made by comparison of the chemical shifts to the chemical shifts of the authentic protonated compounds.

The 2-methyl-1-phenylpropyl acetate **21**-d_4 was assigned as a 1:1 mixture of diasteriomers by the observed doublets of equal intensity at δ 0.93 and 0.76 and the multiplet in the range of *ca.* δ 1.9. The absorption at δ 5.40 for the benzylic proton of 2-methyl-1-phenylpropyl acetate was not observed, which confirms that only acetate **21**-d_4, and no other isomer with the same carbon skeleton, is present.

The *erythro*-3-phenyl-2-butyl acetates **20a** and **20b** give absorptions at δ 4.99, 2.78, 1.22, and 1.00. The 1.22 absorption is coincident with a methyl absorption from the threo acetate **19a** and the intensity for the erythro acetate **20a** which occurs at 4.99. With this analysis the ratios of methine intensities and methyl intensities for **20a:20b** are 2:1 and 1.3:1, which gives an average of 1.7:1 for the ratio **20a:20b**.

The *threo*-3-phenyl-2-butyl acetates **19a** and **19b** give absorptions at δ 5.04, 2.88, 1.22, and 1.08. The ratios for the methine and methyl resonances for **19a:19b** are 2.1:1 and 2.4:1, with the ratios of methyl determined after subtraction of the contribution from the erythro acetate **20a** to the absorption at 1.22. The average value for the ratio of **19a:19b** is 2.3:1.

Another component in the third fraction is *threo*-3-phenyl-2-butyl chloride **22b**, which gave absorptions at δ 3.01 and 1.40. No other absorptions for 3-phenyl-2-butyl chlorides were observed and chloride **22b** was found in trace amounts only.

Supplementary Material Available. The details of the experiments for preparing and identifying **7, 8, 11**, and **13** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-2494.

Solvolysis of Tertiary Tricyclo[3.3.0.0^{8,7}]octyl p-Nitrobenzoates[1]

Ronald R. Sauers* and Elizabeth Mary O'Hara

Contribution from the School of Chemistry, Rutgers University, The State University, New Brunswick, New Jersey 08903. *Received October 13, 1973*

Abstract: Solvolysis rates in 90:10 acetone–water have been measured for the following tertiary *p*-nitrobenzoates of the 2-tricyclo[3.3.0.0^{3,7}]octyl system: methyl, phenyl, *p*-anisyl, and *p*-trifluoromethylphenyl. From considerations of the rates and products of these reactions, it was concluded that all of them react *via* classical ions which may subsequently undergo skeletal rearrangements. Earlier estimates of the anchimeric assistance in the secondary system are shown to have been in error by a factor of 10^4–10^5.

E valuation of the importance of anchimeric assistance has relied heavily on the use of semiempirical calculations[2] and/or rate comparisons involving "model" systems. Interestingly, relatively little discussion of what constitutes a good "model" has appeared in the literature,[3] but it seems generally agreed that a gross structural similarity is important. Thus, differences in rate that might be caused by angle strain, steric effects, torsional strains, and solvent participation might be minimized.[4]

Despite these limitations, the use of model systems has proven to be valuable. For example, the solvolytic behavior of *anti*-7-norbornenyl systems is suitably modeled by the corresponding saturated analogs as

shown by the work of Gassman and Fentiman.[5] These workers demonstrated that participation can be revealed by comparisons of the relative responses of the solvolysis rates to electron demand at the reaction site. Similarly, the relatively strong participation attributable to α-cyclopropyl rings has been demonstrated by the use of isopropyl systems as models.[6] On the other hand, comparisons of the exo–endo rate ratios of tertiary 2-norbornyl derivaties failed to reveal significant σ participation in the secondary derivatives.[7]

While there is little controversy with regard to the importance of participation in the first two examples discussed above, considerable doubt surrounds the interpretation of the rate product data for the *exo*-2-norbornyl system and other systems for which σ participation has been proposed.[8] The present research

(1) Presented in part at the 166th National Meeting of the American Chemical Society, Chicago, Ill., August 1973, Abstracts, ORGN 64.

