

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.

(11) Postdoctoral research associate on a grant (GP 31385) supported by the National Science Foundation.

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

(1) Previously reported rate enhancements relative to *tert*-butyl *p*-nitrobenzoate at 25° are: (a) *p*-nitrobenzoate of perhydro-9 β -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).

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°

<i>p</i> -Nitrobenzoate ^a	$k_1^{25^\circ}$, sec ⁻¹	k_{rel}^{endo}	k_{rel}^{exo}
2-Methyl-2- <i>endo</i> -norbornyl ^b	1.13×10^{-11} ^c	1.0	
2- <i>tert</i> -Butyl-2- <i>endo</i> -norbornyl ^d	4.47×10^{-7} ^c	39,600	
2-Methyl-2- <i>exo</i> -norbornyl ^b	1.00×10^{-8} ^c		1.0
2- <i>tert</i> -Butyl-2- <i>exo</i> -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 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 RCO₂ are similar,¹³ a Goering–

(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).

Table II. Comparison of the Factors Involved in the Goering-Schewene Diagrams for 2-Norbornyl Derivatives

Norbornyl	$\Delta F^{\circ}_{\text{exo}} - \Delta F^{\circ}_{\text{endo}}$ kcal mol ⁻¹	$\Delta F^{\ddagger}_{\text{exo}} - \Delta F^{\ddagger}_{\text{endo}}$ kcal mol ⁻¹	$\Delta\Delta F$ kcal mol ⁻¹	Product ratio	
				Calcd	Obsd
2-Hydrogen ^a	-1.3	4.5	5.8	17,900	5000
2-Methyl ^b	-0.2	4.0	4.2	1,200	999
2- <i>tert</i> -Butyl	1.9	3.6	1.7	17.6	19

^a Reference 9. ^b Reference 8.

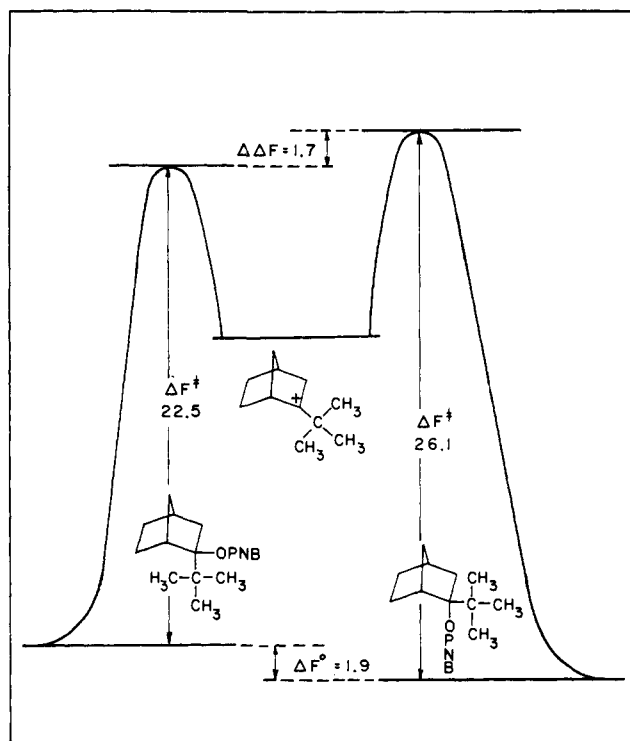


Figure 1. Free-energy diagram for the solvolysis of 2-*tert*-butyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°. (All values in kcal mol⁻¹.)

Schewene diagram can be constructed (Figure 1). The diagram reveals that the difference in energy between the two transition states is small, only 1.7 kcal mol⁻¹. This is consistent with the observed distribution of the cationic intermediate between *exo* and *endo* products of 95:5.

We now have the data to make a highly significant comparison of the factors responsible for the major changes in the *exo*:*endo* product ratios for norbornyl, 2-methylnorbornyl, and 2-*tert*-butylnorbornyl. These are summarized in Table II.

It now becomes clear that the marked difference in the stereoselectivities exhibited by the distribution of the intermediate between *exo* and *endo* products arises not from major differences in the energies of activation for the solvolysis, such as would be anticipated for differences in σ participation, but reflect instead major differences in the ground-state energies of the *exo* and *endo* products. Consequently, it is this factor, rather than differences in σ participation, which appears to be primarily responsible for the major differences in the stereoselectivities of product formation.

A further major implication of the present results should be pointed out. It has been argued that the steric explanation for the high *exo*:*endo* rate ratio for 2-methyl-2-norbornyl^{8,13} cannot be extrapolated to the

high *exo*:*endo* rate ratio for norbornyl itself, in view of the large differences in the steric requirements of the 2-H and 2-Me substituents.¹⁴ This argument for a large α -steric effect is now rendered somewhat questionable in view of the essential constancy in the *exo*:*endo* rate ratio which has now been established for the 2-H, 2-Me, and 2-*t*-Bu norbornyl derivatives, in spite of the large changes in the steric requirements of these 2 substituents.

(14) G. D. Sargent in "Carbonium Ions," Vol. III, G. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, Chapter 24.

(15) Postdoctoral research associate on a grant (GP 31385) supported by the National Science Foundation.

Edward N. Peters,¹⁵ Herbert C. Brown*

Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received September 1, 1973

Exciton Chirality Method as Applied to Conjugated Enones, Esters, and Lactones

Sir:

The chiral interaction between two or more isolated but spatially close chromophores, which give rise to Davydov-split Cotton effects¹ ("exciton chirality method"²) is one of the most reliable optical methods for studies of absolute configurations or conformations. In this communication we have extended this method to conjugated enones, esters, and lactones. The examples shown in Table I demonstrate that a *positive chirality*, **1**, between electric transition moments of diverse carbonyl-containing chromophores 2-4 resulted in exciton-split cd curves having a *positive* first Cotton effect. Experimental curves are corroborated by nonempirical calculations as exemplified for the case of quassin **12** (Figure 2).

Comments on Table I are as follows. (1) The benzoate intramolecular charge transfer transitions³ or the ¹L_a maxima⁴ at 230 nm (ϵ 14,000) interact with enone π - π^* maxima at 230-260 nm (ϵ 7000-15,000) to give split cd curves which determine the enone-hydroxyl chirality (entries 1-7); whether the 205-230 nm enone cd extrema⁵ are involved or not is unclear, but for practical purposes it need not be considered. (2) Note the differences between the exciton-split curve of the enone-benzoate (Figure 1, curve a) and the cd of

(1) (a) S. F. Mason, *J. Chem. Soc. B*, 370 (1966); (b) N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, **91**, 3989 (1969).

(2) See following review: N. Harada and K. Nakanishi, *Accounts Chem. Res.*, **5**, 257 (1972).

(3) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

(4) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962.

(5) (a) L. Velluz, M. Legrand, and R. Viennet, *C. R. Acad. Sci.*, **261**, 1687 (1965); (b) K. Kuriyama, M. Moriyama, T. Iwata, and K. Tori, *Tetrahedron Lett.*, 1661 (1968); (c) A. W. Burgstahler and R. C. Barkhurst, *J. Amer. Chem. Soc.*, **92**, 7601 (1970); (d) R. N. Totty and J. Hudec, *Chem. Commun.*, 785 (1971).