Structural Effects in Solvolytic Reactions. 23. New σ^+ Constants for Activating Substituents. The Solvolysis of 1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates Containing Activating Substituents in the Aryl Group. The Tool of Increasing Electron Demand and I-Strain

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Abstract: The σ^+ constants for *p*-methylthio (*p*-CH_3S) and 5-coumaranyl substituents have been established from the rates of solvolysis of 2-aryl-2-propyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C. The σ^+ constant for *p*-methylthio has been revised to −0.542 and that for 5-coumaranyl determined to be −0.984. 1-Aryl-1-cyclopropyl 3,5-dinitrobenzoates containing activating substituents (*p*-CH_3O, *p*-CH_3S, and *p*-CH_3) were synthesized and their rates of solvolysis measured in 80% aqueous acetone. The system yields a ρ^+ of −5.19, considerably more negative even than the unusual value of ρ^+ observed for the solvolysis of related cyclobutyl derivatives (−4.91), approaching that for 7-norbornyl (ρ^+ = −5.27). The solvolysis products are predominantly the unaltered alcohol for *p*-CH_3O (87%) with only a minor amount of the ring-opened allyl alcohol (13%). The latter increases to 30% for *p*-CH_3S, and becomes the major product, 95%, for *p*-CH_3. The applicability of the tool of increasing electron demand in evaluating I-strain in cycloalkyl systems is discussed. Extrapolation of data from the tertiary derivatives to the secondary cyclopropyl species indicates that the solvolysis of the secondary derivative is enhanced by huge anchimeric assistance, involving a factor of $\sim 10^6$.

The tool of increasing electron demand offers major promise for exploring the effect of structure on the stability of carbocations produced in solvolytic processes.[2] Numerous representative systems have been examined by this tool to establish the effect on the developing carbocationic center of typical cyclic and acyclic groups.[3] Recently we applied this tool to the study of the effect of ring size on solvolysis.[4] 1-Aryl-1-cycloalkyl *p*-nitrobenzoates with ring carbon atoms of four to eight members were examined. A remarkable parallelism was observed to exist between the ρ^+ values realized and the relative reactivities exhibited by these ring systems, previously accounted for in terms of I-strain effects.[5] It seemed highly desirable to have comparable data for the solvolysis of 1-aryl-1-cyclopropyl derivatives in order to permit a direct comparison with the ρ^+ values realized in other cycloalkyl derivatives.

It should be pointed out that De Puy and his co-workers had previously studied the acetolysis of 1-aryl-1-cyclopropyl tosylates and had reported ρ^+ values both for the normal solvolysis and for that involving internal return.[6] Regrettably, we encountered difficulties in attempting to utilize these data to fix ρ^+ at 25 °C for comparison with our values at this temperature. Thus, they reported rate constants at two temperatures only for two substituents, *p*-CH_3 and *p*-H. For *m*-Cl and *m*-CF_3 they reported rate constants only at 108.4 °C. We calculated these to 25 °C, utilizing the frequency factor for *p*-H. Unfortunately, the four data points do not give a satisfactory plot (Figure 1) against σ^+ ($\rho^+ = -4.67 \pm 0.11$). If we use only the two points, *p*-CH_3O and *p*-H, which can be extrapolated directly to 25 °C without approximation, we obtain a ρ^+ value, −5.15, more consistent with our other values.[4]

There is another problem. All of our other values are based upon the solvolysis of substituted benzoates (usually the *p*-nitrobenzoates) as the leaving groups. Indeed, these derivatives are so reactive that it would be impractical to synthesize the tertiary benzylic tosylates for study. The inertness of the 1-aryl-1-cyclopropyl system is such that in this system it is possible, almost uniquely for a tertiary benzylic system, to prepare the tosylates. Unfortunately it has not yet been established whether ρ^+ depends significantly upon the nature of the leaving group.

The desire not to modify the structure of the leaving group at the point of attachment to the alicyclic ring system created a serious experimental difficulty. As already mentioned, cyclopropyl derivatives are extraordinarily resistant to solvolysis,[6] presumably the result of I-strain.[5] Consequently, in order to use substituted benzoates as leaving groups, we were forced to work only with 1-aryl-1-cyclopropyl derivatives containing activating substituents in the aromatic ring. Usually we have utilized only *p*-methoxy as an activating group. In order to obtain more data points in the activated region, we undertook to establish the σ^+ values for the *p*-methylthio and 5-coumaranyl substituents, two groups which would straddle *p*-methoxy on the σ^+ scale. Finally, we shifted from the *p*-nitrobenzoate to the better leaving group 3,5-dinitrobenzoate, further to facilitate the kinetic studies.

