resolution EI spectra: observed *m/z* 398.260 442; calcd 398.260 95. A metastable peak at *m/e* 176.4 corresponds to a 398 → 265 cleavage due to a reciprocal CH$_3$/H transfer, followed by a C$_{10}$H$_{13}$· loss.[1,56]

Anal. Calcd for C$_{29}$H$_{34}$O: C, 87.39; H, 8.60. Found: C ,87.39; H, 8.41.

1-(2,4,6-Tri(methyl-*d*$_3$)phenyl)-2,2-dimesitylethanol (8). Starting from bromomesitylene-*methyl-d*$_9$ (0.22 mL, 1.4 mmol, (98.4% D) and **2** (280 mg, 1 mmol), **8** (50 mg, 12%), mp 208 °C, was obtained by the procedure described for the preparation of **7**.

1-(2,4,6-Tri(methyl-*d*$_3$)phenyl)-2,2-dimesitylethanone (9). Starting from **8** (20 mg, 0.05 mmol) and PDC (60 mg, 0.16 mmol) in DMF (0.3 mL), 15 mg (74%) of **9**, mp 142 °C, was obtained by the procedure described above for formation of **4**.

Acknowledgment. We are indebted to Professor H. Schwarz for the mass spectrum of compound **4**, to Dr. S. Cohen for the

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(56) Biali, S. E.; Depke, G.; Rappoport, Z.; Schwarz, H. *J. Am. Chem. Soc.* **1984**, *106*, 496.

X-ray diffraction of compound **7**, to Dr. M. Kaftory for the X-ray data of compound **4** and for assistance with the Cambridge Structural Data Base, to Dr. D. Cohn for assistance with the IR measurements, and to Professor E. M. Kosower for helpful discussions. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to which were are grateful.

Registry No. 2, 94203-58-4; **4**, 87902-64-5; **5**, 94203-59-5; **6**, 94203-61-9; **7**, 94203-60-8; **8**, 94203-62-0; **9**, 94203-63-1; **10**, 1733-63-7; **11**, 77787-78-1; **12**, 1889-68-5; **13**, 77787-77-0; bromomesitylene, 576-83-0; (bromomesitylene)methyl-*d*$_9$, 87871-32-7; mesityllithium, 5806-59-7.

Supplementary Material Available: Tables S1–S4 giving the crystallographic data for compound **7** (5 pages). Ordering information is given on any current masthead page.

Carbocation Behavior in Norbornyl–Fused Norbornyl Systems. The Kinetic and Chemical Consequences of Fusing Two Norbornane Units Across Framework Bonds of Various Type

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Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. Received August 27, 1984

Abstract: The nature of the *syn,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2-ylium cation was probed both solvolytically and by direct examination (^{1}H and ^{13}C NMR) in superacid solution. This most sterically congested ion is produced in aqueous acetone 3 500 000 times more rapidly than the *tert*-butyl cation and shows no tendency for skeletal rearrangement. Only a propensity for symmetrization via degenerate 2,3-hydride shifting and for conversion to the alkene has been detected. The response of its benzologue **16a** to solvolysis has also been examined. A 1250-fold rate deceleration was determined, and unrearranged products were likewise obtained. The protonation of **8** as an entry to the *anti*-tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-6-ylium cation was investigated in media of increasing acid strength. In contrast to the above, fusion of two norbornyl systems in this matter introduces a propensity for a cascade of cationic rearrangements. The entire range of these isomerizations has been elucidated. The exo/endo rate ratio exhibited by the epimeric *p*-nitrobenzoates **25-OPNB** and **27-OPNB** is the largest yet determined experimentally. The probable causative factors underlying this reactivity extreme and that of the other carbocationic rearrangements are outlined.

The opportunity to uncover fascinating and intricate transformations of heretofore unknown molecular types is customarily not bypassed by organic chemists. In the past, the lure of the unusual structures has yielded notable dividends in new facts that have been of major importance in the building of organic chemistry as a science. When ready access was recently gained in this laboratory to different types of norbornyl-fused norbornyl compounds, a detailed examination of their cationic behavior was undertaken. Our expectation was that these tantalizing structures would contribute in a meaningful way to our knowledge of this class of reactive intermediates.[1]

Recent years have witnessed development of a greatly enhanced appreciation for the special ability of norbornyl carbon atoms to enter into through-space[1a] and through-bond interactions.[2] The unusual reactivity of the norbornene π bond[3] and its outward

deformation have been dealt with from the theoretical[4,5] and experimental vantage points.[6,7] The extent of pyramidalization becomes significantly more pronounced within *syn*-sesquinorbornenes.[8] Whereas distortion angles of 16–18° are commonplace in simple derivatives such as **1**,[9] the bending is still more accen-

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(1) A large number of general accounts of these investigations is available. The most recent is the following set of four companion reviews: (a) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426. (b) Brown, H. C. *Ibid.* **1983**, *16*, 432. (c) Olah, G. A. Surya Prakash, G. K.; Saunders, M. *Ibid.* **1983**, *16*, 440. (d) Walling, C. *Ibid.* **1983**, *16*, 448.

(2) The following photoelectron spectral studies are exemplary: (a) Paddon-Row, M. N.; Patney, H. K.; Brown, R. S.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5575. (b) Jorgensen, F. S.; Paddon-Row, M. N.; Patney, H. K. *J. Chem. Soc., Chem. Commun.* **1983**, 573.

(3) (a) Husigen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *J. Am. Chem. Soc.* **1980**, *102*, 3951. (b) Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171.

(4) (a) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054. (b) Wipff, G.; Morokuma, K. *Chem. Phys. Lett.* **1980**, *74*, 400; *Tetrahedron Lett.* **1980**, 4446. (c) Spanget-Larsen, J.; Gleiter, R. *Ibid.* **1982**, 2435. (d) Ito, S.; Kakehi, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1869.

(5) (a) Mazzochi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6482. (b) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *Ibid.* **1981**, *103*, 2436.

(6) (a) Burnell, E. E.; Diehl, P. *Can. J. Chem.* **1972**, *50*, 3566. (b) Emsley, J. W.; Lindon, J. L. *Mol. Phys.* **1975**, *29*, 531. (c) Cole, K. C.; Gilson, D. F. R. *J. Mol. Struct.* **1982**, *82*, 71.

(7) (a) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095. (b) Paquette, L. A.; Schafer, A. G.; Blount, J. F. *Ibid.* **1983**, *105*, 3642. (c) Mackenzie, K.; Miller, A. S.; Muir, K. W.; Manojlović-Muir, Lj. *Tetrahedron Lett.* **1983**, 4747.

(8) For theoretical discussions of this question, consult: (a) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, 927. (b) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *20*, 3345. (c) Jorgensen, F. S. *Tetrahedron Lett.* **1983**, 5289. (d) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmayer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. (e) Johnson, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1135. (f) For relevant PE spectral data, see: Brown, R. S.; Bushek, J. M.; Kopecky, K. R.; Miller, A. J. *J. Org. Chem.* **1983**, *48*, 3692.

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tuated in *syn*-sesquinorbornadienes (e.g., 2[10]) and benzologues thereof (e.g., 3[11]). X-ray crystal structure analysis has further demonstrated that syn fusion of two norbornene units is not required to attain high levels of rigid pyramidal constraint.[12] One
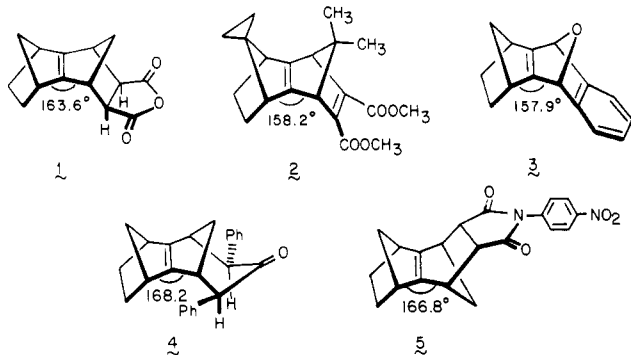
architechturally interesting example is given by 4. In contrast, most,[9a-c] though not all,[13,14] *anti*-sesquinorbornenes possess an essentially flat double bond, consistent with a greater hinge flexibility. Imide 5 is one notable exception.

The obviously unusual character of these molecules is reflected in the chemical reactivity of hydrocarbons 6 and 7. Among the more interesting observations to date, one may cite the ready reaction of 6 and 7 with triplet oxygen,[15] reversible exo addition of acids and of bromine to 6,[16,17] as well as its susceptibility to methanol capture in the presence of TCNE[17] and triplet-state photoreduction from the endo face.[18] Isomeric olefin 8 has been comparably explored.[19] However, as will be shown below, positioning an alkene double bond in this particular matrix does have interesting consequences on chemical reactivity.[20]

syn-Sesquinorbornene (6) is readily available by Diels–Alder addition of phenyl vinyl sulfone to isodicyclopentadiene followed by reductive desulfonylation.[15,21] Benzyne adds to the same diene to provide 7.[21,22] Access to 8 is gained by making recourse to
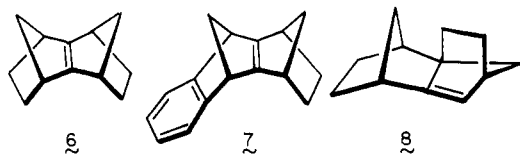
lesser reactive dienophiles such as *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene and *trans*-1,2-dichloroethylene.[19] The resulting angular adducts are subsequently processed to remove the unwanted substituents.

