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Solvolysis of Sterically Compressed *anti*-7-Norbornenyl 3,5-Dinitrobenzoates. Evidence for the Absence of Enhanced Ionic Stabilization in Unsymmetrical (2 + 2 + 0) Laticyclic Cations

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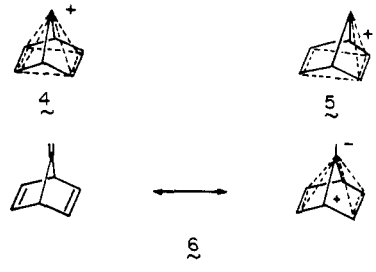
Abstract: The five dinitrobenzoates of generalized structure **24**, prepared according to Scheme I, show solvolysis rates in 80% aqueous acetone which differ by less than a factor of 5 at 114°. The dimethanonaphthadienyl system **10**, previously studied by Allred and Hinshaw, ionizes at a comparable rate. The lack of accelerating influences by the laticyclically positioned double bond, benzene ring, or oxygen atom shows that extended ionic stabilization above that associated with the *anti*-7-norbornenyl moiety is not operative. The products in all cases are the derived alcohols, and these are isolated in >95% yield. Alkyl–oxygen cleavage was established by suitable methanol reactions in one example. The inability of the remote bridges in **10** and **24** to interact during ionization contrasts with the high level of neighboring-group involvement previously observed for the structurally similar brosylates **35–37**. These major differences may derive from the prevailing wide variations in electron-deficiency demand. In the case of **36** and **37**, there is considerable need for laticyclic charge delocalization of the 7-norbornyl cation, and customary neighboring-group influences are manifested. For **10** and **24**, homoaromatic stabilization is appreciable and electron demand is very low such that neighboring-group involvement ceases, and the rate ratios are effectively leveled.

The very low level of solvolytic reactivity associated with 7-norbornyl derivatives,[1] perhaps best reflected in the enormous electron demand ($\rho = -5.64$) of the developing cation center,[2] has for at least a decade been thought to arise chiefly because of energetically unfavorable changes in angle strain upon ionization.[3] The recent theoretical study by Hoffmann and Heilbronner of the 7-norbornyl cation (**1**) has, however, unveiled the alternative possibility that the bicyclo[2.2.1]heptane skeleton with its structurally rigid-boat six-membered ring probably has a symmetry-enforced destabilizing interaction between the C_7 2p orbital and the high-lying cyclohexane σ orbitals.[4] Introduction of a double bond to arrive at the *anti*-7-norbornenyl system has a pronounced effect on the relative ease of ionization, the rate enhancement gained being on the order of 10^{11}.[2a,5] Significantly, interaction of the C_2C_3 π orbital with the vacant orbital at C_7 now permits two-electron delocalization over three centers (cf. **2**) and partially offsets some of the positive charge density at this reaction site.[6] This bishomocyclopropenyl cation interaction leads to approximately 15 kcal/mol of stabilization energy at 25°.[7] An endo-cyclopropane ring in the 2,3 position (**3**) stabilizes positive charge at C_7 to a larger extent than a double bond at the same position,[8] presumably because the vacant C_7 orbital is capable of greater conjugative (trishomoaromatic) interaction with the symmetric e_s Walsh orbital of the cyclopropane moiety than with the π_a orbital of the double bond at the same site.[9] When the double bond becomes part of an aromatic system, the ΔE_π due to bishomoaromatic delocalization is diminished in comparison to **2**.[10,11]

1 **2** **3**

The introduction of a second double bond into the norbornane framework causes a further rate enhancement for ionization at C_7 of 10^3 relative to the already anchimerically accelerated *anti*-7-norbornenyl derivative.[12] The additional ~4.1 kcal/mol stabilization had been initially attributed to the favorable involvement of the double bonds as in **4**.[7] However, because the 7-norbornadienyl cation is now recognized to adopt a distorted geometry more closely resembling **5** than **4**,[13] it would seem that enhanced homoaromatic interaction is of major consequence in the stabilization of this "bicycloaromatic"[14] system. Or, as viewed by Goldstein and Hoffmann,[15] one pericyclic interaction (of the bishomoaromatic type) is favored at the expense of the other [longicyclic (2 + 2 + 0) interaction]. In any event, since the barrier to bridge flipping in **5** is greater than 19.6 kcal/mol at 45°,[13] stabilization of the *symmetrical* (C_{2v}) 7-norbornadienyl cation (**4**) must be quite small and may even be zero.[16] Nevertheless, the exceptional stability of **5**[17] is undoubtedly a function of the spatial orientation and proximity of the π orbitals such that some measurable degree of effective overlap does operate. A perhaps comparable interaction between two vinyl bridges and a C_7 p orbital within a bicyclo[2.2.1]heptyl framework has also been discovered for triene **6**,[18,19] the importance of dipolar ground-state contributions being revealed by its substantial dipole

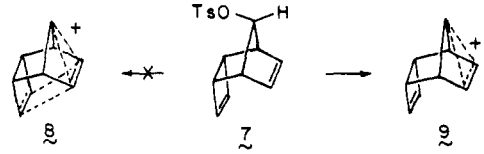


4 **5**

6

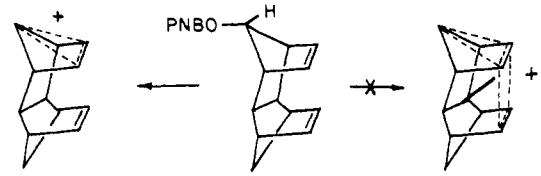
moment (negative terminus at C_8), ^1H NMR and ^{13}C NMR chemical shifts (excessive shielding of C_8 and the two attached protons), photoelectron spectrum, and reactivity toward such electrophiles as chlorosulfonyl isocyanate.