Results

Synthesis. 2-(5′-Coumaranyl)-2-propyl benzoate (**1**) was synthesized according to eq 1. Similarly, 2-*p*-methylthiophenyl-2-propyl *p*-nitrobenzoate was prepared from the tertiary alcohol through the lithium alkoxide. 1-Aryl-1-cyclopropanols (**2**, X = *p*-CH_3O, *p*-CH_3S, *p*-CH_3) were synthesized following the general method described by De Puy et al. (eq 2).[7] The tertiary alcohols were converted into 3,5-dinitro-

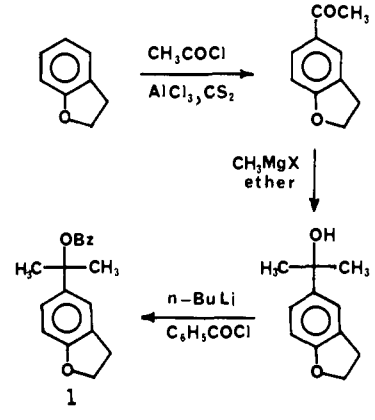

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Table I. The Rates of Solvolysis of 2-Aryl-2-propyl Derivatives in 80% Aqueous Acetone[a]

Aryl substituent	Leaving group	10^6k_1, s^{-1} T_1, °C	T_2, °C	25.0 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	σ^+
5-Coumaranyl	OBz	5.48 (0)		154	21.0	−5.5	
	OPNB			3203[b]			−0.984
p-CH_3O	OBz			17.2[c]			
	OPNB			372[c]			−0.778
p-CH_3S	OPNB	504 (50)		26.1	22.1	−5.5	−0.542
p-H	OPNB	391 (100)	33.6 (75)	0.072[d]	24.8	−8.2	0.00

[a] For related data see Table I, ref 4. [b] Calculated by multiplying the rate constant for the benzoate by the factor 20.8. [c] These values give k_{OPNB}/k_{Bz} = 21.6, in good agreement, within the experimental uncertainty, with the earlier value 20.8 we have been using.[8] For consistency, the value 20.8 will continue to be used. [d] Calculated from data at higher temperatures.

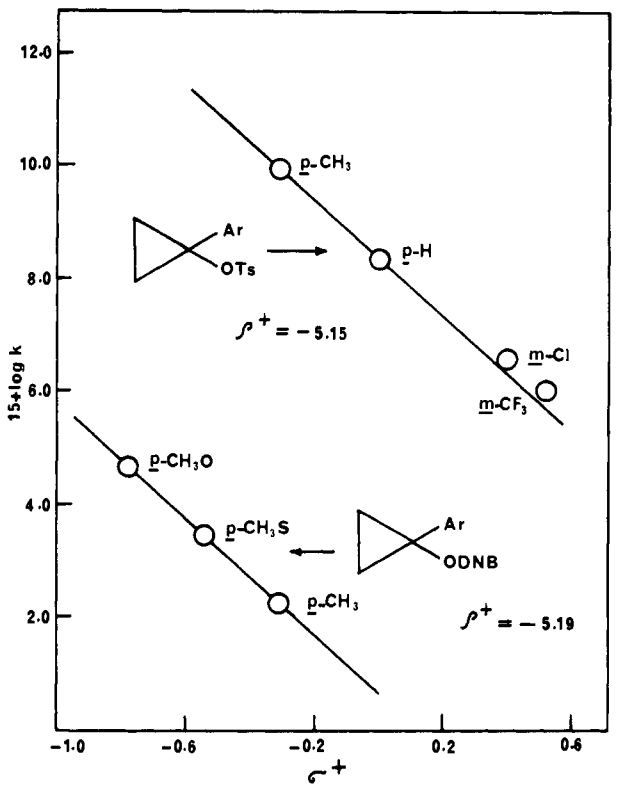
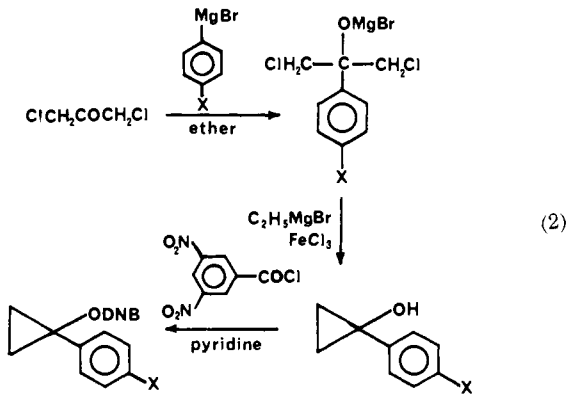


