

Pronounced Catalytic Effect of Micellar Solution of Sodium Dodecyl Sulfate (SDS) for Regioselective Iodination of Aromatic Compounds with a Sodium Iodide/Cerium(IV) Trihydroxide Hydroperoxide System

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Received: March 3, 2005; Accepted: September 5, 2005

Abstract: Micellar solutions of sodium dodecyl sulfate (SDS) catalyze the regioselective iodination of a wide range of aromatic compounds with sodium iodide in the presence of the easily prepared, water-resistant and recyclable cerium(IV) trihydroxide hydroperoxide, $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$, at room temperature. By this protocol, structurally diverse aromatic compounds including benzene and naphthalene were iodinated in good to excellent yields.

Keywords: aromatic compounds; cerium(IV) trihydroxide hydroperoxide; iodination; sodium dodecyl sulfate; sodium iodide

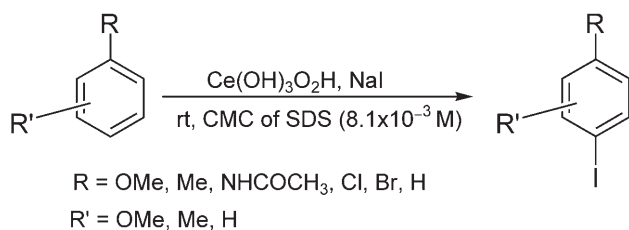
Regarding environmental problems and pollution, clean organic reaction processes which do not use harmful organic solvents are encouraged and are in great demand today.^[1] Water as a cheap and relatively green solvent could be considered as an alternative reaction media for organic processes.^[2,3] However, water with its physical and chemical properties imposes selectivity and reactivity in reactions conducted in this media which cannot be observed in organic solvents.^[4] However, the heat capacity of water is not favourable and isolation and drying of the product sometimes encounter serious problems especially, for large-scale operations. Moreover, organic solvents are still used in most organic reactions for the reasons given below; first of all, most organic substrates are not soluble in water, therefore, it cannot play the role of reaction medium. Second, many reactive substrates, catalysts, reagents and products of the reactions are not stable in water and are decomposed or deactivated in aqueous media. One way to surmount the solubility problem is the use of surface-active compounds which are able to form micelles or vesicular structures in aqueous reaction media.^[5] The use of micellar and vesicle-forming surfactants as catalysts is widespread

and has been investigated in detail for different reactions in aqueous solutions.^[6,7] However, micellar-aided organic reactions are still at their preliminary stages. Recently, we have reported the successful ring-opening of epoxides with various types of nucleophiles^[8] and Michael addition of amines and thiols to α,β -unsaturated ketones in micellar solutions of sodium dodecyl sulfate (SDS).^[9]

Iodoarenes as valuable and versatile synthetic intermediates have found wide applications in medicine and biochemistry.^[10,11] Due to the weaker electrophilic nature of iodine than bromine and chlorine, and also for other reasons, the use of molecular iodine for the synthesis of this important class of compound is not extensively applied.^[11–13] Except for $\text{Pb}(\text{OAc})_4/\text{HOAc}$,^[14] the other reported procedures such as vanadium salts/ $\text{CF}_3\text{SO}_3\text{H}$,^[15] $\text{KMnO}_4/\text{H}_2\text{SO}_4$,^[16] $\text{HIO}_4/\text{H}_2\text{SO}_4$,^[17,18] include highly powerful oxidizing agents which are used in strongly corrosive acidic media. Some other reported methods suffer from using not easily available compounds and others use highly corrosive, toxic or expensive reagents. Examples are: I_2/HgX_2 ,^[12a] $\text{I}_2/\text{Ag}_2\text{SO}_4$,^[19] $\text{NaI}/\text{CF}_3\text{SO}_3\text{H}$.^[12b] Other milder procedures used for the direct iodination of aromatic compounds are NaOCl/NaI ,^[20] $\text{Fe}(\text{NO}_3)_3 \cdot 1.5 \text{N}_2\text{O}_4/\text{charcoal}$.^[21]

We now introduce a system composed of cerium(IV) trihydroxide hydroperoxide [$\text{Ce}(\text{OH})_3\text{O}_2\text{H}$]^[22] and sodium iodide as a cheap, easily prepared, stable, regenerable system for the direct iodination of aromatic compounds in micellar aqueous media. Aqueous solutions of sodium dodecyl sulfate (SDS) at its critical micellar concentration (CMC) catalyze the direct regioselective iodination of structurally diverse aromatic compounds including benzene and naphthalene at room temperature (Scheme 1).

In order to optimize the reaction conditions we chose anisole (1 mmol) as an activated aromatic compound which was reacted with $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$ (1 mmol) and NaI (1 mmol) in dry CH_3CN (4 mL) at room temperature for 24 h. Work-up of the reaction mixture resulted



Scheme 1.

in 4-iodoanisole in only 10% yield. Other solvents such as CH_2Cl_2 and CHCl_3 were also tested but were complete failures. Then we decided to run the reaction in water. The results show that 4-iodoanisole was produced in 5% yield after 24 h. We have also studied a similar reaction in a mixture of CH_3CN and water (1/1 by volume). After 24 h, 4-iodoanisole was detected (GC) in only 20% yield.

