more, it establishes the fact that alkylation occurs on the face of the π-allyl unit opposite to that of the palladium.[2,4,5] This supports our earlier contention that π-allyl palladium cationic complexes are ambident electrophiles and that "soft" nucleophiles which attack directly at carbon are required for successful alkylation.[1a]

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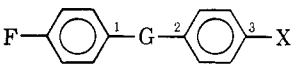
Regarding π-Electron Transmission of Substituent Polar Effects on Fluorine Nuclear Magnetic Resonance Shielding[1]

Sir:

Recent interest centers in the mode of transmission of the σ_I effects of polar substituents[2] on the F NMR shifts of fluoroaromatics. Dewar and students have viewed[3] (and based their FMMF treatment[4]) upon these effects as arising predominantly from field transmission (electrostatic field theory). However, this view is poorly supported by the extremely small magnitude of substituent effects on the F NMR shifts for systems with saturated hydrocarbon molecular cavities.[5] Further, Stock et al.[6] have observed recently that relative to para-substituted fluorobenzenes there is a marked enhancement of the polar effects of 10-substituents in 9-fluoroanthracene. This enhancement was interpreted to mean that the π electron framework connecting the meso positions of anthracene provides a more effective internal transmission of the effects of polar substituents than does that for the para positions of benzene. Dayal et al.[7] have studied extensively the effects of polar substituents, X, in structure I as a function of the variable molecular cavity, G. Greater than 25-fold increase in the effects of corresponding polar substituents was observed, for example, on going from G = $C(CF_3)OH$ to $C(CF_3)^+$. This and similar results led Dayal et al. to conclude that the marked enhancements of substituent polar effects *on the F NMR shifts* arise predominantly from the improved transmission through the π-electron system.[8]



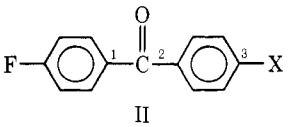
I

Table I. F NMR Substituent Shielding Effects for Ketones in Dilute Methylene Chloride Solutions[a]

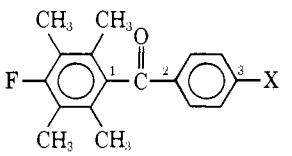
X	Series II[b]	Series III[c]
NMe_2	2.32	1.21
OMe	0.80	0.32
Me	0.46	0.23
F	−0.16	−0.28
Cl	−0.51	−0.44
H	(0.00)[d]	(0.00)[e]
CF_3	−1.29	(−0.94)
CN	(−1.79)[f]	−1.21
NO_2	−2.00	−1.38
$-\rho_I$	2.55	1.82
$-\rho_R$(BA)	2.74	1.49
$\lambda = \rho_R/\rho_I$	1.07	0.82
SD	0.12	0.06
f = SD/RMS	0.091	0.064

[a] Shifts in ppm relative to unsubstituted (H) member. [b] Reference 7. [c] This work. [d] Shift of unsubstituted member relative to external reference of TCTFCB (60 wt % in $HCCl_3$) is −6.42. [e] Shift of unsubstituted member relative to external reference of TCTFCB (60 wt % in $HCCl_3$) is +5.73. [f] Calculated shift by DSP equation, ref 11b.

Comparison of the F NMR shielding effects of polar substituents (X) in ketones II and III and their complexes provides for a definitive decision regarding the relative importance of transmission of the polar effect through field or internal π-electron framework. The extension of π-electron framework beyond a phenyl ring is strongly subject to steric twisting influences.[9] Yet twisting of the phenyl rings of II and III alters but little the X-F distance. In consequence, corresponding polar effects on the F NMR shielding will be little altered in III relative to II if transmission is by field but will be substantially reduced if transmission is by the internal π-electron framework.



II



III

In the compounds of series II and III, attention is directed to three focal points (bonds) in this connection: the positions labeled 1, 2, and 3). Several previous studies have reported the effects on F NMR shifts of directly twisting from the aromatic ring the substituent, X (position 3),[3c,10] We wish to report here the results of steric twisting at positions 1 and 2 which are involved with II and III.

In Table I are given the results for the ketones II and III. Shifts have been obtained as previously reported[7] using 0.03 *M* solutions in methylene chloride and a set of substituents which meets minimum basis set requirements.[11] Analysis of the results by the dual substituent parameter (DSP) treatment[11] is very useful, and the parameters for the $\sigma_{R(BA)}$ scale which gives best fits are also listed in Table I. It is clear from the data of Table I that the substantial increase in twisting that occurs at position 1 in series III compared to that in II causes substantial reduction of substituent shielding effects. The DSP results indicate that (as expected) the π-electron delocalization effect parameter ρ_R is very appreciably reduced (by almost a factor of 2) in III compared to II. Further, there is a 56% reduction in the polar effect transmission parameter, ρ_I. The latter reduction is incompatible with the expectations of field theory.