(9) (a) Watson, M. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022. (b) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818. (c) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 3136. (d) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *Ibid.* **1983**, *105*, 3148.

(10) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schäfer, W.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 8232.

(11) Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625.

(12) Paquette, L. A.; Hsu, L.-Y.; Gallucci, J. C.; Korp, J. D.; Bernal, I.; Kravetz, T. M.; Hathaway, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 5743.

(13) Ermer, O.; Bödecker, C.-D. *Helv. Chim. Acta* **1983**, *66*, 943.

(14) Paquette, L. A.; Green, K. W.; Hsu, L.-Y. *J. Org. Chem.* **1984**, *49*, 3650.

(15) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.

(16) Ohkata, K., unpublished results.

(17) Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J., unpublished results.

(18) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520.

(19) Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 4566.

(20) For preliminary reports of this work, consult: (a) Paquette, L. A.; Ohkata, K.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 3303. (b) Paquette, L. A.; DeLucca, G.; Korp, J. D.; Bernal, I.; Swarzendruber, J. K.; Jones, N. D. *Ibid.* **1984**, *106*, 1122.

(21) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186.

(22) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218.

Table I. Rate Constants and Activation Parameters Obtained for 11a and 16a

| compd	solvent	temp, °C	10^5k, s^{-1} [a]	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	k_{rel} (25 °C)
11a	80% acetone	60.0	22.3			
		50.0	6.67	24.4	−2.3	
		40.0	2.00			
		25.0[b]	0.260			
	80% dioxane	70.0	30.9			
		60.0	8.60			
		50.0	3.33	23.9	−5.5	
		25.0[b]	0.127			1
16a	80% dioxane	110.0	13.8			
		100.0	4.69			
		90.0	1.87	25.7	−9.8	
		25.0[b]	6.22×10^{-4}			8×10^{-4} [c]

[a] The values represented constitute averages from two independent runs; the activation parameters were calculated with use of all individual rate constants. [b] Extrapolated values calculated on the basis of the activation parameters. [c] Calculated on the assumption that 3,5-dinitrobenzoates solvolyze 6 times more rapidly than *p*-nitrobenzoates.

The *syn*,*endo*-Tetracyclo[6.2.1.1³,⁶.0²,⁷]dodec-2-ylium Cation. To arrive at alcohol 10, 6 was oxidized with *m*-chloroperbenzoic acid and epoxide 9 was subsequently reduced with lithium in ethylenediamine. Because the 3,5-dinitrobenzoate of 10 proved especially susceptible to loss of 3,5-dinitrobenzoic acid and reconversion to 6, solvolysis studies were carried out on *p*-nitrobenzoate 11a.

A priori, we viewed the likelihood of σ participation in 11 to form intermediates such as B and C (*the manner in which B–G are drawn should not be construed as denoting nonclassical ion character*) to be low. These limiting rearrangement options differ
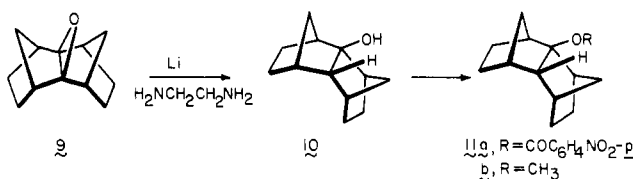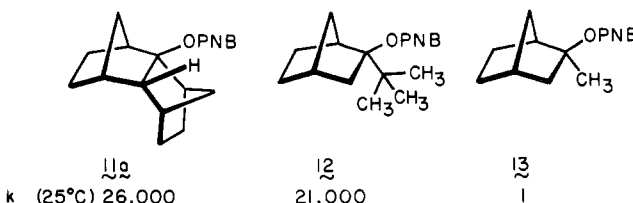

so greatly in energy from classical cation A that the possibility
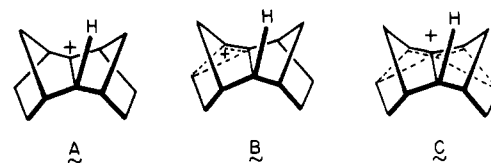
of resonance or rapid equilibration between them was considered very unlikely. These considerations are important because dismissal of structures B and C serves to focus attention solely on localized cation A.

The rate data for solvolysis of 11a in 80% acetone and 80% dioxane are summarized in Table I. As is customary, the decrease in solvent polarity that occurs as one proceeds from the first solvent system (Y = −0.673) to the latter (Y = −0.833)[23] is accompanied by a slight rate decrease. In preparative scale experiments de-

k_{rel} (25°C)   26,000   21,000   1

(23) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; pp 297–299.

signed to give product information, **11a** was seen to behave cleanly. Heating in 80% acetone buffered with 2,6-lutidine at 60 °C for 20 h led to the isolation of **6** (53%) and **10** (21%). Comparable handling in 80% dioxane but for 48 h afforded the same two compounds in yields of 68% and 32%, respectively. Buffered methanolysis (65 °C, 32 h) of **11a** likewise returned a substantial quantity of unrearranged olefin (45%) together with alcohol (7%). In addition, methyl ether **11b** was obtained in 21% yield.

Although the absence of skeletally rearranged products is noteworthy, a more striking finding is the exceptional reactivity of **11a** which ionizes 3 500 000 times more rapdily than *tert*-butyl *p*-nitrobenzoate. More instructive is the comparison with **12** and **13**.[24] *In fact,* **11a** *now replaces* **12** *as the most reactive tertiary system known.*

This behavior conforms to the high ground-state energy of **11**. X-ray structural analysis (see below) has demonstrated that the inner protons of the two ethano bridges engage in severe non-bonded interaction within the framework interior (endo face).[25] As ionization proceeds, the change in hybridization status of a carbon atom common to both norbornyl units from tetrahedral to trigonal is accompanied by steric decompression. The driving force underlying production of olefin **6** is undoubtedly a reflection of the added steric relief that becomes available as *both* internal carbons adopt sp²-like characteristics.

When olefin **6** or alcohol **10** was added to SO_2ClF–FSO_3H (3:1) in CD_2Cl_2 solution at −110 °C, conversion to carbocation A occurred cleanly. Direct comparison with the spectral properties of the epimeric 2,3-dimethyl-2-norbornyl cations that have been directly observed by Olah[26] and Sorensen[27] under superacid conditions proved possible. In our case, the ¹H NMR spectrum was observed to be essentially unchanged over the temperature range −90 to 0 °C,[28] except for some line broadening at the extreme low end. ¹³C NMR spectra, recorded over a comparable ΔT,[28] convincingly reveal that A experiences rapid 3,2-hydride shift. The central C(2–C(3) carbons that appear as a single sharp peak (201.91 ppm) at −15 °C show obvious broadening at −30 °C and are totally time-averaged at −60 °C. Rough estimates place the actual rate of 3,2-*exo*-hydride migration at a level slightly faster than those in polymethyl-substituted norbornyl systems.[26,27,29] This phenomenon may arise as a result of the greater conformational rigidity of A, wherein the empty p-like orbital is more effectively oriented into the ideal 0° dihedral angle relationship with the adjoining C–H bond.[30]

Quenching of these acidic solutions by pouring into cold (−78 °C) methanol containing anhydrous potassium carbonate gave **11b** accompanied by lesser amounts of **6**.

Consequences of Benzo Fusion. Standard reduction of epoxide **14**[15] with lithium in liquid ammonia–tetrahydrofuran at −40 °C or with diisobutylaluminum hydride in ether at 0 °C gave **15** in good yield. Because the *p*-nitrobenzoate derivative proved too
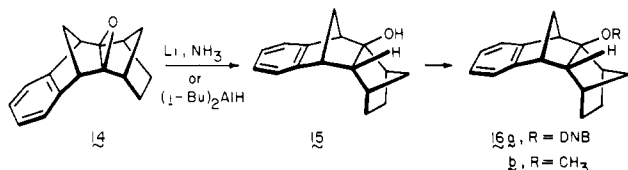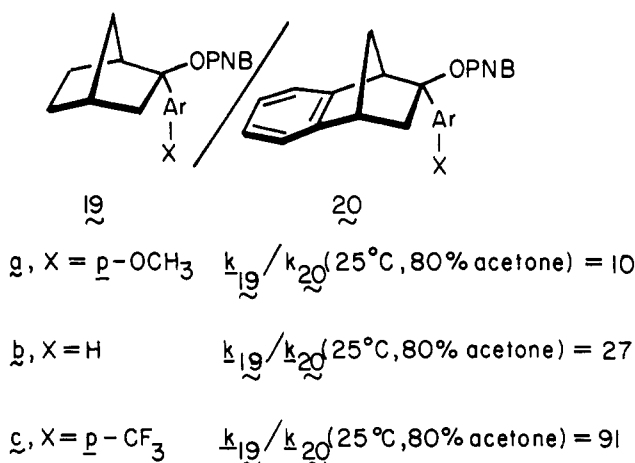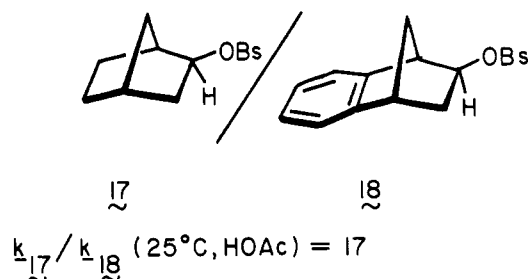
unreactive relative to **11a** under comparable conditions, recourse was made to the 3,5-dinitrobenzoate where solubility considerations

dictated the use of 80% dioxane as solvent. The kinetic results and thermodynamic parameters are collected in Table I.

