Iodoarylation of Arylalkynes with Molecular Iodine in the Presence of Hypervalent Iodine Reagents

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Received: 6 August 2009; in revised form: 18 August 2009 / Accepted: 24 August 2009 / Published: 24 August 2009

Abstract: Iodoarylation of arylacetylenes was performed using a simple reagent system composed of molecular iodine and [bis(benzoyloxy)iodo]benzene. Most arylacetylenes efficiently underwent the iodoarylation reaction with electron-rich arenes to give trans 1,1-diaryl-2-iodoethene adducts regio- and stereoselectively. As an exception, the iodoarylation of p-methoxyphenylacetylene resulted in a mixture of E- and Z-isomers of the corresponding product.

Keywords: iodoarylation; alkyne; molecular iodine; hypervalent iodine; iodoethene

1. Introduction

Alkenyl halides, especially iodides, are synthetically useful compounds and have attracted considerable attention of organic chemists because the iodo group is useful for further elaboration by subjecting the iodoalkene units to metal-catalyzed cross-coupling reactions [1-3]. However, direct iodination of alkenes to iodoalkanes using molecular iodine (I₂) is generally impractical because of the low reactivity of iodine.

We have found that the iodination reaction of aromatic compounds with I₂ proceeds smoothly in the presence of potassium peroxodisulfate (K₂S₂O₈) as an oxidant to give iodoarenes in good yields [4]. To further explore the use of I₂, we extended the iodination reaction of arenes to iodoarylation of alkynes with arenes. It was assumed that an alkyne would be activated by iodine to form a bridged iodonium ion which would then undergo electrophilic substitution with an arene. However, there are
no reports in which molecular iodine is used as an iodine source for the iodoarylation of alkynes. Recently, Barluenga et al. reported the iodoarylation of arenes using bis(pyridine)iodonium(I) tetrafluoroborate as an iodine source [5]. This reagent is commercially available, but very expensive, and its preparation requires the use of toxic mercury oxide [6]. Therefore, a convenient, safe, and simple iodine reagent for the iodoarylation of alkynes is strongly required. Preliminarily, we have found that the iodoarylation of alkynes proceeds effectively in the presence of a simple reagent system: I₂ and a hypervalent iodine species like PhI(OCOPh)₂ [7]. Herein we report the details on the iodoarylation of alkynes with the reagent system consisting of molecular iodine and hypervalent iodine compounds. The results demonstrate a convenient and simple carbon-carbon bond formation process between electron rich arenes and aryl-substituted alkynes using molecular iodine in the presence of hypervalent iodine reagents.

2. Results and Discussion

Molecular iodine and hypervalent iodine compounds have witnessed a large growth in recent years [8-20]. In the present study we confined our attention to the formation of carbon-carbon bonds between arenes and aryl-substituted alkynes in the presence of molecular iodine and hypervalent iodine reagents. Initially, the present work concentrated on the efficiency of the formation of a carbon-carbon bond between pentamethylbenzene (1a) and p-methylphenylacetylene (2) in the presence of I₂ and (diacetoxyiodo)benzene, PhI(OAc)₂ (Scheme 1). PhI(OAc)₂ is one of the most widely available commercial hypervalent iodine compounds and has been widely used in organic synthesis [8,9], making it the first choice among hypervalent iodine reagents tested.

Scheme 1. Reaction of alkyne 2 with arene 1a.

2.1. Optimization of Reaction Conditions

To optimize the reaction conditions the reaction of 1a and 2 using I₂ in the presence of PhI(OAc)₂ was investigated (Table 1). The iodoarylation reaction occurred in different solvent systems: 1,2-dichloroethane (DCE), AcOH, and MeCN to give 1-iodo-2-(4-methylphenyl)-2-(pentamethylphenyl)-ethene (3a; Entries 1-3). MeCN (Entry 3) gave the best results. Increasing the amount of 1a resulted in a better yield of 3a (Entry 4). Elevation of the reaction temperature also improved the yield of 3a (Entry 5). The best overall result (78% yield) was obtained by the reaction at 82 °C using 10 equivalents of 1a (Entry 6). The reaction in EtOAc instead of MeCN resulted in a low yield (13%) of product 3a (Entry 7).
Table 1. Optimization of reaction conditions for the reaction of 1a and 2 in the presence of PhI(OAc)$_2$.

