Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 17 Sep 2007.

To cite this article: Qi-Zeng Shi , Jian-Ge Wang & Kun Cai (1999) Cerium Dioxide Catalyzed Oxidation of Alkylbenzenes with Sodium Bromate, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:7, 1177-1181, DOI: 10.1080/00397919908086088

To link to this article: http://dx.doi.org/10.1080/00397919908086088

SYNTHETIC COMMUNICATIONS, 29(7), 1177–1181 (1999)

CERIUM DIOXIDE CATALYZED OXIDATION OF ALKYLBENZENES WITH SODIUM BROMATE

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Abstract: CeO_2 Catalyzed selective Oxidation of Alkylbenzene with $NaBrO_3$ affords aldehydes and ketones in good yields.

Ce(IV) , an powerful single electron oxidant , has played an important role in organic synthesis[1-3]. The application of Ce(IV) in oxidation reaction has so far been limited for its expensive and the large quantities needed in oxidation [5-7]. CAN(Cerium ammonium nitrate)/$NaBrO_3$ has been reported as a high selectivity and cheap reagent [6-8]. But in the reaction, there is still some CAN be consumed, and the by-product make the siolation difficult. Here, we report that with the cheaper reagent CeO_2 as catalyst, sodium bromate oxidized alkykbenzenes to aldehydes and ketones in good yields. Moreover, being an insoluble powder, CeO_2 can be simply recycled by filtering.

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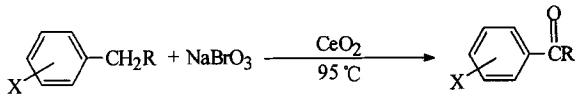
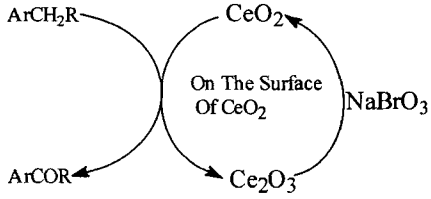


Scheme 1

The possible reacton mechenism mayge as following:

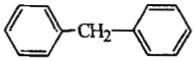
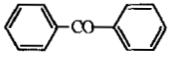
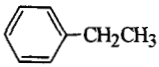
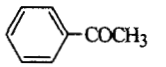
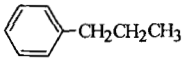
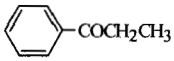
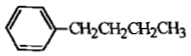
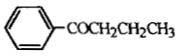
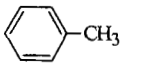
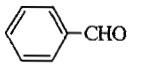
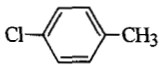
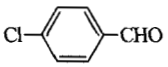
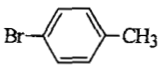
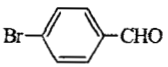
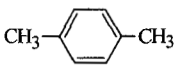
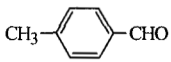
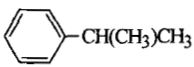
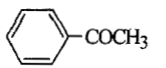


Scheme 2

We have examined a variety of reaction factors. Some alkylbenzenes underwent oxidation, as shown in Table 1. The ethyl, propyl, butyl and benzyl benzenes were oxidized to keton in high yield. While some toluene derivatives gave the methyl oxidation products such as aldehydes and acids. *p*-Nitrotoluene could not be oxidized. We found that *p*-substitution of toluene derivatives gave the corresponding aldehyeds in best yield, and the *o*-substitution in better. The reaction rate and yields also depended on the pH of the system. After adding 15% acetate acid, the reaction was shorten and the yields was increased. It is surprised that t-propylbenzene also gave the ketone product in 15%.

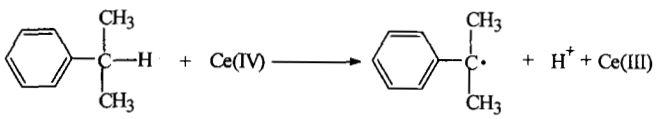
The results of our experiment are superior to those obtained in other uncatalytic systems [8]. The results in the case of isopropylbenzene suggests that the

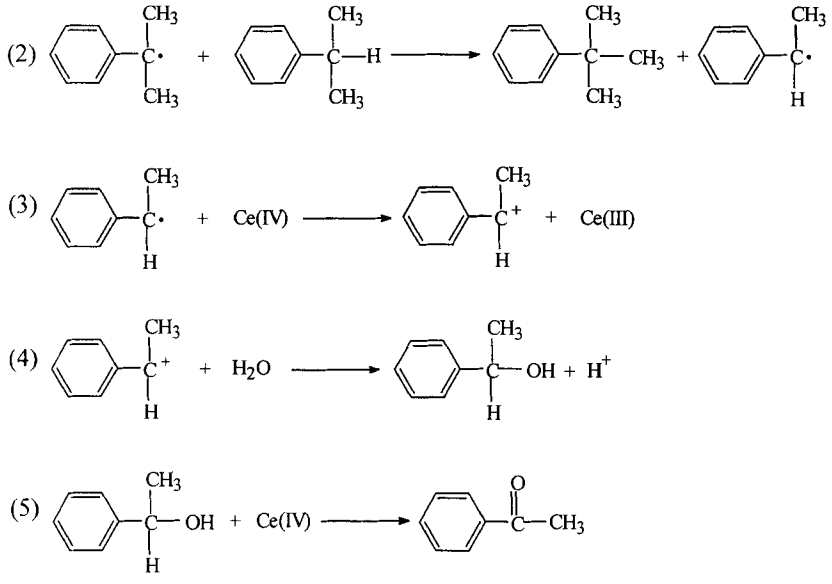
Table 1 Oxidation of Alkylbenzene by CAN/$NaBrO_3$

Substrate	Product	Time(h)	yields [a] (%)
		24	90
		24	85
		24	80
		24	80
		12	25
		24	35
		24	40
		8	45
		24	15

a: Isolated yield as 2,4-dinitrophenylhyrazone and determined by IR.

oxidation reaction involves free radical and benzenylic carbonium ion. It is now generally accepted that the side-chain oxidation of alkylarenes with Ce(IV) occurs via a radical cation [9]. Based on this opinion, we think that the oxidation of isopropylbenzene to phenyl methyl ketone maybe happened as the following five steps:

(1) 



Scheme 3

In summary, $CeO_2/NaBrO_3$ is a good regant for the selective oxidation of alkylbenzenes. It is a convenient and cheap method for the convertiongof alkylbenzenes to aromatic ketones and aldehydes.

Experimental

General procedure: Sodium bromate (25mmol), CeO_2 powder (1g) and alkylbenzene (25mmol) were added to a mixture of water/1,4-dioxane/acetate acids (4:1:1) in a three necked flask. The mixture was stirred at 95 ℃ for 8-24h. The reaction was followed by TLC. Then the reaction mixture was poured into cold water (30ml) and extracted with ether. The extraction was washed with 20ml

water three times, then dried over magnesium sulfate. Evaporation of the solvent furnish the prodcut which was isolated as 2,4-dinitrophenylhydrazone.

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Accepted 8-8-98