Like **11a**, **16a** undergoes ionization without skeletal isomerization to return unrearranged products. When heated in lutidine-buffered 80% dioxane at 100 °C for 40 h, a two-component mixture consisting of **15** (11% isolated) and **7** (59%) was formed. Methanolysis in the presence of 2,6-ludidine (90 °C, 100 h) led to the isolation of methyl ether **16b** (53%) and olefin **7** (20%). Like its non-benzo-fused counterpart **10**, tertiary alcohol **15** proved entirely stable to the reaction conditions employed.

Particularly striking is the factor of 1250 by which the benzene ring in **16a** decelerates ionization of the tertiary exo leaving group (at 25 °C) relative to **11a**. This gap is much larger in magnitude than those values previously recorded for the secondary pair **17**/**18**[31] or the series of tertiary *p*-nitrobenzoates **19**/**20**.[32] This

$$\underset{\underset{\sim}{17}}{} \quad \underset{\underset{\sim}{18}}{}$$

$$\underline{k}_{17}/\underline{k}_{18}\ (25°C,\ HOAc) = 17$$

$$\underset{\underset{\sim}{19}}{} \quad \underset{\underset{\sim}{20}}{}$$

a, X = **p**–OCH₃ $\underline{k}_{19}/k_{20}(25°C,\ 80\%\ acetone) = 10$

b, X = H $\underline{k}_{19}/\underline{k}_{20}(25°C,\ 80\%\ acetone) = 27$

c, X = **p**–CF₃ $\underline{k}_{19}/\underline{k}_{20}(25°C,\ 80\%\ acetone) = 91$

phenomenon is not viewed as the result of decreased levels of anchimeric assistance in **16a** relative to model systems, where it is already recognized to be at a low level or nonexistent.[32–34] Rather, the replacement of an ethano bridge by one that is benzenoid significantly decreases the original level of steric crowding and consequently reduces the ground-state energy of **16a** relative to **11a**, with the usual kinetic consequences. In our opinion, **16a** like its simpler congeners ionizes by an unassisted (k_c) pathway without benefit of k_Δ contributions.

Crystal and Molecular Structure of 10. From the perspective view of **10** shown in Figure 1, its tetracyclodecane framework is seen to closely approach C_{2v} symmetry. As in other structures of this type,[35] the C(1)–C(2)–C(3) and C(6)–C(7)–C(8) angles are about 18° greater than the tetrahedral angle (Table V). The conformation of this molecule places two pairs of carbon atoms within close proximity: C(4)···C(10) = 3.172 (4) Å and C(5)···C(9) = 3.189 (6) Å. These distances are about 0.2 Å less than twice the van der Waals radius for carbon, 3.4 Å.[36] Likewise,

(24) Peters, E. N.; Brown, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 265; **1975**, *97*, 2892.

(25) For another relevant X-ray crystallographic analysis, consult: Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 978.

(26) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 189.

(27) (a) Huang, E.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1972**, *94*, 1780. (b) Jones, A.; Huang, E.; Haseltine, R.; Sorensen, T. S. *Ibid.* **1975**, *97*, 1133.

(28) Illustrations of selected ¹H and ¹³C NMR spectra of A may be found in the preliminary communication.[20a]

(29) Huang, L.; Ranganayakulu, K.; Wong, N.; Sorensen, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 1936.

(30) Chandrasekhar, J.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 4057.

(31) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240.

(32) (a) Takeuchi, T.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2693. (b) Brown, H. C.; Ikegami, S.; Liu, K.-T.; Tritle, G. L. *Ibid.* **1976**, *98*, 2531.

(33) Brown, H. C.; Tritle, G. L. *J. Am. Chem. Soc.* **1964**, *86*, 4904; **1968**, *90*, 2689.

(34) Paquette, L. A.; Dunkin, I. R. *J. Am. Chem. Soc.* **1973**, *95*, 3067.

(35) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 798.

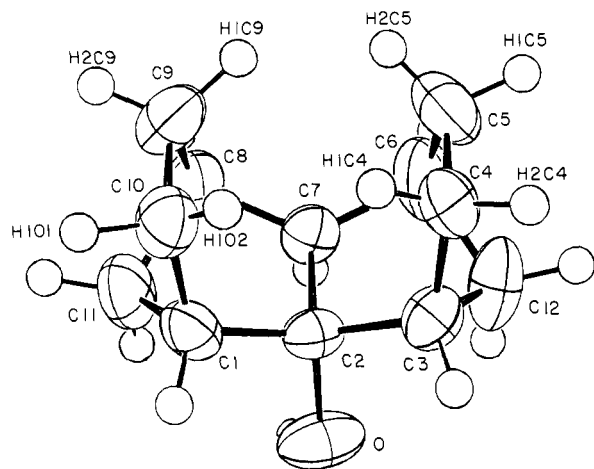(36) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Figure 1. ORTEP drawing of **10** showing the non-hydrogen atoms with 50% thermal probability ellipsoids and the hydrogen atoms with artificially small radii. Only one hydroxyl hydrogen atom has been drawn for clarity.

the hydrogen atoms bonded to these carbon atoms have short contact distances, $H(1C4)\cdots H(1O2) = 1.70$ (4) Å and H-$(1C9)\cdots H(2C5)$: 1.76 (4) Å. Although the positions of the hydrogen atoms are not determined as well as the non-hydrogen atoms, it is of interest to note that these short contact distances are about 0.7 Å less than twice the van der Waals radius for hydrogen, 2.4 Å.[36] Intramolecular H$\cdots$H distances of this magnitude have previously been observed in the neutron diffraction studies of two derivatives of *exo,exo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodecane;[37] the effect of these short distances is to distort the local C_{2v} symmetry about the methylene bridgehead carbons. A similar analysis of the geometry about the ethylene carbons in the structure determined here cannot be done since parameters involving the hydrogen atoms have large standard deviations. For instance the inner C–H bonds, C(4)–H(1C4), C(5)–H(2C5), etc., are not significantly different in length (Table IV) from the outer bonds, C(4)–H(2C4), C(5)–H(1C5), etc., although one would expect them to be shorter. One point which can be made is that the inner H–C–C angles are consistently larger than the outer angles; e.g., H(2C5)–C(5)–C(6) [defined as an inner angle] is 113.8 (18)° in comparison to H(1C5)–C(5)–C(6) [defined as an outer angle] 106.8 (18)°.

The *anti*-Tetracyclo[4.4.0.1^{1,4}.1^{7,10}]dodec-6-ylium Cation. Evidence is beginning to mount that substituents bonded to the exocyclic carbon of a 2-methylenenorbornane are pyramidalized in the exo direction.[38] This π deformation is opposite to that observed in systems such as **1–7**, where the double bond is internally positioned and smaller in magnitude. These considerations cause the recently synthesized hydrocarbon **8** to hold particular fascination because both structural fragments are contained therein. In principle, electrophilic addition to **8** may proceed from either of two directions to delivere initially unrearranged products typified by **21** and **22**. Although the X group in these molecules
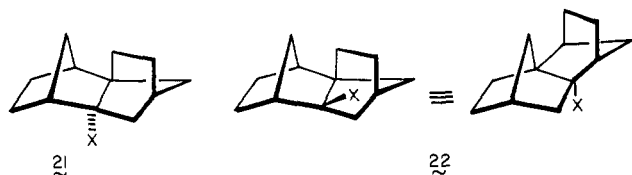

is simultaneously bonded exo to one norbornyl ring and endo to the other, the structures are decidedly not identical, as seen perhaps most clearly by a reorientation of **22** in space. When X is projected in a downward direction as in **21**, the distinctly different manner in which the second norbornyl unit is annealed to the first becomes

(37) Ermer, O.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1983**, 53.
(38) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436 and relevant references cited therein.

apparent. In actuality, the hypothetical conversions of **8** to **21** and **22** just discussed gloss over a number of still less apparent electronic effects. These subleties will be addressed in turn as they are encountered in the studies that follow.

Although **8** is minimally soluble in 60% aqueous dioxane, gradual dissolution occurs at room temperature during 2 h once several drops of 70% perchloric acid have been added. This phenomenon is the result of acid-catalyzed hydration that provides four isomeric alcohols. By means of medium-pressure liquid chromatography on silica gel, the individual products were isolated in pure form. The first two substances to elute were identified as the epimeric tertiary alcohols **23** (50%) and **24** (4%). The
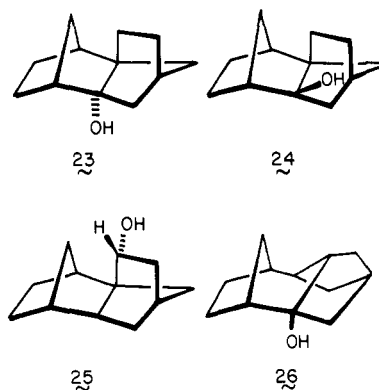

structural assignment to **23** is based on 300-MHz ^{1}H NMR spectral data and the readiness with which this alcohol is isomerized under more strongly acidic conditions. Thus, exposure to perchloric acid in acetic acid followed by reduction of the resulting acetates with lithium aluminum hydride provided **25** (69%) and **26** (31%). These interesting transformations are consistent with an ability of the trans-disposed ethano bridge in **23** to enter efficiently into neighboring group participation when the medium is adequately conducive to ionization. This chemical event leads to carbocation D which is in turn subject to 1,2-hydride migration.
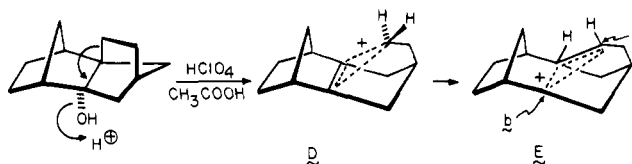
Because of the planar symmetric nature of D, the direction of the hydride shift is inconsequential and E results. Subsequent solvent capture of E can occur at either of two sites. While attack at a delivers **25**-OAc, nucleophile capture at b leads to formation of **26**-OAc.

