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Substituent Effect of the Pentafluorophenyl Group: Is There a Correlation between X-ray Crystal Structures and Reactivity in Carbocation Formation?

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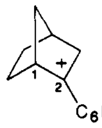
The reactivity of $C_6F_5CH(OTs)CH_3$ (**7**) in various solvents is found to be less than that of $PhCH(OTs)CH_3$ by factors of 6×10^3 to 5×10^5, but the C_6F_5 substituent is still much more activating than hydrogen. The reactivity of **7** gives a poor correlation with the Y_{OTs} measure of solvent ionizing power, with an m value of 0.44, and while the reaction in TFA or HFIP evidently involves initial formation of an ion pair, there is strong nucleophilic assistance to ionization by less ionizing solvents. Crystal structures of $C_6H_5C(CH_3)_2OPNB$ (**10**), $C_6F_5C(CH_3)_2OPNB$ (**11**), and 3,5-$(CF_3)_2C_6H_3CH(OTs)CH_3$ (**12**) have been determined and used to evaluate the proposal of Kirby et al. (*J. Am. Chem. Soc.* **1986**, *108*, 7067-7073) that more reactive phenylethyl systems have geometries that more closely resemble solvolysis transition states. The geometries of **10** and **11** are similar, and the differences are predicted by the Kirby proposal, but the very short C-OTs bond length in **12** is contrary to expectations, although disorder in the CF_3 groups complicates the interpretation. It is concluded that the above simple structure/reactivity correlation should only be applied with due caution.

Introduction

The substituent properties of trifluoromethyl (CF_3) groups in the formation of electron-deficient destabilized carbocations have been under recent investigation in our laboratory[1] as well as others.[2] We have now extended these studies to include the effect of the pentafluorophenyl (C_6F_5) group on reactivity, and to utilize CF_3 and C_6F_5 groups in critical tests of the general applicability of the proposed[3,4] correlation of structure, as measured by X-ray crystallography, with reactivity. Fluorinated groups are well-suited as probes of this correlation, as they can cause drastic changes in reactivity but have rather modest steric requirements.

The study of the pentafluorophenyl substituent has already attracted[5,6] considerable attention, but many of the previous results appear contradictory or unexplained. Thus while $C_6F_5CO_2H$ is a stronger acid than $C_6H_5CO_2H$, as expected for the electron-withdrawing effect of the fluorines, m-$C_6F_5C_6H_4CO_2H$ is a weaker acid than benzoic.[6] This anomaly was attributed[6] to "some unusual solvent interaction associated with the highly fluorinated substituent" and to p–π interactions of the fluorine lone pairs with the aryl π system.

In studies of long-lived carbocations by ^{13}C NMR the chemical shift of C2 of the 2-(pentafluorophenyl)-2-norbornyl carbocation (**1**) was *upfield* from C2 of the 2-*m*-tolyl analogue, while C1 of **1** was *downfield* of C1 for the 3,5-$(CF_3)_2C_6H_3$ ion.[7a] Superficially, the former result indicates that C_6F_5 is acting as a good donor (better than *m*-tolyl) but the latter suggests that C_6F_5 is strongly electron withdrawing (more so than 3,5-$(CF_3)_2C_6H_3$). While it has been emphasized[7a] that ^{13}C chemical shifts cannot be directly equated with charge densities of cations or with donor properties of substituents, nevertheless consistent trends in restricted series of such data were reported,[7a] and the contradictory trends of the chemical shift values for the C_6F_5-substituted carbocation noted have not been explained. Results for the 2,5-diarylnorbornyl carbodications were completely analogous.[7b]



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Protiodetritiation of tritiated pentafluorobiphenyl was slower than the same reaction of benzene, indicating the C_6F_5 group to be electron withdrawing and deactivating relative to hydrogen with σ_m^+ of 0.285 and σ_p^+ of 0.225.[8] The smaller value of the latter was considered noteable and was attributed[8] to modest π-donation by C_6F_5, reducing σ_p^+. However despite the high electron demand in the hydrogen exchange reaction, manifested in the ρ value of -8.0,[8] the net effect of C_6F_5 is strongly electron withdrawing in this system.

Thus the previous studies of the substituent effect of the pentafluorophenyl group lead to widely different conclusions, with an indicated electron donor ability ranging from much poorer than hydrogen to better than *m*-tolyl. Therefore solvolytic reactivity has now been utilized as a measure of substituent properties of C_6F_5, as this process provides a well-established and reliable criterion of such effects.

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Table I. Solvolytic Rate Constants of $C_6F_5CH(OTs)CH_3$ (7)

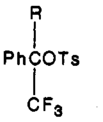
solvent (*Y*)	*k*, s^{-1} (25 °C)	solvent (*Y*)	*k*, s^{-1} (25 °C)
CF_3CO_2H (4.57)	3.90×10^{-4}	HOAc (−0.61)	1.56×10^{-7} [a]
97% HFIP (3.61)	5.42×10^{-5}	80% EtOH (0.0)	1.44×10^{-5} [a]
97% TFE (1.83)	9.04×10^{-6} [a]	100% EtOH (−1.75)	1.40×10^{-6} [a]
HCO_2H (3.04)	1.74×10^{-4}		

[a] Extrapolated from the measured rate constants, s^{-1} (*T*, °C): HOAc, 3.10×10^{-4} (90.6), 8.73×10^{-5} (75.8), 2.36×10^{-5} (65.8), $\Delta H^* = 24.5$ kcal/mol, $\Delta S^* = -7.5$ eu; 80% EtOH, 1.95×10^{-3} (75.7), 8.19×10^{-4} (65.8), 1.99×10^{-4} (50.1), $\Delta H^* = 19.3$ kcal/mol, $\Delta S^* = -16.0$ eu; 100% EtOH, 1.66×10^{-4} (70.4), 5.34×10^{-5} (57.8), 7.95×10^{-6} (40.0), $\Delta H^* = 20.8$ kcal/mol, $\Delta S^* = -15.4$ eu; 97% TFE, 9.34×10^{-4} (72.6), 2.92×10^{-4} (59.2), 8.08×10^{-5} (45.9), $\Delta H^* = 19.5$ kcal/mol, $\Delta S^* = -16.4$ eu.

Crystal structures of suitable substrates bearing C_6F_5 and 3,5-$(CF_3)_2C_6H_3$ groups have also been determined, as we have previously demonstrated that this technique readily detects the effects of steric strain on reactivity in **2**,[9] but did not reveal a simple relationship between molecular geometry and the reactivity differences due to electronic effects in **3–6**.[10] However, it has recently been suggested by Kirby et al.[4] that there is a close relationship between structure and reactivity in 1-phenylethyl derivatives, and the current studies provide further information relevant to this proposal.

