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Solvent-Free Conversion of N,N-Dimethylhydrazones to Nitriles Under Microwave Irradiation

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SOLVENT-FREE CONVERSION OF N,N-DIMETHYLHYDRAZONES TO NITRILES UNDER MICROWAVE IRRADIATION

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Abstract : A variety of aldehyde N,N-dimethylhydrazones are rapidly converted into the corresponding nitriles using oxone supported on wet Al_2O_3 under microwave irradiation in dry media.

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Organic synthesis on solid supported reagents coupled with microwaves (in dry media) is currently a matter of increasing interest due to its greater selectivity, enhanced reaction rates, cleaner reaction products and operational simplicity.[1] Additionally, microwave-assisted reactions are novel, more efficient, convenient and provide solvent free condtions. The conversion of aldehyde to nitrile is an important process in organic synthesis. Several procedures are available for this transformation,[2] among these, the oxidative conversion of N,N-dimethylhydrazones to nitriles is of interest. Aldehyde N,N-dimethylhydrazones are converted into the corresponding nitriles by non-oxidative procedures[3] *via* N,N,N-trimethyl hydrazonium salts or directly in

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hyperbasic media, but they require high temperature and strong basic conditions. Several oxidative methods[4] have been reported to carry out the reaction under mild conditions which include H_2O_2, H_2O_2-SeO_2, H_2O_2-PMA, m-CPBA and MMPP etc. The use of H_2O_2 alone or in combination with other catalysts gave unsatisfactory yields with aliphatic aldehyde hydrazones and also they require several hours to accomplish the reaction. Eventhough, H_2O_2-MTO[5] and dimethyl dioxirane[6] have been employed successfully for conversion of both aromatic and aliphatic aldehyde hydrazones to nitriles, they employ large quantities of organic solvents and hazardous peracids which require aqueous work-up and generates large volumes of effluents.

$$\underset{\mathbf{1(a\text{-}m)}}{R\text{-}CH{=}NN(CH_3)_2} \xrightarrow[\text{M.W.}]{\text{Oxone-wet } Al_2O_3} \underset{\mathbf{2(a\text{-}m)}}{R\text{-}C{\equiv}N}$$

Scheme

In continuation of our work on solid supported reagents coupled with microwaves,[7] herein we report a facile solid state conversion of aldehyde hydrazones to their corresponding nitriles in high yields by oxone- wet Al_2O_3. The reaction proceeds efficiently under microwave irradiation in solvent-free condition. A variety of aldehyde hydrazones are converted into nitriles in good yields in a short reaction time whereas ketone N,N-dimethylhydrazones are simply transformed to the corresponding parent carbonyl compounds under the present reaction conditions. The results summarised in table depict the generality of the reaction for various substrates including aliphatic, aromatic, heterocyclic and α,β-unsaturated aldehydes containing both electron donating and electron withdrawing substituents in the aroamtic ring. It is of interest to observe that oxone-wet Al_2O_3 offers low yield of products after a long

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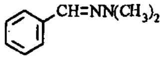
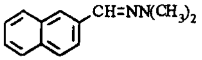
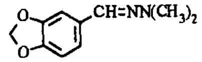
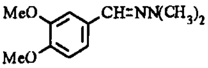
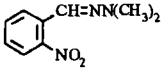
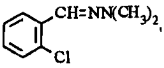
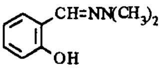
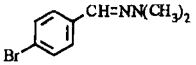
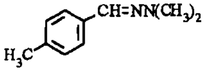
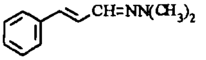
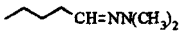
Table : Conversion of N,N-dimethyl hydrazones to nitriles under microwave

entry	Substrate	time (min.)	Yield[a] (%)	m.p(°C) / b.p(°C)/Torr found	m.p(°C) / b.p(°C)/Torr reported[7]
a.		6	78	191-93/760	190-191/760
b.		8	74	64-65	66
c.		5	83	67-68	68-69
d.		5	87	91-92	93
e.		10	72	108-109	110
f.		6	84	41-42	42-43
g.		7	76	93-94	94-95
h.		8	81	112-13	114
i.		5	88	217-19/760	216-217/760
j.		5	83	255-57/760	254-55/760
k.		4	85	192-193/760	192/760
l.		5	68	71-73/10	69-72/10
m.		6	71	223-225/760	224/760

a : Solids were purified by crystallisation and liquids by column chromatography on silica gel and isolated yields after purification.

