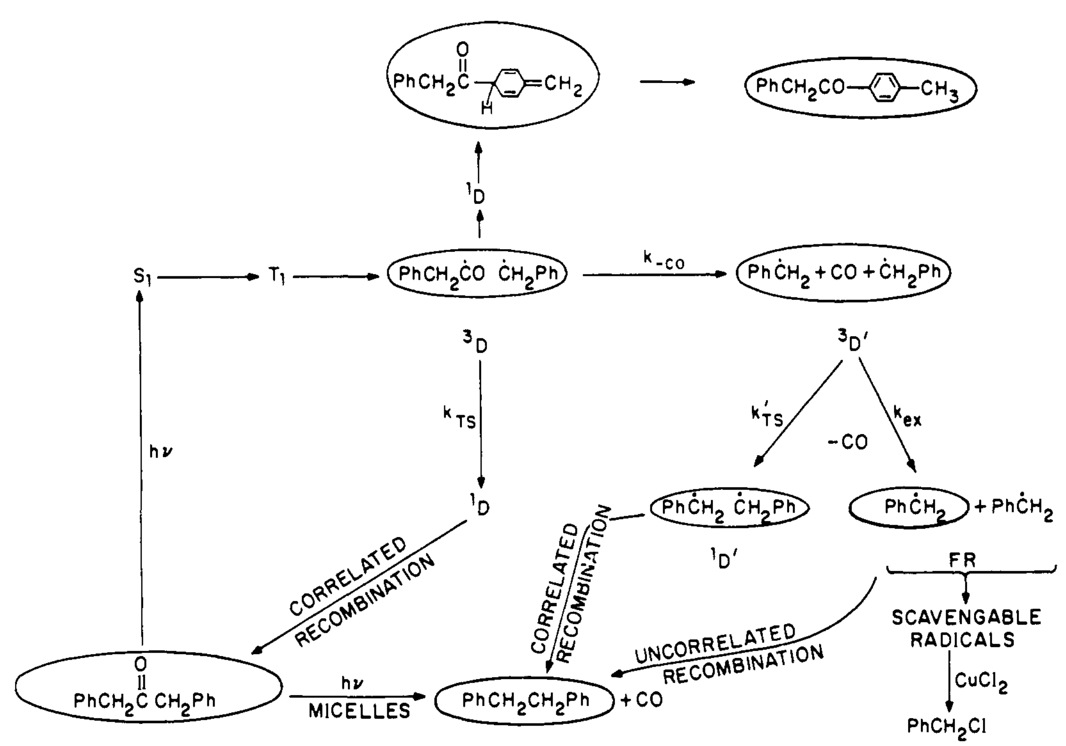
Scheme I



formation of DPE in the presence and absence of Cu^{2+} yields the cage effect for $^3D'$ radical pairs. Intersystem crossing ($^3D' \rightarrow {}^1D'$) presumably precedes efficient coupling to form DPE (Scheme I). The cage effect for the various ketones investigated was measured as a function of magnetic field strength (Figure 2). The "cage effect" was also measured in an alternate manner that did not require a scavenger in order to determine whether aqueous $CuCl_2$ traps all the benzyl radicals which escape from micelles or whether the micellar system is significantly perturbed by the addition of scavenger. A 0.05 M HDTCl solution containing 0.001 M 4-$CH_3C_6H_4CH_2COCH_2C_6H_5$ (A–CO–B) was photolyzed at 0.5 G. The ratio of yields of BB:AB:AA was found to be 1.0:6.52:1.04, from which a cage effect of 52 ± 3% can be computed. In the presence of 0.007 M $CuCl_2$ a solution of 0.05 M HDTCl containing 0.001 M ACOB, a cage effect of 48 ± 4% was computed from the amount of unscavengable coupling product, AB. No AA or BB were detected in the latter experiment. Several salient points are apparent. Only a small difference is noted for DBK and either DBK-*1*-^{13}C or DBK-d_4. However, it is expected from Scheme I that if triplet $Ph^{13}{\cdot}CH_2$ pairs undergo more rapid intersystem crossing than triplet $Ph^{12}{\cdot}CH_2$ pairs this will lead to a higher yield of cage product resulting from recombination of the $Ph^{13}CH_2$ radical pairs as is found experimentally: DBK, cage effect = 32 ± 2%; DBK-α,α'-$^{13}C_2$, cage effect = 46 ± 3%. For each ketone studied, a major decrease in the cage effect occurs only for field strengths less than 1000 G.

In conclusion, the results shown in Figures 1 and 2 provide substantial evidence that nuclear spin isotope effects are significant in the photochemistry of DBK in micellar solution. Fitting the details of the curves to a quantitative theory may provide important information relevant to parameters involved in CIDNP and in micellar structure and dynamics.

