1204)	
	27a	440 (40.5)	134–134.5	7.15 (s, 4 H), 2.98 (m, 2 H), 2.48–2.05 (m, 2 H), 1.42–1.06 (m, 2 H), 1.32 (s, 6 H)		calcd: C, 83.96; H, 8.05 found: C, 83.81; H, 8.07
2 (940)	26b	60 (6)	160–162	6.63 (s, 2 H), 3.80 (s, 6 H), 3.24 (m, 2 H), 1.77 (m, 2 H), 1.40 (s, 6 H), 1.5–1.1 (m, 2 H)	260.1412 (260.1417)	
	27b	620 (62)	138.5–139	6.63 (s, 2 H), 3.80 (s, 6 H), 3.20 (m, 2 H), 2.4–2.02 (m, 2 H), 1.43–1.15 (m, 2 H), 1.34 (s, 6 H)		calcd: C, 73.82; H, 7.74 found: C, 73.92; H, 7.73
3 (75)	26c	33 (41)	183–184	3.32–3.15 (m, 2 H), 2.28–2.0 (m, 2 H), 1.5–1.13 (m, 2 H), 1.4 (s, 6 H)	335.9642 (335.9650)	
	27c	45.4 (57)	165.5–166	3.27 (distorted t, J = 2 Hz, 2 H), 2.47–2.17 (m, 2 H), 1.53–1.15 (m, 2 H), 1.35 (s, 6 H)		calcd: C, 49.74; H, 3.58 found: C, 49.83; H, 3.66
4 (277)	26d	108 (36.5)	91–94	3.4–3.19 (m, 2 H), 2.35–1.9 (m, 2 H), 1.47–1.16 (m, 2 H), 1.43 (s, 6 H)	272.0824 (272.0833)	
	27d	120 (40.6)	106.5–107	3.28–3.08 (m, 2 H), 2.37–2.05 (m, 2 H), 1.43–1.06 (m, 2 H), 1.37 (s, 6 H)		calcd: C, 61.77; H, 4.44 found: C, 61.41; H, 4.62
				C. Allylic Bromination		
1 (430)	30a	32 (5)	146–148.5	7.17 (s, 4 H), 5.2 (m, 1 H), 4.98 (m, 1 H), 3.65 (distorted t, J = 2 Hz, 2 H), 2.17–1.82 (m, 2 H), 2.0 (m, 3 H), 1.35–1.0 (m, 2 H)	262.0357 (262.0364)	
	31a	264 (40)	158.5–159	7.08 (s, 4 H), 4.83 (m, 1 H), 4.7 (m, 1 H), 3.21 (distorted t, J = 2 Hz, 2 H), 2.45–2.1 (m, 2 H), 1.69 (m, 3 H), 1.3–1.0 (m, 2 H)		calcd: C, 63.89; H, 5.74 found: C, 63.69; H, 5.86
2 (75)	30b	trace		6.60 (s, 2 H), 5.25 (m, 1 H), 5.05 (m, 1 H), 3.80 (s, 6 H), 3.5 (m, 2 H), 2.0 (m, 3 H), 2.2–1.80 (m, 2 H), 1.4–1.0 (m, 2 H)		

Table V (*Continued*)

