Cyclopropylcarbinyl Cation Chemistry and Antihomoaromaticity in the Cycloprop[2,3]inden-1-yl Cation System

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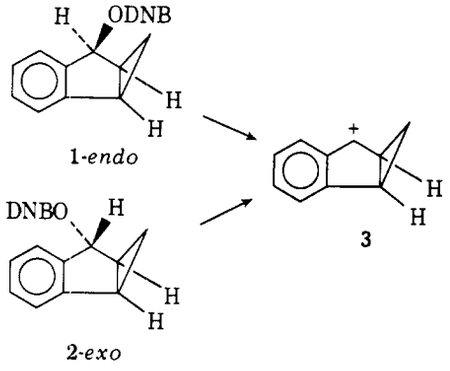
A detailed investigation of the solvolytic behaviors of the *endo*- and *exo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates in 80% aqueous acetone has been carried out. Both esters exhibited closely similar rates of hydrolysis and gave identical mixtures of *endo*- and *exo*-cycloprop[2,3]inden-1-ol products. From kinetic comparisons with model systems, it could be concluded that antihomoaromatic effects cause a rate retardation at 80 °C of approximately 10^3 for the cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate hydrolyses. Also, in accord with the postulation of antihomoaromatic interactions in the cycloprop[2,3]inden-1-yl activated complexes, the effects of methyl substituents on rate indicated that considerable charge is delocalized at C-10 but little at C-3.

For comparison with some of the results of previous work in our laboratory involving studies of stereochemical and electronic effects upon the nature and behavior of cyclopropylcarbinyl cations[1] and free radicals,[2] we have carried out a detailed investigation of the solvolytic behavior of the *endo*- and *exo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates (**1** and **2**) in 80% aqueous acetone. Reactions of these compounds are also of considerable interest for their own sakes because the cycloprop[2,3]inden-1-yl cation intermediate **3** which should be formed in hydrolyses of **1** and **2** is formally a benzo analogue of the monohomocyclopentadienyl cation. Thus, we wished to investigate whether the rates of formation of **3** from **1** or **2**, and the further reactions of **3**, were influenced to a measurable



extent by antihomoaromatic effects.[3] Although some studies of potentially antihomoaromatic systems involving charge delocalization through cyclopropane rings have been reported,[4] most of these were not done under neutral solvolytic conditions.

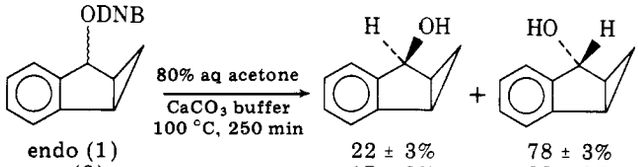
Results and Discussion

Unsubstituted Cycloprop[2,3]inden-1-yl Esters. Synthesis of the isomerically pure *endo*-cycloprop[2,3]inden-1-ol precursor of the 3,5-dinitrobenzoate **1** was accomplished in 41% yield directly through reaction of inden-1-ol[5] with methylene iodide and a zinc–copper couple.[6] Reduction of cycloprop[2,3]inden-1-one[7] with aluminum isopropoxide in 2-propanol[8] gave a 76% yield of a 73:27 exo–endo mixture of cycloprop[2,3]inden-1-ols, from which a 15% yield of the isomerically pure exo alcohol precursor of **2** could be isolated via spinning band distillation followed by fractional recrystallization.

The rates of hydrolysis of **1** and **2** were measured in 80% aqueous acetone both at 80.0 and at 100.0 °C, and the results are listed in Table I. Controls indicated that during the course of hydrolysis both dinitrobenzoates isomerized to small extents due to ion-pair return. Thus, after periods of time sufficient for 50% acid production, the initially pure endo dinitrobenzoate **1** had isomerized to a 75:25 mixture of **1** and **2**, and the initially pure exo dinitrobenzoate **2** had isomerized to a 90:10 mixture of **2** and **1**. However, these amounts of isomerization do not result in producing significant differences between the actual and measured solvolytic rate constants.

As is seen from the data in Table I, the hydrolytic reactivities of **1** and **2** are almost identical. This is in contrast to what we expected from examination of molecular models where it appeared that rate-retarding antihomoaromatic interactions resulting from charge delocalization along the 2,3-cyclopropane bond might be more important when the leaving group has an endo orientation. Apparently, the same types of stabilizing or destabilizing factors are encountered by both isomers owing to sufficient flexibility being present in their activated complexes such that similar types of C-1 orbital overlap with the cyclopropane and benzene ring orbitals can occur. However, from these kinetic results alone it is not possible to conclude if the activated complexes are actually affected by any antihomoaromatic destabilization.

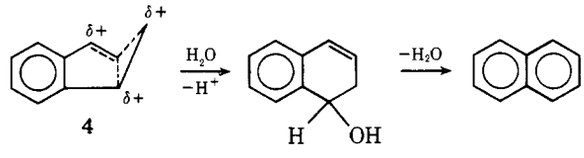
The hydrolysis products of **1** and **2** were determined in 80% aqueous acetone buffered with calcium carbonate at 100 °C after about 5 half-lives for acid production. As is shown below, both isomeric dinitrobenzoates yielded an essentially identical mixture of products within experimental error. Controls run on both the *endo*- and *exo*-cycloprop[2,3]inden-1-ols under



endo (1)	22 ± 3%	78 ± 3%
exo (2)	17 ± 3%	83 ± 3%

the solvolytic conditions indicated that less than 5% isomerization or rearrangement to other materials had occurred. Thus, it is clear that a common carbonium ion intermediate must be involved in product formation from both **1** and **2**.

It should be noted that the exclusive formation of products of solvent attack at C-1, and less than 1% of products such as 1,2-dihydronaphthalen-1-ol or naphthalene expected if solvent attack occurred at C-3, indicates that a delocalized species such as **4** is not important in product formation.



Analogous behavior was observed by Berson and co-workers[4b] in their studies of the methanolysis of the 2-deuterio-*endo*- and -*exo*-bicyclo[3.1.0]hex-3-en-2-yl trifluoroacetates. This

Table I. Rates of Hydrolysis of *endo*- and *exo*-Cycloprop[2,3]-inden-1-yl 3,5-Dinitrobenzoates (1 and 2) in 80% Aqueous Acetone

Compd	Concn, 10^3 M	Temp, °C	$10^5 k_1$, s^{-1}
1 (endo)	8.5	100.0	22.0 ± 0.4
	10.0	80.0	2.77 ± 0.09[a]
2 (exo)	6.5	100.0	25.7 ± 0.7
	4.2	80.0	3.29 ± 0.04[b]

[a] $\Delta H^{\ddagger} = 26.4 \pm 0.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.0 \pm 2.1$ eu. [b] $\Delta H^{\ddagger} = 26.2 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.2 \pm 1.4$ eu.

result thus provides support for an antiaromatic effect in the cycloprop[2,3]inden-1-yl cation. In the absence of an antihomoaromatic effect, considerable delocalization of positive charge at the C-3 position might have been predicted. For example, under conditions identical with those used in the present work, Friedrich and Saleh[1] found that the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates yielded ca. 27% of cyclohexen-4-ol from solvent attack at C-5 of the 2-bicyclo[3.1.0]hexyl cation, which corresponds to solvent attack at C-3 in our system.

Kinetic Comparisons with Model Systems. In order to gather more information regarding whether there are destabilizing antihomoaromatic interactions in the cycloprop[2,3]-inden-1-yl activated complexes, and to assess the magnitude of the effects, the rates of hydrolysis of the cycloprop[2,3]-inden-1-yl 3,5-dinitrobenzoates (1 and 2) were compared with those of various model compounds. The structures of these are shown in Table III. The model compounds were selected so as to provide an estimate of the reactivities of 1 and 2 expected in the absence of antihomoaromatic effects.