Because the symmetrical 7-norbornadienyl cation is so constructed that the closest possible distance between two overlapping π bridges and the C_7 p orbital exists, **4** should be the ion par excellence as concerns maximum "through-space" stabilization. Yet it fails to exhibit this property and is in fact some 20 kcal less stable than **5.** The question may now be raised whether longicyclic stabilization as in **4** or the closely related unsymmetrical laticyclic stabilization (vide infra) will ever gain practical importance in any system. Rather remarkably, far less attention has been accorded to ionic systems endowed with laticyclic topologies composed of more than two ribbons,[15] despite the extensive structural variations possible and the inherent novelty of such species. Quite recent work by Diaz, Harris, and Winstein[20] has shown the cyclobutene double bond in **7** to be too far removed for effective laticyclic participation during ionization at C_7 (cf. **8**), despite the recognized ability of the system to undergo ($_\pi 2 + _\pi 2$) photocyclization.[21] The sixfold greater solvolytic reactivity of **7** relative to *anti*-7-norbornenyl tosylate accords with the belief that homoconjugative longicyclic interaction as in **9** continues as the overriding anchimeric influence.



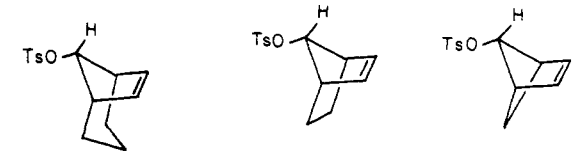
8 7 9

The rate data gained from solvolytic studies of the appreciably more sterically hindered *p*-nitrobenzoate **10** are such that Allred and Hinshaw were prompted to conclude on the basis of kinetic comparisons (k(**10**)/k(*anti*-7-norbornenyl-OPNB) $\approx 10^3$) that this laticyclic π-orbital arrangement was the source of the largest driving force to ionization yet discovered.[22] Enhanced ionic stabilization was presumed and attributed to extended charge delocalization epitomized by nonclassical ion **12.** In view of the above arguments and the dearth of experimental data on relevant model compounds, this theoretical interpretation must be viewed as less than unambiguous. It was of obvious importance to establish whether the approximately equal solvolysis rates of 7-norbornadienyl-OPNB and **10** were in fact due to extend-



11 10 12

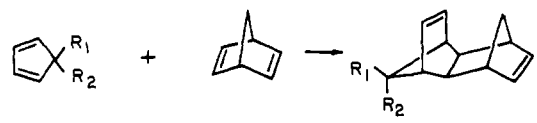
ed charge delocalization as in **5** and **12,** or whether the demonstrably greater ease with which **10** (compared with *anti*-7-norbornenyl-OPNB) reaches the ionization transition state is the result of ca. 4 kcal/mol of ground-state destabilization in **10.** Because the effectiveness of bishomoaromatic π participation in the bicyclo[x.2.1] series seems to be a sensitive function of puckering of the five ring, e.g., **13–15,**[23,24] comparable or even greater effects by more subtle strain influences could be anticipated but remained untested. Were the latter state of affairs prevalent, no reason would exist to invoke laticyclic participation as in **12.** Rather, the bishomocyclopropenyl cation interaction found in **11** would serve adequately to explain the kinetic findings. We now detail evidence which demonstrates convincingly that the enhanced solvolytic reactivity of **10** need not be attributed to laticyclic stabilization arising from involvement of the more remote etheno bridge as in **12,**[26] despite the theoretical attractiveness of the concept.[15]



13 14 15

k_{rel}^{25} 2×10^8 10^{11} 5×10^{14}

Synthetic Considerations. Whereas norbornadiene undergoes cycloaddition with variously substituted cyclopentadienes stereospecifically to give endo,exo adducts such as **16,**[27] the comparable Diels–Alder reaction of 7,7-disubstituted norbornadienes exhibits equally high stereospecificity but *in the opposite direction* with formation of endo,endo products (**17**),[28] presumably as a consequence of non-



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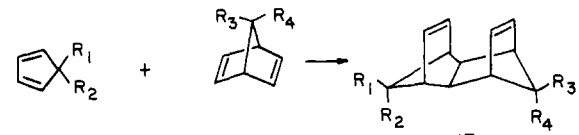


17

avoidable steric factors at the C_7 bridge. Given these observations, the general route adopted for the synthesis of 3,5-dinitrobenzoate esters **24a–24e** was that detailed in Scheme I. As Wege and his coworkers had previously established,[27d,e] benzonorbornadiene (**18d**) and benzo-7-oxabicyclo[2.2.1]heptadiene (**18e**) react with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**19**) in that stereochemical sense anticipated from the earlier observations to give adducts **20d** and **20e.** With benzobarrelene (**18a**), the stereochemistry issue was less clearly defined, the question being one of most ready accommodation of the *syn*-methoxyl group in **19** by the benzo ring or the isolated double bond in the hydrocarbon. In actuality, Diels–Alder reaction of **18a** with ketal **19** gave a single product, dechlorination of which with sodium shot and *tert*-butyl alcohol in anhydrous tetrahydrofuran and subsequent acetone-sensitized irradiation resulted in conversion to caged ketal **25** in high yield. Since the intramolecular photocycloaddition requires a syn orientation of the two etheno bridges, the operation of anal-

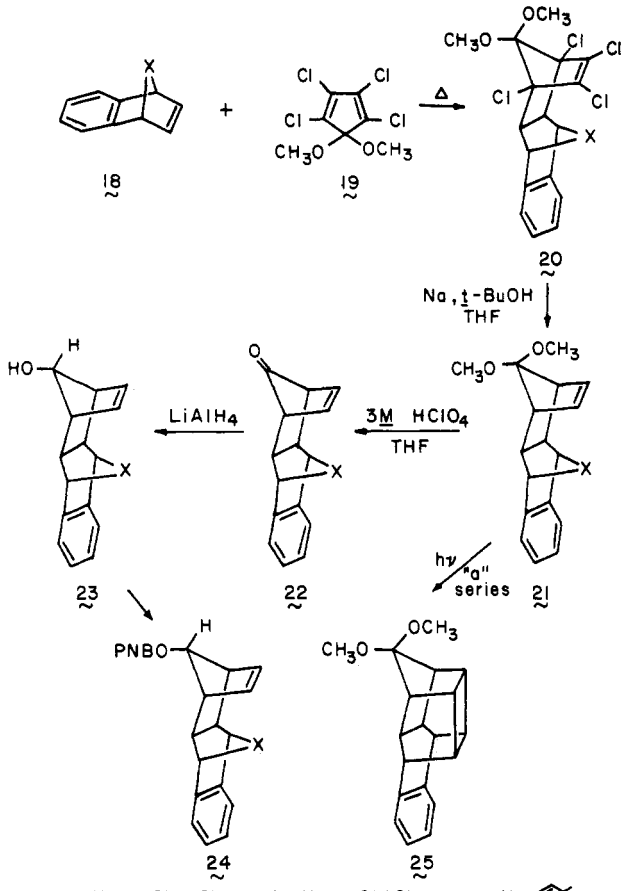
Table I. Lanthanide Shift Data for **23d** and **23e** ($CDCl_3$, 60 MHz)

