Stereochemical Studies on 3,4-Benzobicyclo[4.1.0]hept-3-en-2-ol Systems and Solvolytic Studies on Its *p*-Nitrobenzoates

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Synthesis, geometrical assignment, and solvolysis of 1,6-substituted 3,4-benzobicyclo[4.1.0]hept-3-en-2-yl *p*-nitrobenzoates (**1a–c**) are described. In the stereochemical study of the parent alcohols (**8a–c**), a new comparative method has been proposed together with the previous result for **8d**. The method involves the comparison of relative molar lanthanide-induced shift (RLIS[i]) for certain protons in each alcohol. Anti geometry of the hydroxyl relative to the cyclopropane methylene group was assigned for all the substrates. This method will be promising in application to the other systems in which the framework is similar to each other. The kinetic result was also compatible with the product distribution, in which homoallylic tertiary and syn-secondary alcohols dominated because of the presence of both an aromatic ring and a cyclopropyl group adjacent to the reaction center. The reaction intermediate may be a homonaphthalenium ion.

There is abundant evidence for a stabilization effect of the cyclopropyl group in electron-deficient species.[1] Since a phenyl group shows the similar effect, the difference of the origin between both groups has been the subject of recent investigations.[2] For instance, Traylor et al. suggested that there might be vertical stabilization for the transition state in the solvolyses of some strained substrates,[2a,b] or Olah, Brown, and other investigators discussed the difference of their ability in rate acceleration of solvolysis in these two kinds of groups.[2e,g,h] The authors have been investigating the solvolysis of the unique cyclopropylphenylmethyl system (**1a–d**), in which both groups could competitively exert influence upon the rate as well as upon products. In one example of this system (**1d**),[3] it was suggested that σ participation rather than π conjugation might contribute to the rate acceleration, and that the intermediate of solvolysis might be a nonclassical homonaphthalenium cation in which a positive charge would be delocalized not only in the benzene ring but also in the cyclopropane ring.

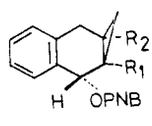
During our solvolytic study of all of the *anti*-3,4-benzobicyclo[4.1.0]hept-3-en-2-yl *p*-nitrobenzoates (**1a–d**), the authors have encountered the serious difficulty of assigning syn/anti geometry between a hydroxyl group and the methylene of a cyclopropane ring in the parent alcohols. In this paper, we wish to report a useful expedient for the purpose of dividing each alcohol into two series of geometric isomers from comparison of the lanthanide-induced shifts in the NMR spectrum and also to discuss the solvolytic reactivity of these esters (**1a–d**), in which the substituent at the C_1 or C_6 position is hydrogen, methyl, or trimethylene group.

Results and Discussion

Synthesis. Each *p*-nitrobenzoate was prepared by the sequence outlined in Scheme I. The *p*-nitrobenzoate **1a** was obtained by esterification of **8a**, which was synthesized by Julia et al.,[4] and the synthesis of **1d** was previously reported.[3] Here, we report the preparation of **1b** and **1c** in detail.

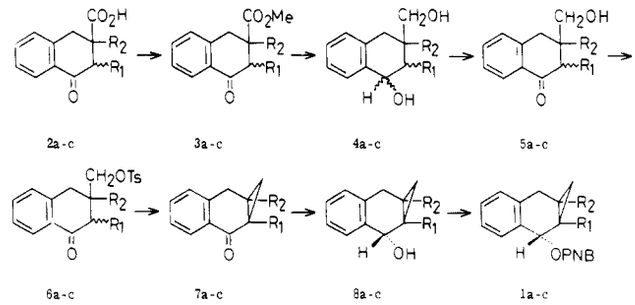
The keto acid **2b** was obtained by the earlier method.[5] In the course of preparation of **2b**, treatment of unsaturated cyano ester **9** with potassium cyanide gave potassium salt **10**

Chart I

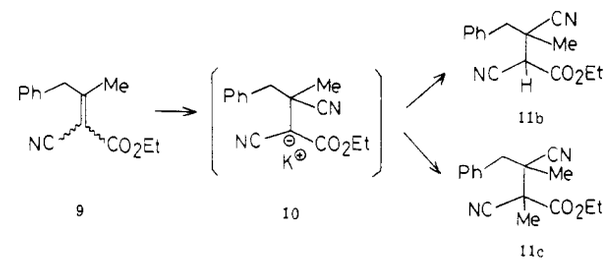


	R_1	R_2
1a	H	H
1b	H	Me
1c	Me	Me
1d	$-(CH_2)_3-$	

Scheme I



Scheme II



(Scheme II), which was quenched by hydrochloric acid to afford monomethyldicyano ester **11b**. Using methyl iodide in place of hydrochloric acid gave rise to dimethyldicyano ester **11c** in 73–76% yield without isolation of **11b** as an intermediate. So **11c** could be obtained directly from **9**.

Intramolecular cyclization of **11c** by means of sulfuric acid in aqueous acetic acid directly gave rise to the keto acid **2c** in moderate yield (30%). Esterification with diazomethane converted **2b** and **2c** almost quantitatively into the esters **3b** and **3c**, which were reduced by lithium aluminum hydride to give a mixture of geometric isomers of diol **4b** and **4c**. Oxidation of **4b** and **4c** with active manganese dioxide gave the keto alcohols **5b** and **5c**. Their tosylates (**6b,c**) were prepared in the general method, then the sulfonic acid was eliminated by potassium hydroxide in aqueous dioxane, giving the ketones **7b** and **7c**. Spectroscopic analysis supported the assigned structure of these cyclopropyl phenyl ketones (**7b,c**) as shown in Table V.[19] Reduction of **7a–c** with lithium aluminum hydride in ether gave the alcohols **8a–c** in 84–96% yield. Although there are two geometric isomers, syn and anti, in these alcohols, only one of the isomers was obtained in each case, judging from spectroscopic analysis. The assignment of signals in the NMR spectra is tabulated along with those of **8d** and **8e** in Table I. The *p*-nitrobenzoates **1a–c** were then prepared from these alcohols by the ordinary method.[3]

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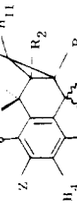
Table I. Chemical Shifts (δ), $(\Delta Eu)_i$ Values, and Relative Lanthanide-Induced Shifts ($RLIS^i$) for 3,4-Benzobicyclo[4.1.0]hept-3-en-2-ol Systems



