

Note

Effect of organized assemblies, Part-III: Micellar catalysed iodo-de-diazoniation reactions

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The iodo-de-diazoniation of benzene diazonium chloride has been carried out in the presence of ionic and nonionic surfactants. Anionic and nonionic micelles do not facilitate the product formation whereas the cationic surfactant gives a reasonable increase in the yield as compared to that in the absence of the surfactants. The results have been attributed to the increase in the effective concentration of the reactants in a reduced volume of Menger's micelle resulting out of both hydrophobic and electrostatic interaction of the reactants and the micelle.

Keywords: Iodobenzene, iodo-de-diazoniation reaction, surfactant assisted reactions, Menger's model, green chemistry, hydrophobic patches

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Indiscriminate use of chemicals in everyday life has threatened the bio-world by presenting a deteriorating image of chemical and especially of synthetic chemicals causing serious health and environment hazards. The awareness of ecofriendly, pollution free and less cost effective chemistry termed as Green Chemistry^{1,2} is of dire need today for sustainable development of the biosystem. Therefore, organic reactions conducted in aqueous media have received much attention from chemists³⁻⁸. Many of the organic reactions like deoxygenation of nitrones to corresponding imines and oximes to nitriles have been carried out in hydrated media^{9,10}. Gogoi *et al.* have reported the selective oxidation of alcohols to carbonyl compounds¹¹ and deprotonation of oximes and imines to carbonyl compounds⁷ in aqueous media.

Aryl iodides are the starting materials for Sonogashira cross coupling reaction¹² which is frequently used as key step for synthesis of pharmaceuticals such as the enediyne antibiotics or the contraceptive pill¹³⁻¹⁶. One of the best methods of introducing iodine into aromatic ring is the reaction of iodine with diazonium salt. Many workers have

cultured the synthesis of halobenzene from benzenediazonium chloride by various modifications to improve the yield. Surfactant aggregates have been found to be suitable biphasic systems for carrying out large number of reactions⁷. The phase transfer catalyzed alkylation at C-3 position of 3,4-dihydrocarbelinones has been reported by Wakebayashi *et al.*¹⁷. Behera *et al.*¹⁸ have prepared an ester of caproic acid in a biphasic system. Substantial increase in the yield of product using biphasic system has been reported^{19,20}. In the present work, we have studied iodo-de-diazoniation of benzene diazonium chloride in the presence of cationic surfactant, cetyltrimethylammonium bromide (CTAB), anionic surfactant, sodium dodecyl sulphate(SDS) and nonionic surfactant, Triton-X-100 to investigate the effect of these micellar media on the yield of the reactions.

Experimental Section

SDS (CDH, New Delhi), CTAB (CDH, New Delhi) were purified by standard methods. Triton-X-100 (CDH, New Delhi) was used without further purification.

Preparation of iodobenzene

Iodobenzene was prepared by the following way and yield in grams was determined. (i) Aniline hydrochloride (2 g in 10 mL of water), cooled NaNO₂ (1 g in 5 mL of water) and solution of potassium iodide (4 g in 10 mL of water) are kept in an ice bath maintaining the temperature at 0-5°C for overnight. The yield of iodobenzene was found to be 0.5424 g. (ii) Aniline hydrochloride (2 g, 10 mL of water, 10 mL of 0.1 M CTAB), cooled NaNO₂ (1 g in 5 mL of water) and solution of potassium iodide (4 g in 10 mL of water) were kept in an ice bath maintaining the temperature at 0-5°C for overnight. The yield was found to be 0.8410 g. (iii) The procedure in (ii) was repeated taking sodium nitrite in CTAB solution instead of aniline hydrochloride. The yield in this case was 0.2907 g. (iv) The procedure in (ii) was repeated taking KI in CTAB solution. The yield of iodobenzene in this case was found to be 0.3699 g.

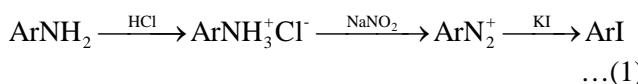
Product analysis

The product was analyzed by TLC on silica gel plate taking benzene and methanol (99:1) as eluent. Test for iodide was done from each isolated product

and positive inferences were made. The product was tested for biaryl with potassium ether keeping overnight in a refrigerator and for phenol with FeCl_3 test. Negative inferences were obtained indicating the product to be iodobenzene.

Results and Discussion

The iodo-de-diazonation reaction is the formation of benzene diazonium chloride by the action of HCl and NaNO_2 on aniline and subsequent reaction of KI to give iodobenzene as shown in Equation 1.



In the present study, the iodo-de-diazonation reactions were carried out by dissolving the three synthons aniline hydrochloride, sodium nitrite and potassium iodide in water and in surfactants solutions containing CTAB, SDS and T-X-100 independently. Aniline hydrochloride did not give any reaction with SDS and Triton-X-100. But CTAB gave a substantial increase in the yield.

The fact that anionic surfactant, SDS does not favour the formation of product can be explained in terms of the incorporation of the benzenediazonium ion into the Hartley's surfactant aggregate²¹ due to both favourable hydrophobic and electrostatic interactions and the non-approachability of the nucleophile I^- to the micelle bound diazonium ion due to electrostatic repulsions. This leads to the distribution of the two reactants in two different phases, I^- in water and benzenediazonium chloride in micellar phase. The nonionic surfactant T-X-100 also provides a negative charge surface due to induced negative charge on the oxygen atom of the polyoxyethylene chains²² thus not allowing the incorporated benzenediazonium chloride to react with the iodide ions. Fernandez and Fromherz²³ have also made similar observations in the measurements of electrical potential and polarity of SDS and T-X-100 micelles using lipoid pH indicators as probe.

In case of the CTAB micelles the surface is positively charged which attracts I^- and is expected to expel out benzenediazonium ion from the micellar phase due to unfavourable electrostatic repulsions with the positive surfacial charge. But the formation of product in a greater yield indicates that the benzenediazonium ions are also found on the micellar surface. Had it been incorporated into the innermost core of the Hartley micelle²¹, having a hexane-like

environment the product would not have been formed. However, it can be conveniently explained by Menger's micelle²⁴. In Menger micellar model some parts of the hydrocarbon tails of the surfactants are exposed to water forming hydrophobic patches^{24,25}. We have calculated that almost 9% of the surface of CTAB micelle to be hydrophobic during the study of hydroxylation of rosaniline hydrochloride by sodium hydroxide in presence of micellar solution²⁵. Thus, the reactants are brought into close proximity and the reaction is favourable thereby increasing the yield. Menger's model for SDS and T-X-100 also explains the unsuitability as a reaction media for those surfactants. Benzendiazonium ions can be placed on the hydrophobic patches of the micelles of SDS and T-X-100 due to favourable hydrophobic and hydrophilic interactions but the nucleophile I^- cannot come into close vicinity of the diazonium ion either by electrostatic or hydrophobic interaction since the nucleophile is oppositely charged and is not nonpolar.

Conclusion

This study is in fact a surfactant catalysed reactions in which the yield of the product has been increased substantially using cationic surfactants CTAB. Many of the surfactants are environmentally compatible, readily biodegradable and easy to handle²⁶. Even though we do not have direct reports on the toxicity and biodegradability of CTAB, still literature survey reveals that cationic surfactants with alkyl and benzyl group are less aquatic toxic, easily biodegradable^{27,28}. The increase of yield is due to increase in the effective concentration of the reactants due to favourable hydrophobic and electrostatic interaction in the vicinity of Menger's CTAB micelles.

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