Proton	Alcohol 23d: Chem shift, δ[a]	Alcohol 23d: ΔEu[b]	Alcohol 23e: Chem shift, δ[a]	Alcohol 23e: ΔEu[b]
Aromatics	6.8–7.3	−1.0 ± 0.2	7.1	−1.45 ± 0.1
Olefinic	6.04	−4.5 ± 0.1	5.95	−6.5 ± 0.2
>C*H*OH	3.59	−27.1 ± 1.0	3.61	−22.6 ± 0.8
Benzylic	3.15	−3.9 ± 0.2	4.97	−10.2 ± 0.4
Allylic	ca. 2.6	−11.9 ± 0.3	2.60	−11.9 ± 0.6
Methine	2.33	−14.5 ± 0.5	ca. 2.4	−15.0 ± 0.4
Hydroxyl	1.90	−76	ca. 2.5	−68
Syn methylene	ca. 2.8	−4.7 ± 0.1		
Anti methylene	1.29	−2.9 ± 0.2		

[a] [Eu(DPM)$_3$] = 0. [b] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Am. Chem. Soc.*, **92,** 5734 (1970).

ogous stereocontrol during $_{\pi}4_s + _{\pi}2_s$ involvement of benzobarrelene is indicated. Catalytic reduction of **20a** over 5% Pd/C led to the uptake of 1 mol equiv of hydrogen and selective saturation of the nonchlorinated double bond. Dechlorination of this substance followed by ketal hydrolysis led to ketone **22b** of unequivocal stereochemistry.

Scheme I



Reduction with lithium aluminum hydride of ketones **22** furnished the anti alcohols **23** in excellent yields. In each instance, only one epimer could be detected by ^{1}H NMR. Three considerations may be cited in support of the indicated stereochemistry. In the first place, steric approach control by the hydride species should be more favored from the exo face of the ketone superstructure. Secondly, comparison of the chemical shifts of the newly introduced bridge proton in **23d** and **23e** (δ 3.59 and 3.61, respectively) with those of the same proton in *anti*-7-norbornenol (δ 3.53) and its syn isomer (3.31)[29] reveals a striking similarity only in the first instance. Lastly, the overall stereochemistry of alcohols **23d** and **23e** was convincingly ascertained by suitable Eu(DPM)$_3$ shift data (Table I).

Kinetic Results. A survey of published data suggested that solvolytic studies would best be carried out on the 3,5-dinitrobenzoate esters (**24**), and these were prepared from **23** in conventional fashion. The solvolyses were performed on 0.002–0.005 *M* solutions of the dinitrobenzoates in 80% aqueous acetone at several temperatures, except for **24c** which, because of its insolubility in this medium at lower temperatures, was studied only at 114.0°. The reactions were followed by titration of the liberated 3,5-dinitrobenzoic acid and exhibited clean first-order behavior. The rates are given in Table II, together with extrapolated results for *anti*-7-norbornenyl-ODNB (**26**-ODNB) and **10**-ODNB.

Products from these hydrolyses were isolated and identified by their ^{1}H NMR and ir spectra as the anti alcohols **23**, with no evidence for other products. Only in the case of the oxygen-bridged ester **24e** was less than a quantitative yield (95%) of alcohol isolated; a minor level of thermal decomposition[30] was suggested by the appearance in the ^{1}H NMR spectrum of a broad low-intensity signal at δ 2.2 which could not be attributed to any product of ascertainable structure. In all other cases, the returned alcohols were isolated in quantitative yield as colorless or off-white crystalline solids.

When **24b** was heated in unbuffered methanol at 175° (sealed tube) for 3 days, the methyl ether of **23b** was obtained in 81% yield together with minor amounts of **23b** and methyl 3,5-dinitrobenzoate. Alkyl-oxygen cleavage is therefore operating. Also, no new σ bonds are being formed

Table II. Kinetic Data for Solvolysis in 80% (v/v) Aqueous Acetone

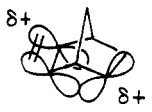
Compd	Temp, °C[a]	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	100° k_{rel}	114° k_{rel}
24a	86.00	$(1.13 \pm 0.09) \times 10^{-5}$	27.3 ± 0.5	−5.5 ± 1.4	2.1	2.1
	100.00	$(5.05 \pm 0.28) \times 10^{-5}$				
	114[b]	1.95×10^{-4}				
	116.00	$(2.33 \pm 0.13) \times 10^{-4}$				
24b	85.00	$(1.13 \pm 0.10) \times 10^{-5}$	27.3 ± 0.6	−5.2 ± 1.9	2.3	2.3
	99.95	$(5.63 \pm 0.60) \times 10^{-5}$				
	112.00	$(1.79 \pm 0.19) \times 10^{-4}$				
	114[b]	2.19×10^{-4}				
24c	114.00	$(2.32 \pm 0.25) \times 10^{-4}$				2.5
24d	84.80	$(4.27 \pm 0.30) \times 10^{-6}$	28.0 ± 2.2	−5.2 ± 5.8	1.0	1.0
	99.90	$(2.41 \pm 0.26) \times 10^{-5}$				
	113.70	$(8.69 \pm 0.35) \times 10^{-5}$				
	114[b]	9.27×10^{-5}				
24e	100.00	$(1.24 \pm 0.04) \times 10^{-5}$	27.1 ± 0.6	−8.9 ± 1.7	0.5	0.5
	114[b]	4.79×10^{-5}				
	114.75	$(5.05 \pm 0.15) \times 10^{-5}$				
	126.03	$(1.44 \pm 0.10) \times 10^{-4}$				
10-ODNB	100[c]	3×10^{-5}			1.2	
26-ODNB	100[d]	1.52×10^{-7}			0.006	

