Structural Effects in Solvolytic Reactions. 49. Steric Effects as a Major Factor in the Exo:Endo Rate Ratios for the Solvolysis of 2,7,7-Trimethyl- and 2,6,6-Trimethyl-2-norbornyl *p*-Nitrobenzoates

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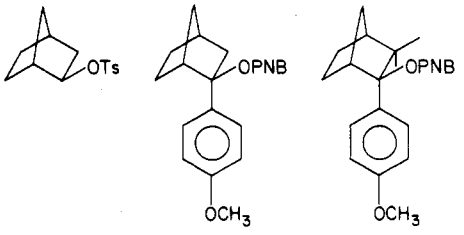
The exo:endo rate ratio for solvolysis, in 80% aqueous acetone at 25 °C, decreases from 885 for 2-methyl-2-norbornyl *p*-nitrobenzoate to 6.1 for 2,7,7-trimethyl-2-norbornyl *p*-nitrobenzoate. On the other hand, it increases remarkably to 3 630 000 in the case of 2,6,6-trimethyl-2-norbornyl *p*-nitrobenzoate. These changes are clearly attributable to steric effects caused by the syn methyl group at the 7- and 6-positions, respectively. In the 2,7,7-trimethyl-2-norbornyl system, the very low exo:endo rate ratio arises primarily from an increased rate of solvolysis of the endo isomer, attributed to relief in steric strain, involving the syn 7-methyl and exo 2-methyl groups, during ionization. The extremely large exo:endo rate ratio in the 2,6,6-trimethyl-2-norbornyl system is attributed to the high rate of solvolysis of the exo isomer, caused by the relief in steric strain involving the endo 2-methyl and endo 6-methyl groups, as well as an especially slow rate for the endo isomer, caused by enhanced steric retardation of ionization. Thus, these results show clearly that exo:endo rate ratios can be strongly affected by steric effects in the rigid norbornyl system.

Winstein proposed that the large exo:endo rate ratio observed in the acetolysis of 2-norbornyl tosylate (280) arises from nonclassical stabilization of the exo transition state by a σ-participation of the C_1–C_6 electron cloud[3] (eq 1). This proposal requires that such a nonclassical sta-

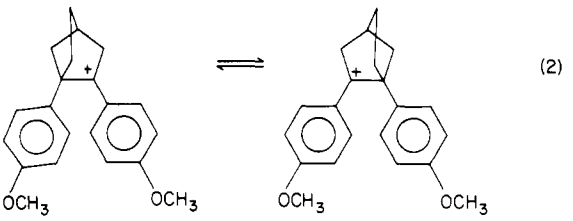
(1)

bilization must be 6.0 kcal mol^{-1}, as revealed by the Goering–Schewene diagram for the solvolysis (Figure 1). We were of the opinion that this proposal, however attractive it might be, required verification, and, therefore, set out to examine it in closer detail.[4] One approach to test this proposal was the study of the rates of solvolysis of tertiary 2-norbornyl substrates. Based on Winstein's proposal for the secondary system, one would expect the tertiary system (PNB = *p*-nitrobenzoate) to exhibit lower exo:endo rate ratios, since the nonclassical stabilization, if present, should be much less in the tertiary ions.[5] Simple experiments soon established that the exo:endo rate ratios, even in highly stabilized tertiary norbornyl derivatives, are comparable to that in the secondary norbornyl solvolysis.[6] Winstein initially maintained that "the older



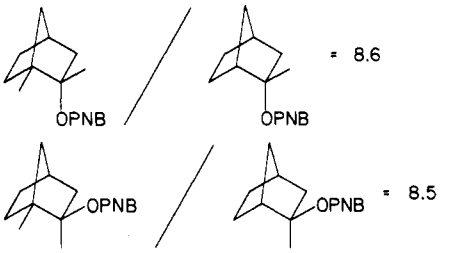
evidence for typical tertiary 2-norbornyl cations is in line with preferred bridged structures." However, a number of developments soon convinced nonclassical adherents that tertiary 2-norbornyl cations must be classical.

For example, Schleyer and his coworkers subjected the 1,2-di-*p*-anisyl-2-norbornyl cation to intensive study.[8] They concluded that their thermochemical, chemical reactivity, and UV and NMR spectral data support the existence of the ion as a rapidly equilibrating pair rather than as a resonance hybrid (eq 2).

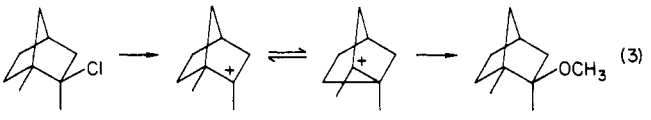


(2)

It appeared that a comparison of the rates of solvolysis of 2-methyl- and 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates should provide evidence for the presence of nonclassical resonance, if present. This should be much more important in the symmetrical species than in the unsymmetrical one. Moreover, it should be present in the exo derivatives but not in the endo. However, the experimental data did not confirm the presence of such nonclassical resonance.[5]



Then Goering and his coworkers solvolyzed optically active 1,2-dimethyl-*exo*-norbornyl chloride (1) and successfully captured up to 14% of the optically active methyl ether **2** (eq 3).[9]



(3)

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(1) Postdoctoral research associate on a grant (GP 6492X) supported by the National Science Foundation.

(2) National Science Foundation Cooperative Fellow, 1965–1967.

(3) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1952**, *74*, 1147, 1154.

(4) (a) Brown, H. C. (with comments by Schleyer, P. v. R.) "The Nonclassical Ion Problem"; Plenum Press: New York, 1977. (b) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432.

(5) Brown, H. C.; Ravindranathan, M.; Gundu Rao, C.; Chloupek, F. J.; Rei, M.-H. *J. Org. Chem.* **1978**, *43*, 3667 and references cited therein.

(6) Brown, H. C.; Takeuchi, K. *J. Am. Chem. Soc.* **1968**, *90*, 2691, 5268, 5270.

(7) Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 381.

(8) Schleyer, P. v. R.; Kleinfelter, D. C.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 479.

