MELDRUM'S ACID IN ORGANIC SYNTHESIS.
NEW SYNTHESES OF INDOLEPROPIONIC ESTERS AND β-KETOESTERS

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Because of the cyclic structure, Meldrum's acid (1), 2,2-dimethyl-1,3-dioxane-4,6-dione, is expected to be more reactive than usual malonic esters and to apply for new malonic ester syntheses. We report here new efficient and widely applicable one-pot syntheses of indolepropionic esters and β-ketoesters; both types of compounds are necessary to synthesize ellipticine analogs.

1) Synthesis of Indolepropionic Esters

An MeCN solution of indole, acetaldehyde, and 1 was allowed to stand at 30° for 7 hr to give a condensation product (2, R=Me) in 98% yield. Under similar conditions, twelve aldehydes involving aliphatic with a straight or branched chain and aromatic ones with an electron-donating or electron-withdrawing substituent gave also the corresponding products (2) in high yields. A pyridine-EtOH solution of 2 (R=Me) was refluxed in the presence of a small amount of Cu-powder to give the *indolepropionic ester* (3, R=Me) in 80% yield. The both reactions were carried out in one-pot. Similarly, other 2 readily gave the corresponding esters (3).

2) Synthesis of β-Ketoesters

Propionyl chloride and 1 reacted nearly quantitatively in the presence of pyridine at 0° to give an acylation product (4, R=Et). Similarly, various chlorides gave the corresponding 4 in high yield. Ethanolysis of 4 without puruification in boiling EtOH easily gave β-keto ethyl esters (5). Alcoholysis with MeOH, $C_6H_5CH_2OH$, and t-BuOH under similar conditions gave Me-, $C_6H_5CH_2$-, and t-Bu-esters, respectively. Alcoholysis with allyl alcohols also gave the corresponding esters, which were applied to Carroll reaction to afford several γ,δ-unsaturated ketones. Finally, 4 was applied to indole synthesis. Thus, heating of 4 with *phenylhydroxylamine gave 2-substituted indoles.*