Registry no.	Compd		H_2	H_3	H_4	Z	H_6	H_7	H_8	H_{10}	H_{11}	OH[a]	R_1	R_2	r[m]
64414-40-0	8a	δ	5.06[a]	7.7-7.5[b]		7.3-7.0[b]		3.00[c]	3.00[c]	0.63-0.17[b]		1.87[d]	1.8-1.3[b]		
		$(\Delta Eu)_i$	23.50	17.30		2.75		4.53		9.43	6.41	85.70	12.79	4.05	
		$RLIS^i$	1.00	0.74		0.12		0.19		0.40	0.27	3.65	0.54	0.17	0.993
64414-41-1	8b	δ	5.02[e]	7.7-7.5[b]		7.3-7.0[b]		2.87[d]	2.87[d]		0.43-0.16[b]	1.83[d]	1.5-1.3[b]	1.28[d]	
		$(\Delta Eu)_i$	22.69	15.90		2.62		3.76		9.94	5.86	79.58	11.85	2.22	
		$RLIS^i$	1.00	0.70		0.12		0.17		0.44	0.26	3.51	0.52	0.12	0.996
64414-42-2	8c	δ	4.73[d]	7.7-7.6[b]		7.3-7.1[b]		2.88[d]	2.88[d]	-0.07[f]	0.27[f]	1.7[d]	1.40[d]	1.30[d]	
		$(\Delta Eu)_i$	23.46	15.44		2.18		4.43		10.80	7.30	87.62	8.99	3.22	
		$RLIS^i$	1.00	0.66		0.09		0.19		0.46	0.31	3.73	0.38	0.14	0.999
58717-76-3	8d	δ[l]	4.83[d]	7.7-7.4[b]		7.3-6.9[b]		2.79[g]	3.15[g]	0.36[d]	0.36[d]	2.5-1.3	2.5-1.3[b]		
		$(\Delta Eu)_i$	23.86	16.06		2.48		4.55	4.58	11.48	7.50	91.20			
		$RLIS^i$	1.00	0.67		0.10		0.19	0.19	0.48	0.31	3.82			
60425-21-0	8e	δ[l]	4.83[d]	7.56[h]	7.03[i]	2.30[d]	6.90[c]	2.82[g]	3.16[g]	0.36[d]	0.36[d]	2.4-1.2	2.4-1.2[b]		
		$(\Delta Eu)_i$	36.26	24.76	2.88	2.25	4.00	6.50	6.63	16.51	11.00	108.04			
		$RLIS^i$	1.00	0.86	0.08	0.06	0.11	0.18	0.18	0.46	0.30	2.98			0.999
64474-23-3	12a	δ	5.03[a]			7.2-7.1[b]		2.90[j]	3.33[k]	0.03-0.2[b]	0.67-0.3[b]	2.15[b]	1.6-1.2[b]		
		$(\Delta Eu)_i$	33.06	11.31		4.78		8.48	14.14	9.57	6.57	110.49	20.88	8.70	
		$RLIS^i$	1.00	0.34		0.14		0.27	0.43	0.29	0.20	3.34	0.63	0.26	0.864

[a] Doublet, $J = 3$ Hz. [b] Multiplet. [c] Doublet, $J = 5$ Hz. [d] Singlet. [e] Doublet, $J = 4$ Hz. [f] AB quartet, $J = 5$ Hz. [g] AB quartet, $J = 16$ Hz. [h] Doublet, $J = 9$ Hz. [i] Double doublet, $J = 9, 2$ Hz. [j] Double AB quartet, $J = 16, 3$ Hz. [k] Double AB quartet, $J = 16, 1$ Hz. [l] Reference 3. [m] The hydroxyl protons were not included in the correlation, since they are known to correlate poorly because of their closeness to the europium ion. [n] Correlation coefficients in the relationship between $RLIS^i$ and $RLIS^i_{8d}$.

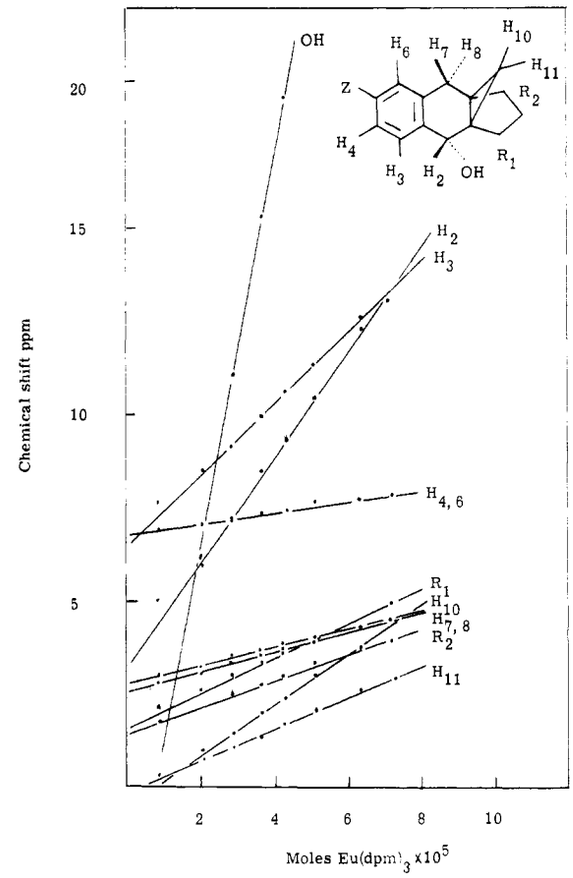
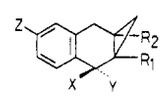


Figure 1. Variation in the chemical shift for the different protons of 3,4-benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2-ol (**8d**) (0.168 mmol in 0.4 mL of $CDCl_3$) with increasing concentration of $Eu(dpm)_3$.

Geometric Assignment of 8a–e. The geometric assignment of syn/anti (or cis/trans) cyclopropane stereochemistry on each alcohol was an important problem in the consideration of the solvolytic reactivity among these esters (**1a–d**). There are many recent applications that the lanthanide-induced chemical shifts observed in rigid oxygenated bicyclic molecules were interpreted by the McConnell–Robertson version of the pseudocontact interaction and then related to the stereochemistry of these molecules.[6,7] We have attempted to apply the somewhat different procedure to our alcohols **8a–d** and



	R_1	R_2	X	Y	Z
8a	H	H	H	OH	H
8b	H	Me	H	OH	H
8c	Me	Me	H	OH	H
8d	$-(CH_2)_3-$		H	OH	H
8e	$-(CH_2)_3-$		H	OH	Me
12a	H	H	OH	H	H
12d	$-(CH_2)_3-$		OH	H	H

its related alcohol **8e**[3a] in which the conformations might not be completely rigid, but be rather *flexible*. According to the generalized method, the dependence of the chemical shifts of all the protons in each alcohol (**8a, 8b, 8c, 8d,** or **8e**) was first studied in NMR measurement by dissolving successively a weighed amount of tris(dipivaloylmethanato)europium, $Eu(dpm)_3$, into a deuteriochloroform solution of the alcohol. For one instance, the result for **8d** is shown in Figure 1. The shift tendency of the corresponding protons in all the other alcohols (**8a–c** and **8e**) was found to be quite similar to this figure. The similarity of these figures suggests that corresponding protons in this series of alcohols are located in sim-

