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TETRACHLOROPYRIDINE: A NEW REAGENT FOR THE DEHYDRATION OF ALDOXIMES UNDER MICROWAVE*

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ABSTRACT

Dehydration of aldoximes to nitriles using tetrachloropyridine under microwave in dry media is described. The procedure is applicable to a variety of aldoximes and the reagent can be recycled and reused.

Dehydration of aldoximes to nitriles is an important transformation in organic synthesis. The classical methods[1–9] of dehydration include trifluoroacetic anhydride, chlorosulphonyl isocyanate, diphosphorus tetraiodide, selenium dioxide, 4,6-diphenyl-2-methylthiopyrylium tetrafluoroborate, copper(II)acetate and the triphenylphosphine carbon tetrachloride system. Most of those methods require excess of solvent for reaction and the catalyst remains as a waste.[10,11] However, zeolites[12] or clay[13–18] are reported as reusable catalysts but they suffer from harsh reaction conditions

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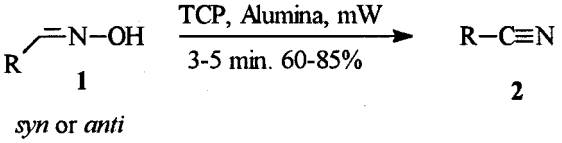
and longer reaction time.[19] Therefore a convenient and eco-friendly method for dehydration is desirable. Recently microwave assisted reactions is an area of growing interest because of its distinct advantages like rapid reaction, non-solvent conditions and operational simplicity with minimum disposal of waste. We have selected tetrachloropyridine (TCP) as an effective catalyst.[20] Herein, we wish to report for the first time the results of dehydration of aldoximes to nitriles using TCP as a reusable catalyst under microwave under non-solvent conditions (Scheme 1).



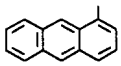
Scheme 1.

The reaction of aldoximes and tetrachloropyridine is carried out on alumina support under microwave irradiation. The products are isolated only by extraction. The aldoximes were prepared according to the literature procedure method.[21] Thus in a typical procedure, the corresponding nitriles (**2a–n**) were isolated in good yields when a mixture of aldehyde oximes **1** and TCP 10 : 1.5 adsorbed on alumina (finer than 200 mesh, 5 equiv.) and taken in a pyrex test tube was subjected to microwave irradiation in a microwave at an output of about 650 W. After cooling the reaction mass to room temperature, the products were isolated by extracting with dichloromethane (DCM) and the solvent DCM was removed under vacuum. The crude products were purified by distillation, crystallisation or column chromatography (Table 1). The catalyst recovered during workup could be effectively reused.

While the nitrile formation is observed using 10% w/w of TCP in the reaction, better yields are obtained by increasing the concentration of TCP to 15% w/w. It is observed that in the case of substrate bearing an electron withdrawing group (Entry **2g**), the reaction is faster with good yield, whereas an electron donating substrate (Entry **2h**) gives lower yield. The heterocyclic (Entry **2j–m**) and polycyclic aldoximes (Entry **2o**) are also effectively converted into nitriles in good yields. An important feature of the reaction is that the catalyst is recovered and reused for two cycles without substantial loss in the yield of product.

The easy workup, convenient handling and availability of the catalyst makes the method highly practical for the dehydration of alkyl, aryl, heterocyclic and polynuclear aldehyde oximes. In conclusion, we are reporting a

Table 1. Dehydration of Aldehyde Oximes **1** to Nitriles **2**

Product	R	Time (h)	Yield[a] (%)	M.P. or B.P./Torr	
				Found[c,d]	Reported[22,23]
2a	Ph	3	72	189–192/760	190.7/760
2b	4-(Cl)C_6H_4	3	80	93–94	94–96
2c	2-(Cl)C_6H_4	3	80	43–44[e]	43–46
2d	2,6-$Cl_2C_6H_3$	4	75	142–145	144–145
2e	4-(OH)C_6H_4	3.5	75	110–112[f]	113
2f	4-(Me)C_6H_4	3	78	216–217/760	217.6/760
2g	4-(NO_2)C_6H_4	3	85	148	149
2h	4-(MeO)C_6H_4	3	79	59–61[g]	61–62
2i	*n*-C_9H_{19}	4	75	233–236/760	235–237/760
2j	Pr	4	70	116–118	118/760
2k		4.5	65[b]	147/738	146/738
2l		4.5	66[b]	190–192	192/760
2m		4.5	60	104.5	103
2o		5	80	174–176	175–177

[a]Yields of isolated products; [b]Purified by column chromatography on silica gel; [c]All products were identified by comparison of their TLC, IR and NMR spectra with those of authentic samples; [d]Crystallised from EtOH unless otherwise noted; [e]From Et_2O/hexane; [f]From benzene; [g]From Et_2O.

new catalyst for the facile dehydration of aldoximes to nitrile a reusable catalyst and dry reaction conditions are remarkable features of the procedure.

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