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Structural Effects in Solvolytic Reactions. 14. Solvolysis of the 2-Aryl-2-benzonorbornenyl *p*-Nitrobenzoates. Application of the Tool of Increasing Electron Demand as a Test for π Participation in the High Exo:Endo Rate Ratios¹

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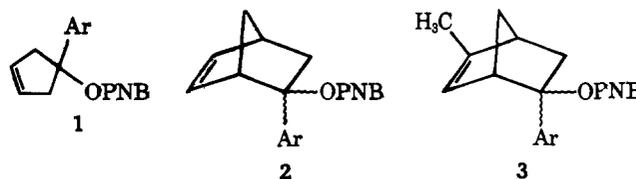
Contribution from the Richard B. Wetherill Laboratory, Purdue University,
West Lafayette, Indiana 47907. Received September 15, 1975

Abstract: 2-Aryl-2-benzonorbornenyl *p*-nitrobenzoates containing representative substituents in the 2-aryl ring were synthesized and their rates of solvolysis in 80% aqueous acetone determined. The exo:endo rate ratios observed are 3300 for *p*-CH₃O; 2900 for *p*-H, 2700 for *p*-CF₃, and 2800 for 3,5-(CF₃)₂. Thus the exo:endo rate ratio fails to exhibit any increase with increasing electron demand as anticipated for π participation as a factor in this ratio. The $\rho^+ \sigma^+$ treatment reveals excellent linear correlations, with ρ^+ of -4.50 for the exo isomers and -4.51 for the endo isomers. The essential constancy of the exo:endo rate ratios with increasing electron demand is consistent with a mechanism involving no significant π participation in the transition state for the solvolysis reaction. It appears, therefore, that the high exo:endo rate ratio of approximately 3000 must arise from major steric difficulties in the ionization of the endo isomer.

The tool of increasing electron demand³ offers promise of providing an unambiguous answer as to the importance in various systems of π or σ participation on the observed rates of solvolysis. Accordingly, we have undertaken an extensive program of testing this tool in the hope of establishing its reliability so that it could be applied to answer the vexing question of the importance of σ participation in the solvolysis of 2-norbornyl derivatives.⁴

We demonstrated that the tool could detect even small effects, as small as 1% of that postulated to be present in the 2-norbornyl system.⁵ It provided an unambiguous answer as to the importance of σ electronic contributions in stabilizing the 3-nortricyclyl cation in solvolytic processes,⁶ resolving conflicting proposals in the literature.⁷

Recently, we applied the tool to test for the importance of π participation in three closely related systems (**1**,⁸ **2**,⁹ **3**¹⁰).



The results reveal the complete absence of π participation in **1**, in complete agreement with the earlier conclusion of Bartlett and Rice based on rate data for the solvolysis of the corresponding secondary derivative.¹¹

Table I. Effect of Increasing Electron Demand on Relative Rates

| Substituent R | Relative rate, 25 °C | | | |
|---------------------------------|----------------------|-------------------|-------------------|-------------------------|
| | A/B | C/D | E/F | G/H |
| <i>p</i> -Anisyl | 3.4 ^a | 0.45 ^c | 312 ^d | 354 ^h |
| Phenyl | 41.5 ^a | 0.31 ^c | 202 ^d | 1260 ^h |
| <i>p</i> -Trifluoromethylphenyl | 34 500 ^a | 0.25 ^c | 282 ^d | 6700 ^{h,i} |
| 3,5-Bis(trifluoromethyl)phenyl | 255 000 ^a | 0.31 ^c | 447 ^d | |
| 2-Methyl | | 0.07 ^d | 885 ^f | 112 000 ^h |
| 2-Hydrogen | 10 ^{11 b} | 0.12 ^e | 7000 ^g | 22 000 000 ⁱ |

^a Reference 3. ^b For tosylate; S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955). ^c Reference 8. ^d Reference 9. ^e For tosylate; S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961). ^f S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 7124 (1968). ^g For the brosylate; S. Winstein, H. Walborsky and K. C. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950). ^h Reference 10. ⁱ Calculated from the log $k-\sigma^+$ plot for other derivatives. ^j For chloride; private communication from Professor C. F. Wilcox.

