Structural Effects in Solvolytic Reactions. 27. Solvolysis of the *exo*- and *endo*-1,2-Diphenyl-2-norbornyl and -1,2-Dimethyl-2-norbornyl *p*-Nitrobenzoates and Chlorides. Definitive Evidence for the Classical Nature of the 1,2-Disubstituted Tertiary 2-Norbornyl Cations and Implications for the Structure of the Parent 2-Norbornyl Cation[1]

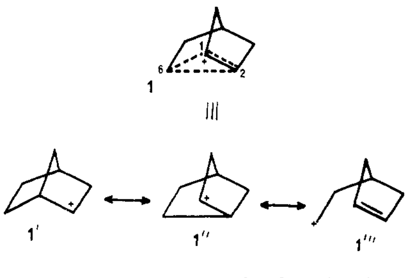
Herbert C. Brown,* M. Ravindranathan,[2] C. Gundu Rao,[2] Frank J. Chloupek,[3] and Min-Hon Rei[3]

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

Received March 27, 1978

exo- and *endo*-1,2-diphenyl- and -1,2-dimethyl-2-norbornyl *p*-nitrobenzoates were synthesized and their rates of solvolysis determined in 80% aqueous acetone. The tertiary chlorides were also synthesized and their rates of solvolysis measured in 100% ethanol. The exo/endo rate ratios for the solvolysis of 1,2-diphenyl-2-norbornyl *p*-nitrobenzoates (350) and of 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates (564) are similar to the ratios observed for the corresponding tertiary 2-phenyl and 2-methyl derivatives, as well as to those for the secondary 2-norbornyl tosylates. Similarly, the exo/endo ratio observed for the 1,2-dimethyl-2-norbornyl chlorides (178) is similar to the value previously determined for the epimeric 2-norbornyl chlorides (170). Consequently, the presence of substituents at the 2 position or at the 1,2 positions has little effect upon the observed exo/endo rate ratios. The introduction of a 1-phenyl substituent into the 2-phenyl-2-norbornyl *p*-nitrobenzoate does not increase, but decreases significantly the rate of solvolysis (by factors of 21 in the exo and 58 in the endo). A 1-methyl substituent, introduced into 2-methyl-2-norbornyl *p*-nitrobenzoate, increases the rate. The effect is the same in both the exo (8.5) and the endo (8.6). Similar effects were realized for the ethanolysis of the corresponding tertiary chlorides. The effects of the 1-phenyl and 1-methyl substituents reveal the absence of significant charge delocalization from the 2 to the 1 position in the solvolytic process. It is concluded that these tertiary derivatives must undergo solvolysis without σ bridging and accompanying charge delocalization to the 1 position associated with such bridging. Yet the free-energy diagram for the solvolysis of 1,2-dimethyl-2-norbornyl *p*-nitrobenzoate is remarkably similar to 2-methyl-2-norbornyl *p*-nitrobenzoate and to 2-norbornyl tosylate. It does not appear reasonable to attribute such similar behavior to the operation of totally different physical phenomena. Yet such has been claimed. Three such proposals which have been advanced are considered and refuted on the basis of available experimental data. Comparison of the rate of solvolysis of 2-methyl-*endo*-norbornyl chloride with that for *endo*-norbornyl chloride reveals a relative rate of 53 000. Ignoring minor differences in the ground state energies, this yields a difference in the energies of the tertiary and secondary transition states of 6.5 kcal mol^{-1}. This corresponds to an estimated difference in energy of the 2-methyl-2-norbornyl cation and 2-norbornyl cation under stable ion conditions of 7.5 kcal mol^{-1} and a difference in the calorimetric heats of ionization of 2-methyl-*exo*-norbornyl chloride and of *exo*-norbornyl chloride in SO_2ClF of 7.4 kcal mol^{-1}. These results establish that the magnitude of the positive charge at the developing cationic center in these transition states must approach that in the intermediate ions or ion pairs, providing strong support for the validity of the Hammond postulate as applied to solvolytic processes. The similarity in the tertiary/secondary rate ratio for the exo isomers to the value for the endo isomers supports the absence of any significant nonclassical resonance contribution to the rate of solvolysis of *exo*-norbornyl derivatives. These data yield essentially identical values of 2-Me/2-H, 5.3 × 10^4 for endo and 5.5 × 10^4 for exo, incompatible with the presence of major nonclassical resonance contributions in the exo secondary and its reduction or absence in the exo tertiary. Other approaches for extrapolating from the tertiary derivatives to the secondary fail to support the presence of a major nonclassical resonance contribution in the exo secondary, absent in the endo secondary and in the exo and endo tertiary derivatives, as postulated in some current proposals.

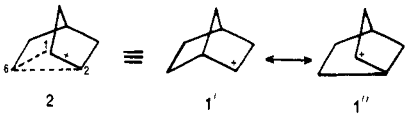
The proposed nonclassical structure (1) for the 2-norbornyl cation distributes positive charge from the 2 position to the 1 and 6 carbon atoms[4] (eq 1). The nonclassical ion (1)



(1)

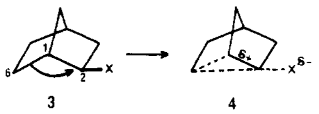
was considered to be a resonance hybrid of the three canonical structures, 1′, 1″, and 1‴. In this interpretation, the charge is not delocalized from the cationic center by hyperconjugation, but involves a specific σ bridge, converting the unsymmetrical classical structure (corresponding to 1′) into the nonclassical structure (1) with a plane of symmetry.

It was later suggested that this last structure (1‴) does not contribute significantly to the resonance hybrid.[5] Consequently, only canonical structures 1′ and 1″ need now be considered as significant contributors to the resonance hybrid (eq 2).



(2)

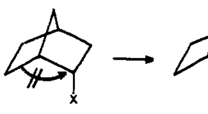
This structure implies that significant portions of the positive charge of the carbocation are distributed equally to C-1 and C-2. The transition state for a solvolytic process leading to such an intermediate is believed to be close to the carbocation produced.[6] Consequently, in the transition state (4) for the solvolysis of an *exo*-norbornyl derivative (3), a significant portion of the developing positive charge at C-2 should be delocalized to C-1 (eq 3). On the other hand, in the



(3)

endo isomer (5) the 1,6-bonding pair is postulated to be stereoelectronically unfavorable for such participation (eq 4).

0022-3263/78/1943-3667$01.00/0

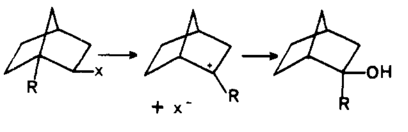


5 **6** (4)

Consequently, the mechanism for the delocalization of charge from C-2 to C-1, which operates in the exo isomer, cannot be effective in the transition state for the endo isomer (**6**). It follows that there should be far less delocalization of charge from C-2 to C-1 in **6**, as compared to **4**. Accordingly, a reasonable test of the nonclassical proposal for 2-norbornyl would appear to be an examination of the relative magnitudes of the charge delocalization from C-2 in the transition states for the solvolysis of appropriate *exo*- and *endo*-norbornyl derivatives.

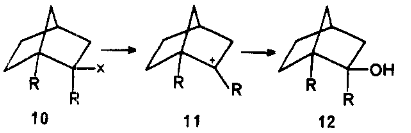
A frequently used test of this kind is the introduction of a phenyl or methyl group into the position being probed.[1b] These substituents provide electron density on demand to satisfy electron deficiencies at the carbon atoms to which they are attached. The 2 position in the transition state for a solvolyzing *endo*-norbornyl derivative should possess a far higher electron deficiency than the 2 position of the corresponding exo isomer, partially satisfied as the latter would be by electronic contributions from the 1,6-bonding pair. Therefore, 2-Me or 2-Ph should exhibit considerably greater activating effects on the endo isomers than on the corresponding exo isomers.

It is not possible to test in this way for such charge delocalization at C-1. The introduction of a phenyl or methyl group at C-1 produces a species (**7**) which undergoes solvolysis only with rearrangement to the tertiary cation[7] (**8**), subsequently converted to the tertiary derivatives (**9**) (eq 5). Consequently, such derivatives contain an internal driving force to produce in the solvolysis the more stable tertiary cation, so that it becomes difficult to utilize the effect of substituents at C-1 as a probe of the magnitude of the charge delocalization to C-1.

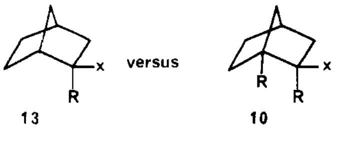


7 **8** **9** (5)

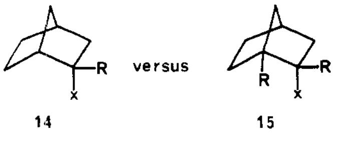
Fortunately, these difficulties can be avoided by introducing the substituent into the related 2-substituted-2-norbornyl derivative. This structural modification converts the molecule into a system (**10**) which undergoes solvolysis into a tertiary cation (**11**), without rearrangement to a more stable structure (eq 6). We are now in a position to observe whether a phenyl or methyl substituent, represented by R, introduced into the exo isomer (**13** → **10**) is far more effective than the same substituent introduced into the endo isomer (**14** → **15**) (eq 7 and 8).



10 **11** **12** (6)



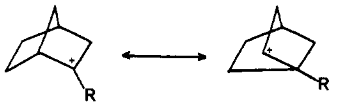
13 **10** (7)



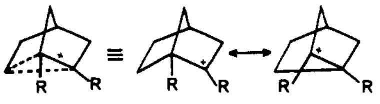
14 **15** (8)

Note that the predicted effects of introducing such groups at C-2 are opposite to those for introducing the groups at C-1 for systems involving nonclassical resonance. At C-2 the rate-enhancing effect of the groups should be larger for the endo isomer. At C-1 the rate-enhancing effects of the groups should be larger for the exo isomer. *In the absence of nonclassical resonance, similar effects of such groups would be anticipated for both epimers.*

There was still another question we wished to answer. It has been argued that resonance is possible in the 2-norbornyl cation because the two canonical structures (**1**′ and **1**″) are equivalent with identical energies (eq 2). On the other hand, in a tertiary cation, such as 2-phenyl- or 2-methyl-2-norbornyl (**16**), the two canonical structures (**16** and **17**) differ greatly in energies. Whatever the level of resonance stabilization in a nonclassical 2-norbornyl system (**1** ≡ **1**′ ↔ **1**″), it should be much less[8] in **16** (eq 9). However, in symmetrically disubstituted 1,2-norbornyl cations, the two canonical structures (**18**′ and **18**″) are again equivalent (eq 10). Will nonclassical resonance, of the kind postulated to be present in 2-norbornyl (eq 2), now return? If so, the 1-R substituent should exhibit an enormously greater effect in the exo isomer (eq 7) compared with the endo isomer (eq 8).



