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Organic Synthesis with Anion-exchange Resins: Reaction of Imines with Active Methylene Compounds†

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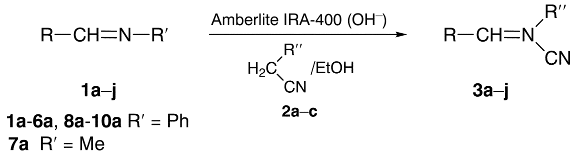
Imines undergo addition–elimination reaction with active methylene compounds in the presence of Amberlite IRA-400 (OH^-) as catalyst to yield arylidenemalononitrile derivatives.

Polymer-supported methods first developed by Merrifield[1] in polypeptide synthesis have been utilised in many transformations in organic chemistry.[2] In recent years the combinatorial chemistry has received much attention in organic synthesis.[3]

Anion-exchange resins, particularly Amberlite IRA-400, have been shown to be excellent catalysts in various organic reactions, for example aldol condensation,[4] Knovenagel and Michael condensation,[5] cyanohydrin formation,[6] *etc*. Recently, they have been in phenyl sulfide formation[7] and selective reduction of alkyl halides to alkanes.[8] We report here an addition–elimination reaction between imines and active methylene compounds in the presence of Amberlite IRA-400 (OH^-) as catalyst to give synthetically useful arylidenemalononitrile derivatives[9] (Scheme 1).



Scheme 1

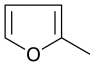
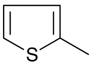
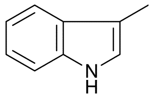
The reaction was carried out by stirring the imines **1a**–**j** and the active methylene compounds **2a**–**c** in the presence of a molar equivalent of Amberlite IRA-400 (OH^-) in ethanol under reflux. The product was obtained by simple filtration evaporation of the solvent under reduced pressure and crystallisation from appropriate solvents. The results are summarized in Table 1.

In conclusion, we have observed that the anion-exchange resin Amberlite IRA-400 (OH^-) can rapidly exchange its labile hydroxide ion with the enolate of the active methylene compounds in ethanol solution producing Amberlite IRA 400 ($HCR''CN^-$) which reacts with the azomethine carbon of the imines and eliminates amines in solution. Work is in progress to understand the mechanism of the reaction.

Experimental

The mps 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 usually purchased from Aldrich as the chloride salt (16–60 mesh). This conversion into the hydroxide form was accomplished by washing with 1 M sodium hydroxide until the eluent gave a negative silver nitrate test for chloride ion. The resin was thoroughly washed with distilled water, dried for several hours at 40 °C and kept in a vacuum desiccator for 24 h. before use. The imines were prepared by the literature method[10] or a slight modification thereof.

Table 1 Synthesis of arylidenemalononitriles **3a**–**j**[a]

Entry	R	R″	*t*/h	Yield (%)
1	Ph	CN	5	82
2	p-ClC_6H_4	CN	4.5	80
3	p-$O_2NC_6H_4$	CN	4	75
4		CN	4.5	70
5		CN	5	65
6	Ph	$CONH_2$	4	79
7	Ph	CN	5	82
8		$CONH_2$	5	65
9	Ph-CH=CH	CO_2Et	6	65
10	Ph	CO_2Et	6	70

[a] All the compounds gave satisfactory spectroscopic analyses and were comparable with authentic samples.

Preparation of Arylidene Malononitrile **3a**.—In a typical experiment, malononitrile (1.32 g, 0.02 mol) in ethanol (25 ml) was mixed with Amberlite IRA-400 (OH^-) (7.3 g, 0.02 mol) having a capacity of 2.8 milliequvalent per dry g and benzylideneaniline **1a** (3.62 g, 0.02 mol) was stirred for 4 h at the reflux temperature of ethanol. The reaction mixture was filtered through a pad of Celite and the solvent evaporated under reduced pressure to give a residue which on crystallisation from light petroleum (bp 40–60 °C) yielded arylidenemalononitrile **3a** as white needles, mp 87 °C (lit.,[11] 87 °C). Yield: 2.5 g (82%). The other nitriles were prepared similarly.

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