The observed product distribution suggests that E experiences charge annihilation at site a twice as rapidly as at site b. This kinetic effect was observed as well when alcohols **25** and **26** were comparably treated with HOAc in CH$_3$COOH. Following hydride reduction, the same 69:31 mixture of alcohols was produced in both cases.

The strong similarity of the 300-MHz ^{1}H NMR spectrum of **24** to that of **23** is one primary consideration underlying our structural assignment to this product. Intriguingly, **24** is transformed cleanly and exclusively into **24**-OAc when ionized in the predescribed manner. Should ion F be involved in this case, pathway d to return the unrearranged acetate is kinetically dominant. The large steric demands imposed upon nucleophile
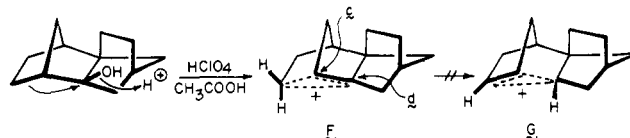
entry from inside the "cage" along pathway c may be responsible for this. No hydride shift to generate G was in evidence.

Norbornyl–Fused Norbornyl Systems

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The original hydration of **8** also furnished **25** (2%) and **26** (4%) as minor products. Although NMR spectral studies clearly revealed these substances to be a secondary and tertiary alcohol, respectively, unequivocal structural definition could not be arrived at on this basis alone. Consequently, their *p*-bromobenzoates were prepared and identified by X-ray crystal structure analysis.[39]

Effect of Increased Acidity. Although the hydration of **8** in acidified aqueous dioxane gives rise predominantly to **23**, this alcohol is particularly susceptible to acid-catalyzed isomerization when water is not present. It was, therefore, not unexpected that the action of $HClO_4$ in CH_3COOH on **8** delivered no **23**. A corresponding increase in the proportion of **25** (35%) and **26** (15%) was observed. Revealingly, although the formation of **25** persisted, the amount remained at a low level (3.3%).

Still more stringent conditions (CF_3COOH, 0 °C, 1 min; $LiAlH_4$) led to the isolation of **25** (8%) and **26** (22%). A quantity of nonpolar material was also produced under these conditions. The characterization of this mixture was not pursued. A heightened preference for formation of the tertiary alcohol is noteworthy.

The stage was now set for examination of the relationship between the hydroxyl group stereochemistry in **25** and the ability of the system to enter the D → E manifold. To this end, **25** was
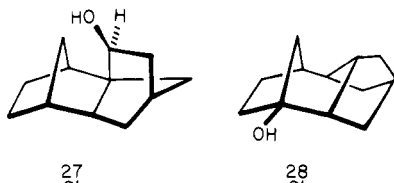
subjected to sequential Jones oxidation and $LiAlH_4$ reduction. When exposed to perchloric acid in acetic acid solution, conditions earlier recognized to cause **25** to equilibrate readily with **26, 27** was cleanly transformed to unrearranged **27**-OAc.

In an additional significant experiment, **26** was found to undergo a remarkable bridgehead → bridgehead cationic rearrangement when exposed to still more acidic conditions (CF_3SO_3H in CH_2Cl_2, 0 °C, 10 min). Since alcohol **28** (85% isolated) shows no penchant
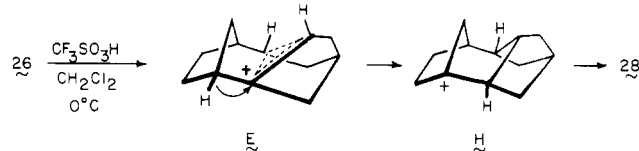
for additional chemical change, it likely represents the end point of the cascade. This isomerization, made possible by good stereoalignment, may be driven by bridghead strain energy considerations related to those found in manxanes and related medium-ring bicyclic compounds.

Solvolysis Studies. The *p*-nitrobenzoate esters of **23, 25, 26**, and **27** were individually solvolyzed in 80% aqueous acetone. The kinetic and thermodynamic data compiled in Table II indicate that there is relatively little difference in the rates and activation energies for secondary derivative **25**-OPNB and the tertiary systems **23**-OPNB and **26**-OPNB. Since the rates for the last two substrates are in line with those of structurally less encumbered tertiary norbornyl derivatives,[40] their reactivity level is considered normal. In this connection, the contrasting high propensity of **25**-OPNB for ionization and the unreactivity of **27**-OPNB is also notable. *In fact, the exo/endo rate ratio exhibited by this pair of epimers may well represent the largest yet determined experimentally.*[41]

Product studies, conducted under $CaCO_3$-buffered conditions, reveal that **23**-OPNB leads at 80 °C to **8** (25%) and **23** (75%). As with **11a** and **16a**, there exists a tendency for elimination. In

(39) Those interested in the details of the X-ray structural analyses are referred to the supplementary material of our preliminary report.[20b]

(40) (a) Brown, H. C.; Chloupek, F. J.; Rei, M.-H. *J. Am. Chem. Soc.* **1964**, *86*, 1248. (b) Brown, H. C.; Rei, M.-H. *Ibid.* **1964**, *86*, 5004.

(41) See: Berson, J. A. In "Molecular Rearrangements"; deMayo, P.; Ed.; Interscience: New York, 1963; p 182.

Table II. Rates of Solvolysis of Selected *p*-Nitrobenzoates in 80% Aqueous Acetone

compd	*T*, °C	*k*, s^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
23-OPNB	55.10	7.24 × 10^{-4}		
	65.00	2.41 × 10^{-5}		
	80.00	1.36 × 10^{-4}	26.5	−1.62
26-OPNB	65.20	3.18 × 10^{-6}		
	79.70	1.81 × 10^{-5}		
	95.00	7.97 × 10^{-5}	26.0	−8.74
25-OPNB	79.70	5.89 × 10^{-6}		
	95.00	2.72 × 10^{-5}		
	110.00	1.06 × 10^{-4}	24.9	−12.2
27-OPNB	130.0	<1.0 × 10^{-7}		

contrast, **25**-OPNB and **26**-OPNB solvolyze at 110 °C to produce identical mixtures of **25** (18%), **26** (70%), and hydrocarbon **29** (12%).

Discussion. In general, carbocations tend to have rather flat potential energy surfaces. As a result, rearrangements involving low-energy barriers are commonly observed. From a different
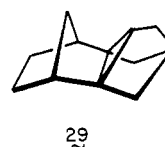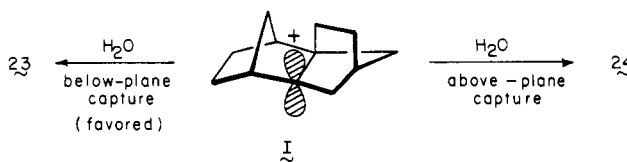

perspective, a reduction in solvent nucleophilicity diminishes the possibility of nucleophilic capture and can lead, where feasible, to passage through a set of progressively more stable positively charged structures. In these uncommon circumstances, gradations in the extent of isomerization are to be expected. The carbocations generated from protonation of **6** and **8** represent widely contrasting case studies.

Let us first consider A. Our recognition of this species as a most sterically congested entity stems from several sources, not the least of which is X-ray analysis of its alcohol precursor. Despite the plight of this intermediate, we have been able to detect only a propensity for symmetrization via degenerate 2,3-hydride shifting and a somewhat less prevalent tendency to lose the same hydrogen atom (though now as a proton) to return to olefin **6**. Evidently, any onset of bridging or heightened hyperconjugation as in B and C is thermodynamically unrewarding in its consequences. In our view, the absence of such intermediates simply reflects the importance of the tertiary doubly norbornyl nature of A and the incipient secondary character of the alternative cations.

Does A possess an inherent electronic stability arising from its unique doubly norbornyl character? This question is difficult to answer with certainty. The 1250-fold faster rate of ionization of **11a** relative to **16a** (after normalization) may have some relevance to this issue. At present, however, it is not possible to dissect cleanly the steric and electronic contributions to the rate constant for **16a**. Also, since the precise role played by the neighboring benzene ring in **18** and **20** has yet to be defined,[32–34] any attempt at more extensive rationalization is unwarranted.

The chemical response of **8** to acidic media is more varied. Under the mildest aqueous acidic conditions examined, carbocation I presumably intervenes. Although this charged entity is subject to low levels of skeletal rearrangement, the medium is sufficiently nucleophilic to promote its capture in unisomerized form. Al-

though the precise geometry of the cationic species is not known, two pathways are imminently available for covalent bonding to the hydroxyl. The experimental evidence is that the below-plane option leading to **23** is favored by a factor of 50:4 over the pathway that delivers **24**. It will be noted that the OH group in either

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alcohol is simultaneously bonded exo to one norbornyl ring and endo to another. On this basis, it would seem unlikely that the empty p orbital in I, which finds itself in a comparable situation, should be distended toward the underside of the molecule for long-range inductive reasons. Rather, a more plausible consideration is one based on greater hyperconjugative release of the type suggested by **D** relative to **F**, although not in the extreme sense of either illustration. The difference in energy between these alternatives, although subtle, presumably has its foundation in improved stereoelectronic alignment, lessened bond angle and steric strain, and the like.

