Photochemistry of Polyhaloarenes. 6. The Fragmentation of Polyfluoroarene Radical Anions

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The quantum yields for photolyses of pentafluorobenzene in the presence of different concentrations of triethylamine in acetonitrile and pentane were determined at 254 nm. Excimer formation was probed through a study of the quantum yield dependence for pentafluorobenzene photolysis upon substrate concentration in the absence of triethylamine. The linear dependence of $1/\Phi$ vs. $1/(ArF)$ is complemented by an analysis of product composition, which revealed the production in a 30-min photolysis of the following: 1,2,3,5-tetrafluorobenzene (2) (0.11%), 1,2,4,5-tetrafluorobenzene (3) (1.09%), 1,2,3,4-tetrafluorobenzene (4) (0.09%), octafluorobiphenyl (four isomers, 0.26, 0.85, 0.91, and 0.8%), and HF (3.01%). The regiochemistry of the monodefluorination of pentafluorobenzene, 1,2,3,5-tetrafluorobenzene, and 1,2,3,4-tetrafluorobenzene in the presence of triethylamine in acetonitrile or pentane (cyclohexane) was determined and is rationalized in terms of fission of the parent radical anion through a bent transition state.

In our previous studies on the photochemistry of polychloroarenes, we have focused our attention on reactions proceeding through the radical anion, the mode of fission of the radical anion (chloride ion loss verses chlorine atom loss), and the regiochemistry of the process.[1] In order to provide additional insight into the photochemistry of polychloroarenes and to test the generality of the mechanistic picture we have developed, an investigation of related aspects of the phototransformations of polyfluorobenzenes was undertaken.

Photochemical transformations of polyfluoroarenes in the presence of an electron donor such as triethylamine should present a simpler mechanistic picture than analogous polychlorarenes, since the C–F bond energy in fluorobenzene is 124 kcal/mol,[2] while λ_{max} for pentafluorobenzene, for example, is 257 nm, suggesting a singlet energy level of less than 111 kcal/mol and thus no competing contribution to product formation from direct fission. As a starting point, the photodefluorination of pentafluorobenzene, in the presence of electron donor triethylamine, might be expected to proceed solely through an exciplex as pictured in Scheme I (UV and NMR experiments provided no evidence for a ground-state charge-transfer complex in either acetonitrile or cyclohexane). If this is accurate, the steady-state assumption yields eq 1, where F

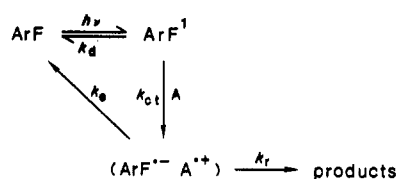$$\frac{1}{\Phi} = \frac{1}{F} + \frac{k_d}{F \cdot k_{ct}(A)} \tag{1}$$

$= k_r/(k_r + k_e)$. A plot of the reciprocal of the quantum yield vs. the reciprocal of the amine concentration should provide a linear relationship with a positive slope.

The quantum yields for photolysis of pentafluorobenzene in the presence of different concentrations of triethylamine in acetonitrile and pentane were determined at 254 nm by using cyclopentanone actinometry. The plots of $1/\Phi$ (Φ representing total product formation) vs. $1/(A)$ in acetonitrile and pentane are presented in Figures 1 and 2 and are curved rather than linear, although there is a linear region for $1/(A) < 2.0$ M^{-1}. The flattening out of the curves with increasing values of $1/(A)$ is reminiscent of the case of the photodecomposition of pentachlorobenzene in the presence of triethylamine and suggests that there is a route to product in the absence of triethylamine[1] in spite of the restriction placed on the system by the strength of the C–F bond.