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[13] Since we now have discovered that α is extremely sensitive to magnetic field strength for fields in the range of 100–300 G, we have reexamined previously reported data.[7] We find that the reported values of α for "control experiments" that were run on samples within the gap of a magnet nominally at 0 G are consistently highr ($\alpha \sim 1.47$) than the values of α (~ 1.35) found for "control experiments" that were run on samples on a bench. It appears likely that a residual field on the order of 100–200 G persisted in the "control experiments" run in the magnet. Also, a better correlation exists between α and quantum yields for disappearance of DBK than for the appearance of DPE. This is because it is now known that an isomer of DBK is also formed[14] in low yield so that the quantum yield for disappearance of DBK does not exactly equal the quantum yield for appearance of DPE. The value of 1.41 reported earlier[9] was based on the quantum yield for formation of DPE. We consider the quantum data reported here, since they are based on DBK disappearance, provide the most accurate values of α (1.35 ± 0.03).

[14] Kraeutler, B.; Turro, N. J. *Chem. Phys. Lett.* **1980**, *70*, 270.

α-Fluorination of Carbonyl Compounds with CF_3OF

Sir:

We have found a convenient, two-step method for the introduction of fluorine adjacent to the carbonyl group of ketones, aldehydes, esters, and amides. This is accomplished by first converting the carbonyl compounds to their trimethylsilyl enol ethers and then treating these resultant ethers with trifluoromethyl hypofluorite (CF_3OF) at −70 °C in an inert solvent to give directly the corresponding α-fluorocarbonyl compound.

Previous investigators[1] have found that enol acetates could be treated with CF_3OF to give mixtures of α,β-difluoroalkyl acetates and α-trifluoromethoxy-β-fluoroalkyl acetates, both of which could be hydrolyzed to α-fluoro ketones. Vinyl ethers and enamines can also be converted to α-fluoro ketones by similar chemistry.[1] These procedures work well for the preparation of α-fluoro ketones, but they appear to lack generality and have not been applied to the syntheses of other α-fluorocarbonyl compounds such as aldehydes, esters, and amides. These procedures also have a further

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[1] Barton, D. H. R.; Godinho, L. S.; Hesse, R. H.; Pechet, M. M. *Chem. Commun.* **1968**, 804–806. Hesse, R. H. *Isr. J. Chem.* **1978**, *17*, 60–70 and references cited therein.

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Table I. α-Fluorocarbonyl Compounds Prepared with CF_3OF

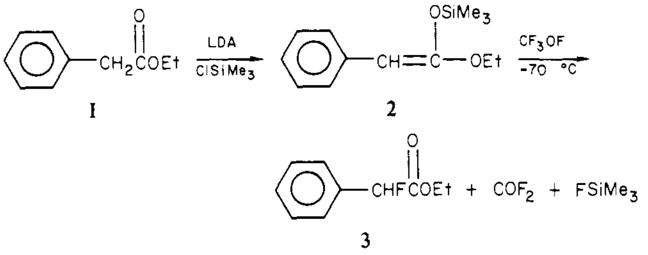
compound[a]	yield, %	mp, °C (recrys solv) [bp (mm), °C]	^{19}F NMR ($CDCl_3$), δ, ppm
esters			
ethyl α-fluorobenzeneacetate (3)	77	[96-98 (4.8)]	−180.1 (d, J = 48 Hz)
ethyl α-fluoro-4-isobutyl-α-methylbenzeneacetate	85	[88-89 (0.4)]	−150.9 (q, J = 22 Hz)
ketones			
α-fluoroacetophenone	70	25-26 [93 (7)]	−231.9 (t, J = 47 Hz)
α,4-difluoroacetophenone	70	48-50 [75 (1.4)]	−232.0 (d, J = 47 Hz) −105.0 (m)
2-fluorocyclohexanone	74	[46 (2.8)]	−188.8 (d, m, J = 51 Hz)
exo-3-fluoronorcamphor	83	99-101 [80 (17)]	−190.0 (d, J = 53 Hz)
α-fluoro-α-phenylacetophenone	72	50-51 (heptane)	−176.5 (d, J = 49 Hz)
aldehyde			
α-fluorobenzeneacetaldehyde[b]	70	[35-36 (1.0)]	−178.8 (d, d, J = 49, 24 Hz)
amides			
α-fluoro-*N*,*N*-dimethylbenzeneacetamide	65	[98-100 (0.45)]	−175.9 (d, J = 50 Hz)
3-fluorodiazepam	80	149-151 (ethanol)	−161.7 (d, J = 57 Hz)
acids			
α-fluorobenzeneacetic acid	90	75-77 (hexane)	−181.4 (d, J = 48 Hz)
α-fluoro-4-isobutylbenzeneacetic acid (6)	80	64-66 (pentane)	−179.9 (d, J = 48 Hz)
3-chloro-α-fluorobenzeneacetic acid	72	61-63 (hexane)	−179.8 (d, J = 47 Hz)
4-chloro-α-fluorobenzeneacetic acid	70	66-68 (hexane)	−182.6 (d, J = 47 Hz)
2-fluoro-2-phenoxyacetic acid	71	61-63 (heptane)	−130.1 (d, J = 59 Hz)
2-fluoro-2-(2,4-dichlorophenoxy)acetic acid	70	89-91 (chlorobutane)	−131.5 (d, J = 59 Hz)
2-fluoro-2-(2,4,5-trichlorophenoxy)acetic acid	76	132 (chlorobutane)	−132.9 (d, J = 59 Hz)
2-fluoro-2-(2-naphthoxy)acetic acid	70	>100 dec	−130.7 (d, J = 60 Hz)