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Table I. Rates of Solvolysis of 2,7,7-Trimethyl- and 2,6,6-Trimethyl-2-norbornyl *p*-Nitrobenzoates and Related Derivatives

p-nitrobenzoate	mp, °C	$10^6 k_1$,[a] s^{-1} 25 °C	rel rate	rate ratio exo:endo
1-methylcyclopentyl[b]	82–83	2.11×10^{-3}	1.00	
2-methyl-*exo*-norbornyl[c]	114–115	1.00×10^{-2}	4.74	885
2-methyl-*endo*-norbornyl[d]	100–100.5	1.13×10^{-5}	0.00536	
2,7,7-trimethyl-*exo*-norbornyl[e]	95.5–96.5	4.01×10^{-2}	19.0	6.1
2,7,7-trimethyl-*endo*-norbornyl[f]	115.5–116.5	6.54×10^{-3}	3.1	
2,6,6-trimethyl-*exo*-norbornyl[g]	90.5–91.5	7.26[j]	3440	3 630 000
2,6,6-trimethyl-*endo*-norbornyl[h]	119.5–120.5	2.00×10^{-6}	0.000948	
2,3,3-trimethyl-*exo*-norbornyl[i]	105.5–106.0	1.04×10^{-1}	49.3	4500
2,3,3-trimethyl-*endo*-norbornyl[i]	144–145	2.31×10^{-5}	0.0109	

[a] Calculated from higher temperatures. [b] Brown, H. C.; Hammar, W. J. *J. Am. Chem. Soc.* **1967**, *89*, 6378. [c] $k_1^{75} = 6.94 \times 10^{-6}$ s^{-1}; $k_1^{100} = 94.6 \times 10^{-6}$ s^{-1}; $\Delta H^{\ddagger} = 26.3$ kcal mol^{-1}; $\Delta S^{\ddagger} = -7.0$ eu. [d] $k_1^{100} = 0.395 \times 10^{-6}$ s^{-1}; $k_1^{125} = 5.41 \times 10^{-6}$ s^{-1}; $\Delta H^{\ddagger} = 30.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -7.5$ eu. [e] $k_1^{75} = 17.6 \times 10^{-6}$ s^{-1}; $k_1^{100} = 212 \times 10^{-6}$ s^{-1}; $\Delta H^{\ddagger} = 24.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -10.2$ eu. [f] $k_1^{75} = 3.93 \times 10^{-6}$ s^{-1}; $k_1^{100} = 53.7 \times 10^{-6}$ s^{-1}; $\Delta H^{\ddagger} = 25.8$ kcal mol^{-1}; $\Delta S^{\ddagger} = -9.5$ eu. [g] $k_1^{50} = 163 \times 10^{-6}$ s^{-1}; $\Delta H^{\ddagger} = 23.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -4.1$ eu. [h] $k_1^{125} = 1.65 \times 10^{-6}$ s^{-1}; $k_1^{150} = 18.2 \times 10^{-6}$ s^{-1}; $\Delta H^{\ddagger} = 31.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -6.4$ eu. [i] From ref 12. [j] Rate constant measured at 25 °C.

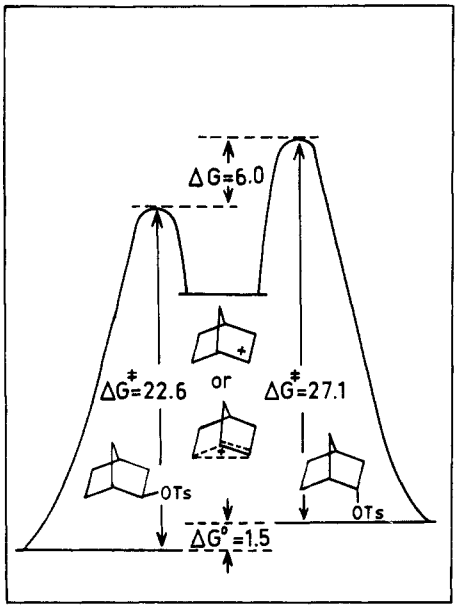
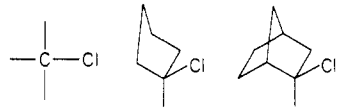


Figure 1. Goering–Schewene diagram for the acetolysis of *exo*- and *endo*-norbornyl tosylates at 25 °C (all numbers in kcal/mol).

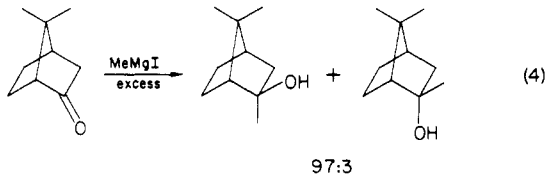
The solvolysis of simple tertiary chlorides is essentially a k_c process. Indeed, simple rate data revealed that there was no major stabilization present in 2-methyl-*exo*-norbornyl chloride not present in 1-methylcyclopentyl chloride.[10] $\Delta\Delta G^{\ddagger}$ for the first two members is 2.3 kcal/mol, for the last two, it is 1.0.



Since the tertiary 2-norbornyl cations are classical, the large exo:endo rate ratio must not arise from σ-bridging. We believed that steric effects might play a major role in this phenomenon. Consequently, we decided to test the possibility of (1) increasing the steric crowding in the exo face of 2-methyl-2-norbornyl *p*-nitrobenzoate, keeping the endo face unperturbed, and (ii) increasing the steric crowding in the endo face, keeping the exo face constant. In terms of our model, we anticipated an exo:endo rate ratio approaching one for the first perturbation and a major increase in the exo:endo rate ratio for the second. We examined the effects of such changes in steric effects by studying the rates of solvolysis of *exo*- and *endo*-2,7,7-trimethyl- and *exo*- and *endo*-2,6,6-trimethyl-2-norbornyl *p*-nitrobenzoates. We report the details of that study in this paper.[11]

Results and Discussion

Synthesis. Apocamphor, treated with a threefold excess of methyl magnesium iodide, gave an exo:endo alcohol mixture of 97:3, with 20% of recovered ketone. Retreatment of the crude product with MeMgI gave 95% of the tertiary alcohol (with the same exo:endo ratio as before) with 5% of residual ketone (eq 4). Purification by chromatography over alumina afforded pure 2,7,7-trimethyl-*exo*-norbornanol. The endo alcohol was obtained by the epoxidation of fenchene with *m*-chloroperbenzoic acid, followed by reduction of the epoxide with lithium in ethylenediamine; the exo:endo alcohols (16:84) were separated by recrystallization from *n*-pentane to afford pure 2,7,7-trimethyl-*endo*-norbornanol (eq 5).



