Notes

Solvolysis Reactions: Relative Abilities of Cyclopentyl/Phenyl Groups To Stabilize an Electron-Deficient Carbon

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It has been established that the *para*-substituent effect on the rates of solvolysis of (1-arylcycloalkyl)carbinyl arenesulfonates can be used to assess the ability of cycloalkyl groups to assist ionization by carbon σ-participation.[2] For example, by measuring the solvolysis rates of *para*-substituted (1-phenylcyclopropyl)carbinyl and (1-phenylcyclobutyl)carbinyl arenesulfonates and comparing their (k^{OMe}/k^{NO_2}) rate ratios with that of similarly substituted neophyl derivatives, we were able to demonstrate the greater ability of both the cyclopropyl and cyclobutyl group over that of neighboring phenyl to stabilize the developing cationic center in the transition state. Since both the test series, (1-phenylcycloalkyl)carbinyl, and the reference series, neophyl, are primary systems—and hence involve high electron demand at the developing cationic center[3,4] —use of the k^{OMe}/k^{NO_2} rate ratios should allow one to assess the small levels of σ-participation expected for such relatively weak neighboring groups as cyclopentyl or cyclohexyl.

Recently, in our continuing assessment of neighboring group ability of small and medium rings in solvolysis reactions, we became interested in extending the k^{OMe}/k^{NO_2} method to the cyclopentyl group. Although the significantly greater ability of the cyclopentyl group over that of methyl to stabilize an adjacent electron-deficient center is well known,[5-7] the assessment of the carbon σ-participation ability of cyclopentyl, relative to that of β-aryl bridging, under both competitive and high electron-demand conditions, remains to be determined.

Thus, we report in this paper the synthesis and solvolytic investigation of a series of [1-(*p*-X-phenyl)-cyclopentyl]carbinyl tosylates.

4a, X = *p*-CH_3O **4b**, X = *p*-CH_3
4c, X = *p*-H **4d**, X = *p*-Cl
4e, X = m,m'-$(CF_3)_2$

The data indicate that **4a–e** undergo solvolysis via a k_Δ process and that the ability of the cyclopentane ring to compete with the β-aryl group in stabilizing the developing cationic center is significant.

The synthesis of the (1-arylcyclopentyl)carbinyl tosylates was accomplished as shown in Scheme 1. Preparation of the *p*-nitro compound was attended with special problems so it was replaced with the *m,m'*-bis(trifluoromethyl) substrate.

The first-order rate constants for solvolysis of **4a–e** are summarized in Table 1. Reaction progress was followed by titrating the liberated *p*-toluenesulfonic acid, and strictly first-order kinetics were observed up to at least 75% conversion furnishing, within experimental error, 100% of the theoretical amount of acid present. In Table 2 we have listed the results of rate data correlations for selected compounds against σ^+, and the calculated k^{OMe}/k^{NO_2} ratios are given in Table 3. The product distribution data for solvolysis of **4a,c–e** are collected in Table 4. Urea was used as a buffer to avoid acid-catalyzed rearrangements of first-formed products, and the product studies were conducted within the temperature range of the kinetic studies. The products of solvolysis were determined by examination of 270-MHz ^{1}H NMR spectra of the oil isolated from the buffered reaction mixture after 10-half-lives at 65 °C. For compounds **4a,c,d**, the integrated peak areas of the benzylic protons gave the composition and established the identity[9a-c] of the aryl-rearranged products. For compound **4e**, the integrated peak areas of the 2,6-aromatic

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(5) For example, in several solvolytic studies[6] of the primary system cyclopentylcarbinyl-OBs, the observed rate enhancements and rearranged products have been used to support a mechanism involving carbon σ-participation by the five-membered ring.

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(7) In earlier papers from this laboratory,[6d,e] we measured, in a wide range of solvents, the response of the cyclopentyl substituent effect to solvent ionizing power. The results clearly support the contention that, in contrast to the usual k_s behavior of such primary substrates as 1-propyl and isobutyl arensulfonates,[8] cyclopentylcarbinyl arenesulfonates undergo solvolysis by a k_Δ pathway.

(8) (a) Hoffmann, H. M. R. *J. Chem. Soc.* **1965**, 6753–6762. (b) McManus, S. P.; Neamat- -Mazraeh, N.; Karaman, R. M.; Harris, J. M. *J. Org. Chem.* **1986**, *51*, 4876–4880. (c) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658–7666. (d) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89. (e) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York 1987; pp 376–378. (f) Winstein, S.; Marshall, H. *J. Am. Chem. Soc.* **1952**, *74*, 1120.

(9) (a) For **4a**, the peaks at δ 2.81 and 3.30 were assigned to the benzylic protons of 1-(*p*-methoxybenzyl)cyclopentyl 2,2,2-trifluoroethyl ether and 1-(*p*-methoxybenzyl)cyclopentene, respectively. A peak at δ 5.30 confirmed the presence of the carbon–carbon double bond and a quartet centered at δ 3.75 established the presence of the 2,2,2-trifluoroethyl group. (b) For **4c**, the peaks at δ 2.80 and 3.31 were assigned to the benzylic protons of 1-benzylcyclopentyl 2,2,2-trifluoroethyl ether and 1-benzylcyclopentene, respectively. The peaks at δ 5.26 and 6.28 were assigned to the vinylic protons of 1-benzylcyclopentene and benzylcyclopentane, respectively, and the integrated peak areas of the vinylic protons gave the alkene composition. [**Note**: the acetolysis products isolated[6a] for **4c**, in the absence of a buffer, at 45 °C were 26% benzalcyclopentane and 76% 1-benzylcyclopentene]. (c) For **4d**, the peaks at δ 2.83, 3.32, and 3.50 were assigned to benzylic protons of 1-(*p*-chlorobenzyl)cyclopentyl 2,2,2-trifluoroethyl ether, 1-(*p*-chlorobenzyl)cyclopentene, and 1-(*p*-chlorobenzyl)cyclopentanol, respectively. The peaks at δ 5.31 and 6.29 were assigned to the vinylic protons of 1-(*p*-chlorobenzyl)cyclopentene and 1-(*p*-chlorobenzyl)cyclopentane, respectively. The integrated peak areas of the vinylic protons gave the alkene composition (peak assignments were made on the basis of values listed for **4a** and **4c** benzylic proton signals plus comparison of the integrated peak areas for the vinylic, 2,2,2-trifluoroethyl, and