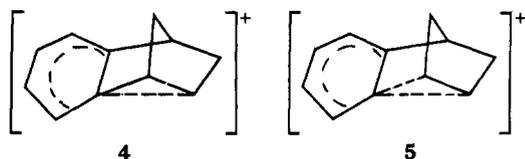
On the other hand, the results with **3** support the presence of major π participation in the *exo* isomer and its absence in the *endo* isomer. Not only are there observed major increases in the *exo:endo* rate ratio with increasing electron demand, but the reaction products strongly support the importance of π participation in the solvolysis.¹⁰

The results indicate **2** to be a borderline case. The *exo:endo* rate ratio remains essentially constant with increasing electron demand for the first three substituents (*p*-OCH₃, *p*-H, *p*-CF₃). Only with greater electron demand [3,5-(CF₃)₂, 2-CH₃, 2-H] are there observed modest increases in the *exo:endo* rate ratios which can be attributed to the inception of π participation. The nature of the reaction products supports these conclusions.⁹

The results are summarized in Table I.

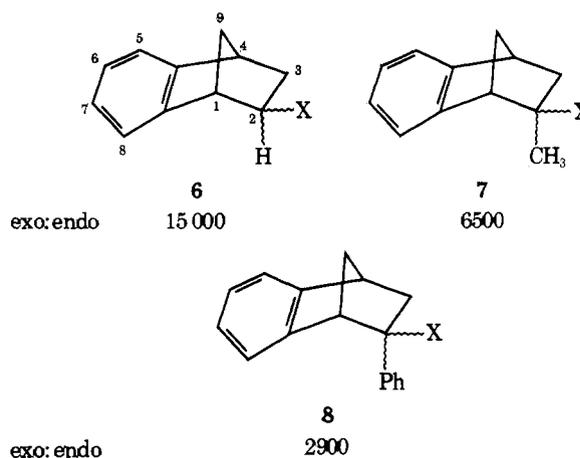
Perhaps the only unexpected feature in these results is the high *exo:endo* rate ratio (~300) observed for the 2-aryl-2-norbornenyl derivatives without evidence for significant π participation provided by the tool of increasing electron demand. If electronic effects are not responsible for the observed high *exo:endo* rate ratio in these stabilized tertiary derivatives (**2**), some other factor must be. It has been proposed that steric hindrance to ionization in rigid U-shaped molecules must be responsible.^{12,13}

The benzonorbornenyl system is an exceptionally versatile one for such structural studies. It has been subjected to extensive study by various groups.¹⁴⁻¹⁹ Originally, Bartlett and Giddings proposed that the acetolysis of the *exo*-benzonorbornenyl brosylate proceeds with carbon participation to give the nonclassical ion **4**.¹⁴ However, Giddings later es-



established that the solvolysis of the optically active derivative yields inactive product. Since the proposed intermediate **4** does not possess a plane of symmetry, he revised the structure of the intermediate as one involving such a plane, the phenonium ion **5**.¹⁵ On this basis, the acetolysis of the parent compound should proceed with π participation to yield the ion **5** as the intermediate.

On the other hand, the near constancy of the *exo:endo* rate ratios in the secondary (**6**), 2-methyl- (**7**), and 2-phenyl-2-benzonorbornenyl (**8**) derivatives originally led to the



conclusion that π participation could not be a major factor in these high *exo:endo* rate ratios.²⁰

The importance of π participation in this versatile system can also be examined by introducing appropriate substituents into the aromatic ring. Thus it is possible to introduce both activating and deactivating substituents into the benzo moiety and then observe the effect on the anti:syn rate ratio at the 9 position^{21,22} or on the *exo:endo* rate ratio at the 2 position.^{17,23} Another possibility is to introduce stabilizing substituents at the 9 position²² or at the 2 position²⁰ and to observe the effect of decreased electron demand at the reaction center on the rate ratios.

