

The ether extract of the filtrate was washed (H₂O), dried (MgSO₄), and evaporated. The residue was chromatographed on 30 g of silica gel (benzene elution), yielding 1.09 g (79%) of *p*-nitrophenol, mp 112–113° (lit.¹⁷ 114°) after recrystallization from benzene. Reaction 11 (Table II) was identical.

2-Pyridone. 2-Chloropyridine (1.14 g, 10 mmol) in DMSO (35 ml) was added to 20 mmol of the benzaldoxime salt in 35 ml of DMSO. No color formation was observed after 30 min at room temperature but when the mixture was heated to 110° it became dark red. The solution was stirred at this temperature for 15 hr, cooled, and poured into 150 ml of ice water. The aqueous solution was saturated with carbon dioxide and extracted twice with chloroform. The aqueous layer was evaporated and the residual solid was triturated twice with CHCl₃. Filtration and evaporation of the chloroform solution produced 0.69 g (72%) of 2-pyridone, mp 104.5–105.5° (lit.¹⁸ 106°) after recrystallization from xylene.

***p*-Hydroxybiphenyl.** To a mixture of 20 mmol of the benzaldoxime salt in 35 ml of DMSO was added 4-nitrobiphenyl (1.99 g, 10 mmol) in DMSO (35 ml). The mixture was heated for 18 hr at 60°, cooled, and poured into 150 ml of ice-water which had been acidified with 2.5 ml of concentrated HCl. The ether extract of this mixture was washed (H₂O), dried (MgSO₄), and evaporated. The residue was triturated with 10% NaOH. Filtration and acidification of the NaOH solution produced 0.34 g (20%) 4-hydroxybiphenyl, mp 159–60° (lit.¹⁹ 160–2°) after sublimation and recrystallization from ethanol-water.

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Registry No.—*O*-(*p*-Nitrophenyl)benzaldoxime, 52540-26-8.

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Solvolysis of *exo*- and *endo*-2-Bicyclo[3.2.0]hepta-3,6-dienyl *p*-Nitrobenzoates. Possibilities of Antiaromatic Interaction in the Resulting Carbocations

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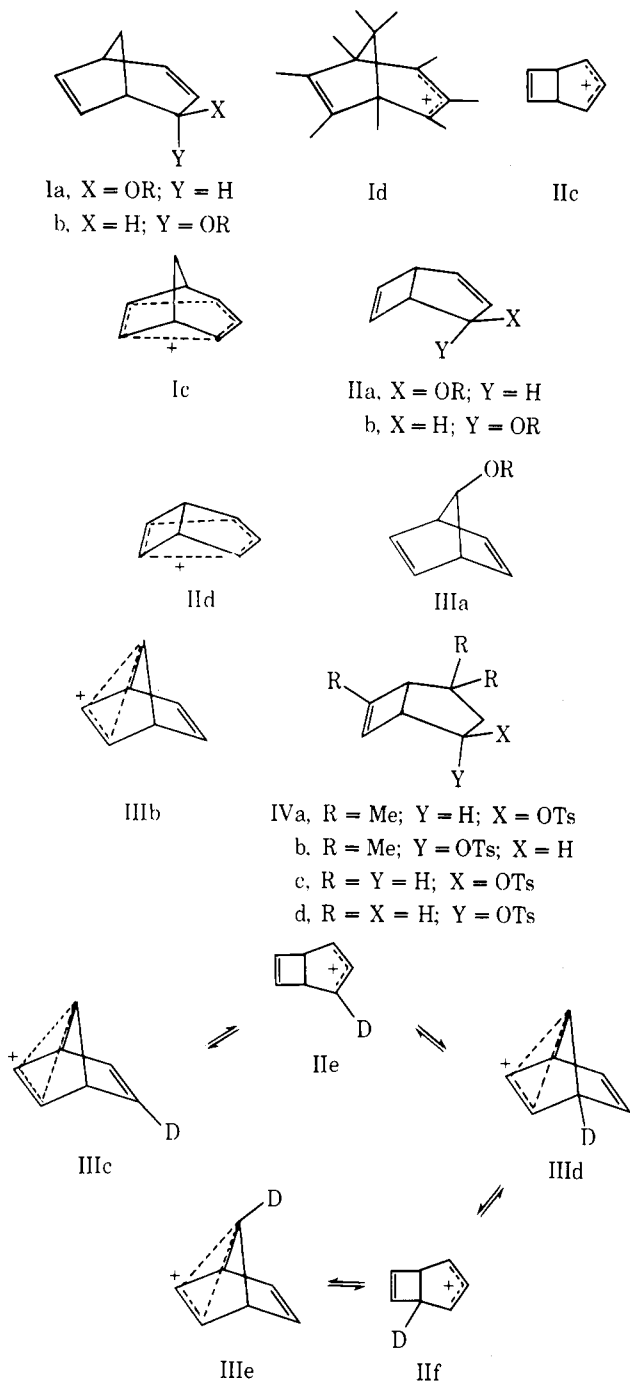
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The kinetics and products of the solvolysis of the title compounds (IIa and IIb, R = PNB) were studied. They were found to undergo hydrolysis (80% aqueous acetone) at virtually identical rates, both being slightly more reactive than 7-norbornadienyl *p*-nitrobenzoate (IIIa, R = PNB). Acetolysis and hydrolysis (50% aqueous acetone) of the title compounds were found to yield only mixtures of the unrearranged *exo* and *endo* acetates and alcohols, with no ring enlarged 7-norbornadienyl derivatives being detected. The possibility of the intermediacy of an antiaromatic bishomocyclopentadienyl cation (IIc) in these solvolyses and in the rearrangement to the 7-norbornadienyl cation (IIIb) observed upon treatment of either *exo* or *endo* alcohols (IIa and IIb, R = H) with FSO₃H is discussed.