The behavior of **23** and **26** under more acidic conditions is particularly noteworthy. Their distinctive rearrangement characteristics further extend the special features which accrue to norbornyl cations. The existent of a significant barrier to that 1,2-hydride shift that leads from D to E is unusual. The observation that an increase in acidity facilitates this migration may be an emergent general one.

A major thrust of norbornyl cation research has involved examination of exo/endo rate ratios. Where **11a** is concerned, such considerations lose their significance because of the major steric alterations which would accompany the changeover to endo stereochemistry. However, this issue reappears in magnified form with the *p*-nitrobenzoate esters of **25** and **27**. In fact, the global collection of data reported herein incorporates two record holders. The widely divergent solvolytic reactivity of **25**- and **27**-OPNB and the unparalleled ionizability of **11a** represent new kinetic limits to carbocation generation and serve as important reference points for limiting behavior in the extreme.

Experimental Section

Epoxidation of *syn*-Sesquinorbornene. A cold (-20 °C) solution of **6** (150 mg, 0.94 mmol) in dichloromethane (5 mL) was treated portionwise over 15 min with *m*-chloroperbenzoic acid (205 mg of 85% purity, 0.98 mmol). After an additional 15 min of stirring, the cold reaction mixture was filtered and the filtrate was washed with saturated sodium bisulfite (5 mL) and 10% sodium carbonate solutions and water prior to drying and evaporation. The residual waxy solid was sublimed at 60 °C and 0.1 torr to give 9 as a white solid, mp 88–89 °C, in 68% yield: IR (CCl₄) 3020, 2960, 1466, 1295 cm⁻¹; ¹H NMR (CDCl₃) δ 2.72 (m, 4 H), 2.08–1.32 (series of m, 10 H), 0.68 (br d, *J* = 8.5 Hz, 2 H); ¹³C NMR (CDCl₃) 58.6 (s), 41.1 (d), 38.9 (t), 27.1 ppm (t); mass spectrum, *m/z* (M⁺) calcd 176.1201, obsd 176.1207.

Anal. Calcd for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.49; H, 9.07.

Reduction of 9. Lithium wire (500 mg, 72 mg atm) was cut into small pieces, washed with petroleum ether, and added with vigorous stirring under a nitrogen atmosphere to a solution of **9** (988 mg, 5.6 mmol) in anhydrous ethylenediamine (50 mL) at room temperature. The reaction mixture was stirred for 3 h and treated with petroleum ether and water. The organic phase was washed with water, saturated ammonium chloride solution, and again water. Following drying and solvent evaporation, there was obtained 940 mg (94%) of **10**: mp 100–101 °C (from petroleum ether); IR (KBr) 3350, 2940, 1480, 1300, 1070, 965 cm⁻¹; ¹H NMR (CDCl₃) δ 2.5–1.7 (m, 11 H), 1.5 (s, 1 H), 1.5–1.1 (m, 6 H); ¹³C NMR (CDCl₃) 86.19 (s), 59.64 (d), 49.21 (d), 45.70 (t), 40.77 (d), 24.65 (t), 23.47 ppm (t).

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.82; H, 10.24.

The 3,5-dinitrobenzoate, prepared in the usual manner, was isolated as pale yellow crystals from petroleum ether–benzene. On melting, these crystals underwent notable change at ca. 130 °C and melted at 205–206 °C which is the melting point of 3,5-dinitrobenzoic acid. Futhermore, a CDCl₃ solution of this derivative, when stored at 37 °C for 20 h, provided a 69% yield of 3,5-dinitrobenzoic acid; IR (KBr) 2945, 1715, 1540, 1345, 1170, 715 cm⁻¹; ¹H NMR (CDCl₃) δ 9.0 (m, 3 H), 3.07 (br, s, 2 H), 2.47 (br, s, 3 H), 2.3–1.7 (m, 6 H), 1.7–1.2 (m, 6 H); ¹³C NMR (CDCl₃) 148.82, 129.95, 129.14, 123.08, 121.94, 101.51, 57.27, 45.85, 45.51, 40.44, 24.75, 23.66 ppm.

The *p*-nitrobenzoate was likewise obtained as a pale yellow solid. When slowly heated, these crystals underwent a morphological change at 144–150 °C and finally melted at 239–240 °C, the melting point of *p*-nitrobenzoic acid; IR (KBr) 2950, 1715, 1530, 1345, 1290, 1115, 865, 715 cm⁻¹; ¹H NMR (CDCl₃) δ 8.10 (s, 4 H), 3.10 (br s, 2 H), 2.43 (br s, 3 H), 2.2–1.7 (m, 6 H), 1.7–1.1 (m, 6 H).

Anal. Calcd for C₁₉H₂₁NO₄: C, 69.71; H, 6.47. Found: C, 69.81; H, 6.61.

Kinetic Studies. A. Preparation of Reagents. Acetone was purified by distillation from potassium permanganate and redistillation after drying over anhydrous potassium carbonate. Dioxane was purified by distillation from calcium hydride and redistribution from sodium metal. Doubly distilled water was utilized, and methanol was distilled from magnesium methoxide. The 80% solutions were prepared on a volume–volume basis.

B. Experimental Procedures. For each run, approximately 35 mg (0.1 mmol) of *p*-nitrobenzoate (0.08 mmol of 3,5-dinitrobenzoate) was weighed into a 10-mL volumetric flask that was subsequently filled to the mark with 80% aqueous acetone or 80% aqueous dioxane. After thorough mixing, the solutions were divided into nine glass ampules (1.00-mL aliquots) which were sealed. All ampoules were simultaneously immersed into a constant temperature bath. After an appropriate time interval (5–30 min), one ampule was removed and placed in an ice–water mixture, at which point an accurate timer was started. The next six ampoules were removed and cooled at appropriate intervals to cover a time span of 2 half-lives. The final two ampoules were removed after approximately 10 and 20 half-lives to provide the average infinity point.

The individual aliquots were diluted with 2 mL of acetone and titrated with standardized 0.0100 N sodium hydroxide solution to a blue end point (3 drops of 0.04% aqueous bromothymol blue as indicator). In the case of **11a**, the infinity titers revealed that 98–104% of *p*-nitrobenzoic acid had been liberated. As concerns **16a**, a substantial excess of base was required for the infinity titers. Therefore first-order rate data in this instance were determined by making use of initial theoretical concentrations.

The reported rate constants for **11a** and **16a** comprise the average of two runs that agreed with 6% at all temperatures.

Preparative Scale Solvolysis of 11a. A solution of **11a** (130 mg, 0.4 mmol) and 2,6-lutidine (0.3 mL) in 20 mL of 80% aqueous acetone was heated at 60 °C for 20 h. The solution was concentrated under reduced pressure, and the resulting suspension was extracted with dichloromethane. The organic phase was washed sequentially with sodium bicarbonate solution, water, 1 N hydrochloric acid, water, and sodium bicarbonate solution before drying. Solvent removal left 59 mg of yellowish oil. Product distributions were determined by using TLC on basic alumina (elution with petroleum ether–ether, 9:1). There was obtained 34 mg of **6** and 15 mg of **10**.

An analogous procedure was employed for **16a**.

Methanolysis of 11a. A sample of **11a** (81 mg, 0.25 mmol) was dissolved in anhydrous methanol (20 mL) containing 2,6-lutidine (0.5 mL), and the solution was heated at 65 °C for 32 h. After removal of the methanol under reduced pressure, the remaining suspension was extracted with petroleum ether. The combined organic layers were washed with sodium bicarbonate solution, 1 N hydrochloric acid, and sodium bicarbonate solution prior to drying. Removal of the solvent left 49 mg of a pale yellow oil. Preparative TLC purification on basic alumina (elution with petroleum ether–ether, 4:1) provided 18 mg of **6**, 3 mg of **10**, and 10 mg of **11b**.

3,5-Dinitrobenzoate **16a** was treated analogously.

Independent Preparation of 11b. A 0.5-mL sample of 50% KH emulsion in mineral oil was washed with petroleum ether and dried under a stream of nitrogen. A solution of **10** (43 mg, 0.24 mmol) in anhydrous tetrahydrofuran (10 mL) was introduced, and the mixture was heated at the reflux temperature for 3 h prior to addition of methyl iodide (0.5 mL). After 2 days at room temperature, the reaction mixture was diluted with cold water, and the product was extracted into petroleum ether. The organic phase was washed with water, dried, and concentrated to give 39 mg of oil. Purification by TLC on basic alumina (elution with petroleum ether) gave 27 mg (59%) of **11b**; IR (neat) 2960, 1480, 1080, 950, 880 cm⁻¹; ¹H NMR (CDCl₃) δ 3.17 (s, 3 H), 2.6–1.0 (m, 17 H); mass spectrum, *m/z* calcd (M⁺) 192.1514, obsd 192.1518.

Control Experiment Involving 10. A solution of **17** (17 mg, 0.09 mmol), 2,6-lutidine (0.3 mL), and *p*-nitrobenzoic acid (15 mg, 0.07 mmol) in 80% aqueous acetone (10 mL) was heated at 60 °C for 16 h. The reaction mixture was diluted with aqueous sodium bicarbonate solution and extracted with dichloromethane. The combined organic layers were washed with 1 N hydrochloric acid and aqueous sodium bicarbonate solution prior to drying. Removal of the solvent left 15 mg of unchanged **10**, thus demonstrating the alcohol to be stable to the solvolysis conditions.

