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OXONE: A CONVENIENT REAGENT FOR FACILE SYNTHESIS OF DIARYLIODONI-UM SALTS

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Oxone® is the trademark name of a stable triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. The active oxidant within the mixture, peroxymonosulfate (HSO_5^-), has been the subject of study in various fields ranging from atmospheric science to physical and computational chemistry. The focus on the salts of Caro acid has not waned for more than one century and has been caused by the extraordinary oxidizing abilities of this compound. This reagent is distinguished by low cost and toxicity and combining with high oxidation properties and facile handling in storage and use. All these aspects make Oxone as a very attractive reagent. Therefore, the Oxone® usage for the synthesis of the most important hypervalent iodine compounds was shown in [2, 3].

Diaryliodonium salts are derivatives of hypervalent iodine compounds have found broad application as reagents in organic synthesis as an analogues of organic-metal catalysts and complexes based on toxic and heavy metals due to their particular structure (Figure 1). Iodine atom in iodine (III) compounds are electrophilic because of the node in the nonbonding orbital of the hypervalent bond. Thus, they react with various nucleophiles by initial Nu – I bond formation and release of the ligands.

A procedure for direct diaryliodonium salts synthesis from iodoarenes, without isolation of an iodine (III) intermediate, is attractive for many reasons. Advantages include reduced reaction time and increased substrate scope, as many intermediates are unstable towards isolation. Furthermore, the applicability is improved when diversely substituted

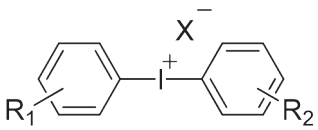

Fig. 1. *Structure of diaryliodonium salts*

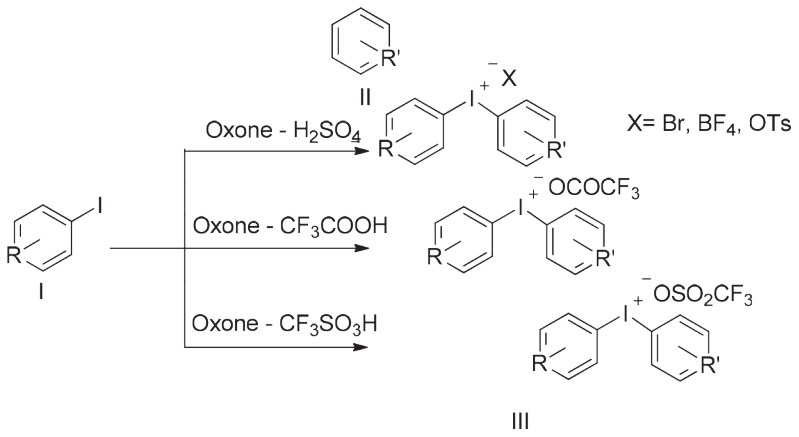

Fig. 2. *General scheme synthesis*
(R=H, CF_3, 5F, R'=H, CH_3, $2CH_3$, $3CH_3$, OCH_3, Cl, Br)

diaryliodonium salts can be obtained by the same method that it was shown at [4]. Thus, a convenient "one-pot" method for the synthesis of diaryliodonium salts was recently developed.

Herein we report the development of a reliable and convenient procedure for the preparation of diaryliodonium salts using Oxone in the presence of sulfuric acid. (Figure 2).

At the first stage, the iodaryl substrate was oxidized with Oxone® reagent in a sulfuric acid medium to produce an iodosyl product (iodine (III) product). Next, the aryl reagent was added to the coupling reaction. The reaction products were diaryliodonium salts, containing in their composition various functional groups. Further, ion exchange with p-toluenesulphonic and triftomethanesulfonic acids was carried out.

Synthesis was carried out “one-pot” without isolation of intermediates. The products were isolated by adding water and dichloro-methane to the mixture. The product yields are following:

$R=H$, $R'=Cl$, $X=CF_3SO_3$ = 23 %
$R=NO_2$, $R'=CH_3$, $X=CF_3SO_3$ = 58 %

$R=H$, $R'=(CH_3)_3$, $X=Br$ = 36 %
$R=H$, $R'=Cl$, $X=OTs$ = 29 %

Thus, Oxone®, as an oxidizing agent for diaryliodonium salts synthesis, was shown. Particularly attractive is the possibility of the onepot synthesis of symmetric bis-aryliodonium salts directly from arenes via an iodination-oxidation sequence.

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