$t\text{-}Bu_3COPNB$

2



$PhC(R)(OTs)CF_3$

3, R = CF_3
4, R = CN
5, R = H
6, R = CH_3

Results

1-(Pentafluorophenyl)ethyl tosylate (**7**) was prepared by the reaction of 1-(pentafluorophenyl)ethanol (**8**) with NaH in ether followed by reaction with *p*-toluenesulfonyl chloride (eq 1).

$$\underset{\mathbf{8}}{C_6F_5CHOHCH_3} \xrightarrow[\text{2. TsCl}]{\text{1. NaH, ether}} \underset{\mathbf{7}}{C_6F_5CH(OTs)CH_3} \qquad (1)$$

The kinetics of reaction of **7** in CF_3CO_2H (TFA), 97% $(CF_3)_2CHOH$ (HFIP), 97% CF_3CH_2OH (TFE), HCO_2H, CH_3CO_2H, C_2H_5OH, and 80% C_2H_5OH/H_2O were monitored by UV spectroscopy or conductivity and the rate constants obtained are given in Table I.

The progress of the reaction of **7** in TFA, HCO_2H, CD_3CD_2OD, and CD_3CO_2D was observed by dissolving **7** in the appropriate solvent in an NMR tube and scanning the ^1H NMR spectrum at intervals. In each case complete conversion to the corresponding substitution product (**9a–d**, respectively), was observed (eq 2), and no signals due to other products could be detected.

$$\underset{\mathbf{7}}{C_6F_5CH(OTs)CH_3} \xrightarrow{SOH(D)} C_6F_5CH(OS)CH_3 \qquad (2)$$

9a, S = CF_3CO
9b, S = HCO
9c, S = C_2D_5
9d, S = CD_3CO
9e, S = C_2H_5
9f, S = CH_3CO

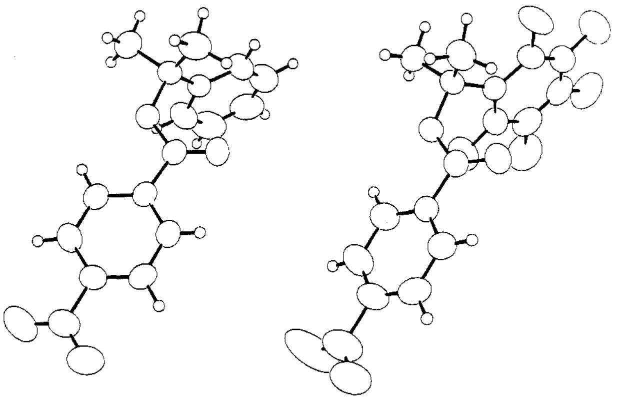


Figure 1. ORTEP views of $C_6H_5C(CH_3)_2OPNB$ (**10**) and $C_6F_5C(CH_3)_2OPNB$ (**11**). The view of **10** is drawn with inverted coordinates.

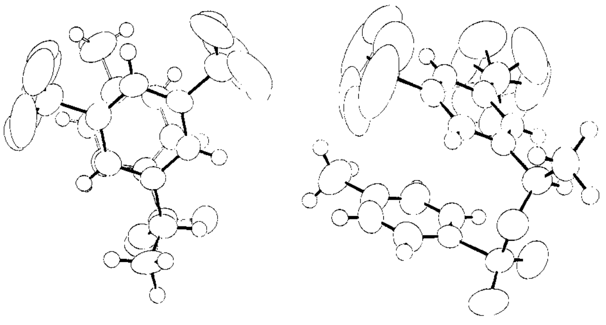


Figure 2. ORTEP views of **12** showing the syn conformation and the overlap of the two ring systems. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are drawn with uniform isotropic temperature factors. Both orientations of the disordered CF_3 groups are indicated.

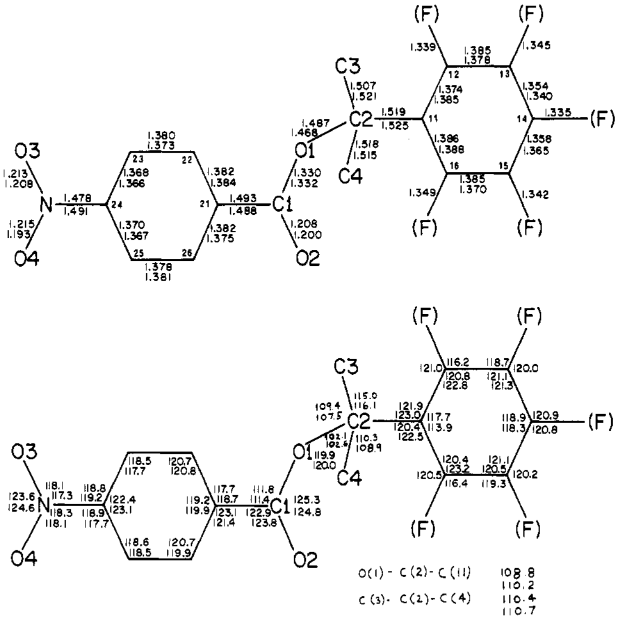


Figure 3. Bond distances (Å) and bond angles (degrees) for $C_6H_5C(CH_3)_2OPNB$ (**10**) and $C_6F_5C(CH_3)_2OPNB$ (**11**). Top values in any paired distances are for compound **10**, the bottom values for **11**.

Authentic samples of **9a** and **9f** were prepared by reaction of **8** with $(CF_3CO)_2O$ and CH_3COCl, respectively, and **9a**, **9b**, and **9e** were isolated from the solvolysis reactions and characterized.

The crystals of **7** were not satisfactory for a structure determination, but structures were obtained for 2-phenyl-2-propyl *p*-nitrobenzoate (**10**), 2-(pentafluoro-

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Table II. Crystal Data, Details of Intensity Measurements, and Structure Refinements[a]

compound	10	11	12
system	monoclinic	monoclinic	monoclinic
a (Å)	6.417 (2)	15.980 (7)	8.014 (3)
b (Å)	10.962 (2)	6.122 (3)	8.862 (2)
c (Å)	20.515 (4)	16.199 (4)	26.275 (3)
β (deg)	91.69 (2)	93.44 (2)	92.63 (2)
U (Å^3)	1442	1582	1864
fw/F(000)	285.3/300	375.3/760	412.4/840
Z/D_x (g cm^{-3})	4/1.31	4/1.58	4/1.46
space group	$P2_1/c$	$P2_1/a$	$P2_1/n$
μ(Mo K$\bar{\alpha}$) (cm^{-1})	0.9	1.4	2.3
reflns used in cell determ (no./θ range in deg)	25 ($9.4 < \theta < 16.5$)	25 ($10.8 < \theta < 15.8$)	25 ($12.1 < \theta < 16.2$)
scan width (deg)	0.65 + 0.35 tanθ	0.65 + 0.35 tanθ	0.75 + 0.35 tanθ
max scan time (s)	75	65	65
std reflns (no. interval in s)[b]	3/7000	3/7500	3/7500
max 2θ (deg)/octants	55/h, k, $\pm l$	50/h, k, $\pm l$	52/h, k, $\pm l$
total no. reflns collected	3898	3267	4292
unique data	2656[c]	2363[d]	3036[e]
no. data $I \geq 3\sigma(I)$	1385	1309	1650
R_1 (R_2)[f]	0.0457 (0.0456)	0.0353 (0.0391)	0.0712 (0.1024)
max Δ/σ	0.31	<0.01	0.33
weights, value of p[g]	0.03	0.025	0.08
esd o.u.w. (e)	1.38	1.49	2.00
max peak final ΔF Fourier (e Å^{-3})	0.17	0.14	0.33
extinction corr.	1.7 (9) × 10^{-7}	2.5 (6) × 10^{-7}	

