SYNTHESES OF DIHYDROXANTHENE DERIVATIVES BY THE INTRAMOLECULAR CYCLIZATION OF 3-SUBSTITUTED-6-(2-ALLYLPHENOXY)PYRIDAZINES

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Heating of 3-phenyl, 3-methyl, and 3-chloro-6-(2-methallylphenoxy)pyridazines (V and IX) in diethylaniline (DEA) produced 2-substituted-9a-methyl-1,9a-dihydroxanthenes (VI and X), previously unknown groups of compounds, by intra-molecular $(4+2)\pi$ cycloaddition reaction followed by the elimination of nitrogen molecule. Similar treatment of 3-phenyl-6-(2-allylphenoxy)pyridazine (XI) gave rise to 2-phenyl-1,9a-dihydroxanthenes (XII). Dehydrogenation of 2-phenyl-1.9a-dihydroxanthene (XIIa) with SeO_2 afforded 2-phenylxanthene (XIIIa) which were also obtained from 3-chloro-6-(2-allyl-4-phenylphenoxy)pyridazine (XIV) under the same condition.

3-Chloro-6-(2-allyl-4-ethoxycarbonylphenoxy)pyridazine (XXIV), with a labile chlorine atom on the heterocyclic ring, produced 2-chloro-7-ethoxycarbonyl-1,9a-dihydroxanthene (XXV) in a low yield at 150-160°. In contrast, XXIV gave 2-ethoxycarbonylxanthene (XXVII) and 2-chloro-7-ethoxycarbonyl-1,4-dihydroxanthene (XXVIII) at more elevated temperature.

The feature of the reaction of 3-methoxy-6-(2-allylphenoxy)pyridazine (XXIX) and the corresponding methylthio analog (XXXIV) were quite different. Heating of XXIX gave dihydroxanthene mixtures (XXX) as major products and trace xanthene (XXXI), while XXIV afforded 2-methylthioxanthene (XXXV) and XXXI in an almost equal ratio, indicating that CH_3S moiety works better as a leaving group than CH_3O moiety.