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Substituent Effect in Solvolysis of Spiro[cyclopropane-1,2′-indan]-1′-yl *p*-Nitrobenzoate

Katsuo Ohkata,* Masaki Akiyama, Kenshi Wada, Shun Sakaue, Yoshiko Toda, and Terukiyo Hanafusa†

Chemistry Department, Faculty of Science, Hiroshima University, Higashi-senda-machi, Naka-ku, Hiroshima 730, Japan

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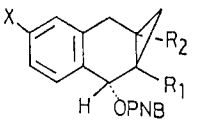
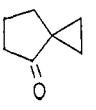
The preparation of a series of substituted spiro[cyclopropane-1,2′-indan]-1′-yl *p*-nitrobenzoates (**4a–g**) is described. The solvolysis rate constant is $k = 8.53 \times 10^{-6}$ s^{-1} at 25 °C in 80% aqueous acetone for the unsaturated derivative (**4e**) and is relatively high in comparison with the related secondary systems. The Hammett treatment ($\rho\sigma^+$) gives a straight line and the ρ value (−3.33) is more negative than that (−2.11) of 3,4-benzotricyclo[4.3.1.0^{1,6}]-dec-3-en-2-*anti*-yl *p*-nitrobenzoate (**1**). On the basis of the results, it can be considered that the mesomeric transmission of substituent effect is very weak in **1** relative to **4**.

The tool of increasing electron demand was initiated by Gassman, Richey, and Winstein to evaluate the electron demand of the electron deficient carbocation center in the 7-aryl-7-norbornenyl cation[1] and extensively exploited by Brown and co-workers.[2] This is generally applied to the solvolysis of a series of arylcarbinyl systems and has proven to be an important criterion for demand of the incipient carbonium ions.

In relation with various solvolytic studies on cyclopropylcarbinyl systems,[3] we have reported the high reactivity of 3,4-benzonorcaren-2-yl derivatives (**1**) in solvolysis and found a smaller ρ-value in Hammett's relationship as compared with its related systems.[4] On the other hand, Kosower et al. showed that spiro[2.4]heptan-2-one (**2**), in which the plane of the cyclopropyl ring is parallel to the π-orbital of the carbonyl group, favors a lower energy transition.[5] Also, Nishida and co-workers reported that such a geometry of the cyclopropyl group leads to an accelerated solvolysis of spiro[2.4]heptyl ester (**3**).[6] Here, we report solvolysis of substituted spiro[cyclopropane-1,2′-indan]-1′-yl *p*-nitrobenzoates (**4a–g**), for the purpose of making a comparison of the extent to which the aromatic portion assists delocalization of the positive charge in the reaction of **1** and of **4**.[5,6]



1



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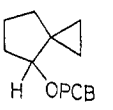

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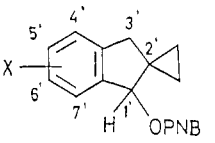

4 a-g

a, X = 5′-MeO
b, X = 6′-MeO
c, X = 5′-Me
d, X = 6′-Me
e, X = H
f, X = 6′-I
g, X = 6′-NO_2

Results

Synthetic Considerations. Spiro[cyclopropane-1,2′-indan]-1′-one (**5e**) was first prepared by Fraisse-Jullien et

† Present address: The Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki, Osaka 567, Japan.

(1) (a) Assman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1545; **1970**, *92*, 2549. (b) Richey, H. G., Jr.; Nichols, D.; Gassman, P. G.; Fentiman, A. F., Jr.; Winstein, S.; Brookhart, M.; Lustgarten, R. K. *Ibid.* **1970**, *92*, 3783. (c) Liu, K.-.; Kuo, M.; Shu, C. *Ibid.* **1982**, *104*, 211.
(2) (a) Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1979**, *44*, 133 and 3536. (b) Brown, H. C.; Periasamy, M. *J. Am. Chem. Soc.* **1982**, *105*, 529. (c) Olah, G. A.; Berrier, A. L.; Arvanagi, M.; Prakach, C. K. S. *Ibid.* **1981**, *103*, 1122.
(3) (a) Birladeanu, L.; Hanafusa, T.; Johnson, B.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 2316. (b) Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1982**, *104*, 2600 and 2605. (c) Harris, J. S.; Moffatt, J. R.; Case, M. G.; Clarke, F. W.; Polley, J. S.; Morgan, T. K., Jr.; Ford, T. M.; Murray, R. K., Jr. *J. Org. Chem.* **1982**, *47*, 2740.
(4) (a) Ohkata, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 235. (b) Ohkata, K. *J. Org. Chem.* **1976**, *41*, 2162. (c) Ogawa, Y.; Matsusaki, H.; Ohkata, K.; Hanafusa, T. *J. Org. Chem.* **1978**, *43*, 849.
(5) Kosower, E. M.; Ito, M. *Proc. Chem. Soc. London* **1962**, 25.
(6) Tsuji, T.; Moritani, I; Nishida, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2338.