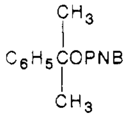
[a] Enraf-Nonius CAD 4 diffractometer; θ–2θ mode; Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å); graphite monochromator; T = 298 K. [b] No systematic variations in intensities of standards observed. [c] 907 systematically absent or zero F_{obsd} data rejected and 203 symmetry equivalent reflections then averaged (R_{merge}(F) = 0.027) to give no. of data indicated. [d] 725 systematically absent or zero F_{obsd} data rejected and 77 symmetry equivalent reflections then averaged (R_{merge}(F) = 0.023) to give no. of data indicated. [e] 934 systematically absent or zero F_{obsd} data rejected and 196 symmetry equivalent reflections then averaged (R_{merge}(F) = 0.027) to give number of data indicated. [f] Structure solutions: direct methods, Fourier, least-squares. Programs: Enraf-Nonius SDP package on PDP 11/23 or SHELX on Gould 9705 computers.[24] Scattering curves stored in programs were taken from International Tables for X-ray Crystallography.[25] Correlation problems between the two orientations of the disordered C(16)F$_3$ group in 12 were eliminated by refining the two orientations in alternating cycles of least-squares. [g] $\omega = 4F^2[\sigma^2(I) + (pF^2)^2]^{-1}$.

Table III. Comparative Bond Lengths and Reactivities of Benzylic Sulfonate Esters

	ArCH(OSO$_2$RO)CH$_3$, Ar =			PhCR′(OTs)CF$_3$, R′ =			
	3,5-(CF$_3$)$_2$(C$_6$H$_3$)[a] (**12**)	4-$_2$NC$_6$H$_4$[b] (**13**)[d]	4-O$_2$NC$_6$H$_4$[a] (**19**)[4h]	CF$_3$ (**3**)	CN (**4**)	H (**5**)	CH$_3$ (**6**)
k_{rel}[c]	1.4 × 10^5	5.6 × 10^6	5.6 × 10^6	1.0	50	54	2.6 × 10^7
C–OTs (Å)	1.413 (5)	1.476 (3)	1.444 (7)	1.436 (7)	1.432 (3)	1.453 (5)	1.457 (4)
O–S (Å)	1.623 (4)	1.573 (3)	1.605 (5)	1.618 (4)	1.619 (2)	1.577 (3)	1.583 (3)
sum (Å)	3.036	3.051	3.049	3.054	3.051	3.030	3.040
C8⋯S (Å)	2.632	2.662	2.652	2.735	2.670	2.602	2.703
COS (deg)	120.0 (3)	121.6 (2)	120.8 (4)	127.1 (4)	122.0 (2)	118.3 (2)	125.5 (2)
ϕ(O3–C8–C10–C11) (deg)	56.0	56.2	64.5	35.1	29.6	42.7	18.8
β(O3–S–C1–C2) (deg)	67.8	66.7	69.0	88.9	83.2	71.9	60.0

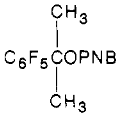
[a] R = 4-CH$_3$C$_6$H$_4$. [b] R = 2-naphthyl, ref 4a. [c] In TFA, 25 °C. [d] The rate constant for 1-(4-nitrophenyl)ethyl 2-naphthalenesulfonate (**13**) can be calculated as 1.1 × 10^{-2} s^{-1} at 25 °C in TFA from $\sigma_{p\text{-}NO_2}{}^+$ of 0.79, the $\rho\sigma^+$ correlation for ArCH(OTs)CH$_3$ in TFA,[13a] and the fact that the leaving group ability of 2-naphthalenesulfonate is essentially identical with that of tosylate in the 2-propyl derivatives at 65 °C (k = 1.15 × 10^{-4} s^{-1} and 1.24 × 10^{-4} s^{-1}, respectively, in 97% HFIP[12,23]).

phenyl)-2-propyl p-nitrobenzoate (**11**), and 3,5-(CF$_3$)$_2$C$_6$H$_3$CH(OTs)CH$_3$ (**12**). The ORTEP views of the three molecules are shown in Figures 1 and 2, and crystallographic details are given in Table II. Bond lengths and angles are given in Figures 3 and 4. It should be noted that the structure of **10** has been determined independently by Liu and co-workers,[11] and the details of the two structures are in good agreement.



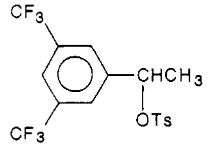
$$\begin{array}{c} CH_3 \\ | \\ C_6H_5COPNB \\ | \\ CH_3 \end{array}$$

10



$$\begin{array}{c} CH_3 \\ | \\ C_6F_5COPNB \\ | \\ CH_3 \end{array}$$

11



12

A disquieting feature of the crystal structure of **12** is that the fluorine atoms of the CF$_3$ groups are disordered so that it was not possible to reduce the R factor below 7%. However, the estimated standard deviations of the bond lengths and angles in the rest of the structure (Figure 4 and Table III) are generally comparable to those reported by us for **3**–**6**[10] and by Kirby et al.[4a,f,h] for 1-(4-nitrophenyl)ethyl 2-naphthalenesulfonate (**13**) and tosylate (**19**), the only other 1-arylethyl sulfonates for which X-ray structure data are available.

Discussion

The dependence of the reaction rates of **7** on the solvent ionizing power parameter Y_{OTs}[12] is seen in Figure 5 to give a highly scattered correlation. The data give a linear correlation log $k = 0.44Y_{OTs} - 5.52$, $r = 0.866$. The low slope of this line and the poor correlation coefficient suggest that the k_c mechanism of rate-limiting carbocation

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[11] Liu, K.-T., unpublished results privately communicated.