[a] All temperatures ±0.1° or better. [b] Extrapolated or interpolated from the activation parameters. [c] Value obtained by assuming solvent change identical in magnitude with that found for **26** (see footnote *d*) and employing the relationship $k_{ODNB}/k_{OPNB} = 6$ [P. v. R. Schleyer and G. W. van Dine, *J. Am. Chem. Soc.*, 88, 2321 (1966), footnote *i* of Table I]. [d] Value obtained by transforming the rate constant of **26**-OPNB in 60% aqueous dioxane and 70% aqueous acetone [M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, ibid., 89, 1954 (1967)] to 80% aqueous acetone by means of the relevant Y values for these media and correction for the ODNB leaving group as in footnote *c*.

in any of the systems examined as a result of possible deep-seated skeletal rearrangement or π-bond reorganization.

Discussion

Geometrical Factors in Carbon–Carbon Double Bond and Oxygen Lone-Pair Nucleophilic Reactivity. Studies of homoallylic systems have demonstrated that the nearby presence of a carbon–carbon double bond can effectively lead to acceleration of ionization. The transition state and first intermediate in these solvolyses have most frequently been inferred to involve unsymmetrical participation by the π system as exemplified by the *exo*-2-norbornenyl cation **27.** This state of affairs requires the sp^2 carbon more remote from the ionization center to acquire a substantial amount of positive charge; the more proximate trigonal carbon plays a quite different role. The unsymmetrical arrangement in **27** is the source of an exo/endo rate differ-



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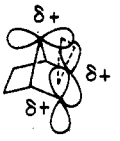

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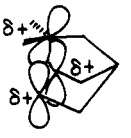

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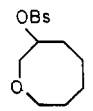
ence of 10^3 (as the tosylates),[31] an order of magnitude which hardly compares with the striking 10^{11}-fold acceleration given by the symmetrical arrangement in the *anti*-7-norbornenyl cation (**2**).[1a,5] The similar accelerating effects engendered upon introduction of one and then two methyl groups at the olefinic site in such systems as **2**[32] and the Δ^3-cyclopentenylethyl cation (**28**)[33] denote that nearly equal amounts of positive charge reside concomitantly on the two original sp^2-hybridized carbons. These results can be taken as supportive evidence for the conclusion that, *where possible,* solvolysis transition states involving symmetrical neighboring $p\pi$-$p\pi$ participation will be energetically preferred to those associated with less symmetrical bridged cation arrangements.

As concerns oxygen lone-pair involvement, Allred and Winstein have shown that anchimerically assisted ionization of ω-methoxy-substituted alkyl brosylates reaches a maximum for the MeO-5 and MeO-6 cases.[34] In cyclic systems, additional complications in the form of inductive and dipolar field effects (arising from the fact that the hetero atom is now constrained to reside significantly closer to the center of incipient positive charge on a time average basis), ring strain influences, and the like can sometimes distort predictability. Perhaps the most spectacular examples of this phenomenon are the 70- and 7-fold rate retardations, respectively, found for **29**[35] and **30**,[36] and the 5×10^4 faster rate of solvolysis exhibited by **31** relative to the cyclooctyl



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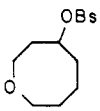

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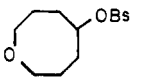
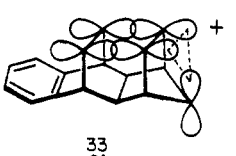


31

derivative.[36] The record high level of kinetic acceleration (for a hetero atom) in **31** is thought on the basis of entropic considerations ($\Delta S^* = -22$ eu) and product distribution to be the result of transannular interaction of the oxygen p orbital with the developing cation center as in **32,** with ultimate generation of the bicyclo[3.3.0]octyl oxonium ion. This end-on mode of intramolecular nucleophilic attack, to be expected for σ-bond formation, is symmetrical for **32** and places significant levels of positive charge density on the oxygen atom.

32

For the structurally rigid dinitrobenzoates **24a** and **24e** to enjoy extended laticyclic delocalization upon ionization, reaction channels involving orbital interactions of the type **33** and **34** would have to develop. The alignment is not only symmetrical but also seemingly such that the developing cationic center could profit by added charge dispersal to the remote double bond and oxygen atom, respectively. Yet, examination of the rate data in Table II shows the 3,5-dinitrobenzoate of **10** and the five esters of structure **24** not to differ in rate by more than a factor of 5 at 100°.



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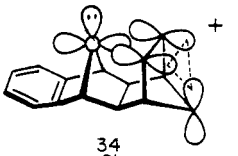

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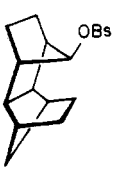
Model System Comparisons. Within the limits of the kinetic measurements, therefore, we see that ionizations of **24a, 24c,** and **24e** are not accompanied by demonstrable rate accelerations. Thus, laticyclic interaction, if operative, must be a minor factor in the overall stabilization of the cations by comparison with dominant homoaromatic stabilization. As is customary, this conclusion relies heavily on the assumption that bridged structures **10** and **24** are sufficiently similar to each other and to *anti*-7-norbornenyl esters that direct comparison of solvolytic behavior is justified. As a consequence of the comparable geometric and structural features, such mutual referencing seems entirely defensible in the present instance.[37]

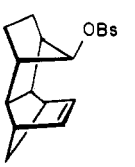
Although orbital overlap and attendant anticipated stabilization fall off rapidly with distance, the remote π double bonds in **10, 24a,** and **24c,** as well as the oxygen atom in **24e,** fall well within the range where interaction is capable of gaining significance. Diaz, Harris, and Winstein have previously made estimates of the intra-π distance between olefinic sites that are necessary in order to achieve a stabilizing interaction.[20] The interatomic π–π distance in cation **8,** for example, approximates 2.91 Å and may be too great to permit effective overlap at this angle. In cation **5,** the olefinic centers are only 2.28 Å from each other; whereas, in **11, 33,** and **34,** the spatial orientation places them some 2.60 Å apart. Perhaps as important as proximity is the mutual orientation of the p orbitals in the several interacting bridges. For the cations under discussion, the overlap integral should increase in the order $\mathbf{5} < \mathbf{8} < \mathbf{11} \sim \mathbf{33} \sim \mathbf{34}$ at equal interatomic distances.[38] However, this trend does not parallel the experimentally determined results.