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Table 1. Summary of Kinetic Data for (1-Arylcyclopentyl)carbinyl Tosylates 4a–e

solvent	substituent	T, °C	k_t, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
AcOH	**a** = *p*-CH_3O	25.0	$(9.0 \pm 0.06) \times 10^{-6}$	24.0	−1.0
		35.0	$(4.0 \pm 0.04) \times 10^{-5}$		
		45.0	$(1.4 \pm 0.1) \times 10^{-4}$		
		55.0	$(4.0 \pm 0.07) \times 10^{-4}$		
		75.0[a]	4.2×10^{-3}		
	b = *p*-CH_3	35.0	$(2.7 \pm 0.01) \times 10^{-6}$	26.2	+0.8
		45.0	$(9.2 \pm 0.01) \times 10^{-6}$		
		55.0	$(3.7 \pm 0.01) \times 10^{-5}$		
		75.0	$(4.0 \pm 0.01) \times 10^{-4}$		
	c = *p*-H	25.0	$(6.2 \pm 0.03) \times 10^{-8}$	27.5	+0.7
		35.0	$(2.3 \pm 0.02) \times 10^{-7}$		
		45.0	$(1.2 \pm 0.01) \times 10^{-6}$		
		65.0	$(1.6 \pm 0.05) \times 10^{-5}$		
		75.0[a]	5.3×10^{-5}		
	d = *p*-Cl	45.0	$(1.8 \pm 0.02) \times 10^{-7}$	27.5	−3.1
		55.0	$(6.6 \pm 0.01) \times 10^{-7}$		
		65.0	$(2.6 \pm 0.01) \times 10^{-6}$		
		75.0	$(8.1 \pm 0.01) \times 10^{-6}$		
	e = *m*,*m*′-$(CF_3)_2$	65.0	$(5.4 \pm 0.01) \times 10^{-8}$	30.3	−2.5
		75.0	$(2.0 \pm 0.05) \times 10^{-7}$		
		85.0	$(7.1 \pm 0.01) \times 10^{-7}$		
		45.0[a]	3.0×10^{-9}		
97% w/w aqueous TFE	**a** = *p*-CH_3O	15.0	$(1.6 \pm 0.05) \times 10^{-4}$	17.4	−15.4
		20.0	$(2.7 \pm 0.05) \times 10^{-4}$		
		25.0	$(4.5 \pm 0.03) \times 10^{-4}$		
		30.0	$(7.6 \pm 0.04) \times 10^{-4}$		
		35.0[a]	1.3×10^{-3}		
		45.0[a]	4.0×10^{-3}		
	b *p*-CH_3	25.0	$(6.4 \pm 0.03) \times 10^{-5}$	19.1	−13.7
		30.0	$(1.2 \pm 0.02) \times 10^{-4}$		
		35.0	$(1.9 \pm 0.04) \times 10^{-4}$		
		45.0	$(5.3 \pm 0.04) \times 10^{-4}$		
	c = *p*-H	30.0	$(1.1 \pm 0.01) \times 10^{-5}$	22.0	−8.8
		35.0	$(2.0 \pm 0.03) \times 10^{-5}$		
		45.0	$(6.5 \pm 0.03) \times 10^{-5}$		
		55.0	$(1.9 \pm 0.04) \times 10^{-4}$		
	d = *p*-Cl	30.0	$(1.2 \pm 0.04) \times 10^{-6}$	21.2	−16.0
		35.0	$(2.4 \pm 0.02) \times 10^{-6}$		
		45.0	$(6.5 \pm 0.03) \times 10^{-6}$		
		55.0	$(2.0 \pm 0.05) \times 10^{-5}$		
	e = *m*,*m*′-$(CF_3)_2$	35.0	$(1.1 \pm 0.06) \times 10^{-8}$	23.6	−18.4
		45.0	$(4.5 \pm 0.06) \times 10^{-8}$		
		55.0	$(1.2 \pm 0.04) \times 10^{-7}$		
		65.0	$(3.9 \pm 0.05) \times 10^{-7}$		

[a] Calculated from data at other temperatures.

