Rates and Products of Solvolysis of Arylmethylcyclobutylcarbinyl p-Nitrobenzoates. Increasing Stabilization with Increasing Electron Demand[1]

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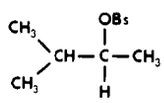
Increasing the electron demand at the carbonium ion center by varying the substituent on the aryl group results in small increases in rates of solvolysis for the arylmethylcyclobutylcarbinyl p-nitrobenzoates, as compared with the corresponding arylmethylisopropylcarbinyl derivatives. The rate increases must reflect increases in the electron supply by the cyclobutyl group under increasing demand of the cationic center. This is the lowest level of stabilization by strained bonds detected by this approach, a factor of 86 for the secondary cyclobutylcarbinyl system, and demonstrates the sensitivity and usefulness in evaluating neighboring group effects by this approach.

A basic tenet of neighboring group effects is that the more stable the carbonium ion center, the less demand that center will make on neighboring groups for additional stabilization through participation.[2] Use of the Hammett–Brown relationship permits one to vary the electron demand at a carbonium ion center over a wide range while maintaining the steric effects around that center essentially constant. This approach can provide definite evidence for the presence or absence of neighboring group participation, e.g., in the 7-*anti*-norbornenyl,[3] 2-norbornenyl,[4] 5-methyl-2-norbornenyl,[5] and the benzonorbornenyl[6] systems.

Unlike π participation, which has been well established,[7] σ participation has been the subject of extensive debate. In particular, the 2-norbornyl system has been the center of controversy.[8,9] The study of the solvolysis of 2-aryl-2-norbornyl p-nitrobenzoates failed to detect any σ participation.[10] It was suggested that this approach may not be sensitive to σ stabilization (σ participation and/or conjugation). Therefore this approach was tested on the strained σ bonds in cyclopropylcarbinyl systems and found to be valid.[11] However, it was argued that cyclopropylcarbinyl systems are too reactive and that results in this system should not be extrapolated to the 2-norbornyl system.[8a] Moreover, there are large differences in the hybridization of the carbon atoms of cyclopropane compared to norbornane. Thus a much less reactive system is needed in order to demonstrate the ability of the approach of varying the electron demand to detect small amounts of stabilization by strained σ bonds.

The cyclobutylcarbinyl system offers such a route. For example, methylcyclobutylcarbinyl brosylate (2) undergoes acetolysis 86 times faster than a model system, 1.[12] This rate enhancement is attributable to stabilization of the developing carbonium ion by the strained σ bonds in the adjacent cyclobutyl group.



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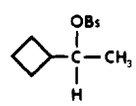


2

	1	2
rel rate (25 °C)	1.0	85.5

Accordingly, the arylmethylcyclobutylcarbinyl p-nitrobenzoates (3) were synthesized and their rates and products of solvolysis in 80% acetone determined. The rates of 3 were compared with a model system which solvolyzes without unusual stabilization, the arylmethylisopropylcarbinyl p-nitrobenzoates (4).[11a]

Results

Synthesis. The arylmethylcyclobutylcarbinols (5) were prepared by the addition of the appropriate Grignard reagent to cyclobutyl methyl ketone. These alcohols were converted into the p-nitrobenzoates by the lithium alkoxide method.[11b]

Kinetic Studies. The rate constants for the solvolysis of 3 in 80% aqueous acetone are listed in Table I. The data reveal an excellent linear correlation with σ^+ constants with a ρ^+ value of −3.94 (correlation coefficient 0.999).

Product Studies. The products of solvolysis were determined in buffered aqueous acetone and analyzed by NMR.

Discussion

The cyclobutylcarbinyl system has been the subject of theoretical and experimental studies,[12–14] and it is generally agreed that the cyclobutyl group stabilizes an adjacent cationic center much less than a cyclopropyl group. Thus the cyclobutylcarbinyl system allows one to test for much smaller amounts of stabilization by strained σ bonds, and should provide a critical test for the ability to detect small levels of neighboring group stabilization by increasing the electron demand.

If neighboring group stabilization is significant in a given system, the rate of solvolysis must be greater than the rate of solvolysis in the absence of such stabilization.[15] Problems can arise in defining an analogous system which reacts without neighboring group stabilization.[11b] In order to accurately address this problem one has to consider numerous factors before choosing an appropriate model. Ground state energies and steric effects (B strain, steric hinderance to ionization, and resonance) are critical. Their neglect can lead to an erroneous assessment of neighboring group effects.[9,11b] For example, 4 has been suggested as a model system for 2-norbornyl.[16] However, it does not appear to be very prudent to compare an aliphatic system with a bicyclic system. Steric effects are much greater in rigid bicyclic systems than in the more flexible aliphatic systems.[17] Moreover, the bond angle strain at the reaction center in 2-norbornyl is greater than in a simple aliphatic system.[18]

However, this is not a problem with 3 and 4. The bond angle strain at the reaction site should be quite similar. Molecular models show that the isopropyl group has about the same steric requirements as a cyclobutyl group. Hence there should not be any significant differences in steric effects during the solvolysis of 3 and 4. Therefore, the best possible model system for 3 which reacts without any neighboring group stabilization is clearly 4.