Of the model compounds selected for these comparisons, the indan-1-yl (**5**), *endo*-5,5-dimethyl-3,4-benzobicyclo[4.1.0]hepten-1-yl (**6**), 4,4-dimethyl-2,3-benzocyclohexen-1-yl (**7**), and phenylcyclopropylcarbinyl (**8**) 3,5-dinitrobenzoates had to be prepared and their solvolytic kinetics studied for the present work. The geminal dimethyl groups were included in **6** and **7** for synthetic convenience, but should have no effects on their rate comparisons with the other systems. The procedures used for synthesis of compounds **5–8** are reported in the Experimental Section. For the other model compounds, suitable kinetic data for the *endo*-2-bicyclo[3.1.0]hexyl (**9**), *endo*-2-bicyclo[4.1.0]heptyl (**10**), 1-cyclopropylethyl (**11**), 1-phenylethyl (**12**), cyclopentyl, cyclohexyl, and isopropyl 3,5-dinitrobenzoates could be estimated from data already available in the literature.

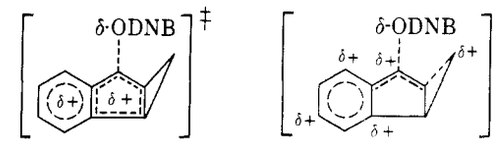
The rate constants for hydrolysis in 80% aqueous acetone of the model compounds **5–8** studied are given in Table II, and the relative rate comparisons of these with the *endo*-cycloprop[2,3]inden-1-yl and other model 3,5-dinitrobenzoates are given in Table III. It is apparent that the cycloprop[2,3]-inden-1-yl system (**1**) on the average is about 10^2 less reactive than either the 5,5-dimethyl-3,4-benzobicyclo[4.1.0]hepten-1-yl (**6**) or phenylcyclopropylcarbinyl (**8**) systems in which antihomoaromatic effects cannot be operating. Also, from comparison of the cumulative effects on rate of phenyl and cyclopropyl substitution in the five-ring, six-ring, and open-chain systems, one can estimate that on the average **1** is about 10^3 less reactive than would be predicted in the absence of antihomoaromatic effects. This rate retardation is not very large. However, it should be pointed out that in potentially antihomoaromatic systems possible molecular distortions which tend to minimize destabilizing cyclic antihomoaromatic orbital overlap would be energetically favorable.[3] Thus, the destabilizing effects might be very much larger in a fully delocalized antihomoaromatic system with normal geometry.

Table II. Rates of Hydrolysis of Some 3,5-Dinitrobenzoates in 80% Aqueous Acetone

Compd	Concn, 10^3 M	Temp, °C	$10^5 k_1$, s^{-1}
5	7.8	100.0	30.6 ± 0.4
	11.5	80.0	4.35 ± 0.07[a]
6		80.0	(3.12×10^3)[b]
	2.4	39.9	6.10 ± 0.7
	2.7	20.0	5.80 ± 0.09
7	4.7	100.0	10.0 ± 0.5
	4.3	80.0	1.28 ± 0.07[c]
8		80.0	(2.38×10^2)[d]
	10.5	60.0	31.3 ± 0.8
	6.7	39.9	3.01 ± 0.03

[a] $\Delta H^{\ddagger} = 24.3 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9.9 \pm 1.1$ eu. [b] $\Delta H^{\ddagger} = 21.0 \pm 0.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.2 \pm 1.1$ eu. [c] $\Delta H^{\ddagger} = 26.2 \pm 1.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -7.1 \pm 4.1$ eu. [d] $\Delta H^{\ddagger} = 23.5 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -4.2 \pm 1.3$ eu.

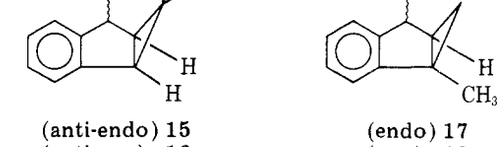
Methyl Substituent Effects. If molecular distortions which minimize cyclic antihomoaromatic orbital overlap are truly operating in the activated complexes for ionization of the cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates, then one might predict little delocalization of charge along the endocyclic cyclopropane bond from C-1 to C-3 as in structure **13**. However, charge delocalization along the exocyclic cyclopropane bond from C-1 to C-10 as in structure **14** would still



13 **14**

appear to be allowed. Thus, to assess these possibilities, a study of the effects on rate of introducing electron-releasing methyl substituents at C-3 and at C-10 in the cycloprop[2,3]-inden-1-yl system were initiated. The methyl group should have a rate-accelerating effect at a carbon where charge is delocalized, but have little or no effect at a carbon where there is no charge delocalization.

Synthesis of the isomerically pure alcohol precursor of the *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate (**15**) was accomplished in 34% yield via reaction of

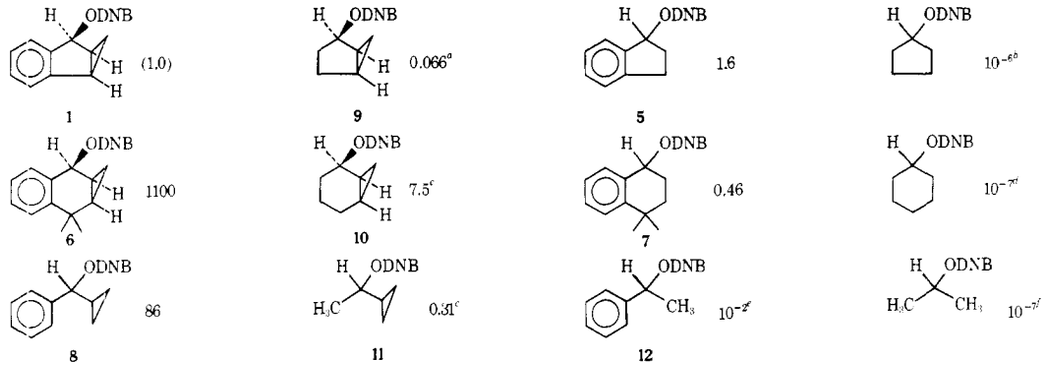


(anti-endo) **15** (endo) **17**
(anti-exo) **16** (exo) **18**

inden-1-ol[5] with ethylidine iodide[14] and ethylzinc iodide[15] in ether followed by fractional recrystallization of the initially obtained mixture of anti-endo and syn-endo-10 methyl alcohols. The anti-endo alcohol was isomerized using aluminum isopropoxide in 2-propanol to give a 66:34 mixture of anti-exo to anti-endo alcohols. Preparation of the 3,5-dinitrobenzoates from this alcohol mixture followed by fractional recrystallization gave a 54% yield of a 90% isomerically pure sample of the anti-exo 10-methyl 3,5-dinitrobenzoate **16**.

Preparation of the 3-methyl-*endo*-cycloprop[2,3]inden-1-ol precursor of **11** proved to be rather difficult as several reasonable approaches were found to be unsatisfactory. One of these approaches involving the anticipated conversion of 3-methylindan-1-one (**19**) to 3-methylinden-1-one (**20**), how-

Table III. Relative Rates of Hydrolysis of Some 3,5-Dinitrobenzoates in 80% Aqueous Acetone at 80 °C



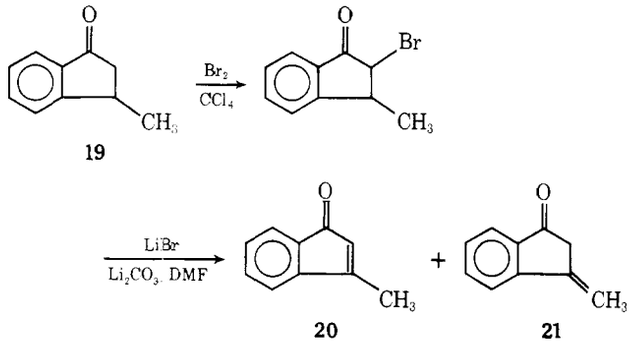
[a] Calculated from data in ref 1. [b] Estimated from data in ref 9. [c] Calculated from data in ref 10. [d] Estimated from data in ref 11. [e] Estimated from data in ref 12. [f] Estimated from data in ref 13.