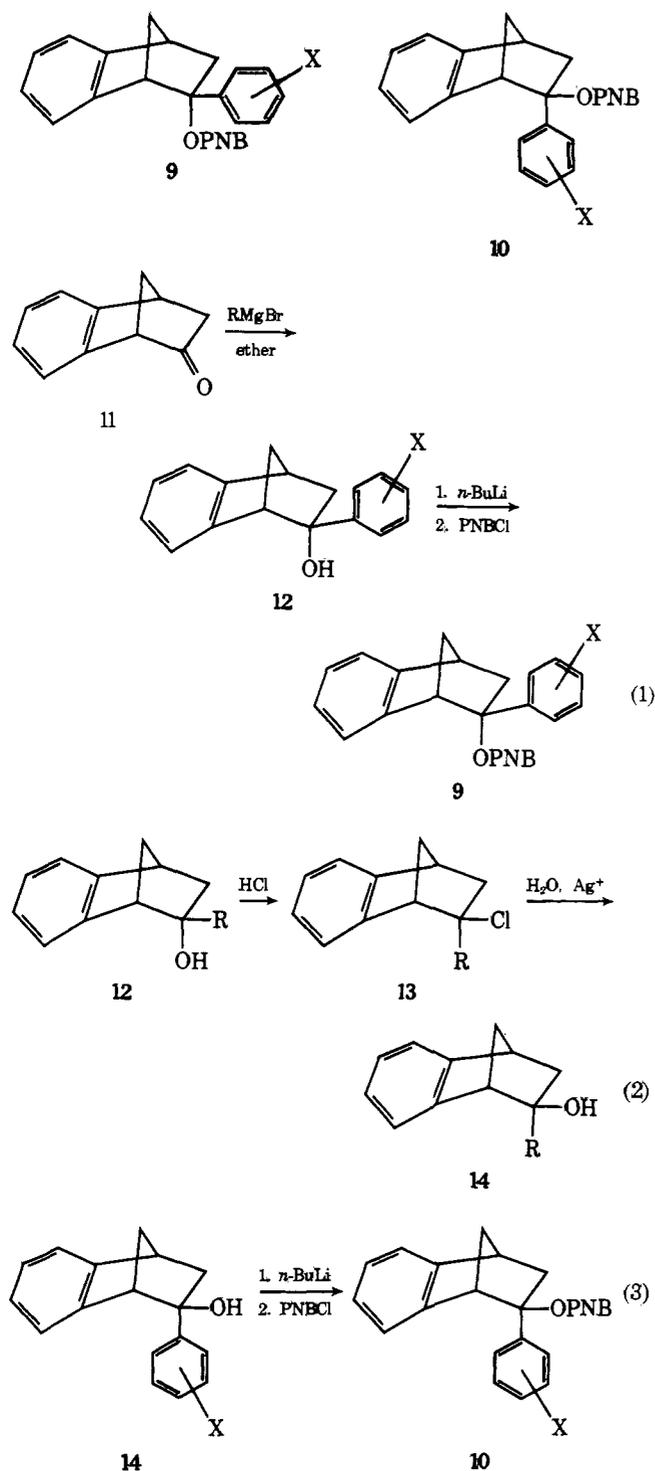
The observation that a 6-methoxy group enhances the *exo:endo* rate ratio by a factor of 55 in the secondary benzo-2-norbornenyl derivative¹⁶⁻¹⁹ is consistent with the incursion of π participation arising from the presence of the activating 6-methoxy substituent. However, the decrease in the *exo:endo* rate ratio to a value of approximately 100 as a consequence of the presence of a nitro substituent at the 6 or 7 position¹⁹ did appear to be inconsistent with the earlier conclusion that π participation must be insignificant in the parent system **6**.

A possible difficulty with the earlier study²⁰ is the difference in the steric requirements of the 2 substituents in **6**, **7**, and **8**: 2-H, 2-Me, 2-Ph. Accordingly, we decided to apply the tool of increasing electron demand, varying the electron demand at the 2 position, while maintaining the steric requirements of the 2 substituent constant (**9**, **10**). The substituents (X) were varied over the usual wide range: *p*-CH₃O, *p*-H, *p*-CF₃, 3,5-(CF₃)₂.

Table II. Kinetic Data for the Solvolysis of the 2-Aryl-2-benzonorbornenyl *p*-Nitrobenzoates in 80% Aqueous Acetone

| Substituent in 2-aryl | Isomer | $10^6 k^1, s^{-1}$ | | | ΔH^\ddagger , kcal mol ⁻¹ | ΔS^\ddagger , eu | Relative rates exo:endo |
|-------------------------------------|--------|---------------------|---------------------|------------------------|---|-----------------------------|----------------------------|
| | | T ₁ , °C | T ₂ , °C | 25.0 °C | | | |
| <i>p</i> -CH ₃ O | exo | | | 1080 ^a | | | 3300 |
| | endo | 144 (75) | 8.69 (50) | 0.328 ^b | 24.5 | -6.0 | |
| <i>p</i> -H | exo | 111 (75) | 7.00 (50) | 0.278 ^b | 24.1 | -7.7 | 2900 |
| | endo | 24.6 (125) | 2.05 (100) | 9.71×10^{-5b} | 28.8 | -8.0 | |
| <i>p</i> -CF ₃ | exo | 93.4 (125) | 8.16 (100) | 4.67×10^{-4b} | 28.2 | -6.6 | 2700 |
| | endo | 3.21 (150) | 0.26 (125) | 1.72×10^{-7b} | 33.0 | -6.3 | |
| 3,5-(CF ₃) ₂ | exo | 29.8 (150) | 3.07 (125) | 7.73×10^{-6b} | 29.8 | -9.3 | 2800 |
| | endo | | | 2.8×10^{-9c} | | | |

