Pergamon

Tetrahedron Letters 39 (1998) 541–542

TETRAHEDRON LETTERS

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

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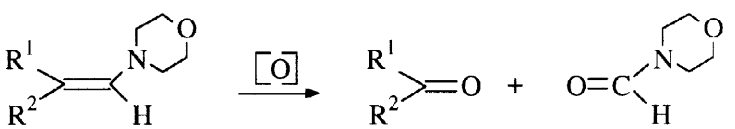
Received 22 October 1997; accepted 10 November 1997

Abstract *:* Ketones and formamides are formed by cleavage of β,β-disubstituted enamines over $KMnO_4/Al_2O_3$ without solvent under microwave irradiation. The comparison was made between, domestic oven, focused oven and classical heating.

The oxidative cleavage of β, β-disubstituted enamines to ketones in homogeneous medium has been extensively studied with various reagents such as $NaIO_4$, $K_2Cr_2O_7/H_2SO_4$, m-$ClC_6H_4CO_3H$, HNO_2 and O_2 with copper ion systems[1]. These procedures lead to moderate to good yields.



As part of our program related to organic synthesis without solvent under microwave irradiation[2] 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 $K_2Cr_2O_7$, 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 alcohols[3-6] 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 reported[7]. 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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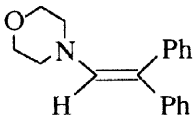
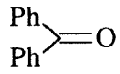
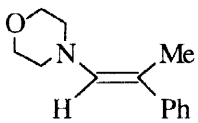
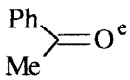
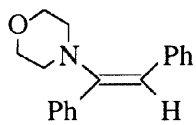
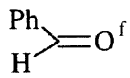
0040-4039/98/$19.00
PII: S0040-4039(97)10623-2

Enamine	Product	Yield[a] % Domestic oven[b]	Yield[a] % Focused oven[c]	Oil bath
		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 microwaves[8], as conventional heating only leads to hydrolysis products. Furthermore, homogeneous irradiation in the focused microwave oven[9] is more efficient than heterogeneous irradiation in the domestic oven. The procedure is very simple : $KMnO_4/Al_2O_3$ is prepared according to the literature[7] and dried 15 minutes in the domestic microwave oven (255 W). Then the mixture of enamine (3 mmol), 1.33g of $KMnO_4/Al_2O_3$ is irradiated or heated.

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