(2) (a) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); (b) P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964); (c) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970).

(3) For discussions on the relative merits of cyclopentyl *vs.* cyclohexyl systems as models for the norbornyl system, see S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1127 (1952), and H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1247 (1964).

(4) A more subtle problem with rate comparisons involves possible complications caused by differences in the relative amounts of internal return. In general, titrimetric rate constants are compared without correction for the return processes.

(5) (a) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549 (1970); (b) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **91**, 1545 (1969).
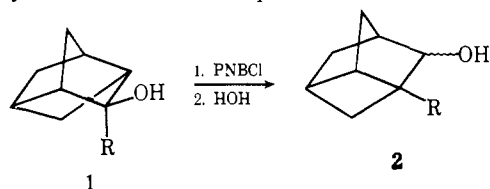
(6) E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, **95**, 2397 (1973).

(7) K. Takeuchi and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2693 (1968).

(8) For some recent examples, see (a) W. G. Dauben and C. H. Schallhorn, *J. Amer. Chem. Soc.*, **93**, 2254 (1971); (b) R. M. Coates and J. L. Kirkpatrick, *ibid.*, **90**, 4162 (1968); (c) P. K. Freeman, R. B. Kinnel, and T. D. Ziebarth, *Tetrahedron Lett.*, 1059 (1970); (d) S. A. Monti and S.-S. Yuan, *J. Org. Chem.*, **36**, 3350 (1971); (e) W. L. Dilling, C. E. Reineke, and R. A. Plepys, *ibid.*, **34**, 2605 (1969); (f) R. R. Sauers, K. W. Kelly, and B. R. Sickles, *ibid.*, **37**, 537 (1972).

was designed to evaluate the utility of the Brown–Gassman technique in systems which do not contain unsaturation or cyclopropyl rings. It was especially desirable to examine a system in which anchimeric assistance was relatively large. Aryl substituents could then be chosen such that their "leveling" effects could bracket the effect of participation. One would thereby have the opportunity to observe changes in behavior with and without participation.

To this end, we initiated synthetic and kinetic studies of tertiary derivatives of the 2-tricyclo[3.3.0.0^{3,7}]-octyl systems 1b–e. The postulated anchimeric as-

a, R = H
b, R = CH$_3$
c, R = C$_6$H$_5$
d, R = p-CH$_3$OC$_6$H$_4$
e, R = p-CF$_3$C$_6$H$_4$

sistance in 1a is sufficiently large, 10^8–10^9, such that the p-trifluoromethylphenyl group ("leveling" effect,[5] 10^6) should be unable to completely inhibit σ participation, but the p-anisyl group with a "leveling" effect of 3 × 10^{10} should be sufficiently stabilizing as to obviate participation. Furthermore, the rearrangement[8c,f] 1 → 2 is known to be facile, and it is anticipated, although not required, that its occurrence will parallel participation.

Results

A. Syntheses. The tertiary systems 1b–e were prepared by the addition of Grignard reagents to tricyclo[3.3.0.0^{3,7}]octan-2-one.[8f] The corresponding alcohols were characterized by spectral means and by the preparation of p-nitrobenzoate esters. The absence of absorptions attributable to H–C–O protons in the nmr spectra was taken as evidence that the esters were unrearranged prior to hydrolysis. In two cases, the original alcohols were recovered after basic hydrolysis.

B. Kinetic Studies. The rates of hydrolysis of the esters of 1b–e in 90% aqueous acetone were followed by titrations with sodium hydroxide solution. Good first-order kinetics were obtained using infinity titers taken after ca. 10 half-lives. The calculated rate constants and values extrapolated to 25° are given in Table I.