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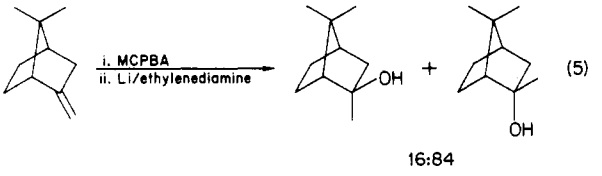

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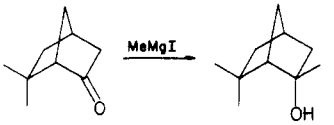
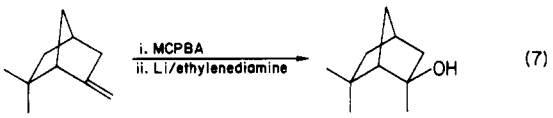
Addition of MeMgI to 6,6-dimethyl-2-norbornanone[12] yielded 2,6,6-trimethyl-*endo*-norboranol (eq 6). The corresponding exo alcohol was prepared as follows. 2-Methylene-6,6-dimethylnorbornane was prepared from 6,6-dimethylnorboranone by Witting olefination. Epoxidation, followed by Li/ethylenediamine reduction, yielded the exo alcohol (eq 7).



(6)

The alcohols were converted to their *p*-nitrobenzoates by standard procedures.

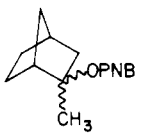
(9) (a) Goering, H. L.; Humski, K. *J. Am. Chem. Soc.* **1968**, *90*, 6213. (b) Goering, H. L.; Clevenger, J. V. *Ibid.* **1972**, *94*, 1010.
(10) Brown, H. C.; Chloupek, F. *J. Am. Chem. Soc.* **1963**, *85*, 2322.
(11) For preliminary communications, see: Brown, H. C.; Ikegami, S. *J. Am. Chem. Soc.* **1968**, *90*, 7122. Ikegami, S.; Vander Jagt, D. L.; Brown, H. C. *Ibid.* **1968**, *90*, 7124.
(12) Brown, H. C.; Chloupek, F. J.; Takeuchi, K. *J. Org. Chem.*, in press.



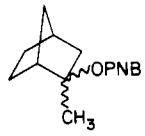
(7)

Rates of Solvolysis. The rates of solvolysis of *exo*- and *endo*-2,7,7-trimethyl- and *exo*- and *endo*-2,6,6-trimethyl-2-norbornyl-*p*-nitrobenzoates in 80% acetone at 25 °C are given in Table I. For the purpose of comparison, data for 1-methylcyclopentyl and *exo*- and *endo*-2,3,3-trimethyl-[12] and *exo*- and *endo*-2-methyl-2-norbornyl *p*-nitrobenzoates are also included.

Solvolysis of 2,7,7-Trimethyl-2-norbornyl *p*-Nitrobenzoates. The exo:endo rate ratio decreases from 885 for 2-methyl-2-norbornyl (**3**) to 6.1 for the 2,7,7-trimethyl-2-norbornyl system (**4**). This large decrease in the

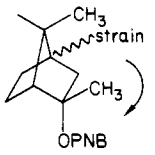


3a, *exo*-OPNB; *endo*-CH_3
3b, *exo*-CH_3; *endo*-OPNB
exo/endo 885



4a, *exo*-OPNB; *endo*-CH_3
4b, *exo*-CH_3; *endo*-OPNB
exo/endo 6.1

exo:endo rate ratio is clearly attributable to changes in the steric environment around the 2-position caused by the syn 7-methyl group. **4a** solvolyses moderately faster (×4) than the parent compound **3a**. This factor is comparable to that (×8.8) observed in the analogous secondary system.[13] Presumably, the relief in steric strain as a result of solvolysis slightly over-balances any steric retardation of ionization[14] caused by the syn 7-methyl group. The major contribution for the decreased exo:endo rate ratio for **4** comes, however, from the remarkably faster rate of solvolysis of the endo isomer **4b**. **4b** reacts 580 times faster than does the corresponding parent derivative **3b**. Obviously, the relief in steric strain accompanying the rotation of the exo methyl group away from the syn 7-methyl group during ionization is responsible for this rate increase (**5**),



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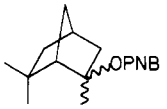
largely overcoming the usual rate-retarding effect of the U-shaped endo structure on the solvolysis of the endo isomer.

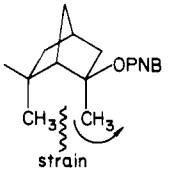
Solvolysis of 2,6,6-Trimethyl-2-norbornyl *p*-Nitrobenzoates. We were encouraged by the results in the 2,7,7-trimethyl-2-norbornyl system and hence studied the rates of solvolysis of *exo*- and *endo*-2,6,6-trimethyl-2-norbornyl *p*-nitrobenzoates (**6a** and **6b**). The exo:endo



6a, *exo*-OPNB, *endo*-CH_3
6b, *exo*-CH_3, *endo*-OPNB
exo/endo 3 630 000

rate ratio increases tremendously from 885 for **3** to 3 630 000 for **6**. The endo isomer **6b** reacts slower (1/5.65) than does the parent derivative **3b**. This is probably due to increased steric retardation of ionization[12] caused by the additional hindrance to ionization afforded by the endo 6-methyl group. The exo compound **6a** reacts much faster (×726) than does the model **3a**. Both of these factors contribute to the phenomenally large value, 3 630 000, for the exo:endo rate ratio.

We wished to ascertain whether the faster rate of **6a** (compared to that of **3a**) is better attributable to steric effects or to σ-participation. As discussed earlier, the evidence from a wide variety of sources is now overwhelming that tertiary norbornyl cations, such as 2-methylnorbornyl, are classical[5,15] (see introduction). Moreover, Schleyer and his coworkers have observed that 6,6-dimethyl-*exo*-2-norbornyl tosylate undergoes acetolysis at a rate considerably slower than does *exo*-2-norbornyl tosylate.[16] They concluded that 6,6-dimethyl substituents should, if anything, decrease the ability of C-6 to participate in the ionization stage. The relief in steric strain accompanying the rotation of the endo 2-methyl group away from the endo 6-methyl substituent must then be responsible for the enhanced rate of solvolysis of **6a**. A comparison of **4b** and **6a** will reveal that the 2-methyl group faces similar steric environments in both **4b** and **6a**. Both compounds undergo solvolysis much faster than do their models, **3b** and **3a**, respectively. If steric assistance to ionization is responsible in both cases, their rate enhancements over the models must be comparable. In fact, **4b**/**3b** is 580 and **6a**/**3a** is 726. Hence, it is certain that the faster rate of **6a** is due to steric assistance to ionization (**7**) rather than to σ-participation.



