

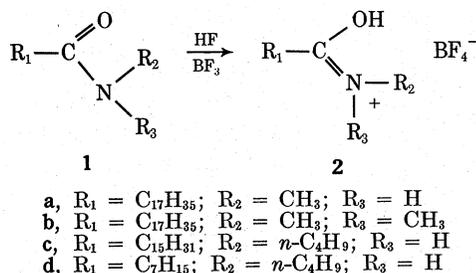
## Amide Hydrofluoroborates

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We have found that aliphatic amides (**1a-d**) react with anhydrous HF and BF<sub>3</sub> to give stable, isolable amide hydrofluoroborates (**2a-d**) in 40–60% yield.<sup>2</sup> Compounds **2a-d** were typically prepared by dissolving the amide in liquid HF at 0–15°, bubbling in BF<sub>3</sub>, and allowing the mixture to stand for 30 min at 15–20°. They were isolated by removal of excess HF and BF<sub>3</sub> and purified by recrystallization.



The structures of these compounds have been established by spectral data and by elemental analysis (see Experimental Section). For example, *N-n*-butylpalmitamide hydrofluoroborate (**2c**) shows ir bands at 3300 [OH or (=NHR)<sup>+</sup>] and 1680 cm<sup>-1</sup> [(>C=N<)<sup>+</sup>], compared to absorptions of 3455 (–NH) and 1660 cm<sup>-1</sup> (>C=O) for the starting amide. The nmr spectrum of **2c** shows two downfield singlets at 10.15 (OH) and 9.12 ppm [(=NHR)<sup>+</sup>]. In addition, a quartet centered at 3.52 [(>C=NHCH<sub>2</sub>CH<sub>2</sub>)<sup>+</sup>] and a triplet at 2.75 ppm [–CH<sub>2</sub>CH<sub>2</sub>C(=NHR)<sup>+</sup>OH] are in agreement with the amide hydrofluoroborate structure.<sup>3</sup> These data are indicative of protonation on oxygen, which has been noted in previous studies of amides in strongly acidic media.<sup>4</sup> The stereochemistry at the quaternary nitrogen in **2a, c**, and **d** is not known.

Amide hydrofluoroborates are quantitatively reconverted to the corresponding amides by treatment with H<sub>2</sub>O and undergo partial decomposition on heating. However, they appear to be indefinitely stable in the absence of H<sub>2</sub>O at room temperature.

In contrast to the above results, *N*-methylstearamide

(**1a**) does not form stable salts with HF alone or upon treatment with HCl in CH<sub>2</sub>Cl<sub>2</sub>. Reaction of **1a** with BF<sub>3</sub> alone in CH<sub>2</sub>Cl<sub>2</sub> results in the formation of a hygroscopic complex.<sup>5</sup> In the case of stearamide (R<sub>1</sub> = C<sub>17</sub>H<sub>35</sub>; R<sub>2</sub> = R<sub>3</sub> = H), reaction with HF and BF<sub>3</sub> yields a less stable salt, which could not be successfully separated from the starting amide. Apparently, the unsubstituted amide is less basic than either **1a** or **1b**.

## Experimental Section

All reactions were performed in a graduated polyethylene bottle with an inlet tube for attachment to HF and BF<sub>3</sub> cylinders<sup>6</sup> and an exit tube protected by Drierite. The ratio of liquid HF to amide in the preparation of **2a-c** is important, since the use of a larger amount of HF results in a different reaction pathway.<sup>7</sup> Caution: To avoid toxicity and severe burns in the handling of HF, appropriate safety precautions should be taken.

*N*-Methylstearamide Hydrofluoroborate (**2a**).—Liquid HF (6 ml) was condensed into the vessel containing *N*-methylstearamide (**1a**) (3.0 g, 0.0101 mol) at 0°. Anhydrous BF<sub>3</sub> was then admitted into the mixture at a moderate bubbling rate for 5 min with occasional warming to maintain solution. The mixture was allowed to stand at 15° for 30 min. Excess HF and BF<sub>3</sub> were removed in a stream of N<sub>2</sub>, and the resulting solid residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to give **2a**: 1.8 g (48%); mp 66–70° dec; ir (CHCl<sub>3</sub>) 3300, 2920, 2860, 1685, 1070 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 9.45 (1 H, s), 8.75 (1 H, s), 3.10 (3 H, d), 2.72 (2 H, t), 1.4–0.9 ppm (33 H, m).

