TABLE I

ABSOLUTE CONFIGURATIONS AND ROTATIONS

Compd	Configuration	Rotation[a] [α]	λ, nm	c, g/100 ml	Solvent
$PhCH(CH_3)CH(CH_3)_2$ (II)	*S*	−36.2	546	1.6	CCl_4
		−30.0	589	1.6	CCl_4
		−24.5	589	0.7	CH_3OH
$PhCH(CH_3)C(CH_3){=}CH_2$ (VI)	*S*	94 ± 2	546	1.9	CCl_4
		79 ± 2	589	1.9	CCl_4
$(PhCH(CH_3)C(CH_3)_2N{=})_2$ (V)	*R,R*	60.2	546	0.86	CH_3OH
$PhCH(CH_3)C(CH_3)_2NH_2$ (IV)	*R*	−30.4[b]	546	3.95	CH_3OH
$PhC(CH_3)$(*i*-Pr)NH_2 (III)	*R*	−22.1[c]	546	1.8	CH_2Cl_2
$(PhC(CH_3)$(*i*-Pr)$N{=})_2$ (I)	*R,R*	10.5[d]	546	1.6	CCl_4
$(PhC(CH_3)$(*i*-Pr)$)_2$ (VII)	*R,R*	4[e]	546	0.59	CCl_4

[a] Samples greater than 98% optically pure except as noted. [b] Greater than 95% optically pure, see text. [c] Judged to contain 8.5% (*S*)-III from meso/nonmeso ratio of oxidation product I. [d] Sample from oxidative coupling of III. 84.4% nonmeso of which 83.7% is *R,R* and 0.7% is *S,S*, since statistical coupling is observed for *rac*-III. [e] Optical purity unknown.

2-Methyl-3-phenyl-2-butylamine (**IV**) was collected as a forerun during a spinning band distillation used to remove this byproduct from amine III after alkaline hydrolysis of the product from a Ritter reaction of 2-methyl-3-phenyl-2-butanol.[17] Combined foreruns from several distillations (115 g) were dissolved in 100 ml of ethanol and added to a hot solution of 160 g of *d*-tartaric acid in 600 ml of ethanol with cooling and stirring. The resulting salt was recrystallized five times from methanol to give 8.3 g of salt which was converted to 4.1 g of amine and distilled [bp 93° (8 mm)]. The resulting (*R*)-(−)-IV had $[\alpha]_{546}$ −31.1° (*c* 3.25, methanol); pmr (20% in CCl_4, 60 MHz) δ 7.30 (5 H, s, Ar H), 2.65 (1 H, q, *J* = 7.3 Hz, $C\mathbf{H}CH_3$), 1.28 (3 H, d, *J* = 7.3 Hz, $CHC\mathbf{H}_3$), 1.03 (2 H, s, NH_2), 1.00 (3 H, s, $C(CH_3)C\mathbf{H}_3$), 0.86 (3 H, s, $C(C\mathbf{H}_3)CH_3$).

Azobis-2-methyl-3-phenyl-2-butane (**V**) was prepared as a mixture of diastereoisomers by oxidative coupling of 11 g of amine mixture containing 85% IV and 15% III with 5 ml of IF_5 in 150 ml of CH_2Cl_2–18 ml of pyridine at −20 to −30°. Washing through Florisil with pentane gave 3.6 g of a yellow oil shown by pmr to contain the diastereomers of V (in equal amounts by peak heights) and a small amount of what are presumably the cross coupling products between III and IV. Preparative tlc (Merck F-254 developed five times with pentane) gave a mixture of the diastereomers of V as a yellow oil free of impurities and showed negligible fractionation of the diastereomers between early and late fractions confirming the absence of asymmetric induction in the coupling reaction. Pmr (CCl_4, 100 MHz): *meso*-V, δ 7.20 (5 H, s, Ar H), 3.19 (1 H, q, *J* = 7.5 Hz, $C\mathbf{H}CH_3$), 1.22 (3 H, d, *J* = 7.5 Hz, $CHC\mathbf{H}_3$), 1.02 (3 H, s, $C(CH_3)C\mathbf{H}_3$), 0.98 (3 H, s, $C(C\mathbf{H}_3)CH_3$); *rac*-V, 7.20 (5 H, s, Ar H), 3.17 (1 H, q, *J* = 7.5 Hz, $C\mathbf{H}CH_3$), 1.22 (3 H, d, *J* = 7.5 Hz, $CHC\mathbf{H}_3$), 1.05 (3 H, s, $CH(CH_3)C\mathbf{H}_3$), 0.96 (3 H, s, $C(C\mathbf{H}_3)CH_3$). The racemate peaks were identified by comparison with the spectrum of (*R,R*)-V.