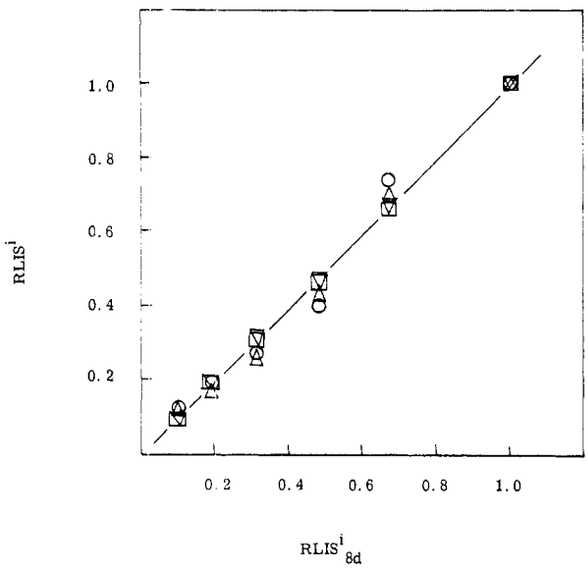


Figure 2. Relationship between relative induced shifts (RLIS^i) for **8a** (○), **8b** (△), **8c** (▽), and **8e** (□) and the standard value (RLIS$^i_{8d}$) for **8d.**

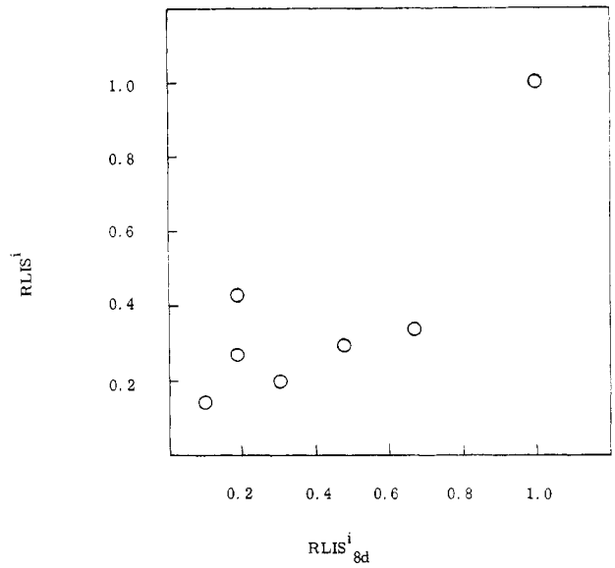


Figure 3. Relationship between relative induced shifts (RLIS^i) for **12a** (○) and the standard value (RLIS$^i_{8d}$) for **8d.**

ilar circumstances with regard to the shift reagents, especially to its metal. The definition of the similarity, however, is ambiguous.

In general, the molar induced shift, $(\Delta Eu)_i$, is defined as the difference between the chemical shift of a given proton, H_i, measured without the reagent and the shift with the equimolar reagent.[8] Also, excellent fits have been reported in various rigid systems for the proportionality of $(\Delta Eu)_i$ with $(3\cos^2\theta_i - 1)/r_i^3$, where r_i is the distance between the metal and the proton (H_i) and θ_i is the angle between the r_i vector and the magnetic axis of the complex.[7,9] Recently, Sullivan suggested that extreme caution should be paid in assigning configurations to nonrigid molecules based on the correlation of observed lanthanide-induced shifts in NMR spectra with those obtained by the McConnel-Robertson equation.[10] Since $(\Delta Eu)_i$ may be sensitive to the experimental conditions and to the character of a given molecule, the suggestion is worthy of attention. Instead of indirect comparison of such figures as Figure 1 obtained for each compound, the following relative ratio, RLIS^i, may serve as a more useful measure to compare molecular structure for one alcohol with that for another, even if these conformations might be considerably *flexible.*

$$\text{RLIS}^i = (\Delta Eu)_i/(\Delta Eu)_2$$

Here, the alcohol **8d** was selected as the reference compound which was investigated in detail in our laboratory.[3] Thus, RLIS$^i_{8d}$ was calculated for each proton of **8d,** using the α proton, H_2, as the standard, which showed the biggest shift with the exception of the hydroxylic proton. The relative induced shift, RLIS^i, was also obtained in the same way for each proton in the other secondary alcohols, **8a, 8b, 8c,** and **8e,** based upon the α proton in each compound. Then the relative induced shifts, RLIS$^i_{8a-c,e}$, of protons H_{3-8} and $H_{10,11}$, in **8a–c** and **8e** were plotted against RLIS$^i_{8d}$ of the corresponding protons in **8d.** As shown in Figure 2, a good linearity is clearly observed. This does mean that relative magnetic environments for each proton bearing on the basic carbon skeleton in one of the series of alcohols (**8a–e**) are quite similar to each other, without any assumption for the coordinated position of the shift reagent. Consequently, it may be deduced that the geometrical structure of these alcohols should be same as far as the syn or anti problem is concerned. Since R_1 and R_2 in the above general formulas provide a variety of groups, such as H, Me, or $-(CH_2)_3-$, the RLIS^i values for these protons were not treated in the first step of this treatment. The plots of H_{10} and H_{11} (methylene protons of the cyclopropane ring) in **8a** and **8b** are slightly deviated from the good linear line obtained by the above treatment. This minute difference might arise from the fact that the relative situation of these protons with H_2 in **8a** and **8b** would be somewhat dissimilar to the situation in the other alcohols, **8c–e.** Presumably the carbon skeleton of both **8a** and **8b** may be more easily modified by coordination of the shift reagent owing to less substitution of alkyl groups at C_1 and C_6. In other words, conformation of coordinating alcohols might be insignificantly different from each other.

Although we could not isolate a sufficient amount of both epimers in all the alcohol pairs in the present experiment, only **12a,** which is the epimer of **8a,** was obtained in a satisfactory degree of purity from the solvolysis of **1a.** The values of RLIS^i for the corresponding protons of this epimer were also plotted against RLIS$^i_{8d}$ as indicated in Figure 3. In this case the plots are markedly scattered and no linear relationship is observed contrary to the above. Since **12a** was characterized as an isomer of **8a** from the other experimental evidence, the geometrical series of this compound may be different from that of **8d.**

From these results it may be suggested that the relative relationship of RLIS^i is expected to be proportional among these geometrically analogous series of alcohols, even though the definite conformation is not clear or considerably *flexible.* The structural assignment by this relationship is based on the assumption that, in the same syn or anti isomeric series of alcohols (**8a–e**), both the distance, r_i, and the angle, θ_i, might be comparably varied with each proton relative to H_2 in these bicyclic alcohols. In the different epimeric series of alcohols, such relationship might be lost, since the relative situation for each proton should be dissimilar to the above. These are criteria of the present proposal to assign these 3,4-benzobicyclo[4.1.0]hept-3-en-2-ol derivatives to which series of geometric isomers.

