Chemical Effects of Steric Strains. XXI. Solvolysis of Tertiary Methyl- and *tert*-Butylcarbinyl *p*-Nitrobenzoates. Evidence that Steric Effects are More Important in Rigid Bicyclic Systems than in Acyclic and Alicyclic Systems[1]

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Abstract: 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 in 80:20 acetone–water. Thus, for a simple aliphatic system, 2-propyl, the rate increases by a factor of 4.4. In simple alicyclic systems, cyclopentyl, cyclohexyl, and cycloheptyl, the rate increases by factors of 112, 134, and 273, respectively. For bicyclic systems, 2-*endo*-norbornyl, 9-bicyclo[3.3.1]nonyl, and 2-*endo*-camphenilyl, the rates increase by factors of 39,600, 104,000, and 1,120,000, respectively. Hence, it is concluded that steric effects increase markedly from the relatively flexible aliphatic, the less flexible alicyclic, to the rigid bicyclics. These results reveal that estimates of steric interactions in norbornyl derivatives based on steric interactions in aliphatic and alicyclic systems can be seriously in error.

In 1946, it was proposed that relief of steric strain accompanying the ionization of sterically crowded tertiary derivatives could provide a potent driving force to enhance the rate of solvolysis.[3] Indeed, today steric assistance to ionization is an accepted factor in calculating rates of solvolysis.[4] Moreover, it has been shown that steric effects can be very large in the rigid norbornyl system.[5,6]

Thus, the presence of *gem*-dimethyls in 2,7,7-trimethyl-2-norbornyl system decreases the exo:endo rate ratio from 885, the value observed in the parent compound, to a value of 6.1 (Figure 1). On the other hand, the presence of *gem*-dimethyls in 2,6,6-trimethyl-2-norbornyl system increases the exo:endo rate ratio to 3,630,000.[5,6]

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.[7] 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 norbornyl system.[5,6] 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.[8]

For example, the effect of steric bulk has been demonstrated by the replacement of one of the methyl groups in *tert*-butyl chloride by a neopentyl group. This results in a 21-fold increase in the reaction rate. Two neopentyl groups raise the rate to 580 times that of *tert*-butyl chloride.[9]

Much larger effects have been realized by Bartlett and coworkers in the solvolysis of derivatives of highly hindered alcohols, such as tri-*tert*-butylcarbinol.[10] For example, at 40°, tri-*tert*-butylcarbinyl *p*-nitrobenzoate solvolyzes 13,500 times faster than *tert*-butyl *p*-nitrobenzoate in 60:40 dioxane–water. Moreover, dineopentyl-*tert*-butylcarbinyl *p*-nitrobenzoate reacts 68,000 times faster.

Thus, it is clear that relief of steric strain can have a large rate-accelerating effect. However, in the replacement of a methyl group by a *tert*-butyl group, one also has to consider the changes in inductive and hyperconjugative effects.

The differences in the inductive effect of alkyl groups are relatively small.[11,12] Consequently, in the study of steric effects, it is frequently possible to assume, as a first approximation, that the polar effects of structure changes in the alkyl group are negligible and to attribute the observed reactivity changes to the altered steric requirements of the alkyl groups.[13] The Baker–Nathan phenomenon is attributed to a small loss in hyperconjugative stabilization of the carbonium ion as the hydrogen atoms of the *tert*-butyl cation are replaced by alkyl groups.[14] In those few cases where the inductive and hyperconjugative effects of groups have been quantitatively resolved, it has appeared that carbon–carbon hyperconjugation is not greatly inferior to that at the carbon–hydrogen bond.[12,15,16]

Therefore, steric effects should play the predominant role in replacing a methyl group with a *tert*-butyl group at a carbonium ion center, and other effects, inductive and hyperconjugative, should be relatively unimportant.

Recently, it was pointed out that F strain involving ionization of *p*-nitrobenzoates can be large in certain systems, much larger than for the corresponding chlorides.[17] Consequently, the chlorides are to be preferred for studies of structural effects. In the present case, it was known that the synthesis of certain of the chlorides would offer major experimental difficulties.[10c] Moreover, we were interested in the effect of the flexibility of the system on the total steric effect without undertaking detailed analyses of the individual F- and B-strain contributions. Consequently, it appeared appropriate to utilize the *p*-nitrobenzoates.