(*R,R*)-(+)-V was prepared by a similar oxidation of 2.74 g of the resolved (−)-amine. Crude chromatography on Florisil gave 1.07 g of a yellow-brown liquid shown by pmr to be IV with less than 5% *meso*-IV. This material was recrystallized three times from ether in a Dry-Ice–acetone bath to give yellow crystals: mp 61.2–61.8°; $[\alpha]_{546}$ 60.2° (*c* 0.86, CH_3OH); λ_{max}^{MeOH} 373 nm (ϵ_{max} 30); pmr as above. ORD showed a Cotton effect at 393 nm.

Anal. Calcd for $C_{22}H_{30}N_2$: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.62; H, 9.18; N, 8.46.

Thermolysis of V was investigated using a Perkin-Elmer DSC-1b calorimeter with a 2.9-mg sample of mixed diastereomers of V sealed in an aluminum volatile sample capsule. A scan from 107 to 257° at 10°/min showed an exotherm beginning near 185° and peaking at 217°.

Photolysis of mixed diastereomers of V was investigated with 30-mg samples degassed by freezing and thawing in benzene solution under vacuum and sealed in nmr tubes. One tube contained 2.8 mol of practical thiophenol per mol of V. The tubes were photolyzed in a 30–40° water bath by light from a 450-W Hanovia L lamp with Pyrex filter. After 80 min pmr showed complete disappearance of starting material in both samples. The pmr spectra were unchanged after another 75 min of photolysis. Both samples showed signals for II and VI, and there were no other appreciable peaks except for solvent and scavenger. In the unscavenged run the II/VI ratio was estimated at 1.1–1.2 on the basis of integration. For the scavenged run this ratio was 3.5–4 implying that 2.5/3.5–3/4 of II was the product of scavenging and that the cage effect was 40–45%.

(*S*)-**2-Methyl-3-phenylbutane** (**II**) **and** (*S*)-**2-methyl-3-phenyl-1-butene** (**VI**) were prepared from 400 mg of pure (*R,R*)-V in 4 ml of benzene, degassed, sealed, and irradiated for 3.5 hr at room temperature. The sample was opened and solvent was removed, and II and VI were bulb-to-bulb distilled under high vacuum. II and VI were separated by preparative vpc using $^3/_8$ in. × 8 ft 20% DEGS on Chromosorb P at 105°. Pmr (100 MHz, CCl_4): II, δ 7.25 (5 H, m, Ar H), 2.38 (1 H, p, *J* = 7.0 Hz, ArCH), 1.76 (1 H, octet, *J* = 7 Hz, $C\mathbf{H}(CH_3)_2$), 1.27 (3 H, d, *J* = 7 Hz, Ar $CHC\mathbf{H}_3$), 0.98 (3 H, d, *J* = 7 Hz, $CH(C\mathbf{H}_3)CH_3$), 0.78 (3 H, d, *J* = 7 Hz, $CH(CH_3)C\mathbf{H}_3$); VI, 7.20 (5 H, s, Ar H), 4.89 and 4.85 (2 H, d, $=CH_2$), 3.34 (1 H, q, *J* = 7 Hz, Ar CH), 1.56 (3 H, s, $CH_3C{=}$), 1.36 (3 H, d, *J* = 7 Hz, $ArCHC\mathbf{H}_3$). See Table I for rotations.

Registry No.—(*S*)-(−)-II, 19643-73-3; (*R*)-(−)-IV, 33686-47-4; *meso*-V, 33686-48-5; *rac*-V, 33686-49-6; (*R,R*)-(+)-V, 33686-50-9; (*S*)-(+)-VI, 25145-46-4.

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[17] For details of this preparation see J. M. McBride, Thesis, Harvard University, 1967. Subsequent preparations by this method have given higher yields of IV as a by-product as did preparation by another method.[10]

The α-Methyl/Hydrogen Reactivity Ratio for the *anti*-7-Norbornenyl and 7-Norbornadienyl Systems

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The very large α-Me/H solvolytic rate ratio for the 7-norbornyl system (4/1) has been attributed to the "enormous demand on substituents for further stabilization" of the unusually strained 7-norbornyl cation.[2,3]

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[1] (a) NIH Postdoctoral Fellow, 1966–1968; address inquiries to Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pa. 15213. (b) Fellow of the French Centre National de la Recherche Scientifique, on leave from the University of Strasbourg, 1967–1968. (c) Deceased, Nov 23, 1969.

[2] (a) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Amer. Chem. Soc.*, **89**, 2928 (1967); (b) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

[3] It has been noted[4] that "steric ground state strain . . . in tertiary tosylates would enhance α-Me/H rate ratios" with the implication that the **4**/**1** tosylate rate ratio may be an inflated value. Comparison of the **4**-Cl/**2**-Cl ratio with the corresponding tosylate ratio (Table II of this paper) would indicate the inflation to be worth *ca.* $10^{1.9}$. On the other hand, the tosylate ratio will be deflated to the extent that solvent nucleophilicity (k_s)

TABLE I

SOLVOLYTIC RATE CONSTANTS FOR SYSTEMS **1**–**6**[a]

Compd	Temp, °C	k, sec^{-1}
1-OTs	25.0	2.1×10^{-14} [b]
2-OTs	25.0	$(3.70 \pm 0.08) \times 10^{-4}$ [c]
2-Cl	25.0	$(8.1 \pm 0.2) \times 10^{-7}$ [d]
2-OPNB	125.0	$(2.84 \pm 0.16) \times 10^{-6}$
	100.0	$(2.05 \pm 0.10) \times 10^{-7}$
	25.0	(5.67×10^{-12}) [e]
3-Cl	25.0	$(1.45 \pm 0.10) \times 10^{-3}$ [f]
3-OPNB	100.0	$(3.93 \pm 0.13) \times 10^{-5}$
	75.0	$(3.26 \pm 0.05) \times 10^{-6}$
	25.0	(6.53×10^{-9}) [g]
4-OTs	25.0	3.36×10^{-6} [h]
4-Cl	125.0	$(7.02 \pm 0.10) \times 10^{-6}$
	100.0	$(7.36 \pm 0.20) \times 10^{-7}$
	25.0	(9.09×10^{-11}) [i]
5-Cl	50.0	$(2.37 \pm 0.04) \times 10^{-3}$
	25.0	$(1.93 \pm 0.03) \times 10^{-4}$ [j]
5-OPNB	100.0	$(2.68 \pm 0.08) \times 10^{-5}$
	75.0	$(1.86 \pm 0.02) \times 10^{-6}$
	25.0	(2.38×10^{-9}) [k]
6-OPNB	75.0	$(3.05 \pm 0.07) \times 10^{-4}$
	50.0	$(2.29 \pm 0.07) \times 10^{-5}$
	25.0	(1.12×10^{-6}) [l]

