Registry No.—**1**, 40723-71-5; **2**, 57252-78-5; **3**, 1767-94-8; **4**, 355-63-5; **5**, 367-36-2; **6**, 79-38-9; *p*-chlorobenzenediazonium chloride, 2028-74-2; *p*-nitrobenzenediazonium chloride, 100-05-0; *p*-carboxybenzenediazonium chloride, 17405-00-4; *p*-dichlorobenzene, 106-46-7; *p*-$ClC_6H_4CH_2CHClCN$, 17849-64-8; *p*-$ClC_6H_4CF_2CFCl_2$, 62448-58-2; *p*-$NO_2C_6H_4CH{=}CHCF_2CF_2H$, 62448-59-3; *p*-chloroaniline, 106-47-8; vinylidene fluoride, 116-14-3; 4,4′-dichloroazobenzene, 1602-00-2; trichlorobiphenyl, 62461-62-5.

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(5) P. L'Ecuyer and C. A. Olivier, *Can. J. Res., Sect. B*, **27**, 689 (1949).
(6) The experiment with chlorotrifluoroethene was performed by Dr. Richard R. Merner of this laboratory.
(7) C. S. Rondestvedt, Jr., unpublished experiments in this laboratory.
(8) L. J. Hals, T. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.*, **73**, 4054 (1951); T. J. Brice, J. D. La Zerte, L. H. Hals, and W. H. Pearlson, *ibid.*, **75**, 2698 (1953); R. N. Haszeldine, *J. Chem. Soc.*, 4026 (1954).
(9) Commercial perfluorooctanoic acid was used for this preparation, and it contained related compounds. The wide boiling range of **4** betokens a mixture of olefins.
(10) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).
(11) GC/MS analyses were performed by Mr. R. H. Weeks in this laboratory.

Metal–Ammonia Reduction of Fluorinated Aromatic Compounds

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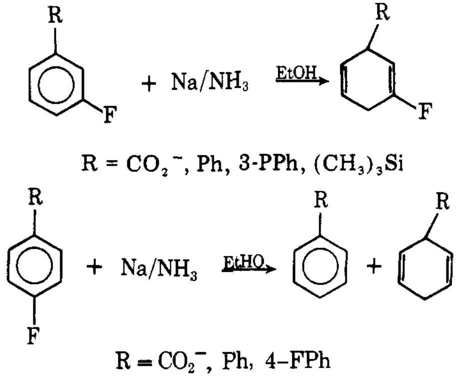
The acceptance of the hydrogenolysis of aryl carbon–halogen bonds (including fluorine) by alkali metals in liquid ammonia is evidenced by three major reviews.[1,2] Since direct metal–halogen exchange is not an attractive mechanism with fluorides,[3] and benzyne processes can be eliminated on other grounds,[4] the most likely pathway appears to be presented in eq 1.

$$ArF \xrightarrow{e^-} [ArF]^{-}\cdot \xrightarrow{-F^-} Ar\cdot \xrightarrow{e^-} Ar^- \xrightarrow{NH_3} ArH \qquad (1)$$

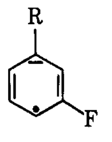
Thus, addition of an electron to the aromatic ring of ArF results in a radical anion which loses fluoride ion producing an aryl radical. This radical is expected to easily accept another electron to form an aryl carbanion which is rapidly protonated by ammonia. Depending on the nature of ArF and reaction conditions (metal supply, proton source, etc.), ArH may also be reduced to cyclohexadienes and related products.

In addition to the firm establishment of the aforementioned mechanism, our results indicate that under proper conditions, the Birch reduction can, in fact, provide an important synthetic pathway for the formation of fluorinated cyclohexadienes. As illustrated in Scheme I, compounds containing fluorine meta to an activating substituent[5] can be successfully reduced with retention of fluorine, whereas fluorine in the para position is lost.[6] Thus, this observed substituent effect rules out any direct electron transfer to the Ar–F bond and establishes electron addition to the ring as the first step. Loss of fluoride from this intermediate seems more attractive than a second electron addition, since dianions are generally not formed with benzene derivatives.[1,2] Protonation of the radical anion followed by a second electron addition and then loss of fluoride may also be ruled out since this would lead to a carbene intermediate which is not consistent with product analysis.