Table 2. ϱ^+ (Hammett–Brown) and ϱ_Δ (Yukawa–Tsuno) Values for Selected Compounds

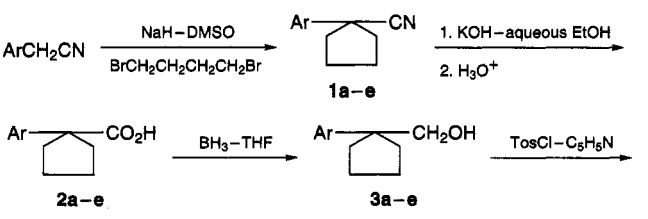
compd	neophyl-OBs	[1-(*p*-G-phenyl)cyclobutyl]carbinyl-OBs	[1-(*p*-G-phenyl)cyclopentyl]carbinyl-OTs
ϱ^+ value (in AcOH at 75 °C)	−3.05[a,b] (r = 0.97)	−1.0[c] (r = 0.99)	−2.3[d] (r = 0.97)
ϱ^+ value (in 97TFE at 45 °C)		−1.7[c] (r = 0.99)	−2.7[d] (r = 0.98)
ϱ value[e] (in AcOH at 75 °C)	−3.83[b] (r = 0.99)	−1.4[c,d,f] (r = 0.99)	−2.7[d] (r = 0.95)
ϱ value[e] (in 97TFE at 45 °C)		−2.0[c,d] (r = 0.99)	−3.1[d] (r = 0.98)

[a] Reference 16a. [b] Reference 15. [c] Reference 2b. [d] This study. [e] Obtained by use of Yukawa–Tsuno equation.[19] [f] At 55 °C.

protons gave the product composition,[9d,10a–c] and the integrated peak areas of the vinylic, 2,2,2-trifluoroethyl, and hydroxy protons[10b,c] confirm this composition and reveal the presence of the ring-expanded products listed in Table 4.

On the basis[11] that primary solvolysis occurs by two discrete pathways—k_s, nucleophilically solvent assisted

Scheme 1



hydroxy protons). (d) For **4e**, the integrated peak areas of the 2,6-aromatic protons indicate a three-compound product composition.[10a] The integrated peak areas of the vinylic, 2,2,2-trifluoroethyl, and hydroxy protons[10b] confirm this composition.

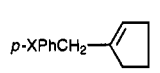
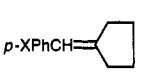
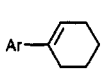
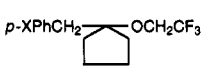
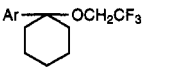
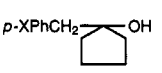
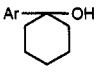
(10) (a) In the aromatic region, the spectra show six peaks (three 2H–1H pairs) ranging from 7.70 to 7.97 ppm. The ^1H chemical shifts of the 2-, 6-, and 4-aromatic protons for compounds **4a–e** are scattered over a similar range. (b) In the range δ 6.5 7 to 2.75, the spectra show the vinylic, 2,2,2-trifluoroethyl signals. The peak at δ 6.28 in the ^1H NMR spectrum of the **4e** solvolysis product mixture was assigned to the vinylic proton of 1-[3,5-bis(trifluoromethyl)phenyl]cyclohexene. The area of this peak relative to that for hydroxy (broad band centered at δ 1.3) and one-half of that for the 2,2,2-trifluoroethoxy (δ 3.40) groups gave the percentage composition of the **4e** product mixture. (c) The absence of a benzyl methylene signal at either δ 2.8 or 3.3 confirms that **4e** rearranges to ring-expanded products.

Table 3. k^{OMe}/k^{X} Ratios of Para-Substituted Neophyl-like Systems

compd	Neophyl-OTs[a,b]	c-PrCarb-OTs[c,d]	c-BuCarb-OBs[e]	c-PnCarb-OTs[f]
solvent/°C	AcOH/75	AcOH/30	AcOH/75	AcOH/75
k_{OMe}/k^{NO_2}	80 000	39	75	7000[g]
Solvent/°C		EtOH/40	TFE/45	97TFE/45
k^{OMe}/k^{NO_2}		23	407	20 000[g]

[a] Reference 15a. [b] Reference 26. [c] Reference 1a. [d] Reference 19a. [e] Reference 19b. [f] This study. [g] Rate constant for the *p*-nitro compound was calculated using the ϱ^+ value reported in Table 2.

Table 4. Summary of Product Runs (% Yield) for [1-(*p*-X-phenyl)cyclopentyl]- and [1-[3,5-Bis(trifluoromethyl)phenyl]cyclopentyl]carbinyl Tosylates in 97% Aqueous TFE

X							
MeO	50			50			
H	51	28		21			
Cl	50	10		20		20	
3,5-bis-CF_3			30		25		45

which leads to only unrearranged products, and k_Δ, neighboring group assisted which leads to only rearranged products—the observation (Table 4) that **4a,c–e** yield almost exclusively rearranged products supports[11–13] a k_Δ pathway. This speculation is corroborated by the linear correlation[14] of log k_t (**4a–e**) with log k_t for the corresponding substituted neophyl brosylates.[2b]

It is generally accepted that the substituent effect on the β-aryl-assisted solvolysis process can be used to establish the mechanistic consistency of a reaction series.[16,17] Therefore, we have analyzed the kinetic data of Table 1 in terms of the usual Hammett–Brown equation (1), where k_t is the titrimetric rate constant, k_o

$$\log k_t/k_0 = \varrho^+\sigma^+ \qquad (1)$$

is the titrimetric constant for *p*-G = H, σ^+ is the Brown substituent constant based on the solvolyses of para-substituted *tert*-cumyl chlorides in 90% aqueous acetone,[18] and ϱ^+ is the slope of the regression line. We also analyzed the same kinetic data by use of the Yukawa–Tsuno equation.[19] The results are summarized in Table 2. The correlation coefficients for these rather small data sets are high ($r = 0.99^+$) for the (1-arylcyclobutyl)carbinyl-OBs series and marginal ($r = 0.97$ in AcOH and 0.98 in 97TFE) for the (1-arylcyclopentyl)carbinyl-OTs series. The most interesting feature of the data in Table 2, however, is the magnitude of the ϱ^+ value for the (1-arylcyclopentyl)carbinyl series, lying between that for the neophyl and (1-arylcyclobutyl)carbinyl series. This result is consistent with the cyclopentyl group's reduced neighboring group assistance relative to that of the four-membered ring but, more importantly, suggests that the ability of the five-membered ring to compete with the β-aryl groups in assisting the ionization of a primary system is significant.