Reduction of 14. A. With Lithium in Liquid Ammonia. To a solution of lithium metal (70 mg, 10 mg atm) in liquid ammonia (50 mL) was added **14** (126 mg, 0.56 mmol) dissolved in dry tetrahydrofuran (10 mL). The reaction mixture was stirred for 1 h, petroleum ether (20 mL) was added, and water (3 mL) was cautiously introduced. The ammonia was allowed to evaporate, the product was extracted into petroleum ether, and the combined organic layers were washed with water prior to drying. Solvent evaporation gave 120 mg of essentially pure **15** as an oil.

Crystallization from petroleum ether produced colorless crystals, mp 95–96 °C (90 mg, 71%); IR (KBr) 3360, 1250, 1035, 965, 740 cm⁻¹; ¹H NMR (CDCl₃) δ 7.2–6.8 (m, 4 H), 3.1 (br s, 2 H), 2.7–1.9 (series of m, 5 H), 2.3 (s, 1 H), 1.3–1.0 (m, 2 H), 0.9–0.5 (m, 4 H); ¹³C NMR (CDCl₃) 147.69 (s), 146.45 (s), 125.35 (d), 125.02 (d), 123.36 (d), 123.17 (d), 88.00 (s), 59.55 (t), 59.12 (d), 54.48 (d), 48.95 (d), 46.18 (d), 44.99 (t), 40.01 (d), 24.04 (t), 22.38 ppm (t).

Anal. Calcd for C₁₆H₁₈O: C, 84.91; H, 8.02. Found: C, 84.74; H, 7.95.

B. With Diisobutylaluminum Hydride. A solution of **14** (609 mg, 2.7 mmol) in dry ether (50 mL) was cooled to 0 °C and treated with 16 mL of 25% diisobutylaluminum hydride in heptane. The reaction mixture was stirred at room temperature for 7 h and quenched with 1 N sodium hydroxide solution (16 mL). After overnight stirring, the inorganic solids were separated by filtration and the filtrate was dried and concentrated. The remaining colorless oil (580 mg) was crystallized and recrystallized from petroleum ether to furnish 380 mg (62%) of **15**, mp 95–96 °C.

3,5-Dinitrobenzoate 16a. A 204-mg sample (0.9 mmol) of **15** in pyridine (5 mL) was treated with 3,5-dinitrobenzoyl chloride (300 mg, 1.3 mmol) for 2 days at room temperature. At this point, an additional 200 mg of the acid chloride was introduced, and stirring was continued for another 24 h. The usual workup afforded 250 mg (66%) of **16a** as pale yellow crystals: mp 225–226 °C (from benzene–petroleum ether); IR (KBr) 2960, 1715, 1550, 1340, 1170, 710 cm⁻¹; ¹H NMR (CDCl₃) δ 9.1 (br s, 3 H), 7.4–7.0 (m, 4 H), 4.00 (br s, 1 H), 3.3 (m, 1 H), 2.9 (m, 2 H), 2.6–1.8 (series of m, 4 H), 1.4–0.8 (m, 6 H).

Anal. Calcd for C₂₃H₂₀N₂O₆: C, 65.71; H, 4.79, N, 6.66. Found: C, 66.05; H, 4.69; N, 6.59.

The preparative scale solvolysis and methanolysis of **16a** were carried out as described for **11a**.

Independent Preparation of 16b. A 70 mg (0.31 mmol) sample of **16b** in dry tetrahydrofuran (10 mL) was treated sequentially with petroleum ether-rinsed potassium hydride and methyl iodide in the predescribed manner. Following the same workup and TLC purification (basic alumina, elution with petroleum ether), there was isolated 38 mg (51%) of **16b**; IR (neat, cm⁻¹) 2960, 1470, 1080, 760; ¹H NMR (CDCl₃) δ 7.2–6.8 (m, 4 H), 3.5–3.0 (m, 2 H), 3.30 (s, 3 H), 2.6–1.8 (series of m, 6 H), 1.3–0.3 (series of m, 5 H); *m/z* calcd (M⁺) 240.1514, obs 240.1519.

Control Experiment Involving 15. A solution of **15** (23 mg, 0.1 mmol), 2,6-lutidine (0.3 mL), and 3,5-dinitrobenzoic acid (21 mg) in 80% aqueous dioxane (20 mL) was heated at 100 °C for 48 h. The reaction mixture was diluted with sodium bicarbonate solution and extracted with dichloromethane. The combined organic layers were washed with 1 N hydrochloric acid and aqueous sodium bicarbonate solution prior to drying. Solvent evaporation left 21 mg (90%) of unchanged **15**.

Treatment of 8 with Perchloric Acid in Aqueous Dioxane. A mixture of **8** (200 mg, 1.25 mmol) in 50% aqueous dioxane (10 mL) was treated with 5 drops of 70% perchloric acid at room temperature. Since the olefin did not dissolve, an additional 3 mL of dioxane was added (to make an approximately 60% solution). Although complete homogeneity was not immediately achieved, a clear soltuion resulted after 2 h of stirring. At this point, the reaction mixture was diluted with ether (70 mL), washed with water and saturated sodium bicarbonate solution, dried, and evaporated. The residual colorless oil was purified by MPLC on silica gel (elution with 13% ethyl acetate in petroleum ether). The following four alcohols were eluted in the order given.

23: 110 mg (50%), colorless solid, mp 86.5–87 °C (not recrystallized), IR (film) 3500, 2960, 2890, 1465, 1350, 1300, 1260, 1195, 1170, 1140, 1055, 975, 910, 880, 855, 805, 740 cm⁻¹; ¹H NMR (CDCl₃) δ 2.4–1.0 (series of m); ¹³C NMR (CDCl₃) 87.05, 61.30, 47.52, 42.93, 42.33, 42.17, 37.79 (2C), 29.48, 29.21, 26.42, 23.03 ppm; mass spectrum, *m/z* calcd (M⁺) 178.1357, obsd 178.1394.

A cold (0 °C) solution of **23** (867 mg, 4.87 mmol) in anhydrous ether (30 mL) was blanketed with nitrogen and treated with 3.6 mL of 1.6 M *n*-butyllithium in hexane. The reaction mixture was stirred for 12 min prior to the addition of solid *p*-nitrobenzoyl chloride (1.20 g, 6.50 mmol) in small portions. Following a reaction time of 1.5 h, water was added and the product was extracted into ether. The combined organic phases were washed with water and saturated sodium bicarbonate solution and brine before drying and evaporation. There was isolated 1.50 g (94%) of the *p*-nitrobenzoate as colorless needles: mp 129–130.5 °C (from ether–petroleum ether); ¹H NMR (CDCl₃) δ 8.29 (d, *J* = 8.76 Hz, 2 H), 8.15 (d, *J* = 8.89 Hz, 2 H), 2.98 (d, *J* = 5.7 Hz, 1 H), 2.30 (br s, 1 H), 2.15 (m, 3 H), 1.79–1.35 (m, 12 H).

Anal. Calcd for C₁₉H₂₁NO₄: C, 69.71; H, 6.47. Found: C, 69.44; H, 6.59.

24: 8.2 mg (4%), colorless solid, mp 83 °C (from petroleum ether); IR (KBr) 3400, 3020, 2960, 2900, 1470, 1400, 1330, 1310, 1280, 1255, 1230, 1180, 1070, 1040, 990, 910, 890, 855, 790 cm⁻¹; ¹H NMR (CDCl₃) δ 2.32 (br s, 1 H), 2.20–2.16 (m, 2 H), 2.05 (d, *J* = 5 Hz, 1 H),

fw, amu	178.28
space group	C2/c – C₂ₕ⁶
a, Å	20.404 (2)
b, Å	10.519 (1)
c, Å	9.352 (1)
β, deg	104.16 (1)
V, Å³	1946
Z	8
density (calcd, g/cm³)	1.22
crystal size, mm³	0.29 × 0.34 × 0.53
radiation	Mo Kα with graphite monochromator H [λ(Kα₁) = 0.70926 Å]
linear abs coeff, cm⁻¹	0.70
temperatire, °C	21
2θ limits	4–50°
scan speed	4–24°/min in 2θ
background time/scan time	0.5
scan range	1.0° below Kα₁ to 1.0° above Kα₂
data collected	+*h*,+*k*,±*l*
unique data	1734
unique data with F₀² > 0.5σ(F₀²)	1394
final number of variables	154
R(F)	0.073
Rᵥᵥ(F)	0.049

1.94–1.90 (m, 1 H), 1.8–1.7 (m, 2 H), 1.63–1.10 (m, 11 H); ¹³C NMR (CDCl₃) 86.85, 59.24, 50.00, 42.33, 41.51, 40.30, 37.19, 36.99, 30.10, 24.52, 24.27, 23.01 ppm; mass spectrum, *m/z* calcd (M⁺) 178.1358, obsd 178.1317.

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 81.13; H, 10.12.

25: 3.7 mg (2%), colorless solid, mp 88–89 °C (from petroleum ether); IR (KBr) 3300, 3990, 3890, 1490, 1470, 1360, 1310, 1270, 1170, 1090, 1050, 1010, 940, 890, 860 cm⁻¹; ¹H NMR (CDCl₃) δ 3.58 (d, *J* = 6 Hz, 1 H), 2.27 (br s, 1 H), 2.22 (s, 1 H), 2.11 (br s, 1 H), 1.76 (m, 1 H), 1.68 (m, 1 H), 1.50–1.40 (m, 8 H), 1.40–1.11 (series of m, 4 H); ¹³C NMR (CDCl₃) 74.97, 59.99, 49.05, 43.53, 41.24, 39.38, 37.36, 35.39, 34.40, 30.47, 29.37, 21.12 ppm.

