Steric Effects of Bulky Leaving Groups in Solvolyses of Crowded Arylsulfonates

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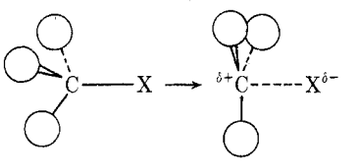
The 2,4,6-trimethylbenzenesulfonate (Mst) and 2,4,6-triisopropylbenzenesulfonate (Tps) esters of 2-propanol (*i*-PrOH), di-*tert*-butylcarbinol (*t*-Bu_2CHOH), 1-adamantanol (1-AdOH), and 2-adamantanol (2-AdOH) have been prepared and their solvolytic reactivities in acetic acid measured and compared to the rates for the corresponding *p*-toluenesulfonates (Ts). Rates relative to the corresponding tosylates at 25° are *i*-PrOMst, 0.23; *i*-PrOTps, 0.25; *t*-$Bu_2CHOMst$, 0.093; *t*-$Bu_2CHOTps$, 0.062; 1-AdOMst, 0.21; 1-AdOTps, 0.17; 2-AdOMst, 0.14; and 2-AdOTps, 0.17. The lower rates of the new leaving groups relative to tosylate are interpreted as being due mainly to inductive effects, but the fact that the leaving group ability of the ortho-substituted sulfonates decreases still more with the more crowded substrates indicates that acceleration due to steric repulsion of the ortho substituent by the alkyl substrate is not a significant factor, but retardation due to solvent exclusion may play a modest role.

Assessment of the contribution of steric factors to the observed reactivity in solvolysis reactions leading to carbonium ions has continued to be a goal of chemical research.[1] At least three discrete steric factors have been considered in proceeding to the transition state in the traditional SN1 mechanism (eq 1). These are relief of steric compression of



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the three groups attached to the central carbon (B strain),[2] relief of the steric interaction of the rest of the molecule with the departing group (F strain),[2,3] and steric inhibition of solvation by the groups surrounding the charged centers.[1a,4] The first two factors would give steric acceleration of the reaction, while the latter would be decelerating.

The possible role of these three factors has been recognized for some time,[1-5] but attention has tended to center on B-strain induced acceleration observed when the bulk of the groups attached to the carbonium ion center is increased. More recently, however, there have been several reports which consider the possibility that differences in leaving group aptitudes may arise partly from repulsion of the bulkier leaving groups by the more crowded substrates, leading to especially rapid rates in such cases.[3-5] The leaving group pairs compared were tosylate/picrate,[3a] tosylate/bromide,[3b] methanol/1-adamantanol,[3c] water/*p*-nitrobenzoate,[4] and chloride/*p*-nitrobenzoate.[5] The authors concluded that F strain was unimportant in the first two cases but was the dominant factor in the latter three.

These studies are persuasive that the leaving group repulsion phenomenon can be significant, and it is of special interest that molecular mechanics calculations promise to quantitatively predict the magnitude of such factors.[5,6] However, it must be noted that these cases involve comparisons of quite dissimilar leaving groups with different electronic character, solvation requirements, shapes, and sizes. Thus it is not obvious how to disentangle the respective contributions of the various probable steric influences on the observed reactivities.

It would appear that the best systematic approach to this question is to maintain the electronic nature of the leaving group as nearly constant as is possible, while varying the bulk of the group in a well-defined way. Experiments on a variety of such systems would permit an assessment of the relative importance of the different steric factors and should provide the best comparison for evaluating the theoretical approaches. Such a program has been initiated in this laboratory, and the present report deals with the first of the systems to be examined.

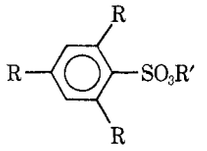
Ortho substituted arylsulfonates were chosen as the first series of leaving groups to be studied. This class has the advantage of being widely used in solvolysis studies and of being capable of a large variation in bulk by using progressively larger ortho substituents. Alkyl groups can be used as the substituents, so that the size of the group is the principal factor being varied, as electronic differences between the different alkyl groups are small. Furthermore the conjugation between the aryl and sulfonyl portions of the molecule should be unaffected by rotation around the aryl–sulfur bond induced by the ortho substituents, so that this factor would not affect the results. Finally alkyl groups have been the most widely studied by theoretical means. Accordingly 2,4,6-trimethylbenzenesulfonate and 2,4,6-triisopropylbenzenesulfonate were chosen as the initial leaving groups for examination.