The k^{OMe}/k^{NO_2} ratios listed in Table 3 show that the (1-arylcyclobutyl)carbinyl and (1-arylcyclopropyl)carbinyl arenesulfonates are, respectively, some two to three powers of 10 less sensitive than neophyl brosylate to a *para*-substituent change from methoxy to nitro. We attributed this reduced sensitivity to changing substituents on the aryl ring to σ-participation by the cycloalkyl groups in the transition state which leads to the first-formed cationic intermediate.[2a,20] Table 3 further reveals that the (1-arylcyclopentyl)carbinyl system is also less sensitive (by about one power of 10) than neophyl brosylate to the measured *para*-substituent effect change. This finding establishes, even more clearly than that of the previous paragraph, that the ability of the five-membered ring to compete with the β-aryl groups in assisting the ionization of a primary system is significant.

As measured by the ϱ^+ or ϱ values given in Table 2, the charge delocalization response of the (1-arylcyclopentyl)carbinyl system to change in solvent ionizing power [$Y_{97TFE} = 1.83$ and $Y_{AcOH} = -0.61$][21] is slight. Also, the relative rate ratio, k_{TFE}/k_{AcOH}, for **4c** (54) is of approximately the same order as that observed for both neophyl tosylate (69) and 1-phenylcyclobutylcarbinyl brosylate (26). This result suggests little sensitivity to solvent change of either the magnitude or type (aryl-bridging or σ-assisted) of neighboring group participation in these neophyl-like substrates.[6d,22]

The product distribution data listed in Table 4 reveal a marked difference between compound **4e** and compounds **4a,c,d**. For compounds **4a,c,d**, at least 98% of

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(14) The acetolysis rate constants (at 75 °C) for the neophyl brosylates were taken from, or in the case of the *m,m'*-$(CF_3)_2$ derived from, the data contained in Tables 1 and 2, ref 15. The calculated correlation coefficient was 0.999, and the slope value was 1.02.

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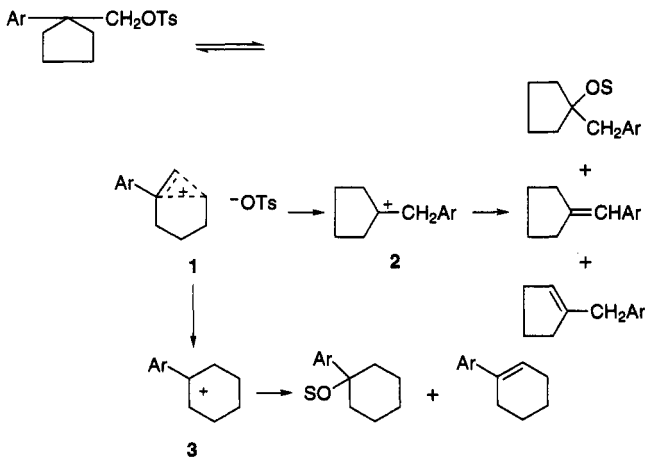
Scheme 2



the solvolysis products are aryl-rearranged products; while, for compound **4e**, at least 98% of the solvolysis products are ring-expanded products. These results indicate that the change from electron-donating (or mildly electron-withdrawing) *para*-substituents to the strongly electron-withdrawing 3,5-bis(trifluoromethyl) groups leads to different cationic intermediates captured by solvent. In the case of **4a,c,d**, a cationic intermediate with appreciable benzylcyclopentyl character must be involved, while in the case of **4e**, solvent capture of a cationic intermediate with appreciable 1-arylcyclohexyl character must be involved. On the other hand, the Hammett–Brown plots of the rate constants for both the acetolysis and trifluoroethanolysis of the (1-arylcyclopentyl)carbinyl tosylates reveal no sharp discontinuity along the correlation line for all substituents, including the point for the 3,5-bis(trifluoromethyl) groups,[23] which indicates that neighboring group participation by the aryl group in the transition state for the rate-controlling step does not change sharply with the change from *p*-X to 3,5-bis(trifluoromethyl) substituents. Also, in view of the proposal[6b,d,e] that the folded geometry of a cyclopentylcarbenium ion is unfavorable for alkene production, the detection of appreciable quantities of cycloalkenes in the trifluoroethanolysis of **4a,c,d**, and the lesser quantity of cycloalkene in the trifluoroethanolysis of **4e**, is mechanistically significant.[6e]

These seemingly contradictory results for the solvolysis of the (1-arylcyclopentyl)carbinyl series are somewhat in common with those obtained for the solvolyses of the (1-arylcyclopropyl)carbinyl and (1-aryl-cyclobutyl)carbinyl reaction series.[2ab,6de,20,25] Here, on the basis that the 1-aryl substituents had little effect upon rate but showed a dramatic effect upon product composition, we proposed a mechanistic scheme involving (1) formation of a tight ion pair, stabilized by σ-bond delocalization of charge into the cycloalkyl ring, and (2) rearrangement to a loose ion-pair, stabilized by delocalization of charge into the aryl group. All of the data presented for the 1-arylcyclopentylcarbinyl series can be explained by Scheme 2, which is somewhat analogous to the mechanism we postulated for the solvolysis of the (1-arylcyclopropyl)carbinyl and (1-arylcyclobutyl)carbinyl arenesulfonates. Thus, in Scheme 2, we propose that σ-participation by the cyclopentyl group takes place in the initial, rate-determining ionization process (k_Δ), leading to bridged intermediate **1**. Intermediate **1** then partitions itself into a minimum of two product pathways: $k_{r\text{-}Ar}$ and $k_{r\text{-}C}$. The $k_{r\text{-}Ar}$ pathway involves rearrangement of **1** to **2** via a transition state with high phenonium character, which when attacked by solvent gives aryl-rearranged ethers, alcohols, and alkenes; while the $k_{r\text{-}C}$ pathway involves rearrangement of **1** to **3** which when attacked by solvent yields the ring-expanded ethers, alcohols, and alkenes.