| Entry | 1a (mmol) | PhI(OAc)$_2$ (mmol) | Solvent (Amt.) | Temp. (°C) | Time (h) | Yield of 3a (%)$^*$ |
|-------|-----------|---------------------|----------------|-----------|---------|------------------|
| 1     | 1         | 1.25                | DCE (2 mL)     | 45        | 28      | 12               |
| 2     | 5         | 3                   | AcOH (2 mL)    | 60        | 48      | 23               |
| 3     | 1.5       | 3                   | MeCN (2 mL)    | 60        | 48      | 31               |
| 4     | 5         | 3                   | MeCN (2 mL)    | 60        | 48      | 52               |
| 5     | 5         | 3                   | MeCN (4 mL)    | 78        | 56      | 67               |
| 6     | 10        | 3                   | MeCN (4 mL)    | 82        | 65      | 78               |
| 7     | 10        | 3                   | EtOAc (4 mL)   | 78        | 65      | 13               |

Reactions conditions: 1a, 2 (1 mmol), I$_2$ (1.25 mmol), PhI(OAc)$_2$ and solvent. $^*$ Isolated yield based on 2.

To improve the yield of iodoarylation product 3a, we further examined the effect of different [bis(acyloxy)iodo]benzenes, PhI(OH)OTs, and AgOCOPh on the iodoarylation reaction. Several [bis(acyloxy)iodo]benzenes were prepared from benzoic acid, $m$- and $p$-chlorobenzoic acids, $p$-nitrobenzoic acid, $p$-toluic acid, and $p$-anisic acid, according to the literature method [21]. The results are given in Table 2. PhI(OCOPh)$_2$ showed the highest activity among all other reagents, giving the product 3a in 86% yield (Entries 1-6). [Bis(4-nitrobenzoyloxy)iodo]benzene also gave 3a in good yield (80%), but we chose [bis(benzoyloxy)iodo]benzene as the activator because of the ready availability of benzoic acid. Koser’s salt, PhI(OH)OTs, and silver benzoate show little effect in the iodoarylation reaction (Entries 7 and 8).

Table 2. Effect of hypervalent iodine reagents on the reaction of 1a with 2.

| Entry | Hypervalent iodine reagent | Yield of 3a (%) |
|-------|---------------------------|----------------|
| 1     | PhI(OCOPh)$_2$            | 86             |
| 2     | [Bis($m$-chlorobenzoyloxy)iodo]benzene | 78             |
| 3     | [Bis($p$-chlorobenzoyloxy)iodo]benzene | 65             |
| 4     | [Bis($p$-nitrobenzoyloxy)iodo]benzene | 80             |
| 5     | [Bis($p$-methylbenzoyloxy)iodo]benzene | 74             |
| 6     | [Bis($p$-methoxybenzoyloxy)iodo]benzene | 70             |
| 7     | PhI(OH)OTs                | $33^a,b$       |
| 8     | AgOCOPh                   | 12$^c$         |

Reactions conditions: 1a (10 mmol), 2 (1 mmol), I$_2$ (1.25 mmol), a hypervalent iodine regent (3 mmol), MeCN (6 mL), 82 °C, and 65 h. $^a$ Iodoarylation product 3a was contaminated with hydroarylation product. $^b$ The reaction was conducted by using 1a (3 mmol) in MeCN (4 mL) at 45 °C for 28 h. $^c$ 1a (2 mmol), 2 (1 mmol), AgOCOPh (1 mmol), MeCN (2 mL), 40 °C and 36 h.
2.2. Scope of the iodoarylation reaction using I₂ and PhI(OCOPh)₂

The iodoarylation reaction of p-methylphenylacetylene (2) in the presence of PhI(OCOPh)₂ was examined with different electron-rich arenes 1 (Scheme 2 and Table 3). The results of the reactions showed that the reaction with electron-rich arenes gave iodoarylation products in good yields. In particular, the electron-rich arene mesitylene (1b) gave iodoarylation product 3b in high yield (Entry 1). The reaction with durene (1c) and bromomesitylene (1d) gave iodoarylation products 3c and 3d in 56 and 42% yields, respectively (Entries 2 and 3). The reaction with p-xylene (1e) gave a low yield of iodoarylation product 3e (Entry 4).

Scheme 2. Reaction of alkyne 2 with arenes 1.