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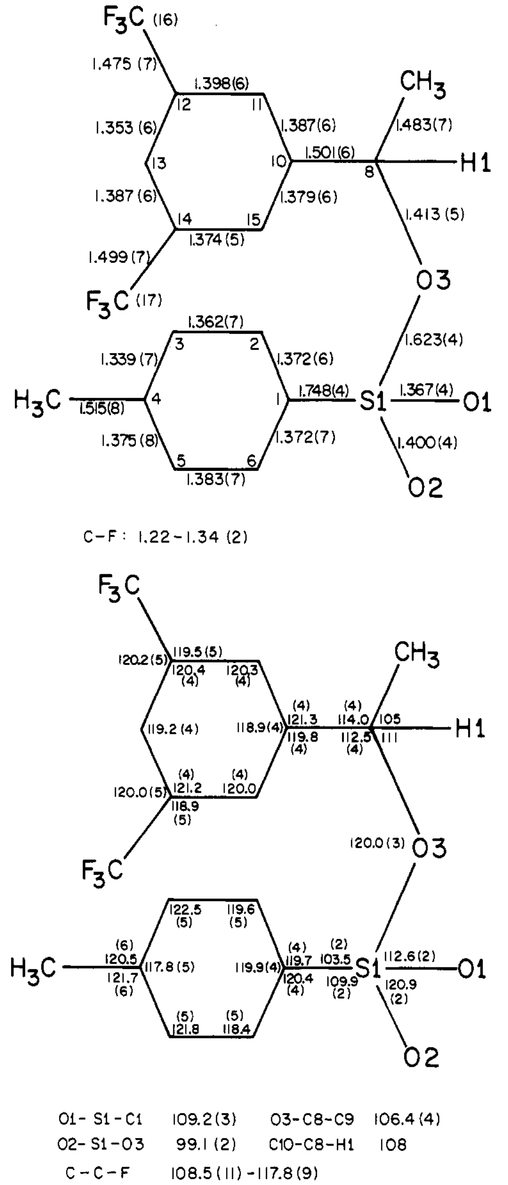

Figure 4. Bond distances (Å) (top) and bond angles (degrees) (bottom) for $3,5\text{-}(CF_3)_2C_6H_3CH(OTs)CH_3$ (**12**).

formation is not followed throughout this series of solvents and that a high degree of nucleophilic solvent assistance occurs for the less ionizing but more nucleophilic solvents.

The dependence of reactivity of **7** on solvent ionizing power closely resembles that reported[13a] for 1-[3,5-bis(trifluoromethyl)phenyl]-1-ethyl tosylate (**12**) and the rate ratio $k(\mathbf{7})/k(\mathbf{12})$ is 1.45 (TFA), 3.98 (HFIP), 2.16 (TFE), 1.05 (HOAc), 1.33 (80% EtOH), and 1.20 (100% EtOH). The ratio $k(\text{TFA}/k(\text{EtOH})$ is 280 for **7** and 230 for **12**. The similarity in reactivity for **7** and **12** indicates that both react by the same reaction mechanism, and **12** was previously[13a] interpreted to react with substantial nucleophilic assistance in the less ionizing solvents. The low value of $k(\text{TFA})/k(\text{EtOH})$ for both these substrates is also indicative of a major enhancement of the reactivities in EtOH due to nucleophilic solvent participation and is in contrast to the value of 1.2×10^6 for $PhC(OTs)(CF_3)CH_3$ (**6**), a fluorinated substrate that has been shown to react by the k_c route of carbocation formation without nucleophilic involvement of the solvent in all solvents.[13b] However, just as was argued for **12**,[13a] the nucleophilic solvent participation in **7** probably involves a number of solvent molecules and not a specific interaction with a single solvent molecule attacking from the rear and expelling the leaving group.

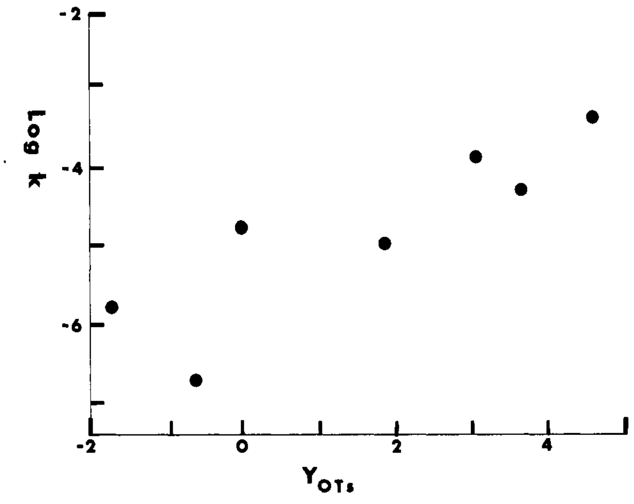

Figure 5. Solvolysis rates of $C_6F_5CH(OTs)CH_3$ (**7**) vs. Y_{OTs}.

In the strongly ionizing and weakly nucleophilic TFA and HFIP **12** was interpreted as reacting through ion pairs because for optically active **12** the polarimetric rate constant exceeded the rate of product formation by factors of 1.4 in TFA and 2.1 in HFIP, and the product had 6% retained configuration in TFA.[13a] Evidently this substrate reacts with some ion pair return in these solvents, and solvent attack to give a dissociated ion pair or products is at least partly rate-determining (eq 3).

$$ArCH(OTs)CH_3 \rightleftarrows ArC^+HCH_3\ OTs^- \xrightarrow{SOH} \text{products} \quad (3)$$

Optically active **7** was not available for study but it appears likely that this substrate also reacts in TFA and HFIP with initial formation of an ion pair that then reacts with solvent to give the products as shown in eq 3, possibly with the intervention of other ion pairs.

The effect of the C_6F_5 group on the reactivity of 1-aryl-1-ethyl tosylates is thus slightly less deactivating than that of the $3,5\text{-}(CF_3)_2C_6H_3$ group. From the $\rho\sigma^+$ correlations established[13a] for 1-arylethyl tosylates in different solvents an average substituent constant of 1.07 for C_6F_5 may be calculated.[14] This corresponds to the combined effect of the five fluorines and such substituent constants for an entire group at the reaction center have been designated by Traylor and Ware as σ_α^+ constants[15a] and more recently as γ^+ constants by Peters, McManus, and Harris.[15b,c]

It should be noted that these $\rho\sigma^+$ correlations were derived by using a revised σ^+ value of 0.56 for $3\text{-}CF_3$,[16a] and by additivity the value for the $3,5\text{-}(CF_3)_2$ grouping was taken as 1.12. However, the original value of σ_m^+ for CF_3 was 0.52,[16b] and a value of 0.946 has been directly measured for the $3,5\text{-}(CF_3)_2$ grouping.[16c] Better precision was ob-

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(13) (a) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4513–4519. (b) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1982**, *104*, 207–211.

(14) Using the equations $\log k = -4.88\sigma^+ + 1.89$ (TFA), $\log k = -5.94\sigma^+ + 1.76$ (97% HFIP), $\log k = -5.05\sigma^+ + 0.26$ (97% TFE), $\log k = -3.93\sigma^+ - 2.44$ (HOAc), $\log k = -3.03\sigma^+ - 1.57$ (80% EtOH), and $\log k = -3.39\sigma^+ - 2.28$ (EtOH).

(15) (a) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304–2316. (b) Peters, E. N. *J. Am. Chem. Soc.* **1976**, *98*, 5627–5632. (c) McManus, S. P.; Harris, J. M. *J. Org. Chem.* **1977**, *42*, 1422–1427.

(16) (a) Taylor, R. *J. Chem. Soc. B* **1971**, 622–627. (b) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979–4987. (c) Takeuchi, K.; Kurosaki, T.; Okamoto, K. *Tetrahedron* **1980**, *36*, 1557–1563.

tained for the 1-arylethyl tosylates by using $\sigma_m{}^+(CF_3)$ of 0.56,[13a] but use of any of the values can be justified, and the derived value for C_6F_5 will be slightly less than that for 3,5-$(CF_3)_2$, but dependent on the value selected for the latter.