The next step is determination of syn or anti geometry for one of the compounds **8a–e.** In order to distinguish the geometry for bicyclic secondary α-cyclopropylcarbinol, some of the following experimental values can be compared: chemical shifts of α-carbinyl proton,[11] coupling constants between α and its adjacent proton,[12] or relative reactivity of its esters in

Table II. Chemical Shift of α Proton and Spin–Spin Coupling Constant between α Proton and Its Adjacent Proton for 3,4-Benzobicyclo[4.1.0]hept-3-en-2-ol Systems

Compd	δ_a[a]	Compd	Registry no.	δ_s[a]	$\Delta\delta$[b]
8a	5.06 (J = 3 Hz)	**12a**		5.05 (J = 3 Hz)	−0.01
8b	5.02 (J = 4 Hz)	**12b**	64474-64-2	5.00 (J = 3 Hz)[c]	−0.02
8c	4.63				
8d	4.83[d]	**12d**	58692-29-8	5.04[d]	0.21[d]

[a] Chemical shifts for α proton are listed in δ (ppm) relative to tetramethylsilane. [b] $\Delta\delta = \delta_s - \delta_a$. [c] This value was observed in a mixture of isomeric alcohols. [d] Reference 3.

solvolysis.[13] In the present case, no decision could be made for the geometry of **8a, 8b, 8c, 12a,** and **12b** from both $\Delta\delta$ and J in Table II. As clearly shown in the previous paper, **8d** has been assigned as the anti epimer from the fact that the α proton of **8d** exhibits its signal at higher field than that of **12d** and that its *p*-nitrobenzoate (**1d**) solvolyzes slower than the epimeric isomer.[3a] Combining this assignment with the above linear correlation, the series of alcohols **8a–e** could be ascribed to the anti isomers. This may be one of the beneficial points in the present treatment of RLIS[i], when other procedures could not be employed for determining geometric relation. This method will be promising in application to the other systems.

Kinetic Studies. The rates of solvolysis of *p*-nitrobenzoates **1a–c** in 80% aqueous acetone were determined by titration of *p*-nitrobenzoic acid. The titration was carried out by employing an automatic titration instrument after quenching by anhydrous acetone in an ice bath. The results and the related values are summarized in Table III.

All four *p*-nitrobenzoates **1a–d** belong to the same anti series of the bicyclo[4.1.0]hept-3-en-2-yl alcohol, so that direct comparison can be made in these solvolyses. As shown from the substituent effect on the benzene ring of **1d,** its absolute value ($\rho = -2.11$) was exceptionally small among many secondary benzylic systems.[3b] The result, together with the other evidence, could be interpreted in terms of σ participation of the 1-bicyclo[3.1.0]hexyl group in **1d** rather than π conjugation.[3] Similar interpretation may be adapted to solvolysis of the other three esters (**1a–c**).

There are small differences in rate among these four esters, **1d** ≳ **1c** > **1b** > **1a.** The following discussion can be taken into account for the explanation. Owing to the steric repulsion of the nonbonded methyl groups, the ground state of **1c** might be destabilized compared with the other esters. Such destabilization decreases in the case of **1b,** resulting in slower rate. Along with a lesser degree of such repulsion, the above σ participation should be reduced especially in **1a,** since the methyl group is lacking at the 1 position of the bicyclo[4.1.0]-heptyl framework where a positive charge develops in the transition state. As a result, the above order or reactivity was observed in the present experiment.

The effect of substitution in the cyclopropyl ring on the rate of solvolysis of cyclopropylmethyl 3,5-dinitrobenzoates was investigated by Schleyer et al. They showed that the introduction of a methyl group at the C_2 position or a trimethylene group between the C_1 and C_2 position results in 10 or 300 times accelerative effect, respectively, in solvolysis.[14] As compared with these primary esters, the magnitude of the rate effects in the 3,4-benzobicyclo[4.1.0]hept-3-en-2-yl system was smaller (three or ten times, respectively). This result indicated that the extent of charge distribution to the cyclopropyl ring at the transition state must be small due to the secondary system, in which the positive charge is also spread in the aromatic ring. However, it is interesting to note that the alkyl substituent effect of the present system (**1a,b,d**) runs well parallel with the effect of Schleyer's system, although the degree decreased one tenth because of partial charge delocalization stated above.

Products Studies. It was confirmed that **8a–c,** the parent alcohols, are stable under the solvolytic conditions if 2,6-lutidine is present. The study on the kinetic solvolysis products of **1a–c** was carried out in 80% aqueous acetone in the presence of 2,6-lutidine. After about 10 half-lives, the products were extracted by usual workup process and analyzed by using NMR spectroscopy. Solvolyses of **1a** and **1c** gave rise to an almost pure sample, secondary alcohol **12a** and tertiary alcohol **13c,** respectively, but solvolysis of **1b** produced a mixture of the secondary and the tertiary alcohols (**12b** and **13b**). The pure sample of **13b** was obtained by acid-catalyzed isomerization of **8b.** These alcohols were assigned by comparison of the NMR spectrum with that of the authentic samples, except **12b.**[15] The product distributions were determined from the ratio of integral intensity for the characteristic signals (α or vinylic protons) in the NMR spectra. The results are summarized in Table IV. The primary alcohols **14a–c** could not be detected in any case.

The product distributions in solvolysis may depend upon a number of effects, for instance the charge density and the

Table III. Rates of Solvolysis of *p*-Nitrobenzoates (1a, 1b, 1c, and 1d) in 80% Aqueous Acetone

Registry no.	Compd	Temp, °C[a]	10^5k, s^{-1} [b]	$\Delta H^{\ddagger}$, kcal/mol[c]	$\Delta S^{\ddagger}$, eu[c]	k_{rel}
64414-43-3	**1a**	55.0	28.6 ± 1.5			
		45.0	8.91 ± 0.27			
		35.0	2.53 ± 0.09			
		25.0	0.667[e]	23.9	−2.0	1.0
64414-44-4	**1b**	45.0	22.6 ± 0.8			
		35.0	7.38 ± 0.27			
		25.0	2.16 ± 0.12	21.1	−9.1	3.2
64414-45-5	**1c**	45.0	89.6 ± 5.0			
		35.0	27.0 ± 1.5			
		25.0	6.96 ± 0.12	22.7	−1.4	10.4
58717-77-4	**1d**	40.0	48.6 ± 0.3[d]			
		30.0	15.1 ± 0.4[d]			
		25.0	8.60 ± 0.5[d,f]	20.6[d]	−8.0[d]	12.9

[a] ±0.03 °C. [b] Kinetic plots were linear to 75% conversion (2 half-lives). [c] Calculated from $\Delta H^{\ddagger} = R(T_1T_2/T_2 - T_1)\ln(T_1k_2/T_2k_1)$, $\Delta S^{\ddagger} = R\ln(k_ih/kT_i) \Delta H^{\ddagger}/T_i$: T_i, absolute temperature; h, Planck's constant; k, Boltzmann's constant. [d] Reference 3. [e] Calculated from $\Delta H^{\ddagger}$. [f] The rate, which was measured by using an automatic titrating apparatus, was $k = (8.81 \pm 0.11) \times 10^{-5}$ s^{-1} at 25.0 °C.

