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REACTION OF PERFLUOROARYL HALIDES WITH REDUCED SPECIES OF SULFUR DIOXIDE (HSO_2^-, SO_2^{2-},$S_2O_4^{2-}$) [1]

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SUMMARY

Rongalite (sodium hydroxymethanesulfinate), sodium dithionite, and aminoiminomethanesulfinic acid (AIMS) reduce perfluoroiodobenzene in N,N-dimethylformamide to pentafluorobenzene. In the presence of added D_2O or CH_3OD, deuteriopentafluorobenzene is formed. p-Dinitrobenzene does not inhibit the reduction, and addition of norbornene did not result in trapping of any radical intermediates. Reaction of pentafluoroiodobenzene with sodium benzenesulfinate gave 1,4-dibenzenesulfonyl-2,3,5,6-tetrafluorobenzene. A halophilic attack mechanism is suggested for the reduction reaction. Chloropentafluorobenzene did not react under the same conditions as the iodide; at elevated temperatures in the presence of sodium bicarbonate and Rongalite the fluorine para to the chlorine was reduced Reduction of the chloride to pentafluorobenzene is minor. In the absence of bicarbonate, the chloride also gave a mixture of sulfides believed to be derived from decomposition of the Rongalite to hydrogen sulfide. Some reaction with dimethylamine from decomposition of DMF also is observed.

INTRODUCTION

Previously, the nucleophilic reactivity and reducing power of reduced species of sulfur dioxide derived from sulfoxylic acid (H_2SO_2) and dithionic acid ($H_2S_2O_4$), e.g. HSO_2^-, $SO_2^=$, $S_2O_4^=$, have been investigated with various compounds [2a-f]. These species have

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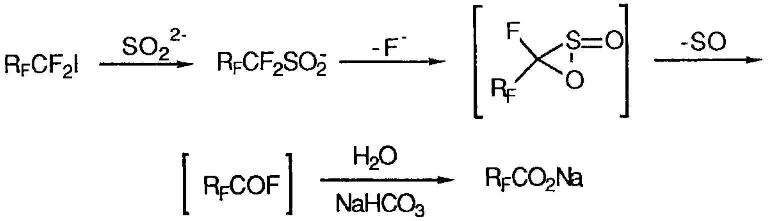
biological and environmental significance with respect to pollution by sulfur dioxide since they are produced on contact of SO_2 with reduced pyridine coenzymes (NADH) [2g] and with models for these important biological reducing agents (1-benzyl-1,4-dihydronicotinamide) [2h]. Except for the work of Huang et al. on perfluoroalkyl derivatives [3], reactions of these anions with fluorinated alkyl and aryl halides have received relatively little attention. Huang and coworkers showed that dithionite effected the addition of perfluoroalkyl iodides to alkenes via electron transfer [3i-l], and Feiring found that reaction of perfluoroalkyl halides with arene- and alkanesulfinates (RSO_2^-) involved electron transfer with the formation of perfluoroalkyl radicals that were trapped with norbornene [4].

Treatment of perfluoroalkyl iodides and bromides with Rongalite-sodium bicarbonate in aqueous DMF or DMSO gave perfluorocarboxylates [3b]. The mechanism for formation of these products was not discussed. One possible mechanism for formation of the carboxylates is via a three-membered cyclic sultine that loses sulfur monoxide to give an acyl fluoride which is hydrolyzed to the carboxylate. These types of sultines have been proposed as intermediates in several reactions of sulfines and sulfenes to explain loss of sulfur [5].



In accord with the reactions reported earlier by Huang and by Feiring, a one-electron transfer process ($S_{RN}1$) is believed to be involved in the reaction of bromotrifluoromethane with sodium dithionite or Rongalite to give sodium trifluoromethanesulfinate [6], a process related to an earlier report on the formation of perfluoroalkylanilines and zinc trifluoromethanesulfinate from the sulfur dioxide anion radical produced from zinc and sulfur dioxide [7]. Kobayashi et al. showed that a p-bromine or iodine in tetrafluoroanilinium ions can be reduced by sodium dithionite in methanol [8]. The reduction was explained either by a halophilic attack mechanism (S_N2X) or an electron transfer mechanism ($S_{RN}1$).

There are several readily available sources of the reduced species of sulfur dioxide. Rongalite ($HOCH_2SO_2Na\bullet 2H_2O$) is the sulfoxylate adduct of formaldehyde and is relatively stable [9] It and its analogs have long been used as bleaching agents in the dye industry [10]. Sodium dithionite ($Na_2S_2O_4$) is a well-known reducing agent [11] and is a dimer of the sulfur dioxide anion radical ($SO_2^{\cdot}$) into which it can dissociate [12]. Thiourea S,S-dioxide has occasionally been used as a reducing agent [13]. Its tautomer, aminoiminomethanesulfinic acid (AIMS) [$H_2NC(=NH)SO_2H$], may be considered an adduct of sulfoxylic acid (H_2SO_2) with cyanamide.

RESULTS AND DISCUSSION

Reactions of Pentafluoroiodobenzene

The reactions of dithionite, Rongalite, AIMS, and sulfite with pentafluoroiodobenzene in aqueous DMF produced a single product, pentafluorobenzene. The data are summarized in Table 1. The reduction could be accomplished efficiently without solvent by the use of the phase transfer catalyst, Adogen 464 [14]. Sodium dithionite was superior to both AIMS and Rongalite in speed of reduction. All reactions were done under argon to avoid air oxidation of the reducing agents. When argon was omitted and the reaction with Rongalite was run open to the air, only 4% of pentafluorobenzene was obtained after 21 hours at room temperature. Purging the system with argon and continuing the reaction for 126 hours resulted in little further reduction. A reasonable explanation of these observations is that the Rongalite is decomposed faster by oxygen than it can react with pentafluoroiodobenzene. The reactions of bromopentafluorobenzene were not extensively investigated, but reduction to pentafluorobenzene (ca 50%) occurred with Rongalite at 90°C

The reduction by Rongalite in DMF at room temperature gave better results than at 90°C. This result is believed to be due to avoiding the decomposition of Rongalite at elevated temperatures to sulfite, thiosulfate, and sulfide [15] The odor of hydrogen sulfide is evident when solutions of Rongalite are heated above 80°C.

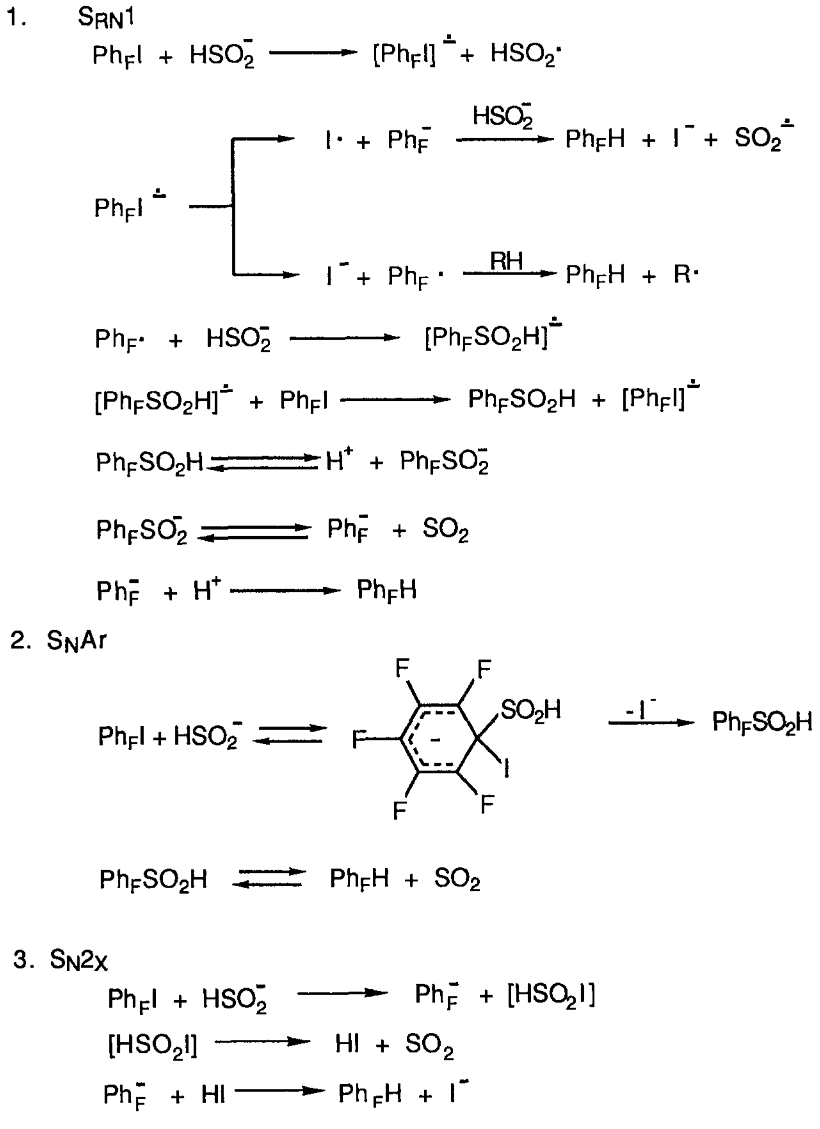
$$5\ HOCH_2SO_2^- \longrightarrow HSO_3^- + SO_3^= + H_2S + S_2O_3^= + H_2O + 5\ CH_2O$$

Although sodium thiosulfate does not react with pentafluoroiodobenzene at room temperature, sodium sulfite, a known reducing agent for halogens [16], gives pentafluorobenzene, but at a slower rate indicating that it is not the major species responsible for the reduction by Rongalite. Sulfite, a derivative of sulfur trioxide, was investigated because of its possible formation by dispro-portionation of sulfoxylate or by the decomposition of Rongalite shown above. Control experiments at room temperature in DMF in the absence of reducing agent and either with or without sodium bicarbonate showed that no reaction occurred with pentafluoroiodobenzene thereby demonstrating the lack of any possible reduction by solvent DMF

TABLE 1 Reactions of pentafluoroiodobenzene with reduced species of SO_2 under argon

Reagent	Conditions	Ph_FH Yield
$Na_2S_2O_4$	$NaHCO_3$, DMF, H_2O, 3 h, RT	100
	Adogen 464, 22 h, RT	100
	C_6H_6, DMF, 6 h, RT	40
	1,4-$(NO_2)_2C_6H_4$, $NaHCO_3$, DMF-H_2O, 1 h, RT	98
	1,4-$(HO)_2C_6H_4$, DMF-H_2O, 1.2 h, RT	100
	$NaHCO_3$, MeCN-H_2O, 12 5 h, 85^{o}	98
$HOCH_2SO_2Na \cdot 2H_2O$	DMF, 19 h, RT	61
	DMF, 22 h, 90^{o}	36
	$NaHCO_3$, MeCN-H_2O, 12 h, 75^{o}	100
	CH_3OD-DMF, 20 h, RT Ph_FD+Ph_FH	100
AIMS	$NaHCO_3$, DMF-H_2O, 5 h, RT	85
Na_2SO_3	DMF-H_2O, 23 h, 83^{o}	100

Three mechanisms (Scheme 1) are possible for the reduction of the iodide with Rongalite or dithionite: (1) radical, nucleophilic substitution ($S_{RN}1$); (2) nucleophilic aromatic substitution (S_NAr); and (3) halophilic (S_N2X). We tend to favor the last mechanism for the reasons that will become clear from the following discussion. In Scheme 1, the hydrogen sulfoxylate ion is used to represent various reduced species of sulfur dioxide and their precursors ($HOCH_2SO_2^-$, $S_2O_4^=$).