Table IV. Rates of Hydrolysis of *anti*-10-Methyl- and 3-Methyl-*endo*- and -*exo*-cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoates in 80% Aqueous Acetone

Compd	Concn, 10^3 M	Temp, °C	$10^5 k_1$, s^{-1}
15 (*anti*-10-Me-*endo*)	6.0	80.0	47.3 ± 1.5
	5.1	60.0	5.72 ± 0.08[a]
16 (*anti*-10-Me-*exo*)	3.2	80.0	52.6 ± 0.7
	2.8	60.0	5.56 ± 0.09[b]
17 (3-Me-*endo*)	5.2	100.0	23.7 ± 1.0
	5.8	80.0	3.52 ± 0.06[c]
18 (3-Me-*exo*)	5.2	100.0	30.3 ± 0.5
	3.4	80.0	3.83 ± 0.08[d]

[a] $\Delta H^{\ddagger}$ = 24.0 ± 0.6 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −6.1 ± 1.8 eu. [b] $\Delta H^{\ddagger}$ = 25.6 ± 0.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −1.4 ± 1.0 eu. [c] $\Delta H^{\ddagger}$ = 24.3 ± 0.8 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −10.4 ± 2.3 eu. [d] $\Delta H^{\ddagger}$ = 26.4 ± 0.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −4.3 ± 1.5 eu.

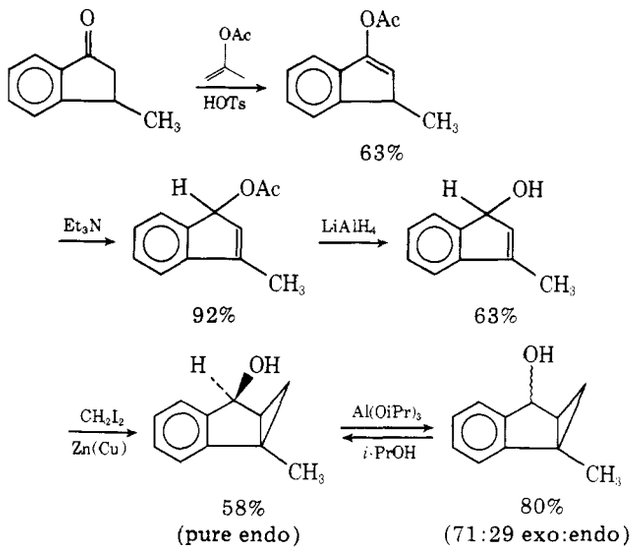
ever, was quite interesting in that it led to a 2:1 mixture of 3-methylinden-1-one (**20**) and 3-methyleneindan-1-one (**21**).



Treatment of this 2:1 mixture of ketones with pyridine at 103 °C for 10 h caused isomerization to a 1:2 mixture in which **21** predominated. The observed thermodynamic instability of the α,β-unsaturated **20** as compared to the β,γ-unsaturated **21** can be attributed to antiaromatic destabilization of **20**.

Thus, a synthesis of the alcohol precursor of **17** had to be devised which avoided **20** as an intermediate. The approach chosen, which proved successful, is shown in Scheme I. Synthesis of the exo alcohol precursor of **18** was then accomplished by aluminum isopropoxide in 2-propanol equilibration with the endo alcohol. Preparation of the 3,5-dinitrobenzoates of the resulting 71:29 exo–endo mixture of 3-methylcycloprop[2,3]inden-1-ols followed by fractional recrystallization provided an isomerically pure sample of the *exo*-3,5-dinitrobenzoate **18**.

Scheme I



The results of studies on the rates of hydrolysis of the *anti*-10-methyl- and 3-methyl-*endo*- and -*exo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates **15**, **16**, **17**, and **18** are given in Table IV. Controls run under the solvolytic conditions showed that none of these dinitrobenzoates rearranged to more than about 10% of isomeric dinitrobenzoates after 1 half-life for acid production. From the data in Table IV, it is seen that both in the *anti*-10-methyl and 3-methyl systems the rates of reaction are essentially independent of leaving group geometry. Similar behavior was observed in the non-methyl-substituted systems. Also, from comparison of the data in Tables I and IV, it is seen that substitution of a methyl group at C-10 of the cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate has an accelerating effect of about 15 for both the endo and exo isomers. However, substitution of a methyl group at C-3 has virtually no effect on rate.

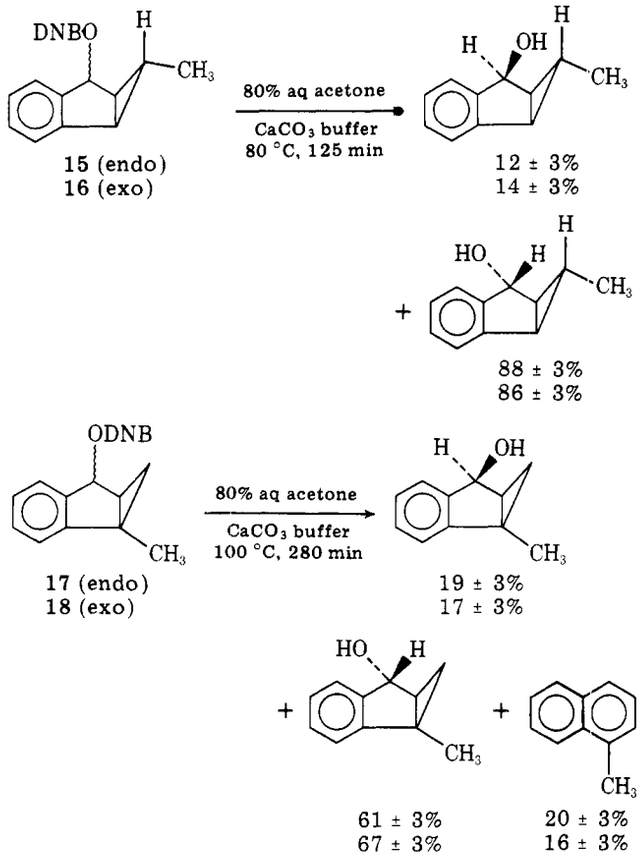
By comparison to the above results, previous work of ours[1] showed that substitution of a methyl group at C-5 in the simple 2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates produced rate accelerations of about 20 in 80% aqueous acetone at 100 °C for both the endo and exo isomers. This corresponds to substitution at C-3 in the cycloprop[2,3]inden-1-yl system.

Thus, one can conclude from these methyl substituent effect studies that there can be little or no delocalization of positive charge at C-3 in the cycloprop[2,3]inden-1-yl activated complexes. However, there is considerable charge delocalization at C-10. These solvolytic data agree with the results of the recently reported NMR studies of Olah and co-

workers[4c] of the cycloprop[2,3]inden-1-yl cation generated from cycloprop[2,3]inden-1-ol in either FSO_3H–SO_2ClF or FSO_3H–SbF_5. Under both our and Olah's conditions it must be concluded that the cycloprop[2,3]inden-1-yl cation is not a fully delocalized antiaromatic species, but that potential antiaromaticity does in some manner prevent otherwise normal charge delocalization to C-3.