Table IV. Product Distributions of Solvolysis of 1a-d in the Presence of 2,6-Lutidine

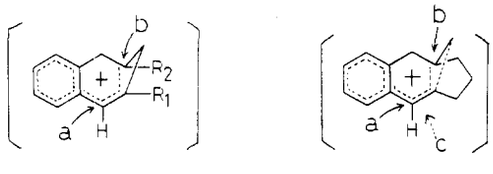
p-Nitrobenzoate 1a-d	Product, %[a] 8a-d	12a-d	13a-d	14a-d
1a (R_1 = H; R_2 = H)	0	~100	0	0
1b (R_1 = H; R_2 = Me)	0	42	58	0
1c (R_1 = Me; R_2 = Me)	0	0	~100	0
1d[b] (R_1, R_2 = -$(CH_2)_3$-)	13	42	45	0

[a] The product distribution was determined by the NMR spectrum and its integral intensity for the α hydrogen of 8a-d and 12a-d or vinyl hydrogen of 13a-d. [b] Reference 3.

circumstances of the carbon atoms attacked nucleophilically by solvent. The *anti*-3,4-benzobicyclo[4.1.0]heptenyl system (**1d**) was solvolyzed not to afford stereoelectronically favorable primary alcohols **14d** (backside participation of the σ bond in the cyclopropane ring), but to produce secondary (**8d** and **12d**) and tertiary alcohols (**13d**). Solvolysis of **1a** and **1b** predominantly gave rise to *syn*-alcohols **12a** and **12b** in contrast with the products obtained from **1d.**

These results might be explained on the basis of the formation of a considerably stable (long lifetime) intermediate in which the positive charge would be highly delocalized not only on the aromatic part but also on the cyclopropane ring, as in the homonaphthalenium cation (**15a-c**). In aqueous media, this intermediate carbocation (**15a-c**) might undergo discharge of water from sides a and b in the formula (**15a-c**) to be converted into the final products.

In the bicyclo[3.1.0]hex-2-yl or bicyclo[4.1.0]hept-2-yl systems in the absence of an aromatic ring adjacent to the reaction center, each solvolysis of these *p*-nitrobenzoates gave rise to a mixture of syn and anti isomer along with the other alcohol.[16] These results indicate that there should be little difference, both electrical and steric, between exo and endo attack of a nucleophile to the cationic intermediate. Since the solvolysis products of **1a** and **1b** contained secondary cyclopropylphenylmethyl alcohol with only syn-type geometry, it is evident that the intermediate may be described as a homonaphthalenium ion in which nucleophilic attack from the exo side (c) is severely hindered by the highly delocalized electrons. However in **1d,** the positive charge might be further delocalized into the primary carbon (C_7) in the intermediate ion **15d** because of the scissors effect by the trimethylene group or the lower stability of bridgehead cation. Furthermore, **15d** would make it possible for the solvent to attack from the side c in the formula to afford the anti secondary alcohol **8d.**[3] The kinetic result was also compatible with the product distribution.



15a-c

15d

Experimental Section

All the melting points are uncorrected. Infrared spectra were recorded with a Hitachi 215 grating IR spectrophotometer. NMR measurements were carried out on a Varian T-60 instrument using tetramethylsilane as an internal reference.

3,4-Benzobicyclo[4.1.0]hept-3-en-2-one (**7a**) was prepared by the modified method of the literature.[4] The details of the synthesis of the 3,4-benzotricyclo[4.3.1.$0^{2,6}$]hept-3-en-2-yl series (**1d, 8d, 8e**) were previously reported.[3] The synthesis of the 6-methyl- and 1,6-dimethyl-3,4-benzobicyclo[4.1.0]hept-3-en-2-yl series is reported in detail in this paper.

2-Benzyl-2-methylsuccinic Acid. To the solution of 27.5 g (0.12 mol) of ethyl 1-methyl-2-phenylethylidenecyanoacetate (**9**)[17] in 60 mL of methanol was added an aqueous solution (35 mL) of potassium cyanide (9.0 g, 0.14 mol) with stirring and cooling by water for several minutes; then the mixture was acidified with diluted hydrochloric acid. The dicyano ester **11b** was obtained by ether extraction. Without further purification a mixture of **11b,** concentrated hydrochloric acid (300 mL), and glacial acetic acid (150 mL) was heated under reflux with vigorous stirring for 20 h. The crude 2-benzyl-2-methylsuccinic acid separated as crystals when the reaction mixture was cooled. The pure sample (15.0 g) was recrystallized from ethanol, mp 143–145 °C (lit. 144 °C),[18] in 57% yield.

3-Carboxy-3-methyl-1-tetralone (2b). A solution of 14.0 g (0.063 mol) of the above dicarboxylic acid dissolved in 140 mL of concentrated sulfuric acid was stirred for 1 day at room temperature. After being poured onto 1.4 kg of crushed ice, the crude keto acid **2b** was obtained by filtration. The product was recrystallized from ethanol to give a pure sample: mp 166–169 °C (lit. 168–170 °C);[5] 10.5 g (82% yield); IR (Nujol) 1720 (CO_2H), 1665 (CO), 1185, 900, 755 cm^{-1}.

Ethyl 2,3-Dicyano-2,3-dimethyl-4-phenylbutyrate (11c). To the solution of **9** (25.6 g, 0.11 mol) in 80 mL of 95% ethanol was added an aqueous solution (39 mL) of potassium cyanide (12.8 g, 0.2 mol) with stirring. After several minutes the solution of methyl iodide (31.2 g, 0.22 mol) in 60 mL of 95% ethanol was added to the above mixture and the stirring was continued for 16 h at room temperature. The distillation of extract gave 22.8 g of dicyano ester **11c** in 76% yield, bp 180–182 °C (3 mm), and then the oil was gradually solidified at room temperature: mp 61–74 °C; IR (Nujol) 2240 (CN), 1745 (CO_2Et) cm^{-1}; NMR ($CDCl_3$) δ 7.36 (s, 5 H, aromatic), 4.35 (q, J = 7.5 Hz, 2 H, methylene), 3.15 and 2.81 (ABq, J = 13.5 Hz, 2 H, benzyl), 1.92 (s, 3 H, methyl), 1.40 (s, 3 H, methyl), 1.35 (t, J = 7.5 Hz, 3 H, methyl).

3-Carboxy-2,3-dimethyl-1-tetralone (2c). A mixture of **11c** (10 g, 0.037 mol), concentrated sulfuric acid (50 g), glacial acetic acid (20 g), and water (9 mL) was heated at 90 °C for 3 h and at 110 °C for 17 h. After the reaction mixture was poured onto crushed ice, 2.3 g of a mixture of geometric isomers (**2c**) was obtained by ordinary workup process in 30% yield. Recrystallization from benzene gave rise to a pure sample: mp 141–143 °C (main product); IR (Nujol) 1700 (CO_2H), 1690 (CO) cm^{-1}; NMR ($CDCl_3$) δ 10.68 (s, 1 H, carboxylic), 7.1–7.7 (m, 3 H, aromatic), 7.9–8.2 (m, 1 H, aromatic), 2.96 and 3.52 (ABq, J = 16.5 Hz, 2 H, benzyl), 3.10 (q, J = 7.5 Hz, methine), 1.20 (d, J = 7.5 Hz, 3 H, methyl), 1.19 (s, 3 H, methyl).