Results and Discussion

The tertiary *tert*-butylcarbinols were prepared by addition of the appropriate ketone to *tert*-butyllithium at −78°.[18] The tertiary methylcarbinols were prepared by the addition of the appropriate ketone to methylmagnesium chloride at 0°. The corresponding *p*-nitrobenzoates were prepared by the reaction of the lithium alkoxides with *p*-nitrobenzoyl chloride.[19]

Rates of solvolysis in 80:20 acetone–water were determined titrimetrically. The data are listed 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 (Figure 2).[20]

Thus in this system, the replacement of a methyl group by the *tert*-butyl group increases the rate by a relatively

Table I. Rates of Solvolysis of Tertiary *p*-Nitrobenzoates in 80% Acetone

p-Nitrobenzoate[a]	$10^6 k_1$, sec^{-1} (T_2, °C)	$10^6 k_1$, sec^{-1} (T_1, °C)	$10^6 k_1$, sec^{-1} 25°[b]	k(*t*-Bu)/k(CH$_3$)	$\Delta H^{\ddagger}$, kcal/mol^{-1}	$\Delta S^{\ddagger}$, eu
tert-Butyl[c]	23.6 (125)	1.85 (100)	7.45×10^{-5}	4.36	29.2	−7.1
tert-Butyldimethylcarbinyl[d]	814 (150)	89.6 (125)	3.25×10^{-4}		29.0	−4.8
1-Methyl-1-cyclopentyl[e]	236 (125)	23.0 (100)	2.11×10^{-3}	112	26.9	−7.9
1-*tert*-Butyl-1-cyclopentyl[f]	1200 (100)	105 (75)	0.236		24.6	−6.5
1-Methyl-1-cyclohexyl[f]	247 (150)	24.9 (125)	5.48×10^{-5}	134	30.1	−4.4
1-*tert*-Butyl-1-cyclohexyl[f]	143 (100)	8.53 (75)	7.35×10^{-3}		28.5	−0.1
1-Methyl-1-cycloheptyl[g]	528 (125)	50.6 (100)	4.21×10^{-3}	273	27.1	−6.0
1-*tert*-Butyl-1-cycloheptyl[g]	518 (75)	30.9 (50)	1.15		24.6	−3.1
3-Methyl-3-nortricyclyl[g]	188 (125)	18.7 (100)	1.81×10^{-3}	1790	26.7	−9.1
3-*tert*-Butyl-3-nortricyclyl[g]			3.24			
2-Methyl-*endo*-norbornyl[h]	5.41 (125)	0.395 (100)	1.13×10^{-5}	39,600	30.2	−7.5
2-*tert*-Butyl-*endo*-norbornyl[f]	243 (75)	13.3 (50)	0.48		25.4	−2.4
9-Methyl-9-bicyclo[3.3.1]nonyl[g]	646 (150)	73.9 (125)	3.34×10^{-4}	104,000	28.4	−6.5
9-*tert*-Butyl-9-bicyclo[3.3.1]nonyl[g]			34.8			
2-Methyl-2-adamantyl[i]	68.8 (124.8)	5.07 (100)	1.43×10^{-4}	225,000	30.2	−2.2
2-*tert*-Butyl-2-adamantyl[i]	7700 (75.4)	631 (50.1)	34.2		21.6	−6.5
2-Methyl-*endo*-camphenilyl[j]	12.0 (125)	0.867 (100)	2.31×10^{-5}	1,120,000	30.4	−5.1
2-*tert*-Butyl-*endo*-camphenilyl[g]			27.7			

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Calculated from data at higher temperatures. [c] H. C. Brown and W. C. Dickason, *J. Am. Chem. Soc.*, 91, 1226 (1969). [d] Reference 20. [e] H. C. Brown and W. J. Hammar, *ibid.*, 89, 6378 (1967). [f] Reference 1. [g] This work. [h] Reference 6. [i] Reference 8. [j] K. Takeuchi, Ph.D. Thesis, Purdue University, 1968.

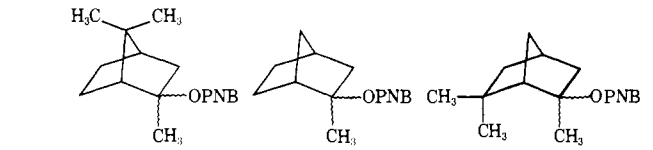


Figure 1.

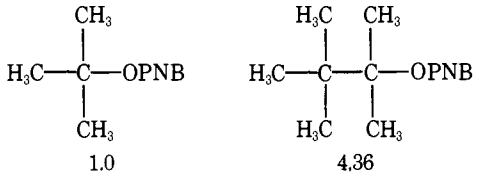
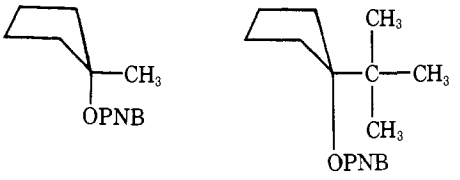


Figure 2.