In summary, we believe that solvolysis of the (1-arylcyclopentyl)carbinyl tosylates takes place via a k_Δ process involving small but significant σ participation by the five-membered ring. The observation of rearranged products and the rate correlation with log k_t (*p*-X-neophyl-OBs) are consistent with this mechanism. Furthermore, the relatively low k^{OMe}/k^{NO_2} ratio and ϱ^+ values are consistent with a first-formed intermediate stabilized by the σ-electrons of a C_α–C_β bond of the cyclopentane ring. Finally, the similar rate response to solvent change observed for (1-phenylcyclopentyl)carbinyl tosylate, (1-phenylcyclobutyl)carbinyl brosylate, and neophyl brosylate suggests little sensitivity to solvent change of either the magnitude or type (aryl-bridging or σ-assisted) of neighboring group participation in these neophyl-like substrates.

Experimental Section

1-(*p*-Methoxyphenyl)cyclopentanecarbonitrile (1a) was prepared using a procedure similar to that for synthesis of 1-*p*-methoxycyclobutanecarbonitrile.[27] Accordingly, a mixture of 39.4 g (0.27 mol) of *p*-methoxyphenylacetonitrile and 58.3 g (0.27 mol) of 1,4-dibromobutane was treated under a nitrogen blanket with 16.2 g of sodium hydride dissolved in 300 mL of DMSO and 35 mL of ether. After the usual workup, distillation of the oily residue gave 36.0 g (0.19 mol, 70% yield) of the nitrile: bp 145–149 °C (1.75 mm); IR (neat) C≡N stretch, 2234 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82–2.10 (broad band with sharp multiplet from 1.88 to 2.10, 6 H), 2.3–2.5 (m, 2 H), 3.8 (s, 3 H, OCH_3), 6.89 (d, J = 8.9 Hz, 2 H, 3,5-Ar), 7.35 (d, J = 8.9 Hz, 2 H, 2,6-Ar); ^{13}C NMR ($CDCl_3$): δ 24.9, 40.2, 46.9, 55.2 (CH_3), 114.0 (3,5-Ar), 124.5 (CN), 127.0 (2,6-Ar), 131.7 (ipso-Ar), 159.9 (ipso-Ar).

1-(*p*-Methoxyphenyl)cyclopentanecarboxylic acid (2a) was prepared using a procedure similar to that for the synthesis of 1-(*p*-methoxyphenyl)cyclobutanecarboxylic acid.[27,28] Thus, 36.0 g (0.19 mol) of 1-(*p*-methoxyphenyl)cyclopentanenitrile, 11.8 g of KOH (88%, 0.21 mol), and 90 mL of diethylene glycol were stirred at reflux temperature for 6 days. After the darkly colored reaction mixture was cooled, acidified with hydrochloric acid, and treated with activated carbon, recrystallization from 160 mL of 40% aqueous EtOH yielded 12 g (55 mmol, 29%) of the acid: mp 160–162 °C; IR (Nujol mull) OH stretch, 3150–2500 (m), C=O stretch, 1757 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65–1.8 (m, 4 H), 1.8–1.95 (m, 2 H), 2.6–2.7 (m, 2 H), 3.8 (s, 3 H, CH_3O), 6.85 (d, J = 8.9 Hz, 2 H, 3.5-Ar), 7.3 (d, J = 8.9 Hz, 2 H, 2,6-Ar); ^{13}C NMR ($CDCl_3$) δ 23.5, 36.0, 55.2, 58.1 (CH_3), 113.7 (3,5-Ar), 128.2 (2,6-Ar), 134.6 (ipso-Ar), 158.5 (ipso-Ar), 182.5 (COOH).

[1-(*p*-Methoxyphenyl)cyclopentyl]carbinol (3a) was prepared using a method similar to that for synthesis of [1-(*p*-methoxyphenyl)cyclobutyl]carbinol.[27,29] Accordingly, to 7.4 g (34 mmol) of 1-(methoxyphenyl)cyclopentanecarboxylic acid dissolved in 15 mL of THF (Aldrich, spectrophotometric grade), under a nitrogen blanket, were added 52 mL of 1 M BH_3–THF

(23) This is particularly true for the correlation with neophyl brosylate data. Some time ago, Schleyer[24] used neophyl tosylate data to define a set of σ^+ constants which he considered more appropriate than the usual Brown values for correlations involving β-aryl participation. We agree with this suggestion.