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.16; H, 6.36.

1-Hydroxy-3-hydroxymethyl-3-methyltetraline (4b). The keto ester **3b** (mp 62–63 °C from benzene) was prepared from 13.7 g (0.067 mol) of **2b** and diazomethane in ether in good yield. Spectral data for **3b:** IR (Nujol) 1715 (CO_2Me), 1680 (CO), 1215, 1110, 770 cm^{-1}; NMR ($CDCl_3$) δ 8.2–7.2 (m, 4 H, aromatic), 3.65 (s, 3 H, methyl), 2.93 and 3.33 (ABq, J = 11 Hz, 2 H, methylene), 2.60 and 3.10 (ABq, J = 17 Hz, 2 H, benzyl), 1.40 (s, 3 H, methyl).

Reduction of 6.5 g (0.03 mol) of **3b** with 3.9 g of $LiAlH_4$ in 100 mL of dry ether was carried out by the ordinary method. Recrystallization from chloroform gave a colorless solid, mp 132–133 °C, **4b** (2.5 g, 43%) and oily residue (2.8 g, 46%) which seemed to be an epimeric mixture of **4b** judging from spectral data. Spectral data for **4b:** IR (Nujol) 3220 (OH), 1045, 1020, 745 cm^{-1}; NMR (C_5H_5N) δ 5.33 (d d, J = 6, 10 Hz, 1 H, α hydrogen), 3.70 (s, 3 H, methyl), 2.93 and 2.63 (ABq, J = 16 Hz, 2 H, benzyl), 2.77 (d, ABq, J = 13, 6 Hz, 1 H, methylene), 1.87 (d, ABq, J = 13, 10 Hz, 1 H, methylene), 1.60 (s, 3 H, methyl) and other signals for aromatic and hydroxy hydrogens: mass m/e 192 ($C_{12}H_{16}O_2$).

1-Hydroxy-2,3-dimethyl-3-hydroxymethyltetraline (4c). The keto ester **3c** was prepared from 9.0 g (0.041 mol) of **2c** and diazomethane in ether in 98% yield. Spectral data for **3c:** IR (neat) 1730 (CO_2Me), 1690 (CO), 1600, 1220, 1100, 740 cm^{-1}; NMR ($CDCl_3$) δ 8.1–7.9 (m, 1 H, aromatic), 7.5–7.1 (m, 3 H, aromatic), 3.68 (s, 3 H, methyl), 3.47 and 2.93 (ABq, J = 16.5 Hz, 2 H, benzyl), 2.7 (q, J = 7.5 Hz, methine), 1.20 (s, 3 H, methyl), 1.17 (d, J = 7.5 Hz, 3 H, methyl).

Reduction of **3c** (5.9 g, 0.07 mol) with $LiAlH_4$ (4.0 g) yielded **4c** (1.4 g, 25% yield) and an oily product (3.3 g, 59% yield) which seemed to be a mixture of **4c** and its epimeric isomer. The crude **4c** purified by

recrystallization from chloroform: mp 149–151 °C; IR (Nujol) 3300 (OH), 1030, 1010, 740 cm^{-1}; NMR (C_5H_5N) δ 5.31 (d, J = 6 Hz, 1 H, α hydrogen), 3.70 (s, 2 H, oxymethyl), 2.89 and 2.75 (ABq, J = 16.5 Hz, 2 H, benzyl), 2.50 (m, 1 H, methine), 1.28 (s, 3 H, methyl), 1.27 (d, J = 7 Hz, 3 H, methyl) and other signals; mass spectrum m/e 206 ($C_{13}H_{18}O_2$).

6-Methyl-3,4-benzobicyclo[4.1.0]hept-3-en-2-one (7b). A suspension of 4.03 g (0.021 mol) of solid diol **4b** and 12 g of active MnO_2 in 450 mL of dry benzene was stirred at room temperature for 30 h. The product **5b** (3.72 g) was obtained by filtration of the reagent and evaporation of the solvent. Spectral data for crude **5b:** IR (neat) 3450 (OH), 1680 (CO), 1600, 1290, 1040, 760 cm^{-1}; NMR ($CDCl_3$) δ 8.2–7.1 (m, 4 H, aromatic), 3.48 (s, 2 H, oxymethyl), 3.13 and 2.77 (ABq, J = 17 Hz, 2 H, benzyl), 2.46 and 2.69 (ABq, J = 17 Hz, 2 H, methylene), 2.03 (br s, 1 H, hydroxyl), 1.03 (s, 3 H, methyl).

The pyridine solution (80 mL) of the crude keto alcohol **5b** (4.0 g) was added into the same solution (30 mL) of p-toluenesulfonyl chloride (12.0 g) under cooling in an ice–water bath. The mixture was then stirred at room temperature for 24 h. Ordinary extraction gave crude tosylate **6b** (7.2 g): IR (Nujol) 1685 (CO), 1600, 1350 (SO_2), 1170 (SO_2), 980, 960 cm^{-1}; NMR ($CDCl_3$) δ 8.2–7.7 (m, 1 H, aromatic), 7.5–7.2 (m, 3 H, aromatic), 7.77 and 7.30 (ABq, J = 8 Hz, 4 H, aromatic), 3.83 (s, 2 H, oxymethyl), 3.10 and 2.70 (ABq, J = 16 Hz, 2 H, benzyl), 2.63 and 2.30 (ABq, J = 16 Hz, 2 H, methylene), 2.47 (s, 3 H, methyl), 1.03 (s, 3 H, methyl).

The above tosylate (**6b**) solution dissolved in dioxane (200 mL) was added to methanolic potassium hydroxide (10 g of KOH in 100 mL of MeOH) solution. The mixture was stirred at room temperature for 5 h and ordinary workup gave rise to a colorless oil (**7b,** 2.4 g) in 66% yield from **4c.** Mass spectrum for **7b:** m/e 172 ($C_{12}H_{12}O$), 157 ($M^+ - 15$), 129 ($M^+ - 43$). NMR and IR data are shown in Table V.[19]