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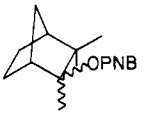
It is instructive to compare the behavior of 2,7,7-trimethyl and 2,6,6-trimethyl-2-norbornyl *p*-nitrobenzoates[12] with that of 2,3,3-trimethyl-2-norbornyl *p*-nitrobenzoates (**8a** and **8b**) (Table I). The exo:endo rate ratio for the last



8a, *exo*-OPNB, *endo*-CH_3
8b, *exo*-CH_3, *endo*-OPNB
exo/endo 4500

system (**8a**, **8b**) differs much less from that of the parent system, 2-methyl-2-norbornyl (**3a**, **3b**) than do the former two systems. This is more or less expected because one would not anticipate very large steric factors in **8a** and **8b** such as we encounter in **6a** or **4b**. The 3,3-dimethyl group appears to increase the rate of the exo isomer by a modest factor (**8a**/**3a** = 10.4), simply attributable to the inductive and steric effects of the 3,3-dimethyl substituent. In the endo isomer, the rate increase with respect to the model **3b** is somewhat less (**8b**/**3b** = 2.0). The small inductive and strain factor in this case may be largely offset by an additional hindrance caused by the endo 3-methyl group to the departing *p*-nitrobenzoate moiety.

(13) Colter, A.; Friedrich, E. C.; Holness, N. J.; Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 378.
(14) Brown, H. C.; Rothberg, I.; Schleyer, P. v. R.; Donaldson, M. M.; Harper, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *56*, 1653.
(15) Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* **1968**, *90*, 6216.
(16) Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375.

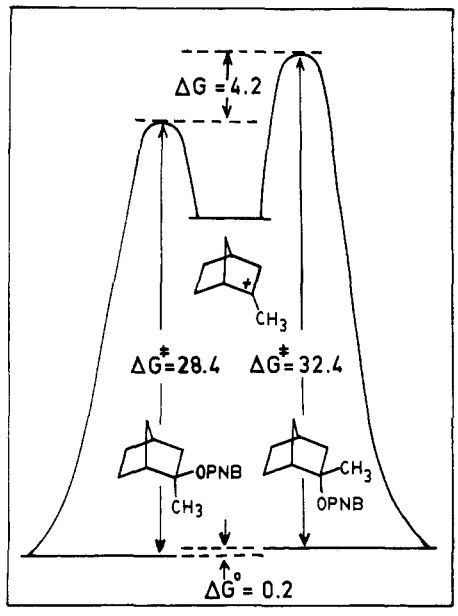


Figure 2. Goering–Schewene diagram for the solvolysis of 2-methyl-*exo*- and 2-methyl-*endo*-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C (all numbers in kcal/mol).

Table II. Products from the Solvolysis of 2,7,7-Trimethyl-2-norbornyl *p*-Nitrobenzoate in 80% Aqueous Acetone at 100 °C

		products,[a] %		
isomer	buffer	2-methylene-7,7-dimethylnorbornane	2,7,7-trimethylnorbornene	ROH[b]
exo	none	82	12	6[c]
exo	NaOAc	79	16	5[d]
endo	none	87	8	5[e]
endo	NaOAc	84	10	6[f]

[a] Normalized. [b] 2,7,7-Trimethyl-2-norbornanol. [c] Exo:endo, 92:8. [d] Exo:endo, 92:8. [e] Exo:endo, 87:13. [f] Exo:endo, 90:10.

Table III. Products from the Solvolysis of 2,6,6-Trimethyl-2-norbornyl *p*-Nitrobenzoates in 80% Acetone

		products, %		
isomer	base[c]	2-methylene-6,6-dimethylnorbornane	2,6,6-trimethylnorbornene	2,6,6-trimethyl-*exo*-2-norbornanol
exo[a]	NaOAc	58.3	31.7	10.0[d]
exo[a]	none	59.3	32.0	8.7[d]
endo[b]	NaOAc	82.0	18.0	~0
endo[b]	none	91.3	8.7	~0

[a] Solvolyzed at 50 °C. [b] Solvolyzed at 150 °C. [c] Equimolar amount of base was employed. [d] More than 99.9% pure exo alcohol.

Products. The solvolysis of the 2,7,7-trimethyl-2-norbornyl *p*-nitrobenzoates gave the same products in almost the same ratios in 95–98% yields, resulting in 95% olefins and 5% alcohols (Table II). In the case of 2,6,6-trimethyl-*exo*-norbornyl *p*-nitrobenzoate, 58% 2-methylene-6,6-dimethylnorbornane, 32% 2,6,6-trimethylnorbornene, and 10% exo alcohol were found (Table III) for a solvolysis at 50 °C. For the endo isomer, for a solvolysis at 150 °C, 82% 2-methylene-6,6-dimethylnorbornane and 18% 2,6,6-trimethylnorbornene were formed.

Goering–Schewene Diagram. The Goering–Schewene diagrams for 2-methyl, 2,7,7-trimethyl, and 2,6,6-trimethyl norbornyl systems are given in Figures 2, 3, and 4, respectively. By equilibration in cyclohexane–2 M H_2SO_4,[17] the ground-state stability of 2,7,7-trimethyl-*exo*-2-norboranol was found to be 0.5 kcal/mol more than that of the endo isomer. On the assumption that the steric requirements of OH and OCOR are similar, the ground-state free energy difference for **4a** and **4b** was taken as 0.5 kcal mol^{-1} (Figure 3). We could not establish equilibrium between the exo and endo isomers of 2,6,6-trimethyl-2-norbornanol due to rapid dehydration of the alcohols. However, we have consistently observed that methyl and hydroxyl (or acyloxy) apparently have similar steric requirements.[17] On that basis we have constructed the Goering–Schewene diagram for the 2,6,6-trimethyl-2-norbornyl system.

