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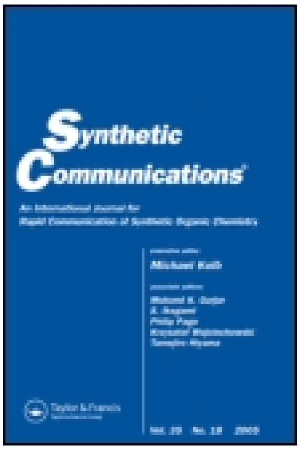

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MICROWAVE-ASSISTED RAPID DEHYDRATION OF ALDOXIMES TO NITRILES ON A SOLID SUPPORT

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MICROWAVE-ASSISTED RAPID DEHYDRATION OF ALDOXIMES TO NITRILES ON A SOLID SUPPORT

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ABSTRACT

p-toluenesulfonyl chloride has been proved out to be an efficient reagent for conversion of aldoximes to the corresponding nitriles under microwave irradiation. Extending the procedure to ketoximes, a 20–40% yield of Beckmann rearranged product was obtained.

Although traditionally other conditions have been used for the dehydration of aldoximes,[1] more recently clays such as Montmorillonites KSF and K-10 have been used with advantage.[2] For example, this transformation has been described using KSF clay under reflux of toluene with yield of 70% within 15 hours,[3] or under microwave irradiation using H_2SO_4–SiO_2 in dry media with yield of 76% in a domestic oven within 4 minutes.[4]

A reduction of reaction time and a mild condition was possible with the use of p-toluenesulfonyl chloride and pyridine or Et_3N. We report here the use of a reagent consisting p-toluenesulfonyl chloride adsorbed on chromatographic grade alumina for rapid, high yield, selective dehydra-

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* Corresponding author.

tion of aldoximes. When alumina (Fluka, basic alumina, type 507C) was mixed with the oxime, p-toluenesulfonyl chloride and pyridine dissolved in a polar volatile solvent such as $CHCl_3$, followed by evaporation at 40–50°C under vacuum (20 mm Hg) for 30 min, a yellowish powder was obtained. The mixture was introduced in a Pyrex flask and submitted to microwave irradiation for 2–15 minutes with a domestic oven. The observed yields of the different dehydration of aldoximes were given in Table 1. In order to explore the scope of this condition, we were interested to consider the possibility of the Beckmann rearrangement of ketoximes[5] using the p-toluenesulfonyl chloride adsorbed on chromatographic grade alumina in the presence of pyridine. We have observed that this condition effectively convert ketoximes to the corresponding p-tosyl derivatives when the migrating group is alkyl residue (entries 6, 7). But in other cases that the migrating group is an aryl group we get a mixture of products. The product of Beckmann rearrangement were less than 40% (entries 8, 9 and 12).

Certain ketoximes can be converted to nitriles by the action of proton or Lewis acids.[6] Among these are oximes of α-diketones, α-ketoacids, α-dialkylamino ketones, α-hydroxy ketones and α-ketoethers. We checked as above the behavior of p-toluenesulfonyl chloride toward the benzoin oxime. In the best condition we separated benzaldehyde and benzonitrile from the mixture of reaction as the main products.

In summary, it is worth noting that carrying out the organic reactions on the solid support has a drawback. It is possible that they can be most useful when their involvement is limited to their outer surface. By monitoring the reaction mixture in all cases, there is only one spot for the product without any trace of starting material, but the isolated yield in the best case cannot exceed from 75%. We think that the remainder of the product is adsorbed into the alumina, and we are hoping to find a means to improve its recovery.