2,4,6-Trimethylbenzenesulfonyl chloride (mesitylenesulfonyl chloride) and 2,4,6-triisopropylbenzenesulfonyl chloride are commercially available materials that are widely used reagents,[7] particularly in nucleotide synthesis.[8] Studies of the solvolytic reactivity of esters of these materials should be useful in understanding their synthetic uses. As is customary for studies of sulfonate leaving groups trivial names and designations for these leaving groups were selected. For mesitylenesulfonate the name mesitylate (Mst) was chosen, which should avoid confusion with mesylate (Ms), commonly used for methanesulfonate. The designation TPS is in general use for triisopropylbenzenesulfonate,[8b] so the name tripsylate (Tps) was adopted for this group.[9]

Results

The sulfonates prepared for kinetic studies were the isopropyl, di-*tert*-butylcarbinyl, 1-adamantyl, and 2-adamantyl esters of 2,4,6-trimethylbenzenesulfonic acid (MstOH) and 2,4,6-triisopropylbenzenesulfonic acid (TpsOH) (**1**–**8**). The mesitylates of isopropyl alcohol (**1**), 1-adamantanol (**3**), and 2-adamantanol (**4**) could be prepared by the conventional Tipson procedure[10] using the acid chloride and pyridine. When this procedure was attempted for the preparation of isopropyl tripsylate (**5**) the acid chloride was recovered; so this ester was prepared from the reaction of sodium isopropoxide and the acid chloride. Di-*tert*-butylcarbinyl mesitylate (**2**) and tripsylate (**6**), and

the adamantyl tripsylates (7 and 8), were prepared by forming the lithium salt of the alcohol by reaction with



1, R = Me; R′ = *i*-Pr
2, R = Me; R′ = *tert*-Bu_2CH
3, R = Me; R′ = 1-Ad
4, R = Me; R′ = 2-Ad
5, R = *i*-Pr; R′ = *i*-Pr
6, R = *i*-Pr; R′ = *tert*-Bu_2CH
7, R = *i*-Pr; R′ = 1-Ad
8, R = *i*-Pr; R′ = 2-Ad

methyllithium, followed by treatment with the sulfonyl chloride.[11] This method also gave **3** in higher purity than the pyridine method.

The sulfonates were all crystalline white solids, whose structures were confirmed by their spectral properties and elemental analyses. The adamantyl derivatives showed a tendency toward contamination by residual sulfonyl chloride, and the elemental analyses of these derivatives showed larger than normal deviations from the expected values, even after repeated crystallization. Some difficulties have also been encountered in the purification of the adamantyl tosylates.[12] The adamantyl tripsylates had rather surprisingly high melting points (126–128° for **7** and 144–145.5° for **8**) and were only soluble with difficulty in pentane or acetic acid at room temperature. The isopropyl methyls in each of the tripsylates had the same chemical shift, but this did not occur in tripsyl chloride.

Acetolysis rates for 1–8 were each measured at three different temperatures by titrimetric methods, and selected rates for isopropyl tosylate were also measured for calibration purposes. The rate data are collected in Table I along with suitable literature data for comparison. Derived relative rates and activation parameters are also collected in Table I.

The trifluoroacetolysis rate of isopropyl mesitylate (**1**) was also measured at 25.0° by observing the change of absorption of the sulfonate chromophore in the ultraviolet. The reaction of isopropyl tripsylate (**5**) in trifluoroacetic acid appeared to proceed initially at a similar rate, but no stable end point could be obtained as the chromophore disappeared entirely. Apparently this crowded aromatic nucleus underwent desulfonation in the moderately strong acid medium. The measured rates for *i*-PrOMst, *i*-PrOTps, and *i*-PrOTs at 25° were 0.439, ~0.4, and 2.12×10^{-5} sec,$^{-1}$ respectively. The latter value compares well with those reported[13a,b] for isopropyl tosylate, 2.14 and 2.49×10^{-5} sec^{-1}.