starting material (mg)	product(s)	mg isolated (yield, %)	mp, °C	^{1}H NMR data (δ, $CDCl_3$)	M$^+$ *m/e* calcd (found)	combustion data
	31b	28.9 (29)	126–126.5	6.6 (s, 2 H), 4.9 (m, 1 H), 4.7 (m, 1 H), 3.8 (s, 6 H), 3.45 (m, 2 H), 2.5–2.1 (m, 2 H), 1.70 (m, 3 H), 1.4–1.0 (m, 2 H)	322.0568 (322.0576)	
3 (44)	30c	20 (36)	143–143.5	5.26 (m, 1 H), 5.08 (m, 1 H), 4.0 (m, 2 H), 2.28–1.88 (m, 2 H), 2.0 (m, 3 H), 1.42–1.14 (m, 2 H)		calcd: C, 41.94; H, 2.76 found: C, 41.75; H, 2.90
	31c	20.3 (37)	185–186	4.95 (m, 1 H), 4.75 (m, 1 H), 3.93 (m, 2 H), 2.7–2.3 (m, 2 H), 1.73 (m, 3 H), 1.4–1.1 (m, 2 H)	397.8798 (397.8805)	
4 (82)	30d	21.6 (20.2)	134–135.5	5.32–4.94 (m, 2 H), 3.99 (m, 2 H), 2.34–1.9 (m, 2 H), 2.0 (m, 3 H), 1.43–1.04 (m, 2 H)		calcd: C, 50.17; H, 3.31 found: C, 50.15; H, 3.34
	31d	12.9 (12)	138–139	4.9–4.63 (m, 2 H), 3.82 (m, 2 H), 2.68–2.34 (m, 2 H), 1.75 (m, 3 H), 1.48–1.18 (m, 2 H)	333.9980 (333.9988)	
				D. NMTAP Addition		
1 (46.5)	33a	46 (61)	318–321	7.15 (s, 4 H), 5.03 (m, 1 H), 4.87 (m, 1 H), 4.07 (m, 2 H), 3.23 (s, 3 H), 2.39–2.02 (m, 2 H), 1.74 (m, 3 H), 1.74–1.27 (m, 2 H)[b]		calcd: C, 68.67; H, 6.44 found: C, 68.97; H, 6.62
	32a	10 (13)	250–260	7.15 (br s, 4 H), 5.4–5.19 (m, 2 H), 4.07 (m, 2 H), 3.0 (s, 3 H), 2.3–1.9 (m, 2 H), 1.92 (m, 3 H), 1.74–1.27 (m, 2 H)[b]	297.1477 (297.1483)	
2 (66)	33b	55 (57)	250–251.5	6.87 (s, 2 H), 5.05 (m, 1 H), 4.88 (m, 1 H), 4.35 (m, 2 H), 4.06 (s, 6 H), 3.21 (s, 3 H), 2.41–2.12 (m, 2 H), 1.7 (m, 3 H), 1.7–1.29 (m, 2 H)[b]	357.1698 (357.1695)	
	32b	9 (9.4)	203–236	6.98 (s, 2 H), 5.48–5.27 (m, 2 H), 4.45 (m, 2 H), 4.03 (s, 6 H), 3.05 (s, 3 H), 2.41–2.05 (m, 2 H), 1.92 (m, 3 H), 1.53–1.21 (m, 2 H)[b]	357.1698 (357.1695)	
3 (200)	32c	139 (51.5)	273–277	5.17 (m, 2 H), 4.3 (m, 2 H), 2.94 (s, 3 H), 2.3–1.96 (m, 2 H), 1.83 (m, 3 H), 1.45–1.1 (m, 2 H)		calcd: C, 46.92; H, 3.47 found: C, 46.92; H, 3.49
	33c	89.4 (33)	215–218	4.9 (m, 1 H), 4.77 (m, 1 H), 4.33 (m, 2 H), 3.03 (s, 3 H), 2.43–2.0 (m, 2 H), 1.63 (m, 3 H), 1.43–1.1 (m, 2 H)	432.9918 (432.9927)	
4 (200)	32d	182 (63)	236–237	9.37 (br s, 1 H), 5.18 (m, 2 H), 4.37 (m, 2 H), 2.93 (br s, 3 H), 2.25–1.6 (m, 2 H), 1.8 (m, 3 H), 1.48–1.02 (m, 2 H)		calcd: C, 55.29; H, 4.09 found: C, 55.18; H, 4.17