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complex (52 mmol) over a 15 min period with cooling. After being stirred for an additional 2 h at room temperature, the mixture was poured with stirring into 300 mL of water. The usual workup yielded 6.3 g (30 mmol, 88.2% yield) of crude [1-(*p*-methoxyphenyl)cyclopentyl]carbinol. Recrystallization from 1:1 EtOH–H_2O gave the purified alcohol: mp 45–46 °C; IR (CCl_4) OH stretch, 3650–3570 (m), CO stretch, 1042 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (s, 1 H, OH), 1.62–1.75 (m, 4 H), 1.75–1.9 (m, 2 H), 1.9–2.0 (m, 2 H), 3.4 (d, J = 5.4 Hz, 2 H, CH_2), 3.7 (s, 3 H, CH_3O), 6.8 (d, J = 8.9 Hz, 2 H, 3,5-Ar), 7.2 (d, J = 8.9 Hz, 2 H, 2,6-Ar); ^{13}C NMR ($CDCl_3$) δ 23.9, 34.5, 52.6, 55.2 (CH_3O), 70.2 (CH_2), 113.6 (3,5-Ar), 128.2 (2,6-Ar), 138.8 (ipso-Ar), 157.9 (ipso-Ar).

[1-(*p*-Methoxyphenyl)cyclopentyl]carbinyl tosylate (4a) was prepared using a standard procedure for the synthesis of tosylate esters.[22c] The alcohol, 3.3 g (16 mmol), was caused to react with 3.24 g (17 mmol) of purified p-toluenesulfonyl chloride dissolved in 40-mL of dry pyridine (Aldrich, spectrophotometric grade) cooled to 0 °C. After the alcohol was allowed to stand for 24 h at 5 °C and the usual workup, recrystallization from 100 mL of 9:1 petroleum ether (bp 30 to 60 °C)–benzene gave 3.3 g (9.2 mmol, 58% yield) of the tosylate: mp 56–57 °C; IR (CCl_4) SO_2 stretch 1370 (s), 1180 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–1.8 (m, 4 H), 1.8–2.0 (m, 4 H), 2.4 (s, 3 H, $ArCH_3$), 3.8 (s, 3 H, OCH_3), 3.9 (s, 2 H, CH_2), 6.75 (d, J = 8.9 Hz, 2 H, Ar), 7.1 (d, J = 8.9 Hz, 2 H, Ar), 7.19 (d, J = 8.9 Hz, 2 H, 3,5-Ar), 7.49 (d, J = 8.9 Hz, 2 H, 2,6-Ar); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 23.6, 34.7, 50.8, 55.2 (OCH_3), 76.3 (CH_2), 113.4 (Ar), 127.7 (Ar), 128.0 (Ar), 129.5 (Ar), 132.8 (ipso-Ar), 137.2 (ipso-Ar), 149.4 (ipso-Ar), 158.1 (ipso-Ar).

1-(*p*-Methylphenyl)cyclopentanecarbonitrile (1b). The procedure described for the synthesis of **1a** was used to prepare **1b** in 57% yield: bp 136–138 °C/0.4 mm; IR (neat) C≡N stretch, 2234 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8–2.1 (m, 6 H), 2.3–2.4 (m, 2 H), 2.3 (s, 3 H, $ArCH_3$), 7.1 (d, J = 8.9 Hz, 2 H, 3,5-Ar), 7.3 (d, 2 H, J = 8.9 Hz, 2,6-Ar); ^{13}C NMR ($CDCl_3$) δ 20.0 (CH_3), 23.3, 39.5, 46.5, 123.6 (2,6-Ar), 125.0 (CN), 128.6 (3,5-Ar), 135.9 (ipso-Ar), 136.5 (ipso-Ar).

1-(*p*-Methylphenyl)cyclopentanecarboxylic Acid (2b). This compound was made by a modified Heyama procedure.[30] Thus, 28 g (150 mmol) of 1-(methylphenyl)cyclopentanecarbonitrile, 150 mL of 50% aqueous KOH, and 250 mL of ethanol were stirred at reflux temperature for 4 days. After removal of most of the alcohol via rotovaporization and acidification with concentrated HCl, 27 g of crude product was isolated. Recrystallization from 200 mL of hot 4:1 EtOH–H_2O gave 15.9 g (85 mmol, 57% yield) of the acid: mp 180–181 °C; IR (Nujol mull) OH stretch, 3250–2500 (m), C=O stretch, 1689 (m) cm^{-1}; ^1H NMR (DMSO) δ 1.6–1.8 (m, 6 H), 1.75–1.9 (m, 2 H), 2.3 (s, 3 H, CH_3), 3.4 (s, small peak), 7.2 (d, J = 7.3 Hz, 2 H, 3,5-Ar), 7.3 (d, J = 7.3, 2,6-Ar), 12.2 (s, small peak); ^{13}C NMR (DMSO) δ 20.5 (CH_3), 23.2, 35.6, 60.1, 126.5 (2,6-Ar), 128.7 (3,5-Ar), 135.1 (ipso-Ar), 140.7 (ipso-Ar), 176.8 (COOH).

[1-(*p*-Methylphenyl)cyclopentyl]carbinol (3b). The procedure described for the synthesis of **3a** was used to prepare **3b** in 71% yield: mp 44–46 °C; IR (CCl_4) OH stretch, 3619–3400 (m), CO stretch, 1050 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6 (s, 1 H, OH), 1.6–1.8 (m, 4 H), 1.80–1.85 (m, 2 H), 1.8–2.0 (m, 2 H), 2.3 (s, 3 H, $ArCH_3$), 3.4 (s, 2 H, CH_2), 7.1 (d, J = 7.8 Hz, 2 H, 3,5-Ar), 7.17 (d, J = 7.8 Hz, 2 H, 2,6-Ar); ^{13}C NMR ($CDCl_3$) δ 20.9 (CH_3), 23.9, 34.4, 52.9, 70.3 (CH_2), 127.2 (2,6-Ar), 129.0 (3,5-Ar), 135.6 (ipso-Ar), 143.8 (ipso-Ar).