16 **17** (9)



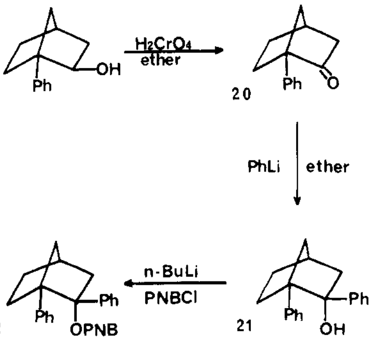
18 **18**′ **18**″ (10)

Accordingly, we undertook to synthesize and to determine the rates of solvolysis of *exo*- and *endo*-1,2-diphenyl-2-norbornyl and 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone and the corresponding chlorides for solvolysis in 100% ethanol.

Finally, attention is called to the study of the related 1,2-di-*p*-anisyl-2-norbornyl,[9] 1,2-diphenyl-2-norbornyl,[10] and 1,2-dimethyl-2-norbornyl[11] cations under stable ion conditions, and to the highly pertinent studies on the solvolysis of optically active 1,2-dimethyl-2-norbornyl derivatives.[12,13] These studies will be incorporated into the discussion of the present results.

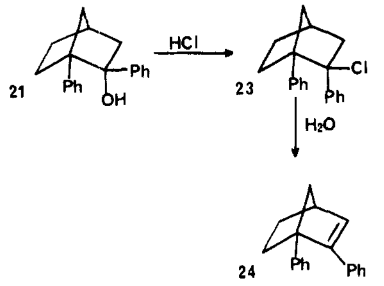
Results

Synthesis. 1-Phenyl-*exo*-norbornanol[14] (**19**) was oxidized to 1-phenylnorbornanone (**20**) by aqueous chromic acid, utilizing the two-phase oxidation procedure.[15] Addition of phenyllithium in ether provided 1,2-diphenyl-*endo*-norbornanol[14] (**21**), converted to the *p*-nitrobenzoate (**22**) by treatment with *n*-butyllithium and *p*-nitrobenzoyl chloride in THF[16] (eq 11).

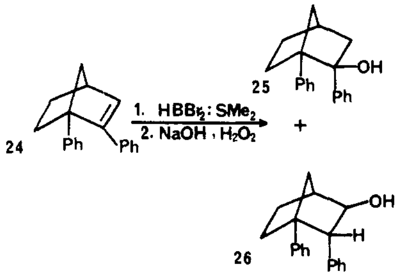


19 **20** **21** **22** (11)

Major problems were encountered in the synthesis of the exo isomer. The standard procedure to obtain the exo isomer through solvolysis of the exo chloride (**23**) or the endo OPNB (**22**) failed. Only the corresponding olefin, 1,2-diphenylnorbornene (**24**), was produced (eq 12). Attempts to hydrate **24** by oxymercuration–demercuration[17] or by synthesis of the epoxide[18] followed by reduction[19] failed. However, hydroboration of **24** by $HBBr_2/SMe_2$[20] followed by oxidation with alkaline hydrogen peroxide gave a mixture of approximately 10% of the desired 1,2-diphenyl-*exo*-norbornanol (**25**) with the isomeric secondary alcohol (**26**) (eq 13). The alcohol mixture was converted into the mixed *p*-nitrobenzoates and most of the secondary isomer was removed by fractional crystallization. The resulting product, containing approximately 40% of the *p*-nitrobenzoate (**27**) of **25**, proved satisfactory for the solvolytic study. The secondary *p*-nitrobenzoate showed no evidence of undergoing solvolysis under the conditions used to solvolyze the desired tertiary isomer.

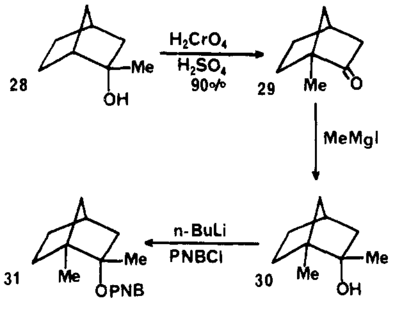


(12)



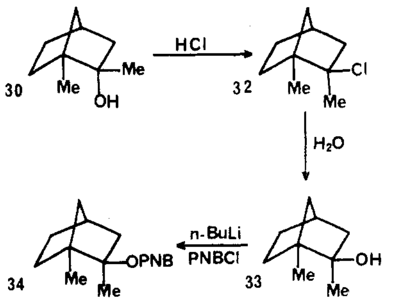
(13)

2-Methyl-*endo*-norbornanol (**28**) was converted to 1-methylnorbornanone (**29**) by means of a combined isomerization–oxidation technique. The ketone (**29**) was treated with methylmagnesium iodide to form 1,2-dimethyl-*endo*-norbornanol[21] (**30**). The alcohol was then converted into the *p*-nitrobenzoate (**31**) by the usual procedure[16] (eq 14). The endo alcohol (**30**) was converted into the exo chloride (**32**) by treatment with hydrogen chloride in an automatic hydrochlorinator.[22] The chloride was then hydrolyzed in buffered aqueous acetone to yield 1,2-dimethyl-*exo*-norbornanol (**33**), which was converted into the *p*-nitrobenzoate[16] (**34**) (eq 15).

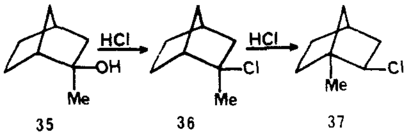


(14)

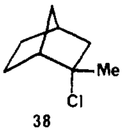
Treatment of 2-methyl-*exo*-norbornanol (**35**) with hydrogen chloride yields 2-methyl-*exo*-norbornyl chloride[21,23] (**36**). On further contact with hydrogen chloride rearrangement occurs to the secondary chloride[24] (**37**) (eq 16). There appears to be no method now available to prepare 2-methyl-*endo*-norbornyl chloride (**38**).



(15)

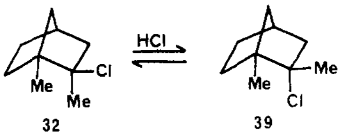


(16)



38

Fortunately, treatment of 1,2-dimethyl-*exo*-norbornyl chloride (**32**) with hydrogen chloride takes another course. Here, isomerization to the secondary chloride is not feasible. Instead, there is an isomerization to another isomer, identified as 1,2-dimethyl-*endo*-norbornyl chloride (**39**) (eq 17).



(17)

The formation of the second isomer can be followed by the appearance of two new methyl peaks in the ^1H NMR spectrum and by the formation of an isomer which undergoes solvolysis at a rate $^1/_{178}$ that of the original chloride. Both isomeric chlorides, which were not separated, undergo hydrolysis to the same alcohol (**33**). At equilibrium the two chlorides are present in the ratio 70% **32**/30% **39**.

Equilibration of 1,2-Dimethyl-2-norbornanols. The exo and endo alcohols, **30** and **33**, were dissolved in cyclohexane (0.2 M solutions) and isomerized under the influence of 6 M sulfuric acid at room temperature. GC analysis of aliquots revealed an equilibrium distribution of 72% exo and 28% endo, similar to the equilibrium distribution for the chlorides, 70% **32** and 30% **39**.

Rates of Solvolysis. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone by the titrimetric procedure.[16] In our earlier studies,[1a] we had utilized 60% aqueous dioxane as the solvolytic medium, following Bartlett and Stiles.[25] However, we observed that this medium was not a satisfactory solvent for the slower compounds. Competitive reaction with oxygen produced acid, resulting in erratic, somewhat high values for the slower endo derivatives. Accordingly, we shifted to aqueous acetone on the recommendation of R. C. Fort and P. v. R. Schleyer and this has proven to be a far superior medium. Accordingly, we redetermined the kinetic data for the isomeric 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates utilizing aqueous acetone and only these data are here reported. The pertinent rate data are summarized in Table I.

The rates of solvolysis of the tertiary chlorides were determined in 100% ethanol. The differential method was employed for determining the rate constants for 1,2-dimethyl-*exo*- and -*endo*-norbornyl chlorides.[26] The available rate data for the

Table I. Rates of Solvolysis of 1,2-Dimethyl-2-norbornyl and 1,2-Diphenyl-2-norbornyl *p*-Nitrobenzoates and Related Derivatives in 80% Aqueous Acetone

OPNB	isomer	$k_1 \times 10^6$ s^{-1} T_1, °C	T_2, °C	25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	exo/endo, 25 °C	rel rate, 25 °C	
2-CH$_3$[a]	exo	94.6 (100)	6.94 (75)	0.010[b]	26.3	−7.0	885	1.00	
	endo	54.7 (150)	5.41 (125)	1.13×10^{-5} [b]	30.1	−7.5			1.00
1,2-(CH$_3$)$_2$	exo[e]	40.0 (75)	1.91 (50)	5.45×10^{-2} [b] (8.44×10^{-2})[c]	26.6	−2.5	564 (875)[c]	5.45 (8.5)[c]	
	endo[f]	41.4 (125)	3.11 (100)	9.67×10^{-5} [b]	30.0	−3.8			8.6
2-Ph[d]	exo		179 (50)	7.56	23.6	−2.7	127	1.00	
	endo	364 (100)	30.2 (75)	0.059[b]	25.1	−7.4			1.00
1,2-Ph$_2$	exo[g]	168 (75)	9.86 (50)	0.36[b]	24.8	−4.9	350	0.048	
	endo[h]	204 (125)	17.9 (100)	1.03×10^{-3} [b]	28.2	−5.2			0.0174

[a] Reference 47. [b] Calculated from data at higher temperatures. [c] Values in parentheses are k_α values, $k_\alpha/k_t = 1.55$ in 90% aqueous acetone at 25 °C (ref 12), assumed to be the same in 80% aqueous acetone. [d] Reference 46. [e] Registry no.: 13351-32-1. [f] Registry no.: 13351-31-0. [g] Registry no.: 67162-93-0. [h] Registry no.: 67162-94-1.

Table II. Rates of Ethanolysis for Norbornyl Chlorides

system	isomer	registry no.	$k_1 \times 10^{-6}$ s^{-1} T_1, °C	T_2, °C	25 °C	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	exo/endo
2-norbornyl	exo[a]	765-91-3	175 (99.7)[b]	38.8 (85)[c]	0.0236[d] (5.42×10^{-4})[f]	26.6	−4.8	170[e]
	endo[a]	2999-06-6		0.56 (85)[c]	1.40×10^{-4} [g] (3.2×10^{-6})[f]			
2-methyl-2-norbornyl	exo	19138-54-6		0.754 (0)	30.0	23.3	−1.2	
	endo	6196-86-7			0.168[h]			178
1,2-dimethyl-2-norbornyl	exo	35033-23-9		6.03 (0)	210	22.6	−0.6	
	endo	6564-96-1			1.18			178
2-phenyl-2-norbornyl	exo	16166-72-6		9080 (0)	158000	17.9	−2.2	
1,2-diphenyl-2-norbornyl	exo	67162-95-2		542 (0)	11300	19.1	−3.5	
2-*p*-anisyl-2-norbornyl	exo[i]				2.55×10^8			

[a] In 80% ethanol. [b] Reference 27b. [c] Reference 27a. [d] Calculated from data at higher temperatures. [e] Calculated from the exo/endo rate ratio at 85 °C (70) assuming constant entropy. [f] Rate constant in ethanol. Calculated from the rate of chloride in 80% ethanol using the factor for the tosylates, $k_{1,\ 80\%\ \mathrm{EtOH}}/k_{1,\ \mathrm{EtOH}} = 43.5$; M.-H. Rei, Ph.D. Thesis, Purdue University, 1967. [g] Calculated from the exo/endo rate ratio of 170 at 25 °C. [h] Calculated from the rate of 1,2-dimethyl-*endo*-norbornyl chloride, assuming the effect of the 1-methyl substituent to be the same as in the exo isomers ($k_{1,2\text{-dimethyl-}exo\text{-}}/k_{2\text{-methyl-}exo\text{-}} = 7.0$). This assumption appears to be valid; see text. [i] H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, 88, 5336 (1966).

ethanolysis of the tertiary and secondary 2-norbornyl chlorides are summarized in Table II.

We wished to compare the rates of ethanolysis of *exo*- and *endo*-norbornyl chlorides at 25 °C with our values for the tertiary chlorides. Data were available for the solvolysis in 80% ethanol of *exo*-norbornyl chloride at 85 and at 99.7 °C and of *endo*-norbornyl chloride at 85 °C.[27] The exo/endo rate ratio of 70 at 85 °C calculates to be 170 at 25 °C, in good agreement with the value of 178 for 1,2-dimethyl-2-norbornyl chloride. The rate constant for the unknown 2-methyl-*endo*-norbornyl chloride was calculated from the rate for 1,2-dimethyl-*endo*-norbornyl chloride by assuming that the effect of the 1-methyl substituent was the same as in the exo isomers ($k_{1,2\text{-dimethyl-}exo\text{-}}/k_{2\text{-methyl-}exo\text{-}} = 7.0$). These values are included in Table II.

Alternatively, we could have estimated the rates for *exo*- and *endo*-norbornyl chlorides by proceeding from the tosylates, correcting from tosylate to chloride.[1b] Similarly, we could have proceeded from the rate constant for 2-methyl-*endo*-norbornyl *p*-nitrobenzoate (Table I) to the value for the chloride by correcting for the leaving group.[28] In fact, the values are very similar. However, the procedure adopted involves much smaller corrections. It also avoids the uncertainty involved in the usual assumption of a constancy in the correction factors for different leaving groups.[29,30]

Discussion

As was pointed out earlier, the nonclassical 2-norbornyl cation (**2**) is stabilized by resonance involving two equivalent canonical structures (**1′** and **1″**). Such resonance should be considerably lower in tertiary 2-norbornyl cations where the two canonical structures (**16** and **17**) differ considerably in their energies.[8] It was a major objective of the present study to examine the possibility that the introduction of a substituent at C-1, identical with that at C-2 (**18**), would again provide two equivalent canonical structures (**18′** and **18″**), resulting in an increase of the nonclassical resonance in the system. Such an increase could readily be detected in the transition state by comparing the effect of the substitutent at C-1 in the exo isomer as compared to that produced in the endo isomer.

The rate constant for ethanolysis of 2-methyl-*endo*-norbornyl chloride is 53 000 times that for *endo*-norbornyl chloride (Table II). Ignoring small differences in the ground-state energies, this means that the transition state for the solvolysis of the tertiary chloride must be 6.5 kcal mol^{-1} more stable than that for the corresponding secondary chloride.

To the extent that solvent participation contributes to the transition state for the secondary chloride, the difference will be even larger. However, recent studies have revealed that solvent participation is not significant in the solvolysis of both *exo*- and *endo*-norbornyl derivatives.[31,32] Consequently, it appears reasonable to ignore what can only be quite minor contributions of this kind by the usual solvolytic media.

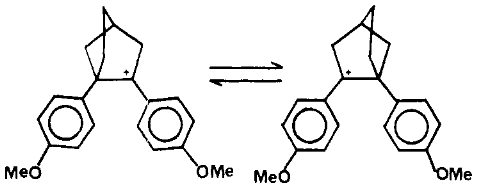
According to the Hammond postulate, the transition state for solvolysis should be close to the first intermediate, the corresponding free ion or ion pair.[6] Therefore, the secondary and tertiary 2-norbornyl cations (or ion pairs) should differ in energy by a quantity somewhat larger than 6.5 kcal mol^{-1}.

Under stable ion conditions, the tertiary 2-methyl-2-norbornyl cation is estimated to be some 7.5 kcal mol^{-1} more stable than the secondary 2-norbornyl cation.[33] Similarly, the difference in the calorimetric heats of ionization of 2-methyl-*exo*-norbornyl and *exo*-norbornyl chlorides in SO_2ClF has recently been determined to be 7.4 kcal mol^{-1}.[34] These values are in excellent agreement with the value derived from the relative rates and the Hammond postulate.[6] Resonance involving canonical structures which differ in energies by 6.5–7.5 kcal mol^{-1} should not be large.

In the same way, the two canonical structures for 2-phenyl-2-norbornyl cation (**16**, R = Ph) can be estimated to differ in energies by somewhat more than 12 kcal mol^{-1}. The corresponding structures for the 2-*p*-anisyl-2-norbornyl cation should differ in energies by some 15 kcal mol^{-1}.

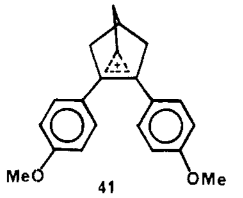
Consider the consequences of introducing a substituent at C-1, identical with the substituent at C-2 (eq 10). In the endo isomer, the substituent will have little effect, since σ bridging is postulated not to occur in the endo isomer (eq 8). However, in the exo isomer (eq 7), return of all or part of the resonance energy should bring about rate increases of 10^3–10^6 or even greater. Thus we should observe large unambiguous effects of the 1-R substituent in systems where nonclassical resonance returns or increases.

The 1,2-Di-*p*-anisyl-2-norbornyl System. We did not undertake an examination of this interesting system. It had been examined under stable ion conditions and unambiguous evidence had been obtained for its classical nature[9] (eq 18).



40 40′ (18)

The ion was generated in concentrated sulfuric acid. The UV spectrum was similar to that of the 2-*p*-anisyl-2-norbornyl cation, without the changes anticipated for extended conjugation in a symmetrical σ-bridged cation (**41**).



41

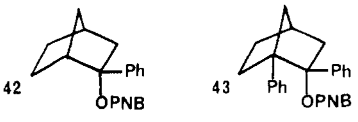
The 2-*p*-anisyl-2-norbornyl cation is half formed from the carbinol in 41% sulfuric acid. To form the ion **40** ⇌ **40′** requires more (51%), not less concentrated sulfuric acid. This is not in accord with greater stabilization of the cation by the cumulative effect of two *p*-anisyl groups, as in **41**.

The 2-*p*-anisyl-2-norbornyl cation does not react easily with bromine, evidently because the *p*-anisyl group is conjugated with the cationic center. The 1,2-di-*p*-anisyl cation takes up bromine in <1 min, corresponding to the presence of a nonconjugated *p*-anisyl group, as in **40** ⇌ **40′**.

Finally, on cooling solutions of the cation to low temperatures (−70 °C), changes in the ^1H NMR spectrum are observed which indicate impending nonequivalence of the two aryl rings.

It has been argued that these results should not be generalized to other systems. First, steric effects could prevent the two *p*-anisyl groups from being coplanar for optimum conjugation in **41**.[35,36] (However, such steric difficulties do not prevent the three *p*-anisyl groups in the more crowded tri-*p*-anisylmethyl cation from stabilizing the system: pK_R for *p*-An_3C^+ 0.82; *p*-An_2CH^+ −1.24).[37] Second, Winstein has suggested that highly stable 2-norbornyl cations, stabilized by extreme groups, such as 2-*p*-anisyl, should be classical.[38] However, he implied that less stabilizing groups, such as phenyl and methyl, could provide nonclassical cations. Accordingly, these were the focus of our studies.

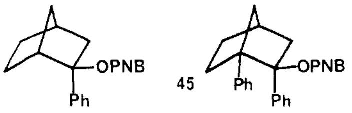
The 1,2-Diphenyl-2-norbornyl System. The introduction of a phenyl group at the 2 position of norbornyl increases the rate of hydrolysis over the parent compound by a factor of approximately 10^9 (Table II). The introduction of a phenyl group into the 1 position (**43**) in 2-phenyl-*endo*-norbornyl *p*-nitrobenzoate (**42**) does not increase the relative rate (RR), but decreases it by a factor of 58 (eq 19). Evidently, the combined inductive and steric effects of the 1-Ph substituent are responsible; no significant electronic contribution is anticipated for this isomer. The critical case is the exo isomer.



42 43 (19)

RR(25°C) 1.00 1/58

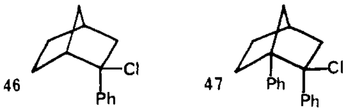
The presence of a 1-Ph substituent in 1,2-diphenyl-*exo*-norbornyl *p*-nitrobenzoate (**45**) does not result in any enhanced rate. Indeed, there is an actual decrease by a factor of 21 over the parent compound (**44**) (eq 20).



44 45 (20)

RR(25°C) 1.00 1/21

In the corresponding chlorides (**46** and **47**), the factor is similar, 16 (eq 21).

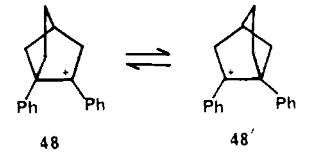


46 47 (21)

RR(25°C) 1.00 1/16

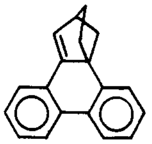
The exo/endo rate ratio for **45**/**43** is 350, slightly larger than the value of 127 realized for the parent system **44**/**42**. This increase in the exo/endo rate ratio arises not from any increase in the rate of the exo isomer (**45**), but from a comparative decrease in the rate of the endo isomer (**43**). Possibly, the decrease arises from the enhanced steric difficulties afforded by the 1-Ph substituent to the departure of the endo leaving group.[39]

Examination of the 1,2-diphenyl-2-norbornyl cation (**48**) by NMR has confirmed the conclusion that the system is best described as a pair of rapidly equilibrating classical cations[10] (eq 22).