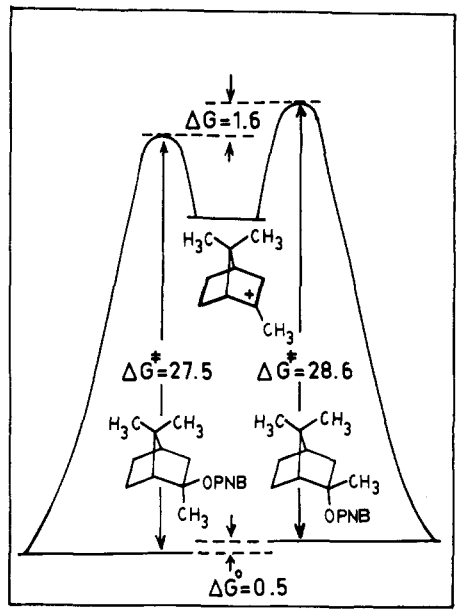


Figure 3. Goering–Schewene diagram for the solvolysis of 2,7,7-trimethyl-*exo*- and 2,7,7-trimethyl-*endo*-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C (all numbers in kcal/mol).

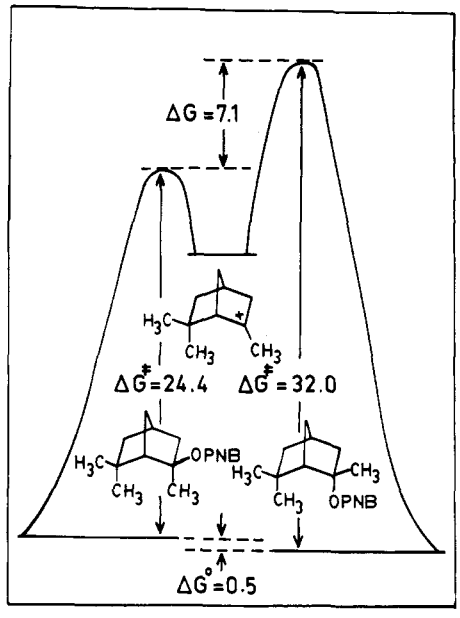
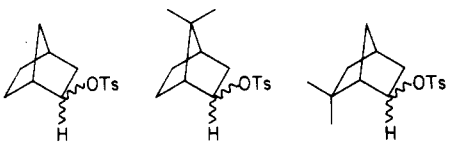


Figure 4. Goering–Schewene diagram for the solvolysis of 2,6,6-trimethyl-*exo*- and 2,6,6-trimethyl-*endo*-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C (all numbers in kcal/mol).

(17) Rei, M.-H.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 5335.

A comparison of these three diagrams will reveal major changes in the $\Delta\Delta G^{\ddagger}$ of the exo and endo isomers. Thus, from 4.2 kcal mol^{-1} for 2-methyl-2-norbornyl, it drops to 1.6 kcal mol^{-1} for 2,7,7-trimethyl and increases to 7.1 kcal mol^{-1} for the 2,6,6-trimethylnorbornyl system. There is a natural reluctance to attribute such large differences in $\Delta\Delta G^{\ddagger}$ to steric effects since steric effects in acyclic and monocyclic systems are normally relatively small,[18] unless exceedingly bulky tertiary groups are introduced.[19] However, in the present case, we are dealing with a rigid, conformationally immobile bicyclic skeleton, which cannot provide a cushion to relieve steric strains[20] as is easily possible with the more flexible acyclic and monocyclic systems.

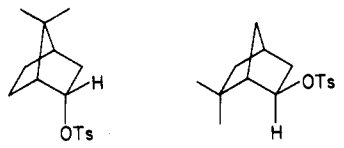
Exo:Endo Rate Ratio in the Solvolysis of 7,7-Dimethyl- and 6,6-Dimethyl-2-norbornyl Tosylates. Analogous to the present study in the tertiary system, Schleyer and co-workers[16] and Winstein and co-workers[13] have compared the exo:endo rate ratio for the acetolysis of 2-norbornyl tosylate with that for 7,7-dimethyl- and 6,6-dimethyl-2-norbornyl tosylates (**9** and **10**). Obviously,



	9	10	11
rel rate	280	4100	206

the results for the secondary systems **10** and **11** are far different from those for the tertiary systems, **4** and **6**. No major changes in the exo:endo rate ratios are observed in the secondary system as we increase the steric congestion around the exo and endo faces, respectively.

The major contribution for the low exo:endo rate ratio in the case of 2,7,7-trimethyl-2-norbornyl *p*-nitrobenzoate comes from the relief of syn CH_3–CH_3 repulsive interactions in the endo isomer **5**. Similarly, the relief of an analogous strain in the exo isomer **6a** is largely responsible



12 **13**

for the large exo:endo rate ratio of **6** (**7**). In the secondary systems, only the CH_3–H interaction, presumably much smaller in magnitude, is involved (12, 13) (compare **5** with **12** and **7** with **13**).

A number of workers have attempted to resolve such differences between secondary and tertiary 2-norbornyl cations by proposing that the secondary derivatives are nonclassically stabilized by 6.0 kcal mol^{-1} in the transition state for the solvolysis (Figure 1) and a somewhat larger factor for the free ion, **4b**, whereas the tertiary ions are classical. On this basis, the exo:endo rate ratio in 2-norbornyl is attributed to σ-participation in the exo isomer and the comparable exo:endo rate ratio in 2-methyl-2-norbornyl is attributed to steric retardation of the solvolysis of the endo isomer.[4a] It should be pointed out that one worker in the field, T. W. Bentley, has argued for a compromise solution, with half of the exo:endo rate ratio in 2-norbornyl arising from σ-participation in the exo derivative and half arising from steric retardation of the endo.[21]

It appeared that a more decisive solution of the primary question in the nonclassical controversy, namely, the factor responsible for the large exo:endo rate ratio in the solvolysis of secondary 2-norbornyl tosylate (**9**) would be provided by a direct search for the nonclassical stabilization energy. Consequently, we focused our efforts on an examination of the available thermochemical data for the solvolysis of norbornyl and related derivatives and the calorimetric heats of ionization under stable ion conditions.[22] The results of that study will be described in a forthcoming paper that will bring our efforts in this area to a close.

