electrophilic reagents were selected because of the high configurational stability of the diastereomers of **3**, **3a** and **3b**, and the presence of diastereotopic CH_3 groups (τ 8.05, 7.82).

1 (four parts) enriched in **1a** or **1b** was treated with a deficiency of the cleaving reagent (one part), solvent was removed, and the resultant mixture was chromatographed on alumina to separate unreacted **1** and **3**. Representative results of these experiments are shown in Table I. The following points deserve emphasis.

Table I. Ratios of Diastereomers and Per Cent Stereoselectivity for the Cleavage Reactions of **1**

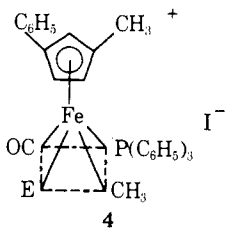
Cleaving reagent	Starting **1a**/**1b**	Recovered **1a**/**1b** (% stereoselectivity)	Isolated **3a**/**3b** (% stereoselectivity)
HI	90:10	73:27 (58)	53:47 (8)
	14:86	27:73 (64)	33:67 (47)
I_2	100:0	90:10 (80)	69:31 (38)
	8:92	20:80 (71)	22:78 (67)
HgI_2	100:0	85:15 (70)	50:50 (0)
	8:92	17:83 (79)	34:66 (38)

In all cases, the recovered **1** has undergone partial epimerization, which is highest for the reaction with HI. In a given cleavage process, the extent of epimerization of **1a** did not greatly differ from that of **1b**. By contrast, the formation of **3** always occurred with greater stereospecificity for **1b** than for **1a**; as a function of the cleaving reagent, the degree of stereospecificity followed the order $I_2 > HI \gtrsim HgI_2$. **1a** and **1b** are configurationally stable under the above reaction conditions and during work-up in the presence or absence of **3**; **3a** and **3b** were shown not to epimerize in the presence of HI, I_2, HgI_2, or CH_3HgI.

The observed epimerization of **1** may be readily accommodated by the reaction scheme

$$\mathbf{1} + EI \rightleftharpoons \text{intermediate} \longrightarrow \mathbf{3} + CH_3E$$

where E = H, I, or HgI. A reasonable intermediate is that derived by oxidative addition of E^+ to **1**. Such an iron(IV) species, analogous to the known h^5-$C_5H_5Fe(CO)(SiCl_3)_2H$,[12] would likely adopt a square pyramidal structure, **4** (or another isomer thereof). From the



4

known fluxional behavior of structurally related complexes of molybdenum(II) of the type h^5-$C_5H_5Mo(CO)_2LX$[13] and h^5-$C_5H_5Mo(CO)L_2X$,[14] one might expect **4** also to exhibit stereochemical nonrigidity. This would give rise to rapid configurational changes at iron, with **4** having E = H likely epimerizing at the fastest rate, as for h^5-$C_5H_5Mo(CO)_2LX$ when X = H.[13]

Factors which give rise to the preferential formation of **3b** over **3a** are not completely clear at present, although molecular models suggest that one isomer may be sterically less hindered than the other. The higher degree of stereospecificity at iron for the cleavage with I_2 than with HI or HgI_2 may be related to differences in the mechanism of conversion of various **4** to **3**. These differences are suggested by the reported stereochemical changes at α carbon which accompany such reactions.[1-4] When E = H or HgI, **3** likely arises *via* reductive elimination of CH_4 and CH_3HgI, respectively, and coordination of ionic iodide. However, when E = I, nucleophilic attack of external I^- at the CH_3 with extrusion of CH_3I[2b] may be operative instead of, or in conjunction with, the former type of reductive elimination.

Several mechanistic proposals have been made concerning reactions of coordinatively saturated transition metal alkyls with acids, halogens, and mercury(II) salts.[1-4,15] The present study is the first to show unequivocally that these processes do not involve direct attack of the electrophile on the alkyl group; instead, addition of the electrophilic species to the metal is occurring.

Acknowledgment. We thank the National Science Foundation for a grant in support of this research.

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(15) See, for example, (a) R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, **10**, 2091 (1971); (b) D. Dodd and M. D. Johnson, *J. Chem. Soc. B*, 662 (1971); (c) G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Lett.*, 275 (1971), and references cited in each.

(16) National Science Foundation Trainee, 1970–1973.