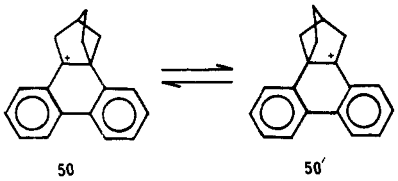


48 48′ (22)

The steric argument for the failure of both aryl groups in **41** and its equivalent phenyl derivative to conjugate and thereby stabilize the nonclassical structure is rendered questionable by a study of the behavior of the phenanthrene derivative[40] (**49**) (eq 23). This olefin **49** dissolves in fluorosulfonic acid to give a pair of classical equilibrating cations,



49

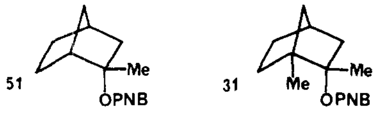


50 50′ (23)

50 $\rightleftharpoons$ **50′**, recognizable by the UV and ^{1}H NMR spectra.[40]

The 1,2-Dimethyl-2-norbornyl System. Aryl groups can, on occasion, be treacherous as a probe for electron delocalizations. If the system makes only a small demand on the aryl substituent for electrons, the −I effect of the aryl group can predominate over the +R effect.[41] As discussed earlier, steric inhibition to resonance can also be a factor.[42] However, methyl substituents appear to be free of these ambiguities. They exert consistent electron-supplying effects, +I and +R, and these effects do not appear to be susceptible to steric influences. Accordingly, the study of the 1,2-dimethyl-2-norbornyl system was emphasized.

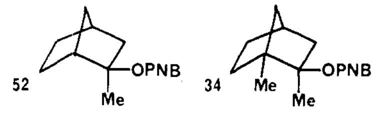
The introduction of a methyl group into the 1 position of the endo isomer (**51**) increases the rate of solvolysis of the *p*-nitrobenzoate (**31**) by a factor of 8.6 (eq 24). Presumably, the increase is the result of the combined steric and inductive effects of the 1-methyl substituent.



(24)

RR(25 °C) 1.00 8.6

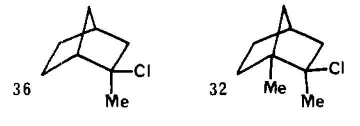
The question is the effect of a 1-methyl substituent (**34**) on the exo isomer (**52**). If the 1-methyl group were to induce the return or increase of nonclassical resonance to the cation and to the transition state modeling the cation,[6] such stabilization should result in a major rate enhancement, as high as 10^3–10^6. However, this is not observed. The rate enhancement (eq 25) is identical with that observed for the endo isomer (eq 24).



(25)

RR(25 °C) 1.00 8.5

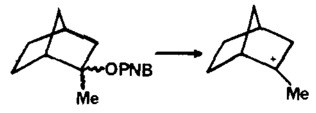
1,2-Dimethyl-*exo*-norbornyl chloride (**32**) exhibits a rate enhancement over **36** by a comparable factor (eq 26).



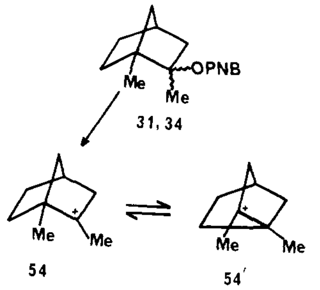
(26)

RR(25 °C) 1.00 7.0

We took advantage of this constancy in the effect of the 1-Me substituent to convert the rate constant for 1,2-dimethyl-*endo*-norbornyl chloride into the rate constant for the presently unknown 2-methyl-*endo*-norbornyl chloride by dividing the rate constant for the former (**39**) by the factor 7 (Table II). These results clearly establish the absence of significant charge delocalization from C-2 to C-1 in the transition state for solvolysis of the 2-methyl-*exo*-norbornyl *p*-nitrobenzoate (**52**). Clearly the solvolyses of the 2-methyl (**51** and **52**) and the 1,2-dimethyl (**31** and **34**) derivatives must proceed without significant participation of the 1,6-bonding pair, leading to the formation of the corresponding classical cations, **53** and **54** $\rightleftharpoons$ **54′** (eq 27 and 28).

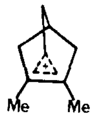


(27)



(28)

This conclusion is supported by results of Goering and his co-workers. Thus the solvolysis of optically active 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate (**34***) in 90% aqueous acetone gives alcohol with 9% retention.[12] Similarly, methanolysis of optically active 1,2-dimethyl-*exo*-norbornyl chloride (**32***) gives the methyl ether with 14% retention.[13,43] Clearly the cation produced cannot be the symmetrical σ-bridged species (**55**). The authors conclude that they are trapping the rapidly equilibrating classical cation or ion pair before complete equilibration has been achieved (eq 28).



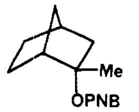
55

MINDO/3 calculations indicate that in the gas phase the classical form of 2-norbornyl (**1′**) is more stable than the nonclassical form (**2**) by approximately 2 kcal mol^{-1}.[44a] A much larger energy difference, 12 kcal mol^{-1}, favors the classical structure for the 2-methyl-2-norbornyl cation[44a] (**53**). MINDO/3 calculations reveal that solvation stabilizes the classical structure over the nonclassical.[44b] Consequently, there can be little reason to question at this time the interpretation that 2-methyl-*exo*- and 1,2-dimethyl-*exo*-norbornyl derivatives undergo solvolysis through classical (unbridged) transition states to classical cations (eq 27 and 28) or ion pairs.

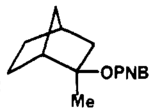
Even under stable ion conditions, the 1,2-dimethyl-2-norbornyl cation exists as a rapidly equilibrating pair of classical cations (**54** $\rightleftharpoons$ **54′**).[11,45] Consequently, we can extend our position to accept the existence of both 2-methyl-2-norbornyl and 1,2-dimethyl-2-norbornyl cations in classical form in solvolytic media, in superacids, and in the gas phase.

Exo/Endo Rate Ratios. In the case of 1,2-diphenyl-2-norbornyl *p*-nitrobenzoates (**45**/**43**), the exo/endo rate ratio is 350, as compared with values of 127 for the parent 2-phenyl derivatives[46] (**44**/**42**) and 280 for the acetolysis of 2-norbornyl tosylate.[5] (Corrected for internal return both the first and last of these would increase modestly.) As discussed earlier, the small increase in the exo/endo rate ratio for **45**/**43** arises primarily because of a decrease in the rate of the endo isomer, **43**. This could arise from a increase in steric effects hindering the departure of the endo leaving group.[39]

The exo/endo rate ratio in the solvolysis of 2-methyl-2-norbornyl *p*-nitrobenzoates (**52**/**51**) is 885[47] (eq 29). Under the same conditions, the exo/endo rate ratio in the solvolysis of the corresponding 1,2-dimethyl derivatives (**34**/**31**) is 564 (Table I). Corrected for internal return,[12] this becomes 875



51

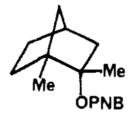


52

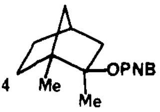
(29)

RR(25°C) 1.00 885

(eq 30). Hence, a methyl substituent in the 1 position has essentially no effect on the exo/endo rate ratio, further evidence



31



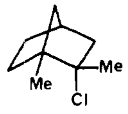
34

(30)

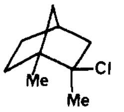
RR(25°C) 1.00 875

for the absence of σ bridging and charge delocalization in the transition state for the solvolysis of the exo isomer **34.**

The ethanolysis of 1,2-dimethyl-2-norbornyl chlorides (**32**/**39**) gives an exo/endo rate ratio of 178 at 25 °C (eq 31).



39

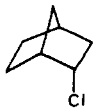


32

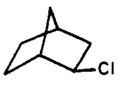
(31)

RR(25°C) 1.00 178

This is similar to the exo/endo ratio of 170 for the solvolysis of *exo*- and *endo*-norbornyl chloride (**57**/**56**) in 80% ethanol (Table II) (eq 32).



56



57

(32)

RR(25°C) 1.00 170

All efforts to obtain independent evidence for σ bridging in the transition state for the solvolysis of 2-methyl- and 1,2-dimethyl-2-norbornyl derivatives have failed. How then are we to account for exo/endo rate ratios as large as 885 and 875 (eq 29 and 30)? Clearly, high exo/endo rate ratios can no longer be considered to require σ bridging.

Free-Energy Diagrams. We are now in position to examine the properties of such classical tertiary 2-norbornyl cations and to compare them with the corresponding properties of the secondary derivatives. The Goering–Schewene diagram provides a quantitative representation of the relationship between the ground-state energies of the exo and endo isomers, the exo/endo rate ratio, and the exo/endo product ratio.[48]

In the case of the secondary tosylate (Figure 1) the difference in the free energies of the exo and endo transition states is 5.8 kcal mol^{-1}. (Because of the greater precision we utilize the free energies rather than the derived enthalpies.[48]) The nonclassical ion interpretation accounts for the lower energy of the exo transition state in terms of its stabilization via σ bridging as the system proceeds along the reaction coordinate to the σ-bridged cation 1 or the equivalent ion pair. The endo isomer is proposed to be stereoelectronically unfavorable for such σ bridging so that ionization proceeds to the classical ion or ion pair.

Since the two transition states differ by 5.8 kcal mol^{-1}, the fully developed nonclassical cation (or ion pair) and the classical cation (or ion pair) must differ by more than 5.8 kcal mol^{-1}. On the basis of the Hammond postulate, fully supported by the experimental data of the present study, the increment need not be large; an estimate of 7 kcal mol^{-1} may be considered reasonable for the difference in energy between the nonclassical and classical structures of the 2-norbornyl cation (solvated). (The difference in energy for the unsolvated ions in the gas phase should be even larger.)[44b] The present study establishes that the solvolysis of 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate proceeds without detectable σ bridging (with accompanying charge delocalization from the 2 to the 1 position). It appears, therefore, appropriate to construct a free-energy diagram for the solvolysis of the 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates for comparison.

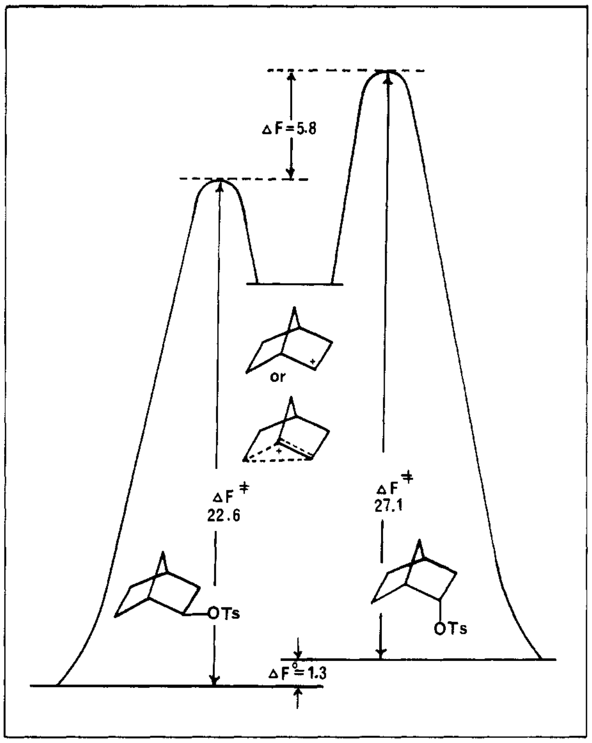


Figure 1. Free-energy diagram for the solvolysis of 2-norbornyl tosylates in acetic acid at 25 °C.