Reactions involving antiaromatically destabilized intermediates have elicited much interest in the recent literature.² Diaz³ has described the solvolysis of *exo*- and *endo*-2-bicyclo[3.2.1]octa-3,6-dienyl *p*-nitrobenzoates (Ia and Ib, R = PNB), noting an *exo/endo* rate ratio of virtual unity, and an apparent rate retardation by the double bond at C-6 of a factor of *ca.* 235. The latter observation suggested the involvement of a bishomoantiaromatic cation, Ic. Hart,⁴ on the other hand, feels that the nmr data from the nonmethylbicyclo[3.2.0]hepta-3,6-dien-2-yl cation (Id) at -90°^{4a} are more consistent with an allylic structure. In a preliminary communication⁵ describing the solvolysis of *exo*- and *endo*-2-bicyclo[3.2.0]hepta-3,6-dienyl *p*-nitrobenzoates (IIa and IIb, R = PNB), we noted an *exo/endo* rate ratio of unity and the observation only of unrearranged products. Winstein,⁶ however, noted that treatment of either 7-norbornadienol (IIIa, R = H) or *exo* and *endo* alcohols IIa and IIb (R = H) with fluorosulfonic acid (FSO₃H) at -78° results in formation of the 7-norbornadienyl cation (IIIb). Using labeled substrates, he found that the interconversion between 7-norbornadienyl and bicyclo-

[3.2.0]heptadienyl cations involves stepwise circumambulation of five carbons with respect to the "bound" vinyl group in IIIb (IIIc = IIe = IIId = IIIf = IIIe).⁶ Hart⁴ noted an analogous degenerate rearrangement in Id at temperatures above -90°, along with other rearrangements detectable only in labeled substrates. We noted, however, that the interconversion between bicyclo[3.2.0]heptadienyl and 7-norbornadienyl cations is quenched in conventional solvolysis media⁵ and rationalized our results on the basis of an allylic (IIc), rather than a bishomoantiaromatic (IIc) intermediate. We also noted that the allylic double bond at C-2 evidently swamps out homoallylic participation as observed by Whitham⁷ in the solvolysis of *exo*-4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-yl tosylate (IVa). This more detailed description of our results, and their relation to our results from a study of *exo*- and *endo*-bicyclo[3.2.0]hept-6-en-2-yl tosylates (IVc and IVd)⁸ shows that allylic cation IIc is probably the solvolytic intermediate, but that the ring enlargement to the 7-norbornadienyl cation probably involves the corresponding bishomocyclopentadienyl cation (IIc) as the transition state.



Experimental Section

Elemental analyses were performed by Midwest Microlabs, Inc. Melting points were determined using a Thomas Hoover capillary melting point apparatus and are uncorrected.

Infrared (ir) spectra were recorded using either a Perkin-Elmer Model 621 or 257 recording infrared spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded using a Varian HA-100 spectrometer. Carbon tetrachloride was employed as solvent for all spectral determinations, unless otherwise stated.