	33d	104 (36)	284–285	9.56 (br s, 1 H), 4.9 (m, 1 H), 4.77 (m, 1 H), 4.3 (m, 2 H), 3.05 (s, 3 H), 2.38–2.08 (m, 2 H), 1.6 (m, 3 H), 1.48–1.08 (m, 2 H)	369.1100 (369.1107)	
5 (300)	35	425 (77)	244.5–246	9.7 (br s, 1 H), 6.0 (m, 2 H), 5.06 (m, 1 H), 4.93 (m, 1 H), 3.77–3.33 (m, 2 H), 3.07 (s, 3 H), 2.23–1.75 (m, 2 H), 1.75 (br s, 3 H), 1.37–0.95 (m, 2 H)		calcd: C, 63.14; H, 6.93 found: C, 62.98; H, 6.95
	34	not isolated pure		6.14 (endocyclic olefinic proton)		
				E. Dichlorocyclopropanation		
1 (250)	39a	153 (55)[c]	173.5–174.5	7.17 (m, 4 H), 3.2 (distorted t, J = 2 Hz, 2 H), 2.2–1.85 (m, 2 H), 1.5–1.2 (m, a distinct s at 1.3, 8 H)		calcd: C, 67.43; H, 6.04 found: C, 67.37; H, 5.99
	40a	80 (29)[c]	121–122.5	7.1 (m, 4 H), 3.14 (distorted t, J = 2 Hz, 2 H), 2.44–2.1 (m, 2 H), 1.47–0.97 (m, a distinct s at 1.22, 8 H)	266.0628 (266.0636)	
2 (200)	39b	147 (55)	147.5–148.5	6.6 (s, 2 H), 3.75 (s, 6 H), 3.42 (distorted t, 2 H), 2.1–1.74 (m, 2 H), 1.45–1.13 (m, a distinct s at 1.3, 8 H)		calcd: C, 62.39; H, 6.16 found: C, 62.38; H, 6.16
	40b	32 (12)	120–125	6.58 (s, 2 H), 3.75 (s, 6 H), 3.33 (distorted t, 2 H), 2.37–2.08 (m, 2 H), 1.43–1.15 (m, a distinct s at 1.15, 8 H)	326.0840 (326.0847)	
4 (100)	39c	36 (49)[c]	156.5–157.5	3.5 (m, 2 H), 2.2–1.9 (m, 2 H), 1.56–1.22 (m, a distinct s at 1.3, 8 H)		calcd: C, 53.12; H, 3.57 found: C, 53.03; H, 3.71
	40c	6 (7.7)[c]	155–161	3.5 (m, 2 H), 2.5–2.12 (m, 2 H), 1.5–1.2 (m, a distinct s at 1.24, 8 H)	338.0252 (338.0259)	
5 (100)	41	29.4 (18.3)	100.5–101	6.24 (t, J = 2 Hz, 2 H), 2.72 (m, 2 H), 1.23 (s, 6 H), 2.0–0.74 (series of m, 4 H)	216.0472 (216.0476)	calcd: C, 60.85; H, 6.50 found: C, 60.57; H, 6.51
	42	6.8 (4.2)	oil	6.1 (t, J = 2 Hz, 2 H), 2.65 (m, 2 H), 1.25 (s, 6 H), 2.35–0.9 (series of m, 4 H)	216.0472 (216.0476)	
				F. Acetylation		
1 (1000)	43a	720 (58.3)	101–105[d]	7.03 (m, 4 H), 5.13 (m, 2 H), 3.66 (m, 2 H), 2.25–1.92 (m, 2 H), 1.93 (s, 3 H), 1.75 (m, 3 H), 1.28–1.0 (m, 2 H)	226.1357 (226.1363)	
2 (250)	43b	150 (51.4)	96.5–97.5	6.55 (s, 2 H), 5.22–5.08 (m, 2 H), 4.05–3.88 (m, 2 H), 3.77 (s, 6 H), 2.2–1.88 (m, a distinct s at 1.93, 5 H), 1.73 (m, 3 H), 1.33–1.15 (m, 2 H)		calcd: C, 75.50; H, 7.74 found: C, 75.46; H, 7.58

