

The Reaction of Trimethylsilylethynyl(phenyl)iodonium Triflate with Some Phenolates: Formation of Substitution and sp^2 C-H Insertion Products

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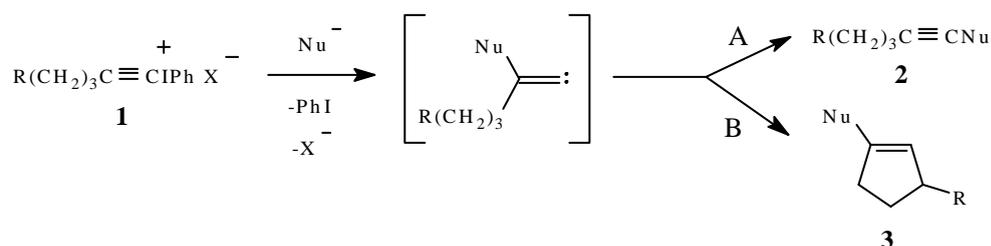
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Abstract: Treatment of trimethylsilylethynyl(phenyl)iodonium triflate with the potassium salts of some acidic phenols results in the formation of substitution products (*O*-trimethylsilylethynylphenols and/or *O*-ethynylphenols), along with sp^2 C-H insertion products which afford eventually 2-aroxybenzo[*b*]furans.

Keywords: Alkynyl iodonium salts, ethynyl phenyl ethers, benzo[*b*]furans

Introduction

The propensity of alkynyl iodonium salts **1** to react with nucleophiles under mild conditions mainly via alkyldiene carbenes is presently well established. Two major reaction modes (A, B) are normally observed: the first involves rearrangement of the carbene (1,2-shift) leading to substituted alkynes **2**, while in the second intramolecular 1,5- sp^3 C-H insertion occurs, resulting in the formation of cyclopentenes **3** (or various heterocycles) (Scheme 1) [1].

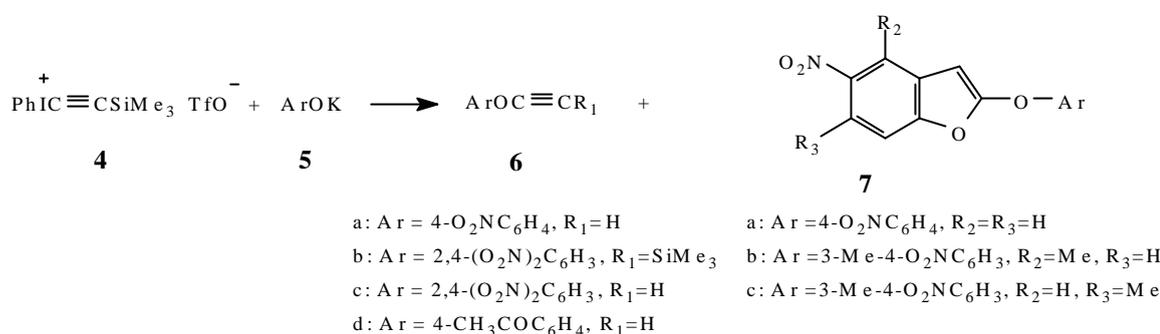


Scheme 1.

It has been recently shown that insertion is also possible into aromatic C-H bonds. Substrates which underwent this type of reaction with various alkynyliodonium salts included sodium *p*-toluenesulfinate [2], salts of some phenols [3] and 4-hydroxypyridine [4], tropolones [5] and 2-hydroxy-1,4-naphthoquinone [5], which gave, respectively, indenenes, benzo and pyridino[*b*]furans, furotropones and furonaphthoquinones.

Results and Discussion

We presently report that the potassium salts of some acidic phenols **5** react with trimethylsilylethynyl(phