SYNTHESES OF SOME HETEROAROMATICS USING ETHOXYCARBONYLACETAMIDINE AND RELATED COMPOUNDS

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The synthesis and several reactions of α-ethoxycarbonylacetamidine (I) were investigated as follows:

1) Treatment of ethyl α-ethoxycarbonylacetimidate (II) with ammonium chloride afforded the pure hydrochloride of I. Based on the spectral data, I(free base) was considered to exist predominantly as the enamine form.

2) Reaction of I with β-dicarbonyl compounds gave ethyl 2-aminonicotinates (IV) instead of the pyrimidine derivatives. This fact suggested that the presence of an active methylene group on the amidines restricted the Pinner type pyrimidine formation.

3) Although the pathway of the reaction is not clear at present, the thermal condensation of I with equimolecular amounts of II afforded 4-amino-2-ethoxycarbonyl-4(3H)-pyrimidone (VI) in good yield.

4) When an ethereal solution of I and acrylonitrile was allowed to stand overnight, the Michael type reaction occurred and 2-ethoxycarbonyl-4-cyanobutyramidine (VIII) was obtained. On the treatment with acetylacetone, VIII was transformed to ethyl α-cyanoethyl-4,6-dimethyl-2-pyrimidineacetate (IX).

5) Based on the results described above, the reactions of I and related imidates with quinoline 1-oxide were examined to introduce a carbon substituent at the 2-position of the quinoline ring. Namely, quinoline 1-oxide reacted with I and II in the presence of benzoyl chloride to give ethyl α-amidino-2-quinolineacetate (XI) and diethyl 2-quinolinemalonimidate (XIIIa), respectively.