[a] Tosylates were solvolyzed in acetic acid. Chlorides were solvolyzed in 80% aqueous acetone. *p*-Nitrobenzoates were solvolyzed in 70% aqueous acetone. [b] Computed by extrapolating data of ref 2a for the corresponding brosylate and assuming a brosylate:tosylate ratio of 2.90. An earlier value of 6.36×10^{-15} [S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77,** 4183 (1955)] had been obtained from a longer temperature extrapolation than that of ref 2a. [c] S. Winstein and M. Shatavsky, *ibid.*, **78,** 592 (1956). [d] S. Winstein and C. Ordronneau, *ibid.*, **82,** 328 (1960). [e] Extrapolated. $\Delta H^{\ddagger} = 30.3 \pm 0.9$ kcal/mol; $\Delta S^{\ddagger} = -8.5 \pm 2.3$ eu. (In 50% acetone, $\Delta H^{\ddagger} = 28.2 \pm 0.8$ kcal/mol; $\Delta S^{\ddagger} = -10.2 \pm 2.2$ eu.) [f] This chloride exhibits common ion rate depression (see Experimental Section) and the (undepressed) value reported here is slightly higher than that previously reported in *d*. D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, **90,** 2561 (1968), report a value of $(1.33 \pm 0.1) \times 10^{-3}$, with $\Delta H^{\ddagger} = 15 \pm 1.5$ kcal/mol; $\Delta S^{\ddagger} = -22 \pm 4$ eu. A. F. Breaziale, Ph.D. Thesis, University of Washington, 1965, reports a value of 1.47×10^{-3}. [g] Extrapolated. $\Delta H^{\ddagger} = 25.0 \pm 0.4$ kcal/mol; $\Delta S^{\ddagger} = -12.2 \pm 1.1$ eu. [h] Extrapolated from data of ref 2a. [i] Extrapolated. $\Delta H^{\ddagger} = 25.9 \pm 0.4$ kcal/mol; $\Delta S^{\ddagger} = -17.7 \pm 1.0$ eu. [j] $\Delta H^{\ddagger} = 18.6 \pm 0.2$ kcal/mol; $\Delta S^{\ddagger} = -13.2 \pm 0.6$ eu. [k] Extrapolated. $\Delta H^{\ddagger} = 26.8 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -8.0 \pm 0.9$ eu. [l] Extrapolated. $\Delta H^{\ddagger} = 22.5 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -10.3 \pm 1.0$ eu.

We report here that similar comparisons for the corresponding *anti*-7-norbornenyl (**5**/**2**) and 7-norbornadienyl (**6**/**3**) systems show a marked attenuation in the demand for stabilization placed by the 7-methyl group.

Except for **6**, the derivatives studied in the present work were prepared from previously described alcohols. Ester **6**-OPNB was prepared from the corresponding quadricyclyl isomer, **7**-OPNB (not shown),[6] which was prepared, in turn, from the corresponding alcohol.[7]

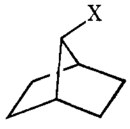
TABLE II

RELATIVE SOLVOLYTIC RATE CONSTANTS FOR **1**–**6** AT 25°[a]

System	OTs	Cl	OPNB
1-X	10^{0}		
2-X	$10^{10.3}$	$10^{4.0}$	10^{0}
3-X		$10^{7.2}$	$10^{3.1}$
4-X	$10^{8.2}$	10^{0}	
5-X		$10^{6.3}$	$10^{2.6}$
6-X			$10^{5.3}$

[a] See Table I, footnote *a*.

Kinetic measurements were made using standard titrimetric procedures, and the collected first-order solvolytic rate constants for **1**–**6** are given in Table I. Table II contains the relative rate comparisons which may be drawn from the data in Table I, tabulated according to leaving group.