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.78; H, 10.26.

The *p*-nitrobenzoate, prepared as described above, was obtained as white flakes, mp 121 °C (from ether–petroleum ether); ¹H NMR (CDCl₃) δ 8.28 (m, 2 H), 8.18 (m, 2 H), 4.86 (d, *J* = 6.4 Hz, 1 H), 2.39 (br s, 1 H), 2.20 (m, 2 H), 2.03 (m, 1 H), 1.80 (d, *J* = 9.6 Hz, 1 H), 1.68 (dd, *J* = 14.4 and 5.2 Hz, 1 H), 1.64–1.26 (m, 10 H).

Anal. Calcd for C₁₉H₂₁NO₄: C, 69.71; H, 6.47. Found: C, 69.56; H, 6.56.

The *p*-bromobenzoate was isolated as colorless crystals, mp 69–71 °C (from methanol).

26: 8.9 mg (4%), colorless solid, mp 140 °C (from petroleum ether); IR (KBr) 3300, 2950, 2890, 1470, 1390, 1320, 1175, 1150, 1090, 1060, 970, 860 cm⁻¹; ¹H NMR (CDCl₃) δ 2.28–1.99 (m, 5 H), 1.89 (dd, *J* = 13 and 3 Hz, 1 H), 1.69–1.05 (m, 12 H); ¹³C NMR (CDCl₃) 81.58, 46.27, 45.72, 43.31, 38.89, 37.74, 34.62, 34.35, 33.86, 29.21, 27.08, 25.55 ppm.

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.61; H, 10.21.

The *p*-nitrobenzoate, prepared as described above, was obtained as fluffy colorless needles: mp 154–155 °C (from methylcyclohexane); ¹H NMR (CDCl₃) δ 8.26 (m, 2 H), 8.14 (m, 2 H), 2.56 (m, 1 H), 2.46 (m, 1 H), 2.38 (m, 2 H), 1.90 (m, 1 H), 1.72–1.33 (m, 11 H), 1.28–1.08 (m, 1 H).

Anal. Calcd for C₁₉H₂₁NO₄: C, 69.71, H, 6.47. Found: C, 69.76; H, 6.57.

The *p*-bromobenzoate was isolated as colorless crystals, mp 112 °C (from methanol).

Acid-Catalyzed Rearrangement of Alcohols 23, 25, and 26. Exemplary Procedure. A solution of **26** (100 mg, 0.56 mmol) in acetic acid (3 mL) was treated with 2 drops of 70% perchloric acid at room temperature. The reaction mixture was stirred for 3 min, poured into 50 mL of petroleum ether, and washed successively with water, saturated sodium bicarbonate solution, and brine. Drying and solvent evaporation left a colorless oil which was dissolved in anhydrous ether (12 mL), cooled in an ice bath, and treated with lithium aluminum hydride (30 mg, 0.9 mmol). This mixture was stirred at 0 °C for 15 min and at 20 °C for 10 min before being quenched with water. The salts were filtered and

Table IV. Final Bond Lengths for **10**

atoms	length, Å	atoms	length, Å
C(2)–C(1)	1.543 (3)	C(2)–C(3)	1.539 (3)
C(1)–C(11)	1.536 (3)	C(3)–C(12)	1.530 (3)
C(1)–C(10)	1.522 (3)	C(3)–C(4)	1.528 (3)
C(7)–C(8)	1.526 (3)	C(7)–C(6)	1.531 (3)
C(8)–C(11)	1.519 (3)	C(6)–C(12)	1.530 (3)
C(8)–C(9)	1.534 (3)	C(6)–C(5)	1.521 (4)
C(9)–C(10)	1.543 (4)	C(4)–C(5)	1.534 (4)
C(2)–C(7)	1.547 (3)		
C(2)–(O)	1.450 (2)		
C(4)–H(1C4)	1.08 (3)	C(10)–H(101)	1.05 (2)
C(4)–H(2C4)	0.98 (2)	C(10)–H(102)	0.98 (2)
C(5)–H(1C5)	0.97 (3)	C(9)–H(1C9)	1.07 (3)
C(5)–H(2C5)	0.97 (3)	C(9)–H(2C9)	0.95 (3)
C(7)–H(C7)	1.00 (2)		
C(4)⋯C(10)	3.172 (4)	C(5)⋯C(9)	3.189 (6)
H(1C4)⋯H(102)	1.70 (4)	H(1C9)⋯H(2C5)	1.73 (4)

rinsed thoroughly with ether. The aqueous phase of the filtrate was separated and extracted with ether. The combined organic solutions were washed with brine, dried, and evaporated to provide 98 mg (98%) of a white solid. MPLC on silica gel (elution with 13% ethyl acetate in petroleum ether) showed **25** (69%) and **26** (31%) to be the only products.

Hydration of 8 in Trifluoroacetic Acid. To ice-cold trifluoroacetic acid (20 mL) was added with stirring 6.2 g of **8** over a period of 30 s. The mixture which turned red was stirred at 0 °C for 1 min, poured into cold 5% sodium carbonate solution, and extracted with ether. The combined organic phases were washed with brine, dried, and evaporated. The procedure was repeated again on an additional 4.8 g of **8**, and the resulting brown oils were combined (15.4 g).

The trifluoroacetic mixture (15.4 g) in anhydrous ether (80 mL) was cooled in an ice bath, treated with lithium aluminum hydride (2.35 g), and stirred at 0 °C for 1.5 h. Water was added, the solids were separated by filtration and rinsed with ether, and the combined filtrates were washed with brine. Drying and solvent evaporation gave a light yellow oil which was purified by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). There were isolated 1.0 g (8%) of **25** and 2.7 g (22%) of **26**. A substantial amount of nonpolar material was also separated, but characterization of this mixture was not pursued.

Alcohol 27. A solution of **25** (1.57 g, 8.8 mmol) in acetone (60 mL) was cooled in an ice bath, and Jones reagent (8.5 mL) was added. The mixture was stirred at 0 °C for 10 min, warmed to room temperature, and treated with isopropyl alcohol to destroy excess oxidant. The in-

solubles were separated by filtration, and the filtrate was diluted with petroleum ether before washing with water, saturated sodium bicarbonate solution, and brine. Drying and solvent evaporation gave the ketone (1.22 g, 79%) as a colorless oil which was homogeneous on TLC: ^{13}C NMR (CDCl$_3$) 211.64, 65.29, 49.77, 44.40, 43.51, 39.42, 37.51, (2C), 33.61, 29.58, 38.56, 20.83 ppm; mass spectrum, m/z calcd (M$^+$) 176.1202, obsd (176.1188).

A cold (0 °C) ethereal solution (80 mL) of this ketone (1.22 g, 6.8 mmol) was stirred with lithium aluminum hydride (260 mg, 6.8 mmol) at 0 °C for 25 min and at room temperature for 15 min. After the usual workup, there was obtained 1.14 g (75% overall) of **27** as colorless crystals: mp 74 °C (from petroleum ether); IR (KBr) 3350, 2960, 2890, 1480, 1460, 1350, 1298, 1270, 1130, 1100, 1070, 1046, 940, 809 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.02 (dd, J = 10 and 5 Hz, 1 H), 2.28 (m, 1 H), 2.16 (br s, 2 H), 2.11–2.04 (m, 2 H), 1.78 (d, J = 101 H), 1.50–1.36 (m, 8 H), 1.26–1.21 (m, 1 H), 1.11–1.01 (m, 1 H), 1.00–0.95 (m, 1 H); ^{13}C NMR (CDCl$_3$) ppm 75.30, 58.13, 44.30, 41.07, 39.05, 38.67, 38.28, 37.68, 37.25, 33.15, 29.81, 21.17 ppm; mass spectrum, m/z calcd (M$^+$) 178.1357, obsd 178.1337.

The *p*-nitrobenzoate was isolated as colorless crystals, mp 141 °C (from ether–petroleum ether).

Anal. Calcd for C$_{19}$H$_{21}$NO$_4$: C, 69.71; H, 6.47. Found: C, 69.56; H, 6.35.

Alcohol 28. A solution of **26** (40 mg, 0.22 mmol) in dichloromethane (9 mL) was cooled in an ice bath and treated with 2 drops of trifluoromethanesulfonic acid. After 5 min at 0 °C, 5 more drops of acid were added, and the reaction mixture turned brown–orange. Five minutes later, not starting material remained. The mixture was poured into 5% sodium carbonate solution, the aqueous layer was extracted with dichloromethane, and the combined organic phases were washed with brine, dried, and evaporated. There was obtained 34 mg (85%) of a pale yellow oil which slowly solidified.

The above procedure was repeated by using 154 mg (0.865 mmol) of **26** and 20 drops of CF$_3$SO$_3$H. After workup, 144 mg of white solid was isolated. MPLC on silica gel (elution with 11% ethyl acetate in petroleum ether) showed **28** to be the only product: colorless crystals, mp 117–120 °C (from petroleum ether); IR (KBr) 3350, 2960, 2880, 1470, 1420, 1340, 1325, 1295, 1270, 1210, 1180, 1165, 1100, 1040, 990 cm^{-1}; ^{13}C NMR (CDCl$_3$) 79.94, 46.49, 43.86, 43.69, 39.92, 37.52, 36.97, 36.43, 31.12, 30.79, 28.77, 24.89 ppm; mass spectrum, m/z calcd (M$^+$) 178.1358, obsd 178.1324.