Scheme I

Scheme II

Scheme III
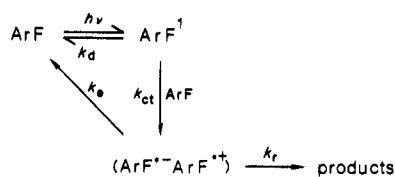
A reasonable adjustment to Scheme I that would provide a fit to the data would be product formation via an excimer, which would operate in competition with electron transfer from triethylamine as illustrated in Scheme II. The steady-state assumption leads to eq 2, where $F =$

$$\frac{1}{\Phi} = \frac{k_{ct}(A) + k_{ex}(ArF) + k_d}{k_{ct}(A)F + k_{ex}(ArF)G} \tag{2}$$

$$\frac{1}{\Phi} = \frac{1}{F} + \frac{k_{ex}(ArF) + k_d}{k_{ct}(A)F} \tag{3}$$

$k_r/(k_r + k_e)$ and $G = k_p/(k_p + k_b)$. As the amine concentration is increased ($1/(A)$ is decreased), the relationship $k_{ct}(A)F \gg k_{ex}(ArF)G$ may hold and eq 2 may be simplified to eq 3, which at constant (ArF) is linear in $1/(A)$. As the concentration of amine is decreased [$1/(A)$ is increased], the plot of $1/\Phi$ vs. $1/(A)$, using eq 2, will be concave downward and flatten out to a slope of zero in harmony with the data presented in Figures 1 and 2.

In order to check on the possibility of product formation through excimer formation, the quantum yield dependence upon pentafluorobenzene concentration was determined
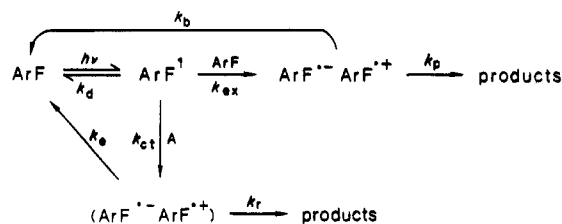
(1) Freeman, P. K.; Srinivasa, R.; Campbell, J.-A.; Deinzer, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5531.

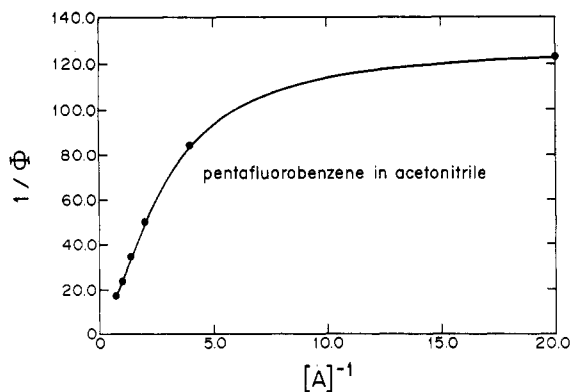(2) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.

Figure 1. Plot of the reciprocal of the quantum yield for pentafluorobenzene photolysis in acetonitrile vs. the reciprocal of triethylamine concentration.
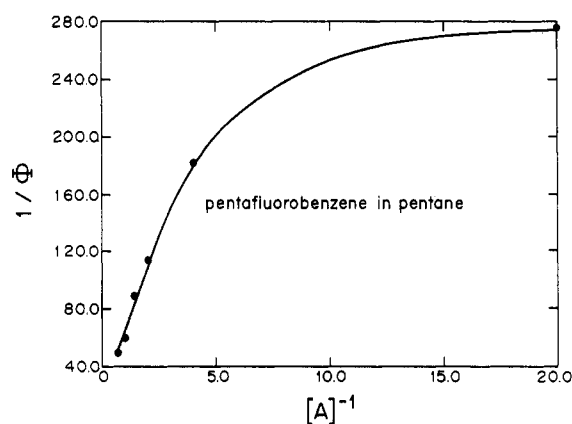

Figure 2. Plot of the reciprocal of the quantum yield for pentafluorobenzene photolysis in pentane vs. the reciprocal of triethylamine concentration.
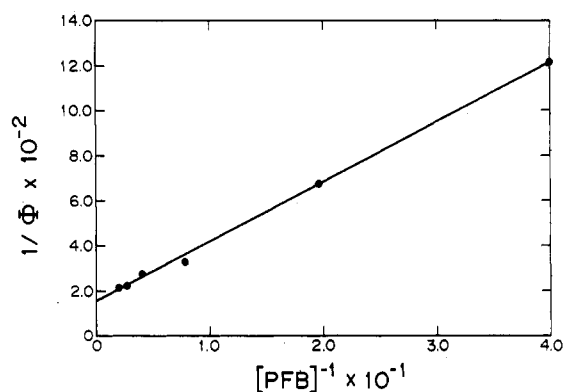

Figure 3. Plot of the reciprocal of the quantum yield for pentafluorobenzene photolysis in acetonitrile vs. the reciprocal of the pentafluorobenzene concentration.

for photolysis at 254 nm in acetonitrile. The simplest mechanistic picture, involving excimer formation, is presented in Scheme III. Using the steady-state assumption, eq 4 may be derived. A plot of $1/\Phi$ vs. $1/(\text{ArF})$

$$\frac{1}{\Phi} = \frac{1}{F} + \frac{k_d}{F \cdot k_{ct}(\text{ArF})} \qquad (4)$$

is provided in Figure 3 and is nicely linear (correlation coefficient $r = 0.999$), providing evidence supporting Scheme III (as well as Scheme II). There would be an equally good fit for the case where the quantum yield for intersystem crossing aproaches 1.00 and triplet state forms product-determining excimer in competition with radiative and nonradiative decay.

Scheme IV
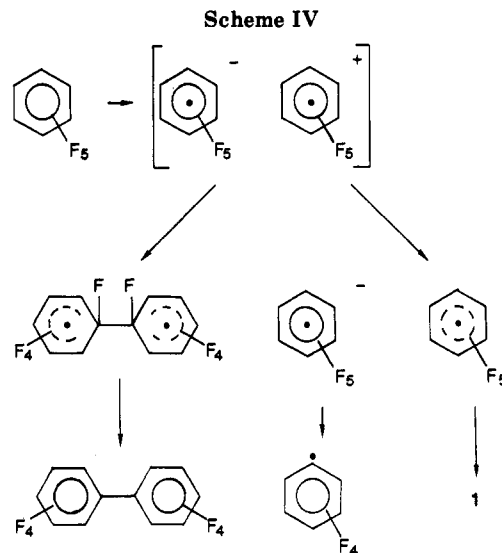
If excimer formation is the key to product formation in the absence of triethylamine, product composition might well provide some interesting evidence pertaining to the mechanism. Irradiation of pentafluorobenzene (1) at 254 nm for 30 min in acetonitrile results in the generation of 1,2,3,5-tetrafluorobenzene (2) (0.11%), 1,2,4,5-tetrafluorobenzene (3) (1.09%), 1,2,3,4-tetrafluorobenzene (4) (0.09%), octafluorobiphenyl (four isomers, 0.26, 0.85, 0.91, and 0.08%, with no detectable nonafluoro or decafluorobiphenyl), and HF (3.01%). Excimer formation might be followed by coupling within the cage to a bis(cyclohexadienyl) diradical, which loses fluorine to form octafluorobiphenyl. Using Benson's group equivalents,[3] the standard enthalpy of reaction (ΔH°_{298}) for the conversion of 2 mol of pentafluorobenzene to octafluorobiphenyl plus fluorine is 85.5 kcal mol^{-1}. It is also possible to estimate that the standard enthalpy of reaction for conversion of 1 into the bis(cyclohexadienyl) diradical is approximately 35 kcal mol^{-1}, while the subsequent conversion to products is endothermic by approximately 51 kcal mol^{-1}. Taking into account vibrational relaxation in the initially formed singlet pentafluorobenzene, the excimer, and the bis(cyclohexadienyl) diradical and the energy available in the intial excitation, generation of excimer followed by formation of bis(cyclohexadienyl) diradical seems quite plausable, but the final conversion to octafluorobiphenyl seems less certain. The lack of formation of nonafluoro- and decafluorobiphenyl is an interesting feature that may be analyzed in terms of the nature of the HOMO (6) and LUMO (7) orbitals of pentafluorobenzene. If these two
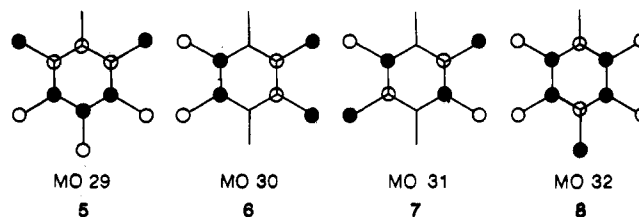
orbitals provided complete control of bond formation within the excimer, consideration of coulombic interactions and overlap of the SOMO of the radical cation with the subjacent orbital of the radical anion (MO 30 with MO 30) and overlap of the LUMO of the radical cation with the SOMO of the radical anion (MO 31 with MO 31) leads to

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(3) Benson, S. W. *Thermochemical Kinetics*, 2nd Ed.; John Wiley: New York, 1976.

