A Convenient One-Step Conversion of Aromatic Nitro Compounds to Phenols

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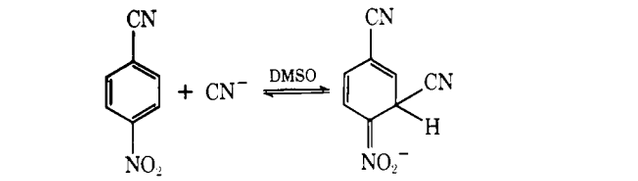
A moderately activated nitro group in a substituted nitrobenzene is displaced by reaction with the anion of an aldoxime in DMSO solution. In the DMSO solution the displacement product, an *O*-arylaldoxime, is rapidly cleaved by a base, yielding the phenol and the nitrile related to the oxime anion. The oxime anion used for the displacement is sufficiently basic to effect the cleavage. Thus, *p*-nitrobenzonitrile is converted to *p*-cyanophenol in excellent yield by reaction with 2 equiv of the salt of benzaldoxime. Similarly, ethyl *p*-nitrobenzoate is converted to ethyl *p*-hydroxybenzoate with little loss resulting from attack at the ester group and subsequent conversion to the nitrobenzoic acid. Displacement of an activated halogen atom followed by *in situ* cleavage of the oxime ether also leads to the phenol. The use of several activating groups in the reactions is reported. Even with the unactivated nitro compound 4-nitrobiphenyl some (~20%) of the phenol has been obtained.

In dipolar aprotic solvents various aromatic nitro compounds undergo the addition of cyanide ion to give adducts, *e.g.*, **1**, similar to Jackson–Meisenheimer complexes, which can be converted to various further transformation products,[1-3] and the anion of 2-nitropropane gives a similar adduct with 9-nitroanthracene.[4] The structural resemblance of the anion of an oxime to that of an aliphatic nitro compound suggests that oximates too might give adducts similar to those observed with cyanide ion. When *p*-nitrobenzonitrile and the sodium salt of benzaldoxime (2 equiv) were brought together in DMSO at ambient temperature the solution rapidly developed an intense purple color, which faded with time, reminiscent of the color changes occurring in reactions of cyanide ion and attributed to the Jackson–Meisenheimer complexes,[4] but when the test was terminated after 48 hr the solution was found to contain an almost quantitative yield of the entirely unexpected product *p*-cyanophenol. Evidently the oximate anion had attacked the aromatic system at the carbon atom bearing the nitro group, displacing it as nitrite ion, rather than adding in the Jackson–Meisenheimer fashion.

The nucleophilic displacement of activated aromatic nitro groups has been studied over many years,[5] but only recently has it found promising application[6] in synthesis. Displacement of a nitro group from a benzene ring carrying only one activating group has been quite rare, and in most such instances the activation has been supplied by a second nitro group. However, very recent studies have shown that a nitro group activated by a single carbalkoxyl, cyano, or carbonyl group, among others, is displaced by a methoxide or a mercaptide anion, sometimes in excellent yield,[6,7] when the reaction is carried out in an aprotic solvent. Cyclization of the diester obtained by the displacement of the nitro group of an ester of 2-nitrobenzoic acid by the anion of methyl mercaptoacetate constitutes a step in a very useful synthesis of methyl 3-hydroxybenzo[*b*]thiophene-2-carboxylates.[6] In the cyanide reactions conducted in this laboratory displacement of an activated nitro group by cyano has been observed only with 9-nitro-10-cyanoanthracene (58% conversion to 9,10-dicyanoanthracene),[1] and none of the displacement product from *p*-nitrobenzonitrile[3] was observed. The nearly complete displacement observed with the anion of benzaldoxime and this nitronitrile suggests that oximate anions may be among the most active displacement agents. Separation of the pure *p*-cyanophenol from the benzaldoxime present at the end of the reaction mentioned above required time-consuming chromatography which could be avoided by the use of the sodium salt of acetaldoxime (2.5 equiv, 45-min reaction time at 30°, 69% yield of pure *p*-cyanophenol isolated by crystallization). The rapid displacement of the nitro group under such very mild conditions suggested the possible successful application of the process to compounds, such as *o*- and *p*-nitrobenzoic esters, in which the activating group is sensitive to attack by base. In a trial with ethyl *p*-nitrobenzoate and the salt of acetaldoxime, reacting for only 20 min at 30°, the yield of ethyl *p*-hydroxybenzoate was 55%, and that of *p*-nitrobenzoic acid was 36% (Table I). Reducing the temperature to 25° increased the yield of the hydroxy ester to 64%, and only 18% nitro acid was obtained. Substantially lower temperatures can be realized with DMF as the solvent (DMSO melts at 18°), but a trial in DMF at 10° gave only 38% hydroxy ester and 45% nitro acid; this solvent evidently favors attack at the ester group rather than at the nucleus. When enough acetonitrile was added to a DMSO solution to permit operation in the liquid state at −3°, the yield of hydroxy ester was also low (31%).



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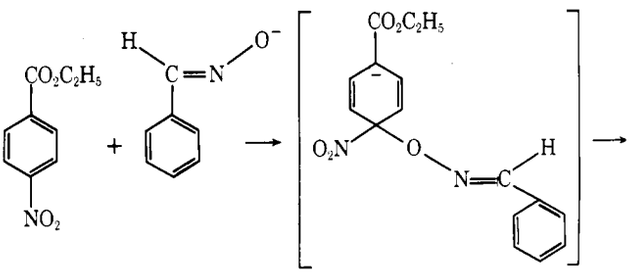

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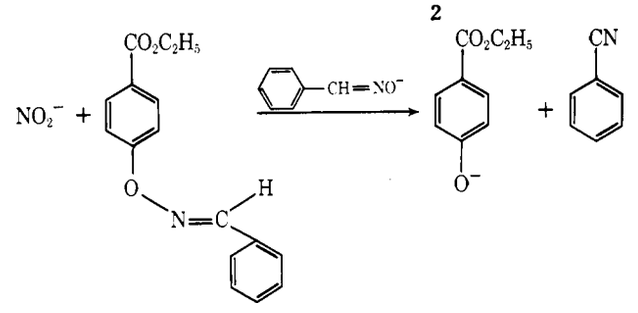

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The salt of benzaldoxime reacted more slowly with the

Table I
Ester Activation of Nitro Displacement

Reaction	Ester	Oxime	Solvent	Time	Temp, °C	Yield, % Hydroxy ester	Yield, % Nitro acid
1	*p*-$O_2NC_6H_4CO_2C_2H_5$[a]	CH_3CHNOH[b,c]	DMSO	20 min	30	55	36
2		*c*	DMSO	10 min	25	64	18
3		*c*	DMF	20 min	25	46	37
4		*c*	DMF	2 hr	10	38	45
5		*c*	DMSO/CH_3CN	1.5 hr	−3	31	
6		C_6H_5CHNOH[c,d]	DMSO	5 hr	20	65	5
7		*e*	DMSO	6.5 hr	20	81	14
8		*e*	ETOH[f]	8 hr	74	<0.2	64
9	*p*-$O_2NC_6H_4CO_2CH_3$[g]	*e*	DMSO	7.5 hr	20	63	14
10	*o*-$O_2NC_6H_4CO_2C_2H_5$[h]	*e*	DMSO	6.5 hr	20	29[i]	37

[a] Registry number, 99-77-4. [b] Registry number, 52540-25-7. [c] Addition of ester to oxime salt. [d] Registry number, 40026-28-6. [e] Addition of oxime salt to ester. [f] Absolute ethanol. [g] Registry number, 619-50-1. [h] Registry number, 610-34-4. [i] Isolated as salicylic acid.