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\text{Scheme 2. Reaction of alkyne } 2 \text{ with arenes 1.}
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Table 3. The reaction of alkyne 2 with arenes 1 in the presence of PhI(OCOPh)₂.

| Entry | Arene | Time (h) | Product | Isolated yield (%) |
|-------|-------|----------|---------|--------------------|
| 1     | Mesitylene (1b) | 65       | 3b      | 75                 |
| 2     | Durene (1c)       | 67       | 3c      | 56                 |
| 3     | Bromomesitylene (1d) | 72   | 3d      | 42<sup>a</sup>     |
| 4     | p-Xylene (1e)     | 72       | 3e      | 33<sup>a</sup>     |

*Reaction conditions:* Arene 1 (10 mmol), p-methylphenylacetylene (2, 1 mmol), I₂ (1.25 mmol), PhI(OCOPh)₂ (3 mmol), MeCN (6 mL), and 82 °C. A mixture of E- and Z-isomers.

Next, we examine the reaction of phenylacetylene (4) with different electron-rich arenes 1 under the same reaction conditions as used for 2 (Scheme 3). The results are given in Table 4. The reaction of arenes such as 1a-1c gave iodoarylation products 5a-5c in good yields (Entries 1-3). Moderately activated arenes 1d and 1e showed a very low reactivity, giving low yields (32 and 24%) of iodoarylation products 5d and 5e, respectively.

Scheme 3. Reaction of alkyne 4 with arenes 1.

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The iodoarylation reaction of arylacetylenes with arenes proceeded regio- and stereospecifically to give a single isomer of the possible \( E \)- and \( Z \)-1,1-diaryl-2-iodoethenes \( 3 \) and \( 5 \). We attempted to determine the stereochemistry of iodoarylation product \( 3a \) by NOE experiments, but only a small enhancement (3%) of the vinylic proton was observed when the \( \text{ortho} \) methyl proton was irradiated. This may be attributed to the deviation of the pentamethylphenyl ring from the olefinic plane. Next, we estimated the chemical shift of the vinylic proton according to the literature [22] and compared it with the observed value. The calculation of the chemical shift concerning the vinylic proton for iodoethenes \( 3 \) and \( 5 \) gives 6.51 ppm for the \( E \) isomer and 6.84 ppm for the \( Z \) isomer. In the \(^1\)H-NMR spectra of \( 3 \) and \( 5 \), a singlet peak of the vinylic proton was observed at the range of 6.30–6.55 ppm. Therefore, the stereochemistry of iodoethenes \( 3 \) and \( 5 \) is considered to be \( E \). This is in accord with the results obtained by Barluenga et al. [5].

The reaction of an internal alkyne, diphenylacetylene (6), with arenes 1 was further examined under the above reaction conditions (Scheme 4). The reaction of electron rich arenes such as 1a and 1b with 6 yielded the expected iodoarylation products 7a and 7b, but the yields were low (14 and 8%, respectively). The low yield of the reaction may be attributable to the low reactivity of diphenylacetylene.

Moreover, we examined the reaction of electron-rich \( p \)-methoxyphenylacetylene (8) with arenes 1 (Scheme 5). The results are shown in Table 5. The reaction of electron-rich arenes 1a-1c gave iodoarylation products 9 in good yields (Entries 1-3). Moderately activated arenes such as 1d and 1e showed a low reactivity and the yields were 32 and 16%, respectively. In the case of arylacetylene 8, the iodoarylation reaction lost its stereospecificity to give a mixture of \( E \)- and \( Z \)-isomers of iodoethenes 9. This behavior is different from that observed in the cases of other arylacetylenes 2 and 4.

### Table 4. The reaction of alkyne 4 with arenes 1 in the presence of PhI(OCOPh)$_2$.

| Entry | Arene | Time (h) | Product | Isolated yield (%) |
|-------|-------|----------|---------|--------------------|
| 1     | 1a    | 65       | 5a      | 71                 |
| 2     | 1b    | 70       | 5b      | 61                 |
| 3     | 1c    | 73       | 5c      | 59                 |
| 4     | 1d    | 76       | 5d      | 32                 |
| 5     | 1e    | 72       | 5e      | 24                 |

*Reaction conditions: Arene 1 (10 mmol), phenylacetylene 4 (1 mmol), I$_2$ (1.25 mmol), PhI(OCOPh)$_2$ (3 mmol), and MeCN (6 mL) at 82 °C.*
Scheme 5. Reaction of alkyne 8 with arenes 1.