Figure 1. Log k–σ^+ plot at 25 °C for the 1-aryl-1-cyclopropyl tosylates in acetic acid and the 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates in 80% aqueous acetone.



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benzoates (**3**) by treating them with 3,5-dinitrobenzoyl chloride in pyridine. Properties of the dinitrobenzoates are given in the Experimental Section.

Solvolysis. The rates of solvolysis of the 2-aryl-2-propyl *p*-nitrobenzoates were determined in 80% aqueous acetone. The rate constant for 2-(5′-coumaranyl)-2-propyl *p*-nitrobenzoate was calculated by multiplying the rate of the benzoate by a factor of 20.8,[8] confirmed by comparing the rates of solvolysis of the two 2-anisyl-2-propyl derivatives. The pertinent rate data and σ^+ constants are summarized in Table I.

The rate constants and activation parameters for the solvolysis of the various 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates are tabulated in Table II.

Product Studies. The products of solvolysis of 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates were determined in buffered aqueous acetone at 150 °C. The products were analyzed by GC and ^1H NMR. The results are tabulated in Table III.

Discussion

The remarkably low reactivity of cyclopropyl derivatives in solvolytic reactions has been accounted for in terms of I-strain, the unfavorable increase in bond angle strain in such small rings in passing from the ground state to the transition state.[5] Thus, from an early study of the rates of solvolysis of the 1-methyl-1-cycloalkyl chlorides, it was predicted on the basis of I-strain that the rate of solvolysis of 1-methyl-1-cyclopropyl chloride should be very much slower than that of 1-methyl-1-cyclobutyl chloride, which itself exhibits a relatively slow rate. Unfortunately, experimental difficulties at the time made it impractical to synthesize 1-methyl-1-cyclopropyl chloride and the prediction could not be tested. Since that time, procedures have been developed for the synthesis of tertiary cyclopropanols[7] and the inertness of such derivatives in solvolysis has been established.[6]

Unfortunately, in all known cases, the solvolysis of tertiary alkyl and aryl cyclopropyl derivatives takes place with ring opening.[6] Consequently, it has not been possible to attain a realistic estimate of the effect of I-strain in a system undergoing solvolysis without participation. For example, it was pointed out that the rate of acetolysis of cyclopropyl tosylate is slower by a factor of 10^5 than that for cyclohexyl tosylate.[9] However, as pointed out later, the acetolysis of cyclopropyl tosylate occurs with ring opening and the rate must be enhanced by a very large factor of the order of 10^6. Thus the difference in reactivity between cyclopropyl and cyclohexyl for a simple ionization process must be a factor very much larger than 10^6.

The extraordinary inertness of the cyclopropyl system toward solvolysis in a system where neither carbon nor solvent participation is significant is revealed by comparing the rate of *p*-methoxy-*tert*-cumyl with that of 1-*p*-anisyl-1-cyclopropyl (Tables I and II). This comparison provides an enormous factor of 1.3×10^8!

Our present interest in the solvolysis of tertiary cyclopropyl derivatives stems from our earlier investigations on the solvolysis of the 1-aryl-1-cycloalkyl *p*-nitrobenzoates.[4] The spread in ρ^+ values in cycloalkyl systems containing rings of four to eight members suggested that the observed variation might have its origin in I-strain. It is evident that the strain accom-

Table II. Rates of Solvolysis of 1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates in 80% Aqueous Acetone

RODNB (3) X	10^6k_1, s^{-1} T_1, °C	T_2, °C	25.0 °C[a]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-CH_3O	212 (150)	21.4 (125)	4.7×10^{-5}	29.9	−11.0
	11.8 (150)[b]	1.21 (125)[b]	2.93×10^{-6} [b]	29.8	−11.0
p-CH_3S	22.7 (150)	2.1 (125)	2.87×10^{-6}	31.3	−6.5
p-CH_3	86.2 (175)	8.23 (150)	1.78×10^{-7}	34.8	−0.1

[a] Calculated from data at higher temperatures. [b] *p*-Nitrobenzoate. This gives $k_{ODNB}/k_{OPNB} = 16.0$.

