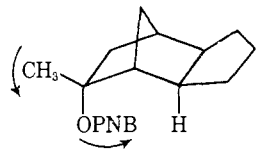
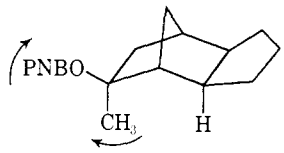


III



IV

The present results make it quite clear that high *exo*:*endo* rate ratios can be observed in norbornyl derivatives where σ participation is not a factor. The problem remains: what is the factor responsible for the low *exo*:*endo* rate ratios in the secondary 5,6- and 4,5-*exo*-trimethylene-2-norbornyl derivatives?[11] We hope to examine this question experimentally.

(10) (a) H. C. Brown and S. Ikegami, *J. Am. Chem. Soc.*, **90**, 7122 (1968); (b) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968).

(11) In the parent norbornyl system, the secondary and tertiary derivatives exhibit very similar behavior. There is a natural reluctance to ascribe such similar behavior to totally different causes. However, we must not overlook the possibility that this may be the case. It is highly important for the theory of solvolysis to attain an understanding of the reason for the low *exo*:*endo* rate ratio in the trimethylene derivatives. It may turn out that this is indeed the result of decreased σ participation. However, caution must be exercised here also. The theory of σ participation is still in an exceedingly qualitative stage. Thus, it was originally predicted that the introduction of methyl groups in the 6 position of norbornyl would result in enhanced σ participation and an enhanced rate. When a decreased rate was observed, it was argued that methyl substituents, for steric reasons, should hinder σ participation (P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, 87, 375 (1965)). Indeed, had the trimethylene derivatives exhibited an enhanced *exo*:*endo* rate ratio, the theory could have accommodated even this. It would merely have been argued that the strain had polarized the C-1–C-6 bond and caused it to be a better donor.

It is important to recognize that the 5,6-trimethylene bridge may have important effects on reactivity other than its postulated influence on σ participation. For example, we have observed that the hydroboration of *exo*-5,6-trimethylenenorbornene yields an *exo*:*endo* product ratio of 10, whereas norbornene exhibits a product ratio of 200. These results are remarkably similar to the *exo*:*endo* rate ratios for the tosylates in the two systems, 11.2 and 280, respectively. Consequently, it is essential that we exercise caution as we grope our way to a better understanding of the chemical behavior of these fascinating rigid polycyclic systems.

(12) National Science Foundation Cooperative Fellow, 1965–1967; Ph.D. Thesis, Purdue University, 1967.

(13) National Science Foundation Predoctoral Fellow, 1963–1964; Ph.D. Thesis, Princeton University, 1964.

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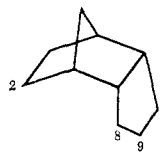
Evidence for Steric Hindrance to Ionization in the Slow Rates of Solvolysis of the Tertiary 2-, 8-, and 9-Phenyl-*endo*-5,6-trimethylene-*endo*-norbornanyl *p*-Nitrobenzoates. An Unusually High *exo*:*endo* Rate Ratio Not Involving σ Participation

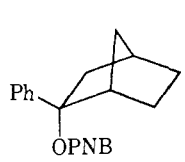
Sir:

The U-shaped structure of the *endo*-5,6-trimethylenenorbornane system (I) appears ideal for the investigation of the possible role of steric hindrance to ionization as a major factor in the rates of solvolysis of bicyclic derivatives.[1,2] Accordingly we undertook to

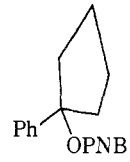


I

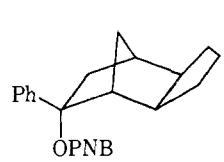
synthesize the tertiary 2-, 8-, and 9-phenyl *p*-nitrobenzoate derivatives (V, VI, VII) and to run their rates of solvolysis in 80% aqueous acetone for comparison with appropriate models (II, III, IV). We also synthesized the *exo* isomer VIII to obtain the *exo*:*endo* rate ratio.