^a The rate was measured in the impure state. However, the rate ratio, k_{OPNB}/k_{OBz} (20.5), is very close to 20.8 observed in the solvolysis of 2-*p*-anisyl-*exo*-norbornyl esters (ref 24). ^b Calculated from data at higher temperatures. ^c Estimated by extrapolation of the log $k-\sigma^+$ plot for other derivatives.



Results

Synthesis. The 2-aryl-*endo*-benzonorbornenols (**12**) were synthesized by addition of the appropriate Grignard reagent to benzonorbornen-2-one (**11**). Conversion of the tertiary alcohols (**12**) to the chlorides (**13**), followed by hydrolysis in the presence of silver ion (eq 2) yielded the *exo* isomers (**14**). The alcohols were converted into *p*-nitrobenzoates (**9**, **10**) by treating their lithium salts with *p*-nitrobenzoyl chloride (eq 1 and 3).

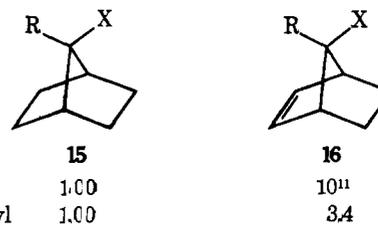
Kinetic Studies. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone. The 2-*p*-anisyl-*exo*-benzonorbornenyl *p*-nitrobenzoate was too unstable to be isolated in the pure state. However, the rate of solvolysis could be determined for the impure material. The validity of the value was confirmed by preparing the corresponding benzoate and measuring its rate of solvolysis. The rate ratio observed, $k_{OPNB}/k_{OBz} = 20.5$, is in excellent agreement with the value of 20.8 observed for the relative rates of solvolysis at 25 °C of 2-phenyl-*exo*-norbornyl *p*-nitrobenzoate and benzoate.²⁴

The rate of solvolysis for 2-[3,5-bis(trifluoromethyl)phenyl]-*endo*-benzonorbornenyl *p*-nitrobenzoate was exceedingly slow. Consequently, its rate constant was calculated from the log $k-\sigma^+$ plot for the other derivatives.

The rate data, together with the activation parameters, are summarized in Table II.

Discussion

It has long been accepted that participation by a neighboring group should decrease with increasing stability of the electron-deficient carbonium ion center and ultimately vanish with a center of sufficient stability.²⁵ Such behavior is revealed by the 7-norbornenyl system (Table I).³ Thus a *p*-anisyl substituent in the 7 position causes the 10¹¹ rate acceleration observed in the secondary derivative essentially to vanish (**15**, **16**).



If a *p*-anisyl group can cause π participation amounting to a factor of 10¹¹ in rate in the secondary derivative essentially to vanish in the stabilized tertiary derivative (**16**), surely it should cause the much smaller *exo:endo* rate factor of $\sim 10^4$, attributed to π participation in the secondary derivative,^{16,17} to vanish likewise in the tertiary derivative sta-

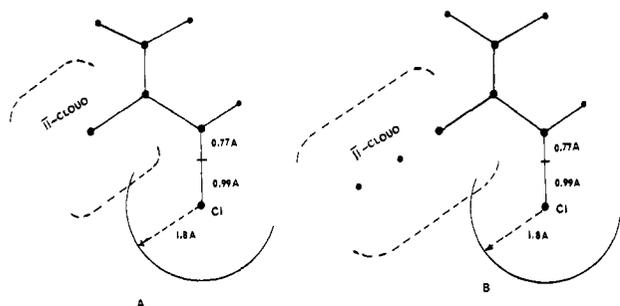


Figure 1. End-on views of (A) *endo*-norbornenyl chloride and (B) *endo*-benzonorbornenyl chloride.

