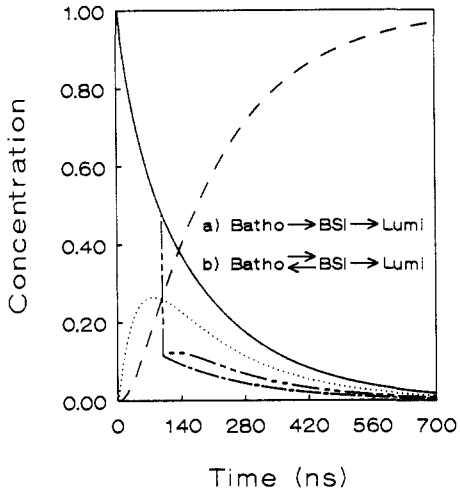

Figure 1. Concentrations of Batho (—), BSI (---), and Lumi (--) predicted by the equilibrium mechanism b. If 75% of the Batho remaining after 93 ns is removed, curves (-·-) and (-···) describe the resulting Batho concentration predicted by the sequential (a) and equilibrium (b) mechanisms, respectively.

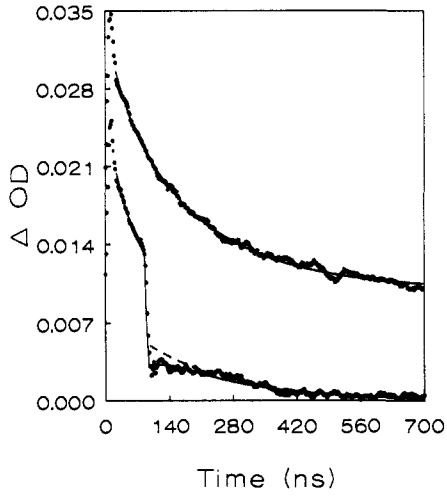

Figure 2. Optical density changes observed at 620 nm. The upper data points (offset 0.01 OD for clarity) show the result of 532-nm photolysis by itself. The line shows the fit using the equilibrium mechanism a with apparent lifetimes of 40 and 190 ns with $K_{eq} = 1.4$. The lower data points are the result of 532-nm photolysis at $t = 0$ followed by 605-nm photolysis 93 ± 3 ns later. (The result of photolysis by 605-nm light alone has been subtracted in order to remove a scattered actinic light artifact.) Using the equilibrium mechanism and assuming 76% photolysis of Batho produces the solid line fit to the data. The dashed line shows the fit assuming the simple sequential mechanism a and 60% photolysis of Batho. This percent was determined by fitting the data starting 93 ns after 605-nm photolysis to an exponential with lifetime 190 ns.

± 3 ns, a 5-mJ, 7-ns pulse of 605-nm light was used to photolyze the remaining Batho. Samples[7] contained 66% glycerol to reduce rotational diffusion and thus increase efficiency of Batho photolysis.

As shown in Figure 2 (top) the data for 532-nm photolysis by itself is extremely well fit by the parameters previously determined from global analysis of spectra taken at different times following rhodopsin photolysis.[1,4] The predictions of the two mechanisms for the two-laser experiment differ significantly. The superior agreement of the kinetic data with the prediction of the equilibrium mechanism demonstrates the existence of back-flow from BSI to Batho, supporting the conclusion that had previously been based on indirect evidence. This raises the question of what structural features in the chromophore/protein pocket environment could be responsible for such a reversible reaction. The answer to this question will require considerably more structural information to be obtained on the new BSI intermediate.

Acknowledgment. This research was supported by Grant EY00983 from the National Eye Institute of the National Institutes of Health.

(6) Einterz, C. M.; Lewis, J. W.; Kliger, D. S. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 3699-3703. Pulses were produced by the second harmonic of a Nd-YAG laser (532 nm) and a dye laser pumped by a second Nd-YAG laser (605 nm). Both were vertically polarized and the probe beam was polarized at the magic angle (54.7°) to avoid kinetic artifacts due to rotational diffusion. The small optical density changes observed make the rotational diffusion effects on absorbance changes negligible under these conditions.