Table III. Products of Solvolysis of 1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates in 80% Aqueous Acetone

RODNB (3) X	Products, % Unrearranged alcohol (2)	Allylic alcohol (9)
p-CH_3O	87	13
p-CH_3S	70	30
p-CH_3	5	95

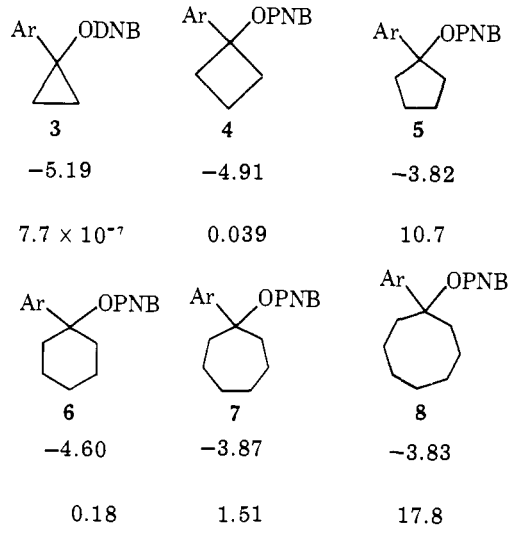
panying the introduction of an sp^2 center in the cyclopropyl system must result in a large demand by that center for additional electronic contributions from the 1-aryl substituent. Hence one would expect both a low rate of ionization and a large negative value of ρ^+, more negative even than the large negative value observed for the 1-aryl-1-cyclobutyl system (ρ^+ −4.91).

As discussed earlier, it is necessary to utilize 1-aryl-1-cyclopropyl derivatives containing activating substituents in the aryl group to measure the rate of solvolysis of derivatives with substituted benzoates as the leaving groups. The tosylates used by De Puy can accommodate deactivating substituents, but we wished to obtain a value of ρ^+ which could be compared directly with our other values.[4] Actually, there is a further possible advantage to the use of derivatives containing activating substituents. Many cyclopropyl derivatives undergo solvolysis with concerted ring opening.[6] All of the tosylates studied by De Puy underwent acetolysis with complete ring opening. Such derivatives with activating substituents may undergo solvolysis without significant concerted ring opening since the substituents contribute greatly to the stability of the developing cationic center.[10-13]

Accordingly, we undertook to establish the σ^+ constants for two highly activating substituents straddling *p*-methoxy. The σ^+ value for the *p*-methylthio group (−0.604) had been determined earlier,[14a] from measurements of the rate of the solvolysis of 2-*p*-methylthiophenyl-2-propyl chloride at low temperatures[14b] with long extrapolations of the data to 25 °C. However, the use of the *p*-nitrobenzoate enabled us to measure the rate constant at 25 °C and the new σ^+ value (−0.542) could be directly calculated from the log $(k/k_H) = \rho^+\sigma^+$ relationship (Table I).[14a] Similarly, the σ^+ value for another activating substituent, 5-coumaranyl, was determined as −0.984 from a study of the rate of solvolysis of 2-(5′-coumaranyl)-2-propyl benzoate (Table I).

Unfortunately, all attempts to synthesize 1-(5′-coumaranyl)-1-cyclopropanol from the 5-bromocoumaran by De Puy's method were unsuccessful. The major product of the reaction is coumaran itself, presumably resulting from a proton abstraction from the solvent by the highly reactive Grignard reagent. Consequently, we were forced to forego this substituent and to utilize only those derivatives containing *p*-CH_3O, *p*-CH_3S, and *p*-CH_3 substituents. The rates of solvolysis of these 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates are summarized in Table II. The data provide an excellent log k-σ^+ relationship (Figure 1), yielding a ρ^+ value of −5.19 (correlation coefficient 0.9999, standard deviation ±0.026), in good agreement with the value of −5.15 calculated as described earlier from De Puy's data for the initial rates of acetolysis of the two tosylates (*p*-CH_3, and *p*-H).

