RING EXCHANGE REACTIONS OF N-SUBSTITUTED 3,5-DINITROPYRIDONE(2 OR 4) WITH SODIUM SALT OF ß-KETOESTERS

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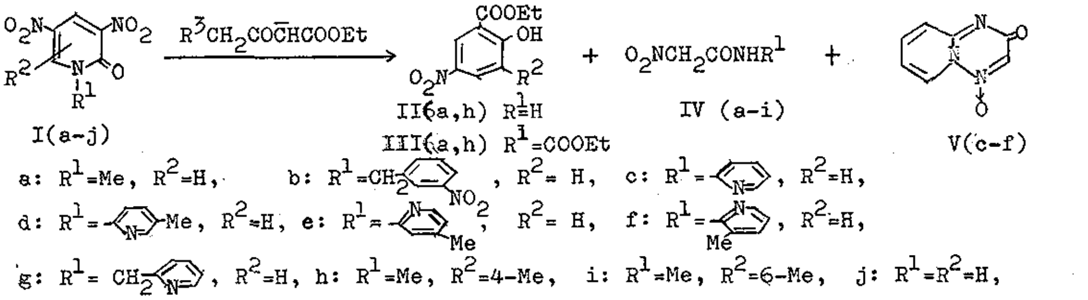
N-Substituted 3,5-dinitro-2-pyridones (Ia-j) underwent a ring exchange reaction, on treatment with sodium salt of ß-ketoesters ($R^3CH_2CO\bar{C}HCOOEt$ R^3=H or COOEt), to give ethyl 2-hydroxy-5-nitrobenzoates (II R^3=H, III R^3=COOEt) and corresponding N-substituted nitroacetamids ((IVa-i). In the case of I(c-f), in addition to II(III) and IV, 2-oxopyrido(1,2-b)triazine(1,2,4) 4-oxides (Vc-f) were obtained, which was assumed to be result of dehydrative cyclization of 1,6-dipole type IV.

The reaction course may be that a C-anion from ß-ketoester sodium salt attacks the 4 or 6-position to form Meisenheimer type complex, then another remaining nucleophilic center attacks 6 or 4-position to give bicyclo type intermediate, which is followed by bond fission in 1-6 and 3-4 bond of mother pyridoneto give II(III) and IV.



Which of the position 4 or 6 took the fast attack of C-anion was not definite, but when either of the two (4 or 6) was substituted by methyl group, the attack occurred at the occupied position.

N-Substituted 3,5-dinitro-4-pyridones(VIa-e) also was subjected to a ring exchange reaction to give corresponding N-substituted 3,5-diethoxycarbonyl-4-pyridones(VIIa-e). In this case the reaction center were 2 and 6-position of pyridone, and the bond fission may occurred at 2-3 and 5-6 bond. Although this reaction is different from the reaction of 2-pyridone in the position of reaction center and of bond fission, the reaction course may be similar to that described above.