Table V (*Continued*)

starting material (mg)	product(s)	mg isolated (yield, %)	mp, °C	^{1}H NMR data (δ, $CDCl_3$)	M$^+$ *m/e* calcd (found)	combustion data
4 (250)	**43c**	118.4 (41)	127.5–128.5	5.2 (m, 2 H), 4.03 (m, 2 H), 2.3–2.0 (m, 2 H), 2.0 (s, 3 H), 1.78 (m, 3 H), 1.35–1.05 (m, 2 H)		calcd: C, 64.64; H, 4.73 found: C, 64.26; H, 4.73
5 (100)	**51**	68.9 (52.5)	44–45.5	6.05 (t, J = 2 Hz, 2 H), 5.17 (m, 1 H), 4.94 (m, 1 H), 3.2 (m, 2 H), 2.02 (s, 3 H), 1.65 (m, 3 H), 2.68–0.75 (series of m, 4 H)		calcd: C, 81.77; H, 9.15 found: C, 81.60; H, 9.11
				G. Prins Reaction		
1 (1000)	**52a**	900 (75)	70.5–71.5	7.13 (br s, 4 H), 4.94 (br s, 2 H), 3.7 (t, J = 6 Hz, 2 H), 3.35 (t, J = 2 H), 3.17 (s, 2 H), 2.45–2.0 (m with a distinct t at 2.3, J = 6 Hz, 4 H), 1.27–0.97 (dd, 2 H)		calcd: C, 84.91; H, 8.02 found: C, 84.81; H, 8.03
2 (300)	**52b**	171.5 (48.4)	120.5–121.5	6.53 (s, 2 H), 4.88 (br s, 2 H), 3.8–3.45 (m, a distinct s at 3.75, 10 H), 3.2 (s, 2 H), 2.39–1.97 (m, a distinct t at 2.26, J = 6 Hz, 4 H), 1.25–0.93 (dd, 2 H)		calcd: C, 75.50; H, 7.74 found: C, 75.59; H, 7.74
4 (250)	**52c**	171 (67)[c]	105.5–106.5	5.02–4.83 (m, 2 H), 3.78–3.55 (m, 4 H), 3.15 (s, 2 H), 2.4–2.03 (m, 4 H), 1.3–0.96 (m, 2 H)		calcd: C, 64.43; H, 4.73 found: C, 64.59; H, 4.72
5 (100)	**55**	75 (57)	oil	5.95 (t, J = 2 Hz, 2 H), 5.86–5.68 (m, 2 H), 3.65 (t, J = 5 Hz, 2 H), 3.58 (s, 2 H), 2.82 (distorted t, J = 2 Hz, 2 H), 2.22 (t, J = 5 Hz, 2 H), 2.0–1.73 (m, 2 H), 1.3–0.95 (m, 2 H)		calcd: C, 81.77, H, 9.15 found: C, 81.90; H, 9.16

[a] Reference 11a. [b] Spectrum recorded in CF_3COOD. [c] Based upon recovered starting material. [d] Reference 35.

absorption corrections was not warranted. *Lp* corrections were applied. The observational weights were derived as previously.[67]

The structure was solved by the heavy-atom Patterson method. The nonhydrogen atoms were quickly located on a Fourier map calculated by using the chlorine atom coordinates. Refinement by standard full-matrix least-squares techniques using the CRYM Computing Package[68] and isotropic thermal parameters for all the nonhydrogen atoms reduced the conventional R factor[69] to 0.20. Refinement using anisotropic temperature factors for the chlorine atoms and for selected carbon atoms permitted all of the hydrogen atoms to be located on difference Fourier maps. Their inclusion and refinement in the calculations eventually reduced the R factors to their final values of R = 0.112, R_{F2} = 0.082, and GOF = 1.22, when refinement was halted. The final shifts for all the heavy-atom parameters averaged less than 1 esd in the last least-squares cycle. A secondary extinction correction coefficient[70] was refined; its final value was $g = 0.66 \times 10^{-6}$. The atomic form factors were taken from the usual source.[71] The final data/parameter ratio was 17.3. The final difference Fourier map showed no features greater than ±0.5 e$^-$/Å^3. The final values of the least-squares parameters comprise Table VI.

Prototypical Acetylation Procedures. A. To a stirred suspension of aluminum chloride (0.82 g, 6.2 mmol) in dichloromethane (10 mL) was added a solution of acetyl chloride (0.53 g, 6.8 mmol) in dichloromethane (10 mL). Most of the aluminum chloride dissolved. The stirred mixture was cooled in an ice–salt bath to −15 °C, and to this mixture was added **1** (1 g, 5.44 mmol) in dichloromethane (10 mL) over a 20-min period. After completion of the addition, the mixture was stirred at −10 °C for 10 min, poured onto ice and a little concentrated hydrochloric acid, and diluted further with dichloromethane. After the ice had melted, the phases were separated and the aqueous layer was extracted twice with dichloromethane. The combined dichloromethane layers were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by chromatography on silica gel (benzene elution). For product data see Table V.

B. To a stirred solution of **1** (100 mg, 0.54 mmol) in acetic anhydride (2 mL) was added anhydrous zinc chloride (74 mg, 0.54 mmol). The mixture was stirred at room temperature for 18 h at which time it was poured into 10% sodium carbonate solution (50 mL) and stirred for 15 min. The aqueous mixture was extracted three times with ether, and the combined organic layers were dried. After solvent removal, the residue was purified by preparative layer chromatography on silica gel (benzene elution) to yield 74 mg (60.3%) of **43a**.

