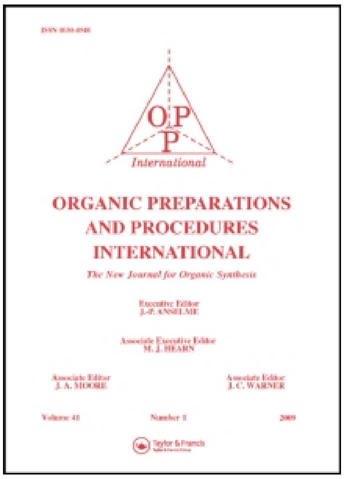

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A CONVENIENT SYNTHESIS OF TOSYLLACTONITRILE AND ITS REACTION WITH BENZENE

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Submitted by (10/24/88)
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Tosyllactonitrile constitutes an important three carbon synthon with a nitrile functionality that can be converted to other useful groups. It can be used to introduce a three carbon chain directly into an aromatic nucleus via the Friedel-Crafts reaction which would lead to biologically important compounds such as ibuprofen, naproxen and hydratropic acid.

$$\mathrm{ArH + CH_3\overset{OTs}{C}HCN \longrightarrow Ar\overset{CH_3}{C}HCN \longrightarrow Ar\overset{CH_3}{C}HCOOH}$$

Tosyllactonitrile is generally prepared by a two-step synthesis. Acetaldehyde is reacted with hydrogen cyanide (HCN) under carefully controlled conditions to give lactonitrile[1] which is isolated and then tosylated using pyridine/tosylchloride.[2] Since lactonitrile is reported to be a very toxic compound,[3] we now report here a simple one-pot synthesis of tosyllactonitrile which has the merit of eliminating the need to use HCN. The method consists of treating a mixture of aqueous acetaldehyde and tosylchloride with sodium cyanide.

$$\mathrm{CH_3CHO + NaCN + TsCl \longrightarrow CH_3\underset{OTs}{C}HCN + NaCl}$$

Tosyllactonitrile thus prepared has been successfully reacted with benzene to get hydratroponitrile in high yield. The reactions of tosyllactonitrile with other aromatic compounds are now being investigated in our laboratories.

EXPERIMENTAL SECTION

Preparation of Tosyllactonitrile.- To a stirred suspension of p-toluenesulfonyl chloride (19.0 g, 0.1 mol) in 25% aqueous acetaldehyde (20 ml; 0.11 mol) cooled to 0° was added a solution of sodium cyanide (4.8 g; 0.1 mol) in 20 ml of water during 1 hr; the pH of the reaction mixture immediately after the addition of sodium cyanide was about 10.5. Stirring was continued and the temperature of the reaction mixture was gradually allowed to rise to room temperature over a period of 4 hrs; the pH of the reaction mixture came down to around 7. TLC examination indicated the total consumption of tosyl chloride (silica gel, 5:1 pet ether: ethylacetate, Rf. of tosyllactonitrile 0.3). The reaction mixture was diluted with water (100 ml) and extracted with dichloromethane (2 x 40 ml). The combined organic extracts were washed with water and dried over sodium sulfate. The solvent was distilled to leave a yellow oil which on distillation gave 16 g. (71%) of tosyllactonitrile as a pale yellow oil, bp. 180-185°/2-3 mm, lit.[2]

Preparation of Hydratroponitrile.- To a stirred suspension of aluminium chloride (6.00 g; 0.45 mol) in benzene (30 ml) was added tosyllactonitrile (6.75 g; 0.03 mol) in one lot. The reaction mixture was stirred and heated at reflux for a period of 5 hrs, cooled to room temperature and decomposed with 10% aq. hydrochloric acid (50 ml) by stirring for 15 min. The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. After removal of excess benzene, the resulting hydratroponitrile was distilled to give 3.55 g. (90%) colorless liquid, bp. 115-117°/20 mm, lit.[4]

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