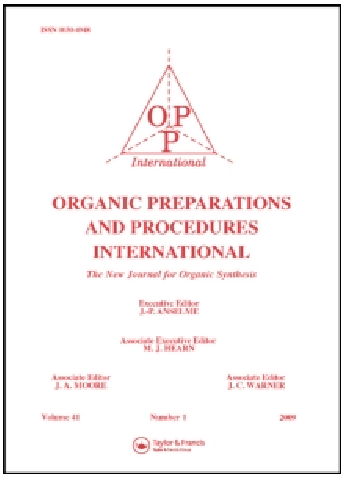

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HETEROGENEOUS SYNTHESIS OF REISSERT COMPOUNDS UTILIZING POTASSIUM CYANIDE ADSORBED ON AMBERLITE XAD RESINS

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UV-vis spectrum (in acetone) exhibits three absorption bands at 327, 393 and 715 nm. These values are in good agreement with those reported for the radical cation generated in solution.[9c]

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HETEROGENEOUS SYNTHESIS OF REISSERT COMPOUNDS UTILIZING POTASSIUM CYANIDE ADSORBED ON AMBERLITE XAD RESINS[†]

Submitted by (06/10/88)
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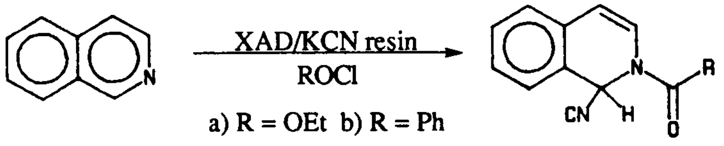
Reagents adsorbed on solid supports have been used in a variety of organic reactions.[1] Sukata has used adsorbed potassium and sodium cyanide on Amberlite XAD resins for the synthesis of aromatic acyl cyanides,[2] cyanosilylation of aldehydes and ketones,[3] and nucleophilic substitution reactions.[4] In light of Sukata's work, we felt that the use of these potassium cyanide impregnated resins could be applied to the synthesis of Reissert compounds.[5,6]

The resins were prepared by the method of Sukata.[4] The Amberlite XAD-2, -4, and -7 resins were used in the preparation of 1a and 1b. We found that the XAD-4/KCN resin in acetonitrile gave the highest yields of 1a and 1b. Refluxing the reaction mixture or using long reaction times decreases the yield of 1a. The spent resin, after appropriate washing and drying, can be reused. The in situ generation of trimethylsilycyanide,[3] a key cyanide source for some Reissert compounds,[5,6] was attempted by carrying out the reaction in the presence of chlorotrimethylsilane. We found, however, the yield of 1a under these conditions decreased when compared to similar runs without chlorotrimethylsilane.



Although, the yields are lower than the more traditional methods of using aqueous potassium cyanide or trimethylsilylcyanide as the cyanide ion source,[5] the method does provide an alternative procedure when one wants to avoid water and also the expense of trimethylsilylcyanide.

EXPERIMENTAL SECTION

Typical Procedure.- To 50 ml of acetonitrile was added 2.0 g of the prepared resin (c.a. 7.5 mmoles KCN). An acetonitrile solution containing 0.35 g (2.71 mmoles) isoquinoline and 259 ml (2.71 mmoles) ethyl chloroformate was poured into the resin suspension. After stirring at room temperature for 23 hrs the mixture was filtered and the resin was washed with benzene and methylene chloride. Evaporation of the solvents under reduced pressure left a residue which was diluted with methylene chloride and washed with 10% HCl, water, 10% NaOH, brine and dried over anhydrous $MgSO_4$. Evaporation of the solvent yielded 0.30 g of a thick pale yellow oil which on tituration with 95% ethanol yielded 0.22 g (36%) of 1a, mp. 82-84°C (95% ethanol), lit.[7] 84-86°C. Compound 1b (10%), mp. 125-126°C (95% ethanol), lit.[8] mp. 124-125°C, was prepared as above from benzoyl chloride and isoquinoline.

The reactions in the presence of chlorotrimethylsilane were carried out as follows. To 2.0 g of XAD-4/KCN resin (c.a. 2.8 mmoles KCN) in methylene chloride was added a 1.39 molar equivalent of chlorotrimethylsilane. The mixture was stirred for 30 minutes. After which time a methylene chloride solution containing 1 molar equivalent each of isoquinoline and chloroethylformate was added. The reaction mixture was then worked up as previously mentioned to give a 22% yield of 1a and a 11% yield of 1a when the reaction was repeated in acetonitrile.

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TRANSFORMATION OF SOME ARYL BENZYL KETONES TO 2-ARYL-1,3-DICHLOROINDENES BY VILSMEIER REAGENT

Submitted by (07/11/88)

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The prototypical Vilsmeier reagents, generated from dimethylformamide (DMF) and phosphorus oxychloride, is a weak, versatile electrophile which can formylate reactive aromatic rings[1] or transform ketones to β-chlorovinyl aldehydes.[2] We have found that desoxyveratroin (1a) is converted by DMF-$POCl_3$ to α-veratryl-β-chloro-3,4-dimethoxycinnamaldehyde (2) under mild conditions (0-60°) while 2-veratryl-1,3-dichloro-5,6-dimethoxyindene (3a) is obtained at elevated temperature (80-100°). Although Pulst et al.[2] prepared compounds analogous to 2, the tricyclic compound 3a is a new Vilsmeier reaction product from aryl benzyl ketones. Compound 2 can also be converted to 3a by hot DMF-$POCl_3$ solution. Cyclization to 3a appears to be facilitated by the p-methoxy group since aryl benzyl ketones (1b-e) with 3,4-dimethoxy substituents in the benzoyl ring readily gave indene derivatives 3b-e; in contrast, desoxybenzoin yields only the β-chlorovinyl aldehyde by our method or as reported by Weissenfels et al.[3]

The preparation of the chlorocinnamaldehyde 2 was carried out in tetrahydrofuran; when