C. Product Studies. The hydrolysis products were analyzed by gas-chromatographic techniques. In all cases, one major (≥88%) product was detected. The product of hydrolysis of 1d-OPNB proved to be the unrearranged alcohol, but in all other systems the major product was rearranged. This was evidenced by the appearance of nmr absorptions attributable to H–C–O protons. Specifically, singlets were found near δ 3.7 and doublets near δ 4.1, the total area of which equaled that expected for one proton. We interpret these data to mean that these products are best represented as mixtures of exo- and endo-tricyclo-[3.2.1.0^{3,6}]octanols 2b, 2c, and 2e.[9] Mass spectral

(9) For comparative data on 1a and 2a, see R. R. Sauers, R. A. Parent, and S. B. Damle, J. Amer. Chem. Soc., 88, 2257 (1966); although there is little doubt concerning the structures of the rearranged products, the arguments to be presented do not depend on these assignments.

Table I. Rates of Hydrolysis of p-Nitrobenzoates in 90:10 Acetone–Water

Compd	Temp, °C	k, sec^{-1}	k_{rel} (25°)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1b-OPNB	126.0	9.99 × 10^{-5}			
	120.0	4.98 × 10^{-5}			
	109.0	1.49 × 10^{-5}			
	(25)^a	1.76 × 10^{-12}	1.0	33.1	−1.12
1c-OPNB	90.0	1.35 × 10^{-4}			
	85.0	8.02 × 10^{-5}			
	75.0	2.97 × 10^{-5}			
	(25)^a	6.49 × 10^{-8}	10$^{4.57}$	24.6	−8.76
1d-OPNB	45.0	1.77 × 10^{-4}			
	40.0	9.43 × 10^{-5}			
	30.0	2.91 × 10^{-5}			
	(25)^a	1.70 × 10^{-5}	10$^{6.99}$	20.7	−10.78
1e-OPNB	125.0	5.58 × 10^{-5}			
	120.0	3.86 × 10^{-5}			
	110.0	1.58 × 10^{-5}			
	(25)^a	7.86 × 10^{-11}	10$^{1.65}$	30.7	−1.83

^{a} Rates at 25° are extrapolated from higher temperatures.

fragmentation patterns were also consistent with these structures.

Discussion

The results presented are consistent with the original interpretations of the behavior of the tricyclo-[3.3.0.0^{3,7}]octyl system. Thus, the magnitude of the α-CH$_3$:H rate ratio can be estimated[10] to be 10^4, a factor which is significantly smaller than the estimated assistance and which is considerably less than the limiting value[11] of 10^8. At least part of this discrepancy could be attributable to σ participation, especially in view of the formation of rearranged product 2b. Similarly, two of the aromatic derivatives (1c and 1e) led to rearranged products in accord with the relative magnitude of their "leveling" effects and the postulated assistance (vide infra). Absence of rearrangement with the p-anisyl system was likewise in accord with expectations.[12]

Despite the general agreement of the data with expectations based on 7-norbornyl systems as models, we were disturbed by the large difference (10$^{2.6}$) in absolute rates between the p-anisyl derivatives in the two systems. It was decided that more definitive evidence was needed to correlate the observed rearrangements with participation. Since neighboring group reactions in general invariably involve rearward attack by the participating electrons, the experimental solution to the problem was to differentiate between migration via rearward attack (path a, Scheme I) and random migration (paths a and b). The implication here is that ionization to a symmetrical intermediate followed by rearrangement would necessarily proceed via paths a and b. Outlined in Scheme II is the synthesis of a suitably deuterium-labeled substrate whose