Thomas G. Attig,[16] Andrew Wojcicki*
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received September 13, 1973

Relative Effects of a Methyl and *tert*-Butyl Group on the Rates of Solvolysis of Tertiary *p*-Nitrobenzoates. Evidence for Major Increases in Steric Effects with Increasing Rigidity of the Parent System

Sir:

The replacement of a methyl group by a *tert*-butyl group at the tertiary position of tertiary *p*-nitrobenzoates results in increases in the rates of solvolysis by a factor of 4 for a simple aliphatic system (2-propyl), by approximately 125 for simple alicyclic systems (cyclopentyl and cyclohexyl), and by 40,000 for a bicyclic system (2-norbornyl). It is concluded that steric effects increase markedly from the relatively flexible aliphatic, to the less flexible alicyclic, to the rigid bicyclics.

Some time ago it was suggested that many of the unusual characteristics of the norbornyl system may have their origin in unusually large steric strains arising from the rigidity of this bicyclic structure.[1] It was proposed that strains arising from the presence of a bulky substituent would be small in the relatively flexible aliphatic system, larger in the less flexible alicyclic system, and enormous in the rigid bicyclic

(1) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).

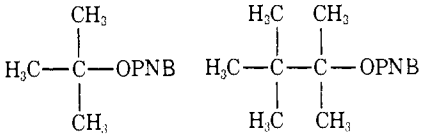
Table I. Rates of Solvolysis in 80% Acetone for Various *p*-Nitrobenzoates at 25.0°

p-Nitrobenzoate[a]	k_1, sec^{-1}	$k^{t\text{-Bu}}/k^{CH_3}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
tert-Butyl[b]	7.45×10^{-11} [c]	4.36	29.2	−7.1
tert-Butyldimethylcarbinyl[d]	3.25×10^{-10} [c]		29.0	−4.8
1-Methyl-1-cyclopentyl[e]	2.11×10^{-9} [c]	112	26.9	−7.9
1-*tert*-Butyl-1-cyclopentyl[f]	2.36×10^{-7} [c]		24.6	−6.5
1-Methyl-1-cyclohexyl[g]	5.48×10^{-11} [c]	134	30.1	−4.4
1-*tert*-Butyl-1-cyclohexyl[h]	7.35×10^{-9} [c]		28.5	−0.1
2-Methyl-2-*endo*-norbornyl[e]	1.13×10^{-11} [c]	39,600	30.2	−7.5
2-*tert*-Butyl-2-*endo*-norbornyl[i]	4.47×10^{-7} [c]		25.4	−2.4
2-Methyl-2-adamantyl[j]	1.43×10^{-10} [c]	225,000	30.2	−2.2
2-*tert*-Butyl-2-adamantyl[j]	3.42×10^{-5} [c]		21.6	−6.5

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] H. C. Brown and W. C. Dickason, *J. Amer. Chem. Soc.*, **91**, 1226 (1969). [c] Calculated from data at higher temperatures. [d] Reference 4. [e] Reference 2. [f] Mp 106.2–106.9°; $k^{100°} = 1.20 \times 10^{-3}$ sec^{-1}; $k^{75°} = 1.05 \times 10^{-4}$ sec^{-1}. [g] Mp 107.3–108.5°; $k^{150°} = 2.47 \times 10^{-4}$ sec^{-1}; $k^{125°} = 2.49 \times 10^{-5}$ sec^{-1}. [h] Mp 112.5–113.0°; $k^{100°} = 1.43 \times 10^{-4}$ sec^{-1}; $k^{75°} = 8.53 \times 10^{-6}$ sec^{-1}. [i] Mp 127.0° dec; $k^{75°} = 2.43 \times 10^{-4}$ sec^{-1}; $k^{50°} = 1.33 \times 10^{-5}$ sec^{-1}. [j] Reference 3.

norbornyl system.[2] It appeared that this proposal could be tested by examining the relative effects of methyl and *tert*-butyl substituents upon the rates of solvolysis of a selected series of derivatives.[3] The rates of solvolysis in 80% acetone are summarized in Table I.

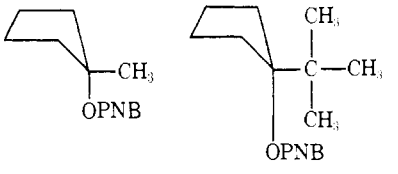
The rate of solvolysis of *tert*-butyldimethylcarbinyl *p*-nitrobenzoate is faster than *tert*-butyl *p*-nitrobenzoate by a factor of 4.4[4]



relative rate (25°) 1.0 4.36

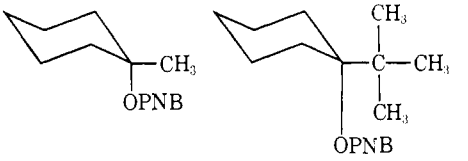
Thus, in this system the replacement of a methyl group by the *tert*-butyl group increases the rate by a relatively small factor, presumably the result of relief of steric strain.[5,6] It should be pointed out that the accumulation of two or three bulky groups at a tertiary center can result in far larger rate enhancements.[7,8]