Table II
Replacement of Nitro and Halogen by Hydroxyl

Reaction	Substrate	Registry no.	Solvent	Time	Temp, °C	Product	Registry no.	Yield, %
11	*p*-Dinitrobenzene[a]	100-25-4	DMSO	50 min	30°	*p*-nitrophenol[b]	100-02-7	78
12	*p*-Nitrobenzonitrile[a]	619-72-7	DMSO	46 hr	25	*p*-hydroxybenzonitrile	767-00-0	94
13	*p*-Nitrobenzonitrile[c]		DMSO	45 min	30	*p*-hydroxybenzonitrile		69
14	*o*-Nitrobenzonitrile[a]	619-24-9	DMSO	2 hr	25	*o*-hydroxybenzonitrile	611-20-1	57
15	*p*-Nitrobenzophenone[a]	1144-74-7	DMSO	8 hr	25	*p*-hydroxybenzophenone	1137-42-4	62
16	*p*-Nitroacetophenone[a]	100-19-6	DMSO	12 hr	25	*p*-hydroxyacetophenone	99-93-4	0
17	*p*-Nitrobenzaldehyde[a]	555-16-8	DMSO	1 hr	30	*p*-hydroxybenzaldehyde	123-08-0	0
18	*p*-Nitrobenzamide[c]	619-80-7	DMSO	17 hr	70	*p*-hydroxybenzoic acid[d]	99-96-7	50
19	4-Nitrobiphenyl[a]	92-93-3	DMSO	18 hr	60	4-hydroxybiphenyl	92-69-3	20
20	*p*-Nitrofluorobenzene[a]	350-46-9	DMSO	50 min	30	*p*-nitrophenol[b]	100-02-7	79
21	Ethyl *p*-fluorobenzoate[a]	451-46-7	DMSO	7.5 hr	20	ethyl *p*-hydroxybenzoate[e]	120-47-8	65
22	Ethyl *p*-fluorobenzoate[a]		ETOH[f]	5 hr	74	*p*-fluorobenzoic acid[g]	456-22-4	33
23	2-Chloropyridine[a]	109-9-1	DMSO	15 hr	110	2-pyridone	142-08-5	72

[a] Benzaldoxime. [b] 12% *O*-(*p*-Nitrophenyl)benzaldoxime was also isolated. [c] Acetaldoxime. [d] Hydrolysis of amide occurred under work-up conditions. [e] *p*-Fluorobenzoic acid (2%) was also isolated. [f] Absolute ethanol. [g] Less than 0.5% ethyl *p*-hydroxybenzoate.

nitro ester, but it proved more selective. Thus, a reaction conducted at 20° for 5 hr gave 65% hydroxy ester and only 5% nitro acid. Inverse addition (oximate salt to ester) in a reaction conducted at 20° for 6.5 hr gave 81% hydroxy ester and 14% nitro acid. It might be expected that the methyl ester would be more susceptible to attack at the carboxylate function, but with the inverse addition it gave a good yield (63%) of the hydroxy ester, along with 14% nitro acid (Table I).

The mutual hindrance of the two groups in ethyl *o*-nitrobenzoate evidently is more effective in deterring displacement of the nitro group than of the alkoxy group. Even with the inverse addition of the benzaldoxime salt the ortho ester gave 37% nitro acid; the hydroxy ester also produced was not readily isolated from the mixture and was converted to salicylic acid, obtained in only 29% yield.

Of the other activating groups tested, *p*-nitro, *p*-benzoyl and *p*-carbamyl promoted the nitro displacement (see Table II). Because of the water solubility of the product (*p*-hydroxybenzamide) from *p*-nitrobenzamide it proved convenient to allow it to undergo hydrolysis and to isolate it as the hydroxy acid. Surprisingly, none of the phenol was isolated from a reaction of the benzaldoximate ion with either *p*-nitroacetophenone (25°, 12 hr) or *p*-nitrobenzaldehyde (70°, 1 hr).

