REACTION OF 3-EXOCYCLIC UNSATURATED 2,5-PIPERAZINEDIONE WITH ALCOHOLIC AND PHENOLIC HYDROXY GROUP

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In connection with the synthetic study on aspirochlorin, we wish to report the facile synthesis of the framework of didethioaspirochlorin and new syntheses of 3-aminocoumarin and -chroman derivatives.

1,4-Diacetyl-2,5-piperazinedione (PDO = 2,5-piperazinedione) was condensed with salicylaldehyde ir the presence of t-BuOK in DMF to give (Z)-3-salicylidene-PDO (1) and another unknown product. Subsequently, the latter was treated with 1 M HCl to give known 3-hydroxycoumarin, which was consistent with the product derived by the reaction of 3-(N-acetyl)-aminocoumarin with 1 M HCl.

On the other hand, when a solution of 1 in MeOH was irradiated by UV, the expected ccumarin derivative was also obtained quantitatively. From the result, it was supposed that the condensation of PDO with salicylaldehyde gave a mixture of (Z)- and (E)-isomers and that the latter was immediately converted into aminocoumarins.

In order to synthesize the desired spiro-PDO derivative, when (Z)-1 was treated with t-BuOCl in $CHCl_3$, spiro[3H-3-chlorobenzofuran-2,3'-(1'-acetyl-2',5'-dioxo)-piperazine] (2) was obtained as a mixture of two diastereomers in an almost quantitative yield. Furthermore, in a similar manner, so many spiro derivatives were synthesized and converted into 3-aminocoumarin derivatives.

Interestingly, it was found that further treatment of 2 with NaOMe or $ZnCO_3$ gave 3-(N-acetylglycyl)amino-3,4-dimethoxy- and 4-chloro-3-methoxychroman in good yields.