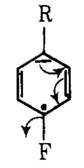
Scheme I



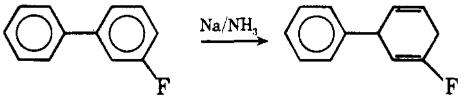
These transformations can be rationalized in terms of the electron density distribution in the intermediate radical anions.[7] Hence, as an oversimplification, if resonance structures 1 and 2 are considered as most important in their respective cases, the process for fluorine loss in 2 can be visualized. Alternatively, we may simply consider that fluorine is expected to be lost when attached to a carbon holding increased electron density in the intermediate anion, and, conversely, when fluorine is on a carbon with decreased electron density (such as 1) it may be retained. This generates particular interest in the biphenyl case, since electron density is distributed between two rings. Nonetheless, fluorine was lost from both 4-fluorobiphenyl and 4,4′-difluorobiphenyl while it was retained with 3-fluorobiphenyl and 3,3′-difluorobiphenyl. The fact that 3-fluorobiphenyl reduces primarily in the fluorinated ring suggests that fluorine is an activating group[8] in metal/ammonia reduction, although not as activating as phenyl or trimethylsilyl in view of our present results. Since fluorine substitution is known to stabilize pyramidal or nonconjugated carbanions[8] but destabilize directly conjugated carbanions, this suggests that the effect of fluorine substitution in this position is largely inductive. However, the deactivating effect of a methyl or methoxy substituent presumably does not shift electron density away from the carbon bearing the fluorine in the intermediate, since the reduction of both *p*-fluorotoluene and *p*-fluoroanisole results in loss of fluorine.

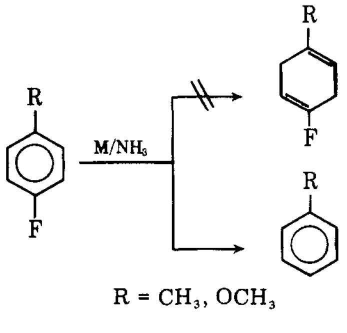


1



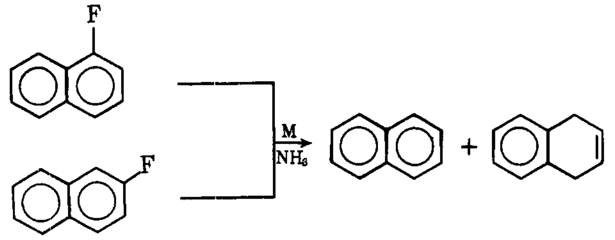
2





R = CH_3, OCH_3

In principle, fluorinated polynuclear aromatic compounds might be reduced successfully, since the reduction of the corresponding hydrocarbons often results in significant localization of the charge in the intermediate radical anions or dianions.[9] However, both 1- and 2-fluoronaphthalene afforded only naphthalene and its reduction products.



Experimental Section

General. Reductions were carried out by adding sodium or lithium metal to the fluoroaromatic compound in liquid ammonia with anhydrous ether as a cosolvent. In the case of polynuclear and biphenyl derivatives, solid ammonium chloride or water was used to quench the reaction whereas absolute alcohol was used with monobenzenoid compounds.

In cases where fluorine was lost (*p*-fluorobenzoic acid, 4-fluorobiphenyl, 4,4′-difluorobiphenyl, *p*-fluorotoluene, *p*-fluoroanisole, 1-fluoronaphthalene, and 2-fluoronaphthalene), the reduction products are identical with those resulting from reduction of the corresponding nonfluorinated derivatives, and these compounds have previously been characterized (i.e., 1,4-dihydrobenzoic acid, 1,4-dihydrobiphenyl, 2,5-dihydrotoluene, 2,5-dihydroanisole, and 1,4-dihydronaphthalene).[5] The absence of fluorinated reduction products in these cases was determined by GLC and/or NMR analysis. In addition, we have previously described the experimental procedure for the preparation of 3-fluoro-1,4-dihydrobenzoic acid.[10]

3,3′-Difluoro-1,4-dihydrobiphenyl. Sodium metal (10.4 mg-atoms) was added to 3,3′-difluorobiphenyl (5.2 mmol, 1 g) in 60 mL of anhydrous ether and 100 mL of anhydrous ammonia at −78 °C. After 20 min, solid ammonium chloride was added and the crude product isolated by ether extraction. The resultant oil was distilled, bp 135 °C (5 mm), to give 0.5 g (50%) of pure material: NMR ($CDCl_3$) δ 7.2 (m, 1 H), 6.9 (m, 3), 5.7 (m, 2, H_5 and H_6), 5.2 (d, 1, H_2), 4.1 (m, 1, H_1), 2.9 (d, 2, H_4).

Anal. Calcd for $C_{12}H_{10}F_2$: C, 74.99; H, 5.24; F, 19.77. Found: C, 74.75; H, 5.32; F, 19.70.