The rate ratio $k(C_6H_5)/k(C_6F_5) = 6 \times 10^3$ can be derived from the directly measured[17] rate of $C_6H_5CH(OTs)CH_3$ in 100% EtOH at 25 °C, and from further values extrapolated for the latter substrate by using $\rho\sigma^+$ correlations for $ArCH(OTs)CH_3$ in various solvents[13a] an average value for the rate ratio of 4.7×10^5 is obtained for TFA, HFIP, and TFE.[18] The value in the fluorinated solvents represents a more carbocationic transition state and should thus be a better indication of the electronic effect of C_6F_5 in such a situation, but the fluorinated substrate is substantially less reactive in all solvents.

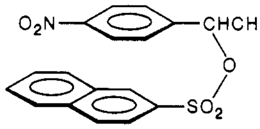
Despite the strong deactivating effect of C_6F_5 relative to C_6H_5 in this system, it is still strongly activating relative to hydrogen. Thus in a compilation[15b] of 15 systems $k(C_6H_5)/k(H)$ rate ratios range from 3×10^4 to 2×10^{13}, and all but two were 10^{10} or greater. The γ^+ constant for hydrogen was determined as 2.53,[15b] as compared to the value derived above of 1.07 for C_6F_5 and 0.0 (by definition) for C_6H_5. Thus the solvolysis of **7** contrasts to the hydrogen exchange of pentafluorobiphenyl discussed above, and the fact that C_6F_5 is a net donor relative to hydrogen in the former process but an acceptor in the latter is another example of the inordinately low donor power of aryl groups derived from studies of biphenyl derivatives. This latter phenomenon may arise from steric inhibition of conjugation.[19]

The low donor ability of C_6F_5 also explains why $C_6F_5C^+Ph_2$ does not undergo the substitution of para fluorine characteristic of other (4-fluorophenyl)diarylmethyl cations in 90% HCO_2H.[20] Thus the low positive charge density on the C_6F_5 ring could preclude nucleophilic attack by water.

Crystal Structures

The most immediate difference between the molecular structure of **12** and the previously determined 2,2,2-trifluoro-1-phenylethyl tosylates, $C_6H_5CR(OTs)CF_3$ (**3**–**6**)[10] is that the overall conformation of **12** involves an almost eclipsed arrangement of the ligands bonded to S1 and C8 when viewed down the S1–C8 vector with the phenyl and tolyl groups syn to one another (Figure 2). In **3**–**6**, however, the ligands bonded to S1 and C8 were approximately staggered about the S1–C8 vector and the aryl groups were approximately anti to one another (dihedral angles 159.2–170.3°).[10] Thus in **12**, the dihedral angle about the S⋯C vector, C10–C8⋯S1–C1 is 7.5°, the angle between the plane of the phenyl and tolyl rings is 19.0°, and C⋯C distances between the rings are 3.24–4.21 Å (center⋯center = 3.72 Å). This conformation means that the lone pairs on O3 are also staggered with respect to the bonds to both S1 and C8 (the smallest lone pair–S1–C8 bond dihedral angle is 34°).

This syn arrangement of the two aryl groups was also observed[4a,f] in the structure of 1-(4-nitrophenyl)ethyl 2-naphthalenesulfonate (**13**) in which the naphthalene is inclined at only 12° to the 4-nitrophenyl ring and the distance between the aromatic systems is ca. 3.4 Å.



13

A detailed comparison of the known C–OSO_2R and CO–SO_2R bond lengths and selected bond angles for benzylic sulfonate esters with reactivities of the substrate in trifluoracetic acid is given in Table III. It is noteable that the CO–Ts and C–OTs distances in **12** are longer and shorter, respectively, than any of the comparable distances in the other compounds. The S–O–C angles of the three secondary substrates in Table III are significantly smaller than the *tertiary* examples and do not appear related to the reactivities. Consistent with the long S–O3 bond length in **12**, it is noteable that both sulfonyl S–O bonds are shorter than those in the other examples. Finally, the O3–S–O angles are significantly larger (112.3 (3)°) and smaller (99.0 (3)°) than those observed in **3**–**6** and **13**, while the O1–S–O2 angle is close to the average value observed in the other compounds.

Refinement of the hydrogen atom at C8 in **12** is not possible and angles involving this atom are based on its position in a ΔF Fourier map, but it is noteable that C8 is again significantly distorted from tetrahedral. Despite the substantial differences in the C–O bond lengths in **12** and **13**, the difference in analogous bond angles at C8 not involving the H atom show only a small increase (2°) in both the O–C–CH_3 and O–C–Ph bond angles in **12**.

The crystal packing in the sulfonates **12** (supplementary figures) and **13**[4f] is similar and involves principally intermolecular interactions between the aryl rings. The shortest O⋯H contact in O3⋯H21 $(1 - x, 1 - y, 1 - z)$ and the length, 2.49 Å, is comparable to the intramolecular O1⋯H1 contact of 2.57 Å. The F⋯F and F⋯H contacts are greater than 2.97 and 2.53 Å, respectively (supplementary tables).

It is also apparent that there are significant angle distortions in the two *p*-nitrobenzoates structures determined (Figures 1 and 3). Concentrating on the geometry at the benzylic carbon C2, the data reveal large deviations from tetrahedral geometry (Figure 3) with differences of 12.9° and 13.5° between the largest and smallest angles for **10** and **11**, respectively. These differences are generally comparable to the angle distortions observed[10] in the previous series of tosylates **3**–**6** (max $\Delta\theta$ = 13.4 (**3**), 11.5 (**4**), 9.6 (**5**), and 13.5 (**6**) and **12** (max $\Delta\theta$ = ca. 9°) but are somewhat less than the difference of 16.7° observed in **2**. However, somewhat surprisingly there is a remarkable similarity in the present structures **10** and **11**, with the largest bond angle at the benzylic carbon involving the aryl and methyl groups in each, and the smallest angle involves the oxygen and the other methyl carbon atom.

The C–OPNB bond distances for **10** and **11** (1.487 (3) and 1.468 (3) Å, respectively) do differ significantly (6σ), with the shorter bond occurring in the least reactive substrate. This distance is even longer (1.496 (5) Å) and the bridging angle C7–O1–C8 is substantially larger (132.8 (3)°) than those in **10** and **11** for the severely crowded and highly reactive *t*-Bu_3COPNB (**2**).[9] Other major differences between the dimensions of the PNB moieties in **2**, **10**, and **11** appear in the angles at C1 and in particular O1–C1–O2, which has opened up to 127.2 (4)° in **2** to reduce O⋯H contacts involving O2 and the *t*-Bu groups. Similarly the C–O bond length in **10** is comparable to those observed[4a] in 1-(4-methyoxyphenyl)ethyl and 1-phenylethyl 3,5-di-

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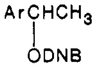
[17] Hoffmann, H. M. R. *J. Chem. Soc.* **1965**, 6753–6761.