1,2,3,4-Tetrahydro-*syn*-9-trideuterioacetyl-*anti*-9-isopropenyl-1,4-methanonaphthalene (44a). To deuterium oxide (2 mL) at 0 °C under nitrogen was added freshly cut sodium (63 mg, 2.72 mmol). To the cold solution was added 30 mg (0.133 mmol) of **43a** in anhydrous tetrahydrofuran (3 mL). The reaction mixture was allowed to warm to room temperature where it was stirred for 3 days. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were dried and evaporated under reduced pressure. The resulting solid product (30.1 mg, 98.7%) was carried on to the next step without further purification. The ^{1}H NMR spectrum was identical with that of the starting material except that the acetyl peak at δ 1.93 was no longer present.

5,8-Dimethoxy-1,2,3,4-tetrahydro-*syn*-9-trideuterioacetyl-*anti*-9-isopropenyl-1,4-methanonapthalene (44b). To deuterium oxide (2 mL) at 0 °C under nitrogen was added freshly cut sodium (52.8 mg 2.3 mmol). To the cold solution was added 25 mg (0.088 mmol) of **43b** in anhydrous tetrahydrofuran (3 mL). After 4 days, the product was isolated by the customary workup procedure to give (19.5 mg, 77%) of solid whose ^{1}H NMR spectrum was identical with that of the starting material except that the acetyl peak at δ 1.93 was no longer evident.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-*syn*-9-trideuterioacetyl-*anti*-9-isopropenyl-1,4-methanonaphthalene (44c). To deuterium oxide (2 mL) at 0 °C under nitrogen was added freshly cut sodium (77 mg, 3.35 mmol). To the cold solution was added 50 mg (0.168 mmol) of **43c** in anhydrous tetrahydrofuran (3 mL). After 4 days, the product was isolated by the customary workup procedure to give (40.9 mg, 81%) of **44c** which was carried on to the next step without further purification. The ^{1}H NMR spectrum was identical with that of starting material except that the acetyl peak at δ 2.0 was no longer present.

Ozonolysis of 43a. A. Ozone was bubbled through a solution of **43a** (400 mg, 1.77 mmol) in methanol (50 mL) with cooling from a dry ice–acetone bath for 15 min. Oxygen was then bubbled through the solution to remove excess dissolved ozone. To the cold reaction mixture was added a solution of sodium iodide (0.88 g), acetic acid (0.4 mL), methanol (1.8 mL), and water (18 mL). After the addition, the mixture was allowed to warm to room temperature, at which time the liberated iodine was destroyed by introduction of solid sodium bisulfite. The resulting solution was extracted three times with ether. The combined ether solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (chloroform elution). For **46a**: 72.5 mg (18%); mp 145–146.5 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 7.07 (m, 4 H), 3.9 (distorted t, J = 2 Hz, 2 H), 2.25–1.8 (m, two distinct s at 2.19 and 1.91, 8 H), 1.34–1.07 (m, 2 H).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.51; H, 6.95.

For **48**: 54.6 mg (13%); mp 91–99 °C; ^{1}H NMR ($CDCl_3$) δ 7.03 (m, 4 H), 3.41 (m, 2 H), 2.94 (d, J = 5 Hz, 1 H), 2.58 (d, J = 5 Hz, 1 H),

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(69) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_{F^2} = [\sum w(F_o^2 - F_c^2)_2/\sum wF_o^4]^{1/2}$ GOF = $[\sum w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2}$. The function minimized in the least-squares refinement was $\sum w(F_o^2 - F_c^2)^2$.
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2.39–2.05 (m, 2 H), 1.9 (s, 3 H), 1.40 (s, 3 H), 1.4–1.07 (m, 2 H); *m/e* calcd 242.1306, obsd 242.1313.

For **47a**: 132 mg (27%) mp 154–156 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 7.14 (s, 4 H), 3.5 (m, 2 H), 3.35 (s, 3 H), 2.46 (br s, 1 H), 2.34–2.06 (m, 2 H), 1.54 (s, 3 H), 1.35–1.05 (m, 2 H), 0.69 (s, 3 H).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found C, 69.66, H, 7.23.

