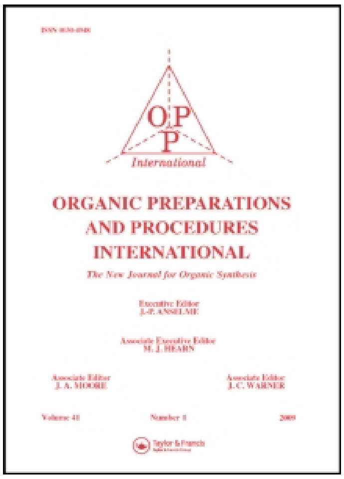

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A CONVENIENT PREPARATION OF 1-BROMO-2-FLUORONAPHTHALENE

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A CONVENIENT PREPARATION OF 1-BROMO-2-FLUORONAPHTHALENE

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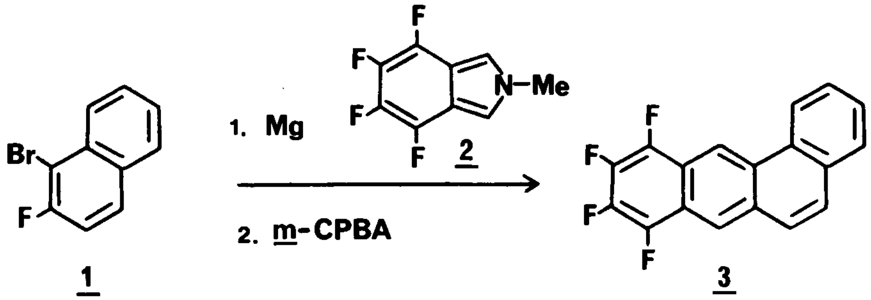
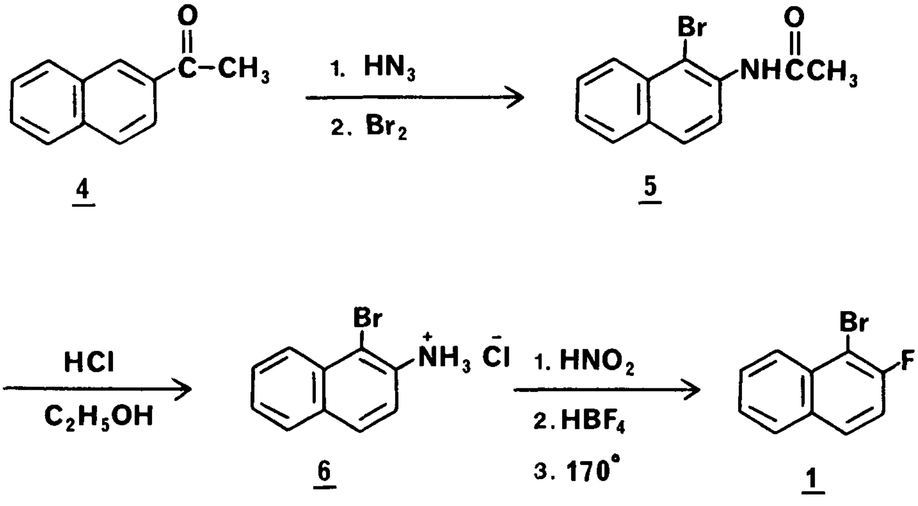
The aryne-azadiene coupling/oxidative deamination methodology is an efficient, convergent route to polycyclic aromatic hydrocarbons.[1,2] For example, the union of 1,2-naphthalyne (as generated from 1-bromo-2-fluoronaphthalene (1)) and 2-methyl-4,5,6,7-tetrafluoroisoindole (2) yields 8,9,10,11-tetrafluorobenz[a]anthracene (3) in 64% yield (two steps).[1]



We here report a convenient synthesis of 1-bromo-2-fluoronaphthalene (1) that avoids starting with the potent bladder carcinogen[3] (and no longer commercially available) 2-naphthylamine, which had been used previously to prepare 1,[4] and avoids purification of the nitrogen-containing intermediates.[5]

A Schmidt reaction[6] with commercially-available 2-acetylnaphthalene (4) followed by bromination in the same flask gives 1-bromo-2-acetonaphthalide (5). Crude 5 is hydrolyzed to 1-bromo-2-naphthylamine hydrochloride (6) (89% yield from 4), which is then subjected to a Schiemann reaction[7] to afford 1-bromo-2-fluoronaphthalene (1) in 47% yield after sublimation (42% yield from 4).



EXPERIMENTAL

1-Bromo-2-fluoronaphthalene (1).- To a magnetically stirred melt of 2-acetylnaphthalene (4) (34.0 g, 0.20 mol) in trichloroacetic acid (100 g) at 60° was added in small portions sodium azide (20.0 g, 0.31 mol), and the mixture was maintained at 60° for 12 h. The resulting foamy, yellow suspension of 2-acetonaphthalide was cooled to 25°, diluted with glacial acetic acid (300 mL), and then treated dropwise with a solution of bromine (32.0 g, 0.20 mol) in glacial acetic acid (50 mL). The resulting orange solution was poured over ice (100 g) and allowed to crystallize at 10° for 24 h. The resulting creamy white 1-bromo-2-acetonaphthalide (5)[8] was collected by filtration, washed with water, suspended in 95% ethanol (200 mL), treated with concentrated hydrochloric acid (100 mL), and then refluxed for 30 min. The clear golden solution was cooled to 25° and the resulting cream colored precipitate was collected by filtration, washed with water, and dried *in vacuo* to afford 40.0 g (77%) of 1-bromo-2-naphthylamine hydrochloride (6), mp 210-211° dec. The filtrate, upon basification and dichloromethane extraction, yielded an additional 5.2 g (12%) of 1-bromo-2-naphthylamine, mp 61-62° (lit.[9] mp 63°).

Without further purification a slurry of 6 (50 g, 0.19 mol) in concentrated hydrochloric acid (250 mL) cooled in an ice bath was treated with sodium nitrite (13.8 g, 0.20 mol) in portions. The mixture was stirred for 30 min at 0-5° and then treated slowly with 50% aqueous fluoboric acid (74 g, 0.42 mol). The resulting orange-brown mixture was stirred for 30 min and then the solid was collected by suction filtration, washed with water, slurried with ethanol, refiltered, and air dried to afford 1-bromo-2-naphthyldiazonium fluoborate as a yellow solid. (This step could also be carried out with a solution of sodium fluoborate (81 g) in water (75 mL)). The salt was placed in a vacuum sublimator and dried at 90°/0.1 torr for 1 h. The temperature was raised to 170° at which point decomposition began and the product deposited on the cold finger. (The evolved boron trifluoride was collected in a liquid nitrogen trap.) The crude sublimate (20.4 g) was resublimed to give 20 g (47%) of 1-bromo-2-fluoronaphthalene (1), mp 66-67°. Recrystallization from 50% ethanol gave colorless crystals, mp 67-68°; lit.[9] mp 69-70°. The original synthesis[4] reported mp 49°. The overall yield from 2-acetylnaphthalene is 42%.

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