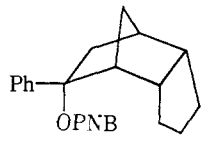
II
1/45



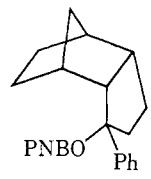
III
1.00



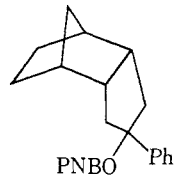
IV
1/63



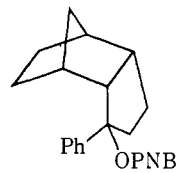
V
1/1030



VI
1/1900



VII
1/27



VIII
6.1

exo:*endo* = 11,600

Addition of phenylmagnesium bromide to 5,6-*endo*-trimethylene-2-norbornanone gave the tertiary *endo* alcohol V-OH, mp 94.7–95.0°. Similarly, the corresponding 8- and 9-norbornanones were converted into the corresponding tertiary alcohols VI-OH, mp 91.5–92.3°; VII-OH, mp 93.5–94.5°. Treatment of VI-OH with hydrogen chloride gave the olefin instead of the chloride. The olefin was epoxidized[3] and the crude unstable epoxide reduced with lithium aluminum hydride to give the *exo*-8-ol, VIII-OH, mp 118.2–118.8°.[4] The rate data are summarized in Table I.

If we consider the 1-phenylcyclopentyl system to constitute a reasonable model for these derivatives, it is apparent that all of the *endo* isomers solvolyze at greatly reduced rates compared to the model. Thus II solvolyzes at $^1/_{45}$ and IV at $^1/_{63}$ the rate of III. It should be noted that there is little difference between II and IV. However, if the 5,6-trimethylene bridge is made *endo*, as in V, the relative rate decreases sharply to $^1/_{1030}$. Presumably this is a reflection of the greater steric hindrance to ionization afforded the *p*-nitrobenzoate moiety by the *endo*-trimethylene bridge as compared to the *exo*.

(1) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966).

(2) H. C. Brown, W. J. Hammar, J. H. Kawakami, J. Rothberg, and D. L. Vander Jagt, *J. Am. Chem. Soc.*, **89**, 6378 (1967).

(3) G. B. Payne, *Tetrahedron*, **18**, 763 (1962).

(4) All compounds exhibited ir and pmr spectra and analytical data in agreement with the assigned structures.

Table I. Rates of Solvolysis of the Tertiary 2-, 8-, and 9-Phenyl-*endo*-5,6-trimethylene-*endo*-norbornanyl *p*-Nitrobenzoates and Related Model Compounds[a]

Compd	Isomer	Temp, °C	Rate constant, $k \times 10^6$ sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate[b]	*exo*:*endo*
II[c]	*endo*-2-OPNB	25.0	5.3×10^{-2}	30.2	−7.5	$^1/_{45}$	
III		25.0	2.37[d]	24.4	−2.8	1.00	
		50.0	55				
		75.0	904				
IV[e]	*endo*-2-OPNB	25.0	3.6×10^{-2}			$^1/_{63}$	
V[e]	*endo*-2-OPNB	25.0	2.3×10^{-3} [d]	27.4	−6.3	$^1/_{1030}$	
		100.0	31.3				
		125.0	338				
VI[f]	*endo*-8-OPNB	25.0	1.25×10^{-3} [d]	28.8	−2.9	$^1/_{1900}$	
		100.0	27.2				
		125.0	330				
VII[g]	*endo*-9-OPNB	25.0	8.7×10^{-2} [d]	25.1	−6.9	$^1/_{27}$	
		75.0	44.7				
		100.0	540				
VIII[h]	*exo*-8-OPNB	25.0	14.5	24.6	2.0	6.1	11,600
		50.0	393				

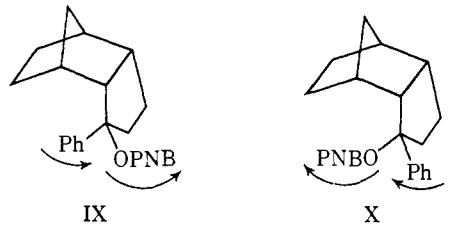
[a] The solvolyses were carried out in 80% aqueous acetone. [b] Rate relative to the cyclopentyl derivative. [c] H. C. Brown, D. L. Vander Jagt, P. von R. Schleyer, R. C. Fort, Jr., and W. E. Watts, *J. Am. Chem. Soc.*, **91**, 6848 (1969). [d] Calculated from data at other temperatures. [e] Mp 151.5–152°. [f] Mp 124–125°. [g] Mp 153 dec. [h] Mp 175° dec.