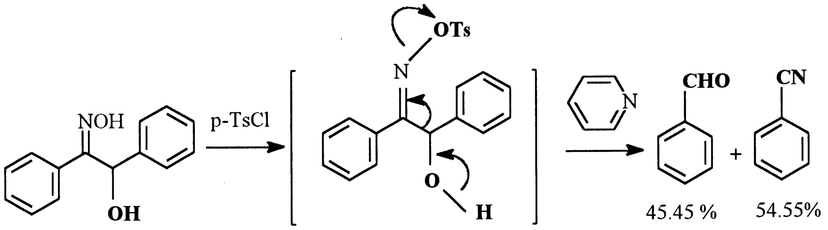

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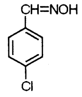
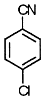
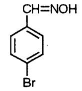
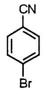
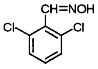
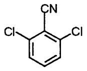
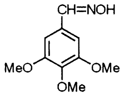
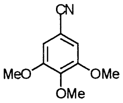
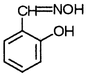
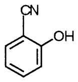
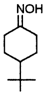
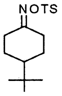
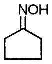
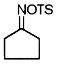
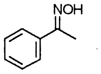
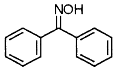
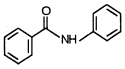
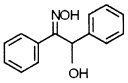
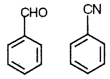
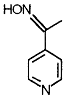
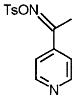
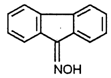
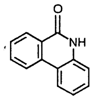
Table 1. Dehydration of Aldoximes to Nitriles

Entries	Substrate	Reaction time (min)	Product	m.p. °C	% Yield (isolated)
1		11		89-90	64
2		2		110	73
3		9		135-7	70
4		15		90-92	55
5		9		90	63
6		3			20
7		3			< 20
8		15	mixture of amides		< 20
9		23		163	40
10		12			70
11		5		–	< 20
12		15			40

EXPERIMENTAL

Typical procedure for the dehydration of aldoximes: A solution of p-chlorobenzaldehyde oxime (1.16 g, 7.5 mmol), p-toluenesulfonyl chloride (2.86 g, 15 mmol) and pyridine (1.2 mL, 15 mmol) in $CHCl_3$ (20 mL) was mixed with 3 g alumina and concentrated under vacuum to give a yellowish solid. The mixture was introduced in a Pyrex flask and submitted to microwave irradiation. After completion of the reaction (TLC, 3–15 min) 50 mL CH_3OH was added. The mixture was filtered and concentrated. To the crude mixture, chloroform (25 mL) was added. The filtrate was washed with brine (2×25 mL), and then with 2×25 mL of 5% sodium bicarbonate. The collected organic phase was dried with $MgSO_4$, filtered and evaporated to give the crude product with good chemical purity. Flash chromatography (cyclohexane–ethyl acetate) gave analytically pure sample in 64% (m.p. 89–90°C) isolated yield.

4-Chlorobenzonitrile: IR (KBr): 2250 (m), 1630 (w), 1580 (m), 1480 (s), 1380 (s), 1080 (m), 820 (s), 780 (w), 750 (m), 700 (m), 680 (m), 550 (m) cm^{-1}. ^1H-NMR ($CDCl_3$, TMS): δ, 7.56 (dd, 4H, $J = 6$ Hz) ppm.

4-Bromobenzonitrile: IR (KBr): 2250 (s), 1580 (s), 1480 (s), 1380 (m), 1060 (s), 820 (s), 770 (m), 700 (w), 550 (s) cm^{-1}. ^1H-NMR ($CDCl_3$, TMS): δ, 7.6 (dd, 4H, $J=3$ Hz) ppm.

2,6-Dichlorobenzonitrile: IR (KBr): 3020 (m), 2250 (s), 1680 (w), 1570 (w), 1550 (w), 1430 (s), 1220 (s), 1100 (m), 980 (w), 800 (m), 780 (s) cm^{-1}. ^1H-NMR ($CDCl_3$, TMS): δ, 7.45 (s, 3H) ppm.

3,4,5-Trimethoxybenzonitrile: IR (KBr): 2880 (m), 2250 (s), 1580 (s), 1520 (s), 1460 (m), 1340 (s), 1240 (s), 1140 (s), 1000 (s), 960 (m), 860 (s), 820 (s), 780 (m), 745 (w), 700 (w), 630 (s) cm^{-1}. ^1H-NMR ($CDCl_3$, TMS): δ, 6.9 (s, 2H), 3.78 (s, 6H), 3.74 (s, 3H) ppm.

2-Hydroxybenzonitrile: IR (KBr): 3020 (m), 2250 (s), 2080 (w), 1990 (m), 1950 (m), 1915 (m), 1660 (s), 1570 (w), 1480 (s), 1450 (s), 1370 (s), 1290 (s), 1080 (s), 1030 (m), 1015 (w), 960 (s), 910 (s), 590 (s) cm^{-1}. ^1H-NMR ($CDCl_3$, TMS): δ, 8.93–7.18 (m, 4H), 2.48 (s, 1H) ppm.

ACKNOWLEDGMENT

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