The free energy of activation for the solvolysis of 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate, corrected for internal return, is 27.2 kcal mol^{-1}; the corresponding value for the endo isomer is 31.1 kcal mol^{-1}. Equilibration of the two epimeric alcohols yields a distribution of 72% *exo*-OH and 28% of *endo*-OH. This establishes that the ground-state energy of the endo isomer is higher than that of the exo isomer by a relatively small quantity, 0.6 kcal mol^{-1}. These data yield a diagram (Figure 2) with a difference in the energies of the two transition states of 4.5 kcal mol^{-1}. Such a difference predicts that the cationic intermediate will distribute itself between exo and endo product in the ratio of 99.8% exo/0.2% endo. Experimentally the observed distribution is $\geq$99.7% exo/$\leq$0.3% endo.

The free-energy diagram for this tertiary system (Figure 2) is remarkably similar to the diagram for the parent secondary system (Figure 1).[48,49]

The high exo/endo rate ratio or the difference in energies between the two transition states for 1,2-dimethyl-2-norbornyl (Figure 2) cannot be attributed to σ bridging and charge delocalization in the exo isomer. The present study has established the absence of these effects in the 1,2-dimethyl system. Consequently, we must find some other explanation. Steric hindrance to ionization has been proposed.[50]

There is now some acceptance of this interpretation (steric hindrance to ionization) of slow rates for the tertiary *endo*-norbornyl system,[51] but a reluctance to extend this interpretation to the parent secondary system.[51,52] Yet is it reasonable to utilize two very different explanations for phenomena which appear so similar? Yet such has been the case. In a later section we shall consider in detail three different proposals of this kind which have been advanced. However, first we shall

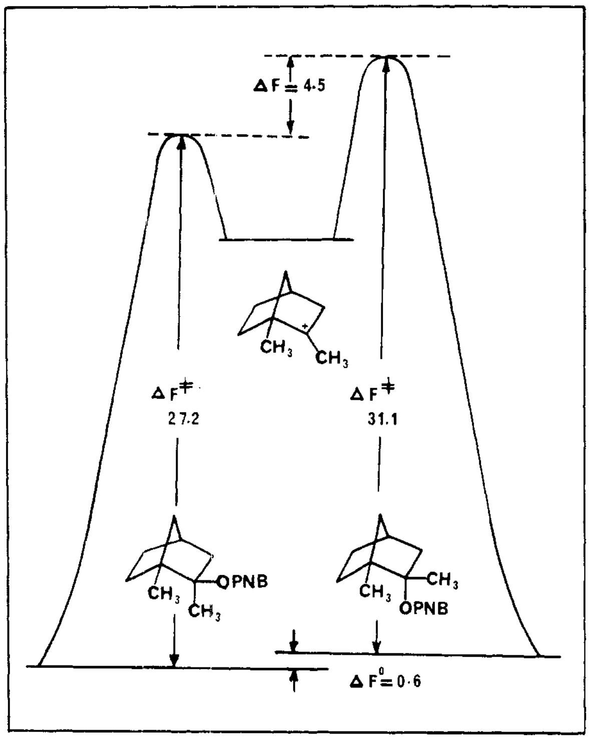


Figure 2. Free-energy diagram for the solvolysis of 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.

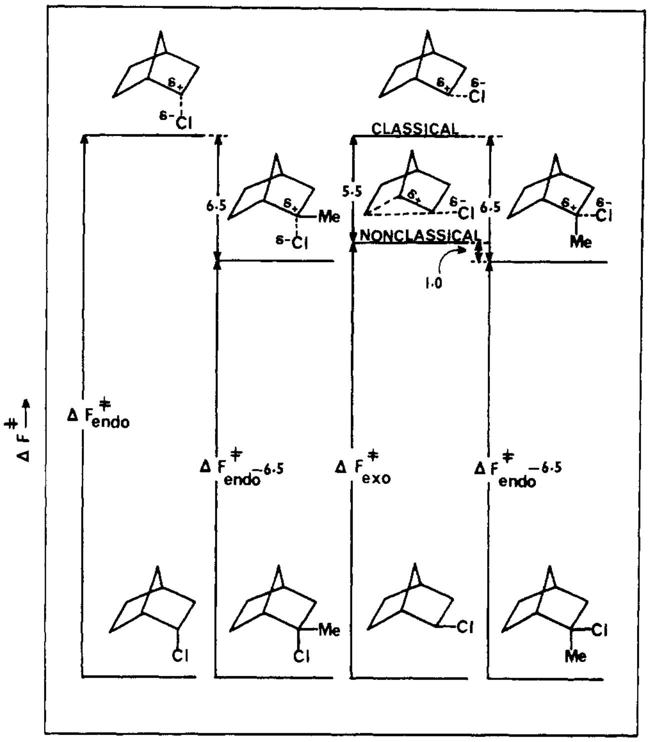


Figure 3. Free energies of activation for the epimeric 2-norbornyl chlorides and 2-methyl-2-norbornyl chlorides assuming the presence of 5.5 kcal mol^{-1} nonclassical stabilization in the exo secondary and its absence in the exo tertiary.

subject to critical test the proposal that the transition state for *exo*-norbornyl solvolysis is resonance stabilized by some 5.8 kcal mol^{-1} (from the Goering–Schewene diagram) as compared to *endo*-norbornyl.

Comparative Energies of Exo and Endo Transition States for Secondary and Tertiary Systems. In recent years there has been a number of attempts to define the stabilities of carbocations in the gas phase[53-55] and in superacids.[33,34,56] Thus it has been observed recently that the calorimetric heat of ionization of 2-propyl chloride (−15.3 ± 0.9 kcal mol^{-1}) is less than that of *tert*-butyl chloride (−25.4 ± 0.8) by some 10.1 kcal mol^{-1}.[34] On the other hand, the values for *exo*-norbornyl chloride (−23.6 ± 0.8) is less than that of 2-methyl-*exo*-norbornyl chloride (−31.0 ± 1.5) by some 7.4 kcal mol^{-1}.[34] Similarly, the difference between 2-propyl chloride and 2-phenyl-2-propyl chloride (−30.3 ± 0.3) is 15.0 ± 1.2 kcal mol^{-1}, whereas the difference between *exo*-norbornyl chloride and 2-phenyl-*exo*-norbornyl chloride (−37.0 ± 1.2) is 13.4 ± 2.1 kcal mol^{-1}.[34]

This change in the secondary–tertiary energy difference for simple alkyl derivatives and the corresponding 2-norbornyl compounds,[57] 2.7 kcal mol^{-1} for the methyl and 1.6 kcal mol^{-1} for the phenyl derivatives, can be interpreted to indicate a modestly higher stability of the secondary 2-norbornyl cation. However, the question must be raised: does such higher stability require σ bridging in the 2-norbornyl cation?

Although such results have been so interpreted in the past, the fact is that this change in the secondary–tertiary energy difference does not require that the secondary 2-norbornyl cation be σ bridged. The 2-norbornyl cations contain a rigid three-dimensional structure which can well delocalize charge from the 2 position by mechanisms other than the σ bridging inherent in the nonclassical interpretation.

Solvolytic data would appear to be more capable of providing an unambiguous answer. The nonclassical concept was introduced in large part to account for the high exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives.[4] Now numerous high exo/endo rate ratios have been observed in the solvolyses of many tertiary 2-norbornyl derivatives where σ bridging has been demonstrated to be absent.[58] There can now be no question but that high exo/endo rate ratios can be realized in stabilized tertiary 2-norbornyl systems not involving σ bridging. The point requiring settling is whether the high exo/endo ratios in 2-norbornyl itself can be accounted for in the same way, or whether we still require σ bridging to account for the parent secondary derivative.

The advantage of the solvolytic approach is that it distinguishes between exo and endo, in contrast to work with the actual ions in superacids. It is a fundamental requirement of the nonclassical phenomenon that σ bridging plays a major role in the solvolysis of the exo isomer, but not of the endo isomer.

As a first approximation, let us ignore the minor differences in the ground-state energies of *exo*- and *endo*-norbornyl chloride (**57** and **56**) and 2-methyl-*exo*- and -*endo*-norbornyl chloride (**36** and **58**). The exo transition state for the solvolysis of representative secondary 2-norbornyl derivatives is more stable than the corresponding endo transition state by some 5.5 kcal mol^{-1}.[59] The introduction of a methyl group into *endo*-norbornyl chloride increases its rate of solvolysis by a factor of 53 000 (Table II). This indicates that the methyl group stabilizes the transition state for the solvolysis of 2-methyl-*endo*-norbornyl chloride by 6.5 kcal mol^{-1}. The introduction of a methyl group into *exo*-norbornyl chloride provides a species which undergoes solvolysis to the classical 2-methyl-2-norbornyl cation. Consequently, the stabilization resulting from the 2-methyl substituent, ~6.5 kcal mol^{-1}, is counterbalanced by the loss of the 5.5 kcal mol^{-1} nonclassical σ bridging in the transition state. There is a net gain in stabilization of only 1.0 kcal mol^{-1}, a factor of only 5!

This analysis predicts that the rate of solvolysis of 2-methyl-*exo*-norbornyl chloride will be faster than *exo*-norbornyl chloride by a factor of only 5. In actual fact, the experimental relative rate is 55 000, almost identical with that of the endo isomers.

The analysis is represented graphically in Figure 3.

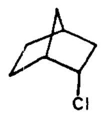
α-Methyl/Hydrogen Ratios in 2-Norbornyl. Schleyer and his co-workers have proposed utilization of α-methyl/hydrogen rate ratios as a diagnostic tool to test for nonclassical resonance stabilization.[60,61] They argued that the limiting value (in the absence of anchimeric and nucleophilic solvent assistance) should be in the neighborhood of 10^8.[60] We had earlier reported that α-methyl/hydrogen ratios for the solvolysis of *exo*-norbornyl chlorides in ethanol at 25 °C is $10^{4.8}$.[1b,62] This diminished value was attributed by other workers to anchimeric assistance (σ bridging) in secondary *exo*-norbornyl[60,63] (solvent assistance is quite unlikely) which increases the rate of the exo isomer "by several powers of 10".