The protonation of the ketones of series II in H_2SO_4 markedly increases electron demand on both phenyl rings[7,12] with an accompanying increase in the π bonding at positions 1 and 2. The consequence in the F NMR shielding substituent effects is an approximately 300% increase in the polar effects ($-\rho_I$ increases from 2.55 to 7.91). This marked enhancement has been attributed[7] to the increased transmission made possible by the increase in π bonding at positions 1 and 2. As expected, the substituent π-delocalization effects are also greatly enhanced as reflected in the DSP treatment by $-\rho_R$ increasing from 2.74 to 7.91 and the best fit changing from the $\sigma_{R(BA)}$ to the σ_R^+ scale (reflecting seectively greater enhancements for para substituents involved in "through conjugation").

F NMR shift measurements for the protonated ketones of series III provide conclusive evidence that the enhancement of polar substituent effects in the protonated ketones of series II result not via space but by the π-bond framework. Steric twisting at position 1 for series III ketones markedly reduces the magnitude of the F NMR shifts (note in Table II in particular the reductions for CF_3, CN, and NO_2 substituents). The value of $-\rho_I$ for series III is 52% of that for II and $-\rho_R$ for series III is 46% of that for II (the results for both series are best fit by the σ_R^+ scale).

Even more dramatic results are obtained for the BCl_3 adducts of series II and III in dilute CH_2Cl_2 solutions as summarized in Table III. Space-filling molecular models indicate that the BCl_3 adducts of series III ketones not only involve substantially greater twisting from coplanarity at position 1 than for corresponding series II ketone adducts but also at position 2. This destruction of the π-bond framework for series III adducts compared to that of corresponding series II adducts is accompanied by a greater than 400% decrease in polar substituent effects ($-\rho_I$ decreases from 7.86 to 1.82) and a nearly 600% decrease in substituent π-electron delocalization effects ($-\rho_R$ decreases from 7.23 to 1.26). Again, the F NMR shielding results for the BCl_3 complexes of both series II and III ketones are significantly better fitted by the σ_R^+ than other scales.

A corollary of these results is that the formation of the BCl_3 adducts of all of series III ketones is accompanied by a nearly constant downfield F NMR shift (Δ) of -5.6 ± 0.1 ppm, except for X = OCH_3, $\Delta = -5.08$ ppm. In contrast, the Δ values for series II ketones vary from -10.26 ppm for X = OCH_3 to ca. -18.8 ppm for X = NO_2. It is also worthy of note that the $-\rho_I$ value (1.82) for the series III BCl_3 adducts has been reduced to a value approaching that for "saturated" G cavities in I, e.g., for G = CH_2, $-\rho_I = 1.31$, and for G = CH(OH), $-\rho_I = 1.68$.[7]

Table II. F NMR Substituent Shielding Effects for Protonated Ketones in H_2SO_4 Solutions[a]

X	Series II[b]	Series III[c]
OME	6.10	2.50
Me	2.38	1.17
F	0.83	−0.04
Cl	−0.45	−0.35
H	(0.00)[d]	(0.00)[e]
CF_3	−3.80	(−2.16)[f]
CN	(−5.46)[f]	−3.09
NO_2	−6.78	−3.09
$-\rho_I$	7.91	4.15
$-\rho_R(+)$	7.91	3.65
$\lambda = \rho_R/\rho_I$	1.00	0.80
SD	0.36	0.18
f = SD/RMS	0.089	0.084

[a] Shifts in ppm relative to unsubstituted (H) member. [b] Reference 12. [c] This work. [d] Shift of unsubstituted member relative to external reference of TCTFCB (60 wt % in $HCCl_3$) is −27.80. [e] Shift of unsubstituted member relative to external reference of TCTFCB (60 wt % in $HCCl_3$) is −4.80. [f] Calculated shift by DSP equation ref 11b.

Table III. F NMR Substituent Shielding Effects for BCl_3 Adducts of Ketones in Dilute Methylene Chloride Solutions[a]

X	Series II[b]	Series III[c]
OMe	5.05	0.85
Me	1.88	0.37
F	(0.19)	−0.25
Cl	−1.05	−0.41
H	(0.00)[d]	(0.00)[e]
CF_3	−4.25	(−0.92)[f]
CN	(−5.34)[f]	−1.05
NO_2	(−6.31)[g]	−1.44
$-\rho_I$	7.86	1.82
$-\rho_R(+)$	7.23	1.26
$\lambda = \rho_R/\rho_I$	0.92	0.69
SD	0.21	0.07
f = SD/RMS	0.069	0.084

[a] Shifts in ppm relative to unsubstituted (H) member. [b] Reference 12. [c] This work. [d] Shift of unsubstituted member relative to external reference of 60 wt % tetrachlorotetrafluorocyclobutane (TCTFCB) in $HCCl_3$ is −6.42. [e] Shift of unsubstituted member relative to external reference of TCTFCB (60 wt % in $HCCl_3$) is 0.12. [f] Calculated shift by DSP equation, ref 11b. [g] Shift calculated from observed *m*-NO_2 shift of −5.33; cf. ref 12.

The conclusion is inescapable from the present results that for series I fluoroaromatics the transmission of polar substituent effects upon F NMR shifts is largely carried internally by the π-bond framework and any transmission through space by comparison is entirely minor. Consequently, the major importance of field transmission of substituent polar effects *upon F NMR shifts* in other fluoroaromatics, e.g., para-substituted fluorobenzenes, is placed in strong doubt. Further, Dewar's FMMF method can no longer be accepted as a valid general treatment.

We cannot overemphasize that the conclusions reached herein apply to *F NMR shielding*, a measurement which directly involves the "unbalance" of the π-electron system in the immediate vicinity of the fluorine nucleus.[13] The conclusions obtained here cannot be necessarily applied to other measurements.[14] In particular, substituent effects on standard free energy changes for aqueous proton transfer equilibria, according to current evidence,[15] are best approximated (in contrast) by field transmission of the polar effects.

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Levulinic Esters. An Alcohol Protecting Group Applicable to Some Nucleosides[1]

Sir:

Protection and mild deprotection of alcohols is of considerable importance in natural products chemistry, especially in carbohydrates, nucleosides, and steroids.[2]

We considered the desirability of a protecting group X so that deprotection occurs after a mild operation (y) that transforms X into a new function Z (see eq 1). Ideally ROZ

$$\mathrm{ROH} \longrightarrow \mathrm{ROX} \xrightarrow{y} \mathrm{ROZ} \longrightarrow \mathrm{ROH} \qquad (1)$$

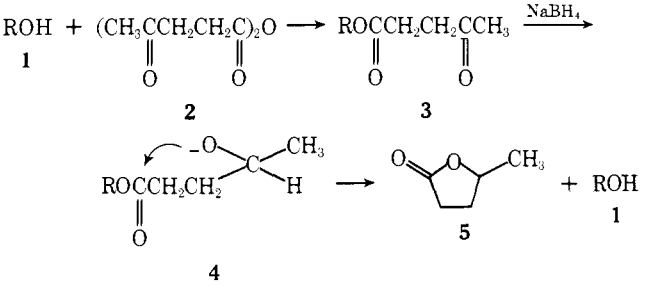
should spontaneously regenerate the alcohol. Such examples include the formation of a tiglic ester[3] which is deprotected by OsO_4-HIO_4 oxidation or benzoylpropionic acid esterification[4] followed by hydrazinolysis.

We wish to report the protection of alcohols by formation of their levulinates, **3**, and the successful mild deprotection of the latter with $NaBH_4$. The method is based on two principles: (1) selective reduction of ketones over esters by borohydride so that ester and other functions can be present in the molecule; (2) facile intramolecular lactone formation from γ-hydroxy esters (see **4**) with concomitant release of ROH. The water soluble lactone **5** is easily separated from the product and was in fact isolated and identified in one of the experiments. In principle any nucleophile capable of attacking the carbonyl group of ketones (cf. **3**) may be suitable. However, only partial success was achieved with the mild nucleophiles CN^- or HSO_3^-, while H^- ($NaBH_4$) in dioxane-water at 25° (30 min) or in alcohol at 65° (1 min) proved to be the most convenient. Another advantage of using $NaBH_4$ is that, if necessary, the pH range of the reaction can be varied between 5 and 8.5 by simultaneous addition of acid,[5] since carbonyl reduction by this reagent occurs readily in this pH range.

Table I. Levulinate Protection and Deprotection of Alcohols

Entry	Alcohol 1	Levulinates[b] % yield[a]	Mp, °C	Yield (%)[a] of pure recovered 1
1	*p*-Nitrobenzyl	80	58	93
2	Cholesterol	74	66.5–68	97
3	Epicholestanol	76	104–105	78
4	6	67	96–97	65
5	7	67	79	94
6	2′,3′-Di-O-benzoyl uridine (8a)	86	156	82
7	2′,3′-Isopropylidene-uridine (8b)	90	45	94
8	5′-O-Tritylthymidine (9)	81	143–145	90

[a] Yield usually refers to recrystallized material. [b] All compounds showed consistent elemental analyses, ir, and NMR spectra.



Successful protection and deprotection of several alcohols shown in Table I was achieved in the presence of nitro, olefin, ester, and acetal (entries 1, 2, 4, and 5) functions. Furthermore, the examples include an axial alcohol (entry 3) as