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Use of a Lithium Amide Suspension in Tetrahydrofuran for Preparation of Some Polyfluorophenyl- and Polyfluorodiphenylamines

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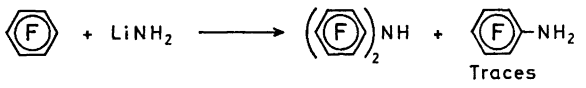
A new direct route for preparation of decafluorodiphenylamine and *N*-methyldecafluorodiphenylamine has been developed. The reactions also indicate a promising route for the preparation of lithium salts of pentafluoroaniline and decafluorodiphenylamine.

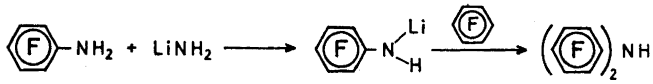
In 1958 Tatlow *et al.*[1] published the preparation of pentafluoroaniline from a reaction between hexafluorobenzene and sodamide in liquid ammonia. Later re-examination of this reaction showed that decafluorodiphenylamine had been formed in approximately 4 % yield.[2] A better yield of decafluorodiphenylamine has been obtained with pentafluoroaniline in ether as the starting material.[3,4] The tertiary amine, *N*-methyldecafluorodiphenylamine, has been prepared from pentafluoroaniline or decafluorodiphenylamine.[4] A direct route for preparation of polyfluoroamines in good yield from hexafluorobenzene will be described.

Through the reaction between equimolar quantities of hexafluorobenzene and lithium amide suspension in tetrahydrofuran decafluorodiphenylamine was formed in good yield, and usually only a faint smell from pentafluoroaniline in the crude product indicated the presence of traces of this compound.



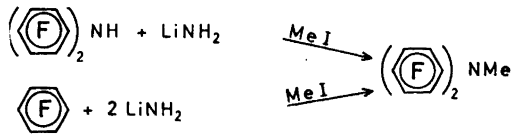
Hexafluorobenzene treated with lithium amide for 20 h at 20° gave no reaction, but good yield of decafluorodiphenylamine was obtained when the temperature was elevated to 70 – 80°. A reaction could also be initiated at room temperature by adding some pentafluoroaniline or *N*,*N*-dimethylaniline to the mixture.

Pentafluoroaniline reacted immediately with lithium amide at 5° by liberating ammonia, and decafluorodiphenylamine was formed by adding hexafluorobenzene.



The reaction between hexafluorobenzene and a lithium amide suspension in tetrahydrofuran shows that the nucleophilic attack from lithium amide on hexafluorobenzene does not terminate with the formation of pentafluoroaniline. A metalation of the aniline may take place as fast as the aniline is formed. The reaction seems to demonstrate that the lithium salt of pentafluoroaniline forms a sufficiently powerful nucleophile [3] in tetrahydrofuran to displace fluorine from hexafluorobenzene, and that this displacement goes faster than the nucleophilic attack from lithium amide, as decafluorodiphenylamine was formed in good yield. It is therefore believed that the reaction between lithium amide and hexafluorobenzene depends upon solution effects on lithium amide. The metal amide is believed to be the strongest of the nucleophilic agents in the reaction. If this amide had been present in dissolved state, most probably pentafluoroaniline would have been formed as the main product, as is the case when the reaction is run in liquid ammonia.[1,2]

N-Methyldecafluorodiphenylamine was prepared from decafluorodiphenylamine or directly from hexafluorobenzene, lithium amide, and methyl iodide in good yield (77.5 %).



Lithium amide was added to decafluorodiphenylamine under liberation of ammonia, which indicates the formation of the lithium salt of decafluorodiphenylamine. The lithium salt of decafluorodiphenylamine reacts with hexafluorobenzene only under more drastic conditions,[3] which may be the reason why no perfluorotriphenylamine resulted.

To investigate the applicability of the reactions further, hexafluorobenzene, lithium amide, and 2,6-dichlorobenzylchloride (1:3:2) were reacted together. A reddish oil was formed, from which only di(2,6-dichlorobenzyl)-pentafluorophenylamine in low yield was isolated.

