SYNTHESES OF 3-BROMO-x-METHYLQUINOLINES AND 2-BROMO-BENZO[f]QUINOLINE, AND REACTIVITIES OF THESE INTERMEDIATES

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Hydrolysis of 3-bromo-1-cyano-1,4-dimethoxy-1,2,3,4-tetrahydroquinoline(I), 3-bromo-1-cyano-1,4-dimethoxy-x-methylquinolines(II) and 2-bromo-4-cyano-1,3-dimethoxy-1,2,3,4-tetrahydrobenzo[f]quinoline(III) gave 3-bromoquinoline(IV), 3-bromo-x-methylquinolines(V) and 2-bromobenzo[f]quinoline(VI), respectively. I, II and III were obtained in excellent yields by addition reactions of bromine in MeOH on $\succ C^{\beta} = {}^{\gamma}C \prec$ bond of 1-cyano-1,2-dihydro-2-methoxyquinoline, 1-cyano-1,2-dihydro-2-methoxy-x-methylquinolines and 4-cyano-3,4-dihydro-3-methoxybenzo[f]-quinoline, which were prepared by treatment of quinoline, x-methylquinolines and benzo[f]quinoline with BrCN in MeOH, respectively. This provides an useful method for the preparation of hardly accessible V and VI.

Similarly 3,x-dibromobenzo[h]quinoline was obtained from benzo[h]quinoline, but 2-bromo-4,6-phenanthroline was not obtained from 4,6-phenanthroline(VII), because 6-cyano-5,6-dihydro-5-methoxy-4,6-phenanthroline was formed only by treatment of VII with BrCN in MeOH.

Furthermore, the reactivities of I was compared with those of III. The reactivity of 2-bromobenzo[f]quinoline N-oxide, which was prepared from VI, was investigated. While only 2-aminobenzo[f]quinoline was formed in excellent yield by treatment of VI with KNH_2 in liq.NH_3 and 1-aminobenzo[f]quinoline was entirely absent.