SYNTHESES OF Δ^2-PYRROLIN-4,5-DIONES AND THEIR REACTION WITH BUTADIENE

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Several Δ^2-pyrrolin-4,5-diones(A) were synthesized by condensation of suitable enamines with oxalyl chloride. Acetophenone methylimine gave 1-Me-2-ph-A in 5% yield. Enamines prepared from β-ketoesters and β-diketones afforded satisfactory results. Thus, 2-ph-3-COOEt-A(I), 1-Me-2-ph-3-COOEt-A(II), 1-Me-2-COOEt-3-phCO-A, 1-ph-2-COOEt-3-phCO-A(III) and 1-ph-2-Me-3-COOEt-A were prepared. Formation of 1-oxo-2-(α-aminobenzylidene)-succinic anhydride(B) was also observed. B was converted to 2-ph-3-COOH-A on short treatment with alkali, and to ph-C(NH_2)=CHCO-COOMe(IV) by heating in MeOH, which afforded 2-ph-A on sublimation. A (yellow ~ red) easily take up protic solvent to form colorless adducts; these changes were illustrated by UV absorptions.

Heating of I with butadiene in CH_2Cl_2 or DMF at 120° gave an 1,2-adduct(10%), 2,3-dioxo-4-carboethoxy-5-vinyl-7-phenyl-4,7-cis-bicyclo[3,2,0]-1-azacycloheptane (V), while at 180° it gave 1,4-adduct(10%), Diels- Alder product (VI). The former was identical with the photoadduct of I and butadiene, and rearranged by acid treatment to VI. The yield of VI markedly increased by changing the solvent to Ac_2O. II gave analogous results, in which Ac_2O was not effective. III yielded at 120-140° an 1,4-adduct, Diels-Alder product (VII) and an abnormal adduct, 1-phenyl-2,3-dioxo-4-phenyl-6-vinyl-7-carboethoxy-2,3,6,7,7a-pentahydropyrano[4,3-b]pyrrole in ratio of 1:5, while at 180° it gave only VII.

These evidence indicated that the first step of the reaction is the formation of 1,2-adduct which rearranged thermally to 1,4-adduct. This apparant violence of the Woodward-Hoffman rule can be explained by nucleophilic addition of butadiene to C_2, then followed electrophilic C-C bond formation at C_3, giving cyclobutane derivative (1,2-adduct), which by 1,3-sigmatropic or ionic manner rearranged to an 1,4-adduct.