Table I
Acetolysis Rates of Arylsulfonates[a]

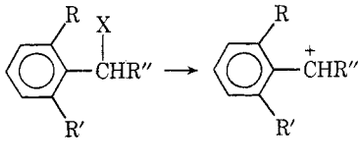
Sulfonate	Temp, °C	k, sec^{-1}	k_{rel}[b] (25.0°)	ΔH^*, kcal/mol	ΔS^*, eu
i-PrOMst (1)	99.8	11.68×10^{-5}			
	84.6	2.62×10^{-5}			
	70.2	5.68×10^{-6}			
	25.0[c]	1.79×10^{-8}	0.23	25.3	−9.2
i-PrOTps (5)	99.7	12.10×10^{-5}			
	84.6	2.72×10^{-5}			
	70.3	6.08×10^{-6}			
	25.0[c]	1.94×10^{-8}	0.25	25.2	−9.4
i-PrOTs	99.7	4.12×10^{-4}			
	99.7[d]	4.07×10^{-4}			
	70.2	2.17×10^{-5}			
	70.2[d]	2.14×10^{-5}			
	25.0[d]	7.74×10^{-8}	1.0	24.7	−8.2
t-Bu_2CHO-Mst (2)	70.4	2.28×10^{-4}			
	55.4	3.44×10^{-5}			
	40.0	4.69×10^{-6}			
	25.0[c]	5.09×10^{-7}	0.093	26.6	2.0
t-Bu_2CHO-Tps (6)	70.8	2.69×10^{-4}			
	55.5	3.17×10^{-5}			
	40.0	3.89×10^{-6}			
	25.0[c]	3.43×10^{-7}	0.062	28.8	8.6
t-Bu_2CH-OTs	25.0[e]	5.49×10^{-6}	1.0	25.7	3.7
1-AdO-Mst (3)	40.0	5.97×10^{-4}			
	25.0	9.16×10^{-5}	0.21	23.1	0.3
	16.7	2.78×10^{-5}			
1-AdO-Tps (7)	40.0	4.46×10^{-4}			
	25.0	7.27×10^{-5}	0.17	22.4	−2.4
	16.7	2.26×10^{-5}			
1-AdOTs	25.0[f]	4.36×10^{-4}	1.0	20.6	−4.7
2-AdO-Mst (4)	115.5	14.64×10^{-4}			
	99.6	2.37×10^{-5}			
	85.0	5.00×10^{-6}			
	25.0[c]	8.57×10^{-10}	0.14[g]	29.9	0.2
2-AdO-Tps (8)	115.8	10.70×10^{-4}			
	99.7	2.15×10^{-5}			
	85.0	4.01×10^{-6}			
	25.0[c]	10.02×10^{-10}	0.17[g]	28.7	−3.3
2-AdOTs	25.0[d]	5.94×10^{-9}	1.0[g]	28.1	−2.1

[a] Rates for 1–8 are averages of duplicate runs. Maximum deviation ±7%. Abbreviations are Mst: mesitylenesulfonate; Tps: 2,4,6-triisopropylbenzenesulfonate. [b] All rates relative to the corresponding tosylate at 25.0°. [c] Extrapolated values. [d] Calculated from data reported in ref 14a. [e] Literature values from ref 1d. [f] Reference 22e; see also ref 22b–d. [g] Calculated relative rates at 100° are 0.27, 0.21, and 1.0, respectively.

