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CONVERSION OF AROMATIC ALDEHYDES INTO NITRILES VIA N-TOSYLIMINES

Richard S. Glass* and Richard C. Hoy
Department of Chemistry, The University of Arizona
Tucson, Arizona 85721

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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

PhCH=NTs

1

into benzonitrile. To test this hypothesis, N-tosylimine **1**[2] 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 CaH_2 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 $NaHCO_3$, dried ($MgSO_4$), 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
o-Chlorobenzaldehyde	o-Chlorobenzonitrile	80
m-Fluorobenzaldehyde	m-Fluorobenzonitrile	78
o-Fluorobenzaldehyde	o-Fluorobenzonitrile	70
p-Hydroxybenzaldehyde	p-Hydroxybenzonitrile	43[b]
m-Methoxybenzaldehyde	m-Methoxybenzonitrile	79
p-Methoxybenzaldehyde	p-Methoxybenzonitrile	100
p-Methylbenzaldehyde	p-Methylbenzonitrile	88
m-Nitrobenzaldehyde	m-Nitrobenzonitrile	44[c]
Piperonal	Piperonylnitrile	98

[a] Based on quantitative glc by comparison with a standard sample.

[b] Run under high dilution conditions.

[c] Run with a 1.1 molar ratio of sodium cyanide to N-tosylimine for 5 min.

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2. N-Tosylimine 1 was prepared by acid catalyzed condensation of benzaldehyde and p-toluenesulfonamide. 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).

3. Taken in part from R. C. Hoy, Ph.D. Dissertation, The University of Arizona, 1976.