(10) The rate of hydrolysis of 1a-OPNB at 25° was estimated to be 10^{-16} sec^{-1} using the factor[5] 6.3 × 10^9 for the ratio of tosylate solvolysis to p-nitrobenzoate hydrolysis in 70:30 dioxane–water, the factor[5] 12 for the conversion to 90:10 acetone–water, and the factor 3 for conversion of tosylate rates to brosylate rates.
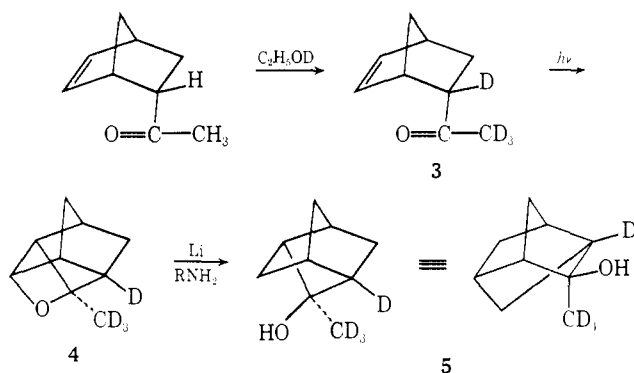
(11) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, J. Amer. Chem. Soc., 92, 2540 (1970).

(12) A Hammett plot of the hydrolysis data vs. σ^+ gave a reasonably good straight line (slope = −3.73, correlation coefficient 0.979). The absence of a "break" in this curve may not be significant in view of the limited data available.
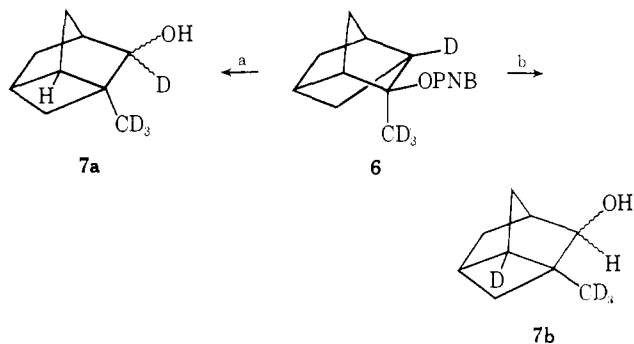
Scheme I
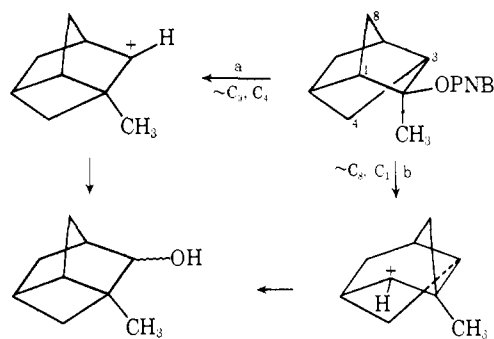
Scheme II

behavior on hydrolysis can be utilized to answer the question posed above.

It was found that the alcohols produced on hydrolysis of **6** were half-protonated at the carbinol carbons, a result which we interpret to mean that paths a and b were involved to essentially the same extent. Thus, a

symmetrical intermediate is required in the methyl system, and, by implication, in the aryl systems also, given the greater stability of the corresponding intermediates.

This finding indicates that the estimated anchimeric assistance for the secondary system is in error by at least a factor of 10^4, the ratio of the estimated assistance and the α-methyl:hydrogen rate ratio. While part or all of the discrepancy may be attributable to other effects, *e.g.*, torsional strain relief,[13] solvent effects,[14] ground state–transition state energy differences,[15a] it is clear that the importance of these additional parameters is difficult to evaluate at best.[15b]

(13) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

(14) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2542 (1970).

(15) (a) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *J. Amer. Chem. Soc.*, **89**, 6381 (1967). (b) P. G. Gassman (private communication) has suggested that **6** might ionize with participation to give a pair of rapidly equilibrating bridged ions. Reaction of the latter with solvent at the secondary center would then

Summary and Conclusions

It is concluded that the tertiary derivatives of the tricyclo[3.3.0.0^{3,7}]octyl system do not ionize with σ participation to form rearranged cations. The results are more consistently interpreted in terms of formation of unrearranged tertiary cations which subsequently may rearrange. While these results do not obviate the conclusion that the secondary system ionizes with participation, it is clear that the use of simple analogies for prediction of solvolyses rates can lead to results which are seriously in error.

