

A Simple Method for the Removal of Phenolic Hydroxy-groups †

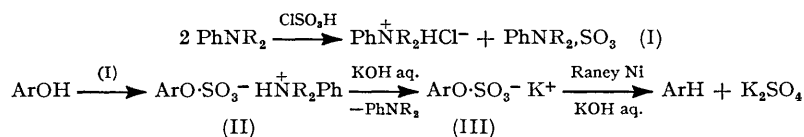
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Catalytic hydrogenation of potassium aryl sulphates affords a new and simple method for cleavage of the phenolic C–O bond.

SEVERAL methods for removing phenolic hydroxy-groups are known. Musliner and Gates¹ prepared phenyl tetrazol-5-yl ethers and subjected them to hydrogenolysis over palladium–charcoal in benzene solution. Clauss and Jensen hydrogenated phenyl alkanesulphonates and thus obtained dehydroxylated products.² Recently, Vowinkel and Wolff³ reported the reductive removal of phenolic OH by catalytical

common reagents, solvent, and catalyst (*i.e.* chlorosulphuric acid, water, and Raney nickel).

The method consists of the catalytic reduction of a potassium aryl sulphate (III) (see Scheme). Formation of the ester salt (III) essentially involves transfer of SO₃ to the phenolic OH. As the SO₃ must not react as a sulphonating agent, the presence of an organic base, such as pyridine⁴ or dimethylaniline,⁵ is necessary



SCHEME

hydrogenation of *O*-arylisoureas and *O*-aryl imidocarbonates. The advantages of the present method are the simplicity of the reaction conditions and work-up procedure, the speed of the reaction, and the use of

to give an addition complex (I). This adduct is able to form an aryl sulphate (II) which easily gives the potassium salt (III) when the reaction mixture is worked up with aqueous potassium hydroxide.

† Dedicated to Professor O. Hoffmann-Ostenhof on the occasion of his 60th birthday.

¹ W. J. Musliner and J. W. Gates, *J. Amer. Chem. Soc.*, 1966, **88**, 4271.

² K. Clauss and H. Jensen, *Angew. Chem.*, 1973, **85**, 981.

³ E. Vowinkel and C. Wolff, *Chem. Ber.*, 1974, **107**, 907.

⁴ M. A. Verley, *Bull. Soc. chim. France*, 1901, **25**, 46.

⁵ G. N. Burkhardt and A. Lapworth, *J. Chem. Soc.*, 1926, 684.

The shift of electron density at the phenolic carbon atom in the sulphuric ester salt (III) as compared with the free phenol would be expected to favour cleavage of the C-O bond by catalytic hydrogenation. These ester salts are water-soluble and in alkaline medium do not undergo hydrolysis, even when heated. Heating in acidic solution, however, gives the phenol and hydrogen sulphate. The potassium aryl sulphates (III) react with freshly prepared Raney nickel in aqueous alkaline solution to afford the corresponding dehydroxylated products.

EXPERIMENTAL

Preparation of Potassium Aryl Sulphates.—The following example is typical. Pyridine (7.4 ml, 0.09 mol) and carbon disulphide (40 ml) were mixed together and cooled to ca. -10 °C in ice-sodium chloride. During 10 min, chlorosulphuric acid (3 ml, 0.045 mol) was added with cooling. 4-Hydroxy-3-methoxybenzyl alcohol (3 g, 0.02 mol) (0.04 mol in the case of monohydroxy-compounds) was then added in one portion and the mixture was stirred for ca. 1 h at room temperature. Carbon disulphide was removed by distillation under reduced pressure (≥ 40 °C). To the resinous residue a solution of potassium hydroxide (7 g, 0.125 mol) in water (50 ml) was added with cooling and stirring. The inorganic precipitate was filtered off. The filtrate was concentrated and cooled to yield the dipotassium salt (6.3 g, 81%), which was dried over P₂O₅.

Hydrogenolytic Cleavage.—Method A. The dipotassium salt (1 g) was dissolved in water (10 ml) containing potassium hydroxide (0.5 g). Freshly prepared Raney nickel* (0.5 g alloy) was added, and the solution was heated to ca. 60 °C with stirring for 5 min. 3-Methoxytoluene was formed almost quantitatively and was identified by chromatographic methods.

Method B. The dipotassium salt (1 g), Raney nickel alloy (0.5 g), and water (20 ml) were mixed together. Solid potassium hydroxide (1.5 g) was added slowly and

the dehydroxylated product was formed immediately. The product could be isolated easily by extraction with ether or other suitable solvents.

Method C. The same results but with much slower reaction rates could be obtained by hydrogenation (at room temperature and pressure) in aqueous solution over palladium-charcoal or Raney nickel (deactivated).

Various phenolic compounds (see Table) were dehydroxylated under these conditions.

Dehydroxylation of phenolic compounds *

Phenolic compound	Yield of potassium aryl sulphate (%)	Yield of dehydroxylated product (%) †	
		(a)	(b)
Phenol	99	96	Benzene 95
2-Methoxy-4-methylphenol	98	91	3-Methoxy-toluene 89
2-Methoxy-4-n-propylphenol	98	70	1-Methoxy-3-n-propylbenzene 69
α -Naphthol	81	78	Naphthalene 63
β -Naphthol	99	94	Naphthalene 93
4-Chlorophenol	63	98	Benzene 62
4-Hydroxy-3-methoxybenzoic acid	84	57	3-Methoxy-benzoic acid 48
4-Hydroxy-3-methoxybenzyl alcohol (di K salt)	81	98	3-Methoxy toluene 79
4-Hydroxy-3-methoxybenzaldehyde	91	96	3-Methoxy toluene 87

* By method B. † Based on the amounts of (a) potassium aryl sulphate or (b) starting material.

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* Organikum; VEB, Deutsch. Verlag d. Wiss., Berlin 1972, 11. Aufl., p. 719.