

Electrophilic Additions of Positive Iodine to Alkynes through an Iodonium Mechanism

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Alkynes react with bis(pyridine)iodonium(I) tetrafluoroborate (1) and nucleophiles (CH_3COOH , HCOOH , Cl^- , pyridine, Br^- , I^-) to give 1,2-iodofunctionalized alkenes. The regiochemistry of the processes is in accordance with the polar effects of the triple bond substituents. With regard to stereochemistry, terminal alkynes yield anti addition products, but internal ones produce anti addition with weaker nucleophiles (CH_3COOH , HCOOH , Cl^- , pyridine), syn with stronger nucleophiles (I^-), and a mixture of anti and syn with borderline nucleophiles (Br^-) or when the internal alkyne bears a bulky group. An ionic mechanism through a vinyleneiodonium ion is proposed to explain the obtained results.

The addition reactions of iodine,^{1,2} interhalogens,^{1,3} and pseudohalogens^{1,3} to alkynes is a relatively well documented process. Their preparative synthetic interest is very limited because, with the exception of a few cases,² mixtures of products are obtained.¹⁻³ On the other hand, several mechanisms had been proposed to interpret these results.² In a recent paper we have described the synthesis of 1,2-iodofunctionalized olefins through the electrophilic addition of bis(pyridine)iodonium(I) tetrafluoroborate (1) to alkynes in the presence of a wide variety of nucleophiles.⁴ These reactions yielded a single stereoisomer, and regiochemistry was fixed by the electronic effect of triple bond substituents.

In this paper we generalize our method, with different nucleophiles and starting alkynes, and to propose an ionic mechanism through a vinyleneiodonium ion intermediate based on the observed regio- and stereochemistry.

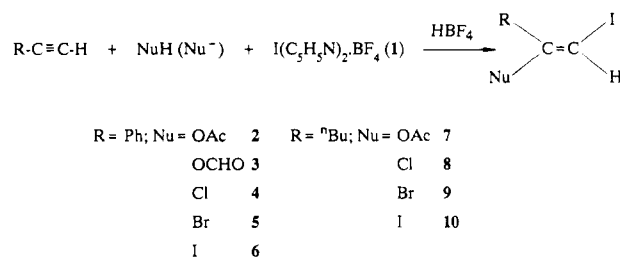
Results and Discussion

The reactions of alkynes with bis(pyridine)iodonium(I) tetrafluoroborate (1) were carried out in the presence of 2 equiv of tetrafluoroboric acid (ethereal 54% solution).

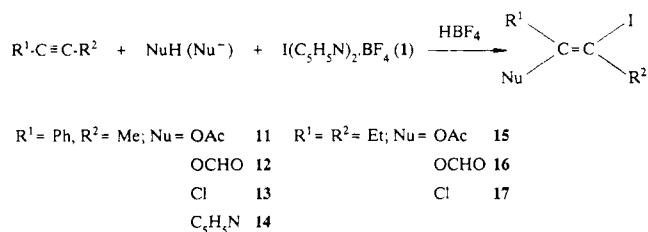
The reaction conditions vary with the starting substrate and nucleophile but, in general, took place in a short time, at room temperature to obtain the corresponding iodoalkene in acceptable yields as a single reaction product (see Table I). When the nucleophile is an organic reagent (CH_3COOH , HCOOH), the reaction was solvolytic, using methylene dichloride as cosolvent ($\text{NuH}-\text{CH}_2\text{Cl}_2 = 1:1$). When the nucleophile was an inorganic salt (LiCl , LiBr , NaI) the best yields were obtained with the system organic solvent-water = 5:1.