[18] Calculated rate constants for $C_6H_5CH(OTs)CH_3$ at 25 °C are 83 s^{-1} (TFA), 54 s^{-1} (97% HFIP), and 1.9 s^{-1} (97% TFE).

[19] (a) Noyce, D. S.; Fike, S. A. *J. Org. Chem.* **1973**, *38*, 2433–2438. (b) Oyama, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1976**, *98*, 947–951.

[20] Andrews, A. F.; Mackie, R. K.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1980**, 96–102.

nitrobenzoates **14** and **15** (1.479 (5) and 1.481 (3) Å, respectively) while that in **11** is similar to the CO distance in 1-(3-fluorophenyl)ethyl 3,5-dinitrobenzoate (**16**) (1.459 (4) Å).[4a]



$ArCHCH_3$ with ODNB below the central C

14, Ar = 4-$CH_3C_6H_4$
15, Ar = C_6H_5
16, Ar = 3-C_6H_4F

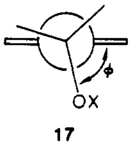
Another significant difference between **10**, **11**, and **14–16** is in the degree of twist of the nitrobenzene ring with respect to the C21–C1–O1–O2 plane. In **11** this is very pronounced (16.2°) while in **10** this angle is only 6.4°. For comparison, this angle is 9.1°, 8.8°, and 7.7° in **14–16**, respectively. In addition, the plane of the nitro group is rotated by ca. 10.1° with respect to the benzene ring in **11** and only 1.6° in **10**. In **14–16** the NO_2 groups are rotated by angles of 3.9–11.0° out of the benzene ring planes.[4a]

Apart from these differences, there does not appear to be any other evidence for enhanced steric interactions in the C_6F_5 derivative compared to C_6H_5, and, tentatively, it may be concluded that the lower reactivity of the former is not affected by steric interactions involving the fluorines. The distortions in the CCF angles in **11** tend to push the ortho and meta F atoms toward each other and are similar to the changes observed in other C_6F_5 groups.[21] Some of the F atoms are slightly out of the plane through C11–16, noteably F3 (by –0.067 (2) Å), as is C2 (by –0.242 (3) Å).

The crystal packings in **10** and **11** (supplementary figures) are both determined by interactions between the phenyl rings. Noteably, in **11**, stacked columns along the *a* axis involve only the *p*-nitrobenzene rings with the C_6F_5 groups on the periphery, whereas in **10**, the stacks are along the [1, 0, 1] direction and involve interspersed *p*-nitrophenyl rings and the phenyl substituent on C8. Presumably this difference in crystal packing is responsible for the 8.6° difference between **10** and **11** (**11** > **10**) in the orientation of the nitro group with respect to the phenyl ring. Despite the different packing arrangements the shortest intra- and intermolecular F···H and H···H contacts involving the Ar substituents are generally comparable in lengths (supplementary table B). There is no evidence in **10** or **11** for the very short intramolecular O···H contact of length 2.14 Å observed in *t*-Bu_3COPNB (**2**)[9] and all O···H contacts are >2.39 Å in length.

Structure/Reactivity Correlations

Kirby et al.[4] have considered the crystal structures and reactivities of a variety of 1-arylethyl derivatives and formulated a general picture that in more reactive systems the ground state tends to more closely resemble the solvolysis transition state, with the C–O bond to the leaving group lengthening, the acute angle ϕ between the C–O bond and the aryl ring approaching 90° (**17**) and the benzylic carbon flattening.

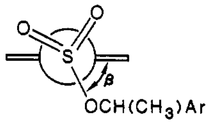


17

Two general rules regarding bond lengths were formulated by Kirby et al.,[4a] for which they have found no exceptions: (1) the longer the bond, in a given system, the faster it breaks and (2) the more reactive the system, the more sensitive is the length of the bond to structural variation. It is instructive to compare all of the reported examples of 1-arylethyl sulfonates to test these rules: the substrates include **3–6**, **12**, **13**,[4a,f] and **19**[4h] (Table III).

If discussion is limited to the $ArCH(O_3SR)CH_3$ derivatives **12** and **13**, then the reactivity/bond length criterion applies. However there are many disturbing additional features to consider. Thus the angle ϕ for **12** and **13** is essentially identical and does not reflect the large difference in the C–O bond lengths. Furthermore the C–O bond length for **12** is extraordinarily short, significantly less than any of the 11 compounds considered by Kirby,[4a] a group in which all the other leaving groups (Ph_3CO, 4-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3CO_2$, $ClCH_2CO_2$, and $(PhO)_2PO_2$) were much poorer than tosylate. Thus in comparison to these other 10 derivatives rule 1 is clearly broken, as it is if **12** is compared to $PhCH(OTs)CF_3$ (**5**) in Table III. Indeed the patterns of C–OTs bond lengths, angles ϕ, and reactivities for the complete group of **12** and **3–6** are essentially random, although it may be argued that the structural differences between **3–6** and **12** are sufficiently great to preclude a fair comparison. Moreover, in the structure of 1-(4-methoxyphenyl)ethyl 4-nitrophenyl ether the difference in C–O bond lengths between the two independent molecules in the asymmetric unit was larger than that between similar ethers with different substituents.[4a,d] The explanation advanced for this observation was that a 10° rotational difference in the nitro group orientations might have effectively reduced the "effective electronegativity" of the ether oxygen atom.[4a,d] Similar rotational differences between molecules have been commented upon above.

In Kirby's analysis the leaving group geometries were not treated in as much detail as the benzylic center. In the series of sulfonates **3–6**, **12**, and **13**, the orientations of the arylsulfonyl group (angle β, **18**) with respect to S–O3 varies from 60.0° to 88.9° (Table III). There is a monotonic increase in β with decreasing reactivity for all six compounds, although there are some deviations from a smooth curve if these variables are plotted. This new correlation is reasonable, as the most stable and least reactive situation in the leaving group has the S–O3 bond at 90° to the plane of the ring thus minimizing n–π repulsive forces between the sulfonyl O lone pairs and the π system as well as maximizing any O···H interactions.[22]



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Furthermore, it is worth noting that the very short C–OTs bond in **12** is reflected in a very long O–S bond (Table III) and that indeed throughout the series the sum of the two bond lengths to this oxygen stays relatively constant while the individual bond lengths change much

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[21] Brock, C. P.; Naae, D. G.; Goodhand, N.; Hamor, T. A. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3691. Goodhand, N.; Hamor, T. A. *Ibid.* **1979**, *B35*, 704. Benghiat, V.; Leiserowitz, L. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1778–1785.

[22] White, D. N. J.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1280–1283. Barrow, M. J.; Cradwick, P. D.; Sim, G. A. *Ibid.* **1974**, 1812–1818. Exner, O.; Fidlerová, Z.; Jehlička, V. *Collect. Czech. Chem. Commun.* **1968**, *33*, 2019.