Discussion

Solvolytic reactions occur by one or a combination of three discrete processes. Solvolysis to a simple open carbonium ion is characterized by the rate constant k_c, whereas ionization assisted by back-side nucleophilic displacement by solvent has rate constant k_s and neighboring group assisted ionization occurs with rate constant k_Δ.[14a] All three processes may occur with or without the initial formation of ion pairs, and the role of such ion pairs is a matter of current study.[15]

Previous investigations of the solvolytic reactivity of esters of aromatic acids substituted with bulky ortho substituents have principally concerned benzoate esters which reacted by bimolecular substitution at the carbonyl group or at the leaving group.[16] In these cases the substitution at the carbonyl group was hindered by the bulky ortho substituents. The role of bulky ortho substituents in unimolecular reactions leading to benzylic cations has also been studied (eq 2).[17] Such substituents have an electronic accelerating effect partly compensated by a rate-retarding tendency to twist the developing π orbital of the carbonium ion out of conjugation with the phenyl ring.



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First-order solvolyses of esters of ortho-substituted arylsulfonate esters include neutral hydrolyses of phenyl esters, which react by S–O cleavage,[18] and methyl mesitylate,[19] which underwent hydrolysis at a rate slower than methyl tosylate by a factor of 0.38 at 80°.

By comparison isopropyl mesitylate and tripsylate are less reactive in acetolysis than the corresponding tosylate

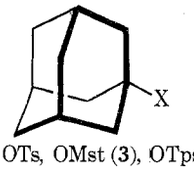
by factors of 0.23 and 0.25, respectively, at 25°. It is known that the acetolysis of simple secondary tosylates occurs by a k_s process, in which back-side displacement by solvent is rate and product determining.[1d,20] However, the fact that the trifluoroacetolysis ratios for the same compound are both about 0.20 shows that the type of solvolysis process does not strongly influence the leaving group aptitude, since the solvent participation is much less important in trifluoroacetolysis, which greatly enhances k_c processes.[13,20] The poorer leaving group ability for mesitylate and tripsylate is what would be expected on the basis of the electron-donating ability of the alkyl substituents, as also reflected in the lower acidity of mesitylenesulfonic acid relative to benzenesulfonic acid.[21]

A quantitative estimate of the anticipated reactivity of isopropyl mesitylate and tripsylate can also be made. The ρ value for ethanolysis of isopropyl arenesulfonates is 1.55.[22a] The combined σ value for 2,4,6-trimethyl substituents can be obtained from a published[21] plot of σ values *vs.* acid strengths in acetic acid and equals −0.54. This value is in agreement with the finding that the effects on solvolyses of methyl arenesulfonates of adding methyl substituents in the 2,4,6 positions are approximately additive.[19] From these data and a σ value for *p*-Me of −0.17 the anticipated rate of isopropyl mesitylate is 0.27 times that of isopropyl tosylate as compared to the observed value of 0.23. The substituent effect of *p*-*i*-Pr is identical with that of *p*-Me in hydrolysis of methyl arenesulfonates;[19] so isopropyl tripsylate has the same calculated rate factor of 0.27, as compared with the measured value of 0.25. Thus the reactivities of isopropyl mesitylate and tripsylate are what would be expected on the basis of the electronic character of the substituents.

Adamantyl arenesulfonates, and other systems that react without solvent participation, tend to have a larger ρ value of around 1.8.[22a] The calculated mesitylate–tosylate ratio is 0.21 for such a ρ value. Thus the adamantyl and di-*tert*-butylcarbinyl mesitylates and tripsylates as noted in Table I appear to have an additional small factor which decreases their reactivity in addition to the electronic character of the substituents.

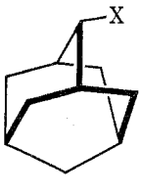
The di-*tert*-butylcarbinyl,[1d] 1-adamantyl,[12,22] and 2-adamantyl substrates serve as critical tests for theories of solvolytic behavior.[14] Di-*tert*-butylcarbinyl sulfonates should be immune from solvent-assisted (k_s) ionization because of the great hindrance to such a process posed by the large groups.[1d] Indeed no substitution products are formed from this material in a variety of nucleophilic solvents.[1d] In addition the *tert*-butyl groups ought to maximize the importance of steric factors of all kinds, including B and F strain, and solvent exclusion. The combination of these factors leads to a 71-fold greater reactivity of *t*-Bu_2CHOTs relative to *i*-PrOTs in acetolysis.