SCHEME 1.

In the first two mechanisms, one step involves the loss of sulfur dioxide from the pentafluorobenzenesulfinate anion, a reaction that has precedent in the decomposition of lithium pentafluorobenzenesulfinate monohydrate to pentafluorobenzene in acetone at room temperature [17] and in water at 80° [18]. However, it was not possible to isolate or detect the sulfinate by ^{19}F nmr. The formation of the pentafluorophenyl anion by these mechanisms is supported by reactions in the presence of D_2O or CH_3OD in which the major product was C_6F_5D (Table 2). The nonisotopic product, C_6F_5H, is believed to be derived from H_2O that was not removed from the reducing agents or solvents It also is possible that the minor protium product is produced by a free radical mechanism in which a hydrogen atom is abstracted from DMF

TABLE 2

Reduction of pentafluoroiodobenzene in deuterated solvents

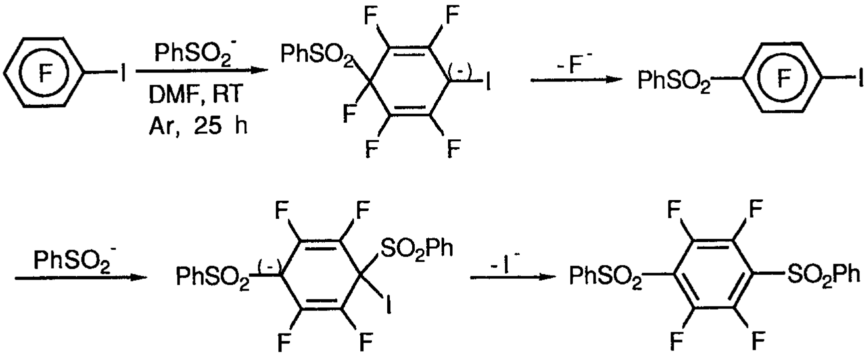
Reagents	Molar Ratio[a]	Solvent System	Overall Yield (%)	Isotope Distribution[b] (%) C_6F_5H	C_6F_5D
Dithionite	2	DMF (30 mL)/ MeOD (7 mL)	17	27	73
Rongalite	2	DMF (15 mL)/ MeOD (7 mL)	100	12	88

[a] Mole ratio of reducing agent to pentafluoroiodobenzene

[b] Yield and isotope distribution were determined by ^{19}F-NMR.

The reduction with dithionite was not inhibited by addition of 10% molar equivalent of p-dinitrobenzene, a known inhibitor of electron-transfer reactions [3f, 19], or by addition of hydroquinone In our system, p-dinitrobenzene is not the best choice of inhibitor since the pentafluorophenyl radical is expected to be difficult to oxidize because of the electronegativity of the fluorine-substituted benzene radical. Also, the dithionite may reduce the nitro groups of the inhibitor, thus diminishing its effectiveness. The lack of effect of hydroquinone is also inconclusive as it may partake in the reaction not only as a scavenger of oxygen but also as a hydrogen atom donor to the pentafluorophenyl radical (see Scheme 1), the resulting quinone being reduced by the dithionite back to hydroquinone. No darkening of the color of the reaction mixture that might be attributed to the formation of quinhydrone (green) or other intermediates in the reduction of quinone was observed. A reaction in which benzene was cosolvent did not reveal any trapping of a pentafluorophenyl radical as had been previously observed in the photolysis of pentafluoroiodobenzene in benzene or toluene [20]. High yields of the biphenyl derivative were obtained in these cases. Norbornene, previously used to trap perfluoroalkyl radicals [4, 21], had no effect on the reaction of pentafluoroiodobenzene and Rongalite, the reduction proceeding as usual.

Since sodium benzenesulfinate was shown to be a one-electron transfer agent to perfluoroalkyl iodides [4], yielding some reduction of the iodide but no sulfone at 90°C, we investigated its reaction at room temperature with pentafluoroiodobenzene. Only substitution occurred to give the known 1,4-dibenzenesulfonyl-2,3,5,6-tetrafluorobenzene, 1, [22] in 19% yield. No pentafluorobenzene was observed The same product was obtained with chloropentafluorobenzene (see below). Although arenesulfinates are said to be unreactive as nucleophiles in aromatic and some aliphatic $S_{RN}1$ reactions [19, 23], they may react by that mechanism with very electron-deficient halides such as pentafluoroiodobenzene. The $S_{RN}1$ reaction will fail, however, if the arenesulfinate ion is a better leaving group (nucleofuge) than the initial leaving group [24]. In fact, arenesulfinate ions undergo electron transfer reactions (leading to substitution) with a number of highly electron deficient compounds [25], and they react with the 2-nitropropyl radical exemplifying a key step in the $S_{RN}1$ mechanism [26]. The formation of the bis-sulfone, 1, may occur stepwise, first by displacement of iodide in an $S_{RN}1$ reaction followed by an S_NAr reaction at the para position. On the other hand, both substitutions may proceed by the S_NAr mechanism in which initial attack is preferentially at the para position and not at the ipso position [27]:



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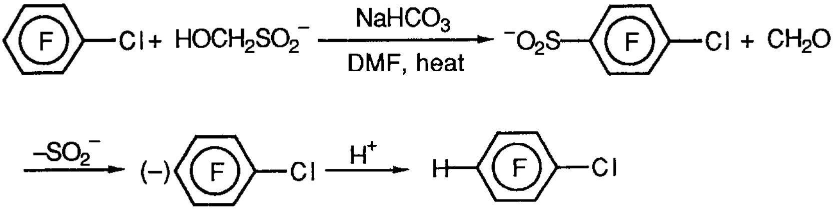
The work of Kobayashi et al. [8] on the reaction of dithionite with p-iodo-N,N,N-trimethyltetrafluoroanilinium ion provides evidence against an $S_{RN}1$ mechanism. The sole product was derived by reduction of the iodide. If the reaction had been of the $S_{RN}1$ type, displacement of the trimethylammonium group should have occurred to some extent [19, 28], but this did not occur even with p-chloro or p-fluoro substituents. A structurally quite different sulfur nucleophile, sodium sulfide, is believed to react by both $S_{RN}1$ and S_NAr mechanisms with hexafluorobenzene [29].

The S_NAr mechanism is unlikely for the reactions in Table I because, as indicated above, such substitutions proceed para and, to a lesser extent, ortho to iodine with loss of fluoride ion [27, 30]. In our reactions, iodide is removed and the p-fluoro group remains except in the reaction with sodium benzenesulfinate.

The halophilic attack mechanism (S_N2_X) has been proposed for the reaction of dithionite with p-halotetrafluoroanilinium ions [8], and the reaction of iodide ion with 4-iodotetrafluoropyridine [31], 3-chloro-2,4,6-trinitrobenzotrifluoride [32], and with picryl chloride [33] The halogen is replaced by a proton. Bunnett has interpreted the reduction by carbanions of certain halobenzenes, e.g 1,2,4-tribromobenzene, and the isomerization, disproportionation, and scrambling of trihalobenzenes (iodides and bromides) in terms of halophilic attack [34]. In a related reaction, bromopentafluorobenzene was reduced to pentafluorobenzene by the enolate ion of 2-butanone [35]. Halophilic attack occurs preferentially at iodine or bromine [36] which explains the different behavior we observe with chloropentafluorobenzene (see below) The pK_a of pentafluorobenzene is 28.8 as compared to 43 for benzene, indicating that $C_6F_5^-$ is a good leaving group that behaves as a pseudohalogen somewhat superior to the trifluoromethyl group [37]. On the basis of these and our observations, we prefer the halophilic attack mechanism to explain the reduction of iodopentafluorobenzene by sodium dithionite, Rongalite, AIMS, and sodium sulfite.

Reactions of Chloropentafluorobenzene

Chloropentafluorobenzene did not react with Rongalite, sodium dithionite, sodium sulfite or sodium thiosulfate in DMF at room temperature. At elevated temperatures the major product with Rongalite in the presence of sodium bicarbonate was chloro-2,3,5,6-tetrafluorobenzene, 2, in which a fluorine para to chlorine was reduced. This result is interpreted on the basis of an S_NAr mechanism.



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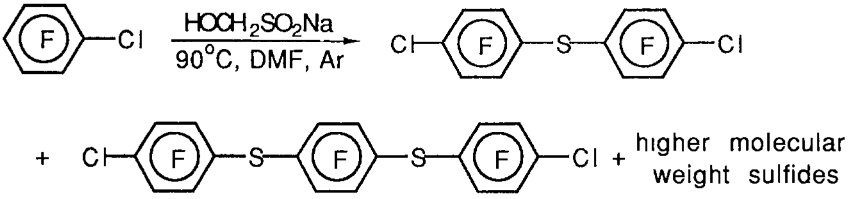
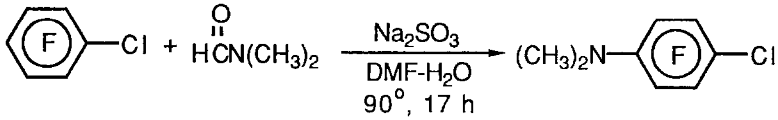
The initially formed sulfinate is expected to lose SO_2 readily to give the anion [17]. A small amount of an unknown, possibly a sulfinate, was observed by ^{19}F nmr in several instances. Dithionite, sulfite, or thiosulfate gives little or no reduction product, 2, suggesting a difference in the major species of reduced sulfur dioxide that are present ($HOCH_2SO_2^-$, HSO_2^-, or $SO_2^=$ for Rongalite and $SO_2^{\dot{-}}$ for dithionite).

Pentafluorobenzene, from the reduction of the chlorine substituent, is a minor product. The halophilic attack that is favored by the iodo- and bromo-derivatives is, as expected [36], much less important for the chloro compound for which reaction by the S_NAr mechanism predominates. Treatment of the chloride with sodium benzenesulfinate gave a 15% yield of the bis-sulfone, 1. No monosubstituted product was obtained indicating that introduction of one benzenesulfonyl group activates the ring for the second nucleophilic attack.