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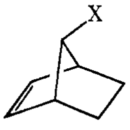

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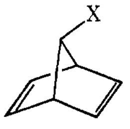

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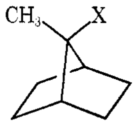

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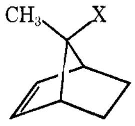

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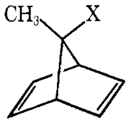

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It would be desirable to keep leaving group and solvent invariant through the entire series **1**–**6**, but the very wide range of reactivity involved presents serious experimental difficulties in that regard. For the particular purpose of comparing α-Me/H ratios from the data in Table II, the uncertainty incurred by variation of leaving group and solvent is not likely to be nearly as large as the gap between the **4**/**1** ratio and the other two α-Me/H ratios.[3] On this basis, it is concluded that there is a real and substantial attenuation of the α-Me/H ratio for the unsaturated systems relative to the saturated model, *i.e.*, from $10^{8.2}$ for 7-norbornyl to $10^{2.6}$ and $10^{2.2}$ for the monoenyl and dienyl OPNB's, respectively. This striking compression is a measure[4] of the diminished extent to which the methyl probe experiences charge in the solvolytic transition states for **2** and **3**, and it represents yet another manifestation of the delocalized nature of these transition states. Indeed, it is now well established that the high reactivities of **2** and **3** are due to π-electron participation which leads to quite stable, bridged carbonium ions.[8] The greater reactivity of **3** (and **6**) relative to **2** (and **5**) may be attributed to the "bicycloaromaticity"[9,10] of the 7-norbornadienyl cation, though strain effects may also play a contributing role.

It is of interest that the α-Me/H ratio diminished only slightly in going from the monoenyl to dienyl systems. The similar responses of **2** and **3** to α-methyl substitution may represent the onset of a "leveling"

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and σ participation[5] contribute selectively to the observed rate for **1**-OTs. We do not expect a quantitative clarification of these effects to significantly alter the present argument.

(4) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92,** 2540 (1970).

(5) (a) F. B. Miles, *ibid.*, **90,** 1265 (1968); (b) P. G. Gassman, J. M. Hornback, and J. L. Marshall, *ibid.*, **90,** 6238 (1968).

(6) Rate data for this compound in 70% acetone are $k_{100°} = (1.30 \pm 0.02) \times 10^{-4}$ sec^{-1}; $k_{75°} = (1.00 \pm 0.03) \times 10^{-5}$ sec^{-1}; $\Delta H^{\ddagger} = 25.8 \pm 0.4$ kcal/mol; $\Delta S^{\ddagger} = -7.7 \pm 1.0$ eu.

(7) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **94,** 2347 (1972).

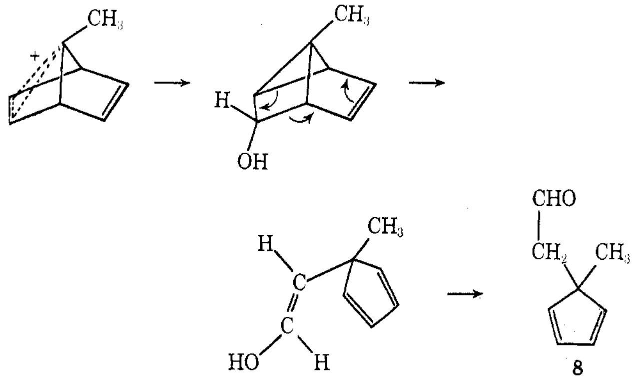
(8) S. Winstein, *Quart. Rev., Chem. Soc.*, **23,** 141 (1969).

(9) (a) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89,** 6357 (1967); (b) H. E. Zimmerman, *Accounts Chem. Res.*, **4,** 272 (1971).[10]

(10) Using the Mobius description for the 7-norbornadienyl cation, one notes that the unsymmetrically bridged ground state,[7,8] with attendant "tetrahedral" hybridization at C$_7$, serves to minimize the localized antibonding overlap between the rear of the vacant ("sp^3") lobe at C$_7$ and the unbridged vinyl function.

phenomenon[11] wherein the stabilization afforded the solvolytic transition states by bridging is sufficiently large that the additional stabilization afforded by methyl has become a minor and diminishing factor.