The 1-adamantyl system gives relatively unreactive tertiary sulfonates for which solvent-assisted ionization is im-



X = OTs, OMst (3), OTps (7)

possible and for which participation routes (k_Δ) are also excluded.[22d] Derivatives of the 2-adamantyl system are also free from major influences of neighboring group participation and solvent assistance.[14,23] The latter is eliminated in this secondary system by axial hydrogens which screen the backside of the molecule from solvent. The adamantyl systems are also subject to appreciable steric interactions be-



X = OTs, OMst (4), OTps (8)

tween the alkyl nucleus and an attached arenesulfonate, and so the effects of F strain and solvent exclusion may be significant.

The mesitylates and tripsylates in every case are less reactive than the tosylate ester of the same substrate, and the factors by which the reactivity is decreased are greater for the larger alkyl substrates than for isopropyl. The factors vary with temperature but this relation holds at any given temperature. Thus there is no evidence for any extra increment of F strain in the esters when the sulfonate portion of the molecule acquires ortho substituents. The lowest reactivity for any of the leaving groups relative to tosylate is 0.062, and this occurs in the most crowded example, di-*tert*-butylcarbinyl tripsylate.

It ought not to be inferred that steric repulsion between the alkyl residue and the sulfonate group is not a major factor in affecting the rates of solvolysis of these compounds. The principal source of strain has been postulated to be the interaction between the alkyl group and the sulfonyl oxygens.[5,22d] This factor is constant throughout the series examined in this study. An examination of molecular models is inconclusive on the relative magnitudes of the interactions of the alkyl portion of the molecule with the sulfonyl oxygens and ortho substituents on the aromatic ring. It is to be hoped that further experimental studies now under way will shed more light on this problem.

The results are suggestive that solvent exclusion may be a factor in the solvolyses of these crowded esters. It is well established that because of steric constraints solvolyses of di-*tert*-butylcarbinyl and adamantyl derivatives do not involve solvent participation,[1c,14] and solvation of the developing positive charge must be hindered as well. The fact that for these systems the presence of ortho methyl or isopropyl groups on the arenesulfonate causes a decrease in reactivity greater than expected on electronic grounds indicates that solvent exclusion by the leaving group may be a factor as well. However, the observed factors are not large so this conclusion is only tentative. Compensating F-strain acceleration and solvent exclusion deceleration due to the leaving group is also a possibility.

It should be noted that there is another way in which steric crowding which destabilizes the ground state may be manifested in the observed reactivity. Geometrical distortions due to strain may result in rehybridization of the carbons. For example, tri-*tert*-butylmethane has bond angles at the central carbon of 101.6° (C–C–H) and 116.0° (C–C–C).[24] Thus the carbon orbital of the central C–H bond in this molecule has greatly increased p character over normal values. It is quite possible that derivatives of crowded molecules which undergo solvolysis may also have enhanced p character in the carbon orbital to the leaving group. Ionization of such a compound should be enhanced due to increased p character at the developing carbonium ion center, just as enhanced s character in an orbital favors carbanion formation.[25] Whether or not strain causes rehybridization in a particular derivative which would favor ionization should be apparent from the molecular structure, and this is under investigation.

In conclusion it should be noted that the mesitylate and tripsylate esters examined usually have higher melting points and always have lower solvolytic reactivities than

the corresponding tosylates. They are readily prepared and show readily interpretable differences from tosylates due to steric differences. Thus these derivatives offer definite advantages as leaving groups for reactivity studies. The importance of leaving group solvent exclusion in solvolysis reactions has received modest support. No evidence has been obtained for F strain between alkyl groups and ortho substituents in arylsulfonates as an accelerating factor in solvolysis, but the evidence obtained does not bear on the possibility of repulsion involving the sulfonyl oxygens. Further study of still more crowded sulfonates appears to be warranted and is being pursued.

Experimental Section

Elemental analyses were carried out by A. B. Gygli at Microanalysis Laboratories, Ltd., Toronto, Ontario. Melting points (obtained on a Fisher hot stage) and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 337 grating spectrophotometer. Nmr spectra were run on a Varian T-60 instrument with tetramethylsilane as an internal standard in CCl_4 solutions.

