Rearrangement fragmentation of aldoxime to isocyanide

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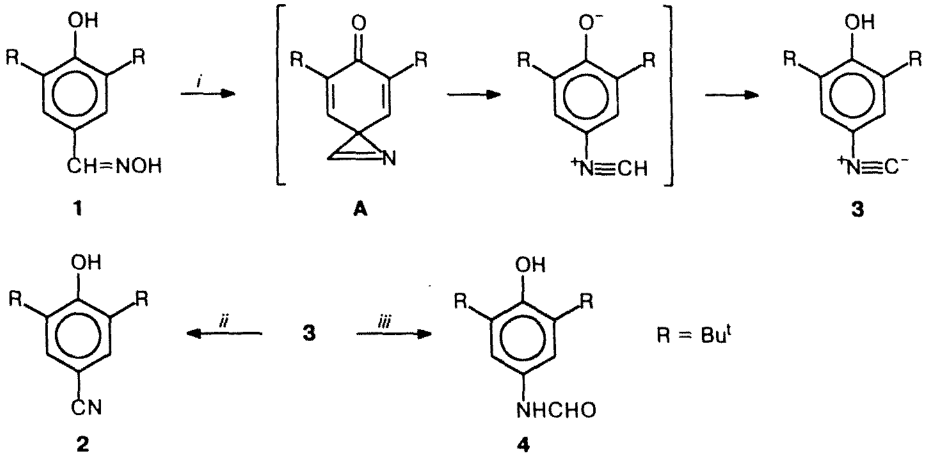
The attempted synthesis of a spiro-fused azirine (**A**) by the cyclization of the known[1] aldoxime **1** under the action of TsCl and Et_3N could be expected to be accompanied by competitive dehydration to form nitrile **2**. However, isocyanide **3** was obtained instead in almost a quantitative yield (Scheme 1).

Scheme 1



Reagents and conditions: *i.* TsCl, Et_3N, CH_2Cl_2, 0.5 h at 5 °C and 1 h at 20 °C; *ii.* PhMe, refluxing, 1 h; *iii.* 90 % AcOH, 0.5 h, 20 °C.

The structure of product **3** was confirmed by spectral methods and the reactions typical of isocyanides[2]: thermal rearrangement to the known[3] nitrile **2** and acid-catalyzed hydration to formanilide **4** described[4] previously (see Scheme 1).

The transformation **1**→**3** observed can likely be explained by the initial formation of a strained intermediate **A** (as in the Neber rearrangement,[2] which gives α-aminocarbonyl compounds under hydrolytic conditions), in which the three-membered cycle undergoes ring-opening followed by the prototropic rearrangement, resulting in the formation of isocyanide **3**.

3,5-Di-*tert*-butyl-4-hydroxyphenyl isocyanide (3). Yield 85 %, light-cream crystals, m.p. 132—134 °C. Found (%): C, 77.95; H, 9.38; N, 5.81. $C_{15}H_{21}NO$. Calculated (%): C, 77.87; H, 9.15; N, 6.05. ^1H NMR (CD_3Cl), δ: 1.43 (s, 18 H, 2 Me_3C); 5.48 (s, 1 H, HO); 7.19 (s, 2 H, H_m). ^{13}C NMR (CD_3Cl), δ: 29.86 (q.hept, Me, ^1J = 126.4 Hz, ^3J = 4.4 Hz); 34.34 (s, $\underline{C}Me_3$); 118.68 (br.s, C=N); 123.25 (dd, HC=, ^1J = 162.8 Hz, ^3J = 5.8 Hz); 137.06 (s, $\underline{C}$—Bu^t); 154.32 (s, $\underline{C}$—N≡C); 160.97 (s, COH).

3,5-Di-*tert*-butyl-4-hydroxybenzonitrile (2). Yield 96 %, m.p. 145—146 °C.[3] ^1H NMR (CD_3Cl), δ: 1.44 (s, 18 H, 2 Me_3C); 5.47 (s, 1 H, OH); 7.46 (s, 2 H, H_m).

3,5-Di-*tert*-butyl-4-hydroxyformanilide (4). Yield 93 %, m.p. 125—126 °C.[4]

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