Anal. Calcd for C$_{12}$H$_{18}$O: C, 80.85; H, 10.18. Found: C, 80.81; H, 10.19.

Control Experiments. A. 26-OPNB. An 84.3-mg sample of **26**-OPNB was placed along with 5 mL of 80% aqueous acetone into a sealed

Table V. Final Bond Angles for **10**

atoms	angle, deg	atoms	angle, deg
Cn2)–C(1)–C(10)	114.9 (2)	C(2)–C(3)–C(4)	115.1 (2)
C(2)–C(1)–C(11)	99.1 (2)	C(2)–C(3)–C(12)	98.7 (2)
C(10)–C(1)–C(11)	99.3 (2)	C(4)–C(3)–C(12)	99.9 (2)
C(1)–C(10)–C(9)	103.5 (2)	C(3)–C(4)–C(5)	103.7 (3)
C(10)–C(9)–C(8)	103.0 (2)	C(4)–C(5)–C(6)	102.8 (3)
C(9)–C(8)–C(7)	115.0 (2)	C(5)–C(6)–C(7)	115.0 (3)
C(9)–C(8)–C(11)	100.0 (2)	C(5)–C(6)–C(12)	99.6 (2)
C(7)–C(8)–C(11)	98.9 (2)	C(7)–C(6)–C(12)	99.9 (2)
C(8)–C(7)–C(2)	103.6 (2)	C(6)–C(7)–C(2)	103.4 (2)
C(6)–C(7)–C(8)	129.3 (2)		
C(1)–C(2)–C(7)	102.7 (2)	C(3)–C(2)–C(7)	102.5 (2)
C(1)–C(2)–C(3)	128.6 (2)		
C(1)–C(2)–O	106.5 (2)		
C(3)–C(2)–O	105.0 (2)		
C(7)–C(2)–O	111.1 (2)		
C(1)–C(11)–C(8)	94.6 (2)	C(3)–C(12)–C(6)	93.9 (2)
H(C7)–C(7)–C(2)	107.4 (11)		
H(C7)–C(7)–C(6)	104.8 (11)		
H(C7)–C(7)–C(8)	106.9 (11)		
H(1C4)–C(4)–C(3)	111.4 (13)	H(1C9)–C(9)–C(8)	113.0 (15)
H(1C4)–C(4)–C(5)	109.3 (13)	H(1C9)–C(9)–C(10)	110.4 (14)
H(1C4)–C(4)–H(2C4)	115.0 (19)	H(1C9)–C(9)–H(2C9)	113.5 (22)
H(2C4)–C(4)–C(3)	107.8 (14)	H(2C9)–C(9)–C(8)	107.6 (15)
H(2C4)–C(4)–C(5)	109.0 (14)	H(2C9)–C(9)–C(10)	108.8 (16)
H(1C5)–C(5)–C(4)	110.2 (16)	H(101)–C(10)–C(1)	107.2 (12)
H(1C5)–C(5)–C(6)	106.8 (18)	H(101)–C(10)–C(9)	110.5 (13)
H(1C5)–C(5)–H(2C5)	111.4 (25)	H(101)–C(10)–H(102)	107.8 (18)
H(2C5)–C(5)–C(4)	111.5 (20)	H(102)–C(10)–C(1)	115.6 (13)
H(2C5)–C(5)–C(6)	113.8 (18)	H(102)–C(10)–C(9)	112.1 (13)

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ampule and heated at 79.7 °C for 3.5 h (30% acid production). The solvent was removed under vacuum, and the residual solid was analyzed by ¹H NMR. The only ester observed was 26-OPNB.

B. 25-OPNB. A solution of 25-OPNB (5.5 mg) in 80% aqueous acetone (5 mL) was placed in a sealed ampule and heated at 95 °C for 22 h (22 half-lives). The cooled ampule was opened and the contents were titrated with a standardized sodium methoxide solution. Acid production had advanced to 87% of the theoretical estimate.

C. Alcohol Stabilities. General Procedure. Alcohol 26 (65.8 mg), *p*-nitrobenzoic acid (64.7 mg), and calcium carbonate (100 mg) were placed in an ampule along with 5 mL of 80% aqueous acetone. The ampule was sealed and heated at 95 °C for 23 h (10 half-lives). The cooled ampule was opened, and the contents were poured into ether. The organic solution was washed with water, 5% sodium carbonate solution, and brine. Following drying and solvent evaporation, the residue was analyzed by ¹H NMR. Only 26 was present. The other alcohols were similarly recovered in intact condition.

General Solvolysis Procedure. A solution of 26-OPNB (200 mg, 0.61 mmol), 2,6-lutidine (or calcium carbonate) (200 mg), and 80% aqueous acetone (5 mL) was heated in a sealed ampule at 110 °C for 22 h and poured into ether. The organic solution was washed with water and dilute hydrochloric acid before drying and evaporation. The solid residue was purified by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). There was isolated in order of elution 12 mg (12%) of 29, 14 mg (18%) of 25, and 65 mg (70%) of 26. 29: IR (neat) 3060, 2960, 3880, 1465, 1295, 1280, 1260 cm⁻¹; ¹H NMR (CDCl₃) δ 2.28 (br s, 2 H), 2.03 (br s, 1 H), 1.45–1.34 (m, 8 H), 1.23–1.11 (m, 4 H), 0.97–0.90 (dd, *J* = 10 and 2 Hz, 1 H); ¹³C NMR (CDCl₃) 36.16, 36.05, 35.89, 35.56, 31.14, 27.69, 26.12, 13.17 ppm; mass spectrum, *m/z* (GC–MS) calcd 160.00, obsd 160.00.

X-ray Crystal Structure Determination of 10. The crystals of 10 were clear and colorless. Preliminary precession photographs with Mo Kα radiation indicated a monoclinic cell, *Z* = 8, with the following systematic absences: *hkl*, *h* + *k* = 2*n* + 1 and *h0l*, *l* = 2*n* + 1. Hence the space group possibilities were restricted to *Cc* and *C2/c*. The crystal used for data collection was cut from a larger crystal. The unit cell constants *a* = 20.404 (2) Å, *b* = 10.519 (1) Å, *c* = 9.352 (1) Å, and β = 104.16 (1)° were determined by the least-squares fit of the diffractometer setting angles for 26 reflections in the 2θ range 20–30° with Mo Kα radiation. Further crystallographic details are reported in Table III–V.

Intensities were measured by the θ − 2θ scan technique on a Syntex P1̄ diffractometer. Six standard reflections were measured after every 100 reflections. During the course of the data collection, the intensities of these standards began to decrease so that at the end of the data collection, each standard had an intensity which measured about 68% of its original value. Visual examination of the crystal at this point did not reveal any unusual features. However, approximately 2 weeks later, a second look under the microscope revealed that the crystal had partly sublimed. Since the crystals appeared stable at room temperature before exposure to X-rays, the decomposition seems to be initiated by the X-ray beam.

Five reflections, the 021, 020, 111, 20̄2, and 31̄1, saturated the detector during data collection and are not included in the data set. The data were corrected for Lorentz and polarization effects and for the observed decay.[42]

The intensity statistics strongly indicated the centrosymmetric space group *C2/c* to be correct. Successful solution and refinement in this space group further supports this choice. MULTAN 80[43] was used to solve the structure. The tetracyclododecane fragment was input to the program as a random group, and the resulting E map clearly revealed the positions of all the non-hydrogen atoms.

The SHELX 76 package[44] was used for full-matrix least-squares refinements. Isotropic refinement of the model converged to an *R* index of 0.181. After one cycle of anisotropic refinement, the hydrogen atoms were located in a difference electron density map. There appeared to be two hydrogen atoms within bonding distance of the oxygen atom and located approximately on opposite sides of it. The oxygen atom is also within hydrogen bonding distance of two symmetry related oxygen atoms (O···O distances are 2.877 (2) and 2.846 (2) Å]. This intermolecular hydrogen bonding chain runs approximately parallel to the *c* axis. The hydrogen atoms in this chain are disordered by means of the inversion center and are included in the model with occupancy factors of 0.5 each at their locations in the difference electron density map. The remainder of the hydrogen atoms were added as fixed contributions in their calculated positions with C–H = 1.00 Å and $B_H = B_{C(2so)} + 1.0$ Å². For the final refinement cycles, the hydrogen atoms on the C(4), C(5), C(7), C(9), and C(10) atoms were allowed to refine. The final refinement cycle based on the 1394 intensities with $F_0{}^2 > 0.5\sigma(F_0{}^2)$ and the 154 variables yielded agreement indexes of *R* = 0.073 and R_w = 0.049. The final difference electron density map contained maximum and minimum peak heights of 0.17 and −0.19 e/Å³. Scattering factors for the carbon and oxygen atoms[45a] and for the hydrogen atom[45b] are from the usual sources.

Supplementary Material Available: Stereodrawing of the unit cell for 10 (Figure 2), final positional and thermal parameters (Tables VI and VII), and observed and calculated structure factors (Table VIII) (10 pages). Ordering information is given on any current masthead page.

(42) The programs used for data reduction are from the CRYM crystallographic computing package (Duchamp, D. J. "Program and Abstracts", American Crystallographic Association Meeting, Bozeman, MT, 1964 American Crystallographic Association: Washington, DC, 1964) and modified by G. C. Christoph at The Ohio State University, Columbus, OH.

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