(7) Detergent suspensions of bovine rhodopsin in 2% octyl β-D-glucoside were prepared as in ref 1. The concentration here was 1 mg of rhodopsin/mL.

The Reactions of CF with Aromatics

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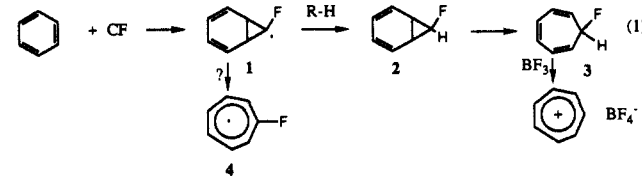
The reaction of C atoms with fluorocarbons gives the monovalent carbon species CF, which can be trapped by addition to alkenes to give a fluorocyclopropyl radical.[1] Subsequent abstraction of hydrogen produces a fluorocyclopropane.[1] We now report evidence that reaction of CF with aromatic compounds gives 7-fluoronorcaradienyl radicals which show some interesting reactions.

When arc-generated carbon and CF_4 are condensed with benzene at 77 K, the predominant fluorine-containing product is fluorobenzene. However, when CF is reacted with benzene in the presence of isobutane as a hydrogen donor and the product treated with BF_3, tropylium fluoroborate is also a product (eq 1, $C_7H_7^+BF4^-$:C_6H_5F = 5.7).[2] This product is consistent with the addition of CF to the aromatic ring to generate a 7-fluoronorcaradienyl radical, **1**, which abstracts hydrogen to give 7-fluoronorcaradiene (**2**),[3a] which then rapidly ring opens to 7-fluorocycloheptatriene (**3**). Subsequent reaction of **3** with BF_3 generates the tropylium fluoroborate.



An interesting question in this system is whether **1** undergoes electrocyclic ring opening to the fluorotropyl radical (**4**). In the reaction of CF with alkenes to give fluorocyclopropyl radicals, we have not observed ring opening to allyl radicals.[1] This electrocyclic ring opening is symmetry forbidden and is generally not observed for cyclopropyl radicals in the absence of a large thermodynamic driving force.[4] However, the ring opening of norcaradienyl radicals should have a large thermodynamic driving force and will not have the symmetry-imposed barrier present in the cyclopropyl radicals. Despite these considerations, several studies of benzonorcaradienyl radicals show that they require high

(1) Rahman, M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 6296.

(2) In a typical reaction, volatile organics (15 mmol each) are mixed on a vacuum line and cocondensed with arc-generated C vapor at 77 K. Products are generally characterized by ^{19}F NMR at 376 MHz. Although product yields calculated from the amount of C lost by the graphite rods are on the order of 1%, they are in fact higher than this as much of the carbon is lost from the rods in large chunks.

(3) (a) A consideration of bond dissociation energies[3b] indicates that this abstraction should be exothermic by 9 kcal/mol. (b) Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1986; Vol. 3, pp 141-191.

(4) Sustmann, S.; Ruchardt, C. *Chem. Ber.* **1975**, *108*, 3043.

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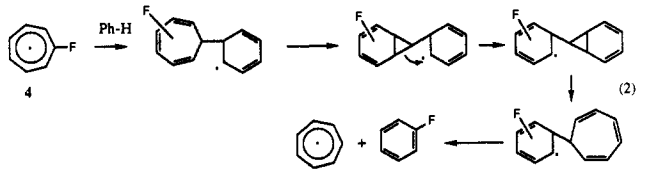
Table I. Ratios of Fluoroaromatics in the Reactions of CF and F Atoms with Aromatics

precursor	rel amt of substitutn at each position			
	% 2	% 3	% 4	% ipso
CF + PhF	13.7	57.5	28.8	–
CF + PhF + O_2	18.5	51.9	29.6	–
F[a] + PhF	36.6	15.5	47.9	–
F[b] + PhF	37.0	18.5	44.5	–
CF + $PhCH_3$	18.4	12.6	10.5	58.5
F[c] + $PhCH_3$	36.1	30.1	33.8	0
CF + $PhCF_3$	11.8	2.8	8.6	76.8
F[d] + $PhCF_3$	27.0	46.0	27.0	0
CF + PhCl	8.3	14.5	8.6	64.9
F[d] + PhCl	33.0	35.0	28.0	0
CF + pyridine	58.8	17.6	11.8	11.8[e]

