SYNTHESES OF HETEROCYCLIC COMPOUNDS THROUGH o-QUINODIMETHANE INTERMEDIATES

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Novel syntheses of heterocyclic compounds and alkaloids by intra- and intermolecular cycloaddition of the imines with o-quinodimethanes or their chemical equivalents are reported.

1',2,2',3,3',4'-Hexahydro-5,6,6',7'-tetramethoxy-1-ketospiro[indene-2,1'-isoquinoline] is synthesized from 3,4-dihydro-1-(4,5-dimethoxybenzocyclobutenyl)-6,7-dimethoxyisoquinoline, whose hydrochloride gives 2,3,10,11-tetramethoxyprotoberberinium chloride on heating. Spirobenzylisoquinoline and ochotensine-type compounds are obtained directly from N-phenethyl-1-methylbenzocyclobutene-1-carboxamide by treatment with phosphoryl chloride. Yohimbones are synthesized from 1-benzocyclobutenyl-3,4-dihydro-β-carboline (I) hydrochloride by thermolysis as follows. Namely, thermolysis of the hydrochloride of I, followed by Birch reduction and acidic treatment and cycloaddition of benzocyclobutene to 3,4-dihydro-β-carboline followed by Birch reaction are carried out. On the other hand, the free base of I gives the spirobenzyl-1,2,3,4-tetrahydro-β-carboline which on photolysis and reduction affords yohimbane. The reaction of indole with pyridoxyl dibromide or pyridoxine diacetate gives a mixture of 3-methyl-10H-pyrido[3,4-b]carbazole and 3-methyl-6H-pyrido[4,3-b]carbazole, the latter of which is a main skeleton of the antitumor indole alkaloids, olivacine and elipticine.