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Scheme I

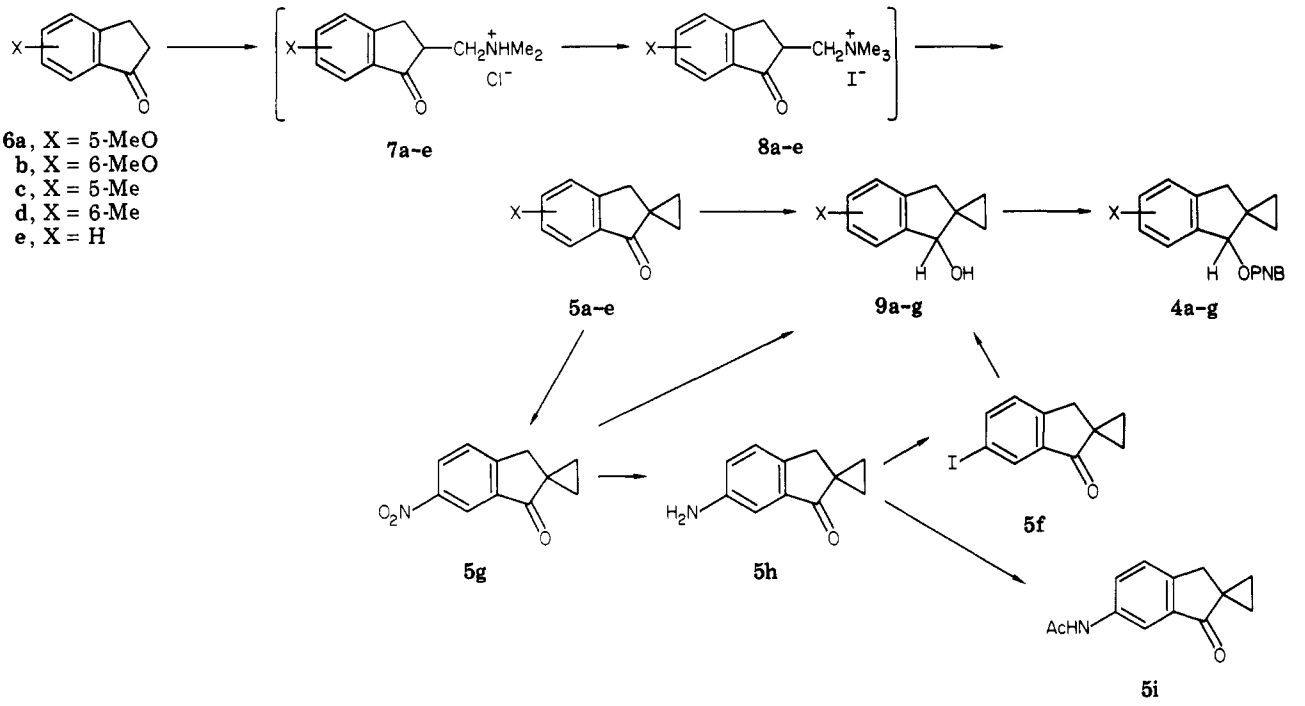

Table IV. Rate Constants and Activation Parameters Obtained from Solvolysis of *p*-Nitrobenzoates (4a–g) in 80% Aqueous Acetone