The α-methyl/hydrogen ratio in the solvolysis of *endo*-norbornyl bromides has been reported as 10^5.[61] The diminished ratio for the endo isomers was then accounted for in terms of an enhanced rate for the secondary endo derivatives resulting from large nucleophilic solvent contributions (k_S).[61]

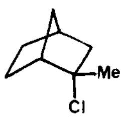
Both Harris, Mount, and Raber[31] and we,[32] by means of independent experimental approaches, have now concluded that the solvolyses of *endo*-norbornyl derivatives proceed without significant solvent participation (k_c). *exo*-Norbornyl derivatives were also shown to solvolyze without significant solvent participation (k_c or k_Δ). In view of this development, we undertook to reexamine the α-methyl/hydrogen ratios in the solvolysis of *exo*- and *endo*-norbornyl chlorides. We restricted ourselves to the chlorides because of growing evidence that there can be large front strain effects in the solvolysis of tosylates and *p*-nitrobenzoates.[29,30]

The fact that we were successful in synthesizing for the first time 1,2-dimethyl-*endo*-norbornyl chloride and determining its rate of solvolysis made it possible to estimate the rate for 2-methyl-*endo*-norbornyl chloride (Table II) with reasonable confidence, without the need for large corrections for different leaving groups.

The α-methyl/hydrogen ratio of 5.3×10^4 for *endo*-norbornyl raises a serious question as to the earlier proposal of 10^8 for this ratio in the absence of either solvent or anchimeric assistance[61] (eq 33). It is probable that this ratio varies with structure, influenced by steric effects, similar to the large variations in the α-*tert*-butyl/α-methyl ratios which have been observed.[64] Harris and his co-workers have come to the same conclusion.[31]



56

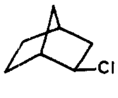


58

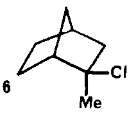
(33)

RR(25°C) 1.00 5.3×10^4

The question now is the magnitude of the α-methyl/hydrogen ratio for *exo*-norbornyl chloride. Will it be a far smaller value, corresponding to the oft postulated σ bridging? In fact the value is 5.5×10^4, almost identical with that for the endo isomer (eq 34).



57



36

(34)

RR(25°C) 1.00 5.5×10^4

The close similarity in the α-methyl/hydrogen rate ratios in *exo*- and *endo*-norbornyl chlorides essentially rules out a k_Δ process for the solvolysis of the exo isomer. The remarkable constancy of the exo/endo rate ratio over an exceptionally wide range of solvents and the similarity in the effects of solvent on the rates of solvolysis of *exo*- and *endo*-norbornyl with those of 2-adamantyl[65] (a model k_c process) argues strongly for the conclusion that *exo*-norbornyl must also undergo solvolysis by a process that is essentially k_c.[32]

These results call for a revision of the previous interpretations that the α-methyl/hydrogen ratio in 2-norbornyl indicates large anchimeric assistance for the solvolysis of *exo*-norbornyl and large solvent assistance for the solvolysis of *endo*-norbornyl derivatives.[63,66] The results are interpreted far more simply in terms of essentially k_c processes in both cases. It should be pointed out that Farcasiu earlier pointed out that α-methyl/hydrogen ratios are not reliable criteria for σ bridging in complex systems.[67]

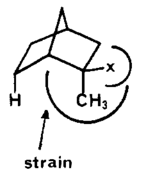
It is appropriate to call attention to the fact that over the years numerous criteria have been advanced in support of σ bridging in the solvolysis of *exo*-norbornyl derivatives. One by one these proposals have crumbled under critical examination. Now the α-methyl/hydrogen criterion joins this growing graveyard.[68]

Effect of Substituents at C-1 and C-2. In the Introduction we pointed out that the presence of σ bridging and accompanying electron delocalization in the exo isomers should result in markedly different effects of substituents at C-1 and C-2. Thus a substituent such as methyl at C-2 should exhibit a much higher activating effect in the endo isomer than in the exo (Figure 2), if charge were delocalized in the latter by a σ bridge. Contrariwise, such a substituent at C-1 would be much more activating in the exo isomer than in the endo isomer. On the other hand, in the absence of nonclassical resonance energy, both in the secondary and tertiary derivatives, we should expect essentially identical effects of substituents, both at C-2 and C-1, in each exo and endo isomer pair.

We have seen that Me/H at C-1 is 8.6 for the endo isomer (eq 24) and 8.5 for the exo isomer (eq 25). We have also seen that Me/H at C-2 is 5.3×10^4 for the endo isomer (eq 33) and 5.5×10^4 for the exo isomer (eq 34). Clearly the observed effects correspond to the absence of a σ-bridged nonclassical species in the transition state for the solvolysis of the exo isomer.

Factor Responsible for the High Exo/Endo Rate Ratios in Secondary and Tertiary 2-Norbornyl Systems. Three different proposals have been advanced to account for the evident similarity in the Goering–Schewene diagrams for secondary and tertiary 2-norbornyl derivatives (Figures 1 and 2) without accepting a common physical origin. (In an earlier section we asked the question: "Is it reasonable to propose two very different explanations for phenomena which appear so similar?" This was answered emphatically by Paul Schleyer: "Yes, it certainly is!")[69]

Proposal No. 1. It was originally proposed back in 1965–1966 that steric effects in the tertiary 2-methyl-2-norbornyl derivatives would be very large, with the steric requirements of the methyl substituent far exceeding the acyloxy group. On this basis large steric strains were estimated for the *endo*-methyl substituent (**59**). Such strain would be relieved during ionization.[70] The smaller strain assumed for the isomer in which the 2-methyl substituent is exo would be less effective in increasing the rate.



59

On this basis, the high exo/endo rate ratio in secondary 2-norbornyl was attributed to an enhanced exo rate, resulting from carbon assistance, with a normal endo rate, whereas the high exo/endo rate ratio in tertiary 2-norbornyl was attributed to a greatly enhanced exo rate, resulting from relief of steric strain, with a comparatively normal endo rate.

This proposal requires that 2-methyl-*endo*-norbornanol be far more stable than 2-methyl-*exo*-norbornanol. However, equilibration experiments soon revealed that the two isomers possess comparable stabilities.[1c]

Proposal No. 2. A later proposal was that the solvolysis of *endo*-norbornyl tosylate is enhanced by large solvent participation comparable in magnitude to carbon participation in the exo isomer. Thus, one of two alternatives considered to account for the 2-Me/2-H reactivity ratios was: "These $\approx 10^5$ values can be rationalized by the postulation of anchimeric assistance in the exo and solvent assistance in the endo secondary cases . . .".[61] This position was adopted and fully discussed by J. M. Harris and S. P. McManus in their interesting attempt to extrapolate from tertiary to secondary 2-norbornyl rates.[63]

However, as was pointed out earlier in the present paper, both J. M. Harris and we, in independent studies, have now concluded that solvent participation is not a significant factor in the solvolysis of *endo*-norbornyl tosylate in solvents of moderate or low nucleophilicities.[31,32]

Proposal No. 3. In "The Nonclassical Ion Problem", Paul Schleyer also discusses another interpretation.[50] He accepts steric hindrance to ionization in the tertiary 2-methyl-*endo*-norbornyl system. However, he argues that such steric hindrance to ionization should not be important in the secondary 2-norbornyl system.[71]

In fact, a careful consideration of the molecular models reveals that even 2-H can serve to trap the anion in the endo cavity.[52] In addition, the ion pair which is presumably the first intermediate in such solvolyses should be far tighter for the secondary system than the stabler tertiary system. This factor may serve to compensate for the smaller size of 2-H.

However, there appears to be little point to a discussion of this proposal on theoretical grounds, when experimental data are available to settle the question. As was pointed out earlier, the nonclassical interpretation of the Goering–Schewene diagram (Figure 1) requires that the nonclassical 2-norbornyl cation be more stable than classical 2-norbornyl cations by some 7 kcal mol^{-1}. However, comparison of the heats of ionization for 2-propyl, *tert*-butyl, and *tert*-cumyl chlorides with 2-norbornyl, 2-methyl-2-norbornyl, and 2-phenyl-2-norbornyl chlorides reveals a total stabilization that is in the neighborhood of 1–2 ± 2 kcal mol^{-1}.

There appears at the present time to be no sound basis to attribute totally different physical causes to the essentially similar behavior of secondary and tertiary 2-norbornyl derivatives (Figures 1 and 2).

Conclusions

The essentially identical effect of a 1-phenyl and a 1-methyl substituent in the solvolysis of the exo and endo isomers of 1,2-diphenyl- and 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates rigorously precludes σ bridging as a significant factor in the rates of solvolysis of the exo isomers. The high exo/endo rate ratios in the solvolysis of 1,2-diphenyl- and 1,2-dimethyl-2-norbornyl derivatives cannot be the result of σ bridging. The close similarity in the Goering–Schewene diagrams for the solvolysis of 1,2-dimethyl-2-norbornyl, 2-methyl-2-norbornyl, and 2-norbornyl itself suggests the operation of similar physical factors. Steric hindrance to ionization of the tertiary 2-norbornyl derivatives offers a reasonable explanation of the high exo/endo rate ratios in the demonstrated absence of σ bridging. The problem is the extension of the analysis to the secondary 2-norbornyl. It is pointed out that the Goering–Schewene diagrams and the exo/endo rate ratios are remarkably similar for both secondary and tertiary 2-norbornyl derivatives. The α-methyl/hydrogen ratio is essentially identical for both *exo*- and *endo*-2-norbornyl. It is no longer possible to account for this in terms of rate enhancements of comparable magnitudes arising from solvent participation in the endo and carbon participation in the exo. The results are more simply accounted for in terms of solvolysis proceeding through essentially k_c processes for both exo and endo secondary and tertiary 2-norbornyl derivatives.

Experimental Section

All melting points are uncorrected. The ^{1}H NMR spectra were recorded on a Varian A60A or T-60 spectrophotometer.

1-Methylnorbornanone (29). 2-Methyl-*endo*-norbornanol (**28**) (51 g, 400 mmol) was oxidized with a solution of chromic acid prepared from sodium dichromate (107 g), sulfuric acid (274 g), and water (840 mL) at 90 °C for 3 h in a 2-L, three-neck, round-bottom flask equipped with mechanical stirrer, condenser, and an additional funnel.

1-Methylnorbornanone (32 g, 65% yield) was isolated by steam distillation. The crude product was redistilled to yield 25.4 g of ketone, n^{20}_{D} 1.4676 [lit.[21] n^{20}_{D} 1.4674].

1,2-Dimethyl-*endo*-norbornanol (30). 1-Methylnorcamphor (25 g, 200 mmol) in ether (150 mL) was treated with 10% excess methyllithium solution in ether. The reaction mixture was decomposed with cold saturated ammonium chloride and extracted with ether. The solvent was removed and the alcohol was purified by distillation. The endo alcohol (**30**) was obtained in 85% yield, bp 50 °C (2 mm).