[1-(*p*-Methylphenyl)cyclopentyl]carbinyl tosylate (4b). The procedure described for the synthesis of **4a** was used to prepare **4b** in 62% yield. Recrystallization from 9:1 petroleum ether (bp 30–60 °C)–benzene gave the ester: mp 78–80 °C; IR (CCl_4) SO_2 stretch, 1373 (s), 1182 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–1.8 (m, 4 H), 1.8 (m, 4 H), 2.3 (s, 3 H, $ArCH_3$), 2.4 (s, 3 H, $ArCH_3$), 3.9 (s, 2 H, CH_2), 7.0 (d, J = 8.9 Hz, 2 H, Ar), 7.05 (d, J = 8.9 Hz, 2 H, Ar), 7.17 (d, J = 8.9 Hz, 2 H, Ar), 7.49 (d, J = 8.9 Hz, 2 H, Ar); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.6, 23.6, 34.7, 50.6, 76.3 (CH_2), 126.85 (Ar), 127.7 (2,6-Ar), 128.8 (Ar), 129.5 (Ar), 132.7 (ipso-Ar), 135.7 (ipso-Ar), 142.0 (ipso), 144.3 (ipso-Ar).

1-Phenylcyclopentanecarbonitrile (1c) was prepared as previously described[6a] in 86% yield: bp 108 °C (at 0.8 Torr); IR (CCl_4) C≡N stretch, 2234 (w) cm^{-1}.

1-Phenylcyclopentanecarboxylic Acid (2c). The procedure described for the synthesis of **2b** was used to prepare **2c** in 68% yield: mp 162–163 °C (lit.[31] mp 162–163.5 °C).

(1-Phenylcyclopentyl)carbinol (3c). The procedure described for the synthesis of **1c** was used to prepare **3c** in 75% yield: mp 43–44 °C (lit.[6a] mp 43–44 °C); IR (CCl_4) OH stretch, 3658–3390 (m), CO stretch, 1050 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (s, 1 H, OH), 1.6–1.7 (m, 4 H), 1.7–1.9 (m, 2 H), 1.9–2.0 (m, 2 H), 3.42 (s, 2 H, CH_2), 7.15–7.25 (m), 7.30 (s), 7.31 (broad peak); ^{13}C NMR ($CDCl_3$) δ 23.9, 34.4, 35.3, 70.38 (CH_2), 126.2 (*p*-Ar), 127.3 (*m*-Ar), 128.4 (*o*-Ar), 146.9 (ipso-Ar).

(1-Phenylcyclopentyl)carbinyl Tosylate (4c). The procedure described for the synthesis of **4a** was used to prepare **4c** in 65% yield: mp 115–116 °C (lit.[6a] mp 115–115.5 °C); IR (CCl_4) SO_2 stretch, 1373 (s), 1178 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–1.76 (m, 4 H), 1.8–2.0 (m, 4 H), 2.4 (s, 3 H, CH_3), 4.0 (s, 2 H, CH_2), 7.17, 7.20, 7.21, 7.22, 7.47 (d, J = 8.9 Hz, 2 H, Ar); ^{13}C NMR ($CDCl_3$) δ 23.0 (CH_3), 25.02, 36.1, 52.37, 77.6 (CH_2), 127.7, 128.4, 129.1, 129.5 , 131.0 (ipso-Ar), 134.1, 145.7 (ipso-Ar), 146.5 (ipso-Ar).

1-(*p*-Chlorophenyl)cyclopentanecarbonitrile (1d). The procedure described for the preparation of **1a** was used to prepare **1d** in 61% yield: mp 36–36.5 °C; IR (CCl_4) C≡N stretch, 2234 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8–2.3 (m, 6 H), 2.4–2.6 (m, 2 H), 7.33 (d, J = 8.1 Hz, 2 H, 3,5-Ar), 7.36 (d, J = 8.1 Hz, 2 H, 2,6-Ar); ^{13}C NMR ($CDCl_3$) δ 24.2, 40.4, 47.3, 123.9 (CN), 127.4 (3,5-Ar), 128.9 (2,6-Ar), 134.8 (ipso-Ar), 138.7 (ipso-Ar).

1-(*p*-Chlorophenyl)cyclopentanecarboxylic Acid (2d). The procedure described for the preparation of **2b** was used to prepare **2d** in 60% yield: mp 162–164 °C; IR (nujol mull) OH stretch, 3200–2500 (m), C=O stretch, 1692 (s) cm^{-1}; ^1H NMR (DMSO) δ 1.6–1.9 (m, 6 H, with a sharp peak at 1.7), 2.5–2.8 (m, 2 H), 3.45 (s), 7.43 (s, 4 H, Ar-H), 12.5 (s, small peak, COOH); ^{13}C NMR (DMSO) δ 23.2, 35.6, 57.9, 128.2 (3,5-Ar), 128.7 (2,6-Ar), 131.3 (ipso-Ar), 141.7 (ipso-Ar), 176.3 (COOH).

[1-(*p*-Chlorophenyl)cyclopentyl]carbinol (3d). The procedure described in the synthesis of **3a** was used to prepare **3d** in 92% yield: mp 42–43 °C; IR (CCl_4) OH stretch, 3627–3581 (w), CO stretch, 1050 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (s, 1H, OH), 1.6–1.8 (m, 6H); 3.4 (s, 2H, CH_2); 7.09–7.27 (m, 4H, Ar, two sharp peaks at 7.18 and 7.20); ^{13}C NMR ($CDCl_3$) δ 23.8, 24.1, 32.5, 34.4, 52.9, 70.0 (CH_2), 128.3 (3,5-Ar), 128.8 (t, 2,6-Ar), 131.9 (ipso-Ar), 145.4 (ipso-Ar).