Reaction between pentafluoroaniline, lithium amide, and 2,6-dichlorobenzylchloride (1:2:1) afforded 2,6-dichlorobenzyl pentafluorophenylamine and di(2,6-dichlorobenzyl)-pentafluorophenylamine.

2,6-Dichlorobenzylchloride and lithium amide in tetrahydrofuran refluxed overnight afforded *trans*-2,2′,6,6′-tetrachlorostilbene in good yield (55.5 %).

The NMR spectrum in $CDCl_3$ showed a complex pattern with all protons in the region δ 7.0 – 7.5 ppm. The vinyl protons showed a signal at δ 7.26 ppm. The reaction mechanism may be similar to that suggested by Karasch *et al.*[5] for the reaction of RCH_2Cl with alkali metal amides in ammonia.

Pentafluorobenzene added to a lithium amide suspension at 0° liberated ammonia under formation of a white, insoluble solid.[6] Pentafluorophenyl magnesium chloride [7] stirred together with lithium amide first at ambient temperature and then for 1 h on reflux, decomposed. This was evidenced by the formation of a white, insoluble solid.[6] Pentafluorophenyl copper [7] refluxed together with lithium amide, gave a small yield of a compound indicating the presence of an NH_2 group by IR.

EXPERIMENTAL

The reactions were carried out in an atmosphere of nitrogen. Tetrahydrofuran was dried over sodium and distilled from sodium benzophenone ketyl prior to use. The lithium amide used contained at least 90 % $LiNH_2$ and approximately 4 % LiH.* All melting points are uncorrected. IR and NMR spectra were determined employing Perkin-Elmer 457-IR and Varian A-60A NMR spectrometers, respectively.

Decafluorodiphenylamine (from hexafluorobenzene and lithium amide, 1:1). To a stirred mixture of lithium amide (3.3 g) in THF (50 ml) cooled to 15°, hexafluorobenzene (24.4 g, 0.131 mol) was added all at once. The temperature was raised to reflux for 2 h. The brown mixture was cooled to 0° and ether (50 ml) was added. The mixture was hydrolyzed with 5 % HCl to acid reaction. The water layer, after separation, was treated twice with ether (30 ml). The gathered organic layers were washed with water, dried with sodium sulphate, and concentrated under reduced pressure. The resultant solid was recrystallized from petroleum ether (b.p. 40 – 65°) to give 14.4 g (61.8 %) decafluorodiphenylamine (m.p. 84 – 86°) (IR in nujol, cm^{-1}: 3423 m, 1520 s, 1030 s, 980 m, 960 w, 825 w). Mixed melting point with an authentic sample showed no depression. IR for the two samples were identical.[3] No pentafluoroaniline was recovered.

Decafluorodiphenylamine (from hexafluorobenzene and lithium amide, 1:2). To a stirred mixture of lithium amide (4.4 g) in THF (30 ml) hexafluorobenzene (14.75 g, 0.079 mol) was added all at once. The temperature was raised to 65°. After 3 h THF (50 ml) was added and the reddish-brown mixture hydrolyzed with 5 % HCl to acid reaction giving a solid. Sublimation of the reaction product gave 0.2 g (1.4 %) of pentafluoroaniline (m.p. 31 – 33°). The compound was identified by mixed melting point and IR with a commercial sample from Imperial Smelting. Recrystallization of the rest after sublimation gave 9.4 g (67.2 %) of decafluorodiphenylamine (m.p. 84 – 85°), identified as described above.

Decafluorodiphenylamine (from hexafluorobenzene and lithium amine, 1:1, activated by N,N-*dimethylaniline).* To a stirred mixture of lithium amide (1.3 g) and *N,N*-dimethylaniline (3 g) in THF (30 ml) at 10°, hexafluorobenzene (10.1 g, 0.05 mol) was added. The mixture was stirred for 16 h on a water bath at 23° giving 5.5 g (63 %) decafluorodiphenylaniline (m.p. 84 – 86°). Work-up and identification were performed as described above.