The reaction products were purified by column chromatography to eliminate the unreacted starting alkyne and analyzed by ^1H and ^{13}C NMR spectroscopy. The regiochemistry was determined based on the ^{13}C chemical shift of the vinylic carbon that bears the iodine atom. The stereochemistry was confirmed by comparison with liter-

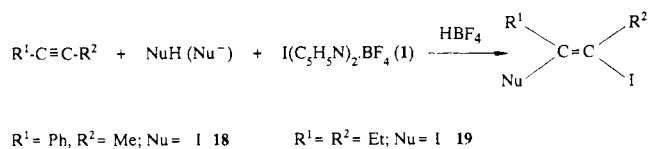
Scheme I



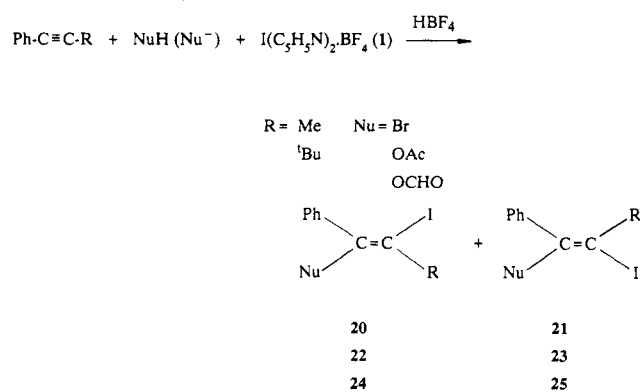
Scheme II



Scheme III



Scheme IV



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ature references^{2a,5} and/or by nuclear Overhauser difference spectroscopy. The irradiation of the vinylic proton (5.6-6.4 ppm) in compounds 2, 3, and 7 resulted in an enhancement of the singlet due to the acetate methyl group

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Table I. Iodo Functionalized Olefins

product-(s)	solvent	time, h	yield, ^a %
2 ^b	CH ₃ COOH/CH ₂ Cl ₂ (1:1)	12	53
3 ^b	HCOOH (aq 85 %)/CH ₂ Cl ₂ (1:1)	12	50
4	CH ₃ CN/H ₂ O (5:1) ^c	5	62
5	CH ₃ CN/H ₂ O (5:1) ^c	7	40
6	CH ₃ CN/H ₂ O (5:1) ^c	14	70
7 ^b	CH ₃ COOH/CH ₂ Cl ₂ (1:1)	12	37
8	CH ₃ CN/H ₂ O (5:1) ^c	14	70
9	CH ₃ CN/H ₂ O (5:1) ^c	14	50
10 ^b	CH ₃ CN/H ₂ O (5:1) ^c	14	53
11	CH ₃ COOH/CH ₂ Cl ₂ (1:1)	12	83
12	HCOOH (aq 85 %)/CH ₂ Cl ₂ (1:1)	12	81
13	CH ₃ CN/H ₂ O (5:1) ^c	14	62
14 ^d	CH ₂ Cl ₂	15	60
15	CH ₃ COOH/CH ₂ Cl ₂ (1:1)	12	71
16	HCOOH (aq 85 %)/CH ₂ Cl ₂ (1:1)	12	75
17	CH ₃ CN/H ₂ O (5:1) ^c	0.5	58
18	CH ₃ CN/H ₂ O (5:1) ^c	14	50
19	CH ₃ CN/H ₂ O (5:1) ^c	14	73
20/21 ^e	CH ₃ CN/H ₂ O (5:1) ^c	8	47 (1/9) ^f
22/23 ^e	CH ₃ COOH/CH ₂ Cl ₂ (1:1)	12	50 (1.7/1) ^f
24/25 ^e	HCOOH (aq 85 %)/CH ₂ Cl ₂ (1:1)	12	50 (1.7/12) ^f

^aYield of isolated products, relative to starting I(C₅H₅N)₂BF₄ and not optimized. The products were purified by column chromatography (silica, hexane-ether, 98:2). Satisfactory microanalyses obtained in all the new compounds: C, ± 0.37 ; H, ± 0.26 . ^bThe product could not be purified because of decomposition. Elemental analyses were not assayed. ^cMole ratio Nu:I = 3:1. ^dAcid treatment was omitted. C₅H₅N from compound 1. ^eE and Z isomers could not be separated. ^fIsomers ratios, determined by ¹H NMR spectra of the crude reaction.