It should be noted that this rate retardation is achieved in spite of the much higher ground-state energy of V, as compared to IV.[2]

There would appear to be little doubt that 1-phenylcyclopentyl *p*-nitrobenzoate should be an excellent model for VI and VII, where the reactive groups are on the *endo* cyclopentyl rings of the structure. Both VI and VII exhibit reduced rates, $^1/_{1900}$ and $^1/_{27}$, again in accordance with expectations in terms of steric hindrance to ionization. Also in terms of this concept, the effect is much larger at the more hindered 8 position (VI) than at the less hindered (more flexible) 9 position.[1,2]

On the other hand, the *exo* isomer VIII actually solvolyzes at a rate 6.1 times greater than that of the parent system. Evidently this is a reflection of the fact that ionization in the *exo* isomer is not hindered. These rates for VI and VIII lead to an enormous *exo*:*endo* rate ratio of 11,600!

We cannot attribute this *exo*:*endo* rate ratio to σ participation in view of the evidence that tertiary benzylic cations are too stable to utilize saturated σ electrons for additional stabilization.[5–7] We cannot attribute this high *exo*:*endo* rate ratio to relief of ground-state strain. All available evidence is that the steric requirements of a phenyl substituent and a *p*-nitrobenzoate group must be very similar.[8] How then can we account for the fact that the two transition states evidently differ greatly in stability, by some 5.5 kcal/mole (Figure 1)?



IX

X

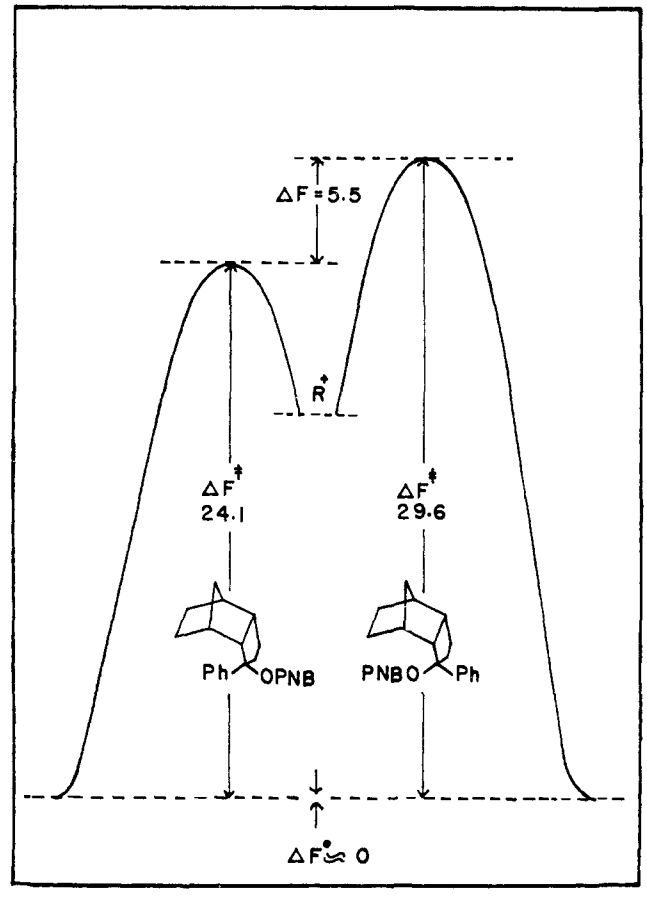


Figure 1. Free energy diagram for the solvolysis of the 8-phenyl-*endo*-5,6-trimethylene-8-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25° (all numbers in kcal/mole).

Again it appears that we must fall back on steric effects. In the *endo* isomer strains will be enhanced in the transition state as the leaving group rotates into the cavity of the U-shaped structure (X), whereas in the *exo*

(5) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **91**, 1545 (1969).
(6) H. C. Brown, S. Ikegami, and K.-T. Liu, *ibid.*, **91**, 5911 (1969).
(7) A detailed pmr study of the 2-phenylnorbornyl cation led the authors to conclude that there is no detectable charge delocalization from the 2- to the neighboring 1 position: D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969).
(8) M.-H. Rei and H. C. Brown, *ibid.*, **88**, 5335 (1966).

isomer such strains will be diminished[9] as both the phenyl and *p*-nitrobenzoate groups rotate away from the crowded environment (IX).