[1-(*p*-Chlorophenyl)cyclopentyl]carbinyl Tosylate (4d). The procedure described in the synthesis of **4a** was used to prepare **4d** in 62% yield: mp 86–88 °C; IR (CCl_4) SO_2 stretch, 1377 (s), 1184 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–1.8 (m, 4 H), 1.8–1.9 (m, 2 H), 1.9–2.0 (m, 2 H), 2.4 (s, 3 H, $ArCH_3$), 3.92 (s, 2 H, CH_2), 7.04 (d, J = 8.9 Hz, 2 H, 7.11 (d, J = 8.9 Hz, 2 H, Ar), 7.18 (d, J = 8.9 Hz, 2 H, 3,5-Ar), 7.45 (2 H, d, J = 8.9 Hz, 2,6-Ar); ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 23.4, 34.5, 50.5, 75.8 (CH_2), 127.5, 127.9, 128.3, 129.6, 132.1 (ipso-Ar), 132.3 (ipso-Ar), 143.6 (ipso-Ar), 144.4 (ipso-Ar).

1-[3,5-Bis(trifluoromethyl)phenyl]cyclopentanecarbonitrile (1e). The procedure described for the synthesis of **1a** was used to prepare **1e** in 64% yield [it was necessary to chromatograph the crude product through a 56 × 2 cm column packed with Florisil (100–200 mesh, 90 g) in petroleum ether (bp 30–60 °C), using petroleum ether as the eluent]. Several fractions were combined to give the semisolid nitrile: mp slightly below 25 °C; IR (CCl_4) C≡N stretch, 2253 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0–2.2 (m, 6 H), 2.5–2.7 (m, 2 H), 7.85 (s, 1 H, Ar), 7.91 (s, 2 H, Ar); ^{13}C NMR ($CDCl_3$) δ 24.0, 40.7, 48.2, 121.1 (CN), 122.1(2,6-Ar), 123.8, 125.1 (ipso-Ar), 126.5 (4-Ar), 132.5(q, CF_3), 142.6 (ipso-Ar).

1-[3,5-Bis(trifluoromethyl)phenyl]cycopentanecarboxylic Acid (2e). The procedure described for the synthesis of **2b** was used to prepare **2e** in 69% yield: mp 156–157 °C; IR (Nujol mull) OH stretch, 3100–2500 (w), C=O stretch, 1709 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 1.76–1.87 (m, 6 H), 2.70–2.78 (m, 2 H), 7.95 (s, 1 H, 4-Ar), 8.02 (s, 2 H, 2,6-Ar); ^{13}C NMR (acetone-d_6) δ 24.3, 37.1, 59.8, 121.5 (2,6-Ar), 122.5, 126.5 (ipso-Ar), 128.5 (4-Ar), 132.0 (q, CF_3), 148.3 (ipso-Ar), 175.8 (COOH).

[1-[3,5-Bis(trifluoromethyl)phenyl]cyclopentyl]carbinol (3e). The procedure described for the synthesis of **3a** was

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used to prepare **3e** in 80% yield: mp 45–6 °C; IR (CCl_4) OH stretch, 3547–3171 (w), CO stretch 1051 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (s, 1 H, OH), 1.7–2.2 (m, 4 H), 2.2–2.4 (m, 4 H), 3.6 (s, 2 H, CH_2), 7.74 (s, 1 H, 4-Ar), 7.76 (s, 2 H, 2,6-Ar); ^{13}C NMR ($CDCl_3$) δ 23.7, 30.7, 34.4, 53.4, 69.3 (CH_2), 120.0 (2,6-Ar), 121.5, 126.2 (ipso-Ar), 127.6 (4-Ar), 131.3 (q, CF_3), 150.2 (ipso-Ar).

[1-[3,5-Bis(trifluoromethyl)phenyl]cyclopentyl]carbinyl tosylate (4e). The procedure described for the synthesis of **4a** was used to prepare **4e** in 67% yield: mp 88–89 °C; IR (CCl_4) SO_2 stretch, 1379 (s), 1178 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7–1.8 (m, 4 H), 1.8–2.0 (m, 2 H), 2.0–2.2 (m, 2 H), 2.38 (s, 3 H, $ArCH_3$), 4.0 (s, 2 H, CH_2), 7.15 (d, J = 8.9 Hz, 2 H, Ar), 7.43 (d, J = 8.9 Hz, 2 H, Ar), 7.54 (s, 2 H, Ar), 7.66 (s, 1 H,); ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 23.4, 34.6, 51.3, 74.8 (CH_2), 125.3, 127.3 (ipso-Ar), 127.45, 128.40, 129.64, 131.3 (q, CF_3), 132.2, 144.8 (ipso-Ar), 148.1 (ipso-Ar).

Solvents were prepared and **rate measurements** were carried out as previously described.[32]

Treatment of Kinetic Data. First-order rate constants were calculated by using the integrated first-order equation: $k_t = 1/t \ln[mL_\infty/(mL_\infty - mL_t)]$. Multiple determinations (8–12) were made for each kinetic run. The activation parameters listed in Table 1 were obtained by regression analysis[33] of ln (k_t/T) versus $1/T$. The ϱ values recorded in Table 2 were also obtained by regression analysis.

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