Accordingly, the present situation with triply bridged laticyclic systems differs in a significant way from the behavior of the somewhat related doubly bridged brosylates **35–37**[39-41] where π-olefinic and cyclopropane ring bonds positioned at rather similar intrabridge distances exert remote stabilizing influences which are convincingly manifested in kinetic acceleration.



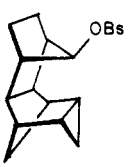
35

k_{rel}^{42} $10^{3.6}$



36

$10^{10.6}$



37

$10^{8.2}$

Differences in rate are known to sometimes arise because of changes in angle and torsional strains, steric effects, or varying degrees of solvent participation and internal return. Because of the identity of leaving group and gross similarity of intrinsic structural features at their ionizing centers, the solvation forces operating during ionization of dinitrobenzoates **24** are expected to be quite comparable throughout the series.[43] However, small differences in the geometries of these highly bridged systems do exist, particularly as the transition from **24a–24c** to **24d–24e** is made. In this connection, **24a–24c** are seen to share the common feature of slightly enhanced (two- to fivefold) reactivity over the group consisting of **10**-ODNB, **24d,** and **24e.** In every case, the additional bicyclic moiety is endo fused (at C_4,C_5) to the 7-substituted norbornenyl framework, but methano bridging as in the latter series increases the angle separating the remaining two-carbon bridges in this appendage.[44] Diminution in intrabridge nonbonded interactions may possibly ensue. The similar reactivity of the monoene (**24b**) and diene (**24a**) compounds suggests that small alterations in compressional factors do not give rise to sizable kinetic inequities. All of these contributions, as well as those originating from differences in field and orbital electronegativity inductive effects for the oxa, methylene, etheno, and ethano bridges, should be overwhelmed if *effective* laticyclic interaction were operative. One is led to conclude that the additional π and oxa bridges in the cations under discussion contribute little, if any, to anchimeric assistance.

The Absence of Extended Laticyclic Interaction in 10 and 24. The solvolytic rate data for **10** and **24** accord with assistance to ionization by the proximate double bond (bishomoaromatic interaction) to the exclusion of more remote stabilizing effects. Why are (2 + 2 + 0) laticyclic ions not formed during these ionization processes? In an attempt to answer this question, it is instructive to return to **35–37** where neighboring bridge influences gain major significance. The incipient 7-norbornyl cation centers in these brosylates should, like **1,** experience substantial destabilization. The electron-deficiency demand will be large and consequently will invite a correspondingly high level of laticyclic interaction during ionization. Some distortion of the relevant bridges may even take place to enhance the homoaromatic character of $\mathbf{36}^+$ and $\mathbf{37}^+$. In any event, stabilization of the unit charge in these systems by delocalization over a proximate vinyl or cyclopropyl bridge is appreciable and contributes measurably to rate enhancement.

In the cations derived from **10** and **24,** delocalization of charge over the three-carbon bishomocyclopropenyl network already prevails, and an abrupt change in electron-deficiency demand has taken place. The need for additional charge stabilization is now small such that participation by other adjacent π-rich centers is not called upon. Thus, homoaromatic delocalization is the major factor involved in the stability of these potentially laticyclic cations.

There would appear to be a definite upper limit to the amount of stabilization which a remote double bond can provide to delocalization of positive charge by laticyclic interaction. If, as is the case with **36** and **37,** massive levels of stabilization are required, all of the traditional characteristics of neighboring-group influences will be made manifest. On the other hand,[45] should the potential stabilization of the adjacent bridge not exceed that already provided to the positive charge (as found for **10** and **24**), neighboring-group involvement will cease, and the rate ratios will be effectively leveled. In many ways, there exists a direct parallelism between the above inferences and those which result from attenuation of electron demand by direct introduction of an aryl substituent at the displacement site.[8c,46] In both instances, double-bond participation and existing stabilization appear to be competitive rather than cooperative.

Lastly, because our data demonstrate in kinetic terms only that anchimeric assistance in **24** above that available from customary homoaromatic interaction generated in the *anti*-7-norbornenyl part structure is not operative, the formation of a laticyclic cation *subsequent to* the rate-determining ionization step cannot be excluded. Should the introduction of such a species ultimately prove necessary, however, we would then be forced to ask why the symmetrical laticyclic ion is not the intermediate produced on the direct lowest energy path for dinitrobenzoate ionization.

Experimental Section

All melting points are corrected. Infrared spectra were recorded on Perkin-Elmer Model 137 and 467 spectrometers, whereas mass spectra were obtained with a CEI-MS9 instrument at an ionizing potential of 70 eV. Proton magnetic resonance spectra were obtained with a Varian A60-A spectrometer. Apparent splittings are given in all cases. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-1,2,3,4-tetrachloro-9,10-etheno-1,4-dimethoxymethanoanthracene (20a).** A solution of 12.1 g (0.078 mol) of benzobarrelene[47] and 32 g (0.12 mol) of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene[48] in 50 ml of toluene was heated at reflux under a dry-nitrogen atmosphere for 42 hr. Solvent was removed in vacuo from the cooled solution, and the residual oil was dissolved in 100 ml of chloroform and shaken with a little activated charcoal. The mixture was filtered, and the filtrate was heated, diluted with methanol to ca. 200 ml, then heated to remove essentially all the chloroform. Cooling of the solution gave 29.3 g of crystals which were recrystallized from chloroform–methanol and sublimed. There was obtained 26.0 g (79%) of **20a** as colorless plates: mp 156–157°; δ_{Me_4Si} ($CDCl_3$) 7.0–7.3 (m, 4, aromatic), 6.38 (t, J = 4 Hz, 2, olefinic), 3.98 (m, 2, bridgehead), 3.50 (s, 6, methoxyl), and 2.85 (m, 2).