Analytical and preparative gas chromatographic (gc) separations were performed using either a Varian A-90-P3, or HiFi-III model recording gas chromatograph. Columns packed with either Carbowax 20M or 1500 on Chromosorb W were used interchangeably for separations described herein.

Samples of *exo*- and *endo*-2-bicyclo[3.2.0]hepta-3,6-dienyl *p*-nitrobenzoates (IIa and IIb, R = PNB) were prepared from the known⁹ alcohols in 81 and 89% yields, respectively, by treatment with *p*-nitrobenzoyl chloride in pyridine at 0–5° for 12 hr. After hydrolytic work-up and recrystallization (pentane) the following physical properties were noted: IIa, R = PNB, mp 67–68.5° (Anal. Calcd: C, 65.30; H, 4.31; N, 5.44. Found: C, 65.59; H, 4.31; N, 5.54); IIb, R = PNB, mp 75–76°C (C, 65.58; H, 4.46; N, 5.61).

A sample of 7-norbornadienyl *p*-nitrobenzoate (IIIa, R = PNB) was prepared in similar fashion (36% yield), mp 103–104° (lit.¹⁰ 101–102°).

Kinetic Determinations. First-order rate constants for hydrolysis of *p*-nitrobenzoates were determined by least-squares treatment of at least eight data points. Weighed samples of ester were added to volumetric flasks, along with 2.0 ml of distilled water and enough acetone to make the volume up to 10.0 ml. Aliquots of 1.0 ml were transferred to ampoules, which were sealed and thermostated at 100.00 ± 0.05° for measured intervals and analyzed titrimetrically for liberated acid. The following rate constants were obtained (sample size given in parentheses): IIa, R = PNB (128.6 mg, 0.5 mmol), $k = (1.56 \pm 0.02) \times 10^{-5} \text{ sec}^{-1}$; IIb, R = PNB (128.6 mg, 0.5 mmol), $k = (1.90 \pm 0.02) \times 10^{-5} \text{ sec}^{-1}$; IIIa, R = PNB (343.4 mg, 1.34 mmol), $k = (1.32 \pm 0.01) \times 10^{-5} \text{ sec}^{-1}$.

Acetolysis of 2-Bicyclo[3.2.0]hepta-3,6-dienyl *p*-Nitrobenzoates (IIa and IIb, R = PNB). A 150-mg (0.59 mmol) sample of *endo-p*-nitrobenzoate (IIb) was treated with acetic acid (15 ml, 5% in acetic anhydride) in a sealed tube at 101° for 6 hr. After hydrolytic work-up, 64.5 mg (0.428 mmol, 73% yield) of 2-bicyclo[3.2.0]hepta-3,6-dienyl acetates (IIa and IIb, R = Ac) was detected using gc. An analytical sample, collected using preparative scale gc, exhibited the following properties: ν_{\max} 3040, 1730, 1365, and 1350 cm^{-1} . Anal. Calcd: C, 71.98; H, 6.71. Found: C, 72.13; H, 6.71. An authentic sample of *exo*-2-bicyclo[3.2.0]hepta-3,6-dienyl acetate, prepared from a sample of the corresponding alcohol and acetic anhydride in pyridine gave gc and ir spectral data identical with that from the acetolysis product. Treatment of the solvolysis product with lithium aluminum hydride in ether resulted in the formation of an 89:11 mixture of *exo* and *endo* alcohols (IIa and IIb, R = H), characterized by gc analysis. A duplicate run was carried out using 0.1 M sodium acetate in acetic acid (5% in acetic anhydride) as solvent. A virtually identical acetate mixture was formed. Hydride reduction yielded a 90:10 mixture of *exo* and *endo* alcohols.

In a similar fashion, 20 mg (0.08 mmol) of *exo-p*-nitrobenzoate (IIa, R = PNB) was acetolyzed (2 ml) for 5 hr. The crude product contained 8 mg (0.05 mmol, 63% yield) of 2-bicyclo[3.2.0]hepta-3,6-dienyl acetate, characterized by gc and ir analysis. Hydride reduction of the acetate mixture yielded an 88:12 mixture of *exo* and *endo* alcohols. A duplicate run using 0.1 M sodium acetate in acetic acid yielded an acetate mixture, which upon hydride reduction formed a 91:9 mixture of *exo* and *endo* alcohol.