3-Fluorotrimethylsilylbenzene. A slight excess of *n*-butyllithium (1.1 equiv, 2 M in hexane) was added to 3-fluorobromobenzene (3 g, 17 mmol) in anhydrous ether at −78 °C. After stirring for 1 h, chlorotrimethylsilane (1 equiv, 1.8 g) was added and the solution was allowed to warm to room temperature (1.5 h). Water was then added followed by ether extraction resulting in an oil which was distilled, bp 60 °C (5 mm), to give pure material (1.2 g, 40%): NMR ($CDCl_3$) δ 7.3 (m, 4 H), 0.25 (s, 9).

Anal. Calcd for $C_9H_{13}FSi$: C, 64.26; H, 7.79; F, 11.30. Found: C, 63.95; H, 8.02; F, 11.55.

3-Fluoro-1,4-dihydrotrimethylsilylbenzene. Lithium wire (0.13 g, 18 mg-atoms) was added to 3-fluorotrimethylsilylbenzene (1.2 g, 7.2 mmol) in 60 mL of anhydrous ammonia containing 5 mL of absolute ethanol. After the blue color had disappeared, saturated ammonium chloride was added and the product was isolated by ether extraction. Distillation gave a colorless oil, bp 37 °C (5 mm), 0.5 g (40%): NMR ($CDCl_3$) δ 5.7 (m, 3 H), 2.8 (m, 2), 2.2 (m, 1), 0.05 (s, 9).

Anal. Calcd for $C_9H_{15}FSi$: C, 63.53; H, 8.88; F, 10.59. Found: C, 64.17; H, 9.05; F, 10.22.

3-Fluoro-1,4-dihydrobiphenyl. 3-Fluorobiphenyl[11] was reduced in the same manner as described above for 3,3′-difluorobiphenyl, to afford 3-fluoro-1,4-dihydrobiphenyl as the major reduction product together with minor products which could not be characterized. An analytical sample was trapped from the gas chromatograph. Structural assignment was based on the appearance of a vinyl proton shifted to higher field and exhibiting large (18 Hz) coupling from the adjacent ^{19}F. NMR ($CDCl_3$) δ 7.2 (m, 5 H), 5.7 (m, 2), 5.27 (d of m, 1), 4.2 (m, 1), 2.8 (d, 2).

Anal. Calcd for $C_{12}H_{11}F$: C, 82.73; H, 6.36; F, 10.90. Found: C, 82.68; H, 6.49; F, 10.75.

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Registry No.—Ammonia, 7664-41-7; 3,3′-difluoro-1,4-dihydrobiphenyl, 62476-43-1; 3,3′-difluorobiphenyl, 396-64-5; 3-fluorotrimethylsilylbenzene, 7217-41-6; 3-fluorobromobenzene, 1073-06-9; chlorotrimethylsilane, 75-77-4; 3-fluoro-1,4-dihydrotrimethylsilylbenzene, 62476-44-2; 3-fluorobiphenyl, 2367-22-8; 3-fluoro-1,4-dihydrobiphenyl, 62476-45-3.

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(6) Depending on the amount of metal used (2 equiv is consumed in the loss of fluoride), the hydrogenolyzed benzene nuclei can be subsequently reduced to non-fluorine-containing cyclohexadienes. Chlorine is lost even from the meta position.

(7) Electrochemical generation of radical anions in the isomeric fluorobenzonitrile have also illustrated unique behavior with the meta isomer: K. J. Hauser, D. E. Bartak, and M. D. Hawley, *J. Am. Chem. Soc.*, **95**, 6033 (1973).

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(11) Prepared by the reaction of 3-fluorobenzenediazonium chloride with sodium hydroxide and benzene.

Steric Effects in Photochemical Intramolecular [$_{\pi}2 + _{\pi}2$] Ring Closure Reaction of Polycyclic Diolefins Leading to Strained Cage Molecules. Empirical Force Field Calculations

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The effect of ground state conformation on photochemical reactivity has rarely been studied[1] expect in the solid state reactions.[2] The [$_{\pi}2 + _{\pi}2$] cycloaddition, one of the most well-studied photochemical processes,[3] of polycyclic dienes leading to strained cage molecules provides an ideal material to probe the possible role of steric requirements. A variety of examples have already been accumulated wherein the steric environments with respect to the reacting double bonds differ considerably. In accordance with expected steric control, recorded yields of such reactions range between zero and quantitative (Table I). We are interested, from a rather practical standpoint, in studying how steric factors in the ground state influence the appalling difference in the yields.

Photochemical yields are also affected by other factors such as nearby substituents and side reactions including cycloreversions.[4] In order to reduce complications arising from these secondary factors to a minimum, we primarily limit our attention to sensitized irradiation of diolefins having no substituent. Diolefins carrying electron-deficient substituents not directly attached to the double bond are considered only for comparison purposes, while those carrying the substituents directly attached to the double bond are not considered except for a homologous series. The effects of side reactions will be discussed when the yield of expected product is poor.