SHORT PAPER

J. Chem. Research (S),
2002, 556–557

Microwave assisted convenient and facile regeneration of carbonyl compounds from oximes, semicarbazones and phenylhydrazones using silica supported ceric ammonium nitrate[1†]

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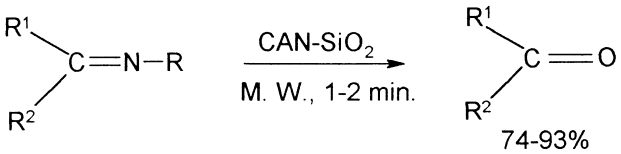
Microwave assisted efficient regeneration of carbonyl compounds from the corresponding oximes, semicarbazones and phenylhydrazones has been developed by using silica supported ceric ammonium nitrate.

Keywords: oximes, semicarbazones, phenylhydrazones, carbonyl compounds, silica supported ceric ammonium nitrate

Oximes, semicarbazones and phenylhydrazones are frequently used as important derivatives for purification, characterisation and protection of carbonyl compounds.[2] The efficient regeneration of carbonyl compounds from these derivatives is very useful. Ceric ammonium nitrate (CAN) is one of the oxidants which has been used[3] earlier for this purpose. The reagent was applied under different conditions. In one of the procedures low reaction temperatures (0°C or below) were employed to get good yields of the carbonyl compounds from the corresponding oximes and semicarbazones.[3a] However, the choice of solvents was a problem due to the low solubility of substrates and reagent at low temperatures. In other method[3b] aromatic aldoximes were oxidised with CAN in acetonitrile or propionitrile at high temperature (70–75°C) to generate aldehydes in low yields along with a mixture of products.

In continuation of our work[4] on solid supported reactions we recently observed that silica supported CAN (CAN-SiO_2) can efficiently be utilised for microwave assisted regeneration of aldehydes and ketones from the corresponding oximes, semicarbazones and phenylhydrazones.



R^1 = alkyl or aryl; R^2 = H, alkyl or aryl
R= -OH, $-NHCONH_2$ or -NHPh

Several oximes, semicarbazones and phenyihydrazones were mixed thoroughly with CAN-SiO_2 and irradiated under microwave irradiation for 1–2 min (Table 1). No any solvent was used. The parent carbonyl compounds were generated in high yields (74–93%). The structures of all the products were settled by direct comparision with authentic samples. CAN-SiO_2 is more convenient to handle than CAN alone as

Table 1 Regeneration of carbonyl compounds from their oximes, semicarbazones and phenylhydrazones

Entry	R^1	R^2	R	Time/min	Isolated yield/%
1	C_6H_5	H	OH	1.5	88
2	4(OH) C_6H_4	H	OH	1.5	82
3	4(OMe) C_6H_4	H	OH	1.0	82
4	3,4$(OMe)_2$ C_6H_3	H	OH	1.0	84
5	C_6H_5	CH_3	OH	1.5	92
6	4(OMe) C_6H_4	CH_3	OH	1.5	90
7	C_6H_5	C_6H_5	OH	2.0	93
8	C_7H_{15}	H	OH	1.5	86
9	C_9H_{19}	H	OH	1.5	84
10	C_6H_5	H	$NHCONH_2$	1.5	89
11	4(OH) C_6H_4	H	$NHCONH_2$	2.0	81
12	4(OMe) C_6H_4	H	$NHCONH_2$	1.0	88
13	3,4$(OMe)_2$ C_6H_3	H	$NHCONH_2$	1.5	84
14	C_6H_5	CH_3	$NHCONH_2$	1.5	88
15	4(OMe) C_6H_4	CH_3	$NHCONH_2$	1.5	85
16	C_6H_5	C_6H_5	$NHCONH_2$	2.0	92
17	C_7H_{15}	H	$NHCONH_2$	1.5	88
18	C_6H_5	H	NHPh	1.5	82
19	4(OH) C_6H_4	H	NHPh	2.0	74
20	4(OMe) C_6H_4	H	NHPh	2.0	76
21	3,4$(OMe)_2$ C_6H_3	H	NHPh	1.5	80
22	C_6H_5	CH_3	NHPh	1.5	84
23	C_6H_5	C_6H_5	NHPh	2.0	82

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

the latter which is hygroscopic when mixed with a carbonyl compound generally forms paste. The yields of the regenerated carbonyl compounds are also somewhat higher (10–20%) when CAN-SiO_2 is used. Moreover, in some cases unsupported CAN produced a mixture of products.

In conclusion, we have developed an efficient microwave promoted solvent free method for regeneration of carbonyl compounds from their oximes, semicarbazones and phenylhydrazones. The reagent can easily be prepared. The experimental process is very simple and environmentally benign. The low solubility of the derivatives will create no problem for their conversions. We hope the present deprotection method will make a useful addition to the existing procedures.

Experimental

4-Hydroxybenzaldoxime (137 mg, 1 mmol) was mixed thoroughly with CAN-SiO_2 (600mg containing 20% CAN, prepared by reported method[5]). The mixture was kept in an alumina bath inside a microwave oven (BPL, BMO, 700T, 466W and irradiated for 1.5 min. The mixture was removed from the oven, cooled and shaken with $CHCl_3$ (10 ml). After filtration the filtrate was concentrated and subjected to column chromatography over silica gel to yield the pure 4-hydroxybenzaldehyde (100 mg, 82%).

The authors thank CSIR, New Delhi for financial assistance.

Received 2 March 2002; accepted 9 June 2002
Paper 02/1271

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