Anal. Calcd for $C_{19}H_{16}Cl_4O_2$: C, 54.58; H, 3.86; Cl, 33.91. Found: C, 54.26; H, 3.85; Cl, 34.41.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-9,10-etheno-1,4-dimethoxymethanoanthracene (21a).** Sodium shot[49] (20 g, 0.87 g-atom) was added under dry nitrogen to a stirred solution of 12.5 g (0.030 mol) of **20a** and 22.2 g (0.30 mol) of *tert*-butyl alcohol in 120 ml of anhydrous tetrahydrofuran, while the mixture was warmed to the reflux temperature. After 5 hr at reflux with continued stirring, the mixture had assumed a purple color, and the sodium had aggregated as a bright lump, indicating completion of the reaction. Heating and stirring was continued for a further 1.5 hr, the mixture was cooled in ice, and excess sodium was destroyed by the cautious addition of methanol (100 ml). Water (600 ml) was introduced, the product was extracted with ether (3 × 150 ml), and the combined extracts were washed with water (2 × 300 ml), dried, and evaporated. The resulting oil crystallized upon trituration with pentane to give 8.4 g of very pale yellow solid. Three recrystallizations from hexane afforded **21a** as colorless prisms: mp 131–132° (3.80 g, 45%); δ_{Me_4Si} ($CDCl_3$) 7.0–7.4 (m, 4, aromatic), 6.06 (dd, J = 4.5 and 2 Hz, 2, vinyl protons nearer benzo ring), 5.71 (t, J = 2 Hz, 2, vinyl protons remote from benzo group), 3.77 (m, 2, benzylic–allylic), 3.18 (s, 3, methoxyl), 3.14 (s, 3, methoxyl), 2.93 (m, 2, allylic), and 2.64 (m, 2).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.36; H, 7.24.

***endo,exo*-1,4-Carbonyl-1,4,4a,9,9a,10-hexahydro-9,10-ethenoanthracene (22a).** A solution of 3.00 g (10.7 mmol) of **21a** in 75 ml of tetrahydrofuran was treated at room temperature with 30 ml of 3 M aqueous perchloric acid, and the resulting solution was allowed to stand for 3 hr. The reaction mixture was poured into 500 ml of water and extracted with ether (3 × 200 ml). The combined extracts were washed with water, saturated sodium bicarbonate solution, and brine, dried, and evaporated to leave 2.51 g (100%) of **22a** as off-white prisms: mp 124–126° (gas evolution); ν_{max} (Nujol) 1762 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.8–7.2 (m, 4, aromatic), 5.7–6.1 (m, 4, olefinic), 3.87 (m, 2, benzylic–allylic), 3.05 (m, 2, allylic), and 2.51 (m, 2).

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-9,10-etheno-*anti*-1,4-hydroxymethanoanthracene (23a).** A solution of 2.50 g (10.7 mmol) of **22a** in 150 ml of anhydrous ether was added during 20 min to an

ice-cooled stirred suspension of 0.4 g (10 mmol) of lithium aluminum hydride in 10 ml of the same solvent. The mixture was stirred at room temperature for 1 hr and processed in the usual manner to furnish 2.43 g (96%) of **23a** as a colorless crystalline solid: mp 158.5–159° (from benzene–hexane); ν_{max} (CCl_4) 3640 cm^{-1}; ν_{max} (Nujol) 3260 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.8–7.2 (m, 4, aromatic), 5.96 (dd, J = 4.5 and 3.5 Hz, 2, vinyls proximate to benzene ring), 5.49 (t, J = 2 Hz, vinyls remote from benzene ring), 3.69 (t, J = 3.5 Hz, 2, benzylic–allylic), 3.46 (br, 1, >C*H*OH), 2.4–2.7 (m, 4), and 2.01 (br, 1, -OH); mol wt 236.1204 (calcd for $C_{17}H_{16}O$, *m/e* 236.1201).

Addition of 1.90 g (8.04 mmol) of **23a** to a solution of 2.23 g (9.7 mmol) of 3,5-dinitrobenzoyl chloride in pyridine (30 ml), followed by storage at 0° overnight and customary work-up, afforded 3.44 g (99%) of **24a** as very pale yellow needles, mp 208–209° dec (from acetone–ethanol).

Anal. Calcd for $C_{24}H_{18}N_2O_6$: C, 66.97; H, 4.22; N, 6.51. Found: C, 67.21; H, 4.09; N, 6.55.

Photocyclization of 21a. A solution of 100 mg (0.36 mmol) of **21a** in 100 ml of deoxygenated acetone was irradiated for 3 hr through Vycor with a bank of nine 15-W germicidal lamps. Evaporation of the resulting solution left 189 mg of brown solid residue. This crude material was dissolved in ether and filtered through a short column of neutral alumina. Evaporation of the eluate gave 97 mg (97%) of **25** as colorless plates: mp 132–132.5° (from hexane); δ_{Me_4Si} ($CDCl_3$) 7.04 (s, 4, aromatic), 3.21 (s, 3, methoxyl), 3.17 (s, 3, methoxyl), 2.8–3.6 (m, 4, bridgehead), and 2.25–2.55 (m, 6).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.18; H, 7.47.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-1,2,3,4-tetrachloro-9,10-ethano-1,4-dimethoxymethanoanthracene (20b).** A 11.0-g (0.026 mol) sample of **20a** in 50 ml of dichloromethane was hydrogenated for 23 hr at room temperature and atmospheric pressure over 5% palladium on charcoal. The mixture was filtered through Celite and evaporated leaving 10.9 g (98%) of **20b,** colorless needles: mp 137–139.5° (from methanol); δ_{Me_4Si} ($CDCl_3$) 7.18 (m, 4, aromatic), 3.54 (s, 3, methoxyl), 3.48 (s, 3, methoxyl), 3.17 (m, 2, bridgehead), 2.68 (m, 2, methines), and 1.0–2.0 (m, 4, methylenes).