The replacement of an activated aromatic nitro group by hydroxyl through reaction with an oximate ion evidently occurs in two steps, displacement of the nitro group to give the *O*-aryl oxime ether (*e.g.*, **3**), and attack of the latter by a second oximate ion acting as a base and converting it to phenoxide ion and benzonitrile. Presumably, an early step in the displacement leads to the intermediate **2**, shown in only one of its resonance forms. Whether the color of the solution is due to such a complex or to a Jackson–Meisenheimer complex similar to **1** but formed reversibly and not leading to products has not been determined. Conversion of the *O*-aryl oxime ethers obtained from 2,4-dinitrochlorobenzene and aldoximes to phenols and nitriles by the action of strong base (KOH) has long been known.[8] In the present work, no attempt to isolate the *O*-(*p*-carbethoxyphenyl)benzaldoxime (**3**) was made, but the benzonitrile shown as arising from its decomposition was isolated in 71% yield. Also, *O*-(*p*-nitrophenyl)benzaldoxime was isolated in quantity sufficient to test its reaction with bases. With refluxing 5% sodium hydroxide it gave a 95% yield of *p*-nitrophenol, along with benzoic acid (75%) and benzamide (5%), formed by hydrolysis of the nitrile, and in DMSO at room temperature the salt of benzaldoxime converted this ether to *p*-nitrophenol in 97% yield at 73% conversion (50 min, room temperature). Thus, in DMSO the oximate ion is able to cleave the ether.

The *O*-aryl oxime ether structure was first proposed by Werner[9] and very recently confirmed by Sheradsky, Salemnick, and Nir,[10] who prepared identical compounds both by

displacement of an activated halogen (as, *e.g.*, in 2,4-dinitrochlorobenzene) by oximate anion and by the reaction of the corresponding *O*-arylhydroxylamine with a carbonyl compound. The *O*-aryl aldoximes reported were assigned the syn configuration,[8,11] but complete spectral data were not presented. In the present work the nmr spectrum of the *O*-(*p*-nitrophenyl)benzaldoxime isolated was found to show only one signal (at δ 8.70, s, 1 H) for the aldoxime proton (CH=NO). Previous work[12] with aldoximes indicates that separate signals would be expected for the syn and anti isomers if both were present. Since the *O*-(*p*-nitrophenyl)benzaldoxime was prepared from the anion of *syn*-benzaldoxime, it seems likely that it too is of the syn configuration.

The powerful directing effect of the aprotic solvent is shown by comparison of the reaction of ethyl *p*-nitrobenzoate and benzaldoxime sodium salt conducted in DMSO with one conducted in ethanol. After 8 hr at room temperature in ethanol there was no indication (tlc) of reaction; so the mixture was heated (74°) for 8 hr. The only product isolated (64%) was *p*-nitrobenzoic acid; if ethyl *p*-hydroxybenzoate was formed vpc tests indicated its yield could not have been more than 0.2%. The response of the oximate ion to the directing effect of the aprotic solvent is shown by comparison of the oximate reaction in DMSO with a sodium hydroxide reaction in the same solvent; only *p*-nitrobenzoic acid (98% yield) was obtained when sodium hydroxide was used.

It would be expected that certain activated aromatic and heterocyclic halogen compounds can also be converted to phenols in a single operation by displacement with oximate in the presence of excess of the reagent. When ethyl *p*-fluorobenzoate was employed with the benzaldoxime salt (7.5 hr, 20°), ethyl *p*-hydroxybenzoate was obtained in 65% yield (Table II). It is interesting that this yield is somewhat lower than that of the same product obtained by nitro displacement. *p*-Nitrofluorobenzene gave *p*-nitrophenol in 79% yield (50 min, 30°), and the intermediate ether, *O*-(*p*-nitrophenyl)benzaldoxime, was also isolated in 12% yield. The yield of the ether was increased to 36% when only 1 equiv of the oximate salt was used. The chlorine atom of 2-chloropyridine was less reactive toward the salt of benzaldoxime, but a reaction at 110° for 15 hr gave 2-pyridone in 72% yield. Although the conditions were among the most vigorous employed in the present study, they are mild compared to some which are used for the same conversion.[13,14]

A trial of the reaction of the benzaldoximate with the unactivated nitro compound 4-nitrobiphenyl resulted in a 20% yield of 4-hydroxybiphenyl after 18 hr at 60°. It seems likely that a more active oximate ion may be found, permitting the useful, direct conversion of an unactivated nitro compound to the phenol.