Table 5. The reaction of alkyne 8 with arenes 1 in the presence of PhI(OCOPh)₂.

| Entry | Arene | Time (h) | Product | Isolated yield (%) |
|-------|-------|----------|---------|-------------------|
| 1     | 1a    | 72       | 9a      | 75                |
| 2     | 1b    | 72       | 9b      | 63                |
| 3     | 1c    | 73       | 9c      | 62                |
| 4     | 1d    | 76       | 9d      | 32                |
| 5     | 1e    | 76       | 9e      | 16                |

Reaction conditions: Arene 1 (10 mmol), alkyne 8 (1 mmol), I₂ (1.25 mmol), PhI(OCOPh)₂ (3 mmol), and MeCN (6 mL) at 82 °C. Products 9 were obtained as a mixture of E- and Z-isomers.

Finally, we examine the reaction of p-fluorophenylacetylene (11) with arenes 1 under the above reaction conditions. The results are given in Table 6. The reaction with electron-rich arenes 1a-1c gave iodoarylation products 12 in good yields (Entries 1-3). The similar reaction of 1d and 1e resulted in low yields (27 and 23%, respectively) of products 12. Arylacetylene 11 showed a similar behavior to 2 and 4 to undergo stereospecific iodoarylation reaction.

Scheme 6. Reaction of alkyne 11 with arenes 1.

Table 6. The reaction of alkyne 11 with arenes 1 in the presence of PhI(OCOPh)₂.

| Entry | ArH   | Time (h) | Product | Isolated yield (%) |
|-------|-------|----------|---------|-------------------|
| 1     | 1a    | 72       | 12a     | 69                |
| 2     | 1b    | 72       | 12b     | 67                |
| 3     | 1c    | 73       | 12c     | 56                |
| 4     | 1d    | 76       | 12d     | 27                |
| 5     | 1e    | 76       | 12e     | 23                |

Reaction conditions: Arene 1 (10 mmol), p-fluorophenylacetylene 11 (1 mmol), I₂ (1.25 mmol), PhI(OCOPh)₂ (3 mmol), and MeCN (6 mL) at 82 °C.
No iodoarylation reaction occurred in the case of 1-hexyne and 3-butyn-2-one, suggesting that this iodoarylation reaction is applicable only to relatively electron-rich alkynes.

2.3. Mechanistic consideration

The proposed mechanism of the iodoarylation reaction of arylacetylenes is shown in Scheme 7. Initially iodine reacts with PhI(OCOPh)$_2$ to form a hypoiodite, IOCOPh [23,24], which actually undergoes iodination of an arylacetylene. The *in situ*-generated IOCOPh adds the arylacetylene to give a cyclic iodonium benzoate. In most cases, the cyclic iodonium form is stable compared with an open vinyl cation due to a significant neighboring participation of iodo group [25]. However, the open vinyl cation governs the reaction process in the case of *p*-methoxyphenylacetylene, where the vinyl cation is strongly stabilized by *p*-methoxyphenyl group and exists as the open form. The cyclic iodonium ion undergoes aromatic electrophilic substitution with an electron-rich arene to afford an iodoarylation product stereoselectively. The presence of the cyclic iodonium ion causes *trans* addition giving the stereochemically defined product. On the other hand, the open vinyl cation has a linear sp-hybridized structure and can react with an arene at both sides of the vacant p orbital. Accordingly, in the case of *p*-methoxyphenylacetylene, a mixture of *E*- and *Z*-isomers is formed. Benzoate anion can trap a proton generated by aromatic electrophilic substitution and prevent the reaction from occurring by protonation.

![Scheme 7. Proposed mechanism of iodoarylation reaction of alkynes.](image)

3. Conclusions

We have demonstrated that arylacetylenes undergo iodoarylation reaction in the presence of a simple reagent system composed of I$_2$ and PhI(OCOPh)$_2$. The iodoarylation reaction of most arylacetylenes with electron-rich arenes proceeds regio- and stereoselectively to give *trans* 1,1-diaryl-2-idoethene adducts in good to high yields. In the case of *p*-methoxyphenylacetylene, the iodoarylation reaction affords a mixture of *E*- and *Z*-isomers of 1,1-diaryl-2-idoethenes 9. The procedure involves a simple and convenient reagent system and provides synthetically valuable iodoalkenes.
4. Experimental

