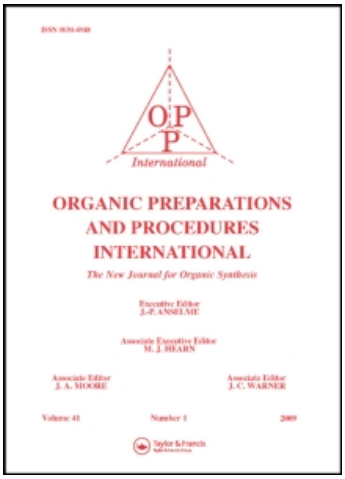

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AN IMPROVED SYNTHESIS OF 2-AMINOCARBAZOLE

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AN IMPROVED SYNTHESIS OF 2-AMINOCARBAZOLE

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(6/8/81)
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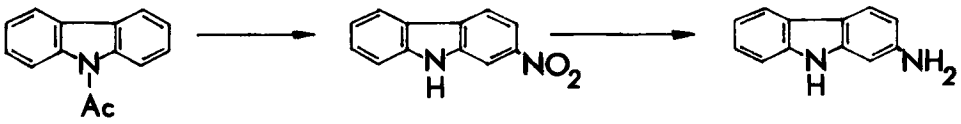
The direct route for the preparation of aromatic amines involving nitration and reduction could not be used for the synthesis of 2-aminocarbazole because nitration of carbazole and its 9-substituted derivatives gives a mixture of 1- and 3-nitro compounds. Friedel-Crafts acylation of 9-acetylcarbazole in the presence of aluminum chloride gives 2,9-diacetylcarbazole which can be converted to 2-aminocarbazole.[1] We now report a simple preparation of 2-aminocarbazole which employs Friedel-Crafts type nitration and subsequent reduction.



Exploratory experiments to determine optimal conditions showed that the best results (57% yield) were obtained with nitration in methylene chloride using two equivalents of nitryl chloride[2] in the presence of six equivalents of anhydrous aluminum chloride; 2-nitrocarbazole wad isolated by preparative thin layer chromatography. Replacement of aluminum chloride with titanium(IV) chloride caused the yield to decrease to 14%; boron trichloride and trifluoride were totally ineffective.

This method should be of practical value since we have found that nitryl chloride, which is hazardous and difficult to handle, could be replaced with silver nitrate without signifi-

cant decrease of the yield. In contrast to hydrogenation, the catalytic reduction of 2-nitrocarbazole with hydrazine hydrate proceeded smoothly to yield 2-aminocarbazole in a high state of purity; pure 2-aminocarbazole is relatively stable when free of impurities formed from reductions using hydrogen.

EXPERIMENTAL

2-Nitrocarbazole.- The mixture of 9-acetylcarbazole (20.0 g, 0.1 mole), aluminum chloride (80.0 g, 0.6 mole) and silver nitrate (34.0 g, 0.2 mole) in 600 ml of methylene chloride was stirred for 2 hrs at room temperature. The dark brown solution was diluted with methylene chloride (500 ml) and poured on ice containing conc. hydrochloric acid (250 ml). The organic layer was separated, dried and the solvent was evaporated to dryness. The yellow residue (16.5 g) was dissolved in 600 ml of 4% methanolic potassium hydroxide and refluxed for 2 hrs. Methanol (450 ml) was distilled, the solution was cooled and neutralized with 10% hydrochloric acid. The crude product (13.5 g) was collected and crystallized from isooctane to yield 9.5 g (45%) of 2-nitrocarbazole, as yellow needles, mp. 170-173°, lit.[3] mp. 174-175.5°.

IR (KBr): 730, 740, 830, 880 (C-H def.); 1350, 1525 (NO_2), 3080 (C-H); 3390 (N-H) cm^{-1}. MS, m/e: 213 (15.0), 212 (M^+, 100.0), 182 (36.6), 166 (77.8), 154 (19.2).

Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.77

Found: C, 67.86; H, 3.89

2-Aminocarbazole.- To the solution of 2-nitrocarbazole (2.12 g, 0.01 mole) in 50 ml of ethanol was added 0.5 g of 10% Pd/C.

Hydrazine hydrate (100%, 5.0 ml) was added dropwise and the mixture was refluxed for 2 hrs. The catalyst was removed by filtration and the crude product (1.69 g) was precipitated by addition of water. Recrystallization from toluene afforded 1.53 g (84%) of 2-aminocarbazole as colorless prisms, mp. 239-241° (sealed capillary), lit.[4] mp. 238-239° (dec.).

IR (KBr): 730, 770, 820, 850 (C-H def.); 1320, 1620, 3320, 3400 (NH_2) cm^{-1}. MS, m/e: 183 (15.1), 182 (M^+, 100.0), 181 (28.3), 154 (13.7), 127 (7.4).

Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53

Found: C, 79.17; H, 5.63

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REACTIONS OF N-AMINOPHTHALIMIDE WITH ELECTROPHILES. PREPARATION AND PROPERTIES OF SOME NEW TRIACYLHYDRAZINES

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In accord with the earlier results of Drew and Hatt,[1] N-aminophthalimide (I) undergoes rearrangement with refluxing di-