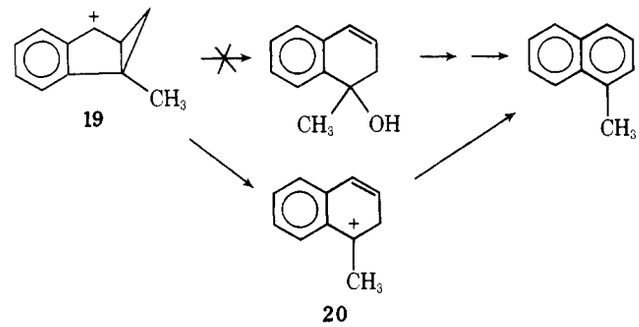
Although the kinetic results from the hydrolysis of the 3-methyl- and *anti*-10-methylcylcoprop[2,3]inden-1-yl 3,5-dinitrobenzoates were readily explainable, upon examining their hydrolysis products some possible ambiguities were observed. These data are shown in Scheme II. In both cases

Scheme II



the major products were unrearranged isomeric cycloprop[2,3]inden-1-ols. Also, within experimental error identical product mixtures were obtained starting with either the endo or the exo dinitrobenzoates. This behavior is similar to that observed with the non-methyl-substituted esters 1 and 2. However, from the 3-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates (17 and 18), significant amounts of 1-methylnaphthalene are formed. On the other hand, no 3-hydroxymethylindene is observed from hydrolyses of the *anti*-10-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates (15 and 16). Controls run on the 3-methyl- and *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-ols under the solvolytic conditions indicated that these underwent less than 5% isomerization or other reactions.

The observation that no 3-hydroxymethylindene is observed from hydrolysis of 15 and 16 is not surprising considering the fact that the C-1 position where major solvent attack occurs is both secondary and benzylic, while even with a methyl substituent the C-10 position is simple secondary. However, formation of 1-methylnaphthalene from 17 and 18 was unexpected and would appear to contradict the interpretation of the results of the kinetic studies that little positive charge is delocalized at the C-3 position in the activated complexes for ionization of 17 and 18. On the other hand, a possible explanation for the formation of 1-methylnaphthalene may be that it does not result directly via solvent attack on a delocalized version of the initially formed cyclopropylcarbinyl cation intermediate 19, but from another carbonium ion species 20 formed by subsequent rearrangement. This species, being both benzylic and tertiary, and having less ring strain, should be much more stable than 19. Reflection of this stability in a lower energy barrier for the rearrangement process of 19 to 20 as compared to the corresponding processes in the unsubstituted and *anti*-10-methyl substituted systems provides an explanation for the lack of formation of naphthalene products from hydrolyses of the latter systems.



Experimental Section

General. Melting points and boiling points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Model 237B grating spectrophotometer. NMR spectra were obtained on a Varian A-60A instrument with chemical shifts measured in parts per million (δ) downfield from Me_4Si internal standard. GLC analyses and separations were carried out using a Varian Series 1400 instrument. Mass spectra were obtained on a CEC 21-104 single beam mass spectrometer by John Voth. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

***endo*-Cycloprop[2,3]inden-1-ol.** Employing the LeGoff[6] modification of the Simmons–Smith reaction, 24 g (0.37 mol) of 30 mesh zinc–copper couple, 103 g (0.38 mol) of methylene iodide, and 20 g (0.15 mol) of inden-1-ol[5] in 250 mL of ether was stirred at reflux for 10 h. After addition of ammonium chloride and extraction with ether, the combined ether solution was washed with saturated sodium chloride solution and dried over magnesium sulfate. Removal of the ether followed by vacuum distillation gave 16.7 g of cycloprop[2,3]-inden-1-ol, bp 100–103 °C (0.6 mm). Recrystallization of the white solid yielded 9.0 g (41%) of white needles of cycloprop[2,3]inden-1-ol: mp 86.5–87.5 °C; NMR ($CDCl_3$) δ 0.5 (m, 1 H, cyclopropyl), 0.9 (m, 1 H, cyclopropyl), 1.9 (m, 1 H, cyclopropyl), 2.3 (m, 1 H, cyclopropyl), 2.8 (s, 1 H, CHO**H**), 5.5 (d, J = 6 Hz, 1 H, C**H**OH), and 7.15 ppm (m, 4 H, aromatic); IR (KBr) 3325 (O–H) and 1015 cm^{-1} (C–O); mass spectrum (70 eV) *m/e* (rel intensity) 146 (20), 145 (38), 131 (48), 128 (64), 117 (100), 116 (39), 115 (50).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.99; H, 7.05.

***endo*-Cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoate.** This was prepared by treatment of 1.8 g (0.012 mol) of cycloprop[2,3]inden-1-ol with 3.8 g (0.017 mol) of 3,5-dinitrobenzoyl chloride in pyridine at 0 °C for 2 h. Workup was followed by recrystallization of the solid to yield 1.6 g (38%) of *endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate: mp 150–152 °C; NMR ($CDCl_3$) δ 1.0 (m, 2 H, cyclopropyl), 2.5 (m, 2 H, cyclopropyl), 6.8 (d, J = 6 Hz, 1 H, C**H**ODNB), 7.4 (m, 4 H, aromatic), and 9.3 ppm (s, 3 H, aromatic); IR (KBr) 1695 (C=O) and 1235 cm^{-1} (C–O).

Anal. Calcd for $C_{17}H_{12}N_2O_6$: C, 60.00; H, 3.55. Found: C, 60.17; H, 3.70.

Cycloprop[2,3]inden-1-one. This material was prepared through the reaction of aluminum chloride with 46.1 g (0.26 mol) of 2-phenylcyclopropanecarboxylic acid chloride[7] in 225 mL of 1,2-dichloroethane at 0 °C for 1 h, 25 °C for 10 h, and 65 °C for 1.5 h. After workup, the mixture was extracted with ether and the ether solution was washed with saturated sodium chloride, then dried over anhydrous magnesium sulfate. Following solvent removal, vacuum distillation yielded 24.5 g (65%) of cycloprop[2,3]inden-1-one: bp 103–105 °C (0.7

mm); n^{23}D 1.5870 [lit.[7] bp 68 °C (0.06 mm)]; NMR (CCl_4) δ 1.1 (m, 1 H, cyclopropyl), 1.5 (m, 1 H, cyclopropyl), 2.2 (m, 1 H, cyclopropyl), 2.8 (m, 1 H, cyclopropyl), and 7.2 ppm (m, 4 H, aromatic).

***exo*-Cycloprop[2,3]inden-1-ol.** Following the method of Eliel,[8] 14.4 g (0.10 mol) of cycloprop[2,3]inden-1-one was stirred with aluminum isopropoxide in isopropyl alcohol for 5 h. The usual workup was followed by vacuum distillation affording 12.4 g (85%) of a light yellow oil, bp 88–91 °C (0.1 mm), which was a 73:27 exo–endo mixture. Spinning band distillation of 7.11 g followed by recrystallization from 20 ml of 1:1 ether–petroleum ether (bp 30–60 °C) yielded 1.24 g (15%) of *exo*-cycloprop[2,3]inden-1-ol: mp 67–68.5 °C; NMR (CCl_4) δ 0.0 (m, 1 H, cyclopropyl), 1.1 (m, 1 H, cyclopropyl), 2.0 (m, 1 H, cyclopropyl), 2.1 (bs, 1 H, OH), 2.4 (m, 1 H, cyclopropyl), 4.8 (bs, 1 H, CHOH), and 7.2 ppm (m, 4 H, aromatic); IR (mineral oil) 3220 cm^{-1} (O–H); mass spectrum (70 eV) *m/e* (rel intensity) 146 (18), 145 (37), 131 (45), 128 (38), 127 (23), 117 (100), 116 (35), 115 (44).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.10; H, 6.80.

***exo*-Cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoate.** This was prepared in the usual manner by the reaction of 0.65 g (0.0045 mol) of *exo*-cycloprop[2,3]inden-1-ol and 1.4 g (0.0062 mol) of 3,5-dinitrobenzoyl chloride in pyridine at 0 °C. Workup and recrystallization of the dinitrobenzoate from ether produced 0.63 g (41%) of *exo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate: mp 113–115 °C; NMR ($CDCl_3$) δ 0.3 (m, 1 H, cyclopropyl), 1.4 (m, 1 H, cyclopropyl), 2.8 (m, 2 H, cyclopropyl), 6.4 (d, J = 2 Hz, 1 H, CHODNB), 7.4 (m, 4 H, aromatic), and 9.2 ppm (bs, 3 H, aromatic); IR (mineral oil) 1725 cm^{-1} (C=O).