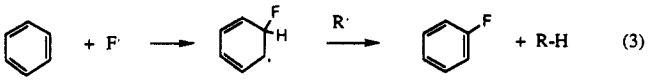
[a] Rowland, F. S.; Cramer, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 6579. [b] Cipollini, R.; Lilla, G.; Pepe, N.; Speranza, M. *J. Phys. Chem.* **1978**, *82*, 1207. [c] Brinkman, G. A.; Visser, J.; Lindner, L. *Radiochim. Acta* **1979**, *26*, 77. [d] Vasek, A. H.; Sams, L. C. *J. Fluorine Chem.* **1973**, *3*, 397. [e] This is the relative amount of fluorobenzene.

temperatures (>180 °C) for ring opening[5] or they do not open at all.[6]

If fluorotropyl radicals are present in these reactions, it is possible that they may abstract hydrogen to give, in addition to **3**, the 1-, 2-, and 3-fluorocycloheptatrienes. Accordingly, we have synthesized these fluorocycloheptatrienes[7] and determined that they are not present among the reaction products. However, a consideration of the heat of formation of tropyl radicals[8] indicates that hydrogen abstraction by **4** from isobutane is endothermic by 15 kcal/mol and would not be expected to occur to a great extent. In order to determine whether **4** is generated in these systems, we must consider other possible reactions of tropyl radicals. In this connection, a very interesting high-temperature reaction of benzotropyl radicals has been reported by Pomerantz and coworkers,[9-12] who observed that such radicals can transfer a CH to another aromatic ring, generating a new tropyl radical and a new aromatic. If fluorotropyl radicals formed here were to transfer a CH in a similar manner, the products would be tropyl radicals and fluorobenzene, a product that we observe. A mechanism, analogous to that proposed by Pomerantz,[9] for this very interesting C–H transfer is shown in eq 2. Addition of **4** to a second benzene



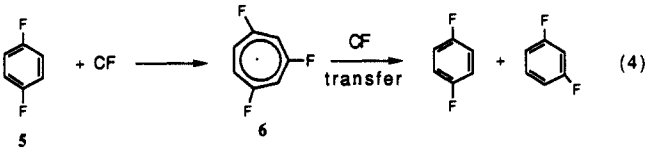
generates a fluorotropyl-substituted cyclohexadienyl radical. Isomerization of the fluorotropyl to a fluoronorcaradienyl group is followed by bond migration to give a fluorocyclohexadienyl radical substituted by a norcaradienyl group. Subsequent ring opening and loss of tropyl radical generates the fluorobenzene. Table I demonstrates that, when substituted benzenes are used as substrates in this system, the products include substituted fluorobenzenes. While it is possible that fluoroaromatics are formed in this system by the reaction of fluorine atoms (perhaps generated by pyrolysis of CF_4 in the carbon arc) with the aromatic (eq 3), a more interesting possibility is that these products result from the transfer of CH by the fluorotropyl radical in eq 2.



Although F atoms, generated by a variety of methods, have been observed to react with aromatics to generate fluorobenzenes, Table I demonstrates that the ratios of isomeric fluoroarenes formed in our system are substantially different from those observed in F atom reactions. Our reactions give ipso substitution products, presumably resulting from transfer of a C–R in eq 2, while such products were not reported in the F atom reactions in Table I.

In an experiment that indicates that C–H transfer and F atom fluorination both generate fluorobenzene in this system, C + CF_4 has been reacted with benzene which is 99.9% ^{12}C. An examination of the ratio of the ^{13}C NMR signals for C_1 and C_2 in the fluorobenzene product of this reaction shows that 38% of this product is formed by attack of CF on the ring followed by CH transfer.

