

Novel Cyclization to Benzofurans in the Reaction of Alkynyl(*p*-phenylene)bisiodonium Ditriflates with Phenoxide Anion

Tsugio Kitamura,* Lei Zheng, and Hiroshi Taniguchi*

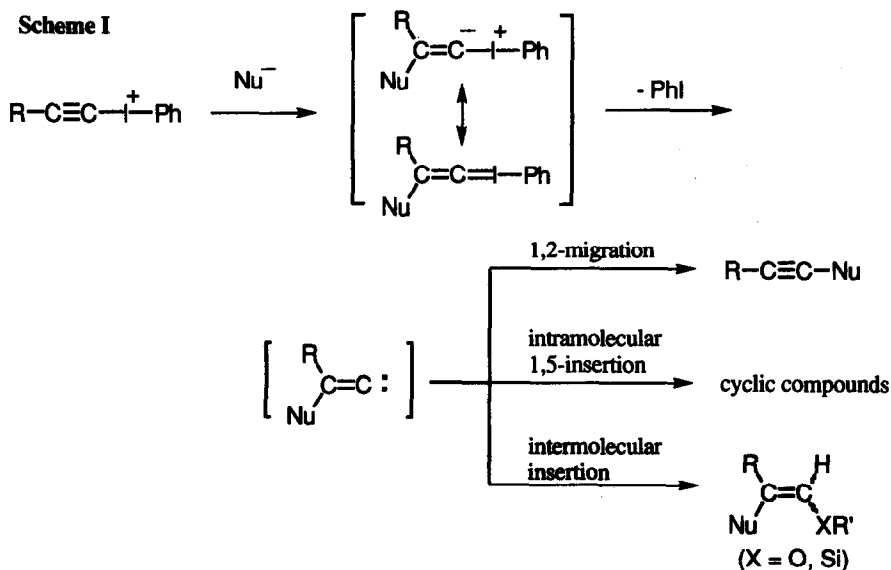
Department of Chemical Science and Technology, Faculty of Engineering,
Kyushu University 36, Hakozaki, Fukuoka 812, Japan

Makoto Sakurai and Ryuichi Tanaka

Department of Chemical Engineering, Faculty of Engineering,
Fukuoka University, Nanakuma, Fukuoka 814-01, Japan

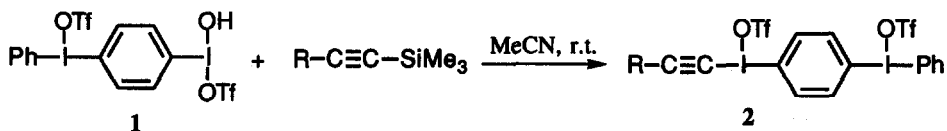
Abstract: Reaction of alkynyl(*p*-phenylene)bisiodonium ditriflates (2) with sodium phenoxide in methanol provides 2-substituted benzofurans (3). This result indicates that β -phenoxyalkylidenecarbenes generated by the reaction with phenoxide anion undergo novel intramolecular aromatic C-H insertion to afford benzofurans.

Recently much interest has been paid to functionalized iodonium salts because of the high synthetic utility and unique property.¹ Alkynyliodonium salts are valuable in organic synthesis and act as Michael acceptors for cyclopentene synthesis, as synthons for "alkynyl cations," and as 1,3-dipolarophiles.²

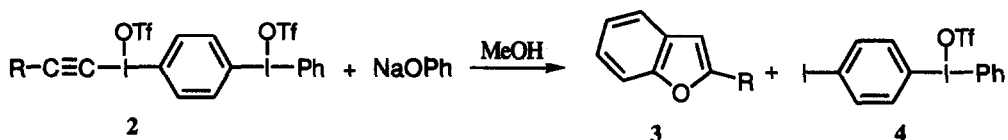


Generally the accepted mechanism for the reaction of alkynyliodonium salts with nucleophiles is composed of nucleophilic β -addition generating a vinyliodonium ylide-iodoallene intermediate and the subsequent reaction of the resulting alkylidenecarbene (Scheme 1).² The reactive alkylidenecarbene undergoes 1,2-migration of the β substituent giving an alkyne,^{3,4a} intramolecular 1,5-insertion,⁴ or intermolecular insertion.^{4c} The intramolecular 1,5-insertion of the alkylidenecarbene has been limited only to a C-H bond of the methylene groups⁴ and an O-H bond of enols and alcohols.^{4a,d} No examples of insertion into aromatic C-H bonds in the reaction of the alkynyliodonium salts have been observed so far. When we conducted the reaction of alkynyl(*p*-phenylene)bisiodonium ditriflates with phenolate anion, we obtained benzofuran derivatives which should be derived from the aromatic C-H insertion of the resulting alkylidenecarbene. In this communication, we describe the novel benzofuran formation derived from aromatic C-H insertion of the alkylidenecarbene.