[23] Yamataka, H.; Tamura, S.; Hanafusa, T.; Ando, T. *J. Am. Chem. Soc.* **1985**, *107*, 5429–5434.

[24] Enraf-Nonius Structure Determination Package (1981). B. A. Frenz and Associates, Inc., College Station, TX. Sheldrick, G. M. SHELX Program for Crystal Structure Determination, University of Cambridge, England, 1976.

[25] International Tables for X-ray Crystallography, Vol. IV; Kynoch Press: Birmingham, England, 1974 (present distributor, D. Reidel, Dordrecht).

more dramatically. This compensating pattern is consistent with a structure–reactivity correlation.

For $C_6H_5C(OPNB)(CH_3)_2$ (**10**) and $C_6F_5C(OPNB)(CH_3)_2$ (**11**), the more reactive **10** has both the longer C–OPNB bond (1.487 (3) and 1.468 (3) Å, respectively) and the larger angle ϕ (43.8° and 36.5°, respectively), in agreement with the simple prediction based on structure–reactivity considerations.

The cautionary note should be added that the *R* value for **12** (7%) is rather high, largely due to the disordered CF_3 groups. However, the set of tosylates **3–6** and **12** have the virtue of meeting the criterion set out by Kirby et al. that one can be "on firm ground when analyzing *trends* in geometrical patterns for a homogeneous set of compounds, with similar thermal parameters, using results obtained in the same laboratory under standard conditions". These substrates have a common leaving group and estimated standard deviations in the bond lengths and angles that are comparable to each other as well as to those reported for **13**[4a,f] and **19**[4h] ($4-O_2NC_6H_4CH(OTs)CH_3$), the only other 1-arylethyl arenesulfonates for which crystal structure data are available. It was stated that **19** shows " a large difference peak near the C–O–S moiety, possibly an unidentified minor disorder or twinning phenomenon" which precluded comparison to other structures.[4h] Some comparative structural data for **19** are included in Table III, and it may be noted that the structure of **19** around the C–O–S atoms is midway between those of **12** and **13** in many respects. While accepting the authors' admonition not to overdraw the comparison of the structure of **19** with others,[4h] we believe all the available structural data deserves consideration, with due regard for the reliability of each set. We conclude that more data is required before a firm conclusion is possible as to the existance of a useful crystal structure reactivity correlation in this series and that this simple relationship should only be applied with great caution.[26]

Experimental Section

Fluorinated solvents were purchased from Aldrich and purified as described previously.[13b] Preparative reactions were carried out under N_2 in glassware that had been flame- or oven-dried. ^1H NMR spectra were measured with a Varian T-60 instrument, and IR spectra were obtained on a NICOLET FT-IR instrument. The elemental analysis was by Galbraith Laboratories. 2-Phenyl-2-propyl *p*-nitrobenzoate (**10**) was prepared by a reported general procedure,[27] and the preparation of **12** was reported previously.[13a]

1-(Pentafluorophenyl)ethyl Tosylate (7). NaH (0.045 mol) was washed three times with pentane in a 100-mL three-necked flask under N_2 and cooled in an ice bath and then washed twice with ether. After addition of 15 mL of ether, 1-(pentafluorophenyl)ethanol (**8**, Aldrich, 5.80 g, 0.0273 mol) in 15 mL of ether was slowly added by a syringe with stirring and copious evolution of H_2. After 1 h of stirring *p*-toluenesulfonyl chloride (5.20 g, 0.273 mol) in 15 mL of ether was slowly added with a syringe and the solution stirred 4 h at room temperature. Then 30 mL of ice water was carefully added and the aqueous solution extracted three times with ether. The combined ether layers were washed successively with $NaHCO_3$ solution, H_2O, and saturated NaCl, dried over $CaSO_4$, and evaporated. The crude solid was recrystallized from pentane/ether to give **7**, 57% yield, mp 94.8–95.5 °C: ^1H NMR (CCl_4) δ 1.68 (d, 3, J = 7 Hz, CH_3CH), 2.40 (s, 3, CH_3Ar), 5.76 (q, 1, J = 7 Hz, CH_3CH), 7.40 (q, 4, C_6H_4); mass spectrum, *m/e* (rel intensity) 366 (7, M^+), 195 (35, M^+ – TsO), 194 (100, M^+ – TsOH), 175 (6), 172 (35, $TsOH^+$), 155 (8, Ts^+), 145 (5), 107 (9). Anal. Calcd for $C_{15}H_{11}F_5O_3S$ (366.31): C, 49.18; H, 3.03. Found: C, 49.12; H, 3.17.

2-(Pentafluorophenyl)-2-propanol was prepared as reported[28] by reaction of C_6F_5Br with Mg followed by addition to acetone: IR (CCl_4) 3667 cm^{-1} (OH); ^1H NMR (CCl_4) δ 1.72 (t, 6, $J(^1H\text{-}o\text{-}^{19}F)$ = 2 Hz, $(CH_3)_2$), 2.50 (s, 1, OH); mass spectrum, *m/e* (rel intensity) 226 (1.5, M^+), 211 (100, $M^+ - CH_3$), 195 (4, $M^+ - CH_3O$), 181 (8, $M^+ - C_2H_5O$), 168 (9, $C_6F_5H^+$). Reaction of this alcohol with pyridine and *p*-nitrobenzoyl chloride using a procedure analogous to one for tosylate preparation[29] gave 2-(pentafluorophenyl)-2-propyl *p*-nitrobenzoate (**11**): mp 82–84 °C; IR (CCl_4) 1734 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 2.00 (t, 6, $J(^1H\text{-}o\text{-}^{19}F)$ = 2 Hz, $(CH_3)_2$), 8.15 (s, 4, Ar); mass spectrum, *m/e* (rel intensity) 375 (16, M^+), 209 (100, M^+ – PNBO), 208 (43, M^+ – PNBOH), 181 (83, $C_6F_5CH_2^+$), 150 (57, PNB^+); high-resolution mass spectrum, *m/e* 375.0522, calcd for M^+ 375.0529.

Product Studies: Trifluoroacetolysis of 7. A sample of **7** (113 mg, 0.31 mmol) was dissolved in 0.5 mL of TFA in an NMR tube and after 35 min was almost completely converted to product identified as the trifluoroacetate **9a**. The solution was poured into a mixture of ether and ice–water and extracted twice with ether, and the combined ether layers were washed successively with H_2O, $NaHCO_3$ solution, and saturated NaCl solution and evaporated. The ether was distilled off and the product purified by VPC using an OV-17 column: IR (CCl_4) 1790 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.78 (d, 3, J = 7 Hz, CH_3), 6.20 (q, 1, J = 7 Hz, CH); mass spectrum, *m/e* (rel intensity) 308 (21, M^+), 293 (3, $M^+ - CH_3$), 265 (7), 195 (100, $M^+ - CF_3CO_2$), 194 (83, $M^+ - CF_3CO_2H$), 175 (17), 145 (20); high resolution mass spectrum, *m/e* 308.0087, calcd 308.0083. An authentic sample of **9a** was prepared by the reaction of **8** with trifluoroacetic anhydride.