Experimental Section

All melting points are uncorrected. The ^{1}H NMR spectra were recorded on a Varian A60A or T-60 spectrophotometer. Analytical data within accepted precision were obtained for all new compounds.

Apocamphor. Apocamphor was prepared from 7,7-dimethoxynorbornene by a reported procedures. 7,7-Dimethylnorbornene,[23] on oxymercuration–demercuration,[24] gave apoisoborneol, oxidized by chromic acid[25] to apocamphor.

2,7,7-Trimethyl-*exo*-2-norbornanol. To a MeMgI solution prepared from 0.12 mol of CH_3I (17.04 g) and 0.12 mol of Mg metal (2.92 g) in anhydrous diethyl ether (EE, 110 mL) was added a solution of apocamphor in EE (5.53 g in 10 mL) at room temperature in an N_2 atmosphere. The reaction mixture was worked up as usual after being stirred for 115 h. GC analysis on a 10% quadrol column showed that 19.5% of apocamphor remained unchanged. Retreatment of the product mixture with excess MeMgI prepared from 15.9 g of MeI (0.112 mol) and 2.7 g of Mg in EE (100 mL) for 60 h led to a product containing only 5% of the unreacted ketone. Column chromatography over alumina led to pure 2,7,7-trimethyl-*exo*-2-norbornanol,[26] mp 41.5–42.5 °C, in 66.3% yield.

2,7,7-Trimethyl-*exo*-2-norbornyl *p*-Nitrobenzoate. To a solution of the above alcohol (20 mmol, 3.08 g) in THF (30 mL) at −30 to −40 °C was added *n*-BuLi in hexane (20 mmol).[27] After being stirred for 30 min, a solution of *p*-nitrobenzoyl chloride (20 mmol) in THF (20 mL) was added to it. The solution became dark brown. After 1 h, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. After stripping off the solvents, 6.0 g of orange substrate was obtained. Recrystallization from EtOH–hexane (1:1) gave 4.0 g of pale yellow crystals, mp 95.5–96.5 °C.

2,7,7-Trimethyl-*endo*-2-norbornanol. To a stirred solution of *m*-chloroperbenzoic acid (5.88 g, 24.3 mmol of a 70% pure sample) in CH_2Cl_2 (50 mL) was added a solution of α-fenchene in CH_2Cl_2 (25 mL) at 10 °C, and the mixture was stirred for 3 h at 10–20 °C. After being cooled with ice–water, the mixture was washed with 10% Na_2CO_3 solution and the organic layer was dried and evaporated to give 3.9 g of a pale yellow oil. The epoxide (3.9 g) was dissolved in ethylenediamine (25 mL) and small pieces of Li metal (0.507 g) were added in a nitrogen atmosphere.[28] The mixture was stirred (1 h) at 50 °C. The color at the end of the reaction was purple. The mixture was treated with ice–water (25 mL) under cooling and the product was extracted with ether (50

(18) Brown, H. C.; Fletcher, R. S. *J. Am. Chem. Soc.* **1949**, *71*, 1845.
(19) Bartlett, P. D.; Stiles, M. *J. Am. Chem. Soc.* **1955**, *77*, 2806.
(20) Brown, H. C.; Muzzio, J. *J. Am. Chem. Soc.* **1968**, *90*, 7124.
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(22) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5402, 5408.
(23) Brown, H. C.; Kawakami, J. H.; Misumi, S. *J. Org. Chem.* **1970**, *35*, 1360.
(24) Brown, H. C.; Kawakami, J. H.; Ikegami, S. *J. Am. Chem. Soc.* **1967**, *89*, 1525.
(25) Brown, H. C.; Garg, C. P.; Liu, K.-T. *J. Org. Chem.* **1971**, *36*, 387.
(26) Hückel and Volkmann Hückel, W.; Volkmann, D. *Liebigs Ann. Chem.* **1963**, *664*, 31 originally assigned the opposite configuration to the predominant alcohol produced in this reaction. However, the validity of the present assignment is established without possible ambiguity by the ^{1}H NMR spectra of the exo and endo alcohols (see Table IV).
(27) Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 1927.
(28) Brown, H. C.; Ikegami, S.; Kawakami, J. H. *J. Org. Chem.* **1970**, *35*, 3243.

Table IV. ^{1}H NMR Spectra of 2,7,7-Trimethyl- and 2,6,6-Trimethyl-2-norbornyl Derivatives[a]

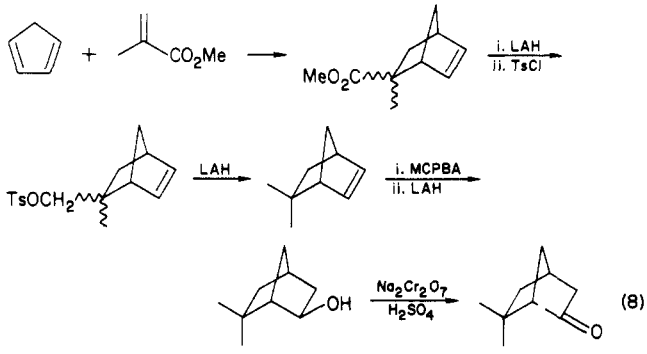
compd	solvent	2-Me	7-*anti*-Me	7-*syn*-Me	C_1-H	C_2-H	OH	OPNB
2,7,7-Trimethyl-2-norbornyl Derivatives								
exo-OH	CCl_4	1.32	0.99	1.28			1.67	
endo-OH	CCl_4	1.42	1.02	1.12			1.73	
exo-OPNB	CCl_4	1.78	1.10	1.22				8.11 (d),[b] 8.29 (d)[b] (J = 9 Hz)
endo-OPNB	CCl_4	1.67	1.06	1.17				8.08 (d),[b] 8.28 (d)[b] (J = 9 Hz)
compd	solvent	2-Me	6-*exo*-Me	6-*endo*-Me	C_1-H	C_4-H	OH	OPNB
2,6,6-Trimethyl-2-norbornyl Derivatives								
exo-OH	CCl_4	1.44	1.03	1.12			1.59	
endo-OH	CCl_4	1.30 or 1.32	1.00	1.32 or 1.30			1.20	
exo-OPNB	CCl_4	1.85	1.12	1.23	2.50 (b)[b]	2.25 (b)[b]		8.05 (d),[b] 8.22 (d)[b] (J = 9 Hz)
endo-OPNB	CCl_4	1.66	1.06	1.15	2.40 (b)[b]	2.23 (b)[b]		8.12 (d),[b] 8.28 (d)[b] (J = 9 Hz)

[a] ppm from Me_4Si as internal standard. [b] b = broad peak; = doublet.

mL). The ether extract was washed with saturated NaCl solution and dried, and the ether was removed to leave 3.0 g of a pale brown oil, which solidified by scratch. On recrystallization from *n*-pentane, 1.2 g of white needles, mp 103.5–104.5 °C was obtained.