Alkynyl(*p*-phenylene)bisiodonium ditriflates (**2**) were prepared readily from interaction of our recently found bisiodine(III) reagent, 1-[(hydroxy)(triflyloxy)iodo]-4-[(phenyl)(triflyloxy)iodo]benzene (**1**), with 1-trimethylsilylalkynes.⁵ The alkynyl(*p*-phenylene)bisiodonium ditriflates **2** react with thiocyanate anion to yield alkynyl thiocyanates.⁵ This reaction indicated that the alkynyl(*p*-phenylene)bisiodonium ditriflates **2** can be used in various reactions as well as the previously investigated and widely used alkynyl(phenyl)iodonium salts.² The advantage of the use of alkynyl(*p*-phenylene)bisiodonium ditriflates (**2**) was indicated for easy workup for isolation of the products.⁵



The reaction of alkynyl(*p*-phenylene)bisiodonium ditriflates (**2**) with phenolate anion was conducted in methanol. A solution of sodium phenoxide (1.1 mmol) in methanol (5 ml) was added dropwise under a N_2 atmosphere at 0°C to a solution of **2** (1 mmol) in methanol (10 ml) and then the mixture was stirred for 1 h at room temperature. Water (20 ml) was added to the mixture, the product was extracted with ether. The product was identified as 2-substituted benzofuran (**3**)⁶ on the basis of the spectral data and the literatures. Alternatively, (*p*-iodophenyl)phenyliodonium triflate (**4**)⁷ was isolated by evaporation of the solvent and filtration after the reaction was completed.



a: R = $n\text{-C}_4\text{H}_9$, b: R = $t\text{-C}_4\text{H}_9$,
 c: R = $n\text{-C}_6\text{H}_{13}$, d: R = $n\text{-C}_{10}\text{H}_{21}$

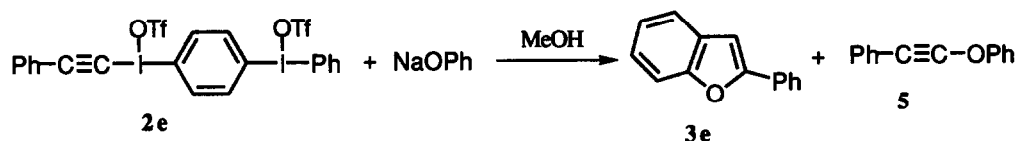
a: R = $n\text{-C}_4\text{H}_9$ (62%)
 b: R = $t\text{-C}_4\text{H}_9$ (59%)
 c: R = $n\text{-C}_6\text{H}_{13}$ (62%)
 d: R = $n\text{-C}_{10}\text{H}_{21}$ (49%)

In the cases of alkyl-substituted ethynyl(*p*-phenylene)bisiodonium ditriflates **2a-d**, benzofuran derivatives **3a-d** were formed selectively. Noteworthy is the selective benzofuran formation even in the cases of *n*-hexyl and

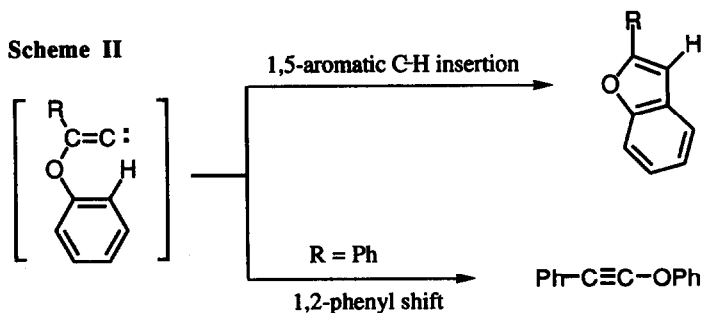
n-decyl-substituted ones **2c** and **d**, since such alkyl-substituted ethynylidonium salts undergo selective 1,5-C-H insertion into the alkyl group in the reactions with enolate anions and azide anion.⁴

The present selective aromatic C-H insertion can be rationalized by taking into account the nature of alkylidenecarbenes. According to the excellent reviews⁸ by Stang, alkylidenecarbenes have an electrophilic character and can interact with olefinic π systems via their empty p orbitals. Although interactions of alkylidenecarbenes with aromatic substrates have not been described, such interaction with the aromatic component should be operated in the present case. Activation of the phenyl group by oxygen atom may assist such interaction. Accordingly, in this situation, it is considered that aromatic 1,5-C-H insertion is more favorable than aliphatic 1,5-C-H insertion.