In the absence of sodium bicarbonate or base, the reactions at elevated temperatures with Rongalite, dithionite, or thiosulfate gave mixtures of sulfides by substitution reactions involving decomposition products (e.g. H_2S) of these reagents. Hexafluorobenzene also gave sulfides at 85°C. Sulfides were obtained by Kobayashi et al. from the reaction of dithionite in methanol at room temperature with pentafluoro-N,N,N-trimethylanilinium ion [8]. Separation of the sulfide mixture by chromatography on silica gel was not successful, but analysis by ^{19}F nmr and by mass spectrometry indicated the approximate composition. In previously reported reactions of hexafluorobenzene with alkyl and aryl thiolates, mixtures of mono-, di-, and tetra-substituted products were obtained [38]. Sulfides also were obtained from the reaction of pentafluorobenzene and Rongalite at 90°C.



In several cases, the solvent, DMF, is involved in the reaction, most likely through hydrolysis to dimethylamine which reacts with chloropentafluorobenzene to give usually small amounts of 4-chlorotetrafluoro-N,N-dimethylaniline. With dithionite and potassium hydroxide, the major product is the dimethylaniline (85%). Sulfite also gives mainly the dimethylaniline (50%) along with a very small amount of pentafluorobenzene Sulfite may aid in decomposing DMF via a bisulfite adduct. Formation of dimethylaniline has been observed previously in reactions of chloropentafluorobenzene in DMF under conditions that favored the formation of dimethylamine from the solvent [39].



EXPERIMENTAL

All halides were used as received (Aldrich Chemical Co.). Pentafluoroiodobenzene was stored in the dark under argon and sodium hydroxymethanesulfinate dihydrate, sodium dithionite, and aminoiminomethanesulfinic acid were stored in the dark at -20°C.

Proton nmr spectra were obtained on a General Electric QE-300 spectrometer (300 MHz) and fluorine nmr spectra (CCl_3F or C_6F_6 as standards) were obtained on a General Electric GN-500 (500 MHz ^1H) spectrometer. Yields of product were determined by nmr and/or gas chromatography (GC) by respective peak integrations. Infrared spectra were run on an IBM-32 FT spectrometer. Mass spectra were recorded on an HP 5890 GC/MS quadrupole instrument. Electron impact mass spectra were obtained with an ionizing voltage of 70 eV and chemical ionization mass spectra were obtained with methane as carrier gas. The data for gas chromatographic analysis (Gow Mac 350) were as follows: 8' x 1/4", 20% DC 710 on chrom P, 80/100 mesh, injection temperature 180°C, column temperature 145°C, detector temperature 170°C, carrier gas helium, flow rate 55 cc/min

Reaction of Pentafluoroiodobenzene with Sodium Dithionite at Room Temperature.

Pentafluoroiodobenzene (5.88 g, 20 mmol), sodium dithionite (6.96 g, 0.04 mol), and sodium bicarbonate (3.36 g, 40 mmol) were stirred in DMF (72 mL) and water (24 mL) at 23°C for 2.5 h under an argon atmosphere. The reaction is accompanied by a change in color from colorless to greenish yellow that dissipates to a yellow color after approximately 3 h (a solution of dithionite in DMF at 85°C is colored blue). A ^{19}F-NMR spectra of the crude mixture revealed no starting material and a sole product, pentafluorobenzene. The mixture was added to ethyl ether (60 mL) and extracted with distilled water (3 x 60 mL). The ether layer was dried over magnesium sulfate and distillation yielded pentafluorobenzene, b.p. 82-83°C (b p of an authentic sample 84-85°C, Aldrich lot 05223JM). The pentafluorobenzene product had ^{1}H, ^{19}F-NMR and infrared spectra identical to those of an authentic sample (Aldrich lot 05223JM). No other fluorine containing organic compounds including water soluble products were detected by ^{19}F-NMR or infrared (FT).

(a) With Dinitrobenzene

In a reaction involving pentafluoroiodobenzene (5 mmol), sodium dithionite (10 mmol), sodium bicarbonate (10 mmol) and p-dinitrobenzene (0.5 mmol) in DMF (36 mL) - water (12 mL) at room temperature only pentafluorobenzene was observed (98% conversion in 60 min).

(b) With Hydroquinone

A similar reaction in the presence of hydroquinone (0.3 mmol), but with the omission of sodium bicarbonate, resulted in complete conversion to pentafluorobenzene in 75 min.

Reaction of Pentafluoroiodobenzene with Sodium Dithionite in DMF-Benzene

Pentafluoroiodobenzene (2.94 g, 0.01 mol) and sodium dithionite (3.48 g, 0.02 mol) were stirred in DMF (50 mL) - benzene (25 mL) as a suspension at room temperature (23°C) for 6 h under an argon atmosphere. A sample was removed and the ^{19}F-NMR spectrum revealed a mixture of unreacted pentafluoroiodobenzene (60%) and pentafluorobenzene (40%). The mixture was added to ethyl ether (50 mL) and extracted with water (4 x 50 mL) The water layer was taken to dryness. An infrared spectrum of the dry solid revealed the absence of benzene rings either fluorinated or non-fluorinated.

Reaction of Pentafluoroiodobenzene with Sodium Hydroxymethanesulfinate Dihydrate (Rongalite) at Room Temperature

Pentafluoroiodobenzene (1.23 g, 4 mmol) and Rongalite (0 65 g, 4.2 mmol) were stirred in DMF (75 mL) at room temperature (23°C) for 19 h under argon. The mixture was added to ether (100 mL), washed with water (3 x 100 mL), and the ether layer was dried over magnesium sulfate. Gas chromatography revealed a mixture of pentafluoroiodobenzene and pentafluorobenzene (61%), whose retention times were compared and yields were determined with reference to authentic standards.