2,7,7-Trimethyl-*endo*-2-norbornyl *p*-Nitrobenzoate. This was prepared in 53% yield by the same procedures used for the exo alcohol.[27]

6,6-Dimethyl-2-norbornanone. This was prepared by a circuitous procedure as outlined in eq 8.



(8)

Methyl 2-Methyl-5-norbornene-2-carboxylate. Diels–Alder reaction of cyclopentadiene with methyl methacrylate by a known procedure[29] afforded this product in 70% purity. The rest was dicyclopentadiene.

2-Methyl-5-norbornene-2-methanol. $LiAlH_4$ reduction of the above ester was carried out by reported procedure[30] to yield this compound in 66% purity (GC).

5,5-Dimethylnorbornene. The tosylate of the above alcohol (152 g) was reduced with $LiAlH_4$ in ether (0.52 mol) at reflux for 70 h. After workup, the crude product was fractionated by a spinning band column. The fraction coming out at 77–79 °C (33.5 g) was 99% pure olefin.

6,6-Dimethyl-*exo*-2-norbornanol. Oxidation of 5,5-dimethylnorbornene with *m*-chloroperbenzoic acid, as mentioned earlier, gave the epoxide (GC pure), which was reduced with $LiAlH_4$ in diglyme. To a stirred solution of $LiAlH_4$ (11.6 g) in diglyme (180 mL) was added 36 g of the epoxide. The mixture was stirred at 100 °C for 2 days. After cooling, NaOH (1 N, 36 mL) was added carefully and the mixture was stirred at room temperature for 3 h. The residue was removed by filtration and was washed with petroleum ether (500 mL). The organic layer (filtrate and washings) was washed with water liberally. Removal of solvents from the organic layer gave 29.2 g of a 97% pure material of 6,6-dimethyl-*exo*-2-norboranol.

6,6-Dimethyl-2-norboranone. Oxidation of the above alcohol (28.0 g) in ether with $Na_2Cr_2O_7$ (100 g) and H_2SO_4 (136 g in 500 mL H_2O) at ~0 °C followed by conventional workup gave 20 g of a crude product. Distillation under reduced pressure afforded a pure sample of 6,6-dimethyl-2-norbornanone whose IR spectrum was superimposable with that of an authentic sample supplied by Professor Schleyer.

(29) Petrow, A. A.; Sapov, N. P. *J. Gen. Chem.* **1948**, *18*, 1781.
(30) Berson, J. A.; Walia, J. S. Remanick, A.; Suzuki, S.; Warnhoff, P. R.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3986.

2-Methylene-6,6-dimethylnorbornane. This was prepared by the Wittig olefination of 6,6-dimethyl-2-norbornanone. To a solution of methyltriphenylphosphonium bromide (18.6 g, 52 mmol) in THF (50 mL) in a 300-mL three-necked flask equipped with a reflux condenser and mechanical stirrer was added slowly *n*-BuLi (15% solution in hexane, 34 mL, 52 mmol) in a nitrogen atmosphere with occasional cooling with ice–water. After stirring for 1.5 h, a solution of 6,6-dimethyl-2-norbornanone (5.53 g, 40 mmol) in THF (50 mL) was added dropwise with stirring and the reaction mixture was refluxed for 20 h. Water (1.0 mL) was added to the cooled reaction mixture. After being stirred for 1 h, the mixture was filtered and the residue was washed with ether. The washings were combined with the filtrate and dried over $MgSO_4$. Removal of the solvents followed by distillation gave 2-methylene-6,6-dimethylnorbornane in 76% yield and 98% purity (GC): bp 93.5–94.0 °C (118 torr); n^{20}_D 1.4667. ^{1}H NMR spectrum showed two CH_2 at δ 4.61 (d) and 4.75 (d) and the *gem*-dimethyl group at δ 0.91 and 0.98. Satisfactory elementary analysis could not be obtained due to the volatile characteristics of the compound.

2,6,6-Trimethyl-*exo*-2-norbornanol. This was prepared by the epoxidation and reduction of 2-methylene-6,6-dimethylnorbornane. The olefin (10 mmol) was oxidized with *m*-chloroperbenzoic acid as described earlier to get 1.4 g of a product which was 91% pure by GC. The crude epoxide was reduced with Li/ethylenediamine[24] again as described earlier in this paper. The crude product (1.1 g) contained 85.5% exo alcohol. It was purified by preparative GC on a Carbowax 20M column to yield 0.4 g of pure sample.

2,7,7-Trimethyl-*exo*-2-norbornyl *p*-Nitrobenzoate. The ester was prepared by the usual procedure of treating the lithium salt of the alcohol with *p*-$NO_2C_6H_4COCl$ but for the fact that the reaction mixture was stirred overnight at room temperature. The crude product was purified by chromatography over alumina to yield pale yellow crystals which were recrystallized from *n*-pentane to yield the pure exo ester, mp 90.5–91.5 °C.

2,6,6-Trimethyl-*endo*-2-norbornanol. The reaction of 6,6-dimethyl-2-norbornanone with MeMgI (25% excess) afforded this alcohol in 74% yield after recrystallization of the crude product. The sample was 99% pure by GC analysis, mp 81.5–82.0 °C.

2,6,6-Trimethyl-*endo*-2-norbornyl *p*-Nitrobenzoate. Esterification with *p*-$NO_2C_6H_4COCl$ by the usual procedure afforded this ester which was purified by two successive recrystallizations from *n*-hexane. The yield of the pure ester was 64%, mp 119.5–120.5 °C.

