(0.5 mole) was added to the silver salt (0.25 mole) in 1-l. of dry benzene. The mixture was stirred and heated under reflux for about 24 hr. The silver iodide was filtered off, the benzene solvent stripped off, and the product distilled under vacuum in an atmosphere of dry nitrogen. The arsonate prepared by this method is much purer than when prepared by method A, only one distillation being required to obtain a pure product.

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Preparation of *N*-1,1-di-H-perfluoroalkyl Amines

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The preparation of *N*-1,1-di-H-trifluoroethyl aniline ($C_6H_5NHCH_2CF_3$) and *N*-1,1-di-H-heptafluorobutyl aniline ($C_6H_5NHCH_2C_3F_7$) has been described in the literature.[1,2] The first of these was prepared by reacting 1,1-di-H-trifluoroethyl chloride with aniline in a sealed ampoule at 185° for 24 hr., while the latter material was prepared in poor yield by the lithium aluminum hydride reduction of heptafluorobutyranilide.

Earlier we reported the preparation of various 1,1-di-H-perfluoroalkyl tosylates (*p*-toluenesulfonates) and their reactions with various alkali halides to give excellent yields of the corresponding 1,1-di-H-perfluoroalkyl halides.[3] It was reasonable to suppose that analogous reactions might occur between these tosyl esters and aliphatic or aromatic amines.

We have found that good yields of pure *N*-1,1-di-H-heptafluorobutyl aniline are readily obtained by heating a mixture of aniline and 1,1-di-H-heptafluorobutyl tosylate for 24 hr. at 230°. It would appear that the previously reported preparation,[2] a liquid, was seriously impure, as our product melted at 38°–39.5°. The corresponding *N*-substituted piperidine was prepared in similar fashion. The use of lower temperatures or shorter reaction times resulted in lower yields of the desired product.

Attempts to react the tosyl ester with ammonia or diethyl amine under similar conditions gave tarry, decomposed mixtures from which the desired products could not be isolated. Similarly, reactions of the iodide, n-$C_3F_7CH_2I$, with aniline at 250° led only to decomposition, none of the desired amine being found.

A highly fluorinated amide has been prepared by treating *N*-1,1-di-H-heptafluorobutyl aniline with heptafluorobutyric anhydride.

EXPERIMENTAL

N-1,1-di-H-heptafluorobutyl aniline. Two hundred grams (2.15 moles) of aniline and 354.2 g. (1.0 mole) of 1,1-di-H-heptafluorobutyl *p*-toluenesulfonate[3] were allowed to react in a 180-ml. Aminco stainless steel autoclave for 24 hr. at 230°. After cooling, the contents of the autoclave were washed out with ether; the mixture was filtered and 200.5 g. (75.5%) of anilinium *p*-toluenesulfonate was obtained. To remove unreacted aniline the filtrate was washed with 250 ml. of 5% hydrochloric acid and then with several portions of water. The ether was boiled off and the residue was subjected to vacuum distillation. One hundred eighty-seven grams of the desired product, n-$C_3F_7CH_2NHC_6H_5$, was obtained, b.p. 86–95° (7–8 mm.), 68% yield. It solidified on cooling, and upon recrystallization from 70% alcohol, melted at 38–39.5°.

Anal. Calcd. for $C_{10}H_8F_7N$: C, 43.6; N, 5.08. Found: C, 43.4; N, 5.08.

N-1,1-di-H-heptafluorobutyl piperidine. In a $^3/_4$-inch o.d. heavy-walled Pyrex No. 7740 ampoule of approximately 30 ml. volume was sealed a mixture of 12.8 g. (0.036 mole) of 1,1-di-H-heptafluorobutyl *p*-toluenesulfonate and 6.2 g. (0.073 mole) of piperidine. The ampoule, placed in an iron pipe shield for safety, was rocked continuously at 175° for 20 hr. The ampoule, still in the iron pipe, was cautiously cracked open at liquid air temperature. After warming to room temperature, the reaction product was treated with petroleum ether and the slurry was filtered to remove piperidinium *p*-toluenesulfonate. The solution was fractionally distilled at 148°–151° and had n_D^{25} 1.3576; there was obtained 4.2 g. (44% yield).

Anal. Calcd. for $C_9F_7H_{12}N$: N, 5.25; F, 49.8. Found: N, 5.10; F, 49.6.

Attempted reaction of aniline with $C_3F_7CH_2I$. In the first two attempts, the sealed, 80-ml. heavy-walled Pyrex ampoules burst when 20 g. (0.064 mole) of $C_3F_7CH_2I$ and 12 g. of (0.129 mole) aniline were heated to 250°. The third reaction was carried out for 24 hr. at 250° in a 43-ml. Aminco stainless steel autoclave, the same quantities of the reactants being used. The reaction product was black and very tarry and none of the desired amine, n-$C_3F_7CH_2NHC_6H_5$, could be isolated by vacuum distillation.

N-1,1-di-H-heptafluorobutylheptafluorobutyranilide. A mixture of 19 g. (0.07 mole) of *N*-1,1-di-H-heptafluorobutylaniline and 41 g. (0.1 mole) of heptafluorobutyric anhydride was refluxed for 7 hr. The mixture was then poured into 250 ml. of water and was neutralized with sodium carbonate. The product was taken up in two 50-ml. portions of ether, washed twice with water, and dried over magnesium sulfate. After distilling off the ether, the product was distilled under reduced pressure, b.p. 90–91° (3 mm.), m.p. 21°, n_D^{20} 1.3834 (supercooled). The yield of pale yellow amide was 20.3 g. (0.043 mole) or 61%.

Anal. Calcd. for $C_{14}H_7F_{14}NO$: C, 35.66; N, 2.97. Found: C, 35.7; N. 2.89.

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