Hydrolysis of IIa and IIb, R = PNB. A 100-mg (0.39 mmol) sample of *endo-p*-nitrobenzoate (IIb, R = PNB) and 10 ml of 50% aqueous acetone were heated at 102° for 6 hr in a sealed tube. After hydrolytic work-up, analysis of the crude product using gc showed the presence of two volatile components in 89:11 proportions, with the minor component eluting first. Subsequent analytical gc injections using weighed portions of 7-norbornadienol as an internal standard, as well as ir analysis of samples of the products obtained from preparative scale gc injections, showed that the volatiles consisted of 17.2 mg (0.16 mmol, 41% yield) of a mixture of *exo*- and *endo*-2-bicyclo[3.2.0]hepta-3,6-dienol (IIa and IIb, R = H). A duplicate run using 50% aqueous acetone 0.1 M sodium bicarbonate as solvent yielded an 89:11 mixture of the same products.

A 30-mg (0.12 mmol) sample of *endo-p*-nitrobenzoate and 3.0 ml of 80% aqueous acetone were sealed in an ampoule, which was thermostated at 102° for 2.5 hr. Isolation and ir analysis of the *p*-nitrobenzoate fraction showed that it consisted of unreacted *exo-p*-nitrobenzoate.

Acid Catalyzed Equilibration of *exo*- and *endo*-2-Bicyclo[3.2.0]hepta-3,6-dienol (IIa and IIb, R = H). A 10-ml ether solution containing 34.9 mg (0.326 mmol) of *endo* alcohol (IIb, R = H) and 10 ml of 5% aqueous sulfuric acid were mixed and stirred for 7.3 hr. Analysis of the ether layer using gc showed the presence of 29.5 mg (0.276 mmol, 85% yield) of a 94:6 mixture of *exo* and *endo* alcohols (IIa and IIb, R = H). A 65-mg (0.61 mmol) sample of *exo* alcohol (IIa, R = H) was treated in identical fashion. Analysis of the ether layer after 9 hr showed the presence only of unchanged *exo* alcohol. The material balance was not determined.

Results and Discussion

Samples of the title compounds (IIa and IIb, R = PNB) were found to undergo hydrolysis in 80% aqueous acetone at virtually identical rates, showing essentially the same reactivity as Diaz's³ 2-bicyclo[3.2.1]octa-3,6-dienyl *p*-nitrobenzoates (Ia and Ib, R = PNB) and 7-norbornadienyl *p*-

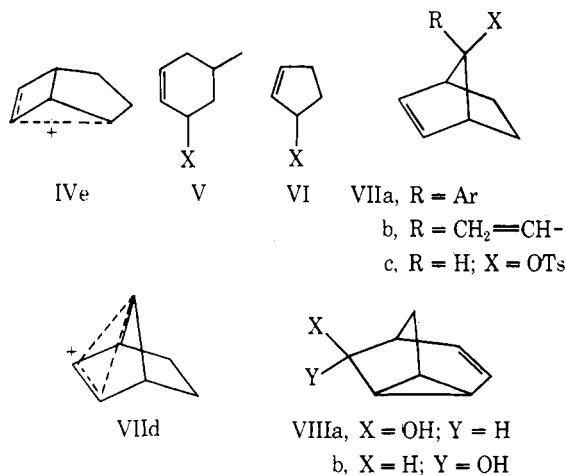
Table I
Kinetics of Hydrolysis of
Various *p*-Nitrobenzoate Esters^a

Substrate	10 ⁵ k, sec ⁻¹	Ref
Ia, R = PNB	2.76 ± 0.05	3
Ib, R = PNB	2.65 ± 0.03	3
IIa, R = PNB	1.56 ± 0.02	b
IIb, R = PNB	1.90 ± 0.02	b
IIIa, R = PNB	1.32 ± 0.01	b
V, R = PNB	0.339	11
VI, R = PNB	178.0 ^c	12

^a In 80% aqueous acetone at 100.0°. ^b This work. ^c Calculated assuming that the reactivity ratio for ethanolysis for V:VI, X = Cl (1:524 applies to hydrolysis of the corresponding *p*-nitrobenzoates in 80% aqueous acetone at 100.0°).

nitrobenzoate (IIIa, R = PNB). Diaz's data showed that his *exo*- and *endo*-*p*-nitrobenzoates undergo hydrolysis with significant acyl-oxygen cleavage and that the double bond at C-6 retards the rate of hydrolysis by a factor of *ca.* 235, indicating the involvement of a bishomoantiaromatically destabilized species (Ic) in the rate-determining step. The product studies described below show that acyl-oxygen cleavage is not involved in the hydrolysis of *p*-nitrobenzoates IIa and IIb, even though they are slightly less reactive than are Diaz's homologous *p*-nitrobenzoates Ia and Ib. Also, the kinetic data in Table I show that a bishomoantiaromatically destabilized species is probably not involved in the solvolysis of either *exo*- or *endo*-*p*-nitrobenzoates IIa and IIb.