The only detectable products from buffered hydrolysis of **4**-Cl, **5**-Cl, and **5**-OPNB were the corresponding (unrearranged) alcohols. Ester **6**-OPNB gave a more interesting result. Three products were detected by glpc in a 1:1:6.3 ratio. One of the minor components was **6**-OH and the other was not identified. The major component proved to be an aldehyde which was isomeric with **6**-OH. Consideration of the spectral data (see Experimental Section) led to the assignment of structure **8** to this compound. The mechanism for conversion of the 7-methyl-7-norbornadienyl cation to **8** is formulated, as shown below, in terms of an endo-directed attack by water at C_2 followed by a retrograde Diels–Alder-like ring opening to give **8** or its enolate.



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This mechanism bears strict analogy to those postulated to explain the formation of tricyclic and cyclopentadienyl derivatives from the reaction of the 7-norbornenyl and 7-norbornadienyl cations with strong nucleophiles.[12] Rearrangement has not been observed, however, for the parent system (**3**–X) under neutral hydrolytic conditions. It may be that tertiary 7-norbornadienyl cations are less susceptible to capture of nucleophile at C_7 than is the secondary system. This circumstance could be a consequence of the bridged nature of these ions which results in the presentation of a nonplanar, relatively crowded face at C_7.[8]

Experimental Section

Melting points are uncorrected. Analyses were performed by Miss H. King. Nmr spectra were recorded on a Varian A-60 instrument for CCl_4 solutions unless noted otherwise. Shifts are referred to internal TMS at τ 10.00. Infrared spectra were recorded for CCl_4 solutions on a Perkin-Elmer Model 421 grating spectrometer.

***anti*-7-Norbornenyl *p*-Nitrobenzoate (2-OPNB)**.[13]—This ester was prepared routinely using *p*-nitrobenzoyl chloride in pyridine: mp 121.5–122.0°; nmr τ 1.84 (4, arom), 3.94 (2 H, vinyl), 5.45 (1 H, bridge), 7.09 (2 H, bridgehead), 8.14 (2 H, *exo*-ethano), 8.86 (2 H, *endo*-ethano).

Anal. Calcd for $C_{14}H_{13}O_4N$: C, 64.86; H, 5.05. Found: C, 65.00; H, 5.16.

7-Norbornadienyl *p*-Nitrobenzoate (3-OPNB).—This compound was described previously.[14]

7-Methyl-7-norbornyl Chloride (4-Cl).—7-Methyl-7-norbornanol (0.450 g, 3.5 mmol) was stirred vigorously with 120 ml of concentrated HCl solution for 35 hr at ambient temperature. The resulting mixture was extracted well with petroleum ether (bp 30–60°), and the combined organic extracts were washed with saturated $NaHCO_3$ solution, with water, and with a saturated NaCl solution and dried over anhydrous K_2CO_3. The solvent was removed by distillation through a Vigreux column leaving a semicrystalline residue which was purified by sublimation (25° at 2 Torr): yield 0.305 g (2.1 mmol, 60%); mp 96.0–97.5°; nmr τ 8.38 (s, methyl), 7.7–8.2 (m, *ca.* 5 H), 8.5–8.8 (m. *ca.* 5 H).

Anal. Calcd for $C_8H_{13}Cl$: C, 66.42; H, 9.06; Cl, 24.52. Found: C, 66.45; H, 9.13; Cl, 24.81.

Attempted preparation of **4**-Cl with $SOCl_2$ in ether gave the corresponding dialkyl sulfite: mp 80.0–81.5°; nmr τ 8.46 (s, methyl), 7.92, 8.65, 8.80 (10 H, broad absorptions).

Anal. Calcd for $C_{16}H_{26}SO_3$: C, 64.38; H, 8.78; S, 10.74. Found: C, 64.91; H, 8.69; S, 10.54.

7-Methyl-*anti*-7-norbornenyl *p*-Nitrobenzoate (5-OPNB).—This was prepared as described above for **2**-OPNB: mp 126.5–127.0°; nmr τ 1.87 (4 H, arom), 3.96 (2 H, vinyl), 6.92 (2 H, bridgehead), 8.44 (3 H, methyl), 8.25 (2 H, *exo*-ethano), 8.97 (2 H, *endo*-ethano).

