Communications

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A General Conversion of Phenols to Anilines[1]

Summary: Phenols are converted to aryl diethyl phosphates which, upon treatment with KNH_2 and potassium metal in liquid ammonia, afford anilines in good yield.

Sir: Methods for the synthetic transformation of phenols to the corresponding anilines, that is, for replacement of the hydroxy group by an amino group in the same position, are few and mostly arduous and/or restricted to narrow classes of phenols. When we recently read of a general method for effecting that transformation,[2] we realized that reactions we had investigated[3,4] should, when properly combined, be adaptable for the purpose of preparative aminodehydroxylation. Accordingly we did a few experiments, now reported, which demonstrate the practicability and suggest the generality of the method.

Operationally, the method involves two steps. First (eq 1), the phenol is converted to the corresponding

$$ArOH + NaOH + (C_2H_5O)_2POCl \longrightarrow ArOPO(OC_2H_5)_2 \quad (1)$$

aryl diethyl phosphate ester through reaction with NaOH and $(C_2H_5O)_2POCl$,[5] an inexpensive chemical. Ester yields are typically 80–90%. Second (eq 2), the

$$ArOPO(OC_2H_5)_2 + KNH_2 + K \longrightarrow ArNH_2 \quad (2)$$

aryl diethyl phosphate reacts with KNH_2 and potassium metal in liquid ammonia, forming the aniline. In the three cases we have examined, yields in the second step are 56–78%.

The aminodephosphation reaction (eq 2) is believed to occur by the $S_{RN}1$ mechanism,[6] as shown in eq 3–6.

$$ArOPO(OC_2H_5)_2 + e_{solv}^- \longrightarrow [ArOPO(OC_2H_5)_2]\cdot^- \quad (3)$$

$$[ArOPO(OC_2H_5)_2]\cdot^- \longrightarrow Ar\cdot + (C_2H_5O)_2PO_2^- \quad (4)$$

$$Ar\cdot + NH_2^- \longrightarrow [ArNH_2]\cdot^- \quad (5)$$

$$[ArNH_2]\cdot^- + ArOPO(OC_2H_5)_2 \longrightarrow ArNH_2 + [ArOPO(OC_2H_5)_2]\cdot^- \quad (6)$$

The phosphate ester accepts an (solvated) electron (eq 3), and the resulting radical anion ruptures to form aryl radical and diethyl phosphate ion (eq 4). The aryl radical combines with amide ion to form the radical anion of an aniline (eq 5), which finally transfers an electron to another phosphate ester molecule (eq 6) or otherwise gets rid of it. Finally, the aniline is converted to an anilide ion in the strongly basic medium.

We have applied this method to phenol, 2,6-dimethylphenol, and 2-methoxy-4-methylphenol. Yields are summarized in Table I.

Among others, this method has the advantage that the two operational steps can be performed quickly at low temperatures. The method is convenient, and it should be feasible for use with thermally labile molecules. It has the disadvantage that some substituents are destroyed or lost on exposure to solvated electrons or to KNH_2. For example, it is unlikely to be serviceable with nitro- or halogen-substituted phenols. Alkyl, alkoxy, aryloxy, and aryl substituents survive, and probably also carbonyl groups of enolizable ketones.

Table I

Syntheses According to Eq 1 and 2

Phenol	Yield of $ArOP(O)(OC_2H_5)_2$, %	Yield of $ArNH_2$,[a] %
Unsubstituted	87	73[b]
2,6-Dimethyl	72	78[c]
2-Methoxy-4-methyl	98	56[c]

[a] Yield from phosphate ester. [b] Yield by glpc. [c] Yield by isolation and weighing.

The method of Scherrer and Beatty[2] involves conversion of the phenol to a 4-aryloxy-2-phenylquinazoline, heating the latter at ~300° to effect O → N aryl migration, and finally alkaline hydrolysis to release the aniline. The last two steps involve long periods of heating, the last in an alkaline environment. Their method is applicable to chloro- and nitro-substituted phenols, but clearly not to thermally labile or alkali-sensitive structures. The two methods are to some extent complementary, but the present method is likely to be chosen when both are feasible.

Aryl Diethyl Phosphates.—Our preparations, by the method of Bliznyuk, *et al.*,[6] and properties of the esters obtained are described elsewhere.[7] Alternatively, these esters may be synthesized by a method due to Kenner and Williams.[8]

Anilines.—In a representative preparation, 0.32 mol of KNH_2 was formed in 320 ml of liquid ammonia by the iron-catalyzed reaction of potassium metal with the solvent. To the stirred solution, at −78°, were added a total of 0.078 g-atom of potassium metal and 0.114 mol of 2,6-dimethylphenyl diethyl phosphate. About a third of the potassium was initially added, then the ester dropwise from a dropping funnel until the blue color was discharged, then another third of the potassium, etc. After addition of the ester was complete, the solution was blue. The mixture was acidified by addition of excess NH_4Cl, 150 ml of diethyl ether was added, and the ammonia was allowed to evaporate. Water was added to the residue, and the ether layer was washed with 10% aqueous NaOH and then with 20% aqueous H_2SO_4. The acidic extract was basified and extracted with ether. The ether extract was dried and evaporated, affording 10.7 g (78%) of 2,6-dimethylaniline, of purity >96% by glpc and structure confirmed by ir, nmr, and mass spectra.

University of California
Santa Cruz, California 95060

Roberto A. Rossi[9]
J. F. Bunnett*

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