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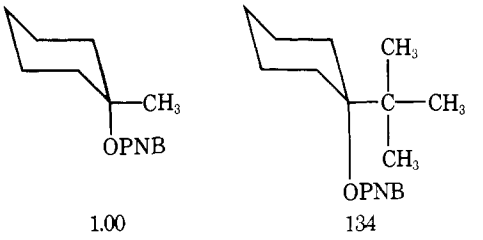

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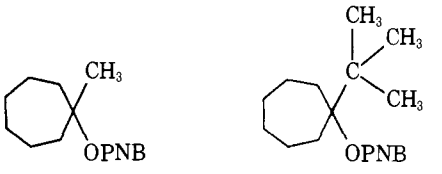


Figure 5.

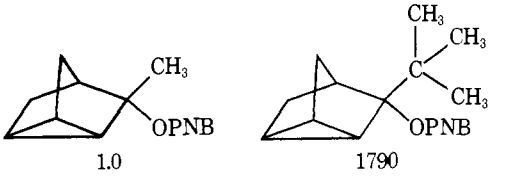


Figure 6.

small factor, presumably the result of relief of steric strain.[3] 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.[10]

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 (Figure 3). 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 (Figure 4). The rate of solvolysis of 1-*tert*-butyl-1-cycloheptyl *p*-nitrobenzoate is faster than that of 1-methyl-1-cycloheptyl by a factor of 273 (Figure 5). These increases in strain over the acyclic system probably result from the loss of some rotational freedom in going to an alicyclic system and result in an increase in nonbonded interactions.

Looking at rigid systems, we see a marked increase in rates by the replacement of a methyl with a *tert*-butyl group in the 3-nortricyclyl, 2-norbornyl, 9-bicyclo[3.3.1]nonyl, and 2-adamantyl systems. Indeed, the rate enhancements due to steric strain reported here are even greater than those reported in the 2,7,7-trimethyl-2-norbornyl and the 2,6,6-trimethyl-2-norbornyl systems (Figure 1).[5,6]

The rate of 3-methyl-3-nortricyclyl *p*-nitrobenzoate is increased by a factor of 1790 by the replacement of the 3-methyl with a 3-*tert*-butyl group (Figure 6).

The rate of 2-*tert*-butyl-*endo*-norbornyl *p*-nitrobenzoate is 39,600 times faster than that of the 2-methyl analog (Figure 7).

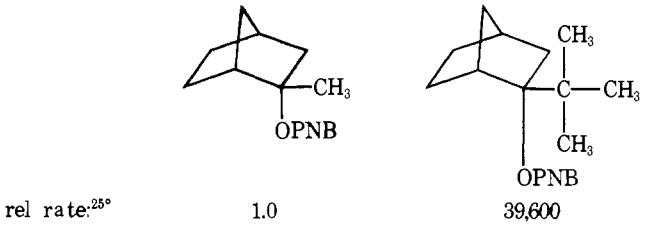
The 9-bicyclo[3.3.1]nonyl *p*-nitrobenzoates show an enormous rate increase of 104,000 in going from the 9-methyl to the 9-*tert*-butyl derivative (Figure 8).

The 2-adamantyl *p*-nitrobenzoates exhibit a somewhat larger rate enhancement than that shown in Figure 8. Thus

