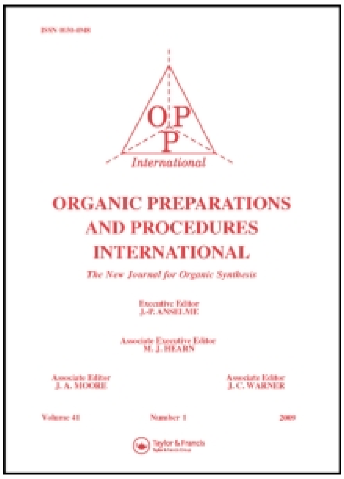

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PREPARATION OF *p*-TOLUENESULFONYL AZIDE. A CAUTIONARY NOTE

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(t, 1, ArH), 7.556 (d, 1, ArH), 7.582 (d, 1, ArH), 8.225 (d, 1, H_5), 8.305 (s, 1, H_6); MS (70 eV, 100°), m/e (relative intensity) 283 ($M^{+\cdot}$, 99.5), 268 (74.2), 267 (37.7), 253 (61.6), 202 (100), 201 (44.7), 200 (80.8), 199 (59.6).

Anal. Calcd for $C_{21}H_{17}N$: C, 88.9; H, 6.0; N, 4.9.
Found: C, 88.9; H, 6.2; N, 4.7

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PREPARATION OF p-TOLUENESULFONYL AZIDE. A CAUTIONARY NOTE

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The utility of p-toluenesulfonyl azide (tosyl azide) for the preparation of diazo compounds is well established.[1] The purpose of this note is to point out that tosyl azide prepared by a standard procedure can be grossly impure. Examination of the *nmr* spectrum of a sample of azide prepared as described in Organic Syntheses[2] revealed the presence of an ethyl-containing impurity. Correspondence with a published spectrum[3] suggested that the impurity was ethyl tosylate. This was confirmed by *tlc* and *hplc* comparison with an authentic sample. Integration of *nmr* spectra established that two different preparations of azide contained 7% and 20% of ethyl tosylate, respectively. The origin of the tosylate ester is not completely clear. However, the Organic Syntheses directions call for adding a warm (45°), approximately 1 M, solution of tosyl chloride in alcohol to sodium azide in aqueous alcohol. When a 1M solution of tosyl chloride in alcohol was held at 45° and sampled periodically over a period of 30 minutes, *hplc* showed that conversion to ethyl tosylate occurred at a rate of approximately 1% per minute. Thus, varying amounts of ethyl tosylate are likely to contaminate the tosyl azide preparations, depending on the times and temperature used to dissolve the tosyl chloride.[4]

An attempt to purify a sample of tosyl azide containing 11% of ethyl tosylate by low temperature crystallization from ether gave, in 70% recovery, azide still contaminated by 6% of ethyl tosylate. Complete removal of the tosylate impurity could be effected by treatment with lithium bromide in acetone, which converted the tosylate to volatile ethyl bromide. However, because of the difficulty and labor involved, it would appear better to employ a preparative procedure which does not produce this by-product. The simple and obvious expedient of conducting the reaction in aqueous acetone[5] rather than aqueous

$$p\text{-}CH_3C_6H_4SO_2Cl + NaN_3 \xrightarrow[\text{Water}]{\text{Acetone}} p\text{-}CH_3C_6H_4SO_2N_3$$

alcohol suffices, and details of a procedure, as well as characterization of the product obtained, are given in the experimental section. In view of the report that impurities enhance the shock sensitivity of azides,[5] prudence dictates that tosyl azide be prepared and stored in as pure a state as possible.

EXPERIMENTAL

Proton magnetic resonance spectra were determined at 60 MHz using a Hitachi Perkin-Elmer R-24 spectrometer. The high performance liquid chromatograph consisted of two Altex model 100 A pumps and model 420 controller, Waters μBondapak C_{18} column, 0.39 x 30 cm, Perkin-Elmer LC75 detector operating at 225 nm, and Hewlett-Packard 3380 A integrator. Mobile phase was 60% MeOH - 40% H_2O at 1 ml/min. Thin layer chromatography was on EM Silica Gel 60 F-254 plates, 5 x 20 cm, using benzene-hexane (1:1) as eluent. Acetone (Fisher Certified), sodium azide (Aldrich), and *p*-toluenesulfonyl chloride (Aldrich) were used as received. Vacuum evaporations were performed on a Buchi rotary evaporator

p-Toluenesulfonyl Azide.- To a mechanically stirred solution of sodium azide (71.5 g, 1.10 mol) in water (300 ml) and acetone (500 ml) was rapidly added a solution of *p*-toluenesulfonyl chloride (190.7 g, 1 mol) in acetone (500 ml). The mixture warmed slightly, the color darkened, and two phases were formed. After stirring at room temperature for 2 hrs, acetone was removed in vacuum (bath temperature 35°), dichloromethane (200 ml) was added, and the organic phase was washed with water (2 x 200 ml), dried over anhydrous Na_2SO_4, and evaporated to a constant weight in vacuum (bath temperature 35°). There was obtained 195 g (99%) of *p*-toluenesulfonyl azide as a colorless oil which, on strong cooling, crystallized to a white solid, mp. 20.4-21.8°, lit.[6] mp. 22°. The *nmr* spectrum in CCl_4 showed a small amount of dichloromethane at 5.2 δ and traces (< 1%) of unidentified impurities at 2.0, 2.1 and 2.6 δ. *tlc* showed only a single spot under UV light, while *hplc* showed 1.5% of a single UV absorbing impurity which eluted at the solvent front and may be p-toluenesulfonic acid or sodium tosylate.

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4. Addition of solid tosyl chloride to sodium azide suspended in cold aqueous alcohol, using the solvent and reactant proportions specified by Organic Syntheses,[2] gave an azide product containing about 1% of an impurity which co-chromatographed (*hplc*) with ethyl tosylate. It thus appears that, in the Organic Syntheses preparation, some ethyl tosylate is formed after the tosyl chloride solution has been mixed with sodium azide.

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