Decafluorodiphenylamine (from pentafluoroaniline, lithium amide, and hexafluorobenzene, 1:1:1). To a stirred mixture of lithium amide (0.78 g) in THF (25 ml) at 5° pentafluoroaniline (5.55 g, 0.03 mol) in THF (25 ml) was added over a period of 10 min. NH_3 was immediately liberated from the reaction mixture. After 1 h, hexafluorobenzene (5.58 g, 0.03 mol) in THF (5 ml) was added to the brownish mixture. The mixture was stirred overnight at room temperature. Subsequent work-up gave a black oil, which was chromatographed on neutral Al_2O_3 (Woelm) with petroleum ether (40 – 65°). 0.4 g of pentafluoroaniline was recovered by sublimation. The rest was chromatographed once

* The lithium amide used was provided from Metallgesellschaft AG, Frankfurt am Main, West Germany.

more and afforded 5.5 g (51 %) decafluorodiphenylamine (m.p. 83 – 85°), identified as previously described.

N-Methyldecafluorodiphenylamine (from decafluorodiphenylamine, lithium amide and methyl iodide, 1:1:1). To a stirred mixture of lithium amide (0.52 g) in THF (30 ml) decafluorodiphenylamine (7.0 g, 0.02 mol) was added. The mixture was refluxed for 3/4 h under liberation of NH_3, and then cooled to 0°. After addition of methyl iodide (2.84 g, 0.02 mol) the mixture was stirred overnight at ambient temperature, and then hydrolyzed with 5 % HCl to acid reaction. The ordinary work-up, after treatment of the organic layer with $Na_2S_2O_3$, afforded a crude that showed no NH band by IR. Subsequent sublimation and recrystallization from petroleum ether (40 – 65°) afforded 6.55 g (90 %) *N*-methyldecafluorodiphenylamine (m.p. 61.5 – 63°) (IR in nujol, cm^{-1}: 1512 s, 1500 s, 1238 m, 1200 m, 1082 s, 1002 s, 990 s, 892 m, 789 m, 732 m, 725 m, 669 m, 571 m). The compound was identical with an authentic sample from Dr. C. Tamborski.[4]

N-Methyldecafluorodiphenylamine (from hexafluorobenzene, lithium amide, and methyl iodide, 1:2:1). To a stirred mixture of lithium amide (5.2 g) in THF (50 ml) hexafluorobenzene (18.6 g, 0.1 mol) was added. The mixture was refluxed slowly for 1 h, then cooled to 0°, whereafter methyl iodide (14.2 g, 0.1 mol) was added all at once. An exothermic reaction took place. The mixture was stirred overnight and worked up as described for the previous reaction, to give a black oil which showed no NH band by IR. Vacuum distillation afforded 1.2 g of an unidentified oil. The distillation rest was sublimated, recrystallized from petroleum ether (40 – 65°) and gave 12.5 g (77.5 %) *N*-methyldecafluorodiphenylamine (m.p. 61 – 63°), identified as above.

2,6-Dichlorobenzyl-pentafluorophenylamine and di(2,6-dichlorobenzyl)-pentafluorophenylamine (from pentafluoroaniline, lithium amide, and 2,6-dichlorobenzylchloride, 1:2:2). To a stirred mixture of lithium amide (4.70 g) in THF (25 ml) pentafluoroaniline (15.55 g, 0.085 mol) in THF (75 ml) was added over 7 min; NH_3 was at once liberated. The reddish-brown mixture was stirred overnight at ambient temperature, cooled to 0°, and 2,6-dichlorobenzylchloride (33.0 g, 0.17 mol) in ether (100 ml) was added. The mixture was refluxed for 2 h, cooled to 0° and hydrolyzed with 5 % HCl to acid reaction, leaving a reddish oil. Vacuum distillation of the oil gave 3.8 g dichlorobenzylchloride and 1.4 g pentafluoroaniline. A subsequent sublimation of the distillation rest gave 5.3 g (20 %) 2,6-dichlorobenzyl-pentafluorophenylamine (m.p. 67.5 – 69.2°) (IR in nujol, cm^{-1}: 3402 w, 1576 w, 1558 w, 1518 s, 1472 sh, 1434 m, 1194 w, 1158 w, 1022 m, 963 m, 942 w, 782 m, 765 m, 731 m). The NMR spectrum in $CDCl_3$ showed bands at δ 7.26 ppm, δ 4.73 ppm, and a broad signal at δ 3.87 ppm, which disappeared on the addition of D_2O. (Found: C 45.94; H 2.18; mol.wt. 342; NMR 3.1:2.0:1.0. Calc. for $C_{13}H_6F_5Cl_2N$: C 45.64; H 1.77; mol. wt. 342.1; NMR 3:2:1.)