In the past high *exo*:*endo* rate ratios in bicyclic systems have invariably been interpreted in terms of σ participation in the *exo* isomers. It should now be clear that we can achieve even higher *exo*:*endo* rate ratios in bicyclic systems in derivatives where σ participation cannot be significant. Consequently, it becomes necessary to consider each case individually in order to decide whether the observed *exo*:*endo* rate ratio is indeed the result of σ participation or whether it is the result of the operation of steric effects.

(9) By introducing methyl groups into the norbornyl system at appropriate positions to alter such strains, it proved possible to change the *exo*:*endo* rate ratio from 885 observed in the parent 2-methyl-2-norbornyl *p*-nitrobenzoates to a low of 6.1 for the 7,7-dimethyl derivative and to a high of 3,630,000 for the 6,6-dimethyl derivative: H. C. Brown and S. Ikegami, *J. Am. Chem. Soc.*, **90**, 7122 (1968); S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968).

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

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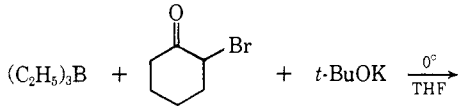
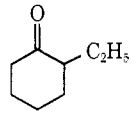
Reaction of Organoboranes with Bromoacetone under the Influence of Potassium 2,6-Di-*t*-butylphenoxide. A Convenient Procedure for the Conversion of Olefins into Methyl Ketones *via* Hydroboration

Sir:

We previously reported that trialkylboranes react with representative α-bromo ketones under the influence of potassium *t*-butoxide in tetrahydrofuran, providing the corresponding α-monoalkylated ketones in good yields[1,2] (eq 1–3).

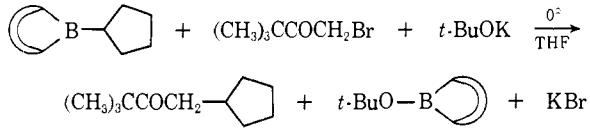


$$(C_2H_5)_3B + \text{cyclohexanone, 2-Br} + t\text{-BuOK} \xrightarrow[\text{THF}]{0^\circ}$$



$$+ t\text{-BuOB}(C_2H_5)_2 + KBr \quad (1)$$

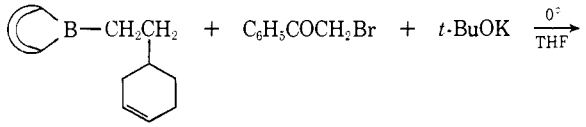
68%



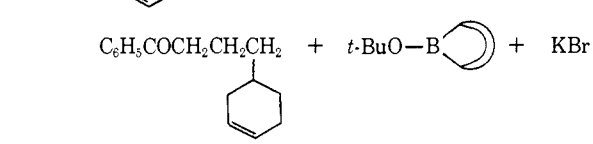
$$\text{B-cyclopentyl} + (CH_3)_3CCOCH_2Br + t\text{-BuOK} \xrightarrow[\text{THF}]{0^\circ}$$

$$(CH_3)_3CCOCH_2\text{-cyclopentyl} + t\text{-BuO-B} + KBr \quad (2)$$

77%



$$\text{B-CH}_2\text{CH}_2\text{-cyclohexene} + C_6H_5COCH_2Br + t\text{-BuOK} \xrightarrow[\text{THF}]{0^\circ}$$



$$C_6H_5COCH_2CH_2CH_2\text{-cyclohexene} + t\text{-BuO-B} + KBr \quad (3)$$

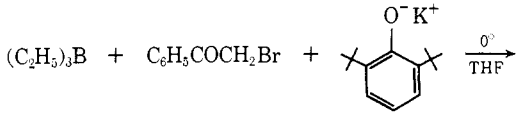
60%

(1) H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Am. Chem. Soc.*, **90**, 6218 (1968).
(2) H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969).