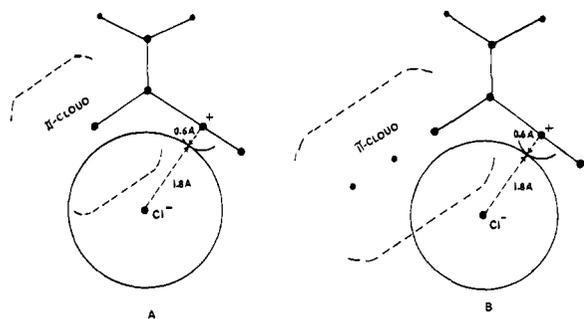
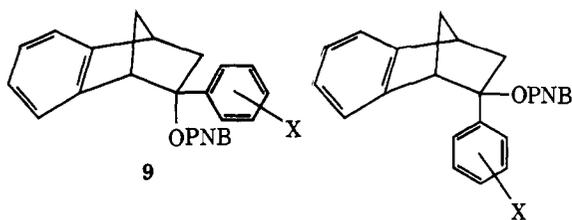


Figure 2. End-on views of the ion pairs from (A) *endo*-norbornenyl chloride and (B) *endo*-benzonorbornenyl chloride.

bilized by a 2-*p*-anisyl group. However, it does not. The *exo:endo* rate ratio remains high, a factor of 3300.

Moreover, with increasing electron demand at the 2 position, over a reactivity ratio of 10^8 , the *exo:endo* rate ratio fails to exhibit any increase such as would be anticipated for the incursion of π participation (9, 10).



| | 10 |
|-------------------------------------|------|
| <i>p</i> -CH ₃ O | 3300 |
| <i>p</i> -H | 2900 |
| <i>p</i> -CF ₃ | 2700 |
| 3,5-(CF ₃) ₂ | 2800 |

In cases where π participation appears unambiguous, as in 16 and in 3, the ρ^+ values clearly reveal the effect of such participation. Thus ρ^+ is -2.30 for the 7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates, as compared with a value of -5.27 for the corresponding saturated derivatives.³ Similarly, *endo*-3 yields a ρ^+ value of -4.19 , in comparison with one of -3.27 for the *exo* derivatives.¹⁰ These ρ^+ values contrast with those of -4.17 for *endo*-2 and -4.21 for *exo*-2.⁹ In the present system, the *endo* derivatives (9) yield a ρ^+ value of -4.51 (correlation coefficient 1.000) and the *exo* series yield one of -4.50 (correlation coefficient 1.000). The data again fail to reveal any differential electronic effect operating preferentially in the *exo* position.

If the high *exo:endo* rate ratio of ~ 3000 is not the result of π participation, what can it be due to? It cannot be attributed to differences in ground-state energies, since the steric requirements of the 2-aryl and the 2-*p*-nitrobenzoyl substituents are reasonably similar.²⁶ Torsional effects ap-

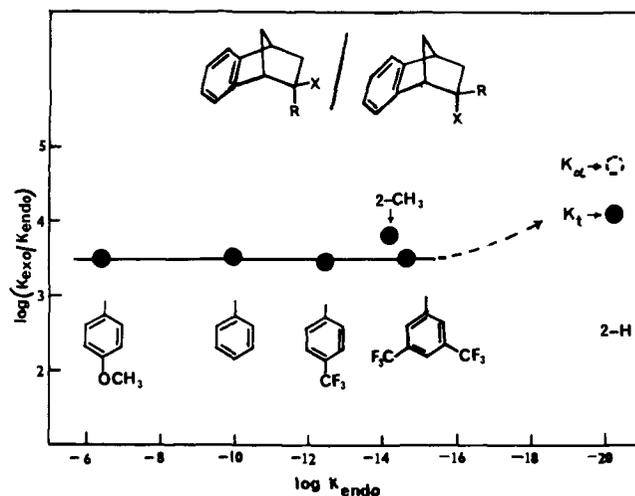


Figure 3. Effect of the increasing electron demand on the *exo:endo* rate ratio in the 2-benzonorbornenyl system.

pear to be far too small to make a significant contribution to the large factor observed.²⁷ The only factor presently proposed which appears to be capable of accounting for such high *exo:endo* rate ratios in these tertiary derivatives appears to be steric hindrance to ionization.^{12,13}