Table II. Summary of Physical and Microanalytical Data for *p*-Nitrobenzoates

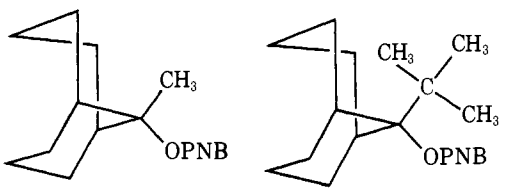
p-Nitrobenzoate	Mp, °C	Calcd, %			Found, %		
		C	H	N	C	H	N
1-*tert*-Butyl-1-cyclopentyl	106.2–106.9	65.95	7.27	4.81	65.86	7.33	4.62
1-Methyl-1-cyclohexyl	107.3–108.5	63.86	6.51	5.32	63.65	6.42	5.44
1-*tert*-Butyl-1-cyclohexyl	112.5–113.0	66.86	7.59	4.59	66.95	7.72	4.56
1-Methyl-1-cycloheptyl	96.5–97.8	64.96	6.91	5.05	64.90	6.69	5.15
1-*tert*-Butyl-1-cycloheptyl	80.5–81.5	67.69	7.89	4.39	67.73	7.74	4.51
3-Methyl-3-nortricyclyl	142.5–144.0[a]	65.93	5.53	5.13	65.67	5.60	5.11
3-*tert*-Butyl-3-nortricyclyl	120–121	68.55	6.71	4.44	68.60	6.96	4.49
2-*tert*-Butyl-2-*endo*-norbornyl	127 dec	68.12	7.31	4.41	68.23	7.39	4.44
9-Methyl-9-bicyclo[3.3.1]nonyl	129–130	67.31	6.98	4.62	67.56	7.20	4.78
9-*tert*-Butyl-9-bicyclo[3.3.1]nonyl	123–124 dec	69.54	7.88	4.06	69.58	7.87	4.16
2-*tert*-Butyl-2-*endo*-camphenilyl	133 dec	69.54	7.88	4.06	69.68	8.05	4.19

[a] Literature mp 141.5–142.5°; G. L. Tritle, Ph.D. Thesis, Purdue University, 1967.



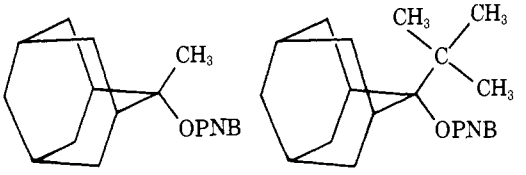
rel rate:[25°] 1.0 39,600

Figure 7.



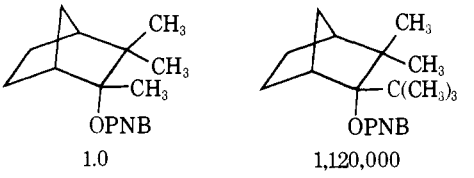
rel rate:[25°] 1.0 104,000

Figure 8.



rel rate:[25°] 1.0 225,000

Figure 9.



rel rate:[25°] 1.0 1,120,000

Figure 10.

the 2-*tert*-butyl derivative reacts 225,000 times faster than the 2-methyl (Figure 9).[8]

The behavior of camphenilyl derivatives possess historical implication for the development of σ participation and the nonclassical ion theory.[21] Thus the very fast rate of ethanolysis of camphene hydrochloride compared with that of *tert*-butyl chloride was considered to provide strong support for the formation of a stabilized synartetic (mesomeric, nonclassical) ion.[22] However, the importance of internal strain in the ground state of camphene hydrochloride has been pointed out, and hence it was concluded that the rates for camphenilyl derivatives are not exceptionally fast but are in accord with the postulated effect of increasing steric strain in enhancing rates of solvolysis of highly branched tertiary chlorides.[23]

Indeed, the rate of solvolysis of 2-*tert*-butyl-2-*endo*-camphenilyl *p*-nitrobenzoate is 1,120,000 times faster than that of 2-methyl-2-*endo*-camphenilyl *p*-nitrobenzoate (Figure 10).

Clearly, steric effects are much greater in the rigid systems than in the more flexible acyclic and alicyclic systems.

Conclusions

In 1966, 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.[7] 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 norbornyl system.

Clearly, from the results presented here, steric effects are indeed much greater in the rigid systems than in the more flexible acyclic and alicyclic systems. Moreover, these results corroborate the belief that the rigid norbornane structure provides an ideal system for the investigation of large steric effects.[7]

In the past, it has not been uncommon to estimate steric interactions in norbornyl derivatives from their magnitudes in aliphatic and especially alicyclic systems.[4,24] The *A* factors determined for alicyclic systems have been an especially fertile source for such estimates.[25] The present results reveal that such estimates can be seriously in error. Steric effects in norbornyl derivatives can be huge compared with the effects we are accustomed to dealing with in the more flexible aliphatic and alicyclic derivatives.

Experimental Section

General Remarks. Melting points (taken in capillary tubes) and boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer Model 137 or 700 spectrometer. NMR spectra were recorded on a Varian T-60 spectrometer. The preparation of most of the *tert*-butylcarbinols, 1-*tert*-butyl-1-cyclohexanol,[18] 2-*tert*-butyl-2-*endo*-norbornanol,[18] 3-*tert*-butyl-3-nortricyclanol,[18] 9-*tert*-butyl-9-bicyclo[3.3.1]nonanol,[26] and 1-*tert*-butyl-1-cyclopentanol,[27] has been described in the literature. Likewise, the preparations of 1-methyl-1-cycloheptanol[28] and 1-methyl-1-cyclohexanol[29] are described in the literature.