Anal. Calcd for $C_{19}H_{18}Cl_4O_2$: C, 54.31; H, 4.32; Cl, 33.75. Found: C, 54.18; H, 4.28; Cl, 33.91.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-9,10-ethano-1,4-dimethoxymethanoanthracene (21b).** Reaction of 10.9 g (0.026 mol) of **20b** with 17 g (0.74 g-atom) of sodium shot and 19.3 g (0.26 mol) of *tert*-butyl alcohol in 100 ml of anhydrous tetrahydrofuran in the predescribed manner gave 9 g of impure crystalline solid. Two recrystallizations from hexane furnished pure **21b** (3.79 g, 52%) as colorless prisms: mp 167.5–169.5°; δ_{Me_4Si} ($CDCl_3$) 7.12 (s, 4, aromatic), 6.27 (t, J = 2.3 Hz, 2, olefinic), 3.11 (s, 3, methoxyl), 3.04 (s, 3, methoxyl), 2.86 (m, 4, bridgeheads), 2.25 (m, 2, methines), and 0.8–1.8 (m, 4, methylenes); mol wt 282.1623 (calcd for $C_{19}H_{22}O_2$; *m/e* 282.1620).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 81.02; H, 7.19.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-9,10-ethano-*anti*-1,4-hydroxymethanoanthracene (23b).** A solution of 3.59 g (12.7 mmol) of **21b** in 75 ml of tetrahydrofuran was treated at room temperature with 30 ml of 3 *M* aqueous perchloric acid and allowed to stand for 3 hr. Processing in the predescribed fashion afforded 3.05 g (100%) of **22b,** mp 115–117°. Reduction of 2.99 g (12.7 mmol) of this ketone with 500 mg (13 mmol) of lithium aluminum hydride in 180 ml of ether yielded 2.93 g (97%) of **23b,** colorless needles, mp 192.5–193° (from benzene–hexane); ν_{max} (CCl_4) 3640 cm^{-1}; ν_{max} (Nujol) 3300 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.12 (s, 4, aromatic), 6.19 (t, J = 2.3 Hz, 2, olefinic), 3.67 (m, 1, >C*H*OH), 2.91 (m, 2, benzylic), 2.57 (m, 2, allylic), 2.30 (m, 2, methine), and 1.0–1.8 (m, 5, methylenes and -OH).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.38; H, 7.56.

Dinitrobenzoate **24b** was obtained in quantitative yield as pale-yellow needles, mp 238–243° dec (from acetone–ethanol).

Anal. Calcd for $C_{24}H_{20}N_2O_6$: C, 66.66; H, 4.66; N, 6.48. Found: C, 66.49; H, 4.68; N, 6.42.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-1,2,3,4-tetrachloro-9,10-benzo-1,4-dimethoxymethanoanthracene (20c).** A mixture of 6.8 g (0.033 mol) of bisbenzobarrelene[50] and 15 g (0.057 mol) of **19** was heated under nitrogen at a bath temperature of 155–165° for 48 hr. The cooled mixture formed a solid mass which was dissolved in 75 ml of hot chloroform, treated with charcoal, and filtered. The filtrate was boiled, and the solvent was partially replaced with methanol, leading to crystallization. After cooling, 11.7 g of needles was collected. These were recrystallized from chloroform–methanol to give 10.1 g (65%) of **20c** as colorless needles: mp 251.5–253.5°; δ_{Me_4Si} ($CDCl_3$) 6.9–7.4 (m, 8, aromatic), 4.34 (m, 2, bridgehead), 3.51 (s, 3, methoxyl), 3.45 (s, 3, methoxyl), and 3.13 (m, 2).

Anal. Calcd for $C_{23}H_{18}Cl_4O_2$: C, 59.00; H, 3.88; Cl, 30.29. Found: C, 58.70; H, 3.91; Cl, 30.14.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-9,10-benzo-1,4-dimethoxymethanoanthracene (21c).** The reductive dechlorination of **20c** (10.1 g, 0.022 mol) with 14 g (0.6 g-atom) of sodium shot and 16.3 g (0.22 mol) of *tert*-butyl alcohol in 120 ml of anhydrous tetrahydrofuran was conducted in the predescribed fashion. There was obtained 7.6 g of crude crystalline product, recrystallization of which from chloroform–methanol and benzene–hexane gave 3.8 g (54%) of pure **21c** as colorless prisms, mp 200–201°; δ_{Me_4Si} ($CDCl_3$) 6.9–7.4 (m, 8, aromatic), 4.95 (t, J = 2 Hz, 2, olefinic), 4.07 (m, 2, benzylic), 3.08 (s, 3, methoxyl), 3.00 (s, 3, methoxyl), and 2.7–2.9 (m, 4, allylic and methine).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.87; H, 6.72.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-9,10-benzo-*anti*-1,4-hydroxymethanoanthracene (23c).** Hydrolysis of **21c** (3.27 g, 9.9 mmol) with 25 ml of 3 *M* perchloric acid in 75 ml of tetrahydrofuran led after 3 hr at room temperature to formation of **22c** in quantitative yield; ν_{max} (Nujol) 1770 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.8–7.3 (m, 8, aromatic), 5.31 (t, J = 2 Hz, 2, olefinic), 4.24 (m, 2, bridgehead), 2.99 (m, 2, allylic), and 2.70 (m, 2).

Lithium aluminum hydride (0.38 g, 10 mmol) reduction of **22c** (2.80 g, 9.8 mmol) in 100 ml of anhydrous tetrahydrofuran afforded 2.74 g (97%) of alcohol **23c** as colorless needles: mp 194.5–196°; ν_{max} (CCl_4) 3640 cm^{-1}; ν_{max} (Nujol) 3595 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.8–7.3 (m, 8, aromatic), 4.86 (t, J = 2.2 Hz, 2, olefinic), 4.09 (m, 2, benzylic), 3.40 (m, 1, >C*H*OH), 2.78 (m, 2, allylic), 2.45 (m, 2, methines), and 1.79 (br, 1, -OH).

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.14; H, 6.71.

Dinitrobenzoate **24c** was obtained in quantitative yield as pale-yellow needles, mp 232–233° dec (from acetone–ethanol).

