

Oxidation of alkyl benzenes to corresponding carbonyl compounds with 1,4-dichloro-1,4-diazoniabicyclo [2,2,2] octane bis-chloride in water

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The 1,4-dichloro-1,4-diazoniabicyclo [2,2,2] octane bis-chloride oxidation of various alkylbenzenes gives the corresponding carbonyl compounds in water as solvent.

Keywords: alkylbenzenes, 1,4-dichloro-1,4-diazoniabicyclo [2,2,2] octane bis-chloride, oxidation, carbonyl compounds

The oxidation of benzylic C–H bonds is a useful transformation in organic synthesis,¹ in the manufacture of various perfumes and medicines. Transition metal oxidants are commonly used. In these cases, the initial oxidation products are often more susceptible to oxidation than the starting material. Once a methyl group is attacked, it is likely to be oxidised to the carboxylic acid.² While such reactions readily give benzoic acids in high yields, they are rather difficult to stop at the aldehyde and ketone stage. Previous oxidations of a methylene group attached to an aromatic ring used stoichiometric quantities of oxidising agents such as benzeneselenic anhydride,³ 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ),⁴ Co/Mn/Br,⁵ Ag(Py)₄S₂O₈,⁶ Ce(NH₄)₂(NO₃)₆,⁷ O₂/NBS,⁸ Ce(IV)/methanesulfonic acid,⁹ RhCl(PPh₃)₃,¹⁰ KMnO₄/Al₂O₃,¹¹ O₂/Laccase/ABTS-(NH₄)₂,¹² CrO₃/Me₃SiCl,^{13,14} Mn(III) Salen complex,¹⁵ ZnO,¹⁶ 4-amino-peroxybenzoic acid,¹⁷ copper(II) complex in the presence of H₂O₂,¹⁸ 3,6-bis(triphenylphosphonium)cyclohexene peroxodisulfate,¹⁹ KMnO₄ or K₂Cr₂O₇.²⁰ The Friedel–Crafts acylation reaction of aromatic rings with an acid halide/anhydride used stoichiometric amounts of AlCl₃ as catalyst²¹ for the production of aromatic ketones. However, all of these procedures have some disadvantages, including drastic reaction conditions, rather poor yields, long reaction times and an environmentally unfriendly procedure.

Recently there has been an increased interest in the development of clean and economical processes for the selective oxidation of alkylarenes to the corresponding carbonyl compounds. In this context, the use of water as a solvent and a reusable reagent are very convenient.

Results and discussion

In continuation of our ongoing programme to develop oxidation reactions involving 1,4-dichloro-1,4-diazoniabicyclo [2,2,2] octane bis-chloride in water,^{22–25} we report here a novel, convenient and mild approach for the oxidation of a C–H benzylic to C=O using 1,4-dichloro-1,4-diazoniabicyclo [2,2,2] octane bis-chloride with water as a solvent under neutral conditions (Scheme 1). This method has many advantages over the existing methodologies offering

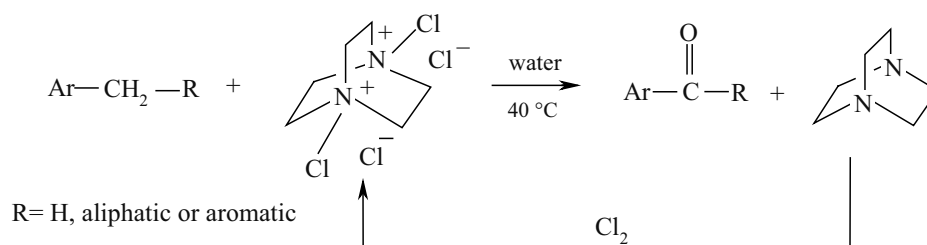
an environmentally benign protocol with the practical convenience of not having to handle flammable and hazardous organic solvents.

The reactions can be carried out effectively in high yields in water (Table 1) without the generation of any toxic waste by products. In the case of 1,3,5-trimethylbenzene and xylene, all of methyl groups converted to the aldehyde groups. Similarly, toluene and *p*-methoxytoluene under the reaction conditions gave high yields of benzaldehyde and *p*-methoxybenzaldehyde, respectively. Introduction of electron-withdrawing groups, such as bromine and nitro groups, on the aromatic ring slowed the oxidation reaction. In the case of ethylbenzene, acetophenone was obtained. In order to investigate the applicability of this procedure in industry, we have carried out the oxidation of *p*-xylene under optimum reaction conditions on a large scale (30–35 mmol) and obtained almost the same yields as in the small-scale reaction. Note also that, unlike other oxidation methods, the major drawback of over-oxidation of the aldehyde to the carboxylic acid was not observed.

In summary, we have reported the efficient and simple method for the oxidation of alkylarenes to phenyl ketones or aldehydes using 1,4-dichloro-1,4-diazoniabicyclo [2,2,2] octane bis-chloride as oxidant. The process exhibited advantages of mild reaction conditions, good yields, ease of work up, and reusability of the DABCO and environmental consciousness because no organic solvent is used in the reaction and only a small amount was needed for the work up.