9-Methyl-9-bicyclo[3.3.1]nonanol. This alcohol was prepared by the addition of methyl Grignard to bicyclo[3.3.1]nonan-9-one and worked up in the normal manner. Recrystallization from hexane gave the desired alcohol (89% yield), mp 175–176°. NMR spectrum ($CDCl_3$) showed a singlet for the 9-methyl at δ 1.33 from Me_4Si.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 78.03; H, 11.88.

1-*tert*-Butyl-1-cycloheptanol. This alcohol was prepared by the addition of cycloheptanone to *tert*-butyllithium at −78° following the procedure described in the literature.[18] Distillation gave the desired product (40% yield), bp 110° (45 mm). NMR spectrum

(CCl_4) showed a singlet for the *tert*-butyl protons at δ 0.92 from Me_4Si.

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.56; H, 13.08.

2-*tert*-Butyl-2-*endo*-camphenilol. This alcohol was prepared by the addition of camphenilone (3,3-dimethyl-2-norbornanone) to *tert*-butyllithium at −78° following the procedure described in the literature.[18] Distillation gave the desired alcohol (93% yield), bp 92–93° (2 mm). VPC analysis (15% Carbowax 20M on Chromosorb W) indicated about 98% purity. Further purification by preparative VPC (20% Carbowax 20M on Chromosorb W) resulted in a solid, mp 33.5–34.5°. NMR spectrum ($CDCl_3$) showed a singlet for the *tert*-butyl hydrogens at δ 1.08 from Me_4Si. Ir spectrum (melt) showed weak absorption at 2.75 μ (sharp).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.75; H, 12.46.

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates were prepared via the lithium alkoxides in tetrahydrofuran similar to the procedure described in the literature,[19] except that, before work-up, an equal volume of diethyl ether was added to the reaction mixture. After washing with cold 5% aqueous sodium bicarbonate, the ethereal layer was dried over anhydrous magnesium sulfate. Good to excellent yields of the *p*-nitrobenzoates were obtained. Physical properties are listed in Table II.

Acknowledgment. The authors thank Dr. Jerry D. Buhler for samples of 1-*tert*-butyl-1-cyclohexanol and 3-*tert*-butyl-3-nortricyclanol, Dr. Gary Lynch for a sample of 1-*tert*-butyl-1-cyclopentanol, and Dr. Bruce A Carlson for samples of 9-*tert*-butyl-9-bicyclo[3.3.1]nonanol and bicyclo-[3.3.1]nonan-9-one.

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Solvolysis of 1-(*p*-Cyclopropylphenyl)- and 1-(*p*-Isopropylphenyl)-1-arylethyl Chlorides. Test of the Tool of Increasing Electron Demand to Systems with Relatively Small Electronic Response[1]

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Abstract: 1-(*p*-Cyclopropylphenyl)-1-arylethyl chlorides and 1-(*p*-isopropylphenyl)-1-arylethyl chlorides were synthesized and their rates of solvolysis in 97.5% aqueous acetone determined in order to establish whether there is, in this highly stabilized cationic system, a detectable difference in the relative abilities of a cyclopropyl and isopropyl group to contribute to the stabilized electron-deficient center. The relative rates of solvolysis of cyclopropyl derivatives compared with the corresponding isopropyl compounds for the usual range of substituents in the aryl group are as follows: *p*-CH_3O, 1.1; *p*-H, 2.8; *p*-CF_3, 8.5; 3,5-$(CF_3)_2$, 13.5. This modest increase in rate is in accordance with the greater ability of the cyclopropyl moiety over isopropyl to react to increasing electron demand by supplying electron density to stabilize the electron-deficient center. The cyclopropyl compounds yield a ρ^+ value of −2.24 as compared with −2.91 for the isopropyl derivatives. It is concluded that the tool of increasing electron demand is quite sensitive, capable of detecting even modest electronic contributions in systems where the electronic demand and supply are relatively small.

The tool of increasing electron demand has been used to detect π or σ contributions in various systems. For example, Gassman and Fentiman have shown that the ability of the π electrons in 7-aryl-*anti*-7-norbornenyl derivatives (**2**) to stabilize the carbonium center increases as the electron demand is increased.[3] Thus, the relative rates of **2** increase from 3.4 for *p*-anisyl to over 10^5 for 3,5-bis(trifluoromethyl)phenyl, compared with the corresponding 7-aryl-7-nor-