Selective Oxidation of Side Chain at C-3 of Indoles and Carbazoles

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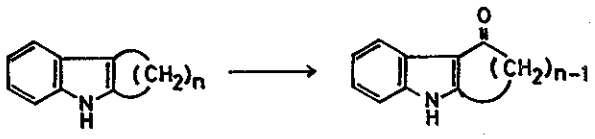
The selective oxidation of side chain at C-3 of indoles and carbazoles with dichlorodicyanobenzoquinone(DDQ) has been investigated.

Cycloalkan[b]indoles(I) were oxidized with 2 equivalents of DDQ in aqueous tetrahydrofuran at 0°C to give II(n=3, 53%; n=4, 83%; n=5, 90%; n=6, 60%; n=10, 96%).
Similarly, 3-substituted indoles(III) were converted to IV{R=H, 55%; R=CO_2Et, 46%; R=CH_2CO_2Et, 38%; R=2-pyridyl, 48%; R=CH(NHAc)CO_2Et, 84%}.

Furthermore, 3-indoleacetonitrile and 5,6,7,8,9,10-hexahydrocyclohept[b]indole-10-carbonitrile were prepared by oxidative cyanation of 3-methylindole and 5,6,7,8,9,10-hexahydrocyclohept[b]indole, respectively, with DDQ in methanol containing potassium cyanide though the yields were not satisfactory.

Carbazole-3-carboxaldehyde, 6-methylcarbazole-3-carboxaldehyde and 5,7-dimethylcarbazole-3-carboxaldehyde were obtained by treatment of 3-methylcarbazole, 3,6-dimethylcarbazole and 3,5,7-trimethylcarbazole in methanol solution with DDQ in 54-63% yields.

This mild and selective oxidation was applied to the syntheses of cycloheptaphylline(80% yield) from dihydrogirinimbine and of murrayacine(81% yield) from girinimbine



I II

III IV