SHORT PAPER

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Ultrasound-promoted samarium/ammonium chloride mediated reductive coupling of aromatic ketones[†]

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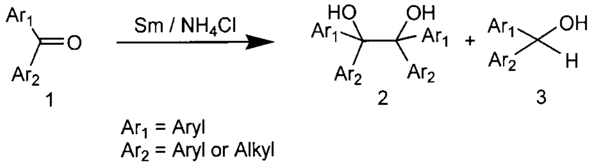
Ultrasound-promoted samarium/ammonium chloride mediated reductive coupling of aromatic ketones was investigated.

The chemistry of samarium metal in organic synthesis is receiving considerable attention because of its ready availability, stability and cost.[1] Recently, samarium has been used for the reduction reaction of ketones in the presence of trimethyl silyl chloride[2] and several lanthanides.[3] We have also used this metal for the reduction of aromatic nitro compounds[4] and imines[5] in the presence of catalytic amounts of iodine. These reports indicate that the reducing ability of samarium depends on its activation by the addition of some other reagents as samarium alone failed to give any products. This prompted us to examine the reducing ability of samarium metal in the presence of other reagents and towards the goal we have already demonstrated a facile pinacol type of coupling of aromatic ketones in the presence of alkyl halides.[6] We envision that such dimerisation of the ketones could be improved in the presence of other activating agents which could improve the reducing ability of the metal. A search of the literature revealed that indium metal in the presence of ammonium chloride greatly enhances the speed of the reaction rates in some cases.[7] We report here a facile reduction of several aromatic ketones to diols by samarium in the presence of ammonium chloride under sonication[8] at room temperature. We believe this is the simplest and most convenient method for the reductive dimerisation of the aromatic ketones.

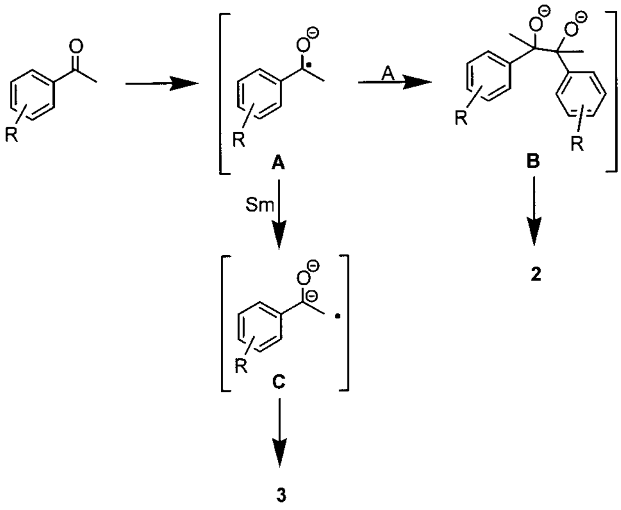
The reaction of acetophenone derivatives (Table 1, entries 1–5) was studied in detail. Untrasonic exposure of a solution of acetophenones in the presence of samarium/ammonium chloride at room temperature produced the resultant diols in excellent yields (66–98%). A small amount of alcohols (Table 1) was isolated. Similarly, benzophenones (Table 1, entries 6–7) could be reduced to the diols along with the alcohols (93–96%) in excellent yield.

The mechanism of the samarium/ammonium chloride mediated reduction has not been investigated. Based on the nature of the products, a most probable mechanism could be suggested which has a close similarity to our samarium-iodine induced reduction reaction of the imines.[5] Single electron transfer to the unsaturated carbon–oxygen bond can generate the ion radical **A** and because of the stability of the benzylic radical, a self-coupling process, **A** to **B** is feasible. As a result of this, a pinacol type of compound **2** is formed (Scheme 2). In concentrated solution further electron transfer to the ion-radical **A** can be a competitive path to the dianion **C** which can be easily protonated by methanol to generate the alcohol **3**. The formation of substantial amounts of alcohols **3** in the benzophenone reduction (entries 6–7) indicates a severe steric hindrance at the ion-radical centre **A** and we assume that this prevents the self-coupling process. However, the formation of considerable amounts of alcohol with 4-methoxyacetophenone (entry 5) could not be explained by using this hypothesis.

The distinct advantages of the reduction of aromatic ketones for the synthesis of the diols reported herein over other methods include a very short reaction time, environmentally benign reagents, less by-products and overall high yield.



Scheme 1



Scheme 2

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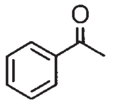
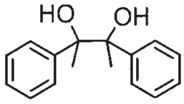
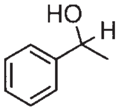
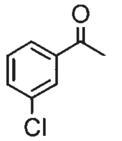
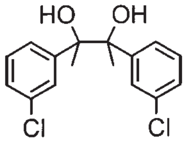
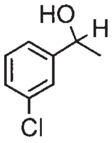
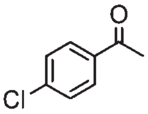
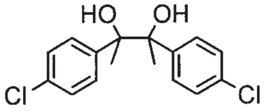
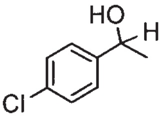
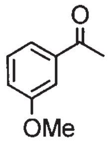
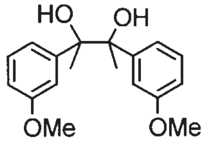
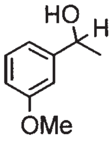
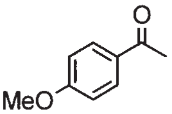
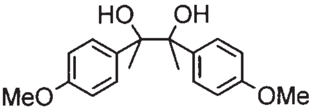
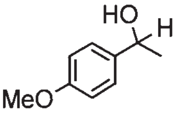
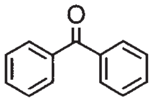
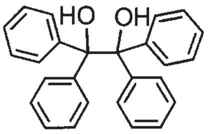
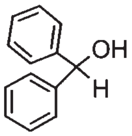
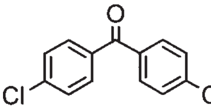
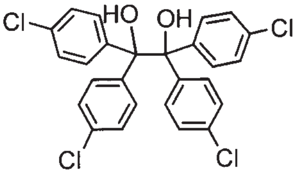
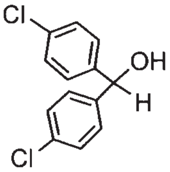
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Ultrasound promoted pinacol coupling of aromatic ketones by Sm/NH_4Cl

Entry	Ketone	Time (min)	**2**	**3**	**2 : 3**	Yield of alcohol (%)	Yield of diol (%)
1		5			82.:18	11	54
2		5			76 : 24	22	69
3		5			76 : 24	22	72
4		5			70 : 30	27	66
5		5			53 : 47	51	46
6		5			51 : 49	48	46
7		5			40 : 60	37	55

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8 For an example of the beneficial effect of ultrasonic irradiation, see: B.H. Han and P. Boudjouk, *J. Org. Chem.*, 1982, **47**, 5030.

9 A representative procedure is as follows: To a solution of ketone (0.5 mmol) in methanol (10 ml), solid ammonium chloride (2.5 mmol) and samarium metal (1.1 mmol, 40 mesh) was added and the reaction mixture was sonicated[10] at room temperature for 5 min. The reaction started immediately as indicated by the evolution of gas and change of colour of the reaction mixture from colorless to greenish yellow. After the reaction was completed as indicated by TLC, the total volume of the reaction mixture was reduced (*ca* 2ml) by evaporation under reduced pressure. Water (5 ml) was added to the residue and the reaction mixture was extracted with dichloromethane (3 × 5 ml). The organic layer was dried over sodium sulfate and concentrated. The pure product was obtained by column chromatography using ethyl acetate and hexane as the solvent. All products have been characterized through mass and NMR spectra and direct comparison with authentic samples prepared earlier in this laboratory.[6]

10 A. Bransonic Model 2210R-DTH was used for sonication.