B. A sample of the crude ozonolysis product (25 mg) in ethyl acetate (3 mL) was stirred with 10% Pd/C (25 mg) at room temperature under 1 atm of hydrogen for a short time. The reaction mixture was filtered through a pad of Celite. After solvent removal from the filtrate, the resulting residue was purified by preparative layer chromatography (chloroform elution) to give 15 mg (53%) of **46a**.

1,2,3,4-Tetrahydro-*syn*-9-trideuterioacetyl-*anti*-9-acetyl-1,4-methanonaphthalene (45a). Ozone was bubbled through a solution of **44a** (30.1 mg, 0.133 mmol) in methanol (5 mL) in the predescribed manner. The customary workup yielded 11.3 mg (37%) of **45a**. The ^{1}H NMR spectrum was identical with that of the crude product from **43a** except that the methyl peak at δ 1.91 was absent.

Ozonolysis of 43c. Ozone was bubbled through a solution of **43c** (154 mg, 0.516 mmol) in methanol (40 mL), with cooling from a dry ice–acetone bath, for 15 min. Application of the previously described workup procedure followed by preparative layer chromatography on silica gel (chloroform elution) gave 71.8 mg (46.4%) of **46b**: mp 122–123 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 4.33–4.17 (m, 2 H), 2.20–1.87 (m, two distinct s at 2.20 and 1.97, 8 H), 1.40–1.17 (m, 2 H).

Anal. Calcd for $C_{15}H_{12}F_4O_2$: C, 60.00; H, 4.03. Found: C, 59.83; H, 4.01.

For **47b**: 30.4 mg (16.9%); mp 123–128 °C; ^{1}H NMR ($CDCl_3$) δ 3.79 (m, 2 H), 3.3 (s, 3 H), 2.61 (br s, 1 H), 2.44–2.1 (m, 2 H), 1.55 (s, 3 H), 1.43–1.07 (m, 2 H), 0.86 (s, 3 H); *m/e* calcd 348.0984, obsd 348.0991.

5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-*syn*-9-trideuterioacetyl-*anti*-9-acetyl-1,4-methanonaphthalene (45c). Ozonolysis of **44c** (40 mg, 0.133 mmol) in a comparable manner afforded 37.3 mg (93%) of **45c**. The ^{1}H NMR spectrum was identical with that of the crude product from **43c** except that the methyl peak at δ 1.97 was absent.

1,2,3,4-Tetrahydro-*syn*-9-hydroxy-*anti*-9-acetyl-1,4-methanonaphthalene (49). Ozone was bubbled through a solution of **20a** (79 mg, 0.393 mmol) in methanol (10 mL) with cooling from a dry ice-acetone bath for 15 min. Oxygen was then bubbled through the solution to remove excess dissolved ozone. To the cold reaction mixture was added a solution of sodium iodide (195 mg), acetic acid (0.1 mL), methanol (0.4 mL), and water (4 mL). After the addition, the mixture was allowed to warm to room temperature, at which time the liberated iodine was destroyed by introduction of solid sodium bisulfite. The resulting solution was extracted three times with ether. The combined ether solutions were washed with saturated sodium bicarbonate and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was purified by preparative layer chromatography on silica gel (chloroform elution) to give 14.3 mg (18%) of **49** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 4 H), 3.35 (m, 2 H), 2.26 (s, 3 H), 2.17–1.8 (m, distinct s at 2.05, 3 H), 1.33–1.15 (m, 2 H); *m/e* calcd 202.0993, obsd 202.0998.

1,2,3,4-Tetrahydro-*syn*-9-acetyl-*anti*-9-hydroxy-1,4-methanonaphthalene (50). Comparable ozonolysis of **21a** (100 mg, 0.5 mmol) in methanol (40 mL) furnished 38.4 mg (38%) of **50**, mp 84–87 °C; ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 4 H), 4.0 (br s, 1 H), 3.25 (distorted t, J = 2 Hz, 2 H), 2.51–2.19 (m, 2 H), 1.67 (s, 3 H), 1.37–1.07 (m, 2 H); *m/e* calcd 202.0993, obsd 202.0998.

In addition, there was isolated 16.3 mg (20.6%) of the 9-benzonorbornanone.

