

Solvent Free Oxidation of β , β -Disubstituted Enamines under Microwave Irradiation.

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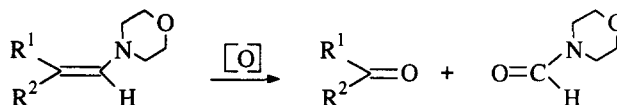
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Abstract : Ketones and formamides are formed by cleavage of β , β -disubstituted enamines over $\text{KMnO}_4/\text{Al}_2\text{O}_3$ without solvent under microwave irradiation. The comparison was made between domestic oven, focused oven and classical heating.

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The oxidative cleavage of β , β -disubstituted enamines to ketones in homogeneous medium has been extensively studied with various reagents such as NaIO_4 , $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$, HNO_2 and O_2 with copper ion systems¹. These procedures lead to moderate to good yields.



As part of our program related to organic synthesis without solvent under microwave irradiation² we studied this reaction using various solid supports under three means of activation : domestic microwave oven, focused microwave oven and oil bath.

Our first experiments realized with $\text{K}_2\text{Cr}_2\text{O}_7$, CrO_3 , MnO_2 and NaIO_4 over montmorillonite clay K_{10} under focused microwave irradiation in various conditions (temperature, power, time) led to the hydrolysis of the enamine. In order to avoid this, we tried MnO_2 over bentonite which was successfully applied to oxidation of alcohols³⁻⁶ but again hydrolysis was the main reaction although small yields of ketones were obtained. During the mean time, this cleavage over alumina supported potassium permanganate in acetone solution during 4 hours at room temperature was reported⁷. Accordingly we tried this reagent without solvent during 15 minutes under microwave or classical heating. The results are summarized in the following table.

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Enamine	Product	Yield ^a %		Oil bath
		Domestic oven ^b	Focused oven ^c	
		73	83	d
		60	77	d
		11	11	d

a) isolated yields. b) 255 W, 82°C. c) 300 W, 140°C. d) 140°C, no ketone. e) ref 7, 60% yield. f) in this case, hydrolysis is the major process.

These experiments clearly show a specific (non thermal) effect of microwaves⁸, as conventional heating only leads to hydrolysis products. Furthermore, homogeneous irradiation in the focused microwave oven⁹ is more efficient than heterogeneous irradiation in the domestic oven. The procedure is very simple : $\text{KMnO}_4/\text{Al}_2\text{O}_3$ is prepared according to the literature⁷ and dried 15 minutes in the domestic microwave oven (255 W). Then the mixture of enamine (3 mmol), 1.33g of $\text{KMnO}_4/\text{Al}_2\text{O}_3$ is irradiated or heated.

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