[a] All new compounds gave satisfactory (±0.4%) elemental analysis (C, H, F). [b] Polymerizes on standing.

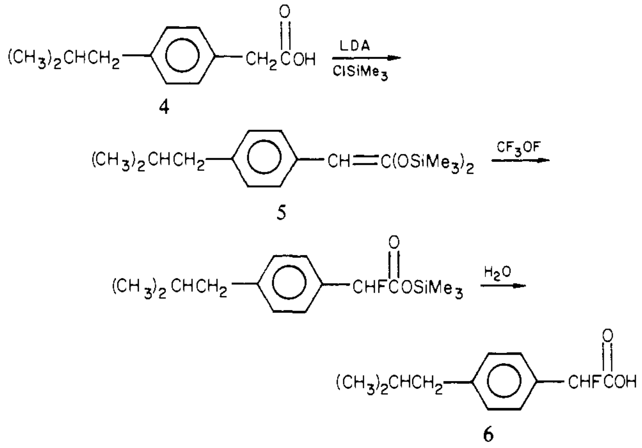
disadvantage in that sometimes a vigorous hydrolysis step is needed to generate the α-fluoro ketones, and yields can be low.

These disadvantages can be overcome by use of trimethylsilyl enol ethers as the fluorinating substrate. In general, trimethylsilyl enol ethers are easy to prepare from most carbonyl compounds, including esters[2] and amides[3] as well as aldehydes and ketones.[4] Silyl enol ethers of all classes of carbonyl compounds react rapidly with CF_3OF at −70 °C in an inert solvent such as CCl_3F to give directly the corresponding α-fluorocarbonyl compound. Workup is simple; no hydrolysis step is required. Since the byproducts of the reaction are all gaseous (carbonyl fluoride and fluorotrimethylsilane), the α-fluorocarbonyl product can be obtained in nearly pure form by a simple evaporation of the reaction mixture.

A sample procedure follows: Ethyl benzeneacetate (1) was converted to its silyl enol ether (2) by treatment with lithium diisopropylamide (LDA) and chlorotrimethylsilane.[2] A solution of 21.28 g (0.09 mol) of this enol ether (2) in 200 mL of CCl_3F was cooled to −70 °C, and 9.4 g (0.09 mol) of CF_3OF[5] was passed into the solution for 3 h. The reaction mixture was warmed to room temperature and distilled to give 12.52 g (77%) of ethyl α-fluorobenzeneacetate (3).



This same chemistry can also be used to convert carboxylic acids to their corresponding α-fluoro derivatives, but an extra hydrolysis step is necessary. The acids are first converted to bis(trimethylsilyl)ketene acetals[6] by reaction with LDA and chlorotrimethylsilane. For example, 5, bp 128–130 °C (0.4 mm), was prepared from ibufenac (4). The ketene acetals are then treated with CF_3OF to give trimethylsilyl α-fluoro esters, which can be easily hydrolyzed to the free α-fluoro acids. Table I shows α-fluorocarbonyl compounds prepared by this new procedure.



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(5) P.C.R. Inc., Gainesville, FL 32602. CF_3OF is an extremely reactive and toxic gas, and proper safety precautions should be followed in its use.

(6) Ainsworth, C.; Kuo, Yu-N. *J. Organomet. Chem.* **1972**, *46*, 73–83.

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^1H and ^{14}N Electron-Nuclear Double Resonance of Oxovanadium(IV) Porphyrin in Solid Solution

Sir:

The oxovanadium(IV) ion, VO^{2+}, is used extensively in ESR studies of metal ion complexes.[1-4] The information derived in