Anal. Calcd for $C_{17}H_{12}N_2O_6$: C, 60.00; H, 3.55. Found: C, 60.13; H, 3.55.

Indan-1-ol. Reduction of 9.1 g (0.069 mol) of indan-1-one with 1.22 g (0.032 mol) of lithium aluminum hydride in ether followed by workup, distillation, and recrystallization from petroleum ether (bp 30–60 °C) produced 4.1 g (68%) of white needles of indan-1-ol: mp 53–55 °C (lit.[17] mp 53–54 °C); NMR (CCl_4) δ 2.0 (m, 2 H, $CHOHCH_2$), 2.7 (m, 2 H, CH_2 aromatic), 3.8 (s, 1 H, OH), 4.9 (t, J = 6 Hz, 1 H, CHOH), and 7.1 ppm (m, 4 H, aromatic).

Indan-1-yl 3,5-Dinitrobenzoate. In the usual manner 2.05 g (0.015 mol) of indan-1-ol was treated with 4.4 g (0.019 mol) of 3,5-dinitrobenzoyl chloride in pyridine at 0 °C for 2 h. Workup and recrystallization from acetone–petroleum ether (bp 30–60 °C) yielded 4.2 g (85%) of indan-1-yl 3,5-dinitrobenzoate: mp 115.5–119 °C (lit.[18] mp 119–120 °C); NMR ($CDCl_3$) δ 2.6 (m, 2 H, $CHODNBCH_2$), 3.2 (m, 2 H, CH_2 aromatic), 6.6 (t, J = 5 Hz, 1 H, CHODNB), 7.4 (m, 4 H, aromatic), and 9.1 ppm (m, 3 H, aromatic).

4,4-Dimethyl-1,4-dihydronaphthalen-1-one. This was prepared from 4,4-dimethyl-2-bromo-1-tetralone[19] by the method of Corey.[20] A mixture of 17.1 g (0.068 mol) of 2-bromo-4,4-dimethyl-1-tetralone, 14.2 g (0.16 mol) of lithium bromide, and 20.0 g (0.27 mol) of lithium carbonate in dry dimethylformamide was heated at 120–125 °C for 60 min. The mixture was poured into ice and extracted with ether. The ethereal solution was washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of the ether followed by recrystallization from mixed hexanes yielded 9.85 g (84%) of 4,4-dimethyl-1,4-dihydronaphthalen-1-one: mp 69–70 °C (lit.[19] mp 69.5–70.5 °C); NMR (CCl_4) δ 1.5 (s, 6 H, CH_3 and CH_3), 6.3 (d, J = 10 Hz, 1 H, CH=CH), 6.7 (d, J = 10 Hz, 1 H, CHC=O), 7.4 (m, 3 H, aromatic), and 8.0 (m, 1 H, aromatic).

5,5-Dimethylbenzobicyclo[4.1.0]hepten-1-one. This material was prepared from 4,4-dimethyl-1,4-dihydronaphthalen-1-one employing the cyclopropanation procedure of Corey.[21] In a flame-dried flask under nitrogen, 1.31 g (0.030 mol) of sodium hydride and 6.9 g (0.030 mol) of trimethylsulfoxonium iodide were combined and dimethyl sulfoxide was added. After 20 min of stirring, 5.2 g (0.030 mol) of 4,4-dimethyl-1,4-dihydronaphthalen-1-one was added. Workup followed by distillation afforded 5.3 g (95%) of 5,5-dimethylbenzobicyclo[4.1.0]hepten-1-one as a colorless liquid: bp 106.5–107.5 °C (1 mm); n^{23}D 1.5637; NMR (CCl_4) δ 0.6 (m, 1 H, cyclopropyl), 1.2 (m, 4 H, CH_3 and cyclopropyl), 1.5 (m, 4 H, CH_3 and cyclopropyl), 2.0 (m, 1 H, cyclopropyl), 7.1 (m, 3 H, aromatic), and 7.4 ppm (m, 1 H, aromatic); IR (neat) 1750 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 186 (26), 172 (14), 171 (100), 152 (12), 146 (18), 144 (19), 143 (29), 131 (22), 129 (12), 128 (36), 127 (11), and 115 (25).

5,5-Dimethylbenzobicyclo[4.1.0]hepten-1-ol. Fourteen milliliters of 0.55 M potassium tri-*sec*-butylborohydride in tetrahydrofuran was utilized to reduce 1.17 g (0.0063 mol) of 5,5-dimethylbenzobicyclo[4.1.0]hepten-1-one at 0 °C. Oxidative workup followed by vacuum distillation yielded 1.02 g (87%) of 5,5-dimethylbenzobicyclo[4.1.0]-hepten-1-ol (greater than 90% endo): bp 104–105 °C (1.0 mm); NMR (CCl_4) δ 0.1 (m, 2 H cyclopropyl), 1.3 (m, 4 H, CH_3 and cyclopropyl), 1.6 (m, 4 H, CH_3 and cyclopropyl), 3.7 (bs, 1 H, OH), 5.1 (bs, 1 H, CHOH), 7.1 (m, 3 H, aromatic), and 7.5 (m, 1 H, aromatic).

5,5-Dimethyl-*endo*-benzobicyclo[4.1.0]hepten-1-yl 3,5-Dinitrobenzoate. The usual procedure involving the reaction of 0.63 g (0.0034 mol) of 5,5-dimethylbenzobicyclo[4.1.0]hepten-1-ol with 1.1 g (0.0048 mol) of 3,5-dinitrobenzoyl chloride in pyridine was used. Workup and recrystallization gave 0.45 g (29%) of 5,5-dimethyl-*endo*-benzobicyclo[4.1.0]hepten-1-yl 3,5-dinitrobenzoate: mp 88–90 °C; NMR ($CDCl_3$) δ 0.5 (m, 2 H, cyclopropyl), 1.3 (s, 3 H, CH_3), 1.5 (s, 4 H, CH_3 and cyclopropyl) 1.8 (m, 1 H, cyclopropyl), 6.7 (d, J = 5 Hz, 1 H, CHODNB), 7.3 (m, 4 H, aromatic), and 9.3 ppm (s, 3 H, aromatic); IR (mineral oil) 1725 cm^{-1} (C=O).

Anal. Calcd for $C_{20}H_{18}N_2O_6$: C, 62.82; H, 4.74. Found: C, 62.62; H, 4.78.

4,4-Dimethyl-1-tetralol. This was prepared in 75% yield by lithium aluminum hydride reduction of 4,4-dimethyl-1-tetralone: bp 107–109 °C (1.9 mm); n^{22}D 1.5465 [lit.[22] bp 102–104 °C (15 mm)]; NMR (CCl_4) δ 1.2 (s, 3 H, CH_3), 1.2 (s, 3 H, CH_3), 1.7 (m, 4 H, CH_2CH_2), 3.5 (bs, 1 H, OH), 4.3 (bs, 1 H, CHOH), and 7.1 ppm (m, 4 H, aromatic).

4,4-Dimethyl-1-tetralyl 3,5-Dinitrobenzoate. A mixture of 0.60 g (0.0035 mol) of 4,4-dimethyl-1-tetralol and 1.1 g (0.0048 mol) of 3,5-dinitrobenzoyl chloride in pyridine was stirred at 0 °C. Workup and recrystallization from 1:10 benzene–mixed hexanes produced 0.45 g (36%) of 4,4-dimethyl-1-tetralyl 3,5-dinitrobenzoate: mp 123–125 °C; NMR ($CDCl_3$) δ 1.3 (s, 3 H, CH_3), 1.4 (s, 3 H, CH_3) 2.1 (m, 4 H, CH_2CH_2), 6.2 (t, J = 4 Hz, 1 H, CHODNB), 7.2 (m, 4 H, aromatic), and 9.0 ppm (s, 3 H, aromatic).