Prototypical Prins Reaction. To 1 (1 g, 5.4 mmol) and paraformaldehyde (1.63 g, 5.4 mmol) was added anhydrous dioxane (55 mL) containing concentrated sulfuric acid (5.33 g, 54 mmol) with external cooling from an ice bath. After completion of the addition, the mixture was stirred at room temperature for 2.5 h, diluted with water, and extracted three times with ether. The combined organic layers were washed with 10% ammonium chloride, saturated sodium bicarbonate, and saturated sodium chloride solutions prior to drying. After removal of solvent, the residue was recrystallized directly or purified by preparative layer chromatography on silica gel. For product data see Table V.

1,2,3,4-Tetrahydro-*anti*-9-isopropenyl-1,4-methanonaphthalene-*syn*-9-carboxylic Acid (53). A solution of **43a** (0.84 g, 3.7 mmol), sodium hydroxide (0.45 g, 11.2 mmol), 5% sodium hypochlorite solution (17 mL, 11.2 mmol), and dioxane (17 mL) were heated at reflux for 7 h. At this point, more sodium hydroxide (0.45 g, 11.2 mmol), 5% sodium hypochlorite solution (17 mL, 11.2 mmol) and dioxane (17 mL) were added and reflux was continued for an additional 12 h. The cooled solution was treated with sodium thiosulfate (6 g) and acidified with concentrated hydrochloric acid with external cooling. The reaction mixture was extracted three times with ether, and the combined ether layers were washed with 10% ammonium chloride solution and extracted three times with 5% sodium hydroxide solution. The basic extracts were acidified with concentrated hydrochloric acid while externally cooled and extracted three times with ether. The combined ether layers were dried and evaporated under reduced pressure to give 0.33 g (76%) of **53** which was carried on to the next step without further purification: ^{1}H NMR ($CDCl_3$) δ 9.73 (br s, 1 H), 7.05 (m, 4 H), 5.1 (m, 2 H), 3.6 (m, 2 H), 2.17–1.81 (m, 5 H), 1.23–0.96 (m, 2 H).

Methyl 1,2,3,4-Tetrahydro-*anti*-9-isopropenyl-1,4-methanonaphthalene-*syn*-9-carboxylate. To a cold (0 °C) solution of **53** (0.33 g, 1.45 mmol) in ether was added an ethereal solution of diazomethane (5.95 mmol). The solution was stirred at 0 °C for 5 min and the solvent was removed under reduced pressure. The residue was purified by recrystallization from ethanol to give 0.25 g (71%) of ester: mp 94.5–95.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.14 (m, 4 H), 5.13 (m, 2 H), 3.72 (t, J = 2 Hz, 2 H), 3.35 (s, 3 H), 2.21–1.84 (m, 5 H), 1.27–0.95 (m, 2 H); ν_{max}^{Nujol} 1722 cm^{-1}.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.25; H, 7.53.

1,2,3,4-Tetrahydro-*syn*-9-hydroxymethyl-*anti*-9-isopropenyl-1,4-methanonaphthalene (54). To a stirred suspension of lithium aluminum hydride (50 mg, 1.32 mmol) in anhydrous tetrahydrofuran (5 mL) was added a solution of the preceding ester (50 mg, 0.21 mmol) in tetrahydrofuran (5 mL). The suspension was refluxed for 1 h and stirred for 12 h at room temperature. The reaction mixture was cooled in an ice bath and 10% sulfuric acid solution was added cautiously at first and then until no precipitated salts remained. The solution was extracted three times with ether, and the combined ether layers were washed with saturated sodium chloride solution prior to drying. Evaporation of the solvent gave 30.4 mg (68%) of **54**, mp 51–58 °C, which was carried on to the next step without further purification: ^{1}H NMR ($CDCl_3$) δ 7.05 (br s, 4 H), 5.1 (m, 1 H), 4.9 (m, 1 H), 3.26 (m, 2 H), 3.08 (s, 2 H), 2.2–1.85 (m, 3 H), 1.80 (m, 3 H), 1.3–0.95 (m, 2 H); *m/e* calcd 214.1357, obsd 214.1362.

Prins Reaction of 54. Treatment of **54** (30 mg, 0.142 mmol) with paraformaldehyde (43 mg, 1.42 mmol) and anhydrous dioxane (2 mL) containing concentrated sulfuric acid (139 mg, 1.42 mmol) in the predescribed fashion gave 22 mg (68.5%) of **52a**.

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Supplementary Material Available: Table VI, final values of the least-squares parameters (1 page). Ordering information is given on any current masthead page.