But what about the relative factor of ~ 3000 observed for the 2-aryl-2-benzonorbornenyl derivatives (9, 10) compared with the factor of ~ 300 observed for the parent 2-aryl-2-norbornenyl derivatives (2)? Clearly this is in the wrong direction to be attributed to π participation. The available evidence is that the π electrons in a carbon-carbon double bond are far more available for participation than the π electrons of an aromatic ring.²⁸

On the other hand, this difference in the *exo:endo* rate ratios can be nicely accounted for on steric grounds. The steric requirements of π electrons are considerable.²⁹ In Figures 1 and 2 are shown end-on views of the *endo* chlorides (for simplicity) of the initial material and the tight ion pair postulated to be the first intermediate in the solvolysis. It is evident that the aromatic ring provides a more extreme U-shaped cavity which can hinder ionization and solvation of the departing anion.

The problem we now face is whether we can extrapolate the present results to the parent secondary 2-benzonorbornenyl derivatives. The *exo:endo* rate ratio for the acetolysis of the secondary brosylates is 15 000.⁷ The value becomes 60 000 corrected for internal return.³⁰ If we take the rate constant for the *endo* isomer as a measure of the electron demand,³¹ the effect of electron demand on the *exo:endo* rate ratio can be examined (Figure 3).

The 2-aryl derivatives cover approximately two-thirds of the range. No significant change in the *exo:endo* rate ratio is observed over this part of the diagram. A relatively small increase in the *exo:endo* rate ratio, by a factor of 5 for k_t and a factor of 20 for k_α , is observed for the secondary derivative. Unfortunately, since the steric requirements of 2-H are so different from those of 2-Me or 2-Ar, it is probably not feasible to attempt a breakdown at this time into contributions resulting from π participation and contributions resulting from steric effects, although it would appear to be a reasonable compromise that both must contribute to the observed ratio.

One major puzzle remains at this time. In the case of the 7-aryl-*anti*-norbornenyl derivatives, Gassman and Fentiman³ demonstrated that with increasing stabilization of the cationic center π participation could be made vanishingly small.

Table III. Preparation and Properties of 2-Aryl-2-benzonorbornenols

| Substituent in 2-aryl | Isomer OH | Yield, % | Mp, °C | Molecular formula | Analyses |
|-------------------------------------|-----------|----------|-------------|--|----------|
| <i>p</i> -CH ₃ O | exo | 78 | 117–117.5 | C ₁₈ H ₁₈ O ₂ | C, H |
| | endo | 69 | 81.5–82 | C ₁₈ H ₁₈ O ₂ | C, H |
| <i>p</i> -H | exo | 69 | 112.8–113.4 | C ₁₇ H ₁₆ O | C, H |
| | endo | 78 | 85.2–86.5 | C ₁₇ H ₁₆ O | C, H |
| <i>p</i> -CF ₃ | exo | 58 | 91.5–92 | C ₁₈ H ₁₅ F ₃ O | C, H, F |
| | endo | 40 | 94.5–95 | C ₁₈ H ₁₅ F ₃ O | C, H, F |
| 3,5-(CF ₃) ₂ | exo | 57 | 82–84 | C ₁₉ H ₁₄ F ₆ O | C, H, F |
| | endo | 66 | 84–85 | C ₁₉ H ₁₄ F ₆ O | C, H, F |

Table IV. Preparation and Properties of 2-Aryl-2-benzonorbornenyl *p*-Nitrobenzoates

| Substituent in 2-aryl | Isomer OPNB | Yield, % | Mp, °C | Molecular formula | Analyses |
|-------------------------------------|------------------|----------|-------------|--|------------|
| <i>p</i> -CH ₃ O | exo ^a | | | C ₂₅ H ₂₁ NO ₅ | |
| | endo | 62 | 130 | C ₂₅ H ₂₁ NO ₅ | C, H, N |
| <i>p</i> -H | exo | 39 | 186–188 dec | C ₂₄ H ₁₉ NO ₄ | C, H, N |
| | endo | 40 | 124.5–126 | C ₂₄ H ₁₉ NO ₄ | C, H, N |
| <i>p</i> -CF ₃ | exo | 40.5 | 147–147.5 | C ₂₅ H ₁₈ NF ₃ O ₄ | C, H, N |
| | endo | 70 | 166–166.5 | C ₂₅ H ₁₈ NF ₃ O ₄ | C, H, N |
| 3,5-(CF ₃) ₂ | exo | 78 | 163.5–164.5 | C ₂₆ H ₁₇ NF ₆ O ₄ | C, H, N, F |
| | endo | 62 | 178–179 | C ₂₆ H ₁₇ NF ₆ O ₄ | C, H, N, F |

^a The *p*-nitrobenzoate could not be isolated in a pure state.