Materials. 2,4,6-Triisopropylbenzenesulfonyl chloride, mesitylenesulfonyl chloride, 1-adamantanol, and 2-adamantanol were obtained from Aldrich Chemical Co. and used as received. Fisher anhydrous pyridine was stored over KOH. Isopropyl tosylate was prepared by the reported procedure with purification by low-temperature crystallization.[26] Other sulfonates were prepared by the modifications noted below of the standard methods.[10,11] The mesitylates showed two characteristic strong infrared bands near 1175 and 1190 cm^{-1}, whereas the tripsylates showed a single strong band near 1175 cm^{-1}. Di-*tert*-butylcarbinol was obtained as a solid, bp 156–158° (lit.[27] mp 46–48°, bp 163°), by overnight reduction of di-*tert*-butyl ketone with sodium borohydride in ethanol.

Isopropyl 2,4,6-trimethylbenzenesulfonate (1) was prepared by the reaction of 10 ml of 2-propanol with 8.5 g (0.028 mol) of mesitylenesulfonyl chloride and 50 ml of pyridine at 25°. After 2 days the mixture was poured into water, collected by filtration, and purified by low-temperature crystallization from pentane: mp 59–61°; nmr δ 1.28 (d, 6, J = 6 Hz, CH**Me**$_2$), 2.28 (s, 3, *p*-Me), 2.58 (s, 6, *o*-Me), 4.62 (heptet, 1, J = 6 Hz, CHO), and 6.92 (s, 2, Ar).

Anal. Calcd for $C_{12}H_{18}O_3S$ (242.34): C, 59.48; H, 7.49. Found: C, 59.56; H, 7.51.

Isopropyl 2,4,6-triisopropylbenzene sulfonate (5) was prepared from the reaction of the sulfonyl chloride with sodium isopropoxide formed by dissolving sodium in 2-propanol. After 2 days at 25° the product was obtained by pouring on ice and recrystallizing from pentane at low temperature: mp 40–41.5°; nmr δ 1.24 (d, 18, J = 7 Hz, aryl CH**Me**$_2$), 1.35 (d, 6, J = 6 Hz, OCH**Me**$_2$), 2.90 (heptet, 1, J = 7 Hz, *p*-CH), 4.14 (heptet, 2, J = 7 Hz, *o*-CH), 4.82 (heptet, 1, J = 6 Hz, OCH), and 7.04 (s, 2, Ar).

Anal. Calcd for $C_{18}H_{30}O_3S$ (326.50): C, 66.22; H, 9.26. Found: C, 66.11; H, 9.14.

Di-*tert*-butylcarbinyl 2,4,6-trimethylbenzenesulfonate (2) was prepared by adding 1 equiv of the sulfonyl chloride in hexane to an ice-cold solution prepared from equivalent amounts of di-*tert*-butylcarbinol and *n*-butyllithium in hexane. After 2 days at room temperature the mixture was poured into water, isolated by extraction, and purified by low-temperature crystallization from pentane: mp 80.5–81.5°; nmr 1.02 (s, 18, *t*-Bu), 2.26 (s, 3, *p*-Me), 2.62 (s, 6, *o*-Me), 4.42 (s, 1, CHO), and 6.88 (s, 2, Ar).

Anal. Calcd for $C_{18}H_{30}O_3S$ (326.50): C, 66.22; H, 9.26. Found: C, 66.37; H, 9.29.

Di-*tert*-butylcarbinyl 2,4,6-triisopropylbenzenesulfonate (6) was prepared by adding 1 equiv of sulfonyl chloride in ether to an ice-cold solution prepared from equivalent amounts of methyllithium and di-*tert*-butylcarbinol in ether. After being stirred for 3 days at 25° the mixture was poured on ice, and the product was isolated by extraction with methylene chloride and evaporation. Trituration of the residue with pentane left a white solid which was discarded and the material soluble in pentane was purified by low-temperature crystallization: mp 102–104.5°; nmr δ 1.04 (s, 18, *t*-Bu), 1.26 (d, 18, J = 7 Hz, CH**Me**$_2$), 2.92 (heptet, 1, J = 7 Hz, *p*-CH), 4.26 (heptet, 2, J = 7 Hz, *o*-CH), 4.54 (s, 1, CHO), and 7.14 (s, 2, Ar).