Anal. Calcd for $C_{15}H_{15}O_4N$: C, 65.92; H, 5.53. Found: C, 66.08; H, 5.67.

7-Methyl-*anti*-7-norbornenyl Chloride (5-Cl).—Alcohol **5**-OH (0.485 g, 3.9 mmol) in 20 ml of anhydrous ether was treated with 0.6 ml of redistilled $SOCl_2$ at 0°. The solution was allowed to stand overnight at 5°, and the solvent was removed at reduced pressure without warming. The residue was taken up in 20 ml of petroleum ether and passed through a column of 5 g of $CaCO_3$. The solvent was removed at reduced pressure leaving 0.395 g (2.3 mmol, 72%) of transparent oil. Purification by sublimation (25° at 2 Torr) or preparative glpc on Carbowax 4000 yielded highly volatile material, mp 40–44°, which failed to give a correct analysis but which was adequate for rate measurements: nmr τ 4.00 (2 H, vinyl), 7.37 (2 H, bridgehead), 7.79 (2 H, *exo*-ethano), 8.41 (3 H, Me), 9.00 (2 H, *endo*-ethano); mass spectrum (70 eV) calcd for parent peak, 142; found, 142.

7-Methyl-7-quadricyclyl *p*-Nitrobenzoate (7).[6]—This was prepared routinely from the corresponding alcohol:[7] mp 147–148°; nmr ($CDCl_3$) τ 1.70 (4 H, arom), 8.05 (3 H, methyl), 8.18 (6 H, mult, cyclopropyl).

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; 4.83; N, 5.16. Found: C, 66.31; H, 4.75; N, 5.00.

7-Methyl-7-norbornadienyl *p*-Nitrobenzoate (6-OPNB).—To a mixture of 0.901 g of **7** in 0.4 ml of CH_2Cl_2 was added 5 mg of μ-dichlorotetraethylenedirhodium(I).[15] The mixture was agitated and monitored by nmr, using the methyl singlets. After 10 hr, conversion to **6**-OPNB was *ca.* 95% complete. A bit more catalyst was added, and the reaction mixture was agitated for 2 days whence none of **7** could be detected. The mixture was diluted with CH_2Cl_2 and filtered, and the product was precipitated by addition of petroleum ether. Crystallization from ether at −20° gave an analytical sample: mp 130.5–132.0°; nmr ($CDCl_3$) τ 1.88 (4 H, arom), 3.31 (2 H, vinyl), 3.40 (2 H, vinyl), 6.12 (2 H, bridgehead), 8.37 (3 H, methyl).

Anal. Calcd: same as **7**. Found: C, 66.32; H, 4.88; N, 4.81.

Kinetics.—All measurements were titrimetric and were done on *ca.* 0.01 *M* solutions. The standard sealed ampoule technique was used for the *p*-nitrobenzoates and for **5**-Cl. Liberated acid was titrated with NaOMe in MeOH using the *p*-bromothymol blue end point. This technique gave unsatisfactory results for **4**-Cl, and so each aliquot was treated using a standard Volhard chloride analysis (back titration of added $AgNO_3$ with KSCN standard solution to the $FeNH_4(SO_4)_2$ end point in the presence of nitrobenzene). The rate for dienyl chloride **3**-Cl was obtained by removing aliquots directly from the master solution which was submerged in the rate bath. In this case, the integrated rate constant was found to decrease with time. A measurement in the presence of added tetrabutylammonium chloride (0.035 *M*) confirmed that common ion rate depression(mass law effect) was being exhibited at the concentration used (0.01 *M*). The data were therefore treated according to the appropriate kinetic ex-

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[11] P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549, 2551 (1970).

[12] (a) P. R. Story, *ibid.*, **83**, 3347 (1961); (b) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); (c) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965); (d) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **88**, 864 (1966); (e) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).

[13] This compound was first prepared at UCLA by C. Ordronneau in 1959.