Table I. Photolysis of Polyfluorobenzenes in the Presence of Triethylamine[a]

|	1[b]		2[c]		4[d]	
	CH$_3$CN	pentane	CH$_3$CN	pentane	CH$_3$CN	C$_6$H$_{12}$
1,2,3,4-F$_4$	13.3 ± 0.7	28.4 ± 1.6				
1,2,3,5-F$_4$	15.2 ± 0.5	21.9 ± 0.6				
1,2,4,5-F$_4$	71.6 ± 0.3	49.7 ± 1.0				
1,2,3-F$_3$			21.0 ± 1.1	7.1 ± 0.7		
1,2,4-F$_3$			35.8 ± 1.3	76.4 ± 2.0		
1,3,5-F$_3$			43.2 ± 2.4	16.5 ± 2.6		
1,2,3-F$_3$					15.0 ± 0.1	12.2 ± 0.8
1,2,4-F$_3$					85.0 ± 0.1	87.8 ± 0.8

[a] The percent compositions listed are the mean and range for two runs. [b] 0.050 M 1, 0.50 M triethylamine. [c] 0.050 M 2, 2.51 M triethylamine in acetonitrile; 0.053 M 2, 2.67 M triethylamine in pentane. [d] 0.052 M 4, 5.27 M triethylamine in acetonitrile; 0.051 M 4, 5.21 M triethylamine in cyclohexane.

the prediction that only three isomeric octafluorobiphenyls would be formed; however, a MNDO calculation places MO 31 only 1.3 kcal below MO 32 (8), whereas MO 30 is 7.3 kcal above MO 29 (5). Thus, participation of MO 32 would explain the fourth isomer. Escape of the radical anion from the cage leads to the monodefluorination products (Scheme IV). Fluoride ion transfer, apparently, does not occur to a significant extent either within or without the cage, since hexafluorobenzene is detectable only in trace amounts (<0.01%). Electron transfer from the solvent to the radical cation may provide a return route to pentafluorobenzene. Alternatively, the octafluorobiphenyl isomers may simply be formed by coupling of the tetrafluorophenyl radicals formed in the defluorination step.

Returning to the dependence of the reciprocal of quantum yield upon the reciprocal of amine concentration portrayed in Figures 1 and 2, and assuming that the mechanistic picture of Scheme II obtains, concentrations of triethylamine greater than 0.5 M should assure the predominance of the exciplex formed by electron transfer from triethylamine. Thus, the regiochemistry, under these conditions, should characterize the radical anion intermediate.

We consider the same two routes [a and b of Scheme V] that we have discussed in the case of the polychlorobenzenes.[1] Heterolytic fission of the C–F bond of the radical anion (9) to generate phenyl radical and fluoride ion through a planar transition state would lead to an excited state (a phenyl cation with an electron in the lowest π* orbital), so that a bent transition state with radical localization (10), which could form aryl radical directly, seems more likely [route a, Scheme V]. A similar argument leads to the suggestion of bent transition state (11) for homolytic fission of radical anion to aryl carbanion and fluorine atom [route b].

In the case of the photolysis of polychlorobenzenes, the regiochemistry of photodechlorination in the presence of triethylamine is consistent with that anticipated for the pathway analogous to route a using the I$_r$ repulsion theory of Burdon,[4,5] originally employed to rationalize orientation in nucleophilic aromatic substitution, or the partial rate factors calculated from the data of Chambers et al.[6] for