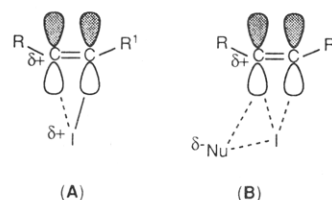
(2.0–2.2 ppm, 2, 7) or formyl proton (8.1 ppm, 3). In a similar way positive NOE was obtained in the products 12, 14, 16, and 18 and in the mixtures 20 + 21, 22 + 23, and 24 + 25. The stereochemistry of the product 19 was assigned by comparison with a similar structure.^{5a}

The regiochemistry of the isomers obtained was in concordance with the inductive and resonance effects of the triple bond substituents. On the other hand, the stereochemistry depended on starting alkyne and nucleophile. With terminal alkynes anti-addition products were isolated (Scheme I), but in the case of internal alkynes addition was anti with weaker nucleophiles⁶ (OAc, OCHO, Cl, pyridine; Scheme II), syn with iodide (Scheme III), and a mixture of anti and syn with bromide (Scheme IV).

In this way, the reaction of 1-phenyl-1-propyne with 1 and lithium bromide gave a mixture of (E)- and (Z)-(-1-bromo-2-iodo-1-propenyl)benzene (20 and 21, 10 and 90% respectively, Scheme IV). When the internal alkyne bore a very bulky group, for example 3,3-dimethyl-1-phenyl-1-butyne, the addition of weak nucleophiles-acetate and formate-yielded mixtures of (E)- and (Z)-iodoalkenes (65 and 35% respectively, Scheme IV).

These results prompted us to assume that reaction occurs through a cyclic iodonium ion intermediate (A). These ions have been previously postulated^{5,7} as intermediates in some electrophilic additions to alkynes. The cationic character may be stabilized by overlap with phenyl p orbitals (when R is phenyl and R¹ is hydrogen or alkyl) or by the inductive effect of an alkyl group (when R is alkyl

and R¹ is hydrogen).^{5b,8} Nucleophilic anti attack yields the E isomer.



When the steric hindrance of R and R¹ groups increases, the bridging by iodine must be weaker and, consequently, the interaction between the carbon and iodine atoms decreases and then, this atom will have a higher positive charge density than with less hindered alkynes. Under these conditions, stronger nucleophiles may interact first with the iodine atom because of the greater positive charge density yielding a syn addition (B). For the same reasons, highly sterically hindered alkynes may even give syn addition with weaker nucleophiles.

Several experimental results confirm this mechanistic interpretation: (1) Terminal alkynes always yield the anti addition products. (2) With internal alkynes the addition is anti with weaker nucleophiles (acetate, formate, chloride, and pyridine), syn with iodide, and mixture of anti and syn with bromide. (3) Greatly sterically hindered alkynes give mixtures of anti and syn addition products with the weakest nucleophiles (acetate and formate).

Studies on cyclic halonium ions verify this mechanism.⁹ A vinyl cation intermediate seems unlikely where anti addition is observed and does not explain the preferred nucleophilic attack syn to the large *tert*-butyl group leading to 22 and 24. The syn process cannot be explained by [2 + 2] concerted addition of I–Nu because it is symmetry forbidden.^{1a,10}

In conclusion, we propose a mechanism through a vinyleneiodonium ion intermediate (A or B).

Experimental Section

General Methods. ¹H NMR spectra were recorded on a Varian FT-80 A or a Bruker AC-300 spectrometer and are reported in ppm from the internal tetramethylsilane (TMS). NOEDIF experiments were carried out on a Bruker AC-300 spectrometer. ¹³C NMR spectra were recorded on a Varian FT-80 A or a Bruker AC-300 spectrometer and chemical shifts are reported in ppm relative to internal TMS. Mass spectra were obtained on a HP 5987 A apparatus. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. All solvents and starting organic compounds were commercial grades and were used without further purification.