Replacement of the 1-methyl group in the solvolysis of 1-methyl-1-cyclopentyl *p*-nitrobenzoate by the more bulky *tert*-butyl group results in a rate enhancement by a factor of 112



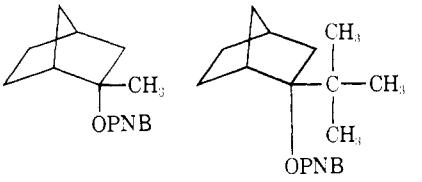
relative rate (25°) 1.00 112

Similarly, the replacement of the 1-methyl group in the solvolysis of 1-methyl-1-cyclohexyl *p*-nitrobenzoate by the *tert*-butyl group increases the rate of solvolysis by a similar factor, 134.



relative rate (25°) 1.0 134

The same structural change in the norbornyl system results in a rate enhancement of 39,600.



relative rate (25°) 1.0 39,600

The 2-alkyl-2-adamantyl *p*-nitrobenzoates exhibit a rate enhancement of 225,000 in going from the 2-methyl to the 2-*tert*-butyl derivative.[3] The rigidity of the adamantyl system is doubtless comparable to, if not greater than, that of norbornyl.

Clearly, steric effects are much greater in the rigid systems than in the more flexible acyclic and alicyclic systems. These results corroborate the belief that the relatively rigid norbornane structure provides an ideal system for the investigation of large steric effects.[1]

In the past it has not been uncommon to estimate steric interactions in norbornyl derivatives from their magnitudes in aliphatic and especially alicyclic systems.[9] The *A* factors determined for alicyclic systems have been an especially fertile source for such estimates.[10] The present results reveal that such estimates can be seriously in error. Steric effects in norbornyl derivatives can be huge compared to the effects we are ac-

(2) For example, the exo:endo rate ratio is altered from 880 for 2-methyl-2-norbornyl *p*-nitrobenzoate to 6 for the corresponding 7,7-dimethyl derivatives and to 3,630,000 for the 6,6-dimethyl derivatives; H. C. Brown and S. Ikegami, *J. Amer. Chem. Soc.*, **90**, 7122 (1968); S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968).

(3) J. L. Ery, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972).

(4) H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973).

(5) H. C. Brown, *Science*, **103**, 385 (1946).

(6) For a detailed discussion of B-strain effects, see H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Chapter VIII.

(7) P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, 77, 2806 (1955).

(8) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968).

(9) For example, see (a) G. D. Sargent in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, Chapter 24; (b) G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 301 (1966); (c) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854, 1856 (1964).

(10) For example, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 236.

customed to dealing with in the more flexible aliphatic and alicyclic derivatives.

Acknowledgment. We wish to thank Mr. Jerry D. Buhler for a sample of 1-*tert*-butyl-1-cyclohexanol and Mr. Gary Lynch for a sample of 1-*tert*-butyl-1-cyclopentanol.

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Edward N. Peters,[11] Herbert C. Brown*
Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907
Received September 1, 1973

An Exceptionally Fast Rate of Solvolysis for 2-*tert*-Butyl-2-*exo*-norbornyl *p*-Nitrobenzoate. Norbornyl Derivatives Which Provide Solvolysis Products with Significant Quantities of the Endo Isomer

Sir:

2-*tert*-Butyl-2-*exo*-norbornyl *p*-nitrobenzoate solvolyzes at a rate 21,000 that of 2-methyl-2-*exo*-norbornyl and 2,820,000 that of *tert*-butyl *p*-nitrobenzoate. Consequently, it is the fastest reacting saturated tertiary derivative known.[1] In spite of the exceptionally fast rate, both it and the corresponding endo isomer undergo solvolysis in aqueous acetone to yield the exo and endo alcohols in an isomer ratio of 95:5. Such a large amount of endo isomer in the solvolysis of a tertiary norbornyl derivative is a hitherto unknown phenomenon and is not compatible with the postulation of a σ-bridged cation. The results are readily interpretable in terms of the relative energies of the species involved.

It was recently pointed out that the great rigidity of the norbornyl structure can introduce steric effects which are huge compared to those encountered in the more flexible aliphatic and alicyclic systems.[5] Indeed, the replacement of the methyl group in 2-methyl-2-*endo*-norbornyl *p*-nitrobenzoate by a *tert*-butyl group results in a rate enhancement by a factor of 39,600.[6] σ participation cannot be a factor in the solvolysis of the endo isomer. Moreover, it has been reported that changes in the inductive and hyperconjugative effects in going from a methyl to a *tert*-butyl group attached to the developing carbonium ion center play only a minor role in the rates of solvolysis.[3,4] Consequently, the enhanced rate must be due to the steric strain in the ground state which is relieved as the 2-*tert*-butyl group rotates away from the syn 7-hydrogen atom during the ionization stage of the solvolysis.

