A New Condensation Reaction of β-Keto-δ-valerolactone with Substituted Aniline

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Abstract: A new condensation reaction of β -keto- δ -valerolactones was developed. The condensation products are composed of a pair of isomers because of the formation of intramolecular hydrogen bond. Their structures were confirmed by ¹HNMR and elemental analysis.

Keywords: Condensation reaction, β -keto- δ -valerolactone, intramolecular hydrogen bond.

Pyrones are important intermediates of pesticides and pharmaceuticals¹. Recently the biological activities of pyrone derivatives have drawn great interest, but few literatures on the biological activities of β -keto- δ -valerolactone derivatives were reported. The 3 position of β -keto- δ -valerolactones is particularly reactive, acylation can take place in this position²⁻³. Here we report a new condensation reaction of β -keto- δ -valerolactone, by means of which new carbon-carbon double bond was formed and a series of new anilinomethylene compounds were obtained.

Synthesis of this type of β -keto- δ -valerolactone **1b** was reported by Tanabe *et al*⁴, which required a separation of intermediate 5-hydroxy-3-oxo-octanoate. We improved the reaction by skipping the intermediate separation, which was more convenient for synthesis of **1b** and **1c**.



3a t $X_{n}=2,6-Cl_2, 2,6-Et_2, 2,6-Me_2, 4-Cl, 4-Br, 2,5-Cl_2, 2,4,5-Cl_3, 4-OMe, 4-Me, 2-Me.$

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In a general procedure, dianion of ethyl acetoacetate reacted with aldehyde in THF for 6h at 0°C, and was poured into ice-cooled water. The solution was allowed to stir overnight at room temperature, then acidified with diluted hydrochloric acid and extracted with ether to give light yellow crystals **1**. Heating **1** and substituted anilines **2** in the presence of ethyl orthoformate led to anilinomethylene compounds **3**. The products **3**, confirmed by ¹HNMR spectra, are composed of a pair of isomers **4** and **5**, the formation of which give rise to two types of intramolecular hydrogen bonds. The Chemical shift of hydrogen atom on nitrogen atom of **4**(**Z**) lies in lower field because of the electron-withdrawing effect of oxygen atom in the 1 position.



In order to elucidate the reaction mechanism, we postulated the structure of intermediate **6**, and by checking with GCD (Gas-Chromatograph Detector) technique the molecular ion m/z 212 was formed.



References and Notes

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