(13) The sequence rule mandates the somewhat confusing difference in stereochemical nomenclature in this substrate-product relationship.

(14) (a) G. Helmchen, H. Völter, and W. Schühle, *Tetrahedron Lett.*, 1417-1420 (1977); (b) G. Helmchen, G. Nill, D. Flockerzi, W. Schühle, and M. S. K. Youssef, *Angew. Chem., Int. Ed. Engl.*, **18**, 62-63 (1979); (c) W. H. Pirkle and J. R. Hauske, *J. Org. Chem.*, **42**, 1839-1844 (1977); (d) W. H. Pirkle and D. L. Sikkenga, *J. Chromatogr.*, **123**, 400-404 (1976). These reports are concerned with model amides[14a,b] or carbamates[14c,d] in which a single polar functional group is present, and the chiral center is always α to the polar group. In our diastereomeric derivatives, three polar functional groups capable of interacting with the adsorbent are present, and the chiral center is β to the amide functionality. Thus, the conformation of diastereomers **5-8a,b**, in solution or adsorbed, is less susceptible to definition than the simpler literature models.

(15) B. J. Bergot, R. J. Anderson, D. A. Schooley, and C. A. Henrick, *J. Chromatogr.*, **155**, 97-105 (1978).

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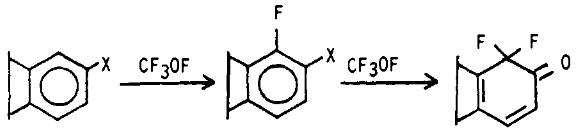
Addition-Elimination Reactions of CF_3OF with Activated Aromatics

Sir:

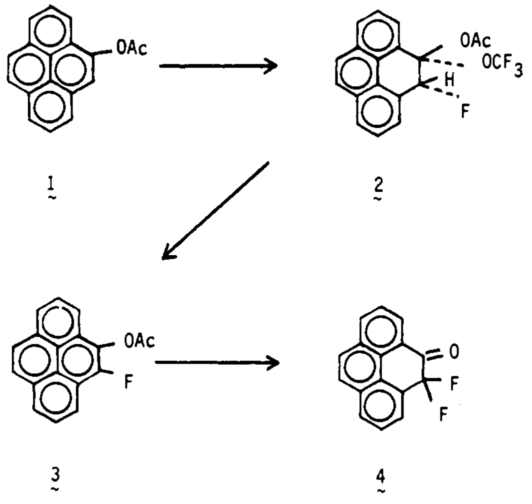
The literature contains a number of examples of fluorination of aromatic compounds with fluoroxytrifluoromethane (CF_3OF). The CF_3OF fluorination of activated aromatic systems can be controlled to produce either monofluoro or *gem*-difluoro products, depending on the amount of CF_3OF used (eq 1).[1-8]



(1)

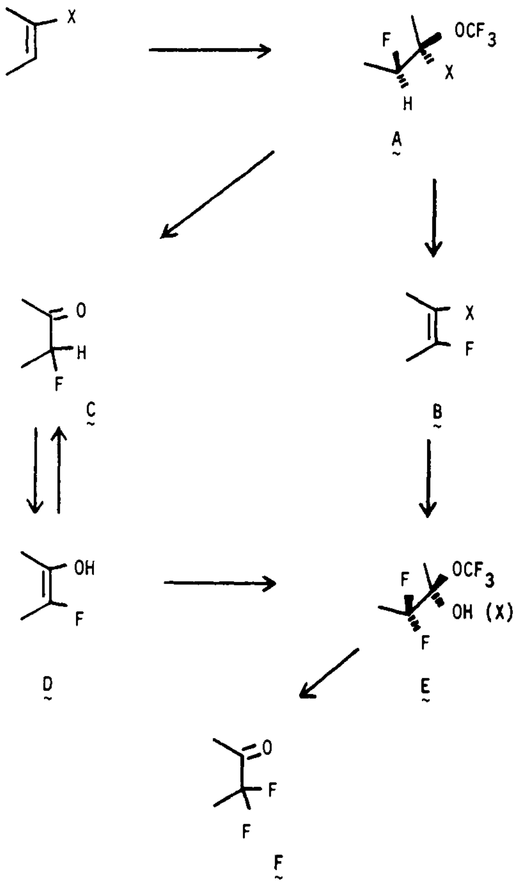
While the path for difluorination is known to involve electrophilic addition of CF_3OF to the monofluoro intermediate,[4] the route for monofluorination is still uncertain. Monofluorination could occur by (a) electrophilic substitution, (b) free-radical substitution, or (c) addition-elimination.[1,3]

In our studies of the reaction of activated aromatics with CF_3OF,[7,8] we have employed 4-acetoxypyrene (**1**) as a mechanistic probe. 4-Acetoxypyrene is especially suitable since it can give stable products from (a) electrophilic substitution[9,10] at the 1 or 5 positions, (b) free-radical dimerization,[11] and (c) molecular addition to the 4,5 position.[9]



Reaction of 4-acetoxypyrene[10] with slightly less than 1 equiv of CF_3OF[12] at −78 °C in methylene chloride furnished a green oil from which were isolated 67% unreacted 4-acetoxypyrene and 27% (82% yield) adduct **2** as a semisolid:[13,14] ^{1}H NMR ($CDCl_3$) δ 7.70-8.60 (m, arom), 6.62 (d, 1 H, CHF, J = 96 Hz), 2.75 (s, 3 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ^* 57.4 (s, 3 F, CF_3O), 57.6 (d, 1 F, CHF, J = 96 Hz); ^{13}C NMR ($CDCl_3$) δ 209.5 (s, C=O), 200.5 (q, CF_3, J = 199.6 Hz), 125.8 (d, CF, J = 188.5 Hz), 125-130.3 (m, arom), 17.5 (s, CH_3); IR (neat) 1760 cm^{-1} (C=O), 1100-1300 (CF_3O); MS (80 eV) m/e 364 amu (calcd mol wt 364). On standing at room temperature for several days, adduct **2** slowly converted into 5-fluoro-4-acetoxypyrene (**3**):[14] ^{1}H NMR ($CDCl_3$) δ 7.5-8.5 (m, arom), 2.7 (s, CH_3); ^{19}F NMR ($CDCl_3$) ϕ^* 57.2 (s); MS m/e 262 amu (calcd mol wt 262); mp 76-79 °C. Extended reaction of **1** or **3** with CF_3OF at −78 °C in CH_2Cl_2 furnished a mixture from which 5,5-difluoro-4-(5*H*)-pyrenone (**4**)[14] was obtained in 20% yield: ^{1}H NMR ($CDCl_3$) δ 6.3-7.95 (m, arom); IR (KBr) 1690 cm^{-1} (C=O); ^{19}F NMR ($CDCl_3$) ϕ^* 101.0 (s); MS m/e 256 amu (calcd mol wt 256); mp 117-120 °C. In a control experiment, 2-acetylaminopyrene,[15] which has an extremely activated 1 position toward electrophilic substitution, failed to give any isolable fluorinated products on reaction with CF_3OF.

Scheme I



Compound **2** represents the first report of a 1:1 adduct between CF_3OF and an activated aromatic system. The isolation of **2** and its conversion to **3** conclusively show that monofluorination occurs by addition of CF_3OF to the aromatic system prior to elimination. Further fluorination of the monofluoroaromatic with CF_3OF produces difluoro products. The pathway illustrated in Scheme I accounts well for all of he experimental data reported.[1-8]

In this scheme, CF_3OF adds to the activated bond to give A which can either eliminate CF_3OH to give B or undergo oxidation-hydrolysis to give C $\rightleftharpoons$ D. Previous work has shown that sterically hindered systems, e.g., benzo[*c*]phenanthrene and 7,12-dimethylbenz[*a*]anthracene, prefer existence as the keto tautomer (C).[8] The difluoro ketone F is obtained through further addition of CF_3OF to B or D to produce E which in turn is oxidized or hydrolyzed to F.[4,7]

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

(13) The stereochemistry of adduct **2** was not determined but the preferred loss of the elements of $HOCF_3$ to give **3** coupled with precedence for cis addition of CF_3OF to alkenes (Barton, D. H. R.; Hesse, R. H.; Jackman, G. P.; Ogunkoya, L.; Pechet, M. M. *J. Chem. Soc., Perkin Trans 1* **1974,** 739) led us to prefer a geometry in which the F and OCF_3 moities are cis to each other.

(14) All new compounds gave satisfactory (±0.3%) elemental analyses (C, H, F).