Preparation of Bis(pyridine)iodonium(I) Tetrafluoroborate (1). To a mixture of methylene dichloride (30 mL), pyridine (40 mmol, 3.2 mL), and HgO/TFBA–SiO₂¹¹ (20 mmol) is slowly added iodine (20 mmol, 5.1 g) with vigorous stirring. After one additional hour of stirring, the solids are filtered off and washed several times with methylene dichloride (3 × 25 mL). The resulting solution is concentrated to half its volume, and the product precipitates when diethyl ether is added (40 mL). The raw compound is filtered and dissolved in methylene dichloride (50 mL) and is precipitated again with cooled ether (40 mL). The process is repeated until a test for Hg(II) is negative. The solid is dried in vacuum and in the dark. Yield 5.2–5.9 g (70–80%),

(6) Nucleophiles may be classified by the n_0 parameter, the nucleophilicity of Swain and Scott (n_0 : OAc⁻ = 4.3; Cl⁻ = 4.33; pyridine = 5.23; Br⁻ = 5.79; I⁻ = 7.42). See, for example: Isaacs, N. S. *Physical Organic Chemistry*; Longman: Harlow, UK, 1987; p 242.

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mp 149–151 °C (dec. from methylene dichloride). Spectral data were previously reported.¹²

General Procedure To Prepare 1,2-Iodo Functionalized Olefins. To a solution of the nucleophile in the appropriate solvent (15 mL) (see Table I) were added HBF₄ (10 mmol, 1.40 mL of ethereal 54% solution), the corresponding alkyne (5 mmol), and 1 (5 mmol, 1.86 g) at room temperature. After stirring, the red solution was hydrolyzed (15 mL), extracted with methylene dichloride (50 mL), washed with 5% aqueous solution of sodium thiosulfate (25 mL) (and twice with 5% aqueous solution of sodium hydrogencarbonate, 25 mL, when the nucleophile was acetic acid), dried over anhydrous sodium sulfate, and evaporated in vacuo. The products were purified by column chromatography (silica, hexane–ether, 98:2). Physical properties and spectral data are recorded below.

(E)-(1-Acetoxy-2-iodoethenyl)benzene (2): ¹H NMR (CCl₄) δ 2.0 (s, 3 H), 6.2 (s, 1 H), 7.2–7.6 (m, 5 H); ¹³C NMR (CDCl₃) δ 21.7 (q), 68.5 (d), 129.1 (d), 129.7 (d), 130.4 (d), 134.7 (s), 151.8 (s), 169.0 (s); MS, *m/e* (M⁺, rel int) 288 (5).

(E)-(1-(Formyloxy)-2-iodoethenyl)benzene (3): ¹H NMR (CDCl₃) δ 6.4 (s, 1 H), 7.3–7.7 (m, 5 H), 8.1 (s, 1 H); ¹³C NMR (CDCl₃) δ 68.2 (d), 129.2 (d), 129.8 (d), 130.5 (d), 134.9 (s), 151.0 (s), 159.7 (d); MS *m/e* (M⁺, rel int) 274 (4).

(E)-(1-Chloro-2-iodoethenyl)benzene (4): bp 117 °C (7 mmHg); ¹H NMR (CDCl₃) δ 6.7 (s, 1 H), 7.2–7.6 (m, 5 H); ¹³C NMR (CDCl₃) δ 74.0 (d), 128.2 (d), 129.0 (d), 129.4 (d), 134.1 (s), 137.8 (s); MS *m/e* (M⁺, rel int) 264 (67), 266 (19).

(E)-(1-Bromo-2-iodoethenyl)benzene (5): oil; ¹H NMR (CDCl₃) δ 7.0 (s, 1 H), 7.4 (s, 5 H); ¹³C NMR (CDCl₃) δ 76.5 (d), 123.2 (s), 129.3 (d), 130.0 (d), 130.3 (d), 140.8 (s); MS *m/e* (M⁺, rel int) 308 (39), 310 (38). Anal. Calcd for C₈H₆BrI: C, 31.07; H, 1.94. Found: C, 31.29; H, 1.84.

(E)-(1,2-Diiodoethenyl)benzene (6): mp 76 °C; ¹H NMR (CDCl₃) δ 7.1 (s, 1 H), 7.2–7.3 (m, 5 H); ¹³C NMR (CDCl₃) δ 80.5 (d), 96.3 (s), 128.3 (d), 128.5 (d), 128.7 (d), 143.3 (s); MS *m/e* (M⁺, rel int) 356 (15).

(E)-2-Acetoxy-1-iodo-1-hexene (7): ¹H NMR (CDCl₃) δ 1.0 (t, 3 H), 1.4 (m, 2 H), 1.6 (m, 2 H), 2.2 (s, 3 H), 2.5 (t, 2 H), 5.6 (s, 1 H); ¹³C NMR (CDCl₃) δ 14.7 (q), 21.6 (q), 22.9 (t), 29.0 (t), 33.8 (t), 68.2 (d), 156.4 (s), 169.5 (s); MS *m/e* (M⁺, rel int) 268 (2).

(E)-2-Chloro-1-iodo-1-hexene (8): bp 71 °C (10 mmHg); ¹H NMR (CDCl₃) δ 1.0 (t, 3 H), 1.4 (m, 2 H), 1.6 (m, 2 H), 2.6 (t, 2 H), 6.3 (s, 1 H); ¹³C NMR (CDCl₃) δ 15.2 (q), 23.1 (t), 30.3 (t), 39.8 (t), 74.5 (d), 139.9 (s); MS *m/e* (M⁺, rel int) 244 (71), 246 (20). Anal. Calcd for C₆H₁₀ClI: C, 29.45; H, 4.09. Found: C, 29.27; H, 4.21.

(E)-2-Bromo-1-iodo-1-hexene (9): oil; ¹H NMR (CDCl₃) δ 1.0 (t, 3 H), 1.4 (m, 2 H), 1.6 (m, 2 H), 2.6 (t, 2 H), 6.5 (s, 1 H); ¹³C NMR (CDCl₃) δ 15.2 (q), 22.6 (t), 30.6 (t), 41.6 (t), 75.3 (d), 129.0 (s); MS *m/e* (M⁺, rel int) 288 (26), 290 (24). Anal. Calcd for C₆H₁₀BrI: C, 24.91; H, 3.46. Found: C, 24.63; H, 3.65.

(E)-1,2-Diiodo-1-hexene (10): ¹H NMR (CCl₄) δ 0.9 (t, 3 H), 1.2–1.6 (m, 4 H), 2.4 (t, 2 H), 6.7 (s, 1 H); ¹³C NMR (CDCl₃) δ 15.2 (q), 22.2 (t), 31.1 (t), 45.2 (t), 80.9 (d), 105.4 (s); MS *m/e* (M⁺, rel int) 336 (10).

(E)-(1-Acetoxy-2-iodo-1-propenyl)benzene (11): bp 120 °C (5 mmHg); ¹H NMR (CDCl₃) δ 2.0 (s, 3 H), 2.6 (s, 3 H), 7.2–7.8 (m, 5 H); ¹³C NMR (CDCl₃) δ 21.9 (q), 28.3 (q), 87.9 (s), 128.9 (d), 129.9 (d), 130.5 (d), 138.2 (s), 147.7 (s), 168.2 (s); MS *m/e* (M⁺, rel int) 302 (11).