Anal. Calcd for C<sub>19</sub>H<sub>40</sub>NOBF<sub>4</sub>: C, 59.23; H, 10.47; N, 3.64; F, 19.72. Found: C, 59.32; H, 10.31; N, 3.56; F, 19.54.

*N,N*-Dimethylstearamide Hydrofluoroborate (**2b**).—*N,N*-Dimethylstearamide (2.0 g, 0.0064 mol) was suspended in liquid HF (3 ml) at 10° and anhydrous BF<sub>3</sub> was admitted at a moderate bubbling rate for 10 min at 10°. The mixture was then warmed briefly to achieve complete solution. After the solution had stood at 0° for 30 min, the excess HF and BF<sub>3</sub> were removed and the residue was crystallized from methylene chloride–hexane (1:1) to give **2b**: 1.5 g (59%); mp 61–65° dec; ir (CHCl<sub>3</sub>) 3480, 2920, 2860, 1670, 1070 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 9.38 (1 H, s), 3.40 (3 H, br s), 2.85 (2 H, t), 1.8–0.9 ppm (33 H, m).

Anal. Calcd for C<sub>20</sub>H<sub>42</sub>NOBF<sub>4</sub>: C, 60.15; H, 10.61; N, 3.51. Found: C, 60.35; H, 10.90; N, 3.30.

*N-n*-Butylpalmitamide Hydrofluoroborate (**2c**).—*N-n*-Butylpalmitamide (**1c**) (3.0 g, 0.0096 mol) was dissolved in liquid HF (4 ml) at 0° and BF<sub>3</sub> was bubbled in at a moderate rate for 5 min. The solution was then allowed to stand at 0–15° for 30 min. The excess HF and BF<sub>3</sub> were removed and the crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–hexane (3:1) to yield **2c** (hygroscopic): 1.5 g (40%); mp 55–59° dec; ir (CHCl<sub>3</sub>) 3300, 2930, 2860, 1680, 1070 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 10.15 (1 H, s), 9.12 (1 H, s), 3.52 (2 H, q), 2.75 (2 H, t), 1.9–0.7 ppm (36 H, m).

Anal. Calcd for C<sub>20</sub>H<sub>42</sub>NOBF<sub>4</sub>: C, 60.15; H, 10.60; N, 3.51. Found: C, 59.96; H, 10.42; N, 3.33.

*N-n*-Butyloctanamide Hydrofluoroborate (**2d**).—*N-n*-Butyloctanamide (**1d**) (2.0 g, 0.01 mol) was dissolved in liquid HF (2 ml) at 0°. The usual procedure was then followed leaving an oily residue, which was dissolved in boiling CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1). On cooling, **2d** separated as an oil which was isolated, filtered to remove a very small amount of inorganic solid, and freed from residual solvent *in vacuo* at 20°. This treatment yielded 1.7 g of **2d** (58%): ir (CHCl<sub>3</sub>) 3300, 2930, 2860, 1680, 1070 cm<sup>-1</sup>;

(1) Agricultural Research Service, U. S. Department of Agriculture.

(2) Certain other examples of isolation of amide salts have been reported. For example, see (a) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6215 (1955); (b) R. Gompper and P. Altreuther, *Z. Anal. Chem.*, **170**, 205 (1959).

(3) The corresponding quartet and triplet in *N-n*-butylpalmitamide occur at 3.30 and 2.25 ppm, respectively.

(4) (a) D. M. Brouwer and J. A. van Doorn, *Tetrahedron Lett.*, 3339 (1971); (b) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 580 (1970), and references cited therein.

(5) See E. L. Muetterties and E. G. Rochow, *J. Amer. Chem. Soc.*, **75**, 490 (1953), for previous examples.

(6) Commercial research grade BF<sub>3</sub> and HF were used directly.

(7) Long-chain aliphatic amides undergo chain-cleavage reactions under these conditions. We will report this in detail separately.

nmr (CDCl<sub>3</sub>) 11.15 (1 H, s), 9.12 (1 H, s), 3.52 (2 H, q), 2.74 (2 H, t), 2.0–0.6 ppm (20 H, m).

*Anal.* Calcd for C<sub>12</sub>H<sub>26</sub>NOBF<sub>4</sub>: C, 50.20; H, 9.13; N, 4.88.  
Found: C, 50.47; H, 9.33; N, 5.01.

**Registry No.**—**2a**, 36955-98-3; **2b**, 36994-06-6;  
**2c**, 36989-94-3; **2d**, 36989-95-4.