Next, we performed the iodination of anisole (1 mmol) with NaI (1 mmol) and $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$ (1 mmol) in 4 mL SDS micellar solution at its CMC ($8.1 \times 10^{-3} \text{ M}$) at room temperature. This reaction proceeded well and produced 4-iodoanisole in 97% yield after 1.5 h with high regioselectivity (Table 1, entry 1). We believe that this rate enhancement is due to the strong catalytic activity of the vesicle of the droplets of micellar SDS. The pronounced effect of micellar SDS solution in the reaction could be explained as follows: molecules of $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$, sodium iodide and the aromatic compound are accumulated inside the vesicle of the droplets of micellar SDS in which the distance between the reacting species could decrease drastically which facilitates the progress of the reaction and rate enhancement is observed. The similar hydrophobic nature of the aryl iodide product with the hydrophobic core of the micellar droplet could be considered as another factor for the rate enhancement of the reaction. These explanations are schematically presented in Figure 1.

We therefore applied similar reaction conditions to benzene, naphthalene and other benzenes substituted with electron-releasing and electron-withdrawing groups (Table 1). The strong feature of this procedure is the preparation of the iodobenzene in good yield. The synthesis of iodobenzene by direct iodination of

benzene is not an easy task and, in most of the methods, it proceeded under harsh conditions with low yields.^[23]

In this report, benzene was iodinated with NaI/ $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$ system at room temperature in 80% yield after 3 h in SDS micellar media (Table 1, entry 7). Using this micellar effect, chloro- and bromobenzenes can be also easily iodinated at room temperature in good yields (Table 1, entries 9 and 10). We have also observed the formation of the *ortho* isomer of the iodinated compounds in 2–8% in the reaction mixture.

The regeneration of $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$ is of practical and economical importance. The regeneration can be easily achieved by the filtration of the pale yellow solid residue of the cerium species from the reaction mixture. This residue upon washing with H_2O_2 (35%) produces the orange-red powder of $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$ immediately in almost quantitative yield. This regenerated reagent is as reactive as the freshly prepared one.

In conclusion, in this study, we have reported the regioselective iodination of benzene, naphthalene and some other aromatic compounds catalyzed by SDS solution at its CMC using the NaI/ $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$ system at room temperature. The protocol could be considered as a relatively eco-friendly procedure which proceeded purely in water.

Experimental Section

Typical Procedure for Iodination of Anisole with NaI

To a mixture of anisole (1 mmol, 0.108 g) and NaI (1 mmol, 0.150 g) in 4 mL SDS micellar solution at its CMC ($8.1 \times 10^{-3} \text{ M}$), cerium(IV) trihydroxide hydroperoxide (1 mmol, 0.224 g) was added at room temperature. After 1.5 h, the reaction mixture was treated with $\text{Na}_2\text{S}_2\text{O}_4$ solution (10%, 10 mL) and extracted with diethyl ether ($2 \times 10 \text{ mL}$). This extract was dried over anhydrous sodium sulfate. After filtration and evaporation of the solvent, the crude product was obtained. Further purification was performed using chromatography over a short column of silica gel which, after evaporation of the solvent, afforded the desired pure *p*-iodoanisole; yield: 0.227 g (97%). ^1H NMR (250 MHz, CDCl_3): $\delta = 3.80$ (s, 3H, OCH_3), 6.94 (d, $J = 8.5 \text{ Hz}$, 2H, Ar), 7.28 (d, $J = 8.5 \text{ Hz}$, 2H, Ar); ^{13}C NMR (63 MHz, CDCl_3): $\delta = 55.2, 87.2, 113.9, 138.2, 160.7$.

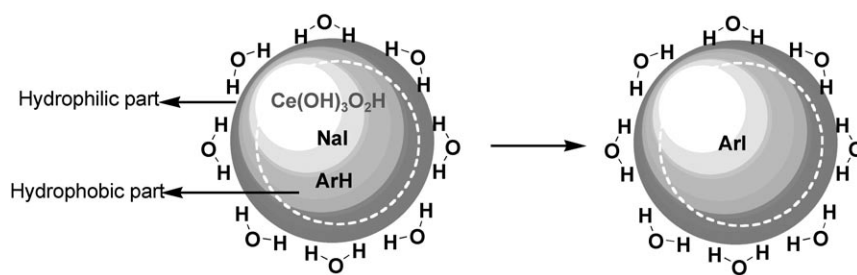
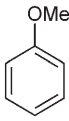
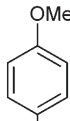
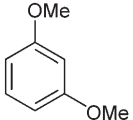
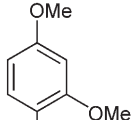
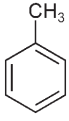
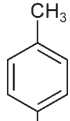
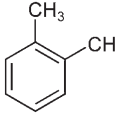
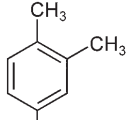
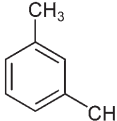
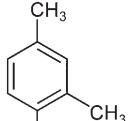
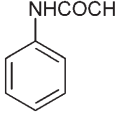
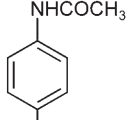
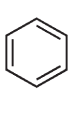
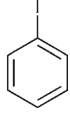
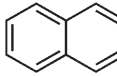
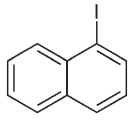
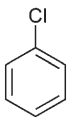
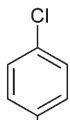
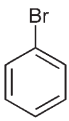
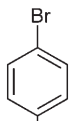


Figure 1.

Table 1. Iodination of aromatic compounds with NaI and $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$ in SDS micellar solution at its critical micellar concentration (CMC) at room temperature.

Entry	Substrate	Product	Time [h]	Yield [%] ^[a]
1			1.5	97
2			1.5	96
3			2	87
4			2	93
5			2	95
6			1	94
7			3	80
8			3	78
9			3	80
10			3	76

^[a] Yields refer to the isolated product.

Acknowledgements

We are thankful to Iran Chapter of TWAS based at ISMO and Shiraz University Research Council and the Grant No. 503614 from the Ministry of Science, Research and Technology of Iran for the support of this work.

References and Notes

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