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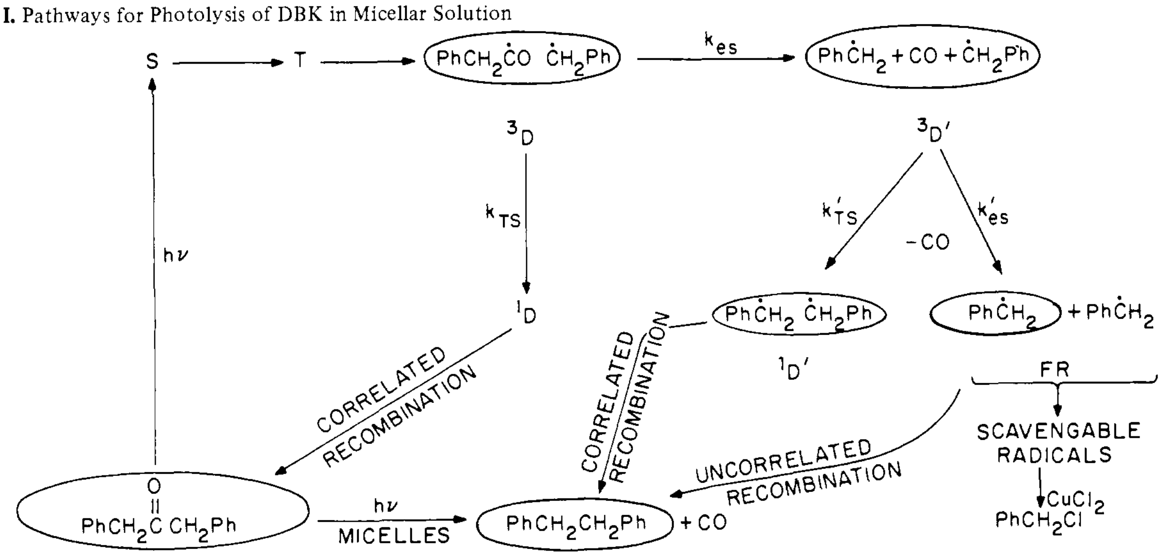
Magnetic and Micellar Effects on Photoreactions. Micellar Cage and Magnetic Isotope Effects on Quantum Yields. Correlation of ^{13}C Enrichment Parameters with Quantum Yield Measurements

Sir:

The photoinduced homolytic α-cleavage reaction of dibenzyl ketone (DBK) produces a geminate triplet radical pair[1] whose reactivity has been shown to be significantly influenced by micellar[2] and magnetic[3] effects (Scheme I). The products derived from the initial $PhCH_2\,COCH_2Ph$ triplet radical pair (^3D) may be classified as geminate (spin-correlated) products which form in a cage process or as free-radical (spin-uncorrelated) products which form after (complete) diffusional separation of the initially formed radical pair. The remarkable ^{13}C enrichment discovered in recovered DBK after partial photolysis in micellar solution was interpreted in terms of an enhanced cage effect of radical pairs in a micelle and a magnetic isotope (^{13}C) effect.[4,5] Both of the latter operate on the reactivity of ^3D by influencing the rate of triplet-singlet crossing via nuclear-electronic hyperfine interaction to yield a singlet radical pair, ^1D, which is presumed to undergo efficient recombination to regenerate DBK. The enhanced cage effects of radical pairs in micelles predicts (1) a decreased quantum yield for disappearance of DBK and appearance of 1,2-diphenylethane (DPE) in hexadecyltrimethylammonium chloride (HDTCl) micelles (Φ_{-DBK}^{HDTCl} and Φ_{DPE}^{HDTCl}) relative to the quantum yields in homogeneous benzene solution ($\Phi_{-DBK}^{benzene}$ and $\Phi_{DPE}^{benzene}$). The magnetic isotope effect concept allows the further extraordinary predictions:[5] (2) the quantum yield for disappearance of DBK and appearance of DPE will be significantly less for a ketone enriched in ^{13}C in the carbonyl carbon; (3) the quantum yield for disappearance of DBK and appearance of DPE will be influenced by the application of an external laboratory magnetic field on the sample during photolysis; (4) the quantum yields for cage reactions will be magnetic field dependent; (5) the magnitude of α, predicted by Bernstein's formula[6] (^{13}C enrichment as a function of percent conversion) is directly related to the value of α derived from quantum yield measurements. In a sufficiently strong magnetic field (provided by a laboratory magnet), intersystem crossing will no longer be determined by hyperfine interactions, but by (isotope independent) differences in g factors of the radicals of ^3D. In this limit, differences in the behavior of DBK that are due to magnetic isotope effects will vanish; i.e., α will decrease to unity.

The absolute quantum yields for total disappearance of DBK and for the appearance of DPE were measured in benzene and in HDTCl solutions. Ratios of these quantum yields were also measured independently and with a higher precision than was possible for the absolute quantum yields. Finally, the influence of added $CuCl_2$ (specific scavenger of free radicals in the aqueous phase) and of laboratory magnetic fields on Φ_{-DBK}^{HDTCl} and Φ_{DPE}^{HDTCl} were obtained. The results are shown in Table I. The notations $^{12}\Phi$ and $^{13}\Phi$ refer to quantum yield measurements of DBK containing 99% ^{12}C and 90% ^{13}C, respectively, in the carbonyl carbon. The values in Table I are adjusted to represent quantum yields of DBK containing 100% ^{12}C and

Scheme I. Pathways for Photolysis of DBK in Micellar Solution



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