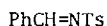


CONVERSION OF AROMATIC ALDEHYDES INTO NITRILES VIA N-TOSYLIMINES

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Many methods have been reported for the conversion of aldehydes into nitriles.¹ In the course of studying the reaction of cyanide ion with sulfonimides a mechanism was postulated, which is presented in detail in the preceding paper, in which N-tosylimine 1 was transformed



1

into benzonitrile. To test this hypothesis, N-tosylimine 1² was subjected to sodium cyanide in anhydrous hexamethylphosphoric triamide (HMPT). Benzonitrile was thus formed in 89% yield. Because of the high yield, mild conditions, and convenience of this reaction it was investigated as a general means for effecting the conversion of aldehydes into nitriles.

Condensation of an aromatic aldehyde with p-toluenesulfonamide catalyzed by p-toluenesulfonic acid afforded the corresponding N-tosylimine. An attempt to prepare an N-tosylimine from n-heptanal and p-toluenesulfonamide was unsuccessful. In general, the N-tosylimine was not purified but dissolved in HMPT and treated with sodium cyanide. The yields of nitriles based on the starting aromatic aldehyde are given in the Table.

A typical experimental procedure for the conversion of aryl aldehydes to nitriles is as follows. A mixture of piperonal (600 mg, 4.00 mmol), p-toluenesulfonamide (822 mg, 4.80 mmol), p-toluenesulfonic acid monohydrate (71 mg, 0.40 mmol) and toluene (25 ml) was heated at reflux under a nitrogen atmosphere in a Soxhlet extractor equipped with a thimble containing CaH₂ for 1 hr. The reaction mixture was then cooled, evaporated to dryness under reduced pressure, and dissolved in HMPT (12 ml). Finely ground 95% NaCN (790 mg, 16 mmol) was added and the reaction

mixture was stirred at room temperature for 24 hr. The reaction mixture was then poured into 5% aqueous HCl and extracted with ethyl ether. The organic layer was washed with water and then saturated aqueous NaHCO₃, dried (MgSO₄), and distilled to near dryness. This residue was analyzed by quantitative glc and showed an amount of piperonylnitrile corresponding to a 98% yield.

Table. Conversion of Aryl Aldehydes to Nitriles via N-Tosylimines

Aldehyde	Nitrile	Yield ^a , %
Benzaldehyde	Benzonitrile	77
<i>o</i> -Chlorobenzaldehyde	<i>o</i> -Chlorobenzonitrile	80
<i>m</i> -Fluorobenzaldehyde	<i>m</i> -Fluorobenzonitrile	78
<i>o</i> -Fluorobenzaldehyde	<i>o</i> -Fluorobenzonitrile	70
<i>p</i> -Hydroxybenzaldehyde	<i>p</i> -Hydroxybenzonitrile	43 ^b
<i>m</i> -Methoxybenzaldehyde	<i>m</i> -Methoxybenzonitrile	79
<i>p</i> -Methoxybenzaldehyde	<i>p</i> -Methoxybenzonitrile	100
<i>p</i> -Methylbenzaldehyde	<i>p</i> -Methylbenzonitrile	88
<i>m</i> -Nitrobenzaldehyde	<i>m</i> -Nitrobenzonitrile	44 ^c
Piperonal	Piperonylnitrile	98

^aBased on quantitative glc by comparison with a standard sample.

^bRun under high dilution conditions.

^cRun with a 1.1 molar ratio of sodium cyanide to N-tosylimine for 5 min.

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- N-Tosylimine **1** was prepared by acid catalyzed condensation of benzaldehyde and *p*-toluene-sulfonamide. For an alternate preparation see: G. Kresze and R. Albrecht, *Angew. Chem. Int. Ed. Engl.*, **1**, 595 (1962); G. Kresze and W. Wucherpfennig, *ibid.*, **6**, 149 (1967).
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