The fact that *m*-difluorobenzene is formed when we condense C + CF_4 with *p*-difluorobenzene (**5**) indicates that CF transfer from fluorotropyl radicals also occurs. If an F atom were displacing F from the benzene ring in this system, we would expect that the only difluorobenzene formed would be the para compound. However, attack of CF on **5** could produce the 1,3,5-trifluorotropyl radical (**6**), which could transfer a CF to another aromatic to give both *m*- and *p*-difluorobenzene (eq 4).[13]



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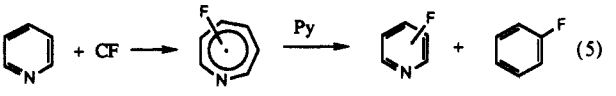
We have also found that cocondensation of C, CF_4, and pyridine at 77 K results in the formation of the three fluoro-substituted pyridines and fluorobenzene (eq 5). The fluoropyridines may be rationalized by postulating a CH transfer by fluoroazatropyl radicals, **7**, while the fluorobenzene results from a transfer of N by **7**. It is difficult to envision a F atom route to fluorobenzene in this system.



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In principle, direct evidence for the intermediacy of fluorotropyl radicals in these reactions could be obtained by isolating their dimers.[14] While the ^{19}F spectra of reaction products show evidence for small amounts of such dimers,[15] analysis is complicated by the fact that a number of isomeric products are expected. However, in the reaction of CF with hexafluorobenzene, we find a product whose ^{19}F NMR spectrum (δ −147.9 (m, 2 F), −152.4 (t of d, J = 19.4 Hz, 5 Hz, 2 F), 155.3 (t, J = 19 Hz, 1 F), −156.5 (m, 2 F)) and mass spectrum (m/e 217 ($C_7F_7^+$)) leads us to conclude that it is perfluoroditropyl.[16]

Acknowledgment. Helpful discussions with Professors M. Pomerantz and K. M. Harmon are gratefully acknowledged. We thank the National Science Foundation for financial support.

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(6) Bartmetler, A.; Ruchardt, C.; Sustmann, R.; Sustmann, S.; Verhulsdonk, R. *Tetrahedron Lett.* **1974**, 4389.
(7) (a) Harmon, K. M. Ph.D. Thesis, University of Washington, Seattle, WA, 1958. (b) Muller, E. v.; Kessler, H. F.; Kiedaish, W. *Justus Liebigs Ann. Chem.* **1964**, *675*, 63.
(8) DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.
(9) Pomerantz, M.; Combs, G. L., Jr.; Fink, R. *J. Org. Chem.* **1980**, *45*, 143.
(10) Pomerantz, M.; Gruber, G. W. *J. Org. Chem.* **1968**, *33*, 4501.
(11) Pomerantz, M.; Ross, A. S.; Gruber, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 1403.
(12) Pomerantz, M.; Ross, A. S. *J. Am. Chem. Soc.* **1975**, *97*, 5850.
(13) Attack of CF on the 1,2 bond of **5** would produce the 1,2,4-trifluorotropyl radical, which could transfer CF to give *o*-difluorobenzene. However, we do not see any more *o*-difluorobenzene than is present in starting **5** as a small impurity. The reason for the apparent preference for attack by CF on the 2,3 bond of **5** is under investigation. We do not detect *m*-difluorobenzene in our starting material by ^{19}F NMR.
(14) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1957**, *79*, 352.
(15) For example, the reaction of CF with benzene generates products with ^{19}F resonances at δ −97.8, −97.9, −104.3, −108.3, −108.5, −108.7, and −116.7. However, these are formed in less than 1% of the fluorobenzene yield.
(16) Dailey and Lemal (Dailey, W. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 1169) have reported perfluorocycloheptatriene whose olefinic fluorines have chemical shifts similar to those we observe for perfluoroditropyl.