Conversely, it would have been anticipated that with the introduction of deactivating substituents into the benzo moiety of the 2-benzonorbornenyl system, π participation would also become vanishingly small. Consequently, with the introduction of deactivating substituents we had anticipated that the exo:endo rate ratio would at first decrease, but would then level off at a constant value as π participation became vanishingly small and no longer a significant factor.

However, this has not been observed. It has been reported that the exo:endo rate ratio of 15 000 for the parent system decreases to 100 for the 6- or 7-nitro derivative¹⁹ and then decreases even further to 4 for the 6,7-dinitro derivative.¹⁸ In the range of the deactivating substituents, both exo and endo isomers give satisfactory Hammett plots. Consequently, extrapolation of the results predicts that the introduction of still more deactivating substituents will cause the exo:endo rate ratio to become less than one!

This feature of the solvolysis of secondary 2-benzonorbornenyl derivatives containing deactivating substituents suggests that the precise interpretation of these solvolytic data for secondary systems should be approached with caution. The data may be complicated by variable solvent participation as the deactivated structure resists ionization. Fortunately, the tertiary derivatives, over the range we have been discussing, appear to be free of this complication.

Conclusion

The essentially constant exo:endo rate ratios in the 2-aryl-2-benzonorbornenyl derivatives argue strongly for the absence of significant π participation. The observed high exo:endo rate ratios (~3000) must result from the operation of some factor other than π participation. The only factor presently available which appears capable of accounting for the observed high exo:endo rate ratio is steric hindrance to ionization.

Experimental Section

Benzonorbornadiene was prepared from cyclopentadiene and *o*-bromofluorobenzene according to literature procedure:³² bp 80–82 °C (2 mm) [lit.¹⁴ bp 88–89 °C (19 mm)]; n_D^{20} 1.5654 [lit.³³ n_D^{20} 1.5647].

exo-Benzonorbornenol was obtained by the hydroboration-oxi-

dation of benzonorbornadiene, mp 75.5–76 °C (lit.¹⁴ mp 74.1–75.4 °C).

Benzonorbornen-2-one (11). To 300 ml of pyridine was added portionwise with stirring 40 g of chromium trioxide maintaining the temperature at 15–30 °C. A solution of benzonorbornenol (48.0 g, 0.3 mol) dissolved in 300 ml of pyridine was added to the chromium trioxide-pyridine complex, cooled in ice. After stirring overnight, 40 g of chromium trioxide was added to ensure completion of the reaction and again stirred overnight. The reaction mixture was poured into water and extracted with pentane. The pentane layer was washed with sodium bicarbonate solution and dried over anhydrous magnesium sulfate, and the solvent was evaporated. Distillation gave 30 g (63.3% yield) of the ketone **11**, bp 114–115 °C (15 mm).

Preparation of 2-Aryl-endo-benzonorbornenols. These alcohols were prepared by the addition of the appropriate arylmagnesium bromides to benzonorbornen-2-one (**11**) following the general procedure described earlier for the synthesis of the related 2-aryl-2-norbornenols⁹ or 3-aryl-3-norbornenols.⁶ The properties of these alcohols are listed in Table III.

Preparation of 2-Aryl-exo-benzonorbornenols. The endo alcohols were hydrochlorinated in methylene chloride in an automatic hydrochlorinator.³⁴ The tertiary chlorides were hydrolyzed in aqueous acetone containing 1 equiv amount of silver nitrate. The acetone was removed using a rotary evaporator and the residue extracted with ether. Removal of solvent and crystallization from hexane furnished pure exo alcohols. Properties of these alcohols are tabulated in Table III.

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates of *exo*- and *endo*-2-arylbenzonorbornenols were prepared by treating the lithium salt of the alcohols with *p*-nitrobenzoyl chloride.⁶ The melting points and analytical data are summarized in Table IV.

