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Metal-Free O-Arylation of Carboxylic Acid by Active Diaryliodonium(III) Intermediates Generated *in situ* from Iodosoarenes

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Abstract. The metal-free arylative coupling of carboxylic acids using iodosoarenes without the use of a catalyst and base, which is applicable to even a highly-polar molecule bearing multiple alcohol groups, is reported. The *in situ* preparation of the reactive diaryliodonium(III) carboxylates is the important key to this approach, and the introduction of the trimethoxybenzene auxiliary enables both the smooth salt formations and the selective aryl transfer events during the couplings.

Keywords: Arylation; Hypervalent compounds; Iodine; Reactive intermediates; Carboxylic acids

Aryl ester structures are ubiquitously found in both naturally-occurring compounds and artificial molecules in fine organic chemicals, and thus their and clean construction from effective the corresponding carboxylic acids is of continuous interest in modern synthetic chemistry and their developments.^[1] Early examples significantly investigated in this area are esterification methods triggered by electrophilic activation of the carboxylic acid functionality by acids and specific derivations, i.e., to the acyl chloride and other activated forms, as represented by the Fischer-Speier esterification,^[2] Schotten-Baumann reaction,^[3] and other sophisticated esterification methodologies using stoichiometric condensation reagents.^[4] With recent significant advances in the metal-catalyzed cross-couplings technologies, a new synthetic approach categorized as the arylative coupling that instead includes carboxylic acids as the O-nucleophile toward aryl coupling partners has become one of the alternative choices to these esterifications for producing aryl esters. Indeed, a series of arylboron compounds (Chan-Lam-Evans type reaction)^[5] and aryl halides^[6] are the typical aryl sources for the couplings by the catalysis of transition metals.^[7] Furthermore, developing the metal-free

variant has attracted attention in modern organic synthesis, and such an elegant coupling chemistry is possible by utilization of the diaryliodonium(III) salts that possess excellent leaving-group abilities for facilitating the nucleophilic arylic substitution processes.^[8] Indeed, the first general methodology regarding the arylation of carboxylates with diaryliodonium(III) salts was reported by Olofsson and co-workers in recent years.^[9,10] Based on this development, we now report a new metal-free arylative coupling method using iodosoarenes without requiring any catalyst or base for enhancing the nucleophilicity of carboxylic acids, and other chemical initiators (Scheme 1). The protocol including the specific in situ facile access to diaryliodonium(III) carboxylates, that is, the reactive coupling intermediates, by dehydrative condensation of a series of iodosoarenes with carboxylic acids would allow the effective couplings, which are applicable to even highly polar molecules bearing multiple alcohol groups.



✓ metal-free ✓ no base activator ✓ single arylation products
✓ improved substrate scope ✓ high chemoselectivity

Scheme 1. Efficient arylative coupling of carboxylic acids based on new approach to reactive diaryliodonium(III) intermediate.

When treating iodosobenzene 2a in the presence of some carboxylic acids (see Scheme 2 for an example of benzoic acid 1a), the reaction with benzene in hexafluoroisopropanol^[11,12] slowly gave the product of

a three-component dehydrative condensation, that is, diphenyliodonium(III) benzoate I (Eq. 1). Upon heating, this benzoate salt I spontaneously decomposed to cause ligand coupling between the phenyl group and the oxygen atom of the benzoic acid 1a (Eq. 2), and the arylative coupling product 3aa was quantitatively obtained from the salt I. However, the entire process for the aryl ester formation was not very productive due to the inefficient access to the salt I that employs the low reactive benzene for the initial condensation.



Scheme 2. Initial attempt for the metal-free arylative coupling involving new preparation of diaryliodonium(III) carboxylate **I** (Eq. 1). Fluoroalcohols = HFIP (1,1,1,3,3,3)-hexafluoro-2-propanol) or TFE (2,2,2-trifluoroethanol).