compd (X)	mp, °C	yield, %	°C	$k \times 10^5$ s^{-1}	$\Delta H^{\ddagger}$, kcal/mol (25 °C)	$\Delta S^{\ddagger}$, eu (25 °C)	k_{rel} (25 °C)
4a (5′-MeO)	105–107	35	25.0	ca. 2600			305
4b (6′-MeO)	109–111	63	35.0	39.7 ± 2.0			
			25.0	13.6 ± 1.5	21.1	−10.0	1.59
			15.0	3.37 ± 0.09			
4c (5′-Me)	122–125	80	25.0	71.7 ± 3.2	20.2	−9.74	8.41
			15.0	21.2 ± 0.5			
4d (6′-Me)	81–83	72	35.0	51.9 ± 0.9			
			25.0	13.2 ± 1.9	21.7	−8.08	1.55
			15.0	4.20 ± 0.33			
4e (H)	95–97	75	45.0	96.1 ± 0.3			
			35.0	24.4 ± 0.1			
			25.0	8.53 ± 0.5	21.9	−8.23	1.00
			15.0	2.22 ± 0.1			
4f (6′-I)	113–115	53	35.0	1.55 ± 0.07			
			25.0	0.475 ± 0.075	21.0	−17.0	0.0557
4g (6′-NO_2)	125–127	46	45.0	0.483 ● 0.035			
			25.0	0.0287 ± 0.0015	26.0	−5.84	0.00336

al. in their spectroscopic investigation,[7] and the interesting photochemical behavior was recently observed by Loutfy and co-workers.[8] A series of substituted substrates (**5a–g**) were prepared by the following synthetic route (Scheme I) in the present study.

Mannich reaction of substituted indanones (**6a–e**) produced the corresponding amino ketone derivatives (**7a–e**) followed by methylation to give quarternary ammonium iodides (**8a–e**). Without further purification at this stage, cyclopropanation with dimethyloxosulfonium methylide afforded spiro[cyclopropane-1,2′-indan]-1′-ones (**5a–e**) in moderate yield. Structural assignment to **5a–e** is founded upon ^{1}H NMR spectral data and elemental analyses.

Nitration of **5e** produced a mixture of two isomeric nitro derivatives in a ratio of 5:1. The major isomer was purified by recrystallization and identified with **5g** on the basis of ^{1}H NMR spectrum. Hydrogenation of **5g** over palladium charcoal gave **7h** in high yield, followed by Sandmeyer reaction to produce iodo substituted compound **5f**. Reduction of **5a–g** with sodium borohydride or lithium aluminum hydride gave alcohols (**9a–g**) in high yield. Each *p*-nitrobenzoate (**4a–g**) was obtained by the reaction with *p*-nitrobenzoyl chloride in dry pyridine. These spectral data are summarized in Tables I, II, and III (supplementary material) for **4a–g**, **5a–h**, and **9a–g**, respectively.

Kinetic Studies. The rates of solvolysis of *p*-nitrobenzoates (**4a–g**) in 80% aqueous acetone were determined by titration of *p*-nitrobenzoic acid with an automatic titration instrument after quenching by anhydrous acetone in an ice bath. Owing to higher reactivity of **4a**, the rate constant at 25 °C was evaluated from its half-life, $\tau_{1/2}$ = 21–35 sec. The rate constants together with thermodynamic parameters for all substrates are collected in Table IV.

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(8) Loutfy, R. O.; Yates, P. *J. Am. Chem. Soc.* **1979**, *101*, 4694.
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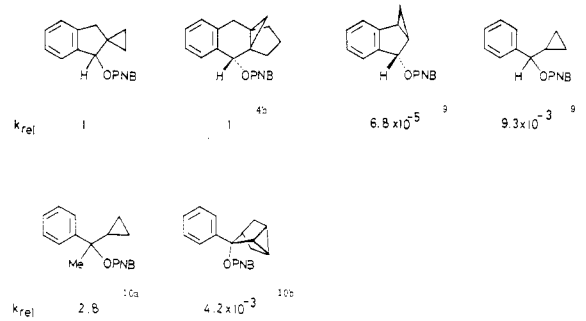
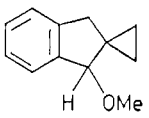


Figure 1. Relative rates of solvolysis of selected cyclopropylphenylmethyl p-nitrobenzoates in 80% aqueous acetone at 25 °C.[11]

Product Studies. After preparative-scale solvolysis of the p-nitrobenzoates (**4a–g**) in 80% aqueous acetone containing 2,6-lutidine for approximately 10 half-lives, each product was isolated almost quantitatively and characterized with the parent alcohol (**9a–g**) by spectroscopic analyses. Methanolysis of **4e** gave the corresponding methyl ether (**10e**) as the sole product, which is indicative



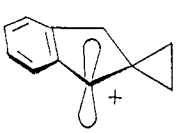
10 e

of exclusive alkyl–oxygen cleavage in the reaction. Since aqueous acetone is clearly more polar than methanol, the esters could be solvolyzed by way of the carbocation intermediates.

Discussion

Kinetic Comparisons with Model System. The rate of hydrolysis of p-nitrobenzoate (**4e**) is compared with those of related compounds as shown in Figure 1. A rate enhancement of 100 is observed for **4e** over that for a simple secondary cyclopropylphenylmethyl system but similar to that of the benzonorcarenyl derivative (**1**).[4b] Despite the higher solvolytic reactivity of **4e**, no rearranged alcohol was obtained in the reaction. This observation clearly showed that exclusive solvent attack occurs at the C-1′ position which is secondary, benzylic, and cyclopropylcarbinyl carbocation.

From the above comparison, it may be deduced that the intermediate cation is stabilized both by the benzene ring and by the symmetric bisected cyclopropane ring such as **11**. Thus, the vacant π orbital of the cation is preferably



11

conjugated with the aromatic π-orbital and two σ-orbitals in the cyclopropane. The rate accelerration as well as exclusive formation of the parent alcohol in solvolysis could thus be explained.

Hammett–Brown Plots of the Solvolysis of 4. The logarithms of the rate constants at 25 °C show a nice linear relationship vs. σ^+ for seven p-nitrobenzoates (**4a–g**), with $\rho = -3.33$ (correlation coefficient, 0.994). Since ρ-values are mostly related with the charge on the transition state, one would expect this degree of electron demand of the electron-deficient carbocationic center. The ρ-value for **4** is almost the same as that (−3.61) of an arylcyclopropylmethyl system[12] but is more negative than that (−2.75) of **1**.[4a] A resonable explanation is that the extensive delocalization by the cyclopropane ring in **1** might leave relatively little net charge on the benzene ring as compared with **4**. Thus, the small value of ρ for **1** suggests that the transmission of resonance from the substituent is very small relative to **4**.

In conclusion, on the basis of the above considerations, it is convenient to imagine the slight mechanistic change in solvolysis between **1** and **4** as the neighboring substituent is changed. Thus, it seems that **4** solvolyzes through a later transition state compared with **1**, so that the phenyl group as well as σ-bond participation might play the part of stabilization in the transition state.

Experimental Section

Infrared spectra were recorded on a Hitachi 215 spectrophotometer. The ^{1}H NMR spectra were determined with Varian T-60 instrument and apparent splitting are given in all cases. Mass spectra were measured with Hitachi Perkin-Elmer RMU 6L spectrometer.

5-Methoxy-1-indanone (6a). Intramolecular Friedel–Crafts reaction of β-(m-methoxyphenyl)propionyl chloride as described by House[13] gave **6a** in 82% yield as a colorless crystalline solid: mp 105–107 °C (from hexane–benzene) [lit.[14] mp 111 °C]; ^{1}H NMR (δ, $CDCl_3$) 2.5–3.2 (m, 4 H), 3.88 (s, 3 H), 6.78–7.00 (m, 2 H), and 7.65 (d, J = 9 Hz, 1 H).

6-Methoxy-1-indanone (6b). Similarly **6b** was prepared in 95% yield as a colorless crystalline solid: mp 106–107 °C (from hexane) [lit.[13] mp 109–110 °C; ^{1}H NMR (δ, $CDCl_3$) 2.5–3.2 (m, 4 H), 3.84 (s, 3 H), 7.15–7.29 (m, 3 H).

