

SYNLETT Spotlight 151

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)

Compiled by Sandip B. Bharate



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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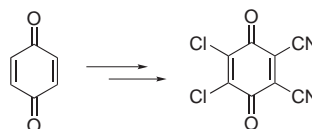
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Introduction

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)¹ is a powerful oxidizing agent and has proved to be versatile reagent for various organic transformations. Apart from its well-known applications as a dehydrogenating and oxidizing agent, in recent years it has found number of other applications in synthetic chemistry, including deprotection of various functional groups, cleavage of linker molecules from solid support, introduction of unsaturation and C–C, C–O and C–N bond-formation reactions. In recent years, it has shown wide potential for oxidative cyclization leading to a variety of heterocyclic ring skeletons such as benzopyrans, xanthenes, alkylindans, benzoxazoles, and oxazolidinones. It has found application in steroid chemistry and in the synthesis of complex natural

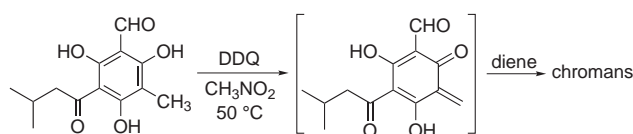
products,² where its unique regioselective properties gave excellent results for the preparation of key intermediates. DDQ was also found to be an excellent reagent to cleave methoxybenzyl ethers³ and an efficient catalyst for the alcoholysis of epoxides⁴ as well as for the hydrolysis of acetals.⁵

DDQ is commercially available and its first synthesis was described by Thiele and Gunther in 1906. It can be prepared by a six-step procedure involving cyanation and chlorination of benzoquinone.⁶

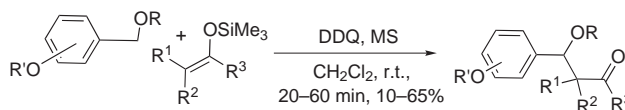


Abstracts

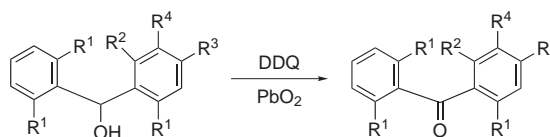
(A) *o*-Quinone methides⁷ are generated in situ by DDQ oxidation from *o*-alkyl phenols, and further undergo Diels–Alder cycloadditions with a variety of dienes to yield chromans and xanthenes.⁸ Similarly, *p*-quinomethanes and heterocyclic quinone methides are also generated by DDQ oxidation.⁹



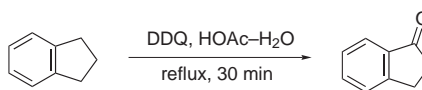
(B) Treatment of an electron-rich benzyl ether with DDQ at ambient temperature followed by addition of a silyl enol ether results in a C–C bond-forming reaction to afford 3-alkoxy-3-phenylpropionyl compounds. This is a general reaction and works well with a variety of silyl enol ethers to give carbonyl products.¹⁰



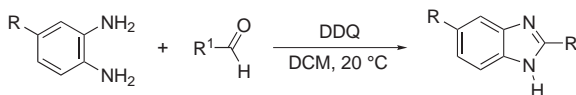
(C) Oxidation of highly hindered electron-rich benzhydrols has been achieved using catalytic amount of DDQ. This method is especially appealing for sterically crowded substrates and furnishes the corresponding benzophenones, which are useful synthons and are difficult to obtain by conventional methods.¹¹



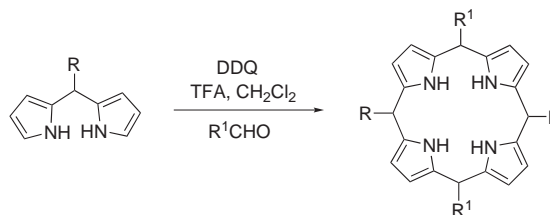
(D) DDQ in aqueous media was found to be a useful reagent for oxidation of arylalkanes to yield aryl ketones and aldehydes. Greater regioselectivity and higher yields were obtained in aqueous acetic acid.¹²



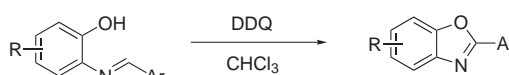
(E) DDQ acts as a Lewis acid to promote the formation of C–O and C–N bonds under very mild conditions. Such methodology enables the preparation of benzimidazoles.¹³



(F) Acid-catalyzed condensation of dipyrromethanes and aldehydes, followed by oxidation with DDQ, has a wide applicability in the synthesis of many complex natural products such as porphyrins (e.g. heme) and corrins (e.g. vitamin B₁₂).¹⁴

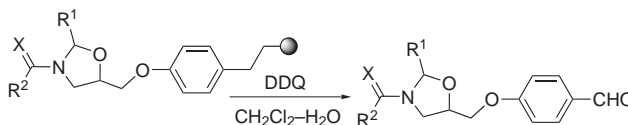


(G) The Schiff base derived from the condensation of *o*-aminophenol with benzaldehydes was induced to undergo oxidative cyclization in the presence of DDQ, leading to formation of 2-arylbenzoxazoles.¹⁵



(H) DDQ has been used for the oxidative cleavage of linker molecule from Wang resin in the solid phase synthesis of 1,3-oxazolidines.¹⁶

Deprotection of prenyl ethers as well as a number of other protecting groups was accomplished with the use of DDQ to give the corresponding alcohol.¹⁷



References

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