In order to improve the synthetic design, it appeared that an alternative selection of the aromatic condensation partner is necessary to facilitate the iodonium(III) carboxylate formation. Recently, Stuart, Olofsson, and we independently reported the effective preparations of aryl(trimethoxyphenyl)iodonium(III) salts.^[13,14] and we have now determined the trimethoxybenzene as a specific promoter for the formation of a series of the carboxylate salts.^[15] In addition, the introduced trimethoxybenzene moiety in the salts is expected to serve as an inert auxiliary group during the ligand coupling of the salts,^[13b,c,14c] and thus, the reaction exclusively involves the aryl ring that originated from the iodosoarene. As a result, a single arylation product 3 was obtained by thermal decomposition of the carboxylate salt after removal of the solvent. An example of the arylation using this strategy is shown in Scheme 3; together with 1,3,5trimethoxybenzene, the reaction of benzoic acid 1a with iodosobenzene 2a to form the salt I' followed by its heating successfully produced the expected aryl ester 3aa in an almost quantitative yield. Such in situ utilizations of diaryliodonium(III) salts and one-pot strategy are the recent topic of interest in the metalfree coupling reactions.^[12a,16]



Scheme 3. Effective coupling protocol utilizing the trimethoxybenzene promoter.

Iodosoarenes are less reactive among the hypervalent iodine reagents due to their polymeric form,^[17] while the high nucleophilicity of the electron-rich trimethoxybenzene would allow the effective dehydrative condensation,^[14a] smoothly producing the corresponding diaryliodonium(III) salts carrying

 Table 1. Phenyl esters 3ba-ra obtained from various carboxylic acids 1b-r and iodosobenzene 2a via formation of phenyl(trimethoxyphenyl)ioodnium(III) carboxylates ^{a)}

Aromatic carboxylic acids





^{a)} The arylative coupling conditions: iodosobenzene (1 equiv relative to carboxylic acids) and 1,3,5-trimethoxybenzene (1 equiv) in 2,2,2-trifluoroethanol for 2 h at room temperature, then heating (110 °C) on toluene for maximum 3 h. Isolated yields of pure aryl ester products after column chromatography on silica-gel are indicated in the parenthesis together with the chemical structures.

various carboxylate counterparts. Consequently, by employment of the trimethoxybenzene auxiliary, a varied series of carboxylic acids becomes applicable using our coupling approach (Table 1). For effective heating of the *in situ* formed salts, toluene^[9a,b] was used for these couplings.^[18] Less nucleophilic and more acidic carboxylic acids, *i.e.*, the 4- and 2nitrobenzoic acids, are better substrates, which is in significant contrast to the outcomes from the reported methods for the couplings using diaryliodonium(III) salts.^[9,10] As well as the product **3da**, the yields of the aryl ester products 3ba and 3ca derived from these carboxylic acids were thus significantly improved to 93% and 92%, respectively.^[19] Meanwhile, 2,3dimethoxybenzoic acid was transformed into the aryl ester 3ea in a good yield. The carbon-halogen bond that is reactive under many cross-coupling conditions did not cleave during the arylation (see product 3fa). Despite the steric bulkiness of the carboxylic acid, which links together with the hindered methoxybenzene auxiliary at the iodonium(III) atom (see Eq. 1), the corresponding aryl ester 3ga was obtained in 83% yield.^[20] The presence of oxidizable and base-sensitive groups, such as the naphthalene ring and aldehyde, were acceptable as the coupling substrates (see 3ha and 3ia), which would suggest that the oxidations of these functionalities are rather slow compared to the rapid salt formations. The carboxylic acids containing thiophene and pyridine rings are also coupling substrates, and the basicity and coordination of these heteroatoms appeared not to influence the reaction processes (see 3ja-3la). The aliphatic carboxylic acids were found to similarly cause the arylations; the selected examples of the products include the aliphatic esters 3ma and 3na, ester 3oa having a quaternary group, keto acid ester 3pa, and even 3ga and 3ra possessing oxidizable alkene moieties.