(E)-(1-(Formyloxy)-2-iodo-1-propenyl)benzene (12): bp 108 °C (6 mmHg); ¹H NMR (CDCl₃) δ 2.6 (s, 3 H), 7.3–7.5 (m, 5 H), 8.0 (s, 1 H); ¹³C NMR (CDCl₃) δ 28.6 (q), 89.0 (s), 130.0 (d),

131.0 (d), 131.3 (d), 138.5 (s), 147.7 (s), 159.9 (d); MS *m/e* (M⁺, rel int) 288 (7). Anal. Calcd for C₁₀H₉IO₂: C, 14.67; H, 3.12. Found: C, 14.98; H, 2.95.

(E)-(1-Chloro-2-iodo-1-propenyl)benzene (13): bp 99 °C (3 mmHg); ¹H NMR (CDCl₃) δ 2.8 (s, 3 H), 7.3 (s, 5 H); ¹³C NMR (CDCl₃) δ 31.3 (q), 92.1 (s), 128.1 (d), 128.5 (d), 128.8 (s), 128.9 (d), 141.3 (s); MS *m/e* (M⁺, rel int) 278 (57), 280 (16).

(E)-[2-Iodo-1-(*N*-pyridiniumyl)-1-propenyl]benzene tetrafluoroborate (14): ¹H NMR (CDCl₃) δ 2.5 (s, 3 H), 7.3–7.6 (m, 5 H), 8.2–8.3 (m, 2 H), 8.7–8.8 (m, 1 H), 9.2–9.3 (m, 2 H); ¹³C NMR (CDCl₃) δ 29.4 (q), 104.8 (s), 128.6 (d), 129.0 (d), 129.1 (d), 130.3 (d), 137.4 (s), 141.8 (s), 144.8 (d), 147.5 (d). Anal. Calcd for C₁₄H₁₃BF₄IN: C, 41.10; H, 3.18. Found: C, 41.03; H, 3.25.

(E)-3-Acetoxy-4-iodo-3-hexene (15): bp 73 °C (8 mmHg); ¹H NMR (CDCl₃) δ 1.0 (t, 6 H), 2.1 (s, 3 H), 2.3 (q, 2 H), 2.5 (q, 2 H); ¹³C NMR (CDCl₃) δ 12.5 (q), 15.6 (q), 21.8 (q), 31.5 (t), 32.8 (t), 97.4 (s), 150.4 (s), 169.0 (s); MS *m/e* (M⁺, rel int) 268 (3). Anal. Calcd for C₈H₁₃IO₂: C, 35.82; H, 4.85. Found: C, 36.14; H, 4.63.

(E)-3-(Formyloxy)-4-iodo-3-hexene (16): bp 64 °C (7 mmHg); ¹H NMR (CDCl₃) δ 1.1 (t, 6 H), 2.4 (q, 2 H), 2.6 (q, 2 H), 8.0 (s, 1 H); ¹³C NMR (CDCl₃) δ 11.9 (q), 15.1 (q), 31.0 (t), 32.2 (t), 97.4 (s), 148.8 (s), 158.8 (d); MS *m/e* (M⁺, rel int) 254 (22). Anal. Calcd for C₇H₁₁IO₂: C, 33.07; H, 4.33. Found: C, 33.34; H, 4.16.

(E)-3-Chloro-4-iodo-3-hexene (17): bp 61 °C (5 mmHg); ¹H NMR (CCl₄) δ 0.9 (t, 3 H), 1.0 (t, 3 H), 2.5 (q, 2 H), 2.53 (q, 2 H); ¹³C NMR (CDCl₃) δ 12.6 (q), 14.0 (q), 36.8 (t), 37.8 (t), 100.4 (s), 132.9 (s); MS *m/e* (M⁺, rel int) 246 (21).