Scheme V

Scheme VI
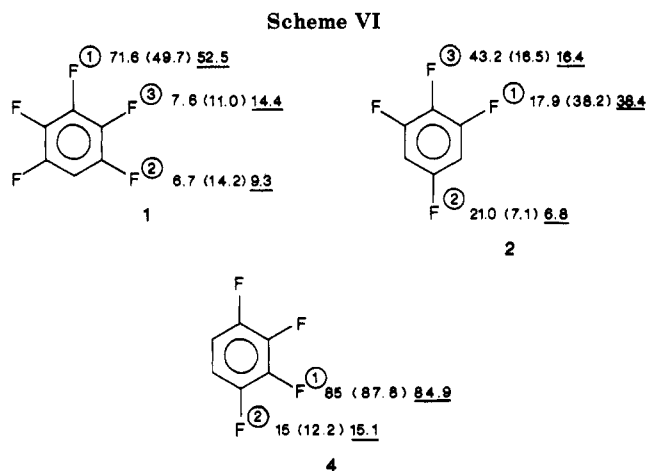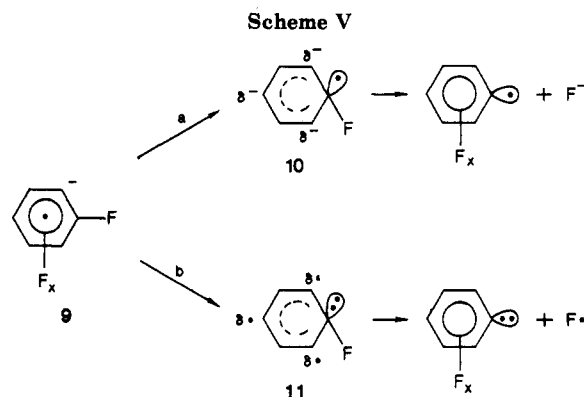
activation by chlorine vs. hydrogen in nucleophilic aromatic substitution. The success of the analysis strongly suggests that a close similarity between the photodechlorination reaction proceeding through a radical anion and nucleophilic aromatic substitution exists.

The regiochemical patterns of monodefluorination were determined for pentafluorobenzene (1), 1,2,3,5-tetrafluorobenzene (2), and 1,2,3,4-tetrafluorobenzene (4) at 254 nm in acetonitrile and pentane in the presence of triethylamine (Table I). Correcting for statistical advantages, the relative rates in acetonitrile are listed directly after the circled numbers, while the relative rates in pentane are in parentheses in Scheme VI. If the reaction

(4) Burdon, J.; Gill, H. S.; Parsons, I. W.; Tatlow, J. C. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1726. Burdon, J.; Parsons, I. W.; Gill, H. S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1351. Burdon, J.; Parsons, I. W. *J. Am. Chem. Soc.* **1977**, *99*, 7445. Burdon, J. *Tetrahedron* **1965**, *21*, 3373.
(5) Burdon, J.; Childs, A. C.; Parsons, I. W.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1982**, 534.

(6) Chambers, R. D.; Close, D.; Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 778.