Our *exo* and *endo* esters (IIa and IIb, R = PNB) are shown to be *ca.* four-five times more reactive than *cis*-5-methylcyclohex-2-enyl *p*-nitrobenzoate (V, X = OPNB).¹¹



As a control experiment, product studies on the hydrolysis of our substrates were carried out under the conditions of the kinetic determinations, and the unreacted *p*-nitrobenzoate fractions were isolated and characterized. In both cases, only unchanged starting material was observed after 2.5 hr, showing that bulk rearrangement of starting material had not occurred and that the titrimetric rate constants truly represent the solvolytic reactivity of our substrates. Goering¹² found that ethanolysis of 2-cyclopentenyl chloride (VI, X = Cl) proceeds some 524 times faster than does ethanolysis of *cis*-5-methylcyclohex-2-enyl chloride (V, X = Cl). Assuming that this reactivity ratio applies to hydrolysis of the corresponding *p*-nitrobenzoates in 80% aqueous acetone, then *exo*-2-bicyclo[3.2.0]hepta-3,6-dienyl *p*-nitrobenzoate (IIa, R = PNB) is only *ca.* 100 times less reactive than 2-cyclopentenyl *p*-nitrobenzoate (VI, X = OPNB). A rate retardation of this magnitude can be easily explained

Table II
Products from the Solvolysis of
Various *p*-Nitrobenzoate Esters at 100°

Substrate	Solvent	Products (% composition)	% total yield	Ref
Ia, R = PNB ^a	60% aq acetone	Ia, R = H(75); Ib, R = H(19); VIIIa(3); VIIIb(3)	83 ^b	3
Ib, R = PNB		Ia, R = H(37.5); Ib, R = H(56); VIIIa(3); VIIIb(3)	89 ^b	3
IIa, R = PNB ^c	50% aq acetone	IIa, R = H(87); IIb, R = H(13)	54	d
IIb, R = PNB ^c		IIa, R = H(89); IIb, R = H(11)	41	d
IIa, R = PNB ^e	HOAc	IIa, R = Ac(88); IIb, R = Ac(12) ^f	63	d
IIb, R = PNB ^e		IIa, R = Ac(89); IIb, R = Ac(11) ^f	73	d

^a Buffered by 3.0-4.5 × 10⁻³ M NaOAc. ^b Other products detected in total yield of 5-8%. ^c Buffered with a threefold excess of NaHCO₃. An unbuffered solvolysis yielded a virtually identical product mixture. ^d This work. ^e Buffered by a threefold excess of NaOAc. An unbuffered acetate mixture yielded a virtually identical product mixture. ^f Composition of acetate mixtures determined by LiAlH₄ reduction of the acetate mixture, followed by gc analysis of the resulting alcohols.

by inductive withdrawal by the double bond at C-6 and steric hindrance toward solvation of the transition state in the more highly substituted bicyclic substrate. Thus, the kinetic results are adequately explained by the intermediacy of allylic cation IIc.

Gassman¹³ found that substitution in the 7-position by electron donating aryl groups, such *p*-anisyl, in *anti*-7-norbornenyl substrates (VIIa, X = OPNB, Ar = *p*-CH₃OC₆H₄-) completely levels the 10¹¹ solvolytic rate difference observed between *anti*-7-norbornenyl tosylate (VIIc) and its saturated analog.¹⁴ This approach has been used to evaluate anchimeric assistance toward solvolysis in other systems.¹⁵ In our preliminary communication⁵ of these results, we noted that the allylic double bond in our esters swamps out homoallylic participation as observed in product studies on the solvolysis of *exo*-4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-yl tosylate (IVa),⁷ but, at that time, there were no rate data available to evaluate the magnitude of this leveling effect. We have completed a study of the solvolysis of *exo*- and *endo*-2-bicyclo[3.2.0]hept-6-enyl tosylates (IVc and IVd)⁸ and find an *exo*/*endo* rate ratio for S_N1 acetolysis at 50.0° of *ca.* 2400. Thus, incorporation of a double bond in the ring system allylic to the reaction center can level solvolytic rate differences of at least 2400. This should be regarded as a lower limit, since Sargent's¹⁶ studies of the solvolysis of 7-vinyl-*anti*-7-norbornenyl 3,5-dinitrobenzoate (VIIb, X = DNB)^{16a} and related substrates showed that an exocyclic vinyl group allylic to the reaction center can level solvolytic rate differences as high as 10⁸ arising from nonvertical stabilization^{16b,c} (*i.e.*, through bridging, rather than hyperconjugation)¹⁷ of the transition state.¹⁸ Studies of other substrates containing allylic double bonds incorporated into the ring system might furnish valuable information concerning anchimeric assistance toward solvolysis in other systems.