1,6-Dimethyl-3,4-benzobicyclo[4.1.0]hept-3-en-2-one (7c). By a method similar to that used in the preparation of **7b, 7c** (oil, 417 mg) was obtained from **4c** (1.43 g). Spectral data for keto alcohol **5c:** IR (neat) 3450 (OH), 1675 (CO), 1030, 740 cm^{-1}; NMR ($CDCl_3$) δ 8.1–7.9 (1 H, m, aromatic), 7.7–7.1 (m, 3 H, aromatic), 3.61 and 3.43 (ABq, J = 10.5 Hz, 2 H, oxymethyl), 3.31 and 2.71 (ABq, J = 16 Hz, 2 H, benzyl), 2.81 (q, J = 7 Hz, 1 H, methine), 2.1 (br s, 1 H, hydroxyl), 1.20 (d, J = 7 Hz, 3 H, methyl), 0.83 (s, 3 H, methyl). Spectral data for tosylate **6c:** mp 129–131 °C; IR (Nujol) 1675 (CO), 1350 (SO_2), 1165 (SO_2), 960, 840 cm^{-1}; NMR ($CDCl_3$) δ 8.2–7.8 (m, 1 H, aromatic), 7.5–7.1 (m, 3 H, aromatic), 7.87 and 7.37 (ABq, J = 8 Hz, 4 H, aromatic), 3.43 and 3.61 (ABq, J = 10.5 Hz, 2 H, oxymethyl), 3.31 and 2.71 (ABq, J = 15.8 Hz, 2 H, benzyl), 2.45 (s, 3 H, methyl), 2.81 (q, J = 7.0 Hz, 1 H, methine), 1.20 (d, J = 7.0 Hz, 3 H, methyl), 0.83 (s, 3 H, methyl). Mass spectrum for **7c:** m/e 186 ($C_{13}H_{14}O$), 171 ($M^+ - 15$), 143 ($M^+ - 43$). NMR and IR data are shown in Table V.[19]

Reduction of the 3,4-Benzobicyclo[4.1.0]hept-3-en-2-one derivatives (7a). 3,4-Benzobicyclo[4.1.0]hept-3-en-2-ol (8a). To a stirred suspension of 420 mg (11 mmol) of $LiAlH_4$ in 30 mL of dry ether was added a solution of 338 mg (2.1 mmol) of **7a**[4] in 40 mL of ether. The mixture was stirred for 1 h at 0 °C and for 20 h at room temperature before the excess hydride was carefully decomposed with 0.5 mL of water. The ether layer was decanted and the precipitate was washed several times with ether. The combined organic layer was dried over anhydrous K_2CO_3. The solvent was removed under reduced pressure to yield 305 mg of a colorless solid. Recrystallization from n-pentane gave a pure product (**8a;** 284 mg, 84%): mp 81.5–82 °C (lit.[4] mp 85–86 °C); IR (Nujol) 3300 (OH), 1030, 730 cm^{-1}; NMR data are compiled in Table I.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.22; H, 7.49.

6-Methyl-3,4-benzobicyclo[4.1.0]hept-3-en-2-ol (8b). Reduction of **7b** (475 mg) with $LiAlH_4$ (550 mg) yielded **8b** (90%), which was recrystallized from n-pentane to give a pure sample: mp 88–90 °C; IR (Nujol) 3350 (OH), 1020, 740 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.43; H, 8.07.

3,4-Benzo-1,6-dimethylbicyclo[4.1.0]hept-3-en-2-ol (8c). Reduction of **7c** (205 mg, 1.1 mmol) with $LiAlH_4$ (210 mg) yielded **8c** (mp 94–95 °C from n-pentane, 133 mg, 65%): IR (Nujol) 3350 (OH), 1030, 740 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.57; H, 8.48.

Europium Shift Reagents Studies. A sample of 30–60 mg of the alcohol (**8a–e** and **12a**) was dissolved in 0.4–0.6 mL of deuteriochloroform and the spectrum was recorded at 1500-Hz sweep width. A weighed sample of commercially available $Eu(dpm)_3$ (from the Wako Co.) was successively dissolved in a deuteriochloroform solution of the alcohol and then the NMR spectrum was measured immediately. Shifts were plotted against the molarity of $Eu(dpm)_3$ (see Figure 1 for the plots in the case of **8d** as one example). The calculation of each $(\Delta Eu)_i$ value,[8] which is defined as the difference between the chemical shift of a given proton, H_i, measured without the reagent and the shifts with the equimolar reagent, was carried out for definite protons and the relative induced shifts, $RLIS^i = (\Delta Eu)_i/(\Delta Eu)_2$, were thus obtained. These values were shown in Table I.

3,4-Benzobicyclo[4.1.0]hept-3-en-2-yl *p*-Nitrobenzoate (1a). The p-nitrobenzoate **1a** was prepared by allowing 367 mg (2.3 mmol) of **8a** to react with 630 mg (3.4 mmol) of p-nitrobenzoyl chloride in 10 mL of dry pyridine at 5 °C for 1 day. The product was extracted with ether and the organic layer was washed with water, 1 M hydrochloric acid, 5% aqueous sodium hydrogen carbonate, and water. The ether layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. A light yellow solid was recrystallized from n-hexane to give **1a** (150 mg, 50%): mp 110–111 °C. NMR and IR data of **1a–c** are summarized in Table V.[19]

Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.70; H, 4.99; N, 4.07.

3,4-Benzo-6-methylbicyclo[4.1.0]hept-3-en-2-yl *p*-Nitrobenzoate (1b) and 3,4-Benzo-1,6-dimethylbicyclo[4.1.0]hept-3-en-2-yl *p*-Nitrobenzoate (1c). By a method similar to that used in the preparation of **1a, 1b** (mp 106.5–107.5 °C, 67%) and **1c** (mp 109.5–110 °C, 72%) were obtained.

Anal. Calcd for $C_{19}H_{17}O_4N$ (**1b**): C, 70.57; H, 5.30; N, 4.33. Found: C, 70.28; H, 5.30; N, 4.41.

Anal. Calcd for $C_{20}H_{19}O_4N$ (**1c**): C, 71.20; H, 5.68; N, 4.15. Found: C, 70.90; H, 5.76; N, 4.16.

General Kinetic Procedures. For each run approximately 100 mg of p-nitrobenzoate was weighed into a 100-mL volumetric flask and dissolved in 80% aqueous acetone; the 80% aqueous acetone mixture was prepared by mixing 80 mL of dry acetone with 20 mL of distilled water. Rates at 25.0 ± 0.03 °C were measured by quenching 5.00-mL aliquots in 25 mL of dry acetone and immediately titrating with a standard aqueous sodium hydroxide (0.01 M) using an automatic titrating apparatus (Hitachi-Horiba automatic titrator using glass electrode). Rates at the other temperatures (35.0, 45.0, 55.0 °C in accuracy, ±0.03 °C) were measured by means of ampules. In each case, 100 mL of ~0.003 M 80% aqueous acetone solution of the p-nitrobenzoate was prepared, and 11-mL portions were sealed into ampules. A set of ampules was immersed in a water bath at the appropriate temperature. After allowing 5–10 min for temperature equilibration, the zero point was taken. The ampules were removed from the bath and immersed into ice–water to stop the solvolyses. After cooling to 0 °C, a 5.00-mL portion of the solution was removed and titrated with aqueous sodium hydroxide in the same method as described above. Kinetic plots were linear to 75% conversion and reported values are the average of two separate runs (Table III). In all cases infinite titers were measured after ~10 half-lives and 95–105% of theoretical p-nitrobenzoic acid was removed.