4.1. General

All solvents and starting materials were used as received without further purification unless otherwise indicated. $^1$H-NMR (300 MHz) and $^{13}$C-NMR (75 MHz) were recorded on a JEOL JNM-Al 300 FT-NMR spectrometer in CDCl$_3$ solution (TMS as an internal standard). Melting points were measured with a YANACO micro melting apparatus and are uncorrected. Column chromatographic separations were carried out using silica gel as the stationary phase. Pre-coated plates (silica gel 60 F$_{254}$, MERCK) were used for TLC examination. All [bis(acyloxy)iodo]benzenes were prepared using a literature procedure [21]. Elemental analysis was performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University.

4.2. General procedure for the iodoarylation of alkynes

A mixture of an arene (10 mmol), an arylacetylene (1 mmol), I$_2$ (1.25 mmol), PhI(OCOPh)$_2$ (3 mmol) and MeCN (6 mL) was placed in a 25 mL round-bottom flask. The reaction mixture was stirred for about 5 min at room temperature and then refluxed at 82 °C with stirring until the completion of the reaction. The reaction mixture was dissolved in CH$_2$Cl$_2$ (20 mL) and water (20 mL) was added to the CH$_2$Cl$_2$ solution. The mixture was then washed with 1M aqueous sodium thiosulphate solution to remove the unreacted iodine. The aqueous reaction mixture was extracted with CH$_2$Cl$_2$ (4 × 10 mL) and the CH$_2$Cl$_2$ extract was dried over anhydrous sodium sulfate. Finally, the solvent was removed under reduced pressure below 40 °C. Individual pure compounds were isolated from the reaction mixture by column chromatography on silica gel using hexane and CH$_2$Cl$_2$ as eluent. Data of 1,1-diaryl-2-iodoethenes 3a-e, 5a-e, and 12a-e were previously reported in the literature [7].

1-Iodo-2-(pentamethylphenyl)-1,2-diphenylethene (7a): Pale yellow crystalline solid; mp 194.5-197 °C; $^1$H-NMR δ: 7.44-6.99 (m, 10H, ArH), 2.20 (s, 6H, 2xMe), 2.08 (s, 3H, Me), 2.03 (s, 6H, 2xMe); $^{13}$C-NMR δ: 149.34, 144.94, 144.66, 137.66, 133.88, 132.35, 130.48, 129.37, 128.35, 127.64, 127.40, 127.31, 100.50, 18.80, 16.67, 16.49 (one peak overlapped); Anal. calcd. for C$_{25}$H$_{25}$I: C, 66.38; H, 5.57. Found: C, 66.34, H, 5.59.

1-Iodo-1,2-diphenyl-2-(2,4,6-trimethylphenyl)ethene (7b): Pale yellow crystalline solid; mp 154-156 °C; $^1$H-NMR δ: 7.42-7.06 (m, 10H, ArH), 2.16 (s, 6H, 2xMe), 2.13 (s, 3H, Me); $^{13}$C-NMR δ: 147.55, 144.50, 144.19, 137.29, 136.77, 135.40, 129.52, 128.93, 128.39, 127.66, 127.60, 127.56, 127.42, 101.39, 20.92, 20.75; HRMS-El: m/z calcd. for C$_{23}$H$_{21}$I: [M]$: 424.0688; found: 424.0689.

1-Iodo-2-(4-methoxyphenyl)-2-(pentamethylphenyl)ethene (9a): Pale yellow crystalline solid; mp 110-111.5 °C; a mixture of E- and Z-isomers (92:8); $^1$H-NMR δ: 7.42 (d, J = 9.0 Hz, ArH), 7.14 (d, J = 9.0 Hz, ArH), 7.02 (s, =CH), 6.82 (d, J = 9.0 Hz, ArH), 6.76 (d, J = 9.0 Hz, ArH), 6.24 (s, =CH), 3.78 (s, OMe), 3.76 (s, OMe), 2.23 (s, Me), 2.23 (s, 2xMe), 2.19 (s, 2xMe), 2.14 (s, Me), 2.04 (s, 2xMe); $^{13}$C-NMR δ: 159.29, 159.01, 152.24, 115.00, 136.99, 138.69, 134.75, 133.95, 131.12, 124.49, 123.49, 119.69, 36.26, 37.38, 21.28, 18.80, 16.67; Anal. calcd. for C$_{23}$H$_{21}$I: C, 66.38; H, 5.57. Found: C, 66.34, H, 5.59.
131.34, 130.45, 130.30, 129.52, 127.65, 113.84, 113.07, 79.28, 75.80, 55.20, 55.14, 18.06, 17.60, 16.94, 16.89, 16.80, 16.58; HRMS-EI: \( m/z \) calcd. for \( C_{20}H_{23}IO \) \([M]^+\): 406.0794; found: 406.0791.