Indeed it was observed that with increasing electron demand at the cationic center the rate of solvolysis of the arylmethylcyclobutylcarbinyl derivatives (3) increases slightly, as compared to the arylmethylisopropylcarbinyl derivatives (4).[11a]

Table I. Solvolysis of Arylmethylcyclobutylcarbinyl *p*-Nitrobenzoates in 80% Aqueous Acetone

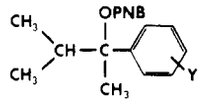
Substituent on aryl group	Registry no.	Temp, °C	$k_1 \times 10^6$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-CH_3O	62861-28-3	25.0	63.2[a]		
p-H	62861-29-4	100.0	389		
		75.0	30.9		
		25.0	5.45×10^{-2} [b]	27.4	−6.0
p-CF_3	62861-30-7	150.0	422		
		125.0	44.3		
		25.0	1.23×10^{-4} [b]	31.0	−4.6
m,m'-$(CF_3)_2$	62861-31-8	150.0	44.1		
		125.0	3.97		
		25.0	4.60×10^{-6} [b]	32.9	−4.3

[a] Rate constant was estimated by multiplying the rate constant for the benzoate by the factor 20.8: H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691 (1968). [b] Calculated from data at higher temperatures.

Table II. Products of Solvolysis of Arylmethylcyclobutylcarbinyl *p*-Nibrobenzoates[a]

Substituent	Products of solvolysis[b] 5	6	7	8
p-CH_3O[c]	(75) (62861-32-9)	(10) (62861-36-3)	(15) (62861-39-6)	(0)
p-H	63 (62861-33-0)	23 (4747-36-8)	14 (4413-14-3)	0
p-CF_3	50 (62861-34-1)	30 (62861-37-4)	15 (62861-40-9)	5 (62861-42-1)
m,m'-$(CF_3)_2$[d]	37 (62861-35-2)	40 (62861-38-5)	12 (62861-41-0)	11 (62861-43-2)

[a] Determined in 80% acetone at 125.0 °C with 10 mol % excess sodium acetate. [b] Analyzed by NMR; values are ±2% unless otherwise noted. Registry numbers are in parentheses. [c] Products of benzoate ester; because of purity of this ester (92%) the product may be in error by more than ±2%, except for 8. [d] Products determined in 50% acetone at 125.0 °C with 10 mol % excess sodium acetate.



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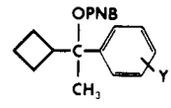


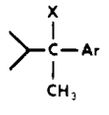
3

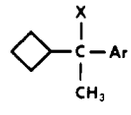
Y	rel rates 4	3
p-CH_3O	1.0	1.0
p-H	1.0	5.7
p-CF_3	1.0	9.0
m,m'-$(CF_3)_2$	1.0	17.6

Clearly the approach is valid for the small electron supply from the carbon–carbon bonds of the cyclobutyl ring. Thus small levels of stabilization (~86) in secondary derivatives can be detected in their analogous tertiary benzylic derivatives.

Let us examine the sensitivity of ρ^+ values to neighboring group effects. The available data reveal that ρ^+ values are very sensitive to neighboring group stabilization. Such stabilization can be classified by their $\Delta\rho^+$ when compared to a suitable model system. For example, large amounts of stabilization found in cyclopropylcarbinyl,[3,11b,19] allylic,[20] and benzylic systems[21] and the π participation found in 7-norbornenyl have $\Delta\rho^+$ between 1.4 and 2.95. Systems with small levels of stabilization such as the 1-(*p*-cyclopropylphenyl)-1-arylethyl,[23] 6-methoxybenzonorbornenyl,[6] and the 5-methyl-2-norbornenyl systems[22] are characterized by $\Delta\rho^+$ of 0.3–0.9. Systems which undergo solvolysis with no significant neighboring group stabilization as in tertiary benzonorbornenyl,[6] 2-norbornyl,[10] 2-norbornenyl,[24] and Δ^3-cyclopentenyl systems[25] have no difference in $\Delta\rho^+$ (0.01 to −0.08).

Let us now examine the cyclobutylcarbinyl system. **4** has a ρ^+ of −4.65, while **3** has a ρ^+ of −3.94. The change in ρ^+ ($\Delta\rho^+$ = 0.71) is in the direction anticipated for a small amount of neighboring group stabilization.