(a) With Norbornene

When the reaction was run in the presence of norbornene the only product was pentafluorobenzene

Reaction of Pentafluoroiodobenzene with Aminoiminomethanesulfinic acid (AIMS)

Aminoiminomethanesulfinic acid (1.08 g, 10 mmol) and sodium bicarbonate (1.68 g, 20 mmol) were stirred in water (50 mL) for 5 min. The water was removed on a roto-evaporator until only 12 mL of the yellow solution remained. DMF (36 mL) was added and the solution purged with argon for 10 min. Pentafluoroiodobenzene (1.47 g, 5 mmol) was added at room temperature under argon The reaction was monitored by gas chromatography, and pentafluoroiodobenzene and pentafluorobenzene were identified by comparison with the retention times of authentic samples. The conversion of pentafluoroiodobenzene to pentafluorobenzene was approximately 50% complete at 40 minutes and was approximately 85% (by GC) complete after 300 min.

Pentafluoroiodobenzene and Sodium Dithionite in Adogen 464 [Methyltrialkyl (C_8-C_{10}) ammonium Chloride]

Pentafluoroiodobenzene (2.94 g, 0.01 mol) and sodium dithionite (3.48 g, 0.02 mol) were stirred in Adogen 464 (10 mL) at room temperature for 22 h under argon. The mixture was added to pentane (25 mL) to form 3 layers (pentane, Adogen and water) which were washed with water (3 x 30 mL) to remove dithionite The pentane layer was roto-evaporated at room temperature and ethyl ether (2 mL) was added to dissolve the adogen/pentane/perfluoroaromatic compounds. The mixture was separated by flash chromatography (silica gel, 70 m, 15 mm x 300 mm, pentane) which allowed the products, minus the adogen to elute. The eluant and products were collected (75 mL) and the solvent was removed on a roto-evaporator. The sole product, pentafluorobenzene, had identical ^{19}F NMR, infrared and ^{1}H-NMR spectra to those of an authentic sample. No starting material was detected by ^{19}F-NMR.

Reaction of Pentafluoroiodobenzene with Sodium Dithionite in Acetonitrile and Water

Pentafluoroiodobenzene (9.11 g, 0.03 mol), sodium dithionite (10.8 g, 0.062 mol), and sodium bicarbonate (5.20 g, 0.062 mol) were stirred in acetonitrile (15 mL) and water (42 mL) at 85°C for 12.5 h under argon. The mixture was added to ether (30 mL), extracted with water (3 x 30 mL), and the ether layer dried over magnesium sulfate. The solvent was removed on a roto-evaporator. The ^{19}F-NMR spectrum revealed a mixture of pentafluoroiodobenzene (<2%) and pentafluorobenzene (>98%), whose ^{1}H- and ^{19}F-NMR spectra were identical with those of authentic samples. No other fluorine containing organic compounds, including water soluble products, were detected by ^{19}F-NMR

Reaction of Pentafluoroiodobenzene in the Presence of MeOD

(a) With Sodium Dithionite

Pentafluoroiodobenzene (5.88 g, 0.02 mol) and sodium dithionite (6.96 g, 0.04 mol) were stirred in a mixture of DMF (30 mL) and methanol-d$_1$ (7 mL) at room temperature for 22 5 h under argon The reaction mixture was added to ethyl ether (30 mL) and water (60 mL), the ether layer was extracted with water (4 x 30 mL), dried over magnesium sulfate, and the ether was removed by distillation. The remaining solution was examined by ^{19}F-NMR and contained unreacted pentafluoroiodobenzene (83%) and pentafluorobenzene (17%). The pentafluorobenzene was composed of pentafluoro[^{1}H]benzene (27%), ^{19}F-NMR (acetone-d$_6$), ortho fluorine δ= 139.19, (quintet, F-1,5), [lit[40] (CFCl$_3$), δ= 139.1] and pentafluoro[^{2}H]benzene (73%), ^{19}F-NMR (acetone-d$_6$), ortho fluorine δ= 139.49, (dd, F-1,5), [lit[17] (acetone-d$_6$), δ= 139.8, (dd, F-1,5)].

(b) With Rongalite

Pentafluoroiodobenzene (1.47 g, 5 mmol) and Rongalite (1.54 g, 10 mmol) were stirred in DMF (15 mL) - methanol-d$_1$ (7 mL) at room temperature for 20 h under argon. The ^{19}F-NMR spectrum of the reaction mixture revealed the presence of only pentafluorobenzene, composed of pentafluoro[^{1}H]benzene (12%), ^{19}F-NMR, (acetone-d$_6$), ortho fluorine δ= 138.50, (quintet, F-1,5), [lit[40], (CFCl$_3$), δ= 139.1], and pentafluoro[^{2}H]benzene (88%), ^{19}F-NMR (acetone-d$_6$), δ= 138.80, (dd, F-1,5) [lit[17], (acetone-d$_6$), δ= 139.8, (dd, F-1,5)]

Reaction of Bromopentafluorobenzene and Rongalite

Bromopentafluorobenzene (2.47 g, 0 01 mol) and Rongalite (1.54 g, 0.01 mol) were stirred in DMF at 90°C for 30 h under argon. The mixture was added to ether (100 mL) and was washed with water (3 x 100 mL). The product, pentafluorobenzene (50%), was identified by ^{19}F-NMR and gas chromatography.

Reaction of Sodium Benzenesulfinate with Pentafluoroiodobenzene

Pentafluoroiodobenzene (1.47 g, 5.00 mmol) and sodium benzenesulfinate (1.23 g, 7.50 mmol) were stirred in DMF (75 mL) at room temperature for 25 h under argon. The mixture was added to ether (100 mL) and was washed with water (2 x 75 mL). Water (75 mL) was added to the ether layer and the two-phase system was allowed to stand 2 days. A white solid that had precipitated was removed by filtration and washed with ethanol. The solid, 2,3,5,6-tetrafluorobis(phenylsulphonyl)benzene (0.31 g, 0.72 mmol, 19.4%), had ^{1}H and ^{19}F NMR spectra identical with those of the product from the reaction of chloropentafluorobenzene and sodium benzenesulfinate.

