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AROMATIC FLUORINE CHEMISTRY. PART 2. PREPARATION OF CHLOROFLUOROBENZENES VIA FLUORINATION OF DICHLOROBENZENES WITH KF

R. G. PEWS AND J. A. GALL
Central Research Laboratory, The Dow Chemical Company, Midland, MI 48674 (U.S.A.)

SUMMARY

The 1,2-, 1,3- and 1,4-chlorofluorobenzenes have been prepared via KF exchange on the corresponding dichlorobenzenes.

INTRODUCTION

Conventional methods of preparing chlorofluoroaromatic compounds are based primarily on diazotization chemistry; i.e. Balz-Schiemann reaction [1]. Alternatively, chlorofluorobenzenes have been prepared by the halogenation of fluorobenzenes, but the fluorobenzene starting materials are themselves prepared by the above mentioned diazonium chemistry. Other methods have been reported for the fluorination of chlorobenzenes but are not practical for commercialization. These procedures include N-fluorosulfonamides [2] and AgF_2 [3]. The nucleophilic substitution of fluoride in perchlorinated compounds (e.g., hexachlorobenzene and pentachloropyridine) is well documented in the literature [4a, b]. However, the literature on the lower chlorinated benzene derivatives is limited. Shiley, Dickerson and Finger [5] investigated the KF exchange reaction of the three isomeric trichlorobenzenes utilizing dimethyl sulfone as solvent [5]. There is no report by either Finger and coworkers or others on the attempted KF exchange reactions on the dichlorobenzenes in dipolar aprotic solvents. However, Yacobson [6] reported on the KF exchange without solvent at 410-420°C. Under these conditions, considerable reduction was observed [6]. Recent success in this laboratory on the KF exchange reaction of 3,4-dichlorobenzotrifluoride in dipolar aprotic solvents [7] prompted us to extend the investigation to the isomeric

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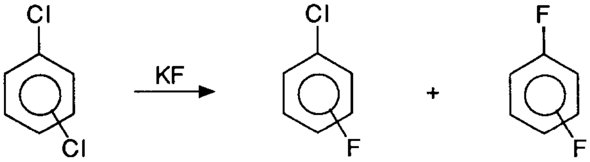
dichlorobenzenes. We now describe the preparation of chlorofluorobenzenes from the corresponding dichlorobenzenes by KF exchange in dipolar aprotic solvents.

RESULTS AND DISCUSSION

The results of our investigations on the KF exchange reaction on the three dichlorobenzenes are summarized in Table 1. The reactions were carried out in a Hastelloy C Parr reactor. The solvents utilized in the study were 1-methyl-2-pyrrolidinone (NMP); 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)pyrimidone (DMTHP), "N,N-dimethylpropylene urea"); 1,3-dimethyl-2-imidazolinone (DME, "N,N-dimethylethylene urea"); and 1-cyclohexyl-2-pyrrolidinone (NCHP). The KF exchange experiments with 1a in NMP, DMTHP and DME gave comparable results. However, NCHP gave very slow rates of conversion, presumably due to the lower solubility of KF in this solvent. The remarkable stability of these solvents is noteworthy. At 350°C for 24 hours in the presence of KF, NMP shows no detectable decomposition by GC analysis, and the solution was only slightly discolored. The preferred reaction temperature for the conversion of 1a → 1b is 310°C. At this temperature, the conversion is 50%, and the ratio of 1a:1b is ~1. The minimum formation of o-difluorobenzene is probably due to the nondipole interactions for activation of ortho fluorine as described by Chambers [8]. This is further substantiated by the formation of small quantities of the difluoro derivatives for the meta and para isomers. The mass balances for the aromatics was



1 2 3

a = 1,2 -
b = 1,3 -
c = 1,4 -

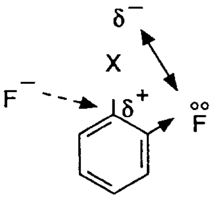


TABLE 1

Preparation of Chlorofluorobenzenes

	Temp. (°C)	Time (Hr)	Solvent (ml)	Reactants (Mol)		Products (Mol)			1:2:3	Mass Balance
				KF	1	1	2	3		
1a	290	66	NMP (250)	0.8	0.4	0.290	0.105	0.000	73:27:0	99
1a	300	70	DMTHP (125)	0.4	0.1	0.063	0.030	0.001	67:32:1	94
1a	300	24	DMI (125)	0.4	0.1	0.058	0.032	0.000	64:36:0	90
1a	310	24	NMP (250)	0.8	0.2	0.092	0.092	0.001	50:50:0	93
1a	320	24	NMP (250)	0.8	0.2	0.068	0.110	0.007	37:59:4	93
1a	320	24	NCHP (250)	0.8	0.2	0.162	0.028	0.000	85:15:0	96
1a	350	24	NMP (250)	0.8	0.2	0.023	0.123	0.021	14:74:12	83
1b	280	24	NMP (125)	0.4	0.1	0.069	0.028	0.002	70:28:2	99
1b	290	24	NMP (125)	0.4	0.1	0.059	0.040	0.003	58:39:3	102
1b	300	24	NMP (125)	0.4	0.1	0.039	0.048	0.007	42:51:7	94
1b	310	24	NMP (125)	0.4	0.1	0.018	0.050	0.014	22:61:17	82
1b	320	24	NMP (125)	0.4	0.1	0.009	0.048	0.023	11:60:29	80
1b	325	24	NMP (250)	0.8	0.2	0.016	0.102	0.039	10:65:25	79
1c	325	24	NMP (250)	0.8	0.2	0.080	0.114	0.006	40:57:3	90

surprisingly high, even for the run at 350°C. As noted above, the exchange reactions for the meta isomer 1b gave detectable amounts of the difluoro derivative 2b. The reaction temperatures appear to be 10-15°C lower for comparable conversion of the meta isomer compared to the ortho derivative. This observation is in good agreement with the +R substituent effect of the meta chlorine.

As noted in the introduction, preparation of the para isomer, 2c, via chlorination of fluorobenzene is probably the preferred route. However, to complete the study, 1c was briefly investigated and found to undergo the exchange reaction. As expected on the basis of the substituent effect of the para chlorine (relative to the meta derivative), 1c yielded considerably less 1,4-difluorobenzene.

In summary, the KF exchange reaction has been demonstrated for the dichlorobenzenes and provides an alternative to diazonium chemistry for the preparation of chlorofluorobenzenes.

EXPERIMENTAL

The experiments were conducted in either a 300 (ml) or 600 (ml) Hastelloy "C" Parr reactor equipped with a magnetic drive stirrer. The KF was dried in a vacuum oven at 150°C for at least 24 hours. Solvents were dried by distillation from calcium hydride. The solvent, KF, and dichlorobenzene were introduced into the pressure reactor along with 20-50 gm of mesitylene which served as the internal standard. The reactor was sealed and pressure tested with N_2, then stirred and heated at the desired temperature. The reactor was cooled and vented, and the reaction mixture was analyzed by gas chromatography, either alone or in conjunction with a mass spectrometer.

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