proceeds according to route a, the similarity of transition state **10** to that for an analogous nucleophilic aromatic substitution suggests that the regiochemistries observed may depend on factors closely related to those that control aromatic substitution. The I_π repulsion theory, which has been used successfully,[4] with one exception,[5] to predict regiochemistry in polyfluoroarenes, may be employed. This approach, which is based upon the assumption that the repulsion between the electron pair on halogen and the filled pentadienyl orbital of the Wheland intermediate provides an order of stability **12 > 13 > 14**,[4,7] leads to the predicted order of rates listed with circled numbers in Scheme VI (1 = fastest, 3 = slowest).
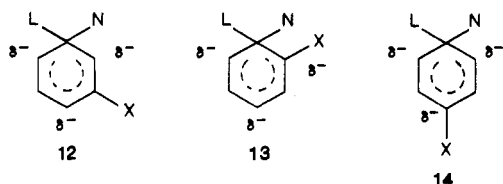
Focusing on the relative rates of fission in acetonitrile listed in Scheme VI, it is clear that overall agreement with the relative rates anticipated using the I_π repulsion analysis is poor. A consideration of the two competing routes of Scheme V, however, reveals that there is a difference in charge dispersion as the reactions proceed. In (a) a radical anion is undergoing fission to a neutral aryl radical and a fluoride ion, so that in the transition state the charge should be dispersed across these two moieties, while in the case of pathway b a delocalized radical anion is undergoing fission to an aryl carbanion, which could well represent a charge concentration process. A switch from a polar to a nonpolar solvent should favor route a over route b and shift the substitution pattern toward that predicted by I_π theory. The regiochemistry for photodefluorination in pentane (numbers in parentheses) is, in fact, in good agreement with that anticipated with the exception of the reversal of second and third place for reaction of 1,2,3,5-tetrafluorobenzene (**2**). Substituent rate factors may be determined from the relative rates observed for pentafluorobenzene, 1,2,3,5-tetrafluorobenzene, and 1,2,3,4-tetrafluorobenzene by minimizing the sum of the square of the residuals for observed and calculated relative rates, weighting each position equally. The substituent rate factors obtained, ortho:meta:para = 5.6:3.6:1.0, may be used to calculate relative rates within each system (underlined values in Scheme VI). The fit seems quite satisfactory, and the *o:m:p* substituent rate factor ratios are similar to those observed for the analogous photodechlorination (ortho:meta:para = 8.0:4.5:1.0)[1] and activation by chlorine of nucleophilic aromatic substitution (ortho:meta:para = 12.1:4.85:1.00),[6] while the order observed is the same as that found for activation by fluorine in nucleophilic aromatic substitution by ammonia in the reactive polyfluoro pyridine system (*o:m:p* = 119:88:1).[8] On the other hand, the orientation observed for the photodefluorination process contrasts strongly with the regiochemistry expected for route b proceeding through pentadienyl radical transition state **11**, using as a model system the radical phenyldefluorination reaction and the partial rate factors (*o:m:p* = 3.0:0.8:1.2).[9] Thus, the predominant rate of attack for phenyldefluorination is at C-2 in pentafluoro-

benzene and also at C-2 in 1,2,3,5-tetrafluorobenzene.[9] In addition, it is interesting to note that the regiochemistry found for irradiation of pentafluorobenzene in acetonitrile in the absence of triethylamine translates to a pattern of relative rates for fission at C-3:C-2:C-1 = 84.5:4.3:3.5, which is reasonably similar to the regiochemical rate pattern found for photolysis of pentafluorobenzene in acetonitrile in the presence of triethylamine (Scheme VI). This provides reinforcement for the view that the pentafluorobenzene radical anion is the product-determining intermediate in this case as well. Therefore, as in the case of the polychlorobenzenes, the regiochemistry of the polyfluorobenzenes seems well rationalized by the two reaction pathways illustrated in Scheme V.

Experimental Section

General. Reagent grade acetonitrile (Baker Chemical Company) was freshly distilled from phosphorous pentoxide and its purity was greater than 99% by GLC analysis. Cyclohexane and pentane were purified by distillation; dodecane (Aldrich, 99%) was used as obtained. Cyclopentanone was distilled just before use.

General Procedure for Photolysis. The photolyses of the polyfluorobenzenes were carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight 2537-Å Rull lamps. A steady, slow stream of air was passed into the reactor to maintain a constant temperature of 40 °C. The photolysis samples were placed in quartz tubes (Ace Glass, 170 mm × 15 mm), each screwed to a nylon adapter bushing containing a Pyrex glass sliding stopper valve, and degassed through three or four freeze–pump–thaw cycles. The tubes were sealed under vacuum and irradiated at 254 nm for 30 min. Quantum yields of products were determined by using the photoconversion of cyclopentanone to 4-pentenal as the actinometer.[10] The cyclopentanone samples in the given solvent were placed in quartz tubes, degassed by freeze–pump–thaw cycles, and irradiated simultaneously with the pentafluorobenzene samples for the same length of time. The λ_{max} values for pentafluorobenzene are 258 nm (cyclohexane, ϵ 787) and 257 nm (acetonitrile, ϵ 587).

