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Synthesis of Nitriles from Aldoximes Using Silica Gel as Catalyst Under Microwave Irradiation

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ABSTRACT

A rapid and efficient synthesis of nitriles via dehydration from the corresponding aldoximes has been carried out in the presence of Silica gel as catalyst under microwave irradiation in 83–95% yield.

Key Words: Aldoximes; Dehydration; Nitriles; MW.

Nitriles can be prepared from the corresponding oximes via dehydration (Sch. 1) by a variety of methods employing reagents like trimethylamine/sulphur dioxide,^[1] zeolites,^[2] sulphuryl chloride fluoride,^[3] etc. But most of them suffer from some limitations such as longer reaction times,

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Scheme 1.

expensive reagents, low yields, drastic reaction conditions and tedious work-up. So, we became interested in developing a new, rapid and efficient method.

We thought of using Silica gel as the inexpensive acidic catalyst in combination with microwave irradiation in dry media. Microwave activation as a non-conventional energy source has become a very popular and useful technology in organic chemistry and reactions under solvent-free conditions do away with the safety hazards associated with low boiling solvents.^[4]

A variety of aldoximes (*syn* as well as *anti*) such as benzaldoximes, *p*-methoxy benzaldoximes, *o*-hydroxy benzaldoximes, *p*-hydroxy-3-methoxy benzaldoximes were dehydrated to the corresponding nitrile in 83–95% yield in 1–3 min. The results obtained are recorded in Table 1. The products were identified on the basis of NMR, IR, and mass spectra and by comparison of their m.p./b.p. and R_f values with those of the authentic samples prepared by standard routes reported in the literature.^[5] Both the *syn* and *anti* forms gave comparable yields.

CONCLUSION

We have developed a new, simple, and efficient method for the dehydration of aldoximes into nitriles under microwave irradiation using silica gel as an inexpensive, easy to handle, and environmentally friendly catalyst.

TYPICAL EXPERIMENTAL PROCEDURE

Benzaldoxime (prepared by standard method reported in the literature),^[5] (0.121 g, 1 mmol) was mixed with Silica gel (3 in an Erlenmeyer flask (100 mL) and irradiated at 560 W for 1–3 min in an unmodified domestic Microwave oven (Kenster OM-9925E, 800 W, operating at 2450 MHz). The flask was taken out, cooled and ether (50 mL) was added. The catalyst was filtered off and the resultant solution evaporated to afford the desired nitrile. Silica gel G used in these studies was from



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Table 1. Dehydration of aldoximes into nitriles in the presence of silica gel under microwave irradiation.

| Entry no. | Product | Irradiation condition | Time (min) | % yield | M.p./b.p. (760 mm) in °C | |
|-----------|----------------------------------|-----------------------|------------|---------|--------------------------|--------------------|
| | | | | | Observed | Lit. |
| 1 | Benzonitrile | 560 W | 2 | 84 | 190 | 191 ^[5] |
| 2 | 4-Methoxy benzonitrile | 560 W | 1 | 91 | 58.5 | 59 ^[6] |
| 3 | Cinnamonitrile (trans) | 560 W | 2 | 85 | 254 | 255 ^[5] |
| 4 | 2-Hydroxy benzonitrile | 560 W | 3 | 83 | 94.5 | 95 ^[6] |
| 5 | 4-Hydroxy benzonitrile | 560 W | 1 | 91 | 110 | 110 ^[6] |
| 6 | 3,4-Dimethoxy benzonitrile | 560 W | 1 | 96 | 62.5 | 63 ^[6] |
| 7 | 2-Nitro Benzonitrile | 560 W | 2 | 83 | 110 | 111 ^[5] |
| 8 | 4-Hydroxy-3-methoxy benzonitrile | 560 W | 1 | 95 | 87 | 88 ^[6] |

Merck. TLC was done on Silica Gel G plates with benzene–ethyl acetate (2:1) system. The physical analysis of the products is as follows:

Benzonitrile (1). ¹H-NMR (CCl₄), 7.5 (m, 5H, Ar-H); IR (neat) 3030 (C-H str.), 2240 (C≡N str.), 1500 & 1450 (C-C str.); b.p. 190°C (bulb to bulb distillation) Rf: 0.33.

4-Methoxy benzonitrile (2). ¹H-NMR (CCl₄), 3.8 (s, 3H, -CH₃), 7.0 (m, 2H, Ar-H), 7.6 (m, 2H, Ar-H); IR (neat) 2940 (C-H str.), 2170 (C≡N str.), 1610 & 1540 (C-C str.); m.p. 58.5°C, Rf: 0.39.

Cinnamonitrile (trans) (3). ¹H-NMR (CCl₄), 5.8 (d, 1H, =CH-CN, *J* = 17 Hz), 7.35 (d, 1H, =CH-Ph, *J* = 17 Hz), 7.4 (m, 5H, Ar-H), IR (neat) 3030 (=CH str.) 2220 (C≡N str.). 1610, 1560 & 1450 (C-C str.); b.p. 254°C (bulb to bulb distillation), Rf: 0.37.

2-Hydroxy benzonitrile (4). ¹H-NMR (CDCl₃), 6.16 (br, 1H, -OH), 6.95–7.04 (m, 2H, Ar-H), 7.4–7.51 (m, 2H, Ar-H); IR (neat) 3264 (OH str.), 2232 (C≡N str.), 1560, 1503 & 1454 (C-C str.); m.p. 94.5°C, Rf: 0.36.

4-Hydroxy benzonitrile (5). ¹H-NMR (DMSO), 7.0 (m, 2H, ArH), 7.6 (m, 2H, ArH) 10.4 (s, 1H, -OH); IR (neat) 3333 (OH str.), 2222 (C≡N str.). 1587, 1493 & 1449 (C-C str.); m.p. 110°C, Rf: 0.35.



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3,4-Dimethoxy benzonitrile (6). $^1\text{H-NMR}$ (CDCl_3), 3.8 (s, 3H, $-\text{OCH}_3$), 3.9 (s, 3H, $-\text{OCH}_3$) 6.9 (m, 1H, ArH), 7.0 (m, 2H, ArH); IR (neat) 2940 (C-H str.), 2220 ($\text{C}\equiv\text{N}$ str.), 1610, 1540 & 1450 (C-C str.); m.p. 62.5°C , Rf 0.41.

2-Nitro benzonitrile (7). $^1\text{H-NMR}$ (CDCl_3), 7.81–7.87 (m, 1H, ArH) 7.91–7.96 (m, 1H, ArH), 8.33–8.39 (m, 1H, ArH), IR (neat) 3050 (C-H str.), 2225 ($\text{C}\equiv\text{N}$ str.), 1540 & 1340 ($-\text{NO}_2$ str., Arom); m.p. 110°C , Rf: 0.34.

4-Hydroxy-3-methoxy benzonitrile (8). $^1\text{H-NMR}$ (CDCl_3), 3.93 (s, 3H, $-\text{CH}_3$), 6.98 (d, $J=8.0$ Hz, 1H, ArH), 7.09 (s, 1H, ArH) 7.23 (d, $J=8.0$ Hz, 1H, ArH); IR (neat) 3364 (OH str.), 2955 (C-H str.), 2225 ($\text{C}\equiv\text{N}$ str.), 1590, 1515 & 1458 (C-C str.); m.p. 87°C , Rf: 0.38.

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