Experimental Section

Either a Perkin-Elmer 521 or a Beckman IR-12 spectrophotometer was used for ir spectra which were run as KBr disks. Nmr spectra were recorded on a Varian A-60A or A-56/60 spectrometer. Mass spectra were recorded by Mr. J. Wrona and associates on an Atlas CH5 mass spectrometer at 70 eV. Microanalyses were performed by Mr. J. Nemeth and associates. Products were identified by comparison of ir and nmr spectra with those of authentic samples unless otherwise noted. All starting materials were either commercially available reagent grade and were used as received or were prepared in this laboratory by well known synthetic routes. DMSO and DMF were stored over Linde Type 4a Molecular Sieves for 2 weeks prior to use.

***p*-Cyanophenol.** A solution of sodium methylsulfinylmethide was prepared by heating sodium hydride (0.48 g, 20 mmol) in DMSO (25 ml) at 70° until a clear solution resulted (20–30 min). To this solution, benzaldoxime (2.42 g, 20 mmol) in DMSO (10 ml) was slowly added and the resulting mixture was stirred at 70° for 0.5 hr. To the thick paste which formed upon cooling was added 1.48 g of *p*-nitrobenzonitrile (10 mmol) in DMSO (35 ml). The deep purple color, which formed almost immediately, faded after the solution had been stirred for 46 hr at 25°. This light yellow solution was poured into 150 ml of ice water which had been acidified with 8.3 ml of concentrated HCl and the resulting aqueous solution was extracted with ether. Acidification of the 5% NaOH extract of the ether solution resulted in the formation of a yellow oil which was separated. Chromatography of this oil on 30 g of silica gel (benzene elution) resulted in the isolation of 1.12 g (94%) of *p*-cyanophenol, mp 111–112° (lit.[15] mp 112°) after recrystallization from benzene. When acetaldoxime was used the ether extract was dried ($MgSO_4$) and evaporated and the resulting oil was recrystallized from water to give *p*-cyanophenol (69%). The procedure for reactions 14–18 (Table II) was similar.

Ethyl *p*-Hydroxybenzoate. The sodium salt of benzaldoxime (81 mmol) in DMSO (175 ml) was prepared as described above. This salt was slowly added (45 min) to a solution of ethyl *p*-nitrobenzoate (7.8 g, 40 mmol) in DMSO (50 ml). The reaction temperature was maintained at 15° by an ice bath. The reaction mixture was stirred for 1 hr at 15° after addition was complete and then for 5.5 hr at room temperature. The resulting DMSO solution was poured into 500 ml of ice water which had been acidified with 8.3 ml of concentrated HCl. This aqueous mixture was extracted with ether. Acidification of a 5% sodium carbonate extract of the ether solution produced 0.94 g (14%) of *p*-nitrobenzoic acid. Further extraction of the ether solution with 5% NaOH and subsequent acidification produced 5.38 g (81%) of ethyl *p*-hydroxybenzoate, mp 115–116° (lit.[16] mp 116°) after recrystallization from water. The ether solution was then extracted with 10% NaOH until the benzaldoxime was completely removed, washed (H_2O), dried ($MgSO_4$), and evaporated. Distillation of the residue resulted in the isolation of 2.94 g (71%) of benzonitrile. The procedures for reactions 1–10, 21, and 22 were similar, with the differences in conditions noted in Tables I and II.