[14] Table I, footnote *d*.

[15] R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

pression,[16] and the true solvolytic rate constant was obtained by graphical analysis. This measurement represents a mild adjustment of a previously determined value which was not corrected for common ion rate depression.[17]

Product Studies. 5-OPNB.—A solution of 10 ml of 70% acetone, 0.5 mmol of **5**-OPNB, and 0.75 mmol of sodium acetate was placed in a sealed ampoule and maintained at 100° for 72 hr (*ca.* 10 half-lives). After cooling, the solution was diluted with petroleum ether and the resulting aqueous phase was saturated with NaCl and extracted with six 5-ml portions of petroleum ether. The combined petroleum ether layers were washed three times with saturated $NaHCO_3$ solution and twice with NaCl solution and dried over anhydrous K_2CO_3. The solution was concentrated to less than 10 ml by careful distillation through a Vigreux column and then brought to value in a 10-ml volumetric flask. An aliquot of this solution was combined with a known quantity of tridecane and analyzed by glpc (5% XF-1150 on Chromsorb W, 75°). A single peak with the same retention time as **5**-OH was detected. After correction for the relative detector response of the standard, the yield of **5**-OH was determined as 89%. The remainder of the solution in the volumetric flask was stripped of solvent leaving a residue whose nmr spectrum was identical with that of **5**-OH.

5-Cl.—An 80% acetone solution (10 ml) that was 0.03 *M* in **5**-Cl and 0.06 *M* in NaOAc was maintained at 25° for 5 hr (*ca.* 5 half-lives) and treated as described above for the PNB. Glpc and nmr analysis revealed only **5**-OH as the product.

4-Cl.—A solution was prepared as described above for **5**-Cl and was maintained at 125° for 90 hr (*ca.* 3.5 half-lives). After work-up as described above, glpc analysis on XF-1150 and Carbowax 4000 columns revealed the presence of **4**-OH, **4**-Cl, mesityl oxide and diacetone alcohol, identified by comparison with authentic materials.

6-OPNB.—A 70% acetone solution (10 ml), which was *ca.* 0.15 *M* in ester and 0.35 *M* in NaOAc, was maintained at 75° for 8.25 hr (*ca.* 12 half-lives). It was worked up as described above. Glpc analysis on 5% Carbowax 4000 operated at 80° indicated the presence of three products in the ratio 6.3:1.0:1.0, with relative retention times of 1.0:2.0:6.0, respectively. In a separate experiment, the absolute yield of the major product was shown to be *ca.* 59%. The peaks were isolated by preparative glpc and the final one proved to be **6**-OH by spectral comparison with authentic material. The other minor product showed *m/e* 122 for the parent ion in a low-resolution mass spectrum but was not further investigated. The major component was a liquid: ir (CCl_4) 1723 (aldehydic carbonyl), 2720 cm^{-1} (aldehydic CH); nmr τ 0.76 (1 H, J = 2.5 Hz, aldehydic H), 3.68 (4 H, broad s, olefinic H's), 7.56 (2 H, d, J = 2.5 Hz, CH_2), 8.79 (3 H, s, CH_3); high-resolution mass spectrum, calcd for $C_8H_{10}O$, 122.073161; found 122.07316. From these data, structure **8** was assigned to this material.

Registry No.—**1**-OTs, 16265-27-7; **2**-OTs, 13111-74-5; **2**-Cl, 1121-10-4; **2**-OPNB, 16558-31-9; **3**-Cl, 1609-39-8; **3**-OPNB, 33686-56-5; **4**-OTs, 33686-57-6; **4**-Cl, 33686-58-7; **4** disulfite, 33686-59-8; **5**-Cl, 33686-60-1; **5**-OPNB, 33686-61-2; **6**-OPNB, 33686-62-3; **7**, 33686-63-4; **8**, 33686-64-5.

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[16] S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, No. 19, 109 (1965); *cf.* eq 1 of this paper.

[17] Table I, footnote *f*.