reaction time at room temperature, this clearly indicates the role of microwave in enhancing reaction rates and yields of the products. We have carried out this transformation using different oxidising agents like H_2O_2-Al_2O_3 and t-butylhydroperoxide-Al_2O_3, which are limited only to the dimethyl hydrazones of simple aromatic aldehydes and aldehydes containing alkoxy groups in the aromatic ring. To know the effect of solid supports in this transformation, oxone has been supported on different solids like SiO_2, KSF or Al_2O_3 and the reactions were carried out with a typical substrate, benzaldehyde N,N-dimethylhydrazone. Oxone supported on SiO_2 gave 60% yield of benzonitrile after 6 min under microwave irradiation operating at 650 watts. Oxone supported on KSF clay afforded 45% yield of benzonitrile whereas oxone supported on wet Al_2O_3 found to offer 78% yield of benzonitrile under similar reaction conditions. Oxone-wet Al_2O_3 is found to be stable, effective and environmentally benign oxidant for this conversion.

In conclusion, we described a novel, efficient and rapid method for the solid state conversion of aldehyde hydrazones to nitriles using solid reagent system, oxone-Al_2O_3, under microwave irradiation. The use of inexpensive oxidising agent and non-solvent reaction conditions makes this procedure more economic and ecofriendly.

EXPERIMENTAL

Aldehyde N,N-dimethylhydrazone (5 mmol) and peroxymonosulfate (5 mmol) were admixed with wet alumina (3 g) and subjected to microwave irradiation at 650 watts (BPL, BMO-700T) for an appropriate time (Table). After complete conversion, as indicated by TLC, the inorganic support was separated by filteration, after triturating the product with dichloromethane (2

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x 20 ml). After removing the solvent *in vacuo,* the resulting crude product was purified on silica gel column chromatography to afford pure corresponding nitrile.

Representative data for Compound 1b : ^{1}H NMR ($CDCl_3$) : δ 3.0 (s, 6H, $N(CH_3)_2$), 7.40-7.50 (m, 3H), 7.85 (s, 1H, CH=N), 7.8-8.05 (m, 4H). IR (KBr) : υ 1595 cm^{-1}, CH=N.

Compound 2b : ^{1}H NMR ($CDCl_3$) : δ 7.45-7.55 (m, 3H), 7.85-8.1 (m, 4H). IR (KBr) : υ 2215 cm^{-1}, C≡N.

Compound 1c : ^{1}H NMR ($CDCl_3$) : δ 2.9 (s, 6H, $N(CH_3)_2$), 5.95 (s, 2H), 6.70 (dd, 1H, J = 8.4 & 0.6 Hz), 6.85 (dd, 1H, J = 8.4 and 2.6 Hz), 7.15 (dd, 1H, J = 2.6 & 0.6 Hz), 7.2 (s, 1H). IR (KBr) : υ 1590 cm^{-1}, CH=N.

Compound 2c : ^{1}H NMR ($CDCl_3$) : δ 6.0 (s, 2H), 6.75 (dd, 1H, J = 8.4 & 0.6 Hz), 6.90 (dd, 1H, J = 8.4 & 2.6 Hz), 7.25 (dd, 1H, J = 2.6 & 0.6 Hz). IR (KBr) : υ 2220 cm^{-1}, C≡N.

Compound 1h : ^{1}H NMR ($CDCl_3$) : δ 2.95 (s, 6H, $N(CH_3)_2$), 7.10 (s, 1H, CH=N), 7.39 (m, 4H). IR (KBr) : υ 1590 cm^{-1}, CH=N.

Compound 2h : ^{1}H NMR ($CDCl_3$) : δ 7.40 (m, 4H). IR (KBr) : υ 2210 cm^{-1}, C≡N.

Compound 1m : ^{1}H NMR ($CDCl_3$) : δ 0.80 (t, 3H), 1.35 (m, 12H), 2.30 (m, 2H), 6.6 (m, 1H), 2.7 (s, 6H, $N(CH_3)_2$). IR (KBr) : υ 1585 cm^{-1}, CH=N.

Compound 2m : ^{1}H NMR ($CDCl_3$) : δ 0.85 (t, 3H), 1.40 (m, 12H), 2.35 (t, 2H). IR (KBr) : υ 2240 cm^{-1}, C≡N.

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