1,2-Dimethyl-*exo*-norbornyl Chloride (32). The endo alcohol (**30**) (19 g, 135 mmol) was treated with hydrogen chloride in an automatic hydrochlorinator.[22] Chloride (20 g, 93% yield) was obtained: mp 120–122 °C [lit.[16] mp 122–123 °C]; ^{1}H NMR (CCl_4) δ 1.23, 1.57 (2 methyls). This "β-chloride" on storing for 6 months at room temperature under hydrogen chloride atmosphere exhibited two additional methyl signals at δ 1.12 and 1.50 due to the formation of an "α isomer." This α isomer was identified as 1,2-dimethyl-*endo*-norbornyl chloride from the ethanolysis studies of the two isomers. The amount of endo chloride in the isomerized crude mixture was approximately 30%.

1,2-Dimethyl-*exo*-norbornanol (33). The tertiary chloride (20 g, 126 mmol) was dissolved in acetone (120 mL) and stirred with 10% sodium bicarbonate (120 mL) for 2 h at 0 °C. The acetone was removed using a rotary evaporator and the organic material was extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and solvent was evaporated. The residual material was crystallized from hexane to give pure exo alcohol (14.2 g, 80% yield), mp 111–112 °C [lit.[21] mp 112–113 °C].

1,2-Dimethyl-*endo*-norbornyl *p*-Nitrobenzoate (31). This compound was obtained by treating the endo alcohol (**30**) with *n*-butyllithium and *p*-nitrobenzoyl chloride in THF in 81% yield: mp 144–145 °C [lit.[21] mp 146–146.5 °C]; ^{1}H NMR (CCl_4) δ 1.22, 1.51 (2 methyls).

1,2-Dimethyl-*exo*-norbornyl *p*-Nitrobenzoate (34). This *p*-nitrobenzoate was obtained from the exo alcohol (**33**) in the usual manner in 72% yield: mp 133–134 °C [lit.[21] mp 132.5–133 °C]; ^{1}H NMR (CCl_4) δ 1.30, 1.58 (2 methyls).

1-Phenylnorbornanone. 1-Phenyl-*exo*-norbornanol (18.9 g, 100 mmol) in ether (50 mL) was oxidized with a solution of chromic acid (100% excess) at 0 °C.[15] The crude material was purified by distillation to give the pure ketone (79% yield), bp 118–120 °C (0.5 mm). This material solidified on standing, mp 41–42 °C [lit.[14] mp 41–42 °C].

1,2-Diphenyl-*endo*-norbornanol (21). Phenyllithium (0.5 M solution in 1:1 ether/benzene mixture, 220 mL) was added to a solution of 1-phenylnorbornanone (19 g, 100 mmol). The reaction mixture was refluxed overnight and then worked up in the usual manner. Crystallization of the crude product from hexane gave 21.1 g (80% yield) of the tertiary alcohol, mp 109–110 °C [lit.[14] mp 109–110 °C].

1,2-Diphenyl-*endo*-norbornyl *p*-Nitrobenzoate (22). This *p*-nitrobenzoate was obtained in 82% yield in the usual manner: mp 162–163 °C; ^{1}H NMR (CCl_4) δ 8.23 (4 H, aromatic), 7.17, 6.92 (10 H, 2 phenyls), 3.05 (1 H, bridgehead), and 1.37–2.51 (8 H, remaining protons).

Anal. Calcd for $C_{26}H_{23}NO_4$: C, 75.54; H, 5.57; N, 3.39. Found: C, 75.49; H, 5.54; N, 3.41.

1,2-Diphenyl-*exo*-norbornyl Chloride. The endo alcohol (5.5 g, 21 mmol) dissolved in methylene chloride (20 mL) was treated with hydrogen chloride in an automatic hydrochlorinator at ice-bath temperature.[22] After the reaction was complete, removal of solvent yielded a light yellow residue. This crude material was crystallized from hexane to yield pure exo chloride (74% yield), mp 65–66 °C.

Anal. Calcd for $C_{19}H_{19}Cl$: C, 80.7; H, 6.75; Cl, 12.55. Found: C, 80.82; H, 6.57; Cl, 12.36.

Solvolysis of 1,2-Diphenyl-*exo*-norbornyl Chloride. The exo chloride (5.25 g, 20 mmol) was solvolyzed in 80% aqueous acetone (100 mL) containing 10% molar excess of sodium bicarbonate. The reactants were stirred overnight at 0 °C and acetone was removed using a rotary evaporator. The residue was extracted with ether, the ether extracts were dried over anhydrous magnesium sulfate, and the solvent was evaporated. The material was crystallized from hexane to give 4.42 g (80%) of 1,2-diphenyl-2-norbornene: mp 97–98 °C [lit.[14] mp 95.4–98 °C]; ^{1}H NMR (CCl$_4$) δ 7.17, 6.90 (10 H, aromatic), 6.24 (1 H, olefinic), 3.04 (1 H, 4-bridgehead), 1.32–2.22 (6 H, remaining protons).

Anal. Calcd for $C_{19}H_{18}$: C, 92.6; H, 7.36. Found: C, 92.53; H, 7.68.

Hydroboration–Oxidation[20] of 1,2-Diphenyl-2-norbornene. In a 250-mL flask equipped with a reflux condenser, a magnetic stirring bar, and a septum inlet was placed the olefin (5.52 g, 20 mmol) dissolved in methylene chloride (20 mL). The hydroboration was achieved by the dropwise addition of $BHBr_2 \cdot SMe_2$ (20.6 mmol). After the addition, the reaction mixture was stirred for 10 min and 1 equiv of BBr_3 was slowly dripped in over a period of 4–5 min to induce fast hydroboration. After stirring at room temperature for 1.5 h, the organoborane was oxidized by the addition of aqueous sodium hydroxide (3 N, 43 mL) and hydrogen peroxide (8.5 mL). The temperature was maintained below 40 °C. The reaction mixture was refluxed for 1 h and the aqueous layer was saturated with K_2CO_3 and the organic layer separated. Removal of solvent furnished a solid, mp 84–94 °C. Most of the secondary alcohol was crystallized out from the crude material (mp 108.5–109.5 °C). The *p*-nitrobenzoate of the crude product (after removing the secondary alcohol) was prepared in the usual manner. The secondary OPNB could be crystallized out from the crude OPNB mixture (mp 154.5 °C) and the rest of the material which contained approximately 40% of *tert-p*-nitrobenzoate was used for solvolytic studies. The *tert*-OPNB could not be obtained in a pure state.

Solvolytic Products of 1,2-Dimethyl-*exo*-norbornyl *p*-Nitrobenzoate. The *exo-p*-nitrobenzoate (5 mmol) was solvolyzed in buffered 60% aqueous acetone at 75 °C. After 5 half-lives, acetone was removed and the solvolysis products were extracted with ether. The ether extract was analyzed by capillary GC. 1,2-Dimethyl-*endo*-norbornanol (0.35 ± 0.05%) was detected among other components, i.e., exo alcohol and hydrocarbons. The same results were obtained in 80% aqueous acetone.

Equilibration of *exo*- and *endo*-1,2-Dimethyl-2-norbornanols. The exo alcohol (10 mL, 0.2 M solution in cyclohexane) was stirred with 10 mL of sulfuric acid (6 M) at room temperature. At appropriate time intervals, 1 mL of organic solution was withdrawn and analyzed by gas chromatography (Perkin-Elmer 226 gas chromatograph, fitted with a 150 ft × 0.01 in. Quadrol column, operated isothermally at 150 °C under a pressure of 20 psi was used for the analysis) until a constant ratio was found for isomeric alcohols. The equilibrium distribution for 1,2-dimethyl-*exo*- and -*endo*-norbornanols was found to be 72% tertiary exo and 28% tertiary endo.

Kinetic Measurements. The rates of solvolysis of the *p*-nitrobenzoates in 80% acetone and the tertiary chlorides in ethanol were determined by the titrimetric method.[16] Sealed ampule technique was used for measuring the rates at higher temperatures. In the case of 1,2-dimethyl-*exo*- and -*endo*-norbornyl chlorides, separate rates were calculated by the differential method.[26] The rate data for the solvolysis of the *p*-nitrobenzoates in 80% aqueous acetone are summarized in Table I and data for the solvolysis of the chlorides in ethanol are tabulated in Table II.

Registry No.—**19**, 14182-93-5; **20**, 7485-54-3; **21**, 67162-96-3; **24**, 67162-97-4; **25**, 67162-98-5; **26**, 67162-99-6; **26** *p*-nitrobenzoate, 67163-00-2; **29**, 10218-04-9; **28**, 3212-16-6; **30**, 13429-45-3; **33**, 23351-29-3; *p*-nitrobenzoyl chloride, 122-04-3; phenyllithium, 591-51-5; $BHBr_2 \cdot SMe_2$, 55671-55-1.

