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Organic Synthesis with Anion Exchange Resins: Synthesis of α-Imino Nitriles from Nitrones†

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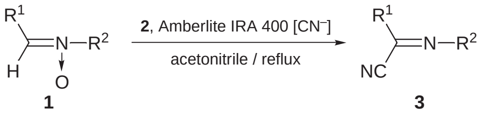
Nitrones react with amberlite IRA 400 [CN⁻] in acetonitrile to produce α-iminonitriles in good yield.

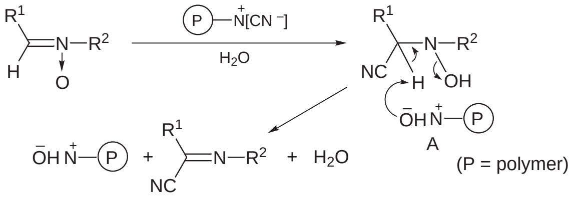
α-Iminonitriles are important intermediates for the synthesis of α-amino acid derivatives and heterocyclic compounds.[1,2] These compounds are prepared by reacting acetals with isocyanates in presence of an $AlClEt_2$ catalyst,[3] reacting dithioacetals with amines,[4] refluxing trimethyl silyl cyanide (TMSCN) with bis-anils,[2] oxidising conjugated imines with chromic anhydrides in the presence of TMSCN,[5] reacting α-chloroimines with hydrogen cyanide[6] and by reacting cyanogen bromide with imines.[7]

In recent years anion exchange resins have been used in many organic transformations. In continuation of our work on anion exchange resin,[8] we now report here the reaction of amberlite IRA 400 [CN⁻] **2** with nitrones **1** to produce α-imino nitriles. The reaction was carried out by stirring a mixture of nitrones **1a–h** and **2** in acetonitrile under reflux. The products **3a–h** were obtained by simple filtration, evaporation of the solvent under reduced pressure and crystallization from appropriate solvents (Scheme 1). The results are summarised in Table 1.



Scheme 1

Regarding the mechanism of the reaction, it is proposed that it proceeds *via* formation of a cyanohydroxylamine intermediate **A** by taking a proton from the trace amount of water present in the solvent which immediately loses a water molecule in presence of the $HO^- \ {}^+N - P$ resin formed *in situ* (Scheme 2). In conclusion, we propose that it is a new method for the preparation of α-imino nitriles using amberlite IRA 400 [CN⁻] as cyanating agent. The reaction has the following advantages over the existing methods: (1) The polymer supported reagent is non-toxic and can be stored for longer periods. (2) It does not require multi-step synthesis, anhydrous conditions, and the product can be obtained simply by filtering out the resin and evaporating off the solvent.



Scheme 2

Experimental

The m.p.s. were measured in a Buchi apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 237B spectrophotometer; ^1H NMR spectra on a Varian T-60 spectrometer with TMS as internal standard; and mass spectra on an AEIMS-30 spectrometer. The anion exchange resin amberlite IRA 400 was purchased from Aldrich chemicals as a chloride salt (16–60 mesh). The conversion of chloride into cyanide was accomplished by following the literature procedure.[9] The nitrones were prepared following a standard method.[10]

Preparation of α-Imino Nitriles.—In a typical experiment a mixture of α-phenyl-*N*-phenylnitrone (**1a**) (1.97 g, 0.01 mol), acetonitrile (50 ml) and amberlite IRA 400 [CN⁻] (10 ml, 0.01 equiv)[9] was stirred magnetically for 3 h in a 100 ml flask at reflux temperature. The reaction was monitored by tlc. The resin was filtered and the solvent distilled under reduced pressure. The residue was crystallized from ethanol to obtain **3a**, 1.89 g, 90%, m.p. 71 °C (lit, 72 °C[4]). Compounds **3b–h** were prepared in similar fashion (Table 1).

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Table 1 Synthesis of α-iminonitriles using amberlite IRA 400 [CN⁻][a]

Entry	Product (**3**)	R^1	R^2	Yield(%)	Time/h	m.p./°C found (lit.)
1	**a**	Ph	Ph	90	3	71 (72[4])
2	**b**	*p*-Cl-C_6H_4	Me	80	3.5	50 (52[4])
3	**c**	*p*-Me-C_6H_4	C_6H_{11}	75	4	67 (67[4])
4	**d**	*o*-Cl-C_6H_4	*p*-NO_2-C_6H_4	78	3.6	117 (116[4])
5	**e**	*p*-NO_2-C_6H_4	*m*-NO_2-C_6H_4	82	4	168 (166[4])
6	**f**	PhCH = CH	Ph	76	6	72 (73[5])
7	**g**	PhCH = CH	*p*-Br-C_6H_4	77	5	141 (142[5])
8	**h**	PhCH = CH	*p*-OMe-C_6H_4	81	5.5	122 (124[5])

[a]All the compounds gave satisfactory IR, NMR, mass spectral and elemental analyses.

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