Anal. Calcd for $C_{19}H_{18}N_2O_6$: C, 61.62; H, 4.90. Found: C, 61.43; H, 4.90.

Phenylcyclopropylcarbinol. A sample of 5.30 g (0.036 mol) of phenyl cyclopropyl ketone was reduced with lithium aluminum hydride in ether. Workup by pouring into 100 ml of ice-cold 1 M sulfuric acid was followed by ether extraction and drying. Subsequent vacuum distillation yielded 4.81 g (89%) of phenylcyclopropylcarbinol: bp 78–79 °C (1.0 mm); n^{22}D 1.5405 [lit.[23] bp 121 °C (12 mm); n^{25}D 1.5390]; NMR (CCl_4) δ 0.2 (m, 4 H, cyclopropyl), 0.9 (m, 1 H, cyclopropyl), 3.4 (bs, 1 H, OH), 4.8 (d, J = 8 Hz, CHOH), and 7.1 ppm (s, 5 H, aromatic).

Phenylcyclopropylcarbinyl 3,5-Dinitrobenzoate. Through the reaction of 1.42 g (0.010 mol) of phenylcyclopropylcarbinol and 3.0 g (0.013 mol) of 3,5-dinitrobenzoyl chloride in pyridine at 0 °C, this dinitrobenzoate was prepared. The usual workup followed by recrystallization from 10:1 methylcyclohexane–chloroform yielded 2.10 g (64%) of phenylcyclopropylcarbinyl 3,5-dinitrobenzoate: mp 92–93 °C; NMR ($CDCl_3$) δ 0.7 (m 4 H, cyclopropyl), 1.6 (m, 1 H, cyclopropyl), 5.5 (d, J = 9 Hz, 1 H, CHODNB), 7.4 (m, 5 H, aromatic), and 9.2 ppm (m, 3 H, aromatic).

Ethylidene Iodide. Following the method of Letsinger and Kammeyer,[14] 15.9 g (0.16 mol) of ethylidene chloride was refluxed with 70.7 g (0.45 mol) of ethyl iodide and 0.3 g of aluminum chloride. Workup and vacuum distillation afforded 30.7 g (67%) of ethylidene iodide: bp 70–72 °C (17 mm); n^{22}D 1.6703 [lit.[14] bp 75–76 °C (25 mm)]; NMR (neat) δ 3.7 (d, J = 7 Hz, 3 H, CH_3) and 6.0 ppm (q, J = 7 Hz, 1 H, CHI_2).

***anti*-10-Methyl-*endo*-cycloprop[2,3]inden-1-ol.** The procedure of Krug and Tang[15] was followed to prepare ethylzinc iodide. After the reaction of 23.4 g (0.070 mol) of cupric citrate monohydrate with 132.0 g (2.0 mol) of powdered zinc, 80 mL (1.0 mol) of ethyl iodide was added. After refluxing in ether, 215 mL of 3.56 M ethylzinc iodide was obtained: NMR (ether) δ 0.4 (m, 2 H, CH_2) and 1.1 ppm (m, 3 H, CH_3). Under a nitrogen atmosphere 5.35 g (0.040 mol) of inden-1-ol was added to 45 mL of 3.56 M ethylzinc iodide. Then 23.0 g (0.081 mol) of ethylidene iodide was added dropwise and refluxing was continued for 12 h. Workup with ammonium chloride and extraction with ether was followed by washing with saturated sodium bicarbonate and saturated sodium chloride solutions and drying over anhydrous magnesium sulfate. Distillation produced 5.2 g of impure *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-ol, bp 81–92 °C (0.7 mm). Recrystallization from 100 mL of 3:1 pentane–ether afforded 2.2 g (34%) of *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-ol, mp 82–85 °C. Further recrystallization from pentane gave white crystals of *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-ol: mp 86.5–87.0 °C; NMR (CCl_4) δ 0.8 (m, 1 H, cyclopropyl), 1.0 (d, J = 5 Hz, 3 H, CH_3), 1.6 (m, 1 H, cyclopropyl), 2.0 (m, 1 H, cyclopropyl), 2.4 (d, J = 7 Hz, 1 H, OH), 5.5 (m, 1 H, CHOH), and 7.2 ppm (bs, 4 H, aromatic); IR (mineral oil) 3350 (O–H) and 3250 cm^{-1} (O–H); mass spectrum (70 eV) *m/e* (rel intensity) 160 (29), 145 (100), 142 (32), 141 (31), 131 (80), 128 (27), 127 (21), 117 (27), 116 (44), 115)61), and 91 (20).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.61; H, 7.63.

***anti*-10-Methyl-*endo*-cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoate.** Employing the usual procedure, 1.0 g (0.0063 mol) of *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-ol was treated with 1.7 g (0.0075 mol) of 3,5-dinitrobenzoyl chloride in pyridine at 0 °C. Workup and recrystallization from 1:1 chloroform–pentane produced 0.95 g (42%) of *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate: mp 148–149 °C; NMR ($CDCl_3$) δ 1.1 (bs, 4 H, C**H**C**H**$_3$), 2.2 (m, 2 H, cyclopropyl), 6.6 (d, J = 6 Hz, 1 H, C**H**ODNB), 7.1 (bs, 4 H, aromatic), and 9.0 ppm (s, 3H, arom); IR (mineral oil) 1710 (C=O) and 1355 cm^{-1} (C–O).

Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.02; H, 3.98. Found: C, 61.11; H, 4.01.

***anti*-10-Methyl-*exo*- and -*endo*-cycloprop[2,3]inden-1-ols.** This material was prepared using the method of Eliel.[8] A mixture of 1.25 g (0.0078 mol) of *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-ol, 2.6 g (0.0127 mol) of aluminum isopropoxide, 50 mg of acetone, and 75 mL of isopropyl alcohol was heated at reflux for 148 h. Then the mixture was cooled, treated with aqueous sodium hydroxide, and extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate and, after removal of the solvent, distillation produced 1.12 g of a 1:1 endo–exo mixture of *anti*-10-methylcycloprop[2,3]inden-1-ols: bp 108–110 °C (3.4 mm); NMR (CCl_4) δ 0.3 [m, 0.5 H, cyclopropyl (exo isomer)], 1.0 [m, 3.5 H, CH_3 and cyclopropyl (endo isomer)], 1.6 (m, 1 H, cyclopropyl), 2.0 (m, 1 H, cyclopropyl), 3.2 (bs, 1 H, OH), 4.6 [bs, 0.5 H, C**H**OH (exo isomer)], 5.3 [d, J = 6 Hz, 0.5 H, C**H**OH (endo isomer)], and 7.1 ppm (m, 4 H, aromatic). Also, when the above mixture was recrystallized from pentane part of the endo isomer was removed to leave 0.62 g (50%) of oil which was a 66:34 exo–endo mixture of *anti*-10-methylcycloprop[2,3]inden-1-ols.

***anti*-10-methyl-*exo*- and -*endo*-cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoates.** This mixture of dinitrobenzoates was prepared in the usual manner from a 66:34 exo–endo mixture of *anti*-10-methylcycloprop[2,3]inden-1-ols. A sample of 0.62 g (0.0039 mol) of the mixture of alcohols was treated with 1.1 g (0.0048 mol) of 3,5-dinitrobenzoyl chloride in pyridine. Workup and recrystallization from 10:1 pentane–chloroform yielded 0.74 g (54%) of an 87:13 exo–endo mixture of *anti*-10-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates: NMR ($CDCl_3$) δ 0.6 (m, 1 H, cyclopropyl), 1.2 (d, J = 6 Hz, 3 H, CH_3), 2.0 (m, 1 H, cyclopropyl), 2.5 (m, 1 H, cyclopropyl), 6.4 [s, 0.87 H, C**H**ODNB (exo isomer)], 6.7 [d, J = 6 Hz, 0.13 H, C**H**ODNB (endo isomer)], 7.3 (m, 4 H, aromatic), and 9.2 ppm (m, 3 H, aromatic).

Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.02; H, 3.98. Found: C, 60.90; H, 4.00.

1-Methylinden-3-yl Acetate. This was prepared by heating a mixture of 20.3 g (0.14 mol) of 3-methylindan-1-one, 21.9 (0.22 mol) of isopropenyl acetate, and 0.3 g of *p*-toluenesulfonic acid at reflux for 10 h. After cooling the solution, 5 g of anhydrous sodium carbonate was added and distillation afforded 15.3 g (63%) of 1-methylinden-3-yl acetate: bp 100–101 °C (1.9 mm); NMR (CCl_4) δ 1.4 (d, J = 8 Hz, 3 H, C**H**$_3$CH), 2.3 (s, 3 H, CH_3C=O), 3.7 (quartet of doublets, J = 3 and 8 Hz, 1 H, C**H**CH$_3$), 6.7 (d, J = 3 Hz, 1 H, C**H**OAc), and 7.7 ppm (m, 4 H, aromatic); IR (neat) 1760 (C=O) and 1190 cm^{-1} (C–O); mass spectrum (70 eV) *m/e* (rel intensity) 188 (10), 147 (11), 146 (100), 145 (22), 131 (58), 117 (10), 115 (19).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.32; H, 6.57.

3-Methylinden-1-ol. Upon treatment of 13.1 g (0.074 mol) of 1-methylinden-3-yl acetate with 1 mL of trimethylamine in 5 mL of ether at reflux for 1 h, rearrangement occurred resulting in an 92:8 ratio of 3-methylinden-1-yl acetate and 1-methylinden-3-yl acetate. After removal of the triethylamine and ether under vacuum, the remaining mixture of acetates was dissolved in ether, cooled to 0 °C, and reduced with lithium aluminum hydride. Workup by pouring the mixture into 1 N sulfuric acid was followed by extraction with ether and drying over anhydrous magesium sulfate. Removal of the ether left a white solid which was recrystallized from 1:1 ether–petroleum ether (bp 30–60 °C) to yield 6.9 g (63%) of short needles, mp 68–71 °C. Further recrystallization from the same solvent mixture yielded 3-methylinden-1-ol: mp 70.5–71.0 °C; NMR (CCl_4) δ 2.0 (t, J = 2 Hz, 3 H, CH_3), 3.2 (bs, 1 H, OH), 4.8 (bs, 1 H, C**H**OH), 5.8 (q, J = 2 Hz, 1 H, C**H**CHOH), and 7.0 ppm (m, 4 H, aromatic); IR (mineral oil) 3280 cm^{-1} (O–H); mass spectrum (70 eV) *m/e* (rel intensity) 147 (10), 146 (92), 145 (32), 132 (10), 131 (100), 128 (17), 127 (13), 117 (14), 115 (25), 103 (18), 77 (12).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.34; H, 6.93.

3-Methyl-*endo*-cycloprop[2,3]inden-1-ol. To 25.0 g (0.39 mol) of a zinc–copper couple, prepared by the LeGoff[6] procedure, in ether was added 27.2 g (0.19 mol) of 3-methylinden-1-ol and 80 g (0.30 mol) of methylene iodide in ether over a 30-min period. This solution was refluxed for 4 h, and workup by the usual method was followed by ether extraction and drying over magnesium sulfate. Distillation afforded 18.6 g of 3-methylcycloprop[2,3]inden-1-ol, bp 92–97 °C (0.8 mm), which was recrystallized from ether–petroleum ether (bp 30–60 °C) to yield 17.4 g (58%) of white crystals, mp 78–80 °C. Further recrystallization from pentane yielded 3-methyl-*endo*-cycloprop[2,3]-inden-1-ol: mp 79–80 °C; NMR (CCl_4) δ 0.6 (m, 2 H, cyclopropyl), 1.5 (s, 3 H, CH_3), 1.7 (m, 1 H, C**H**CHOH), 1.9 (bs, 1 H, OH), 5.4 (bs, 1 H, C**H**OH), and 7.1 ppm (bs, 4 H, aromatic); IR (mineral oil) 3345 and 3250 cm^{-1} (O–H); mass spectrum (70 eV) *m/e* (rel intensity) 145 (100), 142 (34), 141 (28), 131 (66), 130 (22), 129 (25), 128 (38), 127 (25), 117 (50), 116 (24), 115 (58), 91 (24).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.59; H, 7.63.

3-Methyl-*endo*-cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoate. In the usual manner, 1.14 g (0.071 mol) of 3-methyl-*endo*-cycloprop[2,3]inden-1-ol was cooled to 0 °C in pyridine and treated with 2.0 g (0.088 mol) of 3,5-dinitrobenzoyl chloride. Workup and recrystallization from 1:1 chloroform–pentane gave 1.36 g (64%) of 3-methyl-*endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate: mp 118–120 °C; NMR ($CDCL_3$) δ 1.0 (m, 2 H, cyclopropyl), 1.6 (bs, 3 H, CH_3), 2.1 (m, 1 H, cyclopropyl), 6.6 (d, J = 6 Hz, 1 H, C**H**ODNB), 7.1 (m, 4 H, aromatic), and 9.0 ppm (m, 3 H, aromatic); IR (mineral oil) 1725 (C=O) and 1275 cm^{-1} (C–O).

Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.02; H, 3.98. Found: C, 60.98; H, 3.82.

3-Methyl-*exo*- and -*endo*-cycloprop[2,3]inden-1-ols. Again using the method of Eliel,[8] a mixture of 10.1 g (0.063 mol) of 3-methyl-*endo*-cycloprop[2,3]inden-1-ol, 15.1 g (0.073 mol) of aluminum isopropoxide, and 0.1 g of acetone in 2-propanol was heated at reflux for 48 h. Workup by pouring the cooled mixture into ice-cold 2 M hydrochloric acid and extraction with ether was followed by drying over anhydrous magnesium sulfate. Vacuum distillation afforded 8.1 g (80%) of a colorless liquid, bp 89–92 °C (1.0 mm), which was a 75:25 exo–endo mixture of 3-methylcycloprop[2,3]inden-1-ols: NMR (CCl_4) δ 0.0 [t, J = 4 Hz, 0.75 H, cyclopropyl (anti proton of exo isomer)], 0.7 (m, 1.25 H, cyclopropyl), 1.4 (m, 4 H, CH_3 and cyclopropyl), 3.3 (bs, 1 H, OH), 4.4 [s, 0.75 H, C**H**OH (exo isomer)], 5.2 [d, J = 6 Hz, 0.25 H, C**H**OH (endo isomer)], and 7.3 ppm (m, 4 H, aromatic).

3-Methyl-*exo*-cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoate. To 1.83 g (0.011 mol) of a 75:25 exo–endo mixture of 3-methylcycloprop[2,3]inden-1-ol cooled to 0 °C in pyridine was added 3.0 g (0.013 mol) of 3,5-dinitrobenzoyl chloride. Workup and recrystallization produced 2.10 g (52%) of whitish crystals, mp 109–117 °C. Recrystallization twice more from 1:1 methylene chloride–pentane yielded 3-methyl-*exo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate: mp 118–120 °C; NMR ($CDCl_3$) δ 0.4 (t, J = 4 Hz, 1 H, cyclopropyl), 1.2 (doublet of doublets, J = 4 and 8 Hz, 1 H, cyclopropyl), 1.7 (s, 3 H, CH_3), 2.0 (doublet of doublets, J = 4 and 8 Hz, 1 H, cyclopropyl), 6.3 (s, 1 H, C**H**ODNB), 7.3 (m, 4 H, aromatic), and 9.2 ppm (s, 3 H, aromatic); IR (mineral oil) 1725 (C=O) and 1285 cm^{-1} (C–O).

Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.02; h, 3.98. Found: C, 61.13; H, 4.08.

Kinetic Procedures. Acetone (Mallinckrodt AR) was dried by allowing it to slowly drain through a 50 by 2.6 cm column packed with 1/16 in. pellets of Linde 4A molecular sieve. The acetone was distilled from powdered type 4A molecular sieve through a 40-cm Widmer column. The 80 vol % aqueous acetone was then prepared by combining 800 mL of the dry acetone with 200 mL of redistilled water.

As an example of the usual kinetic procedure, 0.1724 g (5.07×10^{-4} mol) of *endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate was dissolved in 50 mL of 80% aqueous acetone in a 50-mL volumetric flask. This solution was then divided into nine portions of ca. 5.5 mL and sealed in ampules. The set of ampules was immersed in a thermostated 5-gal constant-temperature oil bath and at regular intervals they were removed and cooled quickly in ice. After equilibrating to room temperature, a 5-mL aliquot was taken and titrated for acid formed with ca. 0.01 N sodium methoxide in methanol using 2 drops of a 1% methanolic solution of bromothymol blue as the indicator. Infinity titers were determined in duplicate after about 10 half-lives for reaction. All runs were carried out in duplicate and the reported values are the average of two runs. Rate constants were calculated by use of the standard first-order integrated rate equation[23] and thermodynamic parameters were obtained using the Eyring equation.[24] Errors reported for the rate constants represent in each case the standard deviation of the mean. Error values recorded for the activation parameters were determined based on the errors mentioned

above for the rate constants.

Controls on Kinetic Materials. As a typical example of the method employed, 0.0428 g (1.21×10^{-4} mol) of 3-methyl-*endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate was dissolved in 5.0 mL of 80% aqueous acetone. The sample was sealed in an ampule and heated for 15 min (time for hydrolysis of ca. 25% of the ester) at 100.0 °C. The sample was cooled, poured into water, and extracted with ether. The ethereal solution was washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. All traces of solvent were removed on the vacuum pump and the sample was analyzed for 3-methyl-*exo*- and -*endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates by NMR.

Hydrolysis Products. As an example of the procedure, a sample of 0.2902 g (8.52×10^{-4} mol) of *endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate and 0.20 g (2×10^{-3} mol) of calcium carbonate were combined with 5 mL of 80% aqueous acetone and sealed in an ampule. After heating for 250 min at 100.0 °C, the mixture was cooled and poured into 50 mL of ether which contained a weighed amount of indan-1-ol internal standard. The ether solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed using a Widmer column and the products analyzed by GLC using a 5 ft × 0.25 in. 20% diethylene glycol succinate (DEGS) column on Chromosorb W and by NMR.

Controls on Hydrolysis Products. In an example of the general case, 0.0277 g (1.73×10^{-4} mol) of 3-methyl-*endo*-cycloprop[2,3]-inden-1-ol, 0.0406 g (4.06×10^{-4} mol) of calcium carbonate, and 0.0285 g (1.41×10^{-4} mol) of 3,5-dinitrobenzoic acid were combined in 5 mL of 80% aqueous acetone and sealed in an ampule. The ampule was heated at 100.0 °C for 281.0 min (ca. 5 half-lives of the corresponding ester) and then cooled to room temperature. The sample was poured into ether containing indan-1-ol (internal standard) and water was added. After ether extraction, the ethereal solution was washed with saturated sodium bicarbonate and dried over anhydrous sodium sulfate. The solution was concentrated to ca. 0.5 mL using a Widmer column and the sample was analyzed by GLC using a 5 ft × 0.125 in. SF-96/Carbowax on Chromosorb G column and by NMR.

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Registry No.—**1**, 61463-14-7; **2**, 61490-56-0; **5**, 61463-15-8; **6**, 61463-16-9; **7**, 61463-17-0; **8**, 61463-18-1; **15**, 61463-19-2; **16**, 61490-57-1; **17**, 61463-20-5; **18**, 61490-58-2; **19**, 6072-57-7; *endo*-cycloprop[2,3]inden-1-ol, 57378-75-3; methylene iodide, 75-11-6; inden-1-ol, 61463-21-6; 3,5-dinitrobenzoyl chloride, 99-33-2; cycloprop[2,3]inden-1-one, 5771-62-0; 2-phenylcyclopropanecarboxylic acid chloride, 5685-36-9; 1,2-dichloroethane, 107-06-2; *exo*-cycloprop[2,3]inden-1-ol, 57378-74-2; indan-1-ol, 6351-10-6; indan-1-one, 83-33-0; 4,4-dimethyl-1,4-dihydronaphthalen-1-one, 16020-16-9; 4,4-dimethyl-2-bromo-1-tetralone, 17426-90-3; dimethylformamide, 68-12-2; 5,5-dimethylbenzobicyclo[4.1.0]hepten-1-one, 61463-22-7; dimethyl sulfoxide, 67-68-5; 5,5-dimethylbenzobicyclo[4.1.0]hepten-1-ol, 61463-23-8; 4,4-dimethyl-1-tetralol, 53952-18-4; 4,4-dimethyl-1-tetralone, 2979-69-3; phenylcyclopropylcarbinol, 1007-03-0; phenyl cyclopropyl ketone, 3481-02-5; ethylidene iodide, 594-02-5; ethylidene chloride, 75-34-3; ethyl iodide, 75-03-6; *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-ol, 61463-24-9; *anti*-10-methyl-*exo*-cycloprop[2,3]inden-1-ol, 61490-59-3; 1-methylinden-3-yl acetate, 61463-25-0; isopropenyl acetate, 108-22-5; 3-methylinden-1-ol, 23417-85-8; 3-methyl-*endo*-cycloprop[2,3]inden-1-ol, 61463-26-1; 3-methyl-*exo*-cycloprop[2,3]inden-1-ol, 61490-60-6.

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Thermodynamics of Vinyl Ethers. 19. Alkyl-Substituted Divinyl Ethers[1]

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Chemical equilibration studies of isomeric alkyl-substituted divinyl ethers have been carried out. The thermodynamic data obtained are used for discussions concerning the spatial structure of the C=C–O–C=C system in these compounds. Divinyl ethers unsubstituted in the α position probably exist mainly in the planar (or nearly planar) s-trans,s-trans form, the planar s-cis,s-trans form being in any case excluded as the most stable structure. The latter structure is possible for an α-substituted but not for an α,α'-dialkyl-substituted divinyl ether, which assumes a nonplanar structure. The same structure applies to most α,β-dialkyl- and α,β-polyalkyl-substituted divinyl ethers. Electron distribution in the divinyloxy system is rather sensitive to the number and position of alkyl groups present, as revealed by the ^{1}H NMR shift data.

The spatial structure of divinyl ether (**1**) has been of interest ever since the finding of Dolliver et al.[2] that the conjugation energies of **1** and ethyl vinyl ether (**2**) are equal (ca. 15 kJ mol^{-1}). Since the oxygen atom of **1** is interposed between

$CH_2{=}CH{-}\ddot{O}{-}CH{=}CH_2$ (**1**) $\qquad$ $Et{-}\ddot{O}{-}CH{=}CH_2$ (**2**)

two unsaturated linkages, the stabilization due to p–π interaction in **1** might be expected to be higher than that in **2**. The similar conjugation energies of **1** and **2** thus suggest that either the O atom of **1** conjugates effectively with just one of the two vinyl groups or it conjugates with both C=C bonds but with reduced efficiency. The former alternative is reasonable if **1** is markedly nonplanar so that the p orbitals of the O atom can