(Z)-(1,2-Diiodo-1-propenyl)benzene (18): oil; ¹H NMR (CDCl₃) δ 2.7 (s, 3 H), 7.2–7.3 (m, 5 H); ¹³C NMR (CDCl₃) δ 41.3 (q), 97.0 (s), 97.5 (s), 129.0 (d), 129.1 (d), 129.2 (d), 148.5 (s); MS *m/e* (M⁺ – I, rel int) 243 (68). Anal. Calcd for C₉H₈I₂: C, 29.19; H, 2.16. Found: C, 28.82; H, 2.42.

(Z)-3,4-Diiodo-3-hexene (19): bp 67 °C (2 mmHg); ¹H NMR (CCl₄) δ 1.0 (t, 6 H), 2.6 (q, 4 H); ¹³C NMR (CDCl₃) δ 13.9 (q), 46.1 (t), 103.7 (s); MS *m/e* (M⁺, rel int) 336 (42).

(E)- and (Z)-(1-Bromo-2-iodo-1-propenyl)benzene (20 and 21): ¹H NMR (CCl₄) δ 2.7 (s, 0.33 H, E), 2.8 (s, 3 H, Z), 7.2–7.4 (m, 5.55 H, E and Z); ¹³C NMR (CDCl₃) δ 33.9 (q, E) 34.2 (q, Z), 92.8 (s, E), 92.9 (s, Z), 118.1 (s, Z), 118.8 (s, E), 127.2 (d, Z), 127.8 (d, E), 127.9 (d, Z), 128.0 (d, E), 128.1 (d, Z), 128.2 (d, E), 143.4 (s, Z), 144.3 (s, E); MS *m/e* (M⁺, rel int) 322 (32), 324 (31). Anal. Calcd for C₉H₈BrI: C, 33.44; H, 2.48. Found: C, 33.59; H, 2.34.

(E)- and (Z)-(1-Acetoxy-2-iodo-3,3-dimethyl-1-butenyl)benzene (22 and 23): ¹H NMR (CDCl₃) δ 1.2 (s, 5.3 H, Z), 1.4 (s, 9 H, E), 2.0 (s, 3 H, E), 2.1 (s, 1.8 H, Z), 7.2–7.5 (m, 7.9 H, E and Z); ¹³C NMR (CDCl₃) δ 21.1 (q, E), 21.9 (q, Z), 32.2 (q, E), 32.9 (q, Z), 39.1 (s, Z), 39.8 (s, E), 112.8 (s, E), 117.2 (s, Z), 128.4 (d, E), 128.6 (d, Z), 129.5 (d, Z), 129.7 (d, E), 130.9 (d, E), 131.1 (d, Z), 136.2 (s, Z), 141.9 (s, E), 146.8 (s, E), 147.9 (s, Z), 167.8 (s, Z), 168.6 (s, E); MS *m/e* (M⁺, rel int) 344 (7). Anal. Calcd for C₁₄H₁₇IO₂: C, 48.84; H, 4.94. Found: C, 48.73; H, 5.07.

(E)- and (Z)-(1-(Formyloxy)-2-iodo-3,3-dimethyl-1-butenyl)benzene (24 and 25): ¹H NMR (CDCl₃) δ 1.2 (s, 5 H, Z), 1.4 (s, 9 H, E), 7.2–7.5 (m, 7.8 H, E and Z), 7.9 (s, 1 H, E), 8.0 (s, 0.6 H, Z); ¹³C NMR (CDCl₃) δ 31.8 (q, E), 32.4 (q, Z), 38.8 (s, Z), 39.5 (s, E), 112.6 (s, E), 116.5 (s, Z), 127.6 (d, Z), 127.7 (d, E), 128.5 (d, E), 128.7 (d, Z), 129.8 (d, E), 130.0 (d, Z), 134.6 (s, Z), 140.1 (s, E), 144.3 (s, E), 146.0 (s, Z), 157.5 (d, Z), 158.3 (d, E); MS *m/e* (M⁺, rel int) 330 (5). Anal. Calcd for C₁₃H₁₅IO₂: C, 47.27; H, 4.55. Found: C, 47.15; H, 4.70.

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