1-Iodo-2-(4-methoxyphenyl)-2-(2,4,6-trimethylphenyl)ethene (9b): Pale yellow highly viscous liquid; a mixture of E- and Z-isomers (87:13); \(^1\)H-NMR \( \delta \): 7.36-6.76 (m, ArH and \( =CH \)), 3.77 (s, 2xOMe), 2.33 (s, Me), 2.27 (s, Me), 2.21 (s, 2xMe), 2.06 (s, 2xMe); HRMS-EI: \( m/z \) calcd. for \( C_{18}H_{19}IO \) \([M]^+\): 378.0481; found: 378.0479.

1-Iodo-2-(4-methoxyphenyl)-2-(2,3,5,6-tetramethylphenyl)ethene (9c): Pale yellow crystalline solid; mp 108-110 °C; a mixture of E- and Z-isomers (51:49); \(^1\)H-NMR \( \delta \): 7.36-6.77 (m, ArH and \( =CH \)), 3.78 (s, 2xOMe), 2.25 (s, 2xMe), 2.21 (s, 2xMe), 2.14 (s, 2xMe), 1.99 (s, 2xMe); \(^{13}\)C-NMR \( \delta \): 159.37, 159.06, 157.94, 151.51, 144.75, 141.42, 134.16, 133.40, 131.69, 131.05, 130.91, 130.83, 130.51, 130.15, 127.59, 113.89, 113.12, 79.04, 55.22, 55.16, 20.12, 20.11, 16.47, 15.82; HRMS-EI: \( m/z \) calcd. for \( C_{19}H_{21}IO \) \([M]^+\): 392.0637; found: 392.0637.

1-(3-Bromo-2,4,6-trimethylphenyl)-2-iodo-1-(4-methoxyphenyl)ethene (9d): Pale yellow highly viscous liquid; a mixture of E- and Z-isomers (58:42); \(^1\)H-NMR \( \delta \): 7.81-6.68 (m, ArH and \( =CH \)), 3.86 (s, OMe), 3.79 (s, OMe), 2.45 (s, Me), 2.38 (s, Me), 2.37 (s, Me), 2.21 (s, Me), 2.16 (s, Me), 2.01 (s, Me); HRMS-EI: \( m/z \) calcd. for \( C_{18}H_{18}BrIO \) \([M]^+\): 455.9586; found: 455.9583.

1-(2,5-Dimethylphenyl)-2-iodo-1-(4-methoxyphenyl)ethene (9e): Pale yellow highly viscous liquid; a mixture of E- and Z-isomers (60:40), \(^1\)H-NMR \( \delta \): 7.76-6.73 (m, ArH and \( =CH \)), 3.86 (s, OMe), 3.79 (s, OMe), 2.33 (s, Me), 2.32 (s, Me), 2.21 (s, 2xMe); \(^{13}\)C-NMR \( \delta \): 159.08, 157.55, 157.22, 144.44, 143.91, 139.27, 136.44, 135.76, 131.30, 130.55, 130.43, 129.98, 129.93, 129.02, 128.78, 128.39, 113.40, 110.02, 85.30, 77.21, 56.33, 55.20, 20.97, 19.14, 19.09, 17.74; HRMS-EI: \( m/z \) calcd. for \( C_{17}H_{17}IO \) \([M]^+\): 364.0324; found: 364.0327.