It is instructive to compare the value of ρ^+ observed in the solvolysis of the cyclopropyl derivatives (**3**) with the values of ρ^+ realized in the solvolysis of the other cycloalkyl systems (**4, 5, 6, 7,** and **8**).



These changes in the value of ρ^+ with ring size parallel closely the changes in the rates of solvolysis of the 1-*p*-anisyl-1-cycloalkyl *p*-nitrobenzoates (2-*p*-anisyl-2-propyl = 1.00). In this comparison, the *p*-anisyl derivatives are utilized because in the cyclopropyl system it is only the *p*-anisyl compound which undergoes solvolysis without important rearrangement (Table III). A log k-ρ^+ plot of these data reveals a reasonable correlation (Figure 2), with only the cyclopropyl derivative revealing an exceptional deviation. A possible contributing factor to this deviation is discussed later.

An interpretation of the operation of I-strain in influencing the absolute value of ρ^+ was presented in a previous paper from this laboratory.[4] It was suggested that the relative reactivities and the value of ρ^+ may both have their origin in I-strain. The strain accompanying the introduction of an sp^2 center in the cyclopropyl and cyclobutyl rings not only results in a slow rate, but also in a transition state that is closer to the intermediate.[15] This results in an increase in the electron deficiency of the developing cationic center, producing a large demand by that center for additional electronic supply from the aryl group and its substituent. In these systems the low rate of ionization and the large negative ρ^+ values are thereby related.

The solvolytic reactions of simple cyclopropyl derivatives usually yield in the absence of steric or conjugative effects[10] only allylic products[9] through a concerted ionization and ring opening.[16,17] On the other hand, unopened products result only when substituents are present that contribute greatly to the stability of the cationic center.

The major product of solvolysis of 1-*p*-anisyl-1-cyclopropyl 3,5-dinitrobenzoate (**3**, X = *p*-CH_3O) is the unrearranged

Table IV. Properties of 1-Aryl-1-cyclopropanols

Substituent in aryl	Yield, %	Mp or bp (mm), °C	Molecular formula	Anal, % C	H	S
p-CH_3O	35	75-78 (0.5)	$C_{10}H_{12}O_2$	C[b] 73.17	7.31	
				F[c] 73.01	7.22	
p-Ch_3S	40	77-78	$C_{10}H_{12}OS$	C 66.67	6.67	17.78
				F 66.32	6.52	17.60
p-CH_3[a]	47	38-39	$C_{10}H_{12}O$			

[a] Lit. mp 39-40 °C (ref 7). [b]Calculated. [c] Found.

Table V. Properties of 1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates

Substituent in aryl	Yield, %	Mp, °C	Molecular formula	Anal, % C	H	N	S
p-CH_3O	74	109-110	$C_{17}H_{14}N_2O_7$	C[a] 56.98	3.91	7.82	
				F[b] 56.77	4.07	7.63	
p-CH_3S	80	134-135	$C_{17}H_{14}N_2O_6S$	C 54.54	3.74	7.48	8.55
				F 54.76	4.01	7.29	8.76
p-CH_3	57	114-115	$C_{17}H_{14}N_2O_6$	C 59.64	4.09	8.18	
				F 59.85	4.22	8.01	

[a] Calculated. [b] Found.