Anal. Calcd for $C_{24}H_{42}O_3S$ (410.66): C, 70.20; H, 10.31. Found: C, 70.11; H, 10.50.

1-Adamantyl 2,4,6-trimethylbenzenesulfonate (3) was prepared by the methyllithium method to give large prisms from pentane: mp 75.5–77°; nmr δ 1.64 and 2.18 (each broad singlet, 15 Ad H), 2.28 (s, 3, *p*-Me), 2.62 (s, 6, *o*-Me), and 6.90 (s, 2, Ar).

Anal. Calcd for $C_{19}H_{26}O_3S$ (334.48): C, 68.23; H, 7.84. Found: C, 68.43; H, 7.90.

1-Adamantyl 2,4,6-triisopropylbenzenesulfonate (7) was prepared by the methyllithium method to give large prisms from pentane: mp 126–128°; nmr δ 1.28 (d, 18, J = 7 Hz, CH**Me**$_2$), 1.64 and 2.22 (each broad singlet, 15 Ad H), 2.82 (heptet, 1, J = 7 Hz, *p*-CHMe$_2$), 4.20 (heptet, 2, J = 7 Hz, *o*-C**H**Me$_2$), and 6.94 (s, 2, Ar).

Anal. Calcd for $C_{25}H_{38}O_3S$ (418.39): C, 71.72; H, 9.15. Found: C, 72.16; H, 9.33.

2-Adamantyl 2,4,6-trimethylbenzenesulfonate (4) was prepared by the pyridine method to give large prisms from pentane: mp 66.5–68°; nmr δ 1.3–2.1 (m, 14, Ad), 2.32 (s, 3, *p*-Me), 2.60 (s, 6, *o*-Me), 4.54 (broad s, 1, CHO), and 6.92 (s, 2, Ar).

Anal. Calcd for $C_{19}H_{26}O_3S$ (334.48): C, 68.23; H, 7.84. Found: C, 68.98; H, 7.75.

2-Adamantyl 2,4,6-triisopropylbenzenesulfonate (8) was prepared by the methyllithium method to give large prisms from pentane: mp 144–145.5°; nmr δ 1.25 (d, 18, J = 7 Hz, CH**Me**$_2$), 1.5–2.3 (m, 14, Ad), 2.88 (heptet, 1, J = 7 Hz, *p*-C*H*Me$_2$), 4.20 (heptet, 2, J = 7 Hz, *o*-C*H*Me$_2$), 4.72 (broad s, 1, CHO), and 7.10 (s, 2, Ar).

Anal. Calcd for $C_{25}H_{38}O_3S$ (418.39): C, 71.72; H, 9.15. Found: C, 72.20; H, 9.33.

Kinetics. Acetolysis rates for all but the 1-adamantyl sulfonates were carried out by the usual titrimetric procedure[28] using acetic acid purified by distillation from triacetyl borate.[29] The more rapid rates of the 1-adamantyl sulfonates were measured by the original procedure used for 1-adamantyl tosylate.[12a] Aliquots (1 ml) were withdrawn at appropriate intervals from the reacting solution contained in a volumetric flask in the constant temperature bath and were rapidly discharged into 2 ml of chilled pentane. These were promptly titrated to the bromophenol blue end point with 0.05 N NaOAc in acetic acid using a syringe microburet (Micrometric Instrument Co., Cleveland, Ohio). Concentrations of sulfonate utilized ranged from 0.055 to 0.020 M. Duplicate runs were carried out for all acetolysis runs of **1–8**. Rate constants and activation programs were calculated using least-squares programs. Reported rate constants are averages, the maximum deviation of the rate constants was ±7%. The maximum standard deviations were 0.05 kcal/mol for ΔH^* and 0.2 eu for ΔS^*.

Trifluoroacetolysis rates were measured by a modification[13a] of the Peterson method,[13b] using 0.01 M solutions of sulfonates in 0.125 M sodium trifluoroacetate in trifluoroacetic acid by spectrophotometeric observation of the band at 276 nm for the mesitylate and tripsylate.

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Registry No.—**1**, 52873-84-4; **2**, 52873-85-5; **5**, 52873-83-3; **6**, 52873-87-7; *i*-PrOTs, 2307-69-9; 2,4,6-triisopropylbenzenesulfonyl chloride, 6553-96-4; mesitylenesulfonyl chloride, 773-64-8; 1-adamantanol, 768-95-6; 2-adamantanol, 700-57-2; isopropyl alcohol, 67-63-0; di-*tert*-butylcarbinol, 14609-79-1.

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Phenylcinnamalones. II. Some Data Concerning the Preparative Reaction[1]

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Pyrolysis of α-phenyl-*trans*-cinnamic acid (Ia) in the presence of thionyl and sulfuryl chlorides yields phenylcinnamalone (14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (IIIa)). Two intermediates in this reaction appear to be α-phenyl-*trans*-cinnamoyl chloride (IIa) and 14b,14c-dihydro-5a-phenyl-10-(α-phenyl-*trans*-cinnamoxy)benz[*a*]indeno[2,1-*c*]fluoren-5-one (IVa). IVa also can be prepared directly from Ia using phosphorus trichloride in place of thionyl chloride. The 3,12-dichloro, 3,12-dimethyl, and 3,12-dimethoxy analogs of IIIa and the 3,12-dichloro and 3,12-dimethyl analogs of IVa can be prepared using similar techniques. The structures of these compounds and related derivatives were determined using chemical and spectral methods.

In a previous publication,[4] a procedure for the preparation of 14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (phenylcinnamalone, IIIa, see Scheme I) was reported along with a complete crystal and molecular structure proof. Since new procedures for the formation of carbon–carbon bonds are of great general interest and importance in organic chemistry, we have undertaken a detailed study of the reaction, its products, and its mechanism. This report will concern itself with the generality of the reaction and the nature of the reaction intermediates. The unusual chemistry of the phenylcinnamalone ring system (III) will be reported subsequently.

Results and Discussion

The preparative reaction involves a novel one-step reaction which results in the creation of four carbon–carbon bonds between two molecules of α-phenylcinnamoyl chloride (IIa) to yield a complex system of six fused carbocyclic rings. IIa is a known reaction intermediate, but it is not necessary to isolate IIa in order to make IIIa; rather it is more convenient to proceed directly from Ia to IIIa *via in situ* generation of IIa.

In order to clarify subsequent discussions involving proton magnetic resonance (pmr) spectra a brief review of the structure of IIIa as related to its pmr spectrum might be helpful.

Phenylcinnamalone was shown to have the structure of 14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (IIIa) (Figure 1).[4] The previously reported crystal and molecular structure data[4] allow a more complete interpretation of the pmr spectrum of IIIa than would ordinarily be possible. The spectrum displays a singlet at 4.68δ and two well-separated complex multiplets. One multiplet is centered at δ 7.40 and the other at δ8.40. The ratio of integration is 1:16:1, respectively. The singlet is clearly due to resonance of the methine proton of C_{14c}. The intense multiplet at δ7.40 may be reasonably assigned to the collective resonance of all but one of the 17 aromatic protons. Thus, the remaining multiplet must be due to resonance of a single aromatic proton. The shift of this multiplet, away from the bulk of aromatic resonance, toward the deshielded portion of the spectrum points to further strong deshielding. Such deshielding may be caused by a carbonyl group ortho to an aromatic proton.[5] Further, this effect is strongest when both the proton in question and the carbonyl group lie in the same plane. The crystallographic establishment of the coplanarity of the five-membered ring B and its carbonyl oxygen with benz ring A allow assignment of the multiplet at δ8.40 to the resonance of the proton of C_{11}.

If the reaction mixture from the preparation of IIIa is properly treated, a white compound (IVa) can be isolated. When the purified compound (IVa) is again subjected to