The residue after the sublimation was chromatographed on neutral Al_2O_3 (Woelm) with petroleum ether (40 – 65°) and gave 27.5 g (71 %) di(2,6-dichlorobenzyl)-pentafluorophenylamine (m.p. 117 – 119°) (IR in nujol, cm^{-1}: 1580 m, 1560 m, 1500 s, 1435 s, 1100 m, 1025 m, 988 s, 945 s, 780 w, 773 m, 763 m). The NMR spectrum in $CDCl_3$ showed bands at δ 7.22 ppm and δ 4.58 ppm. (Found: C 48.21; H 2.34; mol.wt. 501; NMR 6.0:4.0. Calc. for $C_{20}H_{10}F_5Cl_4N$: C 47.94; H 2.01; mol.wt. 501.0; NMR 6:4.)

Di(2,6-dichlorobenzyl)-pentafluorophenylamine (from hexafluorobenzene, lithium amide, and 2,6-dichlorobenzylchloride, 1:3:2). To a stirred mixture of lithium amide (3.12 g) in THF (40 ml) 2,6-dichlorobenzylchloride (15.6 g, 0.08 mol) and hexafluorobenzene (7.44 g, 0.04 mol) were added. The mixture was stirred overnight at ambient temperature, refluxed for 3/4 h, cooled to 0°, and hydrolyzed with 5 % HCl to acid reaction, leaving a reddish oil. Vacuum distillation gave 2.3 g of unreacted 2,6-dichlorobenzylchloride. The residue formed on standing with some petroleum-ether (40 – 65°) a yellow precipitate which gave 2.2 g (11 %) di(2,6-dichlorobenzyl)-pentafluorophenylamine, which was identified with a sample from the previous reaction.

trans-*2,2',6,6'-Tetrachlorostilbene (from 2,6-dichlorobenzylchloride and lithium amide, 1:1).* To a stirred mixture of lithium amide (1.3 g) in THF (5 ml) 2,6-dichlorobenzylchloride (9.8 g, 0.05 mol) dissolved in THF (25 ml) was added. The mixture was stirred overnight at reflux; the brown mixture was cooled to 0° and hydrolyzed with 70 ml 5 % HCl after the addition of ether (100 ml). The ether layer was worked up in the usual manner. The water layer was made basic with 5 % NaOH and extracted twice with 50 ml ether. The ordinary work-up afforded a compound with the same infrared spectrum as was obtained for the compound from the first organic layer. The compounds were

joined and chromatographed on neutral Al_2O_3 (Woelm) with a petroleum ether (40 – 65°) – chloroform mixture, and gave after recrystallization from petroleum ether (40 – 65°), 4.4 g (55.5 %) *trans*-2,2′,6,6′-tetrachlorostilbene (m.p. 142.5 – 144°) (IR in nujol, cm^{-1}: 1580 w, 1555 w, 1440 m, 1428 s, 1175 m, 1152 w, 1088 w, 962 s, 783 w, 774 s, 721 s). The NMR spectrum in $CDCl_3$ showed bands in the region δ 7.01 – 7.51, with the two highest peaks at δ 7.20 ppm and δ 7.34 ppm. The vinyl protons showed a signal at δ 7.25 ppm. (Found: C 52.83; H 2.68; mol.wt. 318; NMR 6.0:2.0. Calc. for $C_{14}H_8Cl_4$: C 52.87; H 2.53; mol.wt. 318.0; NMR 6:2.) 0.3 g of a mixture of unidentified compounds (m.p. 67 – 83°) was left in the mother liquor.

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