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CERIUM DIOXIDE CATALYZED OXIDATION OF ALKYL BENZENES WITH SODIUM BROMATE

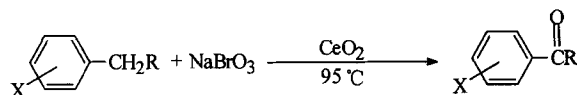
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Abstract: CeO₂ Catalyzed selective Oxidation of Alkylbenzene with NaBrO₃ affords aldehydes and ketones in good yields.

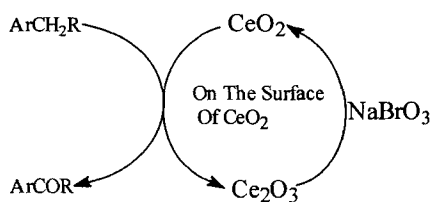
Ce(IV), an powerful single electron oxidant, has played an important role in organic synthesis¹⁻³. The application of Ce(IV) in oxidation reaction has so far been limited for its expensive and the large quantities needed in oxidation⁵⁻⁷. CAN(Cerium ammonium nitrate)/NaBrO₃ has been reported as a high selectivity and cheap reagent⁶⁻⁸. But in the reaction, there is still some CAN be consumed, and the by-product make the isolation difficult. Here, we report that with the cheaper reagent CeO₂ as catalyst, sodium bromate oxidized alkylbenzenes to aldehydes and ketones in good yields. Moreover, being an insoluble powder, CeO₂ can be simply recycled by filtering.

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Scheme 1

The possible reaction mechanism may be as following:

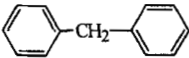
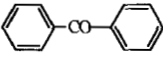
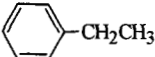
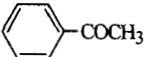
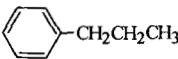
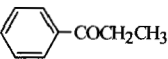
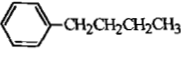
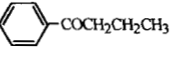
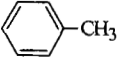
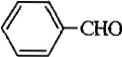
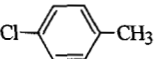
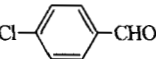
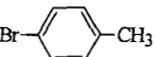
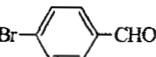

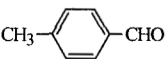
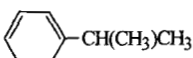
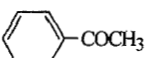


Scheme 2

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 ketone 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 aldehydes 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 shortened and the yields were increased. It is surprising that *t*-propylbenzene also gave the ketone product in 15%.

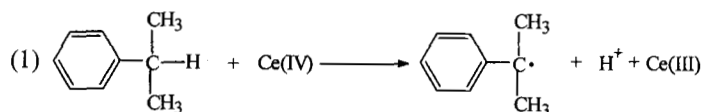
The results of our experiment are superior to those obtained in other uncatalytic systems⁸. The results in the case of isopropylbenzene suggest that the

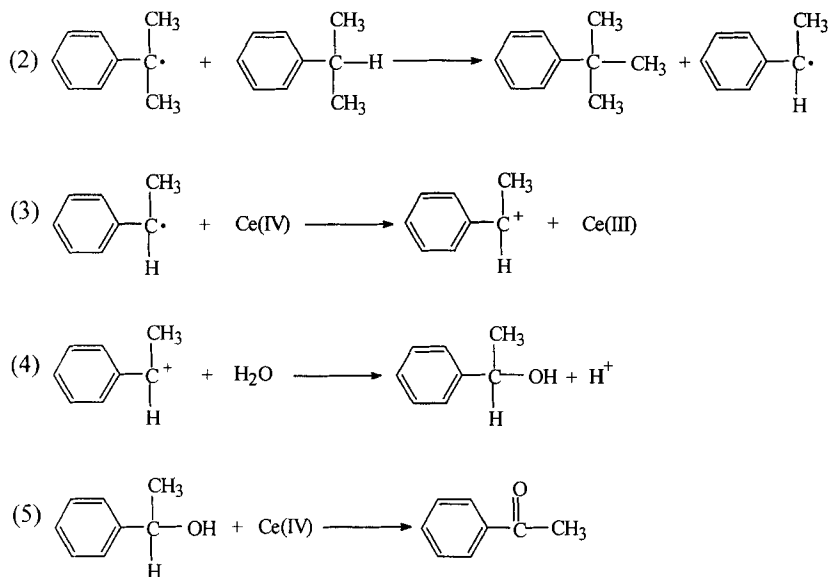
Table 1 Oxidation of Alkylbenzene by CAN/NaBrO₃

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-dinitrophenylhydrazone and determined by IR.

oxidation reaction involves free radical and benzylic carbonium ion. It is now generally accepted that the side-chain oxidation of alkylarenes with Ce(IV) occurs via a radical cation⁹. Based on this opinion, we think that the oxidation of isopropylbenzene to phenyl methyl ketone maybe happened as the following five steps:





Scheme 3

In summary, $\text{CeO}_2/\text{NaBrO}_3$ is a good reagent for the selective oxidation of alkylbenzenes. It is a convenient and cheap method for the conversion of 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 °C 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 product which was isolated as 2,4-dinitrophenylhydrazone.

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