Formolysis of **7** was carried out by a similar procedure and the purified formate **9b** showed the following: ^1H NMR (CCl_4) δ 1.68 (d, 3, J = 7 Hz, CH_3), 6.15 (q, 1, $CHCH_3$), 7.86 (s, 1, CHO); mass spectrum, *m/e* (rel intensity) 240 (27, M^+), 197 (38), 195 (70, $M^+ - HCO_2$), 194 (100, $M^+ - HCO_2H$), 175 (15), 145 (18).

Ethanolysis of **7** in C_2D_5OD was observed by ^1H NMR to give the C_2D_5 ester **9c**, and solvolysis of **7** (0.5 g, 1.37 mmol) in 5 mL of C_2H_5OH for 1 day at 60 °C followed by extraction and purification as above gave the C_2H_5 ether **9e**: ^1H NMR (CCl_4) δ 1.16 (t, 3, J = 7 Hz, CH_3CH_2), 1.56 (d, 3, J = 7 Hz, CH_3CH), 3.36 (q, 2, J = 7 Hz, CH_3CH_2), 4.78 (q, 1, J = 7 Hz, CH_3CH); mass spectrum, *m/e* (rel intensity) 240 (2, M^+), 225 (60, $M^+ - CH_3$), 197 (100, $M^+ - C_3H_7$), 195 (55, $M^+ - C_2H_5O$), 175 (8), 145 (10); high resolution mass spectrum, *m/e* 240.0568, calcd 240.0573 (M^+).

Acetolysis of **7** in CD_3CO_2D was observed by ^1H NMR to give the deuterioacetate **9d**, and reaction of **8** (0.20 g, 0.94 mmol) in 5 mL of ether with 1 mmol of CH_3COCl and 1 mmol of pyridine, followed by extraction and purification as above, gave the acetate **9f**: IR (CCl_4) 1755 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.62 (d, 3, J = 7 Hz, CH_3CH), 2.02 (s, 3, CH_3CO), 6.00 (q, 1, J = 7 Hz, CH_3CH); mass spectrum, *m/e* (rel intensity) 254 (33, M^+), 239 (2, $M^+ - CH_3$), 211 (5), 195 (75, $M^+ - CH_3CO_2$), 194 (100, $M^+ - CH_3CO_2H$), 192 (20), 175 (13), 145 (14); high resolution mass spectrum, *m/e* 254.0382, calcd 254.0365 (M^+).

Kinetics. Reaction rates were measured as previously by UV spectroscopy[1a,b,13] on a Cary 210 spectrophotometer. The absorbance change was measured (nm) at 275 (TFA), 260 (HFIP), 263 (TFE, HCO_2H, 80% C_2H_5OH), and 250 (CH_3CO_2H). The rates in 100% C_2H_5OH were measured by conductivity.

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Registry No. **7**, 109390-63-8; **8**, 830-50-2; **9a**, 109390-65-0; **9b**, 109390-66-1; **9c**, 109390-67-2; **9d**, 109390-68-3; **9e**, 90095-68-4; **9f**, 32019-38-8; **10**, 7429-06-3; **11**, 109390-64-9; **12**, 109432-21-5; C_6H_5Br,

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Supplementary Material Available: Views showing the crystal packing in **10**, **11**, and **12** and tables of positional and anisotropic thermal parameters, molecular contacts, and selected torsional angles for **10**–**12** and related compounds (13 pages). (Final structure factor amplitudes for **10**–**12** are available from the authors.) Ordering information is given on any current masthead page.

The Octant Rule. 21.[1] Antioctant Effects in δ,ε-Unsaturated Ketones

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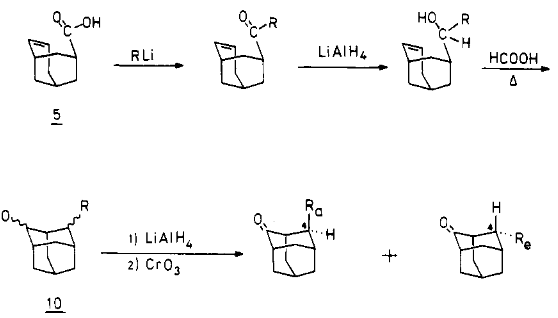
Optically active (1*S*,3*R*)-4(*S*)(a)- and (1*S*,3*R*)-4(*R*)(e)-phenyl- and -benzyladamantan-2-ones have been synthesized, and their n → π* circular dichroism spectra have been recorded. The equatorial benzyl substituent shows greatly enhanced Cotton effect magnitudes over those expected for equatorial alkyl perturbers of the same size, and β-axial phenyl and benzyl substituents are found to be powerful front octant (dissignate) perturbers.

Introduction

Since its formulation over 25 years ago,[2] the octant rule for the n → π* transition of saturated alkyl ketones has enjoyed wide application in extracting stereochemical and conformational information from chiral ketones. The octants are derived from the local symmetry (C_{2v}) of the carbonyl group and a consideration of the relevant orbitals of the n → π* transition. The two carbonyl symmetry planes divide all space about the C═O into quadrants, and a third, nonsymmetry-derived nodal surface divides all space into front and back octants (as viewed down the C═O bond from O to C, Figure 1).[3,4] In practical application,[5] alkyl perturbers lying in lower right and upper left back octants make a (+) contribution to the sign and magnitude of the n → π* rotatory strength, and reflection of a perturber across either of the C═O C_{2v} symmetry planes leads to a mirror image molecular fragment and hence to a (–) contribution. Since the third nodal surface does not follow from symmetry, reflection of a perturber into front octants leads to a sign change without necessarily the same magnitude.

Most of the relatively few cases of antioctant (dissignate[6]) behavior have derived from atoms or groups lying close to the octant rule nodal surfaces, especially the third nodal surface.[7] Antioctant behavior in back octants has almost always been associated with a breakdown of the (orbital) symmetry due to α,β-conjugation[8] or β,γ-homoconjugation,[9] such that the carbonyl group is no longer inherently symmetric but becomes a component of an inherently dissymmetric chromophore.[5c] Because interchromophoric interaction falls off with increasing distance, evidence for nonoctant behavior in back octants is rare for γ,δ-conjugated ketones, and only one case has been reported for a δ,ε-unsaturated ketone.[10] Their unusual octant behavior has been rationalized in terms of "through-bond" interaction of the two chromophores.

Scheme I



We have pursued an investigation of γ,δ-bis-homoconjugation and δ,ε-tris-homoconjugation effects of the ketone carbonyl with phenyl chromophores using the adamantanone system. Adamantanone possesses C_{2v} molecular symmetry, which coincides with the local symmetry of the C═O chromophore, and β-equatorial substituents probe back octants (whereas β-axial substituents can probe front octants).[3] In this work, we describe the synthesis and circular dichroism (CD) spectra of β-equatorial and β-axial phenyl- and benzyladamantanones **1**–**4**. These compounds provide additional evidence for long-range interchromophoric interaction.

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