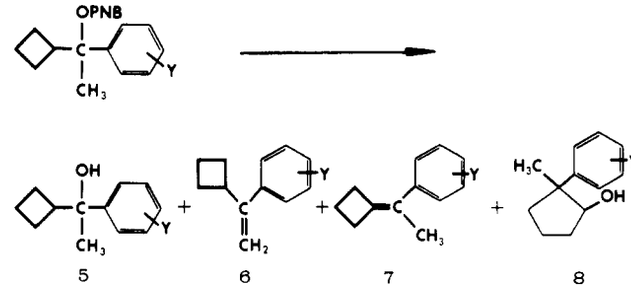




ρ^+ −4.65 −3.94 $\Delta\rho^+$ = 0.71

The amount of σ stabilization by the 1,6 carbon–carbon bond of 2-*exo*-norbornyl brosylate is reported to be 350. Since the approach of varying the electron demand can detect the factor of 86 attributable to σ stabilization in the cyclobutylcarbinyl system, it is of major importance that this approach reveals no significant stabilization by the 1,6 carbon–carbon bonds in the tertiary arylnorbornyl derivatives. Consequently, the high exo/endo rate ratio in the solvolysis of 2-norbornyl must be due to some factor other than participation. Steric hindrance to ionization has been suggested as an alternative explanation.[9a]

The products of solvolysis of **3** were determined in buffered aqueous acetone at 125.0 °C and appear in Table II. The predominant products are those with no skeleton rearrangement **5, 6,** and **7**. The derivatives with increased electron demand [*p*-CF_3 and *m,m'*-$(CF_3)_2$] exhibit a small amount of rearranged product **8**. These results are consistant with the kinetic arguments.



5 6 7 8

The fact that the phenyl derivative reacts with a rate enhancement of almost six but gives no rearranged product suggests that the formation of **8** in the *p*-trifluoromethylphenyl and *m,m'*-bis(trifluoromethyl)phenyl derivatives occurs after the rate determining step.

In conclusion, neighboring group stabilization by carbon–carbon bonds in the cyclobutylcarbinyl system is a linear function of the electron demand of the carbonium ion center. Moreover, the technique of increasing the electron demand of a cationic center was able to detect the small amount of σ

Table III. Preparation of Arylmethylcyclobutylcarbinols[a]

Aryl group	% yield	Bp, °C	n^{20}_D
p-Anisyl	82	75–76 (0.001 mm)	1.5332
Phenyl	89	94–96 (1 mm)	1.5381
p-Trifluoromethylphenyl	85	67–70 (0.05 mm)	1.4814
3,5-Bis(trifluoromethyl)-phenyl	87	64–66 (0.03 mm)	1.4460

[a] Boiling points are uncorrected; all new compounds gave spectral and microanalytical data (±0.4% for C, H. F) consistent with the proposed structure.

Table IV. Preparation of Arylmethylcyclobutylcarbinyl p-Nitrobenzoates[a]

Aryl group	% yield	Mp, °C
p-Anisyl	*b*	*b*
Phenyl	89	107.0–107.5
p-Trifluoromethylphenyl	91	124.8–126.0
3,5-Bis(trifluoromethyl)phenyl	85	95.5–96.5

[a] Melting points are uncorrected; all new compounds gave spectral and microanalytical data (±0.4% C, H, N, F) consistent with the proposed structure, except the p-anisyl derivative which was not pure enough for microanalysis. [b] This p-nitrobenzoate was too unstable to isolate. The benzoate would not solidify. The NMR indicates that this ester was about 92% pure.

stabilization, a factor of 86, in the cyclobutylmethylcarbinyl system. Clearly, this approach is sensitive in detecting small amounts of π and σ participation and/or conjugation and is a valuable tool for the physical organic chemist.

Experimental Section

Cyclobutyl methyl ketone was prepared from cyclobutylcarboxylic acid in 90% yield following the general procedure for the preparation of methyl ketones from carboxylic acids:[27] bp 134–136 °C (lit. bp 137 °C).[28]

General Procedure for the Preparation of Arylmethylcyclobutylcarbinols. The Grignard reagents of p-bromoanisole, bromobenzene, p-bromobenzotrifluoride, and 3,5-bis(trifluoromethyl)-bromobenzene were prepared by the reaction of the respective bromides with magnesium in anhydrous ether under nitrogen. A solution of cyclobutyl methyl ketone in ether was added to a stirred solution of the Grignard reagent (10 mol % excess) at 0 °C. After hydrolysis of the reaction mixture with saturated ammonium chloride solution, the organic layer was separated and the aqueous layer extracted twice with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered, and solvent was evaporated. The resultant arylmethylcyclobutylcarbinols were purified by distillation and characterized by NMR and IR; properties are listed in Table III.

Preparation of p-Nitrobenzoates. The arylmethylcyclobutylcarbinyl p-nitrobenzoates were prepared from the lithium alkoxide and p-nitrobenzoyl chloride as described by Brown and Peters.[11] The benzoate of p-anisylmethylcyclobutylcarbinol was obtained in a similar manner. The properties of these derivatives are listed in Table IV.

Kinetic Procedure. The procedure utilized for the determination of rate constants was similar to that previously reported by Brown and Peters.[11]

Registry No.—2, 62861-44-3; p-bromoanisole, 104-92-7; bromobenzene, 108-86-1; p-bromobenzotrifluoride, 402-43-7; 3,5-bis(trifluoromethyl)bromobenzene, 328-70-1; cyclobutyl methyl ketone, 3019-25-8.

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