Data from the product studies on the solvolysis of our substrates (IIa and IIb, R = PNB) are also adequately ex-

plained by the intermediacy of allylic cation IIc. These results, along with those from product studies on hydrolysis of Diaz's³ homologous esters (Ia and Ib, R = PNB) are presented in Table II. The product from hydrolysis of both bicyclooctadienyl esters (Ia and Ib, R = PNB) consists mainly of mixtures of the corresponding *exo* and *endo* alcohols, along with small amounts of tricyclic alcohols VIIIa and VIIIb. The unrearranged alcohols are thought to arise from acyl-oxygen and alkyl-oxygen cleavage. Diaz³ calculated that hydrolysis of these substrates in 60% aqueous acetone in the presence of $3.0\text{--}4.5 \times 10^{-3} M$ sodium acetate as buffer occurs with 60% alkyl-oxygen and 40% acyl-oxygen cleavage, where the alkyl-oxygen cleavage yields 90% unrearranged dienyl alcohols consisting of a 2:1 *exo*:*endo* product mixture (Ia:Ib, R = H). The solvolysis of *exo*- and *endo*-2-bicyclo[3.2.0]hepta-3,6-dienyl *p*-nitrobenzoates (IIa and IIb, R = PNB), on the other hand, yields *ca.* 90:10 mixtures of the corresponding *exo* and *endo* derivatives, whether buffered or unbuffered media are used, and for solvents ranging from aqueous acetone to acetic acid. This indicates the absence of acyl-oxygen cleavage, and that the title compounds (IIa and IIb, R = PNB) solvolyze *via* formation of a common intermediate, presumably allylic cation IIc. The difference in product ratio in the unrearranged alcohols from solvolysis of the bicycloheptadienyl and bicyclooctadienyl substrates can be explained on steric grounds. In the latter case, the *syn*-proton in the methylene bridge hinders the *exo*-side of cation IIc toward nucleophilic attack. This type of interaction is absent in cation IIc.

Consideration of the energetics of the solvolyses of our *exo*- and *endo*-*p*-nitrobenzoates (IIa and IIb, R = PNB), as well as the ring enlargement of the 2-bicyclo[3.2.0]hepta-3,6-dienyl cation (IIc) to the 7-norbornadienyl cation (IIIb) is informative in several respects. Data pertaining to the latter case are presented graphically in Figure 1, along with energy differences and activation parameters from the hydrolysis of *exo*-*p*-nitrobenzoate (IIa, R = PNB) and 7-norbornadienyl *p*-nitrobenzoate (IIIa, R = PNB). The former case is elaborated as follows.

Acid catalyzed equilibration in diethyl ether-5% sulfuric acid of *endo* alcohol (IIb, R = H) resulted in a 94:6 mixture of *exo* and *endo* alcohols (IIa:IIb, R = H), indicating that, at ambient temperatures, the *exo* alcohol is the more stable by *ca.* 1.64 kcal/mol. It should be noted in passing that, even under acidic conditions such as these, which should favor rearrangement, no 7-norbornadienol (IIIa, R = PNB) was detected. Calculation directly from the kinetic data yields free energies of activation (ΔG^*) of 30.3 and 30.1 kcal/mol for the hydrolysis of *exo*- and *endo*-*p*-nitrobenzoates (IIa and IIb, R = PNB), respectively. Assuming that the energy difference for the alcohols applies also to the *p*-nitrobenzoates at 100°, then the solvolytic transition states differ in energy by *ca.* 1.44 kcal/mol, with the *exo* transition state being favored. Calculation directly from the product ratios (ranging from 87:12 to 89:11), which represent the partitioning of allylic cation IIc between *exo* and *endo* products (IIa and IIb, R = H or Ac) *via* the solvolytic transition states, yields values of 1.37-1.55 kcal/mol, in excellent agreement for such approximate methods. If bishomoantiaromatic cation IIc were involved in the solvolysis of the title compounds, then the transition state for solvolysis of the *exo* substrate would be somewhat higher than that of the *endo* substrate. Since the converse is true, the intermediacy of allylic cation IIc, rather than bishomoantiaromatic cation IIc, in the solvolysis of *exo*- and *endo*-2-bicyclo[3.2.0]hepta-3,6-dienyl *p*-nitrobenzoates (IIa and IIb, R = PNB) now seems well established. That the bisho-