Anal. Calcd for $C_{28}H_{20}N_2O_6$: C, 69.99; H, 4.20; N, 5.83. Found: C, 70.27; H, 4.15; N, 5.50.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-9,10-methano-*anti*-1,4-hydroxymethanoanthracene (23d).** A solution of 1.66 g (7.5 mmol) of **22d**[27d,51] in 50 ml of anhydrous ether was added dropwise during 10 min to a cold stirred suspension of lithium aluminum hydride (0.2 g, 5 mmol) in 20 ml of the same solvent. Work-up in the usual manner gave 1.62 g (96%) of **23d** which, after recrystallization from benzene–hexane and sublimation, was obtained as colorless needles, mp 147.5–148.5°; ν_{max} (CCl_4) 3640 cm^{-1}; ν_{max} (Nujol) 3250 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.8–7.3 (m, 4, aromatic), 6.04 (t, J = 2.2 Hz, 2, olefinic), 3.59 (m, 1, >C*H*OH), 3.15 (m, 2, benzylic), 2.5–3.0 (m including d with J = 9 Hz, 3, allylics and syn methylene proton), 2.33 (m, 2, methines), 1.90 (s, 1, -OH), and 1.29 (d, J = 9 Hz, 1, anti methylene proton).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.83; H, 7.21.

Dinitrobenzoate **24d** was isolated in 98% yield as very pale-yellow needles, mp 221.5–222.5° (from acetone–ethanol).

Anal. Calcd for $C_{23}H_{18}N_2O_6$: C, 66.02; H, 4.34; N, 6.70. Found: C, 65.90; H, 4.49; N, 6.77.

***endo,exo*-1,4,4a,9,9a,10-Hexahydro-9,10-epoxy-*anti*-1,4-hydroxymethanoanthracene (23e).** Lithium aluminum hydride (0.38 g, 0.010 mol) reduction of 4.0 g (0.018 mol) of ketone **22e**[27e,51] in ether (20 ml)–tetrahydrofuran (50 ml) gave rise to alcohol **23e** in 99% yield, colorless needles: mp 164–168° (from benzene–hexane); ν_{max} (CCl_4) 3640 cm^{-1}; ν_{max} (Nujol) 3385 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.1 (m, 4, aromatic), 5.95 (t, J = 2 Hz, 2, olefinic), 4.97 (s, 2, benzylic), 3.61 (m, 1, >C*H*OH), 2.60 (m, 2, allylic), and 2.35–2.55 (m, 3, methines and -OH).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.62; H, 6.31.

Dinitrobenzoate **24e** was obtained in 95% yield as pale-yellow plates, mp 202–203° dec (from acetone–alcohol).

Anal. Calcd for $C_{22}H_{16}N_2O_7$: C, 62.86; H, 3.84; N, 6.66. Found: C, 62.50; H, 3.98; N, 6.61.

Kinetic Procedure. Acetone was purified by heating at reflux with a small quantity of potassium permanganate, followed by drying ($CaSO_4$) and distillation at atmospheric pressure under dry nitrogen. Water used in the kinetic studies was demineralized and doubly distilled. 80% aqueous acetone (v/v) was prepared at 25° by mixing 4 volumes (accurately pipetted) of purified acetone with 1 volume of purified water.

An accurately weighed amount of dinitrobenzoate was dissolved in a weighed amount of 80% aqueous acetone by warming in a well-stoppered flask to give solutions in the concentration range of 0.002–0.005 mol kg^{-1}. Aliquots of the solutions were transferred as quickly as possible to glass ampoules which were in turn sealed and immersed simultaneously into a constant-temperature bath. After approximately 15 min, one ampoule was removed, an accurate timer started, and the ampoule was immediately plunged into an ice–water bath. A weighed aliquot of the solution was then titrated gravimetrically with 0.00467 ± 0.00008 mol kg^{-1} of aqueous potassium hydroxide, using a Fisher Accumet pH meter and microprobe electrode to determine the end point accurately. The remaining ampoules were removed at appropriate intervals and titrated in the same manner. One ampoule was allowed to remain in the bath for at least 10 solvolytic half-lives and was then titrated to provide an infinity titer.

Ester **24c** was sparingly soluble in 80% aqueous acetone, and dissolution was effected only by heating the compound and solvent to approximately 110° in a sealed tube. The ester remained in solution long enough after cooling to allow its transfer to ampoules without inducement of crystallization. The low solubility of **24c** at temperatures below 110°, at which point the solvolysis rate was already substantial, restricted the range of temperatures at which kinetics could be conveniently carried out. One temperature only was therefore employed.

Product Studies. The dinitrobenzoate (300–500 mg) and 50–100 ml of 80% aqueous acetone were sealed in a thick-walled glass tube together with a thermometer and heated in a cylindrical oven for a period equivalent to at least 10 solvolytic half-lives. After cooling, most of the acetone was removed in vacuo, and the residue was diluted with 300 ml of 3% aqueous sodium hydroxide solution. Extraction with ether and washing of the combined organic layers with 3% aqueous sodium hydroxide solution and brine were followed by drying and evaporation. The products were thus isolated in 95–100% yields as colorless or off-white solids and were readily identified as the anti alcohols **23** by ^1H NMR and ir spectral comparisons.

Methanolysis of 24b. A 306-mg sample (0.708 mmol) of **24b** dissolved in 10 ml of methanol was sealed under reduced pressure (30 mm) in a thick-walled Pyrex tube and heated in a copper-tube furnace at 175° for 3 days. The solvent was evaporated, ether was added, and the organic phase was extracted with 3% potassium hydroxide solution, dried, and evaporated. The residue was chromatographed on basic alumina. Ether elution furnished 144 mg (81%) of **23b** methyl ether, 24 mg (10%) of **23b**, and ca. 10% of methyl dinitrobenzoate.

Recrystallization of the ether from hexane gave colorless prisms, mp 145–146°; δ_{Me_4Si} ($CDCl_3$) 7.18 (s, 4, aromatic), 6.22 (t, J = 2.2 Hz, 2, olefinic), 3.15 (m, 1, >CH—O-), 3.06 (s, 3, $-OCH_3$), 2.85 (m, 2, benzylic), 2.67 (m, 2, allylic), 2.21 (m, 2, methine), and 1.0–1.65 (m, 4, methylenes).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.37; H, 7.92.

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