5-Methyl-1-indanone (6c). Polyphosphoric acid was prepared by the reaction of phosphoric acid (330 mL) with phosphorus pentaoxide (500 g) at 95 °C for 2 h. To the mixture was added β-(m-methylphenyl)propionic acid[15] (30.0 g, 0.18 mol) at room temperature. The mixture was stirred at 95 °C for 3 h before quenching with ice. The product was extracted into ether and the combined organic layers were washed with a saturated sodium bicarbonate solution before drying. Solvent removal left 20 g of a yellowish oil which was crystallized and fractionally recrystallized from hexane to give a pure **6c** (6.0 g, 22%) as a colorless crystalline product: mp 65–66.5 °C [lit.[16] mp 70–71 °C]; ^{1}H NMR (δ, $CDCl_3$) 2.43 (s, 3 H), 2.5–3.2 (m, 4 H), 7.15 (d, J = 8 Hz, 1 H) 7.25 (s, 1 H), 7.63 (d, J = 8 Hz, 1 H).

6-Methyl-1-indanone (6d). By a similar procedure to that used in the preparation of **6c**, **6d** (mp 58–59.5 °C (lit.[16] mp 59 °C), 14.6 g, 82%) was obtained from β-(p-methylphenyl)propionic acid[16] (20.0 g, 0.12 mol): ^{1}H NMR (δ, $CDCl_3$) 2.38 (s, 3 H), 2.5–3.2 (m, 4 H), 7.38 (s, 2 H), 7.53 (bs, 1 H).

5′-Methoxyspiro[cyclopropane-1,2′-indan]-1′-one (5a). A mixture of 5-methoxy-1-indanone (**6a**) (9.88 g, 0.075 mol), dimethylamine hydrochloride (25 g, 0.35 mol), and paraformaldehyde (7.0 g, 0.23 mol) in 95% ethanol (100 mL) was heated in the presence of a catalytic amount of concentrated hydrochloric acid (1 mL) under reflux for 2.5 h. After the solution was cooled and diluted with 400 mL of acetone, a precipitate was filtered to give 16.5 g (86%) of a product (**7a**).

Treatment of the crude **7a** (4.5 g, 0.02 mol) with excess sodium carbonate in water (50 mL) gave an oil. The aqueous phase was extracted with ether. The combined organic layers were washed

(11) The values cited from ref 9 are extrapolated on the basis of the assumption that 3,5-dinitrobenzoates solvolyze six times faster than p-nitrobenzoates [Schleyer, P. v. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321].

(12) Shono, T.; Oku, A.; Oda, R. *Tetrahedron* **1967**, *24*, 421.
(13) House, H. O.; Hudson, C. B. *J. Org. Chem.* **1970**, *35*, 647
(14) Bone, A. H.; Cort, L. A. *J. Chem. Soc.* **1962**, 1986.
(15) Miller, W. v.; Rohde *Chem. Ber.* **1890**, *23*, 1887.
(16) Elvidge, J. A.; Foster, R. G. *J. Chem. Soc.* **1963**, 590.

with water, dried, and concentrated to furnish a yellow amino ketone. Methylation of the amino ketone with methyl iodide (5.7 g, 0.04 mol) in acetonitrile gave a white precipitate (7.3 g) after evaporation of solvent and excess methyl iodide. The product was used for the following cyclopropanation without further purification.

A mixture of oil-free sodium hydride (0.48 g, 0.02 mol) and trimethyloxosulfonium iodide (4.4 g, 0.02 mol) was treated dropwise with dimethyl sulfoxide (25 mL) at room temperature. After the solution was stirred for 1 h, a solution of the crude ammonium iodide (**8a**) was added dropwise in the same solvent (25 mL). Stirring was continued for 3 h at room temperature and 1 h at 40–50 °C before the mixture was poured onto ice and extracted with ether. The organic layers were washed with water, dried, and concentrated to yield a yellow oil. Trituration with benzene and hexane afforded 3.0 g (79% based on **7a**) of **5a** as a colorless solid, mp 130–132 °C.