References and Notes

1. Diederich, F.; de Meijere, A. Metal-Catalyzed Cross-Coupling Reactions, 2nd ed.; Wiley-VCH: New York, NY, USA, 2004.
2. Miyaura, N. Cross-Coupling Reactions: A Practical Guide; Springer: Berlin, Germany, 2002.
3. Diederich, F.; Stang, P.J. Metal-Catalyzed Cross-Coupling Reactions; Wiley-VCH: New York, NY, USA, 1998.
4. Hossain, M.D.; Oyamada, J.; Kitamura, T. Direct Synthesis of Iodoarenes from Aromatic Substrates Using Molecular Iodine. Synthesis 2008, 690-692.
5. Barluenga, J.; Rodriguez, M.A.; Gonzalez, J.M.; Campos, P.J. Iodo-carbofunctionalization of Alkynes with Aromatic Rings and Ipy2BF4. Tetrahedron Lett. 1990, 31, 4207-4210.
6. Barluenga, J.; Rodriguez, M.A.; Campos, P.J. Electrophilic Addition of Positive Iodine to Alkynes through an Iodonium Mechanism. J. Org. Chem. 1990, 55, 3104-3105.
7. Rahman, M.A.; Kitamura, T. Regio- and Stereoselective Iodoarylation of Arylacetylenes Using Molecular Iodine Promoted by Hypervalent Iodine. Tetrahedron Lett. 2009, 50, 4759-4761.
8. Varvoglis, A. Hypervalent Iodine in Organic Synthesis; Academic Press: San Diego, CA, USA, 1997.
9. Zhdankin, V.V.; Stang, P.J. Chemistry of Polyvalent Iodine. Chem. Rev. 2008, 108, 5299-5358.
10. Togo, H.; Iida, S. Synthetic Use of Molecular Iodine for Organic Synthesis. Synlett 2006, 2159-2175.
11. Stavber, S.; Jereb, M.; Zupan, M. Electrophilic Iodination of Organic Compounds Using Elemental Iodine or Iodides. Synlett 2008, 1487-1513.
12. Finet, J.-P. Ligand Coupling Reactions with Heteroatomic Compounds; Pergamon: Oxford, UK, 1998; pp. 205-247.
13. Zhdankin, V.V.; Stang, P.J. Alkynyliodonium Salts in Organic Synthesis. Tetrahedron 1998, 54, 10927-10966.
14. Wirth, T.; Hirt, U.H. Hypervalent Iodine Compounds: Recent Advances in Synthetic Applications. Synthesis 1999, 1271-1287.
15. Ochiai, M. Organic Synthesis Using Hypervalent Organoiiodanes. In Chemistry of Hypervalent Compounds; Akiba, K.-Y., Ed.; Wiley-VCH: New York, NY, USA, 1999; pp. 359-388.
16. Zhdankin, V.V.; Stang, P.J. Recent Developments in the Chemistry of Polyvalent Iodine Compounds. Chem. Rev. 2002, 102, 2523-2584.
17. Wirth, T. Hypervalent Iodine Chemistry; Springer: Berlin, Germany, 2003.
18. Tohma, H.; Kita, Y. Hypervalent Iodine Reagents for the Oxidation of Alcohols and Their Application to Complex Molecule Synthesis. Adv. Synth. Catal. 2004, 346, 111-124.
19. Wirth, T. Hypervalent Iodine Chemistry in Synthesis: Scope and New Directions. Angew. Chem. Int. Ed. 2005, 44, 3656-3665.
20. Zhdankin, V.V. Hypervalent Iodoarenes and Aryliodonium Salts. In Science of Synthesis; Thieme, Stuttgart: Germany, 2007; Volume 31a, pp. 161-234.
21. Stang, P.J.; Boehshar, M.; Wingert, H.; Kitamura, T. Acetylenic Esters. Preparation and Characterization of Alkynyl Carboxylates via Polyvalent Iodonium Species. J. Am. Chem. Soc. 1988, 110, 3272-3278.
22. Pretsh, E.; Clere, T.; Seibl, J.; Simon, W. Tables of Spectral Data for Structure Determination of Organic Compounds, 2nd ed.; Springer-Verlag: New York, NY, USA, 1989; p. H215.
23. Varvoglis, A. Hypervalent Iodine in Organic Synthesis; Academic Press: San Diego, CA, USA, 1997; p. 42.
24. Madsen, J.; Viuf, C.; Bols, M. A New Method for the Deprotection of Benzyl Ethers or the Selective Protection of Alcohols. Chem. Eur. J. 2000, 1140-1146.
25. Bassi, P.; Tonellato, U. Reactivity of Vinyl Sulfonic Esters. XVI. Solvolytic Reactivity of β-Halovinyl Derivatives. J. Chem. Soc. Perkin Trans. 2 1974, 1283-1288.

Sample Availability: Samples of the compounds 3a-e, 5a-e, 9a-e and 12a-e are available from the authors.

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