***O*-(*p*-Nitrophenyl)benzaldoxime.** The sodium salt of benzaldoxime (80 mmol) in DMSO (175 ml) was prepared as described previously. This mixture was slowly added to *p*-fluoronitrobenzene (11.28 g, 80 mmol) in 50 ml of DMSO. The reaction mixture was cooled in an ice bath. After addition was complete, stirring was continued for 0.5 hr at room temperature. The mixture was poured into 500 ml of ice water which had been acidified with 8.3 ml of concentrated HCl. The light tan precipitate which formed was filtered, washed (H_2O), and dried; it weighed 6.95 g (36%). After recrystallization from cyclohexane (Darco) it showed mp 124.5–125.5°; ir (KBr) 1595, 1518, 1485, 1348, 1245, 910, 835, 740, 675 cm^{-1}; nmr ($CDCl_3$) δ 7.55 (d, 2 H), 8.48 (d, 2 H), 8.70 (s, 1 H), 7.6–8.2 (m, 5 H); mass spectrum (rel intensity) *m/e* (I) 242 (14), 104 (100), 77 (90), 51 (16).

Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.13; N, 11.57. Found: C, 64.63; H, 4.13; N, 11.83.

Base Decomposition of *O*-(*p*-Nitrophenyl)benzaldoxime. A. To a solution of 20 ml of 5% NaOH and 20 ml of ethanol was added *O*-(*p*-nitrophenyl)benzaldoxime (300 mg, 1.24 mmol). The mixture was refluxed for 1.5 hr and the ethanol was then removed by distillation. The resulting basic solution was extracted with ether, which upon evaporation produced 7.2 mg (5%) of benzamide (ir identical with that of an authentic sample). Acidification and ether extraction of the aqueous solution resulted in the isolation of 270 mg of a light yellow solid upon evaporation of the ether extract. Nmr comparison with a known mixture showed *p*-nitrophenol and benzoic acid to be present in 95% and 70% yields, respectively.

B. *O*-(*p*-Nitrophenyl)benzaldoxime (600 mg, 2.48 mmol) in DMSO (10 ml) was added to 2.48 mmol of the benzaldoxime salt in 15 ml of DMSO. This mixture was stirred for 50 min at 25° and was then poured into 50 ml of ice water which had been acidified with 0.5 ml of concentrated HCl. Unchanged *O*-(*p*-nitrophenyl)benzaldoxime (163 mg, 27% recovery) was collected by filtration. The ether extract of the filtrate was washed (H_2O), dried ($MgSO_4$), and evaporated. Chromatography of the residue on 10 g of silica gel (benzene elution) resulted in the isolation of 246 mg (97% yield based on unrecovered starting material) of *p*-nitrophenol, mp 112–113° (lit.[17] 114°).

***p*-Nitrophenol.** The sodium salt of benzaldoxime (20 mmol) in DMSO (35 ml) was prepared as usual. *p*-Fluoronitrobenzene (1.41 g, 10 mmol) in DMSO (35 ml) was added; an intense color developed immediately. The dark solution was stirred at 30° for 50 min and then poured into 150 ml of ice water which had been acidified with 2 ml of concentrated HCl. *O*(*p*-Nitrophenylbenzaldoxime (0.28 g, 12%) was separated from the aqueous mixture by filtration.

The ether extract of the filtrate was washed (H_2O), dried ($MgSO_4$), 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 $CHCl_3$. 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 (H_2O), dried ($MgSO_4$), and evaporated. The residue was tritrated 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*-Nitrophenylbenzaldoxime, 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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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 (IId) 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 FSO_3H is discussed.

Reactions involving antiaromatically destabilized intermediates have elicited much interest in the recent literature.[2] Diaz[3] 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 nonamethylbicyclo[3.2.0]hepta-3,6-dien-2-yl cation (Id) at −90°[4a] are more consistent with an allylic structure. In a preliminary communication[5] 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 (FSO_3H) 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 ⇌ IIf ⇌ IIIe).[6] Hart[4] 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 media[5] and rationalized our results on the basis of an allylic (IIc), rather than a bishomoantiaromatic (IId) intermediate. We also noted that the allylic double bond at C-2 evidently swamps out homoallylic participation as observed by Whitham[7] 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 (IId) as the transition state.