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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

CONVERSION OF ALKYLBENZENES TO CARBONYL COMPOUNDS BY NaBrO₃ IN THE PRESENCE OF NH₄CI AND Bu₄NHSO₄

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Version of record first published: 16 Aug 2006

To cite this article: Ahmad Shaabani, Ayoob Bazgir & Masoomeh Abdoli (2002): CONVERSION OF ALKYLBENZENES TO CARBONYL COMPOUNDS BY NaBrO₃ IN THE PRESENCE OF NH₄CI AND Bu₄NHSO₄, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:5, 675-678

To link to this article: http://dx.doi.org/10.1081/SCC-120002504

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SYNTHETIC COMMUNICATIONS, 32(5), 675-678 (2002)

CONVERSION OF ALKYLBENZENES TO CARBONYL COMPOUNDS BY NaBrO₃ IN THE PRESENCE OF NH₄Cl AND Bu₄NHSO₄

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ABSTRACT

Alkylbenzenes are oxidized selectively to their carbonyl compounds by sodium bromate in the presence of NH_4Cl or Bu_4NHSO_4 .

Bromate ion has recently been studied, as an oxidizing agent in connection with oscillating reactions, such as Belousov-Zhabotinsky reaction.¹ However bromate ion as a cheap, light and simple multi oxidant system in organic syntheses are rarely employed in the literature.

Standard redox potential of the bromate ion, BrO_3^- , is 0.61 V in neutral and alkaline aqueous solution while in aqueous acidic media it has a potential of $1.52 \text{ V}.^{2,3}$ Therefore, pH of the media drastically affect standard redox potential and oxidation ability of BrO_3^- ion. Due to low standard redox potential in neutral or weak acidic media, BrO_3^- have usually

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been used under strong acidic media such as HBr,⁴ H_2SO_4 ,⁵ $HClO_4^6$ and $HOAc^7$ for the oxidation of organic compounds.

Recently, we have introduced a new method⁸⁻¹⁰ for oxidation of organic compounds under mild reaction conditions by using NaBrO₃/NH₄Cl⁸ as oxidizing agent. We wish to report application of NaBrO₃ for the oxidation of alkylbenzenes in the presence of NH₄Cl or Bu₄NHSO₄ to extend the synthetic use of NaBrO₃ (Scheme 1). The results of oxidation of alkylbenzenes to carbonyl compounds by NaBrO₃/NH₄Cl and NaBrO₃/Bu₄NHSO₄ are summarized in Table 1.



We have observed that NaBrO₃/Bu₄NHSO₄ is a more efficient oxidizing agent than NaBrO₃/NH₄Cl for the conversion of alkylbenzenes to aldehydes and ketones. Moreover, tetrabutylammonium bromate as a phase transfer reagent was produced in situ from tetrabutylammonium hydrogensulfate and sodium bromate which was suitable for application in our two-phase system. Monosubstituted alkylbenzenes were oxidized at the benzylic carbon and corresponding aldehydes and ketones were isolated (Entries 1–4). While *o*-xylene resisted to oxidation (Entry 6), only one of the two methyls on *p*-xylene was oxidized (Entry 5). Diphenylmethane was also oxidized into benzophenone by NaBrO₃/Bu₄NHSO₄ in high yield (Entry 8).

We found that, the present method is cheap, safe and convenient for the oxidation of alkylbenzenes to carbonyl compounds in comparison with cerium ammonium nitrate (CAN),¹¹ NaBrO₃/CAN¹² and NaBrO₃/CeO₂/HOAc,¹³ in which large quantities of the expensive cerium compounds are needed.

EXPERIMENTAL

All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. Melting points were determined in open capillaries using an oil-bath and are not corrected. IR spectra were run at neat films or as KBr pellets on a

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Table 1. Oxidation of Alkylbenzenes to Carbonyl Compounds by $NaBrO_3 \cdot NH_4Cl$ and $NaBrO_3 \cdot Bu_4NHSO_4$ in Acetonitrile–Water at $80^{\circ}C$

Entry	Reactant	Product	NaBrO ₃ / NH ₄ Cl		NaBrO3/Bu4NHSO4	
			Time(hr) Yield(%)	Time(hr)	Yield(%)
1	CH,		12	15	12	35.
2	CH,		24	30	24	85
3			24	60	24	80
4			24	70	24	89
5	п,сСп,	и,с -{\}-{	8	25	8	60
6	СН,	-	24	No reaction	24	No reaction
7	Br -CH,	Br	24	40	24	53
8			24	45	24	91

Shimadzu 470 spectrometer. ¹H NMR spectra were recorded at 90 MHz on a JEOL EX-90 instrument with $CDCl_3$ as solvent and Me_4Si as an internal standard.

Typical procedure: Diphenylmethane (0.842 g, 5 mmol) was added to a mixture of NaBrO₃ (0.750 g, 5 mmol) and Bu₄NHSO₄ (0.400 g, 0.118 mmol) in aqueous acetonitrile (CH₃CN/H₂O = 7:3, (v/v), 10 ml). The mixture was stirred at 80°C for 24 h, while was followed by TLC. Then the reaction



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mixture was extracted with methylene dichloride $(2 \times 10 \text{ ml})$. The combined organic layers were dried over MgSO₄. Evaporation of the solvent furnished the product which was isolated as its 2,4-dinitrophenylhydrazone derivative.

ACKNOWLEDGMENT

Financial support by the Research Council of Shahid Beheshti University is acknowledged.

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Received in the UK September 19, 2000

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