SYHTHESES AND REACTIONS OF AZA- AND OXA-ANALOGUES OF NAPHTHO[a]CYCLOBUTENE

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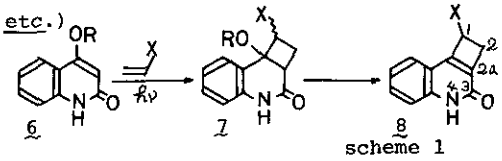
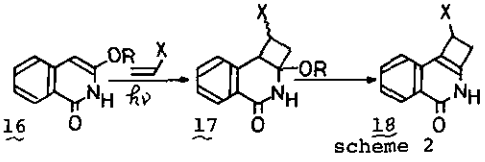
Syntheses: Intermolecular 2+2 cycloaddition of heteroaromatics (6, 13, etc.) having a β-alkoxy-enone function in their skeleton to olefins could be effected photochemically and the resulted adducts (7, 14) afforded the corresponding cyclobutane-fused heteroaromatics [e.g., 1,2-dihydrocyclobuta[c]quinolin-3(4H)-ones (8), 1,2-dihydrocyclobuta[c]coumarins (15), etc.] by elimination of an alcohol under appropriate conditions (scheme 1). In a similar manner, 1,2-dihydrocyclobuta[c]isoquinolin-4(3H)-ones (18) from 3-alkoxyisoquinolin-1(2H)-one (16) were accomplished (scheme 2). The two-step syntheses could be carried out in a preparative scale and proceeded in high overall yields (80-90%) from readily available starting materials (e.g. 6, 13, 16, etc.)



6 7 8

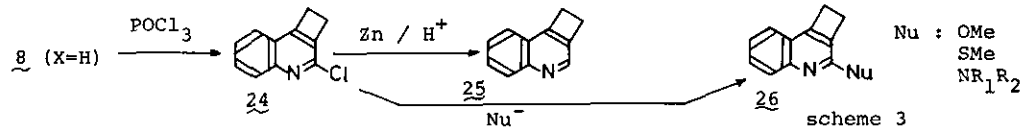
scheme 1



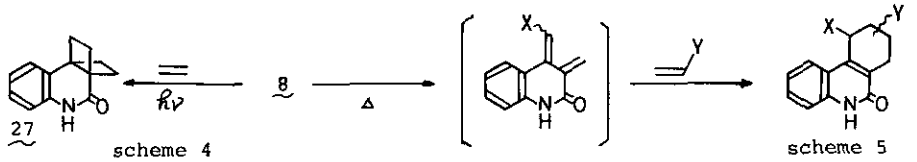
16 17 18

scheme 2

Reactions [Reactions are described using 1,2-dihydrocyclobuta[c]quinolin-3(4H)-ones (8) as typical examples]: a) Using 3-chloro-1,2-dihydrocyclobuta[c]quinoline (24) obtained by chlorination of 8 (X=H) by $POCl_3$ as a key intermediate, 1,2-dihydrocyclobuta[c]quinoline (25) and a variety of its 3-hetero-functionarized derivatives (26) were synthesized (scheme 3). b) Intermolecular photo 2+2 cycloaddition of 8 to olefins afforded novel benz[d]-3-aza-2-oxotricyclo[4.2.2.0]decanes (27, etc.) (scheme 4). c) 1,2-Dihydrocyclobuta[c]quinolin-3(4H)-ones (8) reacted with olefins via aza-o-quinodimethanes and hence can be used as synthons for organic synthesis for aza-analogues of benzocyclobutenes (scheme 5).



scheme 3



scheme 4 scheme 5