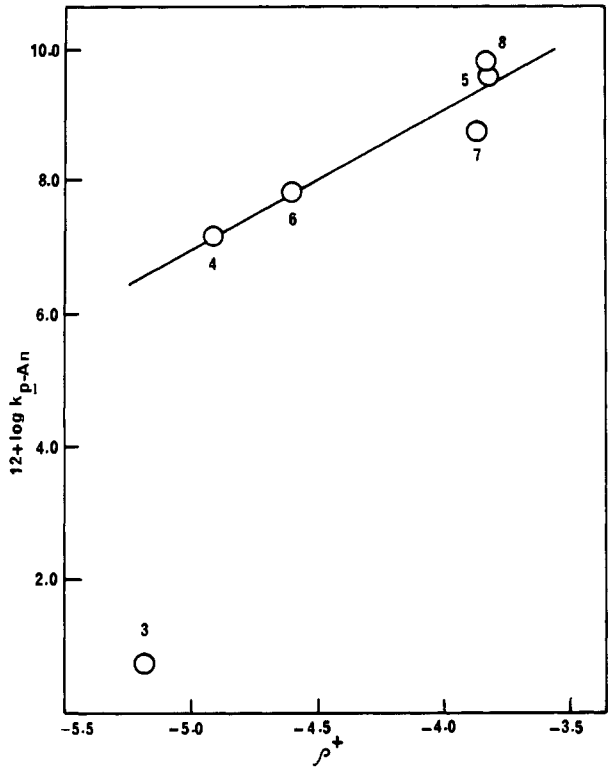


Figure 2. Log k-ρ^+ plot at 25 °C for the 1-*p*-anisyl-1-cycloalkyl *p*-nitrobenzoates in 80% aqueous acetone.

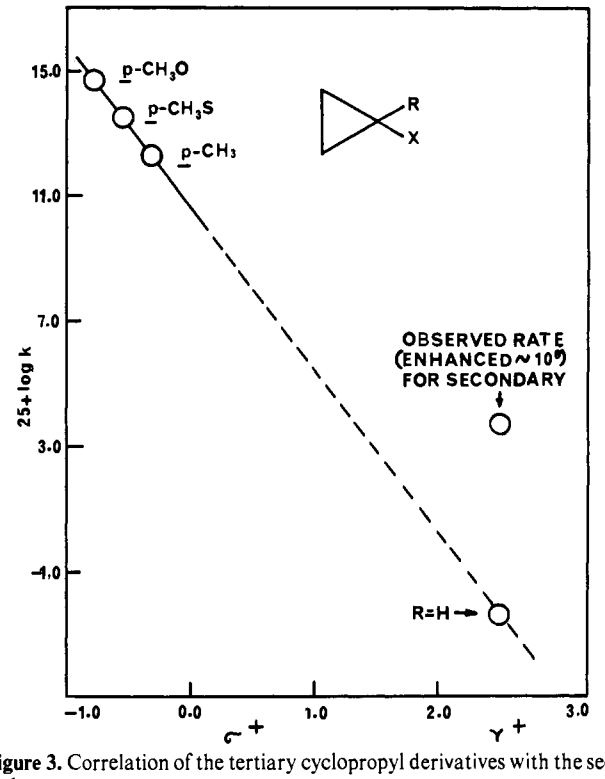
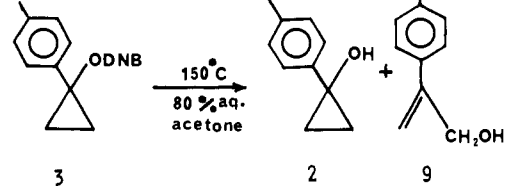


Figure 3. Correlation of the tertiary cyclopropyl derivatives with the secondary.

alcohol (**2**, X = *p*-CH_3O, 87%, Table III), with a minor amount (13%) of the ring-opened product **9**. The amount of



unrearranged alcohol decreases with less activating substituents, 70% for X = *p*-CH_3S, and 5% for X = *p*-CH_3. If the ring opening were to occur subsequent to the ionization, this would involve no significant effect upon the value of ρ^+. However, the possibility that the solvolysis involves concurrent k_c and k_Δ processes must be considered. Indeed, the observed large changes in $\Delta S^\ddagger$ (Table II) correspond to that anticipated for an increasing k_Δ component

In theory we could multiply the observed values of k_1 at the experimental temperatures (175 and 150 °C for *p*-CH_3; 150 and 125 °C for *p*-CH_3S and *p*-CH_3O) by the fractions of the two products to obtain values for k_c and k_Δ at these temperatures. We could then extrapolate these values down to 25 °C to obtain individual values for k_c and k_Δ. A plot of the logarithms of these constants against σ^+ should then yield individual values of ρ_c^+ and ρ_Δ^+.