On the other hand, phenyl-substituted ethynyl(*p*-phenylene)bisiodonium ditriflate **2e** showed a different behavior from the alkyl-substituted ones **2a-d**. Interaction of **2e** with phenoxide anion gave a 59:41 mixture of 2-phenylbenzofuran **3e**⁹ and phenyl phenylethynyl ether **5**⁹ in 59% yield. The comparable formation of benzofuran **3e** even in the β -phenylalkylidenecarbene indicates that aromatic C-H insertion occurs as easily as 1,2-phenyl shift, although aliphatic 1,5-C-H insertion cannot absolutely compete with the 1,2-phenyl shift and alkyne formation.^{4a}



Scheme II



In conclusion, we found novel intramolecular aromatic C-H insertion of alkylidenecarbenes generated by the reaction of alkynyl(*p*-phenylene)bisiodonium ditriflates with phenoxide anion. The intramolecular aromatic C-H insertion takes place selectively and provides 2-substituted benzofuran derivatives. Further chemistry and application are now in progress.

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 6. **3a**: ¹⁰oil; ¹H NMR (CDCl₃) δ 0.95 (t, J = 7.3 Hz, 3 H, Me), 1.37-1.51 (sext, J = 7.5 Hz, 2 H, CH₂), 1.69-1.75 (quint, J = 7.5 Hz, 2 H, CH₂), 2.75 (t, J = 7.5 Hz, 2 H, CH₂), 6.35 (d, J = 0.7 Hz, 1 H, CH), 7.15-7.48 (m, 4 H, ArH); ¹³C NMR (CDCl₃) δ 13.82, 22.29, 28.14, 29.79, 101.74, 110.67, 120.14, 122.35, 123.00, 129.02, 154.61, 159.73. **3b**: ¹¹oil; ¹H NMR (CDCl₃) δ 1.36 (s, 9 H, Me), 6.33 (s, 1 H, CH), 7.11-7.48 (m, 4 H, ArH); ¹³C NMR (CDCl₃) δ 28.83, 32.92, 98.89, 110.78, 120.32, 122.27, 123.05, 128.89, 139.29, 154.58. **3c**: ¹²oil; ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.7 Hz, 3 H, CH₃), 1.26-1.44 (m, 6 H, CH₂CH₂CH₂), 1.72 (quint, J = 7.4 Hz, 2 H, CH₂), 2.73 (t, J = 7.5 Hz, 2 H, CH₂), 6.33 (d, J = 0.8 Hz, 1 H, CH), 7.11-7.47 (m, 4 H, ArH); ¹³C NMR (CDCl₃) δ 14.10, 22.59, 27.66, 28.46, 28.90, 31.60, 101.73, 110.69, 120.14, 122.34, 123.00, 129.03, 154.63, 159.74. **3d**: oil; ¹H NMR (CDCl₃) δ 0.88 (t, J = 6.8 Hz, 3 H, Me), 1.27-1.45 (m, 14 H, (CH₂)₇), 1.73 (quint, J = 7.5 Hz, 2 H, CH₂), 2.75 (t, J = 7.6 Hz, 2 H, CH₂), 6.35 (d, J = 0.7 Hz, 1 H, CH), 7.14-7.48 (m, 4 H, ArH); ¹³C NMR (CDCl₃) δ 14.12, 22.71, 27.73, 28.49, 29.24, 29.35, 29.40, 29.57, 29.63, 31.93, 101.75, 110.70, 120.15, 122.36, 123.01, 129.09, 154.68, 159.80.
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 9. **3e**: mp 120-121 °C (EtOH) (lit., 119-120 °C, ¹²120-121 °C¹⁰). **5**: oil; ¹H NMR (CDCl₃) δ 6.50-7.62 (m, ArH); ¹³C NMR (CDCl₃) δ 66.37 and 115.03 (C≡C); IR (neat) 2268 cm⁻¹ (strong, C≡C).
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