The observed factor accompanying the replacement of the methyl group in 2-methyl-2-*exo*-norbornyl by a *tert*-butyl group is comparable in magnitude, 21,000. Here it is the decrease in strain accompanying rotation of the *tert*-butyl group away from the endo 6-hydrogen atom in the course of the ionization stage that must be responsible.

The results are summarized in Table I.

Table I. Rates of Solvolysis for 2-Methyl- and 2-*tert*-Butyl-2-norbornyl *p*-Nitrobenzoates in 80% Acetone at 25.0°

p-Nitrobenzoate[a]	$k_1^{25°}$, sec^{-1}	k_{rel}^{endo}	k_{rel}^{exo}
2-Methyl-2-*endo*-norbornyl[b]	1.13×10^{-11} [c]	1.0	
2-*tert*-Butyl-2-*endo*-norbornyl[d]	4.47×10^{-7} [c]	39,600	
2-Methyl-2-*exo*-norbornyl[b]	1.00×10^{-8} [c]		1.0
2-*tert*-Butyl-2-*exo*-norbornyl[e]	2.10×10^{-4}		21,000

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Reference 8. [c] Calculated from data at higher temperatures. [d] Reference 6. ROH, see J. D. Buhler, *J. Org. Chem.*, **38**, 904 (1973). [e] Mp 109° dec, ROH mp 83–84°.

The exo:endo rate ratio is 470. In view of the extraordinarily large steric accelerations observed in both isomers, it is evident that these large steric effects must largely cancel, yielding an exo:endo rate ratio comparable to that observed in the acetolysis of 2-norbornyl brosylates, 350,[7] and in the solvolysis of the 2-methyl-2-norbornyl *p*-nitrobenzoates, 885.[8]

On the other hand, the exo:endo product ratio realized in the solvolysis of these 2-*tert*-butyl derivatives is highly unusual for norbornyl derivatives. The acetolysis of 2-norbornyl brosylates yields 99.98% *exo*- and and 0.02% *endo*-norbornyl acetate.[9] The solvolysis of 2-methyl-2-norbornyl *p*-nitrobenzoates yields 99.9% *exo*- and 0.1% 2-methyl-2-*endo*-norbornanol.[10] As was pointed out earlier, the solvolysis of 2-*tert*-butyl-2-norbornyl *p*-nitrobenzoates yielded the exo and endo alcohols in a ratio of 95:5.[11]

Clearly such a ratio is incompatible with significant σ bridging in the cationic intermediates.[12]

Equilibration of 2-*tert*-butyl-2-*endo*-norbornanol in a heterogeneous system (cyclohexane–6 *N* sulfuric acid)[13] gave the two epimeric alcohols in the ratio exo:endo = 1.0:24, corresponding to a greater ground-state stability of the endo alcohol of 1.9 kcal mol^{-1}.

With the usual assumption that the steric requirements of OH and RCO_2 are similar,[13] a Goering–

(1) Previously reported rate enhancements relative to *tert*-butyl *p*-nitrobenzoate at 25° are: (a) *p*-nitrobenzoate of perhydro-9β-phenalenol,[2] 2,030,000; (b) 2-*tert*-butyl-2-adamantyl *p*-nitrobenzoate,[3] 460,000; and (c) *tert*-butyldineopentylcarbinyl *p*-nitrobenzoate,[4] 129,500.

(2) H. C. Brown and W. C. Dickason, *J. Amer. Chem. Soc.*, **91**, 1226 (1969).

(3) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972).

(4) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968).

(5) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).

(6) E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, **96**, 263 (1974).

(7) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, **74**, 1147, 1154 (1952).

(8) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 7124 (1968).

(9) (a) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, **87**, 376 (1965); (b) H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

(10) M.-H. Rei, Ph.D. Thesis, Purdue University, 1967.

(11) Normalized. Products derived from methyl migration were present in less than 4%.

(12) For example, the isolation of ~10% of optically active 1,2-dimethyl-*exo*-norbornanol from the solvolysis of the corresponding *p*-nitrobenzoate led the authors to conclude that the cationic intermediate must be classical; H. L. Goering and K. Humski, *J. Amer. Chem. Soc.*, **90**, 6213 (1968). For a similar study using 1,2-dimethyl-2-*exo*-norbornyl chloride, see H. L. Goering and J. V. Clevenger, *ibid.*, **94**, 1010 (1972).

(13) M.-H. Rei and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 5335 (1966).