

SYNTHESIS OF HETEROCYCLES USING ACYL MELDRUM'S ACIDS
REACTIONS WITH AROMATIC HYDROXYLAMINES

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Acyl Meldrum's acids (1, acyl; CH_3CO , $\text{C}_2\text{H}_5\text{CO}$, $\text{C}_3\text{H}_7\text{CO}$, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{CO}$, $\text{CH}_3\text{COC}_2\text{H}_4\text{CO}$, $\text{CH}_3\text{O}_2\text{CC}_2\text{H}_4\text{CO}$, $\text{CH}_3\text{O}_2\text{CC}_4\text{H}_8\text{CO}$, $\text{C}_6\text{H}_5\text{CO}$, $\text{C}_6\text{H}_5\text{CH}_2\text{CO}$), synthetic equivalent of "mixed diketene", are now applied to new syntheses of 2-substituted indoles and isoxazolones.

Treatment of phenylhydroxylamine (2) with 1 gave quite easily β -ketoamides (3), which were converted to N,O-diacylacetylated compounds (4) by another treatment with 1. When heated in toluene, 4 gave 2-substituted indoles (5, ~58%) accompanied by the formation of 5-substituted isoxazolones (6). N-Benzoylphenylhydroxylamine (7) was converted to the O-acylacetylated compound (8), which gave readily 2-substituted N-benzoylindoles (9). N-Acetyl and N-benzyloxycarbonylphenylhydroxylamines also gave similar results. When β -ketoamides (3) were heated in anhydrous xylene, 2-substituted indoles (5) were isolated in fair yields (~67%). This simple thermal formation of indoles presumably involves a radical mechanism, because the reaction was markedly accelerated by the addition of a little azobisisobutyronitrile and inhibited by diphenylpicrylhydrazyl.

When heated in benzene in the presence of acid, 3 gave 5-substituted isoxazolones (6) instead of 5 in good yields (~97%).