The ^{1}H NMR spectra for the 2,7,7-trimethyl- and 2,6,6-trimethyl-2-norbornanols and their *p*-nitrobenzoates are given in Table IV.

Product Study. The conditions and the products obtained in the solvolyses are given in Tables II and III. The general procedure employed was to solvolyze the given *p*-nitrobenzoate in a sealed ampule. After sufficient time, the ampule was opened and anhydrous K_2CO_3 was added to separate the organic and aqueous layers. The organic layer, after drying, was subjected to GC analysis. The results are provided in Tables II and III.

Equilibration of 2,7,7-Trimethyl-2-norbornanols. To a solution of 61.7 mg (0.4 mmol) of the endo alcohol in cyclohexane (2.0 mL) containing tridecane (0.2 mmol) as an internal standard

was added 2.0 mL of 2.0 M H_2SO_4.[17] The mixture was vigorously stirred and a small aliquot of the organic layer was subjected to GC analysis. Equilibrium was reached after 700 min and the equilibrium mixture consisted of 2,7,7-trimethylnorbornene, (3.0%) α-fenchene (81.5%), 2,7,7-trimethyl-*exo*-2-norbornanol (10.7%), and the endo alcohol (4.8%). The exo alcohol could not be studied in this fashion due to rapid dehydration. However, the equilibration of a mixture of 40.0 mg of the exo alcohol and 21.7 mg of the endo alcohol by the same procedure led to an equilibrium mixture of 2,7,7-trimethylnorbornene (2.1%), α-fenchene (61.8%), the exo alcohol (26.4%), and the endo alcohol (9.7%).

Kinetics Measurements. The rates of solvolysis of the *p*-nitrobenzoates in 80% acetone were determined by the titrimetric method.[27] The sealed ampule technique was employed for measuring the rates at higher temperatures. The data are summarized in Table I.

Acknowledgment. We are deeply indebted to Professor Paul von R. Schleyer for relinquishing his own plans for a closely related problem. He generously supplied us with a sample of 6,6-dimethyl-2-norboranone, which facilitated the initial experiments. We also thank the National Science Foundation (Grant GP 6492X) for their financial support.

Solvomercuration-Demercuration. 12. The Solvomercuration-Demercuration of Olefins in Alcohol Solvents with Mercuric Trifluoroacetate—An Ether Synthesis of Wide Generality

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Studies on the solvomercuration–demercuration (SM–DM) of olefins in methyl, ethyl, isopropyl, and *tert*-butyl alcohols with mercuric trifluoroacetate have been extended. 1-Dodecene undergoes the SM–DM sequence with typical results for a monosubstituted olefin. Cyclopentene similarly exhibited behavior characteristic of a 1,2-disubstituted olefin in methanol, ethanol, and 2-propanol, giving high yields, >90% of the corresponding ethers. However, in *tert*-butyl alcohol, the yields of ether were lower than normal and decreased somewhat with time. 2-Methyl-1-butene gives >90% yields of the Markovnikov methyl ether. On the other hand, the yields of ethyl, isopropyl, and *tert*-butyl ethers are lower and decrease with time. Major improvements in yields, however, are possible by lowering the reaction temperature from room temperature to 0 °C. Cyclooctene, surprisingly, behaves more like a tri-, tetra-, or isosubstituted olefin than a 1,2-disubstituted olefin. The yields of cyclooctyl methyl ether are >90% and do not decrease with time. However, yields of the ethyl, isopropyl, and *tert*-butyl ethers are lower and drop with time. Again, lowering the reaction temperature from room temperature to 0 °C markedly improves the yields of the cyclooctyl ethers. These results, coupled with those of a previous study, clearly reveal the exceptional superiority of mercuric trifluoroacetate for the SM–DM of olefins in alcohol solvents.

The results of the previous paper[1] revealed mercuric trifluoroacetate to be a remarkably effective reagent for the etherification of olefins using the solvomercuration–demercuration (SM–DM) sequence in alcohols. Consequently, we felt it desirable to expand on the SM–DM of olefins with this mercuric salt.[2] 1-Dodecene, cyclopentene, 2-methyl-1-butene, and cyclooctene were chosen for examination. We also examined scaling up representative reactions to a preparative scale.

Results and Discussion

1-Dodecene is converted in near quantitative yield to the corresponding methyl, ethyl, and isopropyl Markovnikov ethers. Trace amounts of 2-dodecanol accompany the formation of the isopropyl ether. The *tert*-butyl ethers are synthesized in somewhat lower but nevertheless good yields.

The results are essentially identical with those of 1-hexene. However, one important difference was noted. Initially, in methanol, low and irreproducable yields of the 2° ether (ca. 75–85%) were obtained. An investigation revealed the problem to be in the demercuration step. Apparently the oxymercurials produced from 1-dodecene are somewhat insoluble in the reaction media following the addition of aqueous sodium hydroxide (see Experimental Section). By rapidly stirring the reactions for ca. 2 min

Table I. Solvomercuration–Demercuration of 1-Dodecene[a]

ROH	R	time, min	% products[b] n-$C_{10}H_{21}$CH(OR)CH_3	% products[b] n-$C_{10}H_{21}$CH(OH)CH_3
methanol	Me	5, 60	91	0
ethanol	Et	5, 60	94	0
2-propanol	*i*-Pr	5, 60	100	trace
2-methyl-2-propanol	*t*-Bu	5	76	21
		80, 180	87	10

[a] Reaction at room temperature, 22–23 °C. [b] Quantitative VPC analysis.

Table II. Solvomercuration–Demercuration of Cyclopentene[a]

ROH	R	time, min	% products[b] 	% products[b] 
methanol	Me	5, 60	94	0
ethanol	Et	5, 60	93	0
2-propanol	*i*-Pr	5, 60	100	trace
2-methyl-2-propanol[d]	*t*-Bu	5	79	*c*
		60	72	*c*
		165	67	*c*

[a] Reaction at room temperature, 22–23 °C. [b] Quantitative VPC analysis. [c] Cyclopentanol present but not analyzed quantitatively as it was partially lost during workup. [d] Trace amounts of one other product.

(1) Brown, H. C.; Kurek, J. T.; Rei, M-H.; Thompson, K. L. *J. Org. Chem.* **1984**, *49*, 2551.

(2) A preliminary communication was published earlier: Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* **1969**, *91*, 5646.

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