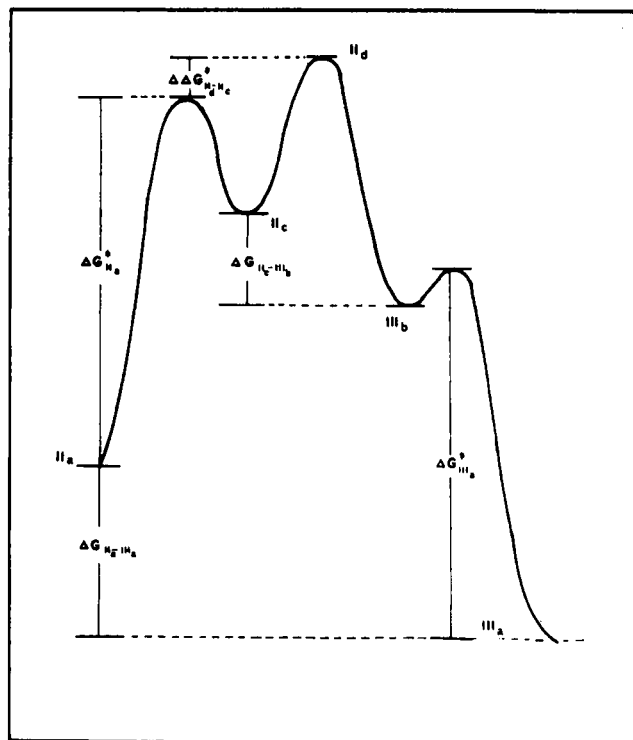
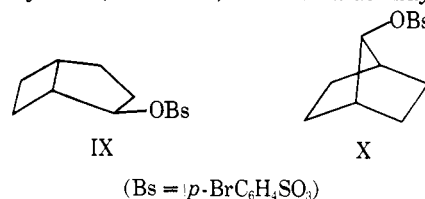


Figure 1. Free energy diagram for solvolysis of *exo*-2-bicyclo[3.2.0]hepta-3,6-dienyl and 7-norbornadienyl *p*-nitrobenzoates and the resulting cations: $\Delta G_{IIa-IIIa}^* = 14.4$, $\Delta G_{IIIa}^* = 30.4$, $\Delta G_{IIa}^* = 30.2$, $\Delta G_{IIc-IIIb} \geq 7.5$, $\Delta \Delta G_{IIc-IIIc}^* > 3.5$ kcal/mol.

moantiaromatic cation is probably involved in the ring enlargement will now be demonstrated.

The energy diagram in Figure 1 was constructed as follows. The free energy difference between our *exo*-*p*-nitrobenzoate (IIa, R = PNB) and 7-norbornadienyl *p*-nitrobenzoate (IIIa, R = PNB) ($\Delta G_{IIa-IIIa}^*$) was taken as 14.4 kcal/mol, the difference observed in the corresponding saturated brosylates (IX and X).²⁰ This value may be some-



what low, since IIa contains double bonds in a cyclobutane, as well as a cyclopentane ring, while the double bonds in IIIa are both contained in less strained cyclopentane rings, but serves as an adequate approximation for this discussion. Calculation directly from the kinetic data described above yielded free energies of activation (ΔG_{IIa}^* and ΔG_{IIIa}^*) of 30.2 and 30.4 kcal/mol for hydrolysis of IIa and IIIa, R = PNB, respectively. Winstein's⁶ value for the free energy difference between cation IIc and the 7-norbornadienyl cation (IIIb) ($\Delta G_{IIc-IIIb}$) of 7.5 kcal/mol was used but should be regarded as a lower limit. The published value for the free energy of activation for the ring enlargement (not given in Figure 1), equal to *ca.* 10 kcal/mol in FSO₃H at -120°,⁶ appears to be too low by several kilocalories. This discrepancy can be easily explained, since cation IIc (and presumably cation IIIb) is stabilized by solvation in media such as acetic acid or aqueous acetone, thereby lowering its energy relative to the transition state for ring enlargement. Such interaction is, of course, minimal in FSO₃H. A lower limit for the free energy difference between the solvolytic transition state from *exo*-*p*-nitrobenzoate and the transition state for ring enlargement

