SYNTHESIS OF POLYCYCLIC INDOLES BY INTRAMOLECULAR RING-CLOSURE OF 1- AND 3-BENZOYLINDOLES BY PALLADIUM ACETATE

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Treatment of 1-benzoylindole in acetic acid with 0.5 equiv. of palladium(II) acetate at 110°C for 15 hr under nitrogen atmosphere afforded isoindolo[2,1-a]indol-6-one in 47% yield. Under similar conditions 1-aroylindoles (aroyl= p-methyl-, o-methyl-, p-chloro-, and o-chloro-benzoyl) reacted with palladium acetate to give the corresponding isoindolo[2,1-a]indol-6-ones in good yields, although a steric hindrance due to the ortho-substitution led to decreased yields of the ring-closed products.

Oxidation of 3-benzoylindoles by palladium acetate also afforded ring-closed products. Oxidation of 3-benzoyl-1-methylindole resulted in 60% yield of 5-methyl-5,10-dihydroindeno[1,2-b]indol-10-one. Furthermore, 3-benzoyl-1,2-dimethylindole reacted to give 4,5-dimethyl-4,6-dihydronaphth[3,2,1-c,d]indol-6-one in 31% yield, which, to our knowledge, belongs to a new class of compounds bridged at the peri-position of indole and is of interest in connection with framework synthesis for the formation of the ergot alkaloids. Under similar conditions 3-p-methylbenzoyl-1,2-dimethylindole reacted to give 4,5,9-trimethyl-4,6-dihydronaphth[3,2,1-c,d]indol-6-one in 23% yield. Attempted intramolecular coupling reactions of benzophenone and benzil led to failure, suggesting that the amide structure of 1-aroylindoles and the vinylog amide (β-amino-α,β-unsaturated ketone) structure of 3-aroylindoles might facilitate the intramolecular coupling.

No intramolecular ring-closure of 1- and 3-benzoylindoles by the other metal acetate, such as silver(I) acetate, cupric(II) acetate, nickel(II) acetate, and cobalt(II) acetate, was observed. However, when the oxidation of 3-benzoyl-1,2-dimethylindole was carried out with silver acetate, the 2-methyl group of the indole was converted into the formyl group.