Note

Reduction of Quinones with
2-Propanol over Hydrous
Zirconium Oxide

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Received May 23, 1985

Hydroquinones are important intermediate products or starting materials for the preparation of coenzyme Qn,¹⁾ vitamin K₂,²⁾ and many other naturally occurring quinones.³⁾ For example, the bromination of 2,3-dimethoxy-5-methylhydroquinone¹⁾ proceeds smoothly and selectively,^{*1} and the alkylation of the same compound with polyprenyl alcohol is a key step in the preparation of coenzyme Qn (the Friedel-Crafts reaction).⁴⁾

Quinones constitute one of the most easily reducible systems, and many methods for the reduction of quinones to hydroquinones have been reported (H₂/Pt, H₂/Pd, LiAlH₄, NaBH₄, LiAlH(OR)₃, SnCl₂, Sn/HCl, Zn/CH₃COOH, Zn/NH₄OH, TiCl₃, VCl₂, CrCl₂, ((CH₃)₂CHO)₃Al/(CH₃)₂CHOH, C₆H₅NHNH₂, H₂S, SO₂ and Na₂S₂O₄).⁵⁾ It is important for the choice of methods to consider the selectivity for carbonyl reduction, the compatibility with other types of functional groups, the low cost, and easy product isolation. New methods and new reagents which offer alternatives to those already known are constantly being sought.⁶⁾

In this paper, we describe the reduction of quinones with 2-propanol over hydrous zirconium oxide. The hydrous zirconium oxide was employed in the form of hard granules. It was a translucent polymer, and amorphous to X-ray diffraction. The surface area was 300 to 400 m²/g. It was stable at room temperature in air for 7 years, and could be used at any time for the reduction. The preparation of the catalyst has already been mentioned,⁷⁾ and a typical procedure of the reduction is as follows: In a 100 ml round-bottomed flask equipped with a reflux condenser were placed 2 g of hydrous zirconium oxide (8~14 mesh), 522 mg (2 mmol) of 6-bromo-2,3-dimethoxy-5-methyl-1,4-benzoquinone, and 10 ml of 2-propanol. The contents were heated under gentle reflux, and the color of the solution gradually changed from red to pale yellow. After a two-hour heating, the contents were cooled and filtered. The hydrous zirconium oxide was washed with hot 2-propanol, the solution was dried over anhydrous sodium

TABLE I. REDUCTION OF QUINONE WITH 2-PROPANOL
OVER HYDROUS ZIRCONIUM OXIDE

Quinone	Yield of product ^a (%)
2,5-Dimethyl- <i>p</i> -quinone	100
2,6-Dimethyl- <i>p</i> -quinone	99
2-Methyl-1,4-naphthoquinone	95
1,4-Naphthoquinone	93
<i>p</i> -Quinone	98
2,3-Dimethoxy-5-methyl-1,4-benzoquinone	93
6-Bromo-2,3-dimethoxy-5-methyl-1,4-benzoquinone	95

^a Isolated yield.

sulfate and the solvent was removed. The residue was crystallized from petroleum ether to afford 498 mg (95%) of 6-bromo-2,3-dimethoxy-5-methylhydroquinone.

The results of the reduction of several quinones are shown in Table I.

The Meerwein-Ponndorf-Verley reduction⁸⁾ is similar to this reaction in using 2-propanol as the hydride source. The disadvantage in the reduction is the need for a strong acidic treatment to neutralize the alkoxide salt as well as tedious other workups. The advantages of the method mentioned in this paper are 1) easy product isolation, 2) progress of the reaction in a neutral condition, 3) high-yield, 4) low cost of 2-propanol, and 5) stability of the oxide which can be stored at room temperature in air and used at any time. The substituted bromine atom on the quinone was not affected, but we are interested in the compatibility with many other types of functional groups.

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*1 Direct bromination of 2,3-dimethoxy-5-methylbenzoquinone has been reported.¹⁾ However, the addition of hydrogen bromide to the double bond in the quinone was observed.