Experimental Section

Nuclear magnetic resonance data was obtained from a Varian Model T-60 spectrometer in carbon tetrachloride or deuteriochloroform using tetramethylsilane as an internal standard. Infrared spectra were taken on a Perkin-Elmer Model 137 spectrometer. Gas chromatograms were determined on a Varian Aerograph Model A-90-P using the following columns: A, 10% Apiezon L (5 ft × 0.25 in.); B, 10% QF-1 (5 ft × 0.25 in.); C, 18% Carbowax 20M (5 ft × 0.25 in.); D, 4% FFAP: 16% QF-1 (12 ft × 0.25 in). Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-7 mass spectrometer (70 eV).

Tricyclo[3.3.0.0^{3,7}]octan-2-one was prepared by chromic acid oxidation[8f] of the corresponding alcohol.[8f] The product had mp 106° (lit.[8f] 106–110°).

2-Methyltricyclo[3.3.0.0^{3,7}]octan-2-ol (1b).[16] A solution of 3.5 g (0.060 mol) of the above ketone in 20 ml of anhydrous ether was added to the Grignard reagent prepared from 1.44 g (0.060 g-atom) of magnesium and 8.53 g (0.060 mol) of methyl iodide in 30 ml of ether. After stirring for 3 days at 25° the reaction mixture was hydrolyzed with saturated ammonium chloride solution, and the product was extracted into ether. A yellow oil was obtained on evaporation of the ether. Evaporative distillation gave 2.0 g (50%) of a white solid: mp 56° (lit.[16] mp 55.5–57°); nmr δ 2.7–0.85 (m), 1.28 (s, CH$_3$); ir (Nujol) 2.95 μ (OH); mass spectrum. molecular ion m/e 138, base peak m/e 71, M$^+$ − 18 at m/e 120 (rel intensity 0.1).

This compound was characterized by the preparation of the p-nitrobenzoate derivative, mp 84–86° (lit.[16] 86–88°).

Anal. Calcd for C$_{16}$H$_{17}$NO$_4$: C, 66.48; H, 6.04; N, 4.87. Found: C, 66.8, H, 6.0; N, 5.0.

2-Phenyltricyclo[3.3.0.0^{3,7}]octan-2-ol (1c) was prepared similarly from phenylmagnesium bromide and the ketone. Purification was effected by chromatography on alumina (elution with 50:50 ether–pentane) and preparative gc (A, 195°): mp 64–66°; yield 38%; nmr δ 7.27 (s, ArH), 3.0–0.8 (m); ir (Nujol) 2.98 (OH), 13.00 and 14.40 (5 ArH) μ; mass spectrum, molecular ion at m/e 200, base peak at m/e 133, M$^-$ − 18 at 182 (rel intensity 0.085).

The p-nitrobenzoate derivative was prepared in anhydrous pyridine and had mp 137–138° after crystallization from petroleum ether (bp 60–90°).

Anal. Calcd for C$_{21}$H$_{19}$NO$_4$: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.21; H, 5.48; N, 3.77.

The original alcohol could be regenerated in 72% yield upon treatment with methanolic KOH for 5 days.

2-p-Methoxyphenyltricyclo[3.3.0.0^{3,7}]octan-2-ol (1d) was prepared as described above and was purified by alumina chromatography (benzene and 1:9 chloroform–benzene), yield 20%. Preparative gc (A, 200°) gave a solid: mp 66–67°; nmr δ 6.97 (q, ArH), 3.74 (s, CH$_3$), 3.0–0.8 (m); ir (Nujol) 2.90 (OH) and 12.00 μ (s, o-ArH$_2$); mass spectrum, molecular ion at m/e 230, base peak at m/e 163, M$^-$ − 18 at m/e 212 (rel intensity 0.28).