Treatment of 8a–c with *p*-Nitrobenzoic Acid. A solution of 200 mg (1.15 mmol) of **8b** and 196 mg (1.15 mmol) of p-nitrobenzoic acid dissolved in 100 mL of 80% aqueous acetone was warmed at 45 °C for 2 days. Into the solution was added 190 mg (2.2 mmol) of $NaHCO_3$ and most of the acetone was removed under reduced pressure followed by extraction with ether, washing the ether layer with water, and drying it over anhydrous K_2CO_3. The solvent was removed at reduced pressure to give 165 mg (82%) of a yellow oil. Spectral data showed that the oil was 1-methyl-3,4-benzohepta-3,5-dien-1-ol (**13b**). Spectral data for **13b:** IR (CCl_4) 3450 (OH), 1100 cm^{-1}; NMR ($CDCl_3$) δ 7.12 (s, 4 H, aromatic), 6.51 (d, J = 11 Hz, 1 H, vinyl), 5.86 (dt, J = 11 and 5.5 Hz, 1 H, vinyl), 2.79 (s, 2 H, benzyl), 2.32 (d, J = 5.5 Hz, 2 H, methylene), 2.22 (s, 1 H, hydroxyl), 1.27 (s, 3 H, methyl); mass m/e 174 ($C_{12}H_{14}O$), 131 ($M^+ - 43$).

By the method similar to that used in the reaction of **8b,** 1,6-dimethyl-3,4-benzohept-3,5-dien-1-ol (**13c,** an oily product, 35 mg) was obtained from **8c** (40 mg). Spectral data for **13c:** IR (CCl_4) 3400 (OH), 1100 cm^{-1}; NMR ($CDCl_3$) δ 7.23 (s, 4H, aromatic), 6.47 (br s, 1H, vinyl), 2.79 (s, 2H, benzyl), 2.15 (s, 2H, methylene), 2.04 (s, 3H, methyl), 1.70 (s, 1H, hydroxyl), 1.37 (s, 3 H, methyl); mass m/e 188 ($C_{13}H_{16}O$), 145 ($M^+ - 43$).

Under the same conditions, **8a** was not isomerized appreciably after 1 month.

Preparative Solvolysis of 1a–c. A solution of 87 mg (0.28 mmol) of **1a** and 0.15 mL (~1.4 mmol) of 2,6-lutidine in 100 mL of 80% aqueous acetone was heated at 35 °C for 80 h (~10 half-lives). The solution was concentrated under reduced pressure, 200 mL of water was added, and the resulting suspension was extracted with ether. The combined ether extracts were washed with water and dried over anhydrous K_2CO_3. Removing the solvent under reduced pressure gave

39 mg (85%) of a light yellow oil. It was found from its NMR spectrum that the oily residue consisted almost entirely of one component, the epimer of **8a**, *syn*-3,4-benzobicyclo[4.1.0]hept-3-en-2-ol (**12a**): IR (neat) 3350 (OH), 1030, 980, 740 cm^{-1}; NMR is shown in Table I.

The other esters (**1b** and **1c**) were solvolyzed by the method similar to that used in solvolysis of **1a** and the product distribution was determined by the NMR spectrum and its integral intensity for α hydrogen or vinyl hydrogen. The results was shown in Table IV. The NMR spectrum of the epimer of **8b** was assumed from that of products **12b** and **13b**. NMR spectrum for **12b** ($CDCl_3$): δ 7.12 (s, 4 H, aromatic), 5.00 (d, J = 3 Hz, 1 H, α hydrogen), 3.20 and 2.88 (ABq, J = 16 Hz, 2 H, benzyl), 1.30 (s, 3 H, methyl), 1.48–0 (m, 3 H, cyclopropyl), and the other signals.

A mixture containing 100 mg of **8b** (0.58 mmol), 300 mg (2.9 mmol) of 2,6-lutidine, and 100 mg (0.6 mmol) of *p*-nitrobenzoic acid in 100 mL of 80% aqueous acetone was heated at 45 °C for 1 day. After usual workup, 93 mg of colorless solid was obtained. A comparison of the NMR spectrum before and after heating showed that **8b** was stable to the reaction conditions. Similar treatment of **8a** and **8c** gave the same results.

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Registry No.—*cis*-**2b**, 64425-83-8; *trans*-**2b**, 64414-48-8; **2c**, 64425-29-2; **3b**, 64414-49-9; **3c**, 64414-50-2; *cis*-**4b**, 64414-51-3; *trans*-**4b**, 64414-52-4; **4c**, 64414-53-5; **5b**, 64414-54-6; **5c**, 64414-55-7; **6b**, 64414-56-8; **6c**, 64414-36-4; **7a**, 27346-16-3; **7b**, 64414-46-6; **7c**, 64414-47-7; **9**, 7148-59-6; **11b**, 29840-37-7; **11c**, 64414-37-5; **13b**, 64414-38-6; **13c**, 64414-39-7; 2-benzyl-2-methylsuccinic acid, 32980-47-5; *p*-toluenesulfonyl chloride, 98-59-9; *p*-nitrobenzoyl chloride, 122-04-3; *p*-nitrobenzoic acid, 62-23-7; 2,6-lutidine, 108-48-5.

Supplementary Material Available: infrared and proton NMR data for **1a–c** and **7a–c** (Table V) (4 pages). Ordering information is given on any current masthead page.

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A Carbon-13 Nuclear Magnetic Resonance Investigation of Substituted 4-X-2,6-Dinitroanisoles and Related Meisenheimer 1,1-Complexes

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Carbon-13 NMR chemical shifts for various substituted 4-X-2,6-dinitroanisoles **1** (X = SO_2CF_3, NO_2, CN, SO_2CH_3, COC_6H_5, CF_3, Cl, H) and related *gem*-dimethoxyl adducts **2** (X = SO_2CF_3, NO_2, CN, SO_2CH_3, COC_6H_5, CF_3) are reported. In the case of anisoles **1** the deviations from additivity of substituent effects observed for $C_{2,6}$ and C_1 together with the absence of a deshielding of C_4 indicate an inhibition of resonance of the *o*-nitro groups. Good linear correlations with the Swain and Lupton reactivity parameters are observed for δ_{C_1}, $^1J_{^{13}C_7H}$, $^1J_{C_3H_3}$ in these tetrasubstituted benzenes. ^{13}C chemical shifts measured for adducts **2** reveal an increase in the negative charge located at $C_{2,6}$ and C_4, but a decrease at $C_{3,5}$, in agreement with SCFMO calculations. However, no relation exists between these shifts and the known thermodynamic stability of adducts **2**.

The reaction of methoxide ions with substituted 4-X-2,6-dinitroanisoles **1** usually gives the *gem*-dimethoxyl 1,1-complexes **2** as the stable products.[2] From thermodynamic and kinetic studies on the one hand[2-6] and crystallographic and ^1H NMR studies on the other hand,[2-7,11] it appears that the electron-withdrawing ability of the ring substituents and the release of steric compression which exists between the methoxyl group and the adjacent nitro groups in the parent ethers **1** are two major factors responsible for the stability of complexes **2**. Since they are known to depend on steric and charge distribution effects, ^{13}C chemical shifts could be reasonably expected to yield further information on both of these

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