Substituted Spiro[cyclopropane-1,2′-indan]-1′-one (5b–e). By a method similar to that used in the preparation of **5a**, **5b** (mp 72–73.5 °C, 69%), **5c** (mp 52–54 °C, 56%), **5d** (mp 50–52 °C, 52%), and **5e** (mp 51–53 °C (lit.[7] mp 49–52 °C), 51%) were obtained from the corresponding substituted 1-indanone (**6a–e**).

6′-Nitrospiro[cyclopropane-1,2′-indan]-1′-one (5g). A mixture of concentrated nitric acid (3 mL) and concentrated sulfuric acid (4.5 mL) was added dropwise to a precooled solution of spiro ketone (**5e**, 4.5 g, 0.028 mol) in 20 mL of concentrated sulfuric acid at 0 °C. After 40 min of stirring, the solution was poured onto ice and the product was extracted into ether. The organic layers were washed with water, dried, and evaporated to yield a yellow solid, which was recrystallized from a mixture of ether and petroleum ether to afford 4.0 g (69%) of **5g** as a colorless solid, mp 114.5–117 °C.

6′-Aminospiro[cyclopropane-1,2′-indan]-1′-one (5h). A mixture of **5g** (4.0 g, 0.02 mol) dissolved in acetic acid (50 mL) and 10% palladium–charcoal catalyst (1 g) was stirred under hydrogen atmosphere at room temperature; slightly excess hydrogen was absorbed. After filtration, the solution was neutralized with 1 M NaOH and extracted with ether. The organic layers were washed with water, dried, and concentrated to yield crystalline product. Recrystallization from benzene afforded 3.8 g of **7h** (mp 161–163 °C, 95%).

A solution of 1.00 g (5.8 mmol) of **5h** in acetic acid (10 mL) was heated under reflux for 5 h. After cooling, the mixture was poured onto ice. Crystalline product was filtered and dried. Recrystallization from benzene gave 0.9 g (72%) of 6′-(*N*-acetylamino)spiro[cyclopropane-1,2′-indan]-1′-one (**5i**).

6′-Iodospiro[cyclopropane-1,2′-indan]-1′-one (5f). To a solution of **5h** (2.0 g, 12 mmol) in concentrated sulfuric acid (20 mL) was added dropwise a precooled solution of sodium nitrite (0.92 g, 0.10 mmol) in the same acid (10 mL) at −5 °C. After 5 h of stirring, the mixture was poured onto water and ice. To the solution was added dropwise urea until evolution of gas was no longer observed before filtration. The filtrate was treated with saturated aqueous potassium iodide (2.7 g, 16 mmol) at −5 °C. After 5 h of stirring, the product was extracted into ether. The organic layers were washed with aqueous sodium thiosulfate, aqueous 1 M sodium hydroxide, and water before drying. Evaporation of the solvent left a yellow solid. Chromatography of the residue on alumina gave 0.8 g (25%) of **5f** as a colorless crystals, mp 85–89 °C.

Reduction of Spiro Ketone (5a–g). Method A. Spiro[cyclopropane-1,2′-indan]-1′-ol (9e). To a stirred suspension of lithium aluminum hydride (630 mg, 17 mmol) in anhydrous ether (3 mL) was added dropwise a solution of **5e** (1.00 g, 6.3 mmol) in the same solvent (30 mL). The mixture was stirred at 0 °C for 1 h and at room temperature for 20 h before the excess hydride was carefully decomposed with water (2 mL). The inorganic solids were separated by filtration. Concentration of the dried filtrate gave a colorless oil. The residual material was crystallized and recrystallized from hexane to give 0.78 g (79%) of **9e**, mp 55.5–57 °C (see Table III).

Method B. 5′-Methylspiro[cyclopropane-1,2′-indan]-1′-ol (9c). A solution of **5c** (2.0 g, 12 mmol) in anhydrous ethanol (50 mL) was cooled to 0 °C and treated with sodium borohydride (1.5 g, 0.04 mol). The reaction mixture was stirred at 0 °C for 3 h and at room temperature for 20 h and poured onto water and ice (150 mL). A colorless precipitate was separated by filtration and recrystallized from hexane to give 2.0 g (98%) of **9c**, mp 63–65 °C (see Table III).