Experimental

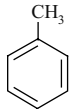
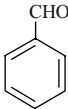
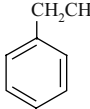
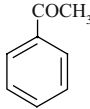
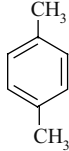
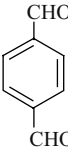
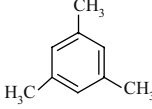
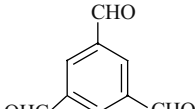
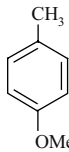
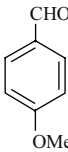
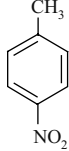
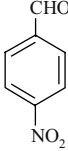
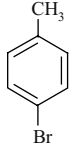
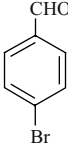
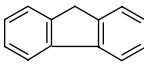
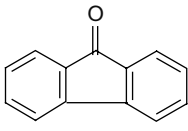
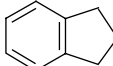
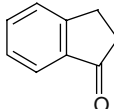
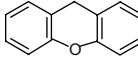
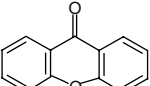
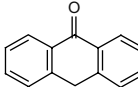
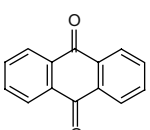
All the starting materials were purchased from Fluka and Merck companies.²⁶ The reaction was monitored by TLC using silica gel plate and the products were identified by comparison of their spectra and physical data with those of the authentic samples. ¹H NMR spectra were recorded at 300 MHz on a JEOL spectrometer with tetramethylsilane (Me₄Si) as an internal reference and CDCl₃ as solvent. Melting points were determined using a Mettler FP 5 apparatus and were uncorrected. IR spectra were recorded on Pye-unicam SP 1100 spectrophotometer. Elemental analysis was performed on a LECO 250 instrument. All yields refer to isolated products.



Scheme 1

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Table 1 Oxidation of alkylbenzenes to carbonyl compounds

Entry	Substrate	Product ^a	Time/min	Yield/% ^b	M.p./°C or b.p./°C/Torr	
					Found	Reported ²⁵
1			10	90	177–1769	177–179
2			10	95	200–201/760	202/760
2			15	91	114–115	114–116
3			20	90	oil	–
4			10	90	120–121/12	118–121/12
5			40	86	104–105	104–106
6			35	88	54	55–57
7			30	93	82	80–83
8			20	89	40–42	39–41
9			30	88	172–173	172–174
10			30	91	284–287	283–287

^aAll products were characterised spectroscopically (¹H NMR, IR) and by comparison with authentic samples, showing physical and spectral data in accordance with expected structures.

^bThe yields refer to isolated products.

Preparation of 1,4-dichloro-1,4-diazoniabicyclo [2,2,2] octane bis chloride

Chlorine gas was bubbled through a solution of 1,4-diazabicyclo[2,2,2] octane (DABCO) (6.72 g, 60 mmol) in chloroform (100 mL) for 10 minute at room temperature. The solvent was evaporated under reduced pressured to afford almost pure product (14.94 g, 98%), m.p. decomp. 125–130 °C. Anal. Calcd for C₆H₁₂N₂Cl₄: C, 28.3; H, 4.7; N, 11.0; Cl, 55.9. Found: C, 27.9; H, 4.6; N, 11.2; Cl, 55.6%. ¹H NMR (D₂O) δ 3.2 (s, 12H, 6CH₂). ¹³C NMR (D₂O) δ 91.3. IR 2800, 1500, 1380, 1000 and 750 cm⁻¹.

General procedure for oxidation of benzylic hydrogens

A substrate (4 mmol) and 1,4-dichloro-1,4-diazoniabicyclo[2,2,2]-octane bischloride (0.51 g, 2.0 mmol) was added to H₂O (10 mL) in a flask. The reaction mixture (pH = 7) was warmed to 40 °C. After completion of the reaction (TLC), ether was added to the reaction mixture and the extract was washed with solution of 1% HCl (2 × 10 mL). The aqueous layer (**1**) was separated and the organic layer was washed with 3% sodium bicarbonate (2 × 10 mL) and water (1 × 10 mL) respectively. The organic solution was dried over MgSO₄, filtered and evaporated to dryness under reduced pressure to afford the pure corresponding carbonyl compound.

Regeneration of 1,4-diazabicyclo [2,2,2] octane (DABCO)

The aqueous layer (**1**) from above procedure was further treated with 10% sodium bicarbonate solution (2 × 10 mL) and 1,4-diazabicyclo[2,2,2]octane (DABCO) was extracted with ether (2 × 10 mL). The ether layer was dried over MgSO₄, and evaporated to give pure 1,4-diazabicyclo[2,2,2]octane (0.21 g, 95%), which can be chlorinated and reused several times.

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