Product Analyses. The photolysis mixtures were analyzed by GLC on a Varian 3700 gas chromatograph equipped with an FID using a series combination of a 10% SE-30 on Chromsorb P (80/100) AW/DMCS and a 7% Carbowax 20 M on Chromsorb P (80/100) AW/DMCS column. The column was programed from 35 to 180 °C at a rate of 8 °C/min increase with an injection port temperature of 150 °C and detector temperature of 230 °C. Helium was used as the carrier gas at about 30 mL/min flow. The photoproducts were identified by comparing their retention times with those of known compounds[11] and by mass spectrometry. The mass spectral analyses were carried out on a Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 gas chromatograph. Dodecane was used as an internal standard in the determination of yields of products.

Photolysis of Pentafluorobenzene in the Presence of Triethylamine. A 25.0-mL acetonitrile solution of pentafluorobenzene (0.210 g, 1.25 mmol, 0.050 M) and dodecane (0.101 g, 0.593 mmol) was prepared. Six 3.0-mL samples were transferred into quartz tubes and triethylamine was added to each of the tubes to establish the following triethylamine molarities: 0.05, 0.25, 0.50, 0.75, 1.0, 1.5 M. After being degassed by three or four freeze–pump–thaw cycles and sealed in vacuum, the samples were irradiated at 254 nm for 30 min. At this point, in order to reduce the amount of triethylamine and the solvent, due to their interference with the GLC analysis, each sample was treated with dilute sulfuric acid, followed by dilution with distilled water and extraction with pentane. The combined pentane extracts were then analyzed by GLC. Quantum yields were determined by using cyclopentanone as the actinometer.

The photolysis of pentafluorobenzene in pentane in the presence of varying amounts of triethylamine was carried out in a completely analogous manner by using the same quantities and

(7) Streitweiser, A.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444.

(8) Chambers, R. D.; Waterhouse, J. S.; Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 585.

(9) Allen, K. J.; Bolton, R.; Williams, G. H. *J. Chem. Soc., Perkin Trans. 2* **1983**, 691.

(10) Dunion, P.; Trumbore, C. N. *J. Am. Chem. Soc.* **1965**, *87*, 4211.

(11) Huang, Y. M.S. Thesis, Oregon State University, 1986.

molarities of substrate and amine.

Photolysis of Pentafluorobenzene in Acetonitrile in the Absence of Triethylamine. A 25.0-mL solution in acetonitrile of pentafluorobenzene (1.04 g, 0.245 M) and dodecane (250 μL, 1.10 mmol) was prepared. Exactly 10.0 mL of this solution was pipetted out into a quartz tube with a side arm (25.0 mL) fitted with a nitrogen inlet adapter (19/14) with a long stem whose tip almost touched the bottom of the tube. The side arm was connected to an absorption unit containing a known excess of standard NaOH solution. The quartz tube was placed inside the merry-go-round reactor chamber and irradiated with the eight 254-nm lamps surrounding the tube for a period of 30 min, while nitrogen gas was passed through the reaction mixture in a slow stream (1 to 2 bubbles per s for 1 h). Cold air was passed through the chamber during the photolysis in order to maintain the temperature constant at 40 °C. Hydrogen fluoride gas that was evolved during the reaction was swept out by nitrogen into the absorption unit and was converted to NaF. The inlet tube dipping in the NaOH solution was rinsed with distilled water and removed. The aqueous solution containing NaF and excess alkali was titrated with standard potassium hydrogen phthalate solution to the phenolphthalein end point. In a second run, the aqueous solution containing NaF was subjected to quantitative determination of F^- by a modified Volhard's method.[12] Analysis of the product mixture and the sodium hydroxide trap solution

revealed the following product components: 1,2,3,5-tetrafluorobenzene (2) (0.11%), 1,2,4,5-tetrafluorobenzene (3) (1.09%), 1,2,3,4-tetrafluorobenzene (4) (0.09%), octafluorobiphenyl (A 0.26, B 0.85, C 0.91, D 0.08%), and HF [3.15% (Volhard's method), 3.01% (titration)].