Kinetic Procedure. The solvolysis conditions and procedures are the same as previously reported.⁶

References and Notes

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General Acid Catalysis of the Hydrolysis of Acetal Analogues of High Basicity. The Hydrolysis of 2-(Substituted phenyl)-*N,N*-dimethyl-1,3-imidazolidines

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Abstract: The rates of hydrolysis of a series of 2-(substituted phenyl)-*N,N*-dimethyl- and -diphenyl-1,3-imidazolidines to the corresponding aldehydes have been measured in H₂O at 30 °C. With 2-(*p*-methoxyphenyl)-*N,N*-dimethyl-1,3-imidazolidine, a cationic Schiff base intermediate can be observed at pH values below 4.7 (λ_{\max} 330 nm). This Schiff base hydrolyzes rapidly in moderately concentrated HCl solutions in comparison with analogous intermediates formed during hydrolysis of 2-(*p*-methoxyphenyl)-*N*-ethylloxazolidine and -thiazolidine. High reactivity is due to lack of reversibility of the ring-opening reaction after protonation of the nitrogen leaving group subsequent to ring opening. The order of reactivity for intramolecular nucleophilic attack on a cationic Schiff base is SH > OH > N⁺H₂CH₃. The rate of cationic Schiff base hydrolysis decreases with increasing acidity in moderately concentrated HCl solutions. From pH 2–4, formation of *p*-methoxybenzaldehyde is pH independent. Kinetic general base catalysis occurs in that pH region. At pH values greater than 4.7, a Schiff base intermediate can no longer be observed, and the rate of aldehyde formation decreases with increasing pH. A plot of log k_{obsd} vs. pH is linear from pH 8.5–11 with slope of -1.0 . At pH values greater than 11, the reaction again becomes pH independent ($k_0^{\text{H}_2\text{O}}/k_0^{\text{D}_2\text{O}} = 1.5$). The acid-catalyzed reaction involves rapid acid-catalyzed ring opening (at near diffusion-controlled rates) followed by rate-limiting Schiff base hydrolysis. Kinetic general acid catalysis is observed. An intermediate is not observed because of facile reversibility of the ring-opening reaction. That this interpretation is correct is shown by the behavior of the analogous open-chain compound *N,N,N',N'*-tetramethyl-*p*-methoxytoluenediamine. This compound gives a cationic Schiff base at rates too fast to measure at all pH values. The Schiff base hydrolyzes to *p*-methoxybenzaldehyde in a pH-independent reaction which involves proton transfer in the critical transition state ($k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 2.39$). General base catalysis is observed with $\beta = 0.42$. Hydroxide ion catalysis takes place at pH values greater than 7. 2-(*p*-Methoxyphenyl)-*N,N*-diphenylimidazolidine hydrolyzes slowly to aldehyde in an acid-catalyzed reaction which is $\sim 10^7$ -fold slower than in the case of the *N,N*-dimethyl derivative. The reaction is considerably faster in D₂O than H₂O ($k_{\text{D}}/k_{\text{H}} = 2.9$). Thus, it is likely that the ring is opening in an A-1 reaction involving preequilibrium protonation of the substrate by hydronium ion. The relative unreactivity of this compound is due to the low basicity of the ring nitrogens ($\text{p}K_{\text{a}} < 1$). Therefore, protonation is not appreciable, and the nitrogen does not readily release electrons to stabilize a carbonium ion intermediate.

The structural features in acetals that will allow general acid catalysis in their hydrolytic reactions have been determined.² General acid catalysis by buffer acids will be observed in cases where the leaving group is good (a phenol) and the intermediate carbonium ion is of moderate stability.³ General acid catalysis will also occur when the leaving group is poor (an aliphatic alcohol) if the intermediate is of exceedingly great stability, approaching that of an alkoxytropylium ion,⁴ or if there is steric strain in the ground state which is relieved in the transition state of the reaction.⁵ In all of these cases, ease of bond breaking is the key factor in facilitating general acid catalysis, with basicity considerations apparently of secondary importance. That even very

low basicity of the substrate will not by itself permit general acid catalysis was shown by the fact that general acid catalysis could not be observed in hydrolysis of benzaldehyde methyl *S*-phenyl thioacetals where thiophenol is the leaving group in the reaction.⁶ The exactly analogous oxygen acetals are subject to general acid catalyzed hydrolysis.⁷

In an early discussion of general acid catalyzed hydrolysis of orthoesters,⁸ low basicity was stressed as the primary cause. However, it was later demonstrated that with orthoesters, as with acetals, ease of bond breaking is of greater importance in facilitating general acid catalysis.⁹

Jencks¹⁰ has recently proposed that concerted general acid catalysis will be seen in cases where the $\text{p}K_{\text{a}}$ of the sub-