Reaction of Chloropentafluorobenzene and Sodium Dithionite

(a) At >90°C

Chloropentafluorobenzene (1.01 g, 5 mmol) and sodium dithionite (0.87 g, 5 mmol) were stirred in DMF (37 mL) at 110-115°C for 54 h under argon. The reaction mixture was added to ethyl ether (50 mL) and washed with water (3 x 50 mL). The ether layer was analyzed by ^{19}F-NMR (CDCl$_3$): chloro-2,3,5,6-tetrafluorobenzene (7%), δ= 138.2 (quintet, F-3,5), 141.4 (quintet, F-2,6) [lit[41] (tetrahydrofuran), δ= 138.6 (m, F-3,5), 142.2 (m, F-2,6)]; 4-chloro-2,3,5,6-tetrafluoro-N,N-dimethylaniline, δ= 144.2 (d, F-3,5), 150.9 (d, F-2,6) [lit[39a] 145 2 (d), 151.7 (d)]; pentafluorobenzene (22%), δ= 139.0 (quintet, F1,5), 154.4 (t, F-3), 162.6 (m,F-2,4); unreacted chloropentafluorobenzene (50%), δ= 140.8 (d, F-2,6), 156.3 (t, F-4), 161 5 (m, F-3,5) [lit[43] 140 9, 156.3, 161.6]; a mixture of sulfides (14% by ^{19}F NMR), δ= 132.4 (m), 139 5 (m) [Calculated* bis(4-chloro-2,3,5,6-tetrafluorophenyl)sulfide δ= 131 (F-2,6), 138 (F-3,5), 1,4-bis(4-chloro-2,3,5,6-tetrafluorothiophenoxy) tetrafluorobenzene δ= 131 (F-2,6), 138 (F-3,5), 130 (F'-2,3,5,6)]; mass spectrum (70 eV) of the sulfide mixture: m/e (relative intensity, %), bis(4-chloro-2,3,5,6-tetrafluorophenyl)sulfide, 398 (M$^+$, 100), 363 (5), 344 (7), 328 (10), 241 (14), 215 (13),180 (29), 171 (12), 149 (5), 135 (15), 117 (20), 111 (21); 1,4-bis(4-chloro-2,3,5,6-tetrafluorothiophenoxy)tetrafluorobenzene, m/e (relative intensity, %) 578 (M$^+$,18), 395 (21), 328 (16), 241 (21), 215 (25), 180 (82), 171 (16), 133 (14), 117 (22), 111 (24), 87 (25), 72 (17), 69 (21), 63 (16), 58 (15). The presence of 1,2,3,5-tetrakis(4-chloro-2,3,5,6-tetrafluorothiophenoxy)-4,6-difluorobenzene was suspected because of m/e greater than 578 and by analogy with known substitution patterns [38].

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*Calculated, estimating a -SC$_6$F$_4$Cl (para substituent) group as a -SC$_6$F$_5$ group, and reported shifts of [18] and [43].

(b) At 67°C

There was no reaction.

(c) At 90°C in the Presence of Potassium Hydroxide

In the presence of potassium hydroxide (0.84 g, 15 mmol), the chloroperfluoroaniline derivative, 4-chloro-2,3,5,6-tetrafluoro-N,N-dimethylaniline, was formed in good yield (85-90%): ^{19}F NMR (acetone-d_6) δ= 141.3 (d, F-3,5) and 147.2 (d, F-2,6) [lit [39a], NMR solvent not specified, δ= 145.2 (d, F-3,5) and 151.7 (d, F-2,6)].

Reaction of Chloropentafluorobenzene with Rongalite

Chloropentafluorobenzene (2 03 g, 0 01 mol) and Rongalite (1.54 g, 0.01 mol) were stirred in DMF (75 mL) at 90°C for 20 h under argon. The mixture was added to ethyl ether (100 mL) and washed with water (3 x 100 mL): ^{19}F-NMR (ether layer) ($CDCl_3$); chloro-2,3,5,6-tetrafluorobenzene (10%), δ=138.25 (m, F-3,5), 141.43 (t, F-2,6) [lit[41], (tetrahydrofuran), δ=138.6 and 142.2]; a mixture of sulfides (25%) whose ^{19}F NMR is identical to that of the reaction of chloropentafluorobenzene with sodium dithionite (see above), unreacted chloropentafluorobenzene (64%), δ=140.85 (d, F-2,6), 156.30 (t, F-4), 161.51 (t, F-3,5).