Quantum Yield Dependence of Pentafluorobenzene Photolysis upon Pentafluorobenzene Concentration. Solutions of pentafluorobenzene in acetonitrile (10.0 mL each) were prepared containing the following concentrations of pentafluorobenzene (internal standard dodecane in parentheses): 0.0256 M (0.643 mM), 0.0504 M (0.756 mM), 0.127 M (0.678), 0.251 M (0.584 mM), and 0.376 M (0.688 mM), and 0.500 M (0.622 mM). Duplicate 3.0-mL samples of each solution were degassed in quartz tubes and irradiated at 254 nm for 30 min. Similarly, two 3.0-mL samples of a solution containing cyclopentanone (2.01 M) and dodecane (1.27 mmol) in acetonitrile were degassed and irradiated simultaneously with the pentafluorobenzene samples. At the end of the photolysis period, the pentafluorobenzene samples were extracted six times with pentane (2.0 mL) and the pentane extract was concentrated carefully and then analyzed by gas chromatography.

(12) Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*, 3rd ed.; Wiley: New York, 1966; p 269.

Use of Biological Systems for the Preparation of Chiral Molecules. 3. An Application in Pheromone Synthesis: Preparation of Sulcatol Enantiomers

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Both enantiomers of sulcatol, an aggregation pheromone, are prepared by microbial asymmetric reduction of prochiral 6-methylhept-5-en-2-one. Bacteria, yeast, fungi, and commercial enzymes which give high optical purities are used. Enzymatic resolution of (±)-sulcatol by pig pancratic lipase is carried out in anhydrous ether. The use of biological systems in organic chemistry to prepare chiral alcohols is discussed in terms of availability, cost, specific equipment, and chemical and optical yields.

The use of biological systems (enzymes or microorganisms) to prepare chiral alcohols is widespread and very efficient. The alcohol is obtained by reduction of the corresponding ketone.[1] It can be difficult to obtain both enantiomers since most microorganisms obey Prelog's rule and so give the same enantiomer, with *S* configuration.

However, since Sih[2] showed that several alcohol dehydrogenases could be implicated in the reduction of β-keto esters by *Saccharomyces cerevisiae* several authors have succeeded in controlling the stereochemistry of microbiological reductions. Reversibly modifying the substrate can allow the other enantiomer to be obtained.[3]

Besides, given the immense variety of reducing microorganisms, one or more species or strains can be expected to occur that yield alcohols with stereochemistry opposite to that predicted by the Prelog's rule.

In addition, whenever racemic mixtures of alcohols can be readily obtained, separation of the enantiomers can be envisaged. Here again, biological systems are especially useful because of their operational simplicity. Lipases are well-suited to the resolution of chiral alcohols[4] and a very simple procedure was recently developed by A. M. Klibanov.[5]

In the course of work on the stereospecific synthesis of pheromones, we set out to prepare the two enantiomers of sulcatol by means of various biological systems and procedures.

Sulcatol (6-methylhept-5-en-2-ol) is the aggregation pheromone of an ambrosia beetle, an economically important pest in the coniferous forests of the North Pacific

(1) Jones, J. B.; Beck, J. F. "Applications of Biochemical Systems in Organic Chemistry" *Techniques of Chemistry*; Jones, J. B., Sih, C. J., Perlman, D., Eds.; Wiley: New York, 1976; Vol X, p 107. Sih, C. J.; Chen, C. S. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 570.

(2) Shieh, W. R.; Gopalan, A. S.; Sih, C. J. *J. Am. Chem. Soc.* 1985, *107*, 2993.

(3) Mori, K.; Mori, H.; Sugai, T. *Tetrahedron* 1985, *41*, 919. Nakamura, K.; Ushio, K.; Oka, S.; Ohno, A. *Tetrahedron Lett.* 1984, *25*, 3979. Fuganti, C.; Grasselli, P. *Tetrahedron Lett.* 1985, *26*, 102.

(4) Cambou, B.; Klibanov, A. M. *J. Am. Chem. Soc.* 1984, *106*, 2687. Ladner, W. E.; Whitesides, G. M. *J. Am. Chem. Soc.* 1984, *106*, 7250. Hamaguchi, C. S.; Asada, M.; Hasegawa, J.; Watanabe, K. *Agric. Biol. Chem.* 1984, *48*, 2331. Langrand, G.; Baratti, J.; Buono, G.; Triantaphylides, C. *Tetrahedron Lett.* 1986, *27*, 29.

(5) Kirchener, G.; Scollar, M. P.; Klibanov, A. M., *J. Am. Chem. Soc.* 1985, *107*, 7072.