We pointed out that once the reaction had been demonstrated to proceed satisfactorily with a particular α-halo ketone, it appeared to proceed satisfactorily with a wide variety of alkyl groups in the form of R_3B or B-R-9-BBN derivatives.[2] Unfortunately, the reaction proved to be quite sensitive to the structure of the α-halo ketone, and all our attempts to extend it to α-bromoacetone failed. This was especially disappointing because the successful alkylation of this derivative would provide a new, highly convenient synthesis of methyl ketones, very useful synthetic intermediates.

It appeared to us that the difficulty might lie in the use of potassium *t*-butoxide as the base. This is an exceptionally strong base, and α-halo ketones are extraordinarily sensitive to the action of such bases.[3] Accordingly, we decided to screen a large number of bases, using the reaction of phenacyl bromide and triethylborane as a model system. Although a number of promising bases were discovered, the most satisfactory proved to be 2,6-di-*t*-butylphenoxide, a base which does not appear to have been previously utilized for condensation reactions in organic chemistry.

Presence of the large alkyl substituents in the *ortho* positions appears to be highly favorable for the desired reaction. Thus the yield of product (*n*-butyrophenone) was 2% with potassium phenoxide, 24% with the 2-methyl derivative, 75% with the 2,6-dimethyl, and 98% with the 2,6-di-*t*-butyl compound (eq 4). Possi-

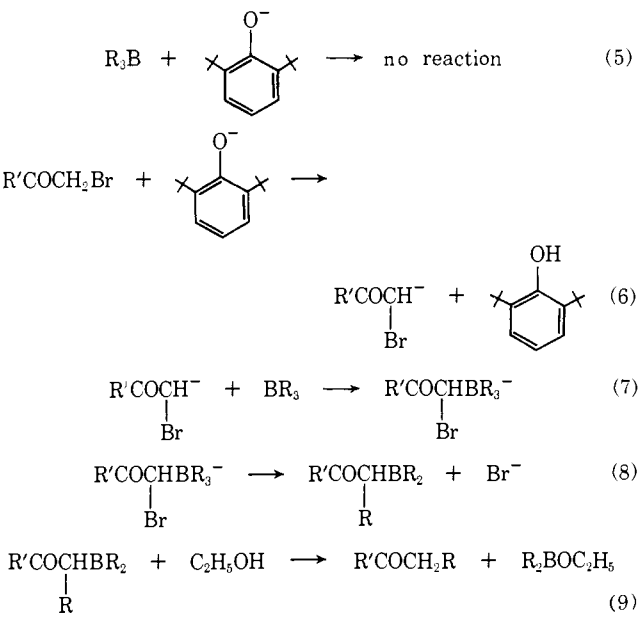


$$(C_2H_5)_3B + C_6H_5COCH_2Br + \text{2,6-di-t-Bu-C}_6\text{H}_3\text{O}^-K^+ \xrightarrow[\text{THF}]{0^\circ}$$

$$C_6H_5COCH_2CH_2CH_3 + (C_2H_5)_2BOR + KBr \quad (4)$$

98%

bly, the bulky substituents prevent the organoborane from coordinating with the base (eq 5). Consequently, when the base acts on the α-halo ketones to produce the α-halo carbanion (eq 6), the latter is immediately removed by reaction with the free, uncomplexed organo-



$$R_3B + \text{2,6-di-t-Bu-C}_6\text{H}_3\text{O}^- \longrightarrow \text{no reaction} \quad (5)$$

$$R'COCH_2Br + \text{2,6-di-t-Bu-C}_6\text{H}_3\text{O}^- \longrightarrow$$

$$R'\underset{\underset{Br}{|}}{C}HCO^- + \text{2,6-di-t-Bu-C}_6\text{H}_3\text{OH} \quad (6)$$

$$R'\underset{\underset{Br}{|}}{C}HCO^- + BR_3 \longrightarrow R'\underset{\underset{Br}{|}}{C}HCOBR_3^- \quad (7)$$

$$R'\underset{\underset{Br}{|}}{C}HCOBR_3^- \longrightarrow R'\underset{\underset{R}{|}}{C}HCOBR_2 + Br^- \quad (8)$$

$$R'\underset{\underset{R}{|}}{C}HCOBR_2 + C_2H_5OH \longrightarrow R'COCH_2R + R_2BOC_2H_5 \quad (9)$$

(3) See H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, for a discussion of the use of various bases for condensations, with pertinent literature references.