($\Delta\Delta G^*_{\text{IIc-IId}}$) can be fixed with some certainty, however. Assuming that the hydrolysis of *exo-p*-nitrobenzoate in 50% aqueous acetone formed, along with the 54% observed yield of unrearranged products, as much as a 0.5% yield of 7-norbornadienol (IIIa, R = H) that escaped detection, then the solvolytic transition state is lower than that for ring enlargement by at least 3.5 kcal/mol. The bridged 2-bicyclo[3.2.0]hept-6-enyl cation (IVe), on the other hand, undergoes ring enlargement to the 7-norbornenyl cation (VIIId) at an exceedingly rapid rate, as shown by the fact that solvolysis of *exo*-2-bicyclo[3.2.0]hept-6-enyl tosylate (IVc) yields only products derivable from the 7-norbornenyl cation,⁸ even in the presence of strong nucleophiles, such as methoxide, added to trap²¹ cation IVe prior to rearrangement. Although no reliable value for the free energy of activation for this ring enlargement can be assigned, it is certainly lower than that for the ring enlargement involving cation IIc by several kilocalories per mole. This difference is explained as follows. The ring enlargement of the 2-bicyclo[3.2.0]hepta-3,6-dienyl cation (IIc) must involve initial interaction between the incipient p orbital at C-4 and either the π -system at C-7, or the σ -bond connecting it to the bridgehead. Although Dewar²² cautions against the rigorous use of arguments of this type, it seems likely that such interaction would involve the π -system, occupying frontier orbitals,²³ rather than a portion of the lower lying σ -system. This type of interaction would yield bishomocyclopentadienyl cation IIId, and is thought to be destabilizing.^{2,3,24} This interaction can be minimized by flattening of the concave carbon skeleton in bicyclo[3.2.0]heptadienyl derivatives (II) and is, therefore, unimportant in either the rate-determining or product-forming steps in the solvolysis of the title compounds. Incidentally, such flattening should be less favored in Diaz's³ homologous bicyclooctadienyl cation (Ic), rendering it a more likely candidate for antiaromatic interaction.

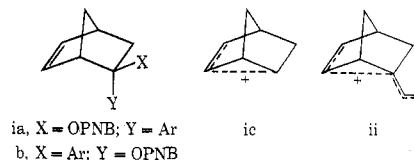
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Registry No.—IIa (R = PNB), 21654-38-6; IIa (R = Ac), 52393-61-0; IIa (R = H), 35826-10-9; IIb (R = PNB), 21654-39-7; IIb (R = Ac), 52438-20-7; IIb (R = H), 35826-09-6; IIIa (R = PNB), 33686-56-5; V (X = OPNB), 52393-62-1; VI (X = OPNB), 21985-86-9; *p*-nitrobenzoyl chloride, 122-04-3.

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- (18) It should be pointed out that Brown¹⁹ has found that the *exo/endo* rate ratio from solvolysis of 2-aryl-2-norbornenyl *p*-nitrobenzoates (Ia, Ib) remains constant (ca. 350) for aryl groups of widely differing electron demand. This calls the bridged structure for the 2-norbornenyl cation (Ic)



- and the closely related bicyclic cation IVe into serious question and suggests that the high *exo/endo* rate differences can be explained on steric grounds. Sargent¹⁶ has found some evidence for the intermediacy of cation II in the product forming step in the solvolysis of 2-(2'-ethylidene-yl)bicyclo[2.2.1]hept-5-enyl 3,5-dinitrobenzoate, suggesting that, in the 2-norbornenyl system, allylic centers of unsaturation can act cooperatively with homoallylic centers to vertically stabilize^{16b,c,17} the cationic center. In any case, the allylic double bond in our substrates (Ia and Ib, R = PNB) acts competitively with the homoallylic double bond, suggesting that IVa, like the 7-norbornenyl cation (VIIId), is stabilized by a non-vertical process (*i.e.*, bridging).
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