(a) With Sodium Bicarbonate

Chloropentafluorobenzene (2.03 g, 0.010 mol), Rongalite (1.54 g, 0.01 mol), and sodium bicarbonate (0.84 g, 0.01 mol) were stirred in DMF (75 mL) under argon. Temperatures were varied from 43°C to 113°C with times from 57 h to 1 week. The reaction mixture was added to ether (75 mL) and washed with water (3 x 75 mL). The ether layer was dried with magnesium sulfate, and the majority of solvent was removed on a roto-evaporator: ^{19}F-NMR (ether layer) ($CDCl_3$), pentafluorobenzene (8-18%), δ= 162.7 (m, F-2,4), 154.5 (t, F-3), 139.0 (quintet, F-1,5); chloro-2,3,5,6-tetrafluorobenzene (51-64%), δ= 138 4 (quintet, F-3,5), 141.6 (quintet, F-2,6), [lit[41] (tetrahydrofuran), 138.6 (m, F-3,5), 142.2 (m, F-2,6)]; unreacted chloropentafluorobenzene (13-40%), δ= 141.0 (d, F-2,6), 156.5 (t, F-4), 161.7 (t, F-3,5); an unknown (1-4%) (possibly chloro-2,3,4,5-tetrafluorobenzene) δ=157.4 (m F-4), 154.1 (m, F-3), 139.7 (m, F-2), 138.9 (m, F-5) [lit[41] (tetrahydrofuran), δ= 158.0, 154.6, 139.8, 139.0]. The ether layer was removed and chloro-2,3,5,6-tetrafluorobenzene was separated by preparative gas chromatography: b.p. (micro) 124-125°C [lit [42] b.p. 123.0-123.5°C].

Reaction of Chloropentafluorobenzene with Sodium Sulfite

Chloropentafluorobenzene (1.01 g, 5 mmol), sodium sulfite (0.63 g, 5 mmol), and sodium bicarbonate (0 42 g, 5 mmol) were stirred in DMF (25 mL) - water (25 mL) at 85°C for 17 h under argon. The mixture was added to ether (70 mL) and extracted with water (1 x 70 mL, 2 x 30 mL): ^{19}F-NMR (ether layer) ($CDCl_3$), unreacted chloropentafluorobenzene (46%), δ = 140.9 (d, F-2,6), 156.4 (t, F-4), 161 6 (t, F-2,5); 4-chloro-2,3,5,6-tetrafluoro-N,N-dimethylaniline (50%), δ = 144.2 (d, F-3,5), 150.8 (d, F-2,6), [lit[39a] 145.2 (d), 151.7 (d)]; 4% unknown (probably chloro-2,3,4,5-tetrafluorobenzene). The ether and the chloropentafluorobenzene were removed by distillation to leave 4-chloro-2,3,5,6-tetrafluoro-N,N-dimethylaniline, b.p. 192.5-193.0°C [lit[39a], b.p. 77-79°C, 3mm; b.p. 203-204°C]; ^{1}H-NMR ($CDCl_3$), δ= 2.95 (m) (lit[27b], δ=2.85 (t), no solvent reported) and a small amount of an impurity δ= 2.89 (s). The water layer contained a new fluorinated product, probably 4-chloro-2,3,5,6-tetrafluorobenzenesulfonate, ^{19}F NMR, (D_2O) δ= 136.66 (dd), 136.37 (dd), and an unknown at δ= 119.46 suspected to be NaF [lit[40b] (H_2O), 124.8 (s)].

Reaction of Chloropentafluorobenzene with Sodium Benzenesulfinate

Chloropentafluorobenzene (2.03 g, 0.01 mol) and sodium benzenesulfinate (2.46 g, 0.015 mol) were stirred under argon in DMF (75 mL) at 50°C for 41 h. Water (25 mL) was added and a solid precipitated. The mixture was stirred for an additional 5.5 h at 50°C, added to ether (75 mL), and extracted with water (2 x 75 mL). A solid, 2,3,5,6-tetrafluorobis(phenylsulphonyl)benzene, was removed by filtration and recrystallized from acetic acid (0.50 g, 1.2 mmol,15%): mp (hot stage, corr.) 301-305°C [lit[22] m.p. 285° C]; ^{1}H-NMR (acetone-$\underline{d}_6$), δ = 7.71(t, 2H, H-3,5), 7.84 (t, 1H, H-4), 8 74 (d, 2H, H-2,6 $J_{2,3}$=25 Hz); ^{19}F-NMR (acetone-$\underline{d}_6$), δ = 134.86 ppm (s); IR (KBr) 3080 (w), 1487 (s), 1348, 1165 (m, vs, SO_2), 1261 (s), 1084 (m), 981 (m), 796 (m), 725 (s), 681 (m), 634 (m), 590 (vs), 526 (m) cm^{-1} [lit[22] 1490, 1480, 1351 (SO_2), 1164, cm^{-1}]; mass spectrum, chemical ionization (CH_4^+), m/e (relative intensity,%) 471 (9, M+C_3H_5), 459 (20, M+C_2H_5), 433 (13), 432 (22), 431 (100, M+H), 429 (21).

Reaction of Pentafluorobenzene with Rongalite

Pentafluorobenzene (1.68 g, 0.01 mol) and Rongalite (1.54 g, 0.01 mol) were stirred in DMF at 85°C for 5 h under argon. More Rongalite (1.54 g, 0.01 mol) was added and stirring was continued for an additional 16 h. The mixture was added to ether (50 mL) and extracted with water (2 x 75 mL). The ether layer was dried and the ether removed to give a liquid that was chromatographed (silica gel) to give a white solid. The solid was recrystallized from propanol-water (1:1): m.p. 35.5-44.0°C (lit[22] m.p. 44 5°C for bis-2,3,5,6-tetrafluorophenyl sulfide). The filtrate produced more crystals after 7 days. This material was not homogeneous and showed three distinct melting points, 36-44.5°C, 93-96°C and 103-107°C; ^{1}H-NMR (acetone-d_6), 7 69 (tt); ^{19}F-NMR (acetone-d_6) 133.65 (m), 137.60 (quintet), 139.41 (m); chemical ionization mass spectrum (CH_4^+), m/e (relative intensity, %) [bis-2,3,5,6-tetrafluorophenylsulfide] 371 (8, M+C_3H_5), 359 (21, M+C_2H_5), 332 (13), 331 (100, M+H).

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