Preparation of *p*-Nitrobenzoates (4a–g). General Procedure. A solution of **9e** (600 mg, 3.75 mmol) in dry pyridine (20 mL) cooled to 5 °C was treated with 740 mg (4.0 mmol) of *p*-nitrobenzoyl chloride. After 3 h, the reaction mixture was allowed to warm to room temperature for 16 h. The product was extracted into ether and washed with water, 1 M hydrochloric acid, 5% aqueous sodium bicarbonate solution, and water before drying. Evaporation of the solvent left a yellow solid which was recrystallized from hexane to give a pure sample of **4e** (see Table I).

Kinetic Studies. Preparation of Reagents. Acetone was prepared by distillation from potassium permanganate and redistillation after drying over anhydrous potassium carbonate. Double distilled water was employed.

General Kinetic Procedure. The methodology employed followed that described previously.[4c]

Preparative-Scale Solvolysis. A solution of **4e** (200 mg, 0.65 mmol) and 2,6-lutidine (0.5 mL) in 80% aqueous acetone (100 mL) was allowed at 25 °C for approximately 20 half-lives. The reaction mixture was concentrated under reduced pressure and the resulting suspension was extracted with dichloromethane. The organic phase was washed with sodium bicarbonate solution and water prior to drying. Solvent removal gave 96 mg (92%) of a pale yellow solid whose spectra were superimposable upon those of **9e**.

By similar methodology, product analysis for the other *p*-nitrobenzoates (**4a–d** and **4fg**) was carried out. Each esters solvolyzed to give the parent alcohols (**9a–d** and **9fg**), respectively.

Methanolysis Studies. In a typical procedure, 106 mg (0.34 mmol) of **4e** was dissolved in anhydrous methanol (50 mL) containing 0.2 mL of 2,6-lutidine and the mixture was allowed at 25 °C for 5 days. After removal of the methanol under reduced pressure, the resulting residue was treated with dichloromethane. The organic layers were processed in the predescribed manner to give 52 mg (88%) of **10e** as a colorless oil: ν_{max} (neat) 3080, 3000, and 1080 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 0.45–1.38 (m, 4 H), 2.56 and 3.32 (AB, J = 17 Hz, 2 H), 3.22 (s, 3 H), 4.31 (s, 1 H), 7.23–7.46 (m, 4 H); m/e 174 (M^+).

Registry No. **4a**, 90321-41-8; **4b**, 90343-27-4; **4c**, 90321-42-9; **4d**, 90321-43-0; **4e**, 90321-44-1; **4f**, 90321-45-2; **4g**, 90321-46-3; **5a**, 90321-53-2; **5b**, 90321-54-3; **5c**, 90321-55-4; **5d**, 90321-56-5; **5e**, 22228-23-5; **5f**, 90321-60-1; **5g**, 90321-57-6; **5h**, 90321-58-7; **5i**, 90321-59-8; **6a**, 5111-70-6; **6b**, 13623-25-1; **6c**, 4593-38-8; **6d**, 24623-20-9; **6e**, 83-33-0; **6g**, 24623-24-3; **7a**, 90321-68-9; **7b**, 42348-55-0; **7c**, 42348-48-1; **7d**, 42348-52-7; **7e**, 16931-84-3; **7g**, 90321-47-4; **8a**, 90321-48-5; **8b**, 90321-49-6; **8c**, 90321-50-9; **8d**, 90321-51-0; **8e**, 76919-83-0; **8g**, 90321-52-1; **9a**, 90321-61-2; **9b**, 90321-62-3; **9c**, 90321-63-4; **9d**, 90321-64-5; **9e**, 90321-65-6; **9f**, 90321-66-7; **9g**, 90321-67-8; dimethylamine, 124-40-3; formaldehyde, 50-00-0.

Supplementary Material Available: Physical (mp and elemental analysis) and spectral data (^{1}H NMR and IR) for **5a–g**, **5a–i**, and **9a–g** are summarized in Tables I, II, and III (3 pages). Ordering information is given on any current masthead page.