Unfortunately, the solvolysis temperatures are so high and the necessary extrapolations so great that one could have little confidence in the precision of the results. Consequently, we did not undertake such a dissection of the observed solvolysis

constants. It should, however, be recognized that if the solvolysis of these 1-aryl-1-cyclopropyl dinitrobenzoates proceeds through such concurrent processes, then the large negative value realized for ρ^+, −5.19, may in fact be an even larger, negative number for the unassisted ionization process. This would improve the fit of the cyclopropyl derivative in the log k–ρ^+ plot (Figure 2). Irrespective of this uncertainty, it is worth noting that this value of −5.19 for the 1-aryl-1-cyclopropyl system, possibly increased somewhat by participation, is more negative than that for any other system previously examined with the sole exception of 7-norbornyl (ρ^+ = −5.27).[2]

Finally, it is of interest to examine extrapolation of the data from the tertiary 1-aryl-1-cyclopropyl derivatives to the parent secondary tosylate.[18,19] The extrapolation using the substituent constant for hydrogen[20] reveals that the solvolysis of the secondary derivative proceeds with exceptionally large anchimeric assistance (Figure 3). Even though this extrapolation is far longer than in other cases examined,[21] because of the absence of deactivating substituents, it shows that anchimeric assistance in the secondary cyclopropyl derivatives must be large, in the neighborhood of a rate factor of 10^6. Schleyer and coworkers have recently concluded from two independent experimental criteria [m, $(k_{aq\ alc}/k_{AcOH})_y$], together with low α-methyl/hydrogen ratios, that the solvolyses of simple cyclopropyl derivatives are k_Δ processes.[16] They have also estimated the magnitude of anchimeric assistance to be at least a factor of 10^4–10^5 in rate at 25 °C.[16]

In conclusion, the high negative value of ρ^+ observed in the solvolysis of cyclopropyl derivatives is attributed to the destabilization of the cationic center by angle strain effects (I-strain) resulting in a large demand by that center for additional electronic stabilization. The large deviation (increase) in the observed rate constant over the extrapolated value (Figure 3) supports the conclusion that the secondary cyclopropyl derivative solvolyzes by a pathway involving huge (~10^6) anchimeric assistance.

Experimental Section

2-(*p*-Methylthiophenyl)-2-propyl *p*-Nitrobenzoate. This *p*-nitrobenzoate was prepared by treating the tertiary alcohol with *n*-butyllithium and *p*-nitrobenzoyl chloride[22] in THF in 30% yield, mp 96–97 °C.

Anal. Calcd for $C_{17}H_{15}O_4NS$: C, 61.63; H, 5.14; N, 4.23; S, 9.67. Found: C, 61.58; H, 5.12; N, 4.25; S, 9.58.

2-(5′-Coumaranyl)-2-propanol. The procedure followed is essentially the same as described by Brown and Inukai.[23] The tertiary alcohol was crystallized from hexane, mp 41–42 °C (lit.[23] mp 42–43 °C).

2-(5′-Coumaranyl)-2-propyl Benzoate. The benzoate was prepared from *n*-butyllithium and benzoyl chloride in THF. It was used for solvolysis without further purification.

1-Aryl-1-cyclopropanols (2). The procedure described by De Puy et al.[7] was followed. 1,3-Dichloroacetone (1 equiv) in ether was added to an ethereal solution of the arylmagnesium bromide (1 equiv). After the addition was complete, an ethereal solution of ethylmagnesium bromide (3 equiv) and a solution of ferric chloride (0.10 equiv) in ether were added simultaneously over a period of 1 h. The reaction mixture was hydrolyzed with ice-cold ammonium chloride and worked up in the usual way. The properties of the 1-aryl-1-cyclopropanols synthesized are summarized in Table IV.

1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates (3). The dinitrobenzoates of the tertiary alcohols were prepared by treating them with 3,5-dinitrobenzoyl chloride in pyridine following the general procedure described earlier.[24] The properties of the dinitrobenzoates are listed in Table V.

Kinetic Procedure. The procedure employed in determining the rate constants followed that described earlier.[22] All temperatures in the kinetic measurements were controlled to within ±0.02 °C.

Product Analyses. The 3,5-dinitrobenzoates (1 mmol) were solvolyzed at 150 °C in 80% aqueous acetone containing a 10% molar excess of sodium acetate (sealed ampules). After 10 half-lives, the ampules were cooled and opened. The acetone was evaporated and the residue extracted with ether. The methyl derivative was solvolyzed only for 2–3 half-lives. The solvent was removed and the products were analyzed by GC and ^{1}H NMR. The product compositions are tabulated in Table III.

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