References and Notes

(1) Preliminary accounts of portions of this study have appeared earlier: (a) H. C. Brown and Min-Hon Rei, *J. Am. Chem. Soc.*, **86**, 5004 (1964); (b) *ibid.*, **86**, 5008 (1964); (c) *ibid.*, **90**, 6216 (1968).
(2) Postdoctoral research associates on a grant provided by the Exxon Research and Engineering Co.
(3) Graduate research assistant on grants (G 19878 and GP 6492X) supported by the National Science Foundation.
(4) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).
(5) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965).
(6) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(7) D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960.
(8) For a more extreme position see C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom", Elsevier, New York, N.Y., 1963.
(9) P. v. R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963).
(10) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **96**, 195 (1974).
(11) G. A. Olah, J. R. De Member, C. Y. Liu, and R. D. Porter, *J. Am. Chem. Soc.*, **93**, 1442 (1971).
(12) H. Goering and K. Humski, *J. Am. Chem. Soc.*, **90**, 6213 (1968).
(13) H. L. Goering and J. V. Clevenger, *J. Am. Chem. Soc.*, **94**, 1010 (1972).
(14) D. C. Kleinfelter and P. v. R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).
(15) H. C. Brown, C. P. Garg, and K.-T. Liu, *J. Org. Chem.*, **36**, 387 (1971).
(16) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 1927 (1975).
(17) H. C. Brown and P. Geoghegan, Jr., *J. Am. Chem. Soc.*, **89**, 1522 (1967).
(18) K. Ishikawa, H. C. Charles, and G. W. Griffin, *Tetrahedron Lett.*, 427 (1977).
(19) S. Krishnamurthy, R. M. Schubert, and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 8486 (1973).
(20) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **99**, 7097 (1977). This hydroborating agent exhibits an unusually high propensity for placing the boron atom at a tertiary position during the hydroboration stage. Research in progress with J. B. Campbell, Jr.
(21) H. Toivenen, *Suom. Kemistil. B*, **33**, 66 (1960).
(22) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966). An improved model is now available from the Ace Glass Co., Vineland, New Jersey.
(23) H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963).
(24) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **97**, 600 (1975).
(25) P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955).
(26) H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845 (1949).
(27) (a) J. D. Roberts and W. Bennett, *J. Am. Chem. Soc.*, **76**, 4623 (1954); (b) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).
(28) E. N. Peters, *J. Am. Chem. Soc.*, **98**, 5627 (1976).
(29) J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickason, and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 969 (1974).
(30) J. S. Lomas, P. K. Luong, and J. E. Dubois, *J. Am. Chem. Soc.*, **99**, 5478 (1977).
(31) J. M. Harris, D. L. Mount, and D. J. Raber, *J. Am. Chem. Soc.*, **100**, 3139 (1978).
(32) H. C. Brown, M. Ravindranathan, F. J. Chloupek, and I. S. Rothberg, *J. Am. Chem. Soc.*, **100**, 3143 (1978).
(33) R. Hasaline, E. Huang, K. Ranganayakulu, T. S. Sorensen, and N. Wong, *Can. J. Chem.*, **53**, 1876 (1975); R. Hasaline, N. Wong, T. S. Sorensen, and A. J. Jones, *ibid.*, **53**, 1891 (1975); T. S. Sorensen, *Acc. Chem. Res.*, **9**, 257 (1976).
(34) E. M. Arnett and C. Petro, *J. Am. Chem. Soc.*, **100**, 2563 (1978).
(35) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965, p 474.
(36) G. D. Sargent, *Carbonium Ions*, **3**, 1132–1136 (1972).
(37) N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3051 (1955).
(38) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).
(39) A similar interpretation was offered to account for the exceptionally high exo/endo rate ratio, 44 000, observed for the 2-*p*-anisyl-2-camphenilyl derivatives: H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **99**, 2679 (1977).
(40) R. M. Cooper, M. C. Grossel, and M. J. Perkins, *J. Chem. Soc., Perkin Trans. 2*, 594 (1972).
(41) R. A. Sneen, K. M. Lewandoski, I. A. I. Taha, and B. R. Smith, *J. Am. Chem. Soc.*, **83**, 4843 (1961).
(42) W. J. le Noble, "Highlights of Organic Chemistry", Marcel Dekker, New York, N.Y. 1974.
(43) It had been shown earlier that the hydrochlorination and deuteriochlorination of deuterio-tagged 1-methyl-2-methylenenorbornane gives tagged 1,2-dimethyl-*exo*-norbornyl chloride (**32**) with only partial scrambling of the tag: H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 466 (1967).
(44) (a) M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. Rzepa, *J. Am. Chem. Soc.*, **99**, 377 (1977); (b) W. L. Jorgensen, *ibid.*, **99**, 280 (1977).
(45) T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 2447 (1972).
(46) H. C. Brown, K. Takeuchi, and M. Ravindranathan, *J. Am. Chem. Soc.*, **99**, 2684 (1977).
(47) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 7124 (1968).
(48) H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87**, 3516 (1965); H. L. Goering, C. Brown, and C. B. Schewene, *ibid.*, **90**, 6214 (1968).
(49) H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973); H. C. Brown *Tetrahedron*, **32**, 179 (1975).
(50) H. C. Brown (with comments by P. v. R. Schleyer), "The Nonclassical Ion Problem", Plenum Press, New York, N.Y., 1977, Chapter 8.
(51) See comments by P. v. R. Schleyer to Chapter 8, ref 50.
(52) H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 1653 (1966).
(53) J. J. Solomon and F. H. Field, *J. Am. Chem. Soc.*, **98**, 1567 (1976).
(54) F. Kaplan, P. Cross, and R. Prinstein, *J. Am. Chem. Soc.*, **92**, 1446 (1970).
(55) R. D. Wietig, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974).
(56) E. W. Bittner, E. M. Arnett, and M. Saunders, *J. Am. Chem. Soc.*, **98**, 3734 (1976).
(57) The calorimetric data of E. M. Arnett and C. Petro[34] in SO_2ClF is of major importance in placing upper limits to possible stabilization of the 2-norbornyl cation (2.7 and 1.6 kcal mol^{-1}), values that are far smaller than that required to account for the difference in the energies of the two transition states in the free-energy diagram for the acetolysis of 2-norbornyl tosylates (Figure 1).
(58) See, for example, Figures 7.1, 7.2, 8.5, and 8.8 in ref 50.
(59) We use here the more general value 5.5 (Figure 6.4, ref 50) rather than the slightly higher value of 5.8 kcal mol^{-1} of Figure 1.
(60) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2540 (1970).
(61) D. Lenoir, D. J. Raber, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 2149 (1974).
(62) The α-methyl/hydrogen ratio for the solvolysis of the chlorides in 80%

ethanol at 85 °C is reported to be $10^{4.3}$: K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968).

(63) J. M. Harris and S. P. McManus, *J. Am. Chem. Soc.*, **96**, 4693 (1974).

(64) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 2892 (1975).

(65) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2538 (1970).

(66) Schleyer has recently suggested that the low α-methyl/hydrogen ratio for *endo*-norbornyl could arise from a slow rate for the tertiary derivative attributable to steric hindrance to ionization. See comments in ref 50, Chapter 14, and discussion of Proposal No. 3 in the following section.

(67) D. Fărcasiu, *J. Am. Chem. Soc.*, **98**, 5301 (1976).

(68) The following provide ten representative examples of such proposals: (a) the exceptionally high rate of solvolysis of camphene hydrochloride, F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature (London)*, **168**, 65 (1951); (b) high exo/endo rate ratios in the solvolysis of 2-norbornyl derivatives, ref 4 and 38; (c) high exo/endo product ratios in 7,7-dimethyl-2-norbornyl, J. A. Berson, "Molecular Rearrangements", Vol. 1, P. de Mayo, Ed., Interscience, New York, N.Y., 1963, Chapter 3; A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 378 (1965); (d) low exo/endo rate ratio in 7-oxo-2-norbornyl derivatives, P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966); (e) the Foote–Schleyer correlation, P. v. R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964); (f) the Goering–Schewene energy diagram for 2-norbornyl, ref 48; (g) symmetrical substituent effects in the acetolysis of 2-(Δ^3-cyclopentenyl)ethyl derivatives containing none, one, and two methyl groups on the double bond, P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297 (1965); (h) the enhanced rate of acetolysis of *exo*-norbornylmethylmercury (1.3 times the rate for endo!), W. A. Nugent, M. M.-H. Wu, T. P. Fehlner, and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 456 (1976); (i) the Harris–McManus correlation, ref 63; (j) the α-methyl/hydrogen ratio, ref 61. See ref 50 for discussion of most of these proposals and the basis for their elimination, with pertinent references.

(69) Private communication.

(70) G. D. Sargent, *Q. Rev., Chem. Soc.*, **20**, 301 (1966).

(71) Reference 50, pp 119–120, 146–149, 214–215, 277.

Solvolysis of *p,p'*-Dichlorobenzhydryl Chloride in Ethanol–2,2,2-Trifluoroethanol Mixtures

Zvi Rappoport,* Hadassah Ben-Yacov, and Joseph Kaspi

Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

Received April 25, 1978

The solvolysis of *p,p'*-dichlorobenzhydryl chloride (1) in the nearly isodielectric EtOH–TFE mixtures gives a Grunwald–Winstein *m* value of 1.30. The solvolysis is subject to common ion rate depression and the mass law constants α increase with the increase in the mole fraction of TFE. A $k_{\mathrm{TFE}}/k_{\mathrm{EtOH}}$ ratio of ~0.025 was calculated from the product distribution by assuming reaction of the solvent components with a free cationic intermediate. Ionizing power parameters *Y* for EtOH–TFE mixtures were calculated from the solvolysis of 1 and from the solvatochromic shifts of the charge-transfer band of 1-(*p*-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine. It is suggested that the reaction proceeds via a selective free *p,p'*-dichlorobenzhydryl cation.

Solvent effects on solvolytic displacement reactions involve several solvent properties such as nucleophilicity, electrophilicity, and dielectric constant. A linear free energy relationship for describing these reactions (eq 1) was suggested by Winstein, Grunwald, and Jones,[1] where k and k_0 are the rate constants in a certain solvent and in 80% EtOH, and Y and N are the solvent ionizing power and nucleophilicity, respectively, m and l being the sensitivities to these parameters.

$$\log (k/k_0) = mY + lN \tag{1}$$

$$\log (k/k_0) = mY \tag{2}$$

However, in the absence of a scale of N values a more restricted form (eq 2)[2] is usually applied where the nucleophilicity is either assumed to be unimportant (k_c process[3]) or nearly constant in the solvents studied. Only recently have scales of N values become available.[4] Schleyer and co-workers who presented an extensive list of N values[4d] showed the superiority of eq 1 over eq 2 in analyzing solvent effects in solvolysis.[4d]

A useful way to gradually change the solvent properties is by studying binary solvent mixtures. Only one solvent property may be changed significantly as in aqueous EtOH mixtures where the change in N is small compared with the change in Y.[4d] On the other hand, in aqueous TFE mixtures both N[4,5] and Y[4b,6] (which are based on solvolytic data) increase with the increase of the water content.

The ionization power parameter Y involves contributions from two solvent properties: from the dielectric constant which is related to electrostatic solvation and from electrophilic solvation, mainly via hydrogen bonding to the leaving group. In aqueous EtOH the two effects are in the same direction since water has a higher dielectric constant and a higher electrophilicity than EtOH. In aqueous TFE the two properties operate in opposite directions since water has higher dielectric constant, but TFE is probably a better electrophilic solvator.[7] The nonlinear log k vs. Y plots found for solvolysis of α-arylvinyl derivatives in aqueous TFE were ascribed to this reason.[7]

The different bulk of the solvent components in a binary mixture was invoked for explaining the selectivity in the product-forming process in terms of different stabilities of solvent separated ion pairs.[8]

It is therefore surprising that more attention was not paid to the binary solvent mixtures EtOH–TFE. Mukherjee and Grunwald showed that these are nearly isodielectric mixtures, where the dielectric constants of TFE (26.14) and EtOH (24.32) are the extremes.[9] The bulk of the two solvents is also very similar. On the other hand, the nucleophilicity of TFE is much lower[4d] and its acidity[10] and probably its electrophilicity are higher than those of EtOH. Nevertheless, only three solvolytic studies in EtOH–TFE mixtures appeared so far.[11–13] da Roza, Andrews, and Keefer measured several Y and N values and studied the solvolyses of several benzyl halides.[11] They found that Y increases and N decreases on increasing the molar fraction of TFE in EtOH–TFE and that eq 2 gives nonlinear correlations, as expected since the lN term was neglected. From the dependence of the shape of these plots, of the product distribution, and of the $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ ratios on the substituent in the aryl ring, the extent of solvent involvement as a nucleophile and an electrophile in the transition state was probed.[11] Ando and Tsukamoto used the product distribution in the solvolysis of 1- and 2-adamantyl systems in 50% EtOH–TFE as a tool for evaluating various proposals concerning the product-forming selectivities in binary mixtures.[12] Kaspi and Rappoport[13] found a nearly linear N vs. Y correlation in the region of 20–90% TFE with a slope of −0.83.

0022-3263/78/1943-3678$01.00/0