The p-nitrobenzoate derivative had mp 122–123° after crystallization from petroleum ether.

Anal. Calcd for C$_{22}$H$_{21}$NO$_5$: C, 69.65; H, 5.58; N, 3.69. Found: C, 69.87; H, 5.75; N, 3.71.

lead to the observed products. While the available data cannot rule out this possibility, we doubt that the lifetimes of such ions could be sufficient to allow for equilibration. For example, under comparable reaction conditions, even the 1,2-dimethylnorbornyl cations do not completely equilibrate: see H. L. Goering and J. V. Clevenger, *J. Amer. Chem. Soc.*, **94**, 1010 (1972). More crucially, the absence of high stereospecificity in product formation rules out bridged intermediates.

(16) This alcohol was first prepared by B. R. Sickles, M. S. Thesis, Rutgers University, 1970.

2-*p*-Trifluoromethylphenyltricyclo[3.3.0.0^{3,7}]octan-2-ol (1e) was prepared from the ketone and the Grignard reagent of *p*-trifluoromethylphenyl bromide and was obtained as a white solid, mp 78–80°, after preparative gc (B, 180°): nmr δ 7.05 (q, ArH), 2.8–0.8 (m); ir (film) 2.90 (OH), 11.85 μ (s, *o*-ArH$_2$); mass spectrum, molecular ion at *m/e* 268, base peak at *m/e* 80, M$^+$ − 18 at *m/e* 250 (rel intensity 0.085).

The *p*-nitrobenzoate had mp 156° after crystallization from petroleum ether (60–90°).

Anal. Calcd for C$_{22}$H$_{18}$F$_3$NO$_4$: C, 63.31; H, 4.35; N, 3.36. Found: C, 63.29; H, 4.45; N, 3.27.

Hydrolysis of this ester with methanolic KOH regenerated alcohol 1e.

Preparation of 2-Methyltricyclo[3.3.0.0^{3,6}]octan-2-ol-*d*$_4$ (5). 5-Acetyl-2-norbornene (2.0 g, 80% endo) was heated at reflux for 17 hr in a solution of sodium ethoxide prepared by reaction of *ca.* 0.07 g of sodium with 20 ml of ethanol-*O-d*.[17] The alcohol was removed by evaporation and the residue was dissolved in chloroform. This solution was filtered and washed with aqueous sodium bicarbonate and water and then dried over sodium sulfate. The solvent was removed by evaporation and the residue was purified by gc (D, 125°) to give partially deuterated *endo*-5-acetylnorbornene. Repetition of the exchange reaction yielded the tetradeuterated ketone 3 as shown by the loss of the peak at δ 2.02 (CH$_3$) in the nmr spectrum and the relative area of the vinyl peaks. Gc analysis revealed that a 50:50 mixture of exo:endo ketone was obtained as a result of the exchange conditions.

The deuterated oxetane 4 was prepared by a photocycloaddition reaction[18] of 22 g of the mixture of isomers in 1.5 l. of benzene which contained 11 g of piperylene. There was obtained 7.1 g of oxetane 4. The nmr spectrum of this product was almost identical with that of a sample of the undeuterated material except for the absence of a broad singlet at δ 2.10 and the methyl resonance at δ 1.30.

The alcohol 5 was prepared by reduction with lithium in ethylenediamine.[19] From 7.5 g of oxetane there was obtained 0.23 g of alcohol 5 after preparative gc (C, 150°); the nmr spectrum was similar to that of 2b except that the methyl resonance was totally absent.

Kinetic Studies. A stock solution of 90% aqueous acetone was prepared from purified acetone[20] and triply distilled water. Solvolyses were carried out in sealed ampoules into which 2.00 ml of *ca.* 0.01 *M* ester solutions had been measured. The samples were immersed in a constant-temperature bath for the appropriate times after which they were withdrawn, cooled, and quenched with 5 ml of purified acetone. They were titrated immediately with standardized 0.01 *N* sodium hydroxide solution using Thymol Blue as indicator. Infinity titers were taken after 10 or more half-lives and gave values in good agreement with expectations.[21]

Product Studies. A. General. Samples of the esters were hydrolyzed to completion at the appropriate temperatures. The resulting solutions were reduced in volume by partial evaporation, and the organic products were extracted into ether. The extracts were washed with aqueous sodium bicarbonate solution and water and dried (Na$_2$SO$_4$); gc analyses utilized the columns and conditions already mentioned.

B. Hydrolysis of 1c-OPNB. Gc analysis revealed three products in the ratios 1:92:7. The minor component was not isolated. The 7% peak was collected and shown by comparative ir and nmr to be alcohol 1c. The structure of the major constituent (2c) was assigned on the basis of the following data: nmr δ 7.02 (m, ArH), 4.07 (m), and 3.75 (s, 1 H total, HCO), 2.9–0.87 (m); ir (Nujol) 2.91 (OH), 13.05, and 14.3 (s, 5 ArH) μ; mass spectrum, molecular ion at *m/e* 200, M$^+$ − 18 at 182.

Anal. Calcd for C$_{14}$H$_{16}$O: C, 83.96; H, 8.05. Found: C, 83.75; H, 8.34.

C. Hydrolysis of 1d-OPNB. The gas chromatogram of the hydrolysis product showed only one component which displayed nmr and ir spectra identical with those of 1d.

D. Hydrolysis of 1e-OPNB. Three components appeared in the gc trace of the hydrolysis, two of which (12% total) were very volatile and were not collected. The major component (88%) was collected and assigned structure 2e: nmr δ 7.40 (q, ArH), 4.13 (m, 0.25 HCO), 3.80 (s, 0.75 HCO), and 2.90–0.80 (m); ir (film) 2.80 (OH) 12.00 (s, *o*-ArH$_2$) μ; mass spectrum, molecular ion at *m/e* 268, M$^+$ − 18 at *m/e* 250.

Anal. Calcd for C$_{15}$H$_{15}$OF$_3$: C, 67.14; H, 5.64. Found: C, 67.15; H, 5.90.

E. Hydrolysis of 1b-OPNB. Hydrolysis of this ester gave two components in the ratio 94:6 on gc analysis (C, 160°). The minor component proved to be identical with 1b. The structure of the major constituent was consistent with formula 2b: nmr δ 4.16 (m, 0.13 HCO), 3.58 (s, 0.87 HCO), 1.00 (s, CH$_3$), and complex absorptions between 2.50 and 0.98; mass spectrum, molecular ion at *m/e* 138, base peak at *m/e* 71, M$^+$ − 18 at *m/e* 120 (rel intensity 0.10).

F. Hydrolysis of 6. Similarly, 6 gave two products in a 94:6 ratio. The minor component proved to be the unrearranged alcohol 5. The major component is believed to be an equimolar mixture of 7a and 7b and showed HCO absorptions in the nmr spectrum at δ 4.1 (0.1 H) and 3.60 (0.4 H); mass spectrum, molecular ion at *m/e* 142.

(17) D. J. Pasto and G. R. Meyer, *J. Org. Chem.*, 33, 1257 (1968).

(18) R. Srinivasan, Ed., "Organic Photochemical Syntheses," Vol. I, Wiley-Interscience, New York, N. Y., 1971, p 76.

(19) R. R. Sauers, W. Schinski, M. M. Mason, E. O'Hara, and B. Byrne, *J. Org. Chem.*, 38, 642 (1973).

(20) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 171.

(21) The experimental results may be found in the thesis of E. O'H. which will be available on microfilm from University Microfilms, Ann Arbor, Mich.