As many types of iodosoarenes 2 are available by simple and reliable preparations,^[21] the method can possibly attach various aryl moieties to the carboxylic acids by changing the aryl source. Thus, we examined an extended series of iodosoarenes 2b-h, which were prepared from the corresponding iodine(III) diacetates or dichlorides (Table 2). The reactions with benzoic acid 1a for these iodosoarenes were carried out under the same conditions, and all the expected aryl esters **3ab-ah** can be obtained in yields ranging from 56-93%. Hence, different electronic and steric structures of the iodosobenzene derivatives **2b-h** had little influence on the method. Among the examined reactions, the production of the aryl ester 3ah using the nitrogencontaining aryl source 2h showed a decrease due to the reduced yield during the iodonium(III) salt formation. all the cases, incorporation In of the trimethoxybenzene into the carboxylic acid 1a was not detected. Regarding the ligand coupling selectivity of the diaryliodonium(III) salts, both the electronic and steric factors of the two aryl groups should be considered,^[22] in which the strong electronic characteristics of the introduced trimethoxybenzene would overwhelm the steric "ortho-effect", causing

the one ligand coupling course and observed aryl ester selectivities from the intermediates ($ArI^+Ar^X^-$, Ar =aryl groups from iodosoarenes **2**, $Ar^2 = 2,4,6$ trimethoxyphenyl, X^- = benzoate).

Table 2. Several iodosoarenes **2** for the couplings initiated by thermal decomposition of *in situ* formed diaryliodonium(III) carboxylates ^{a)}



^{a)} Conditions: iodosoarene (*Ar*I=O, 1 equiv relative to benzoic acid **1a**) and 1,3,5-trimethoxybenzene (1 equiv) in 2,2,2-trifluoroethanol (TFE) for maximum 2 h at room temperature, then heating (110 °C) on toluene for 3 h. ^{b)} oxidant = NaBO₃/AcOH (for **2b**, **2d**, **2e**, and **2g**), *m*CPBA/AcOH (for **2c**), NaIO₄/AcOH (for **2f**), Cl₂ (for **2h**).

The conventional esterification procedures for the carboxylic acids^[2-4] sometimes suffered from an uncontrolled chemoselectivity during the condensation, if multiple numbers of alcohol groups are present in the molecule. We were encouraged to note that this type of chemoselectivity issue can be generally ruled out by the diaryliodonium(III) strategies;^[23] for example, it was revealed that the three hydroxyl groups of cholic acid 1s have no effect on the coupling event, and when reacting with the iodosoarenes 2a and 2g non-protected aryl esters 3sa and 3sg were obtained as the sole arylation product with outstanding yields (Scheme 4). Note that no other arylation product at the hydroxy groups was observed during the reaction. This agrees with the fact that the corresponding iodonium(III) salt formation for cholic acid **1s** occurred only with the acidic carboxyl group rather than the alcohol moieties. On the other hand, attempts to esterifications using our other representative methods (EDC, Mitsunobu, Corey-Nicolaou, Mukaiyama, Yamaguchi, etc.)^[4] were all disappointing, resulting in low-yield formations of the target aryl ester 3sa (For details, see the Suppring Information) due to the competing alcohol nucleophilicities and/or scarce solubilities of the

cholic acid **1s** in organic solvents, except for the highly polar solvents, i.e., fluoroalcohols, employed in our strategy.



Scheme 4. Caroboxylic acid versus alcohol functionalities: selective arylation of carboxy-fuctional group of cholic acid 1s.

In summary, we have established the efficient metal-free arylation of carboxylic acids 1 based on the new generation of reactive diaryliodonium(III) intermediates for the couplings. The reagent system consisting of iodosoarenes 2 and a specific promoter, the trimethoxybenzene, is efficient for the arylation of carboxylic acids having low pKa values and compatible for conversions of a highly-polar molecule bearing multiple alcohol groups. We expect that the extension of this synthetic concept will appear in the near future along with further detailed studies of this work.

Experimental Section

General procedure for arylative coupling of carboxylic acids 1 using iodosoarenes 2 (Tables 1 and 2)

To a stirred solution of carboxylic acid 1 (0.30 mmol) and 1,3,5-trimethoxybenzene (1 equiv) in TFE (3 mL), iodosoarene 2 (1 equiv) was added in one portion under N₂ atmosphere at 0 °C. The reaction mixture was then warm up to room temperature, and stirred for 1 h. The solvent was removed by rotary evaporator, and to the resulting residue 3 mL of toluene was added, which was then heated at 110 °C for 3 h. After cooling to room temperature, the reaction mixture was directly subjected to column chromatography on silica-gel (eluent: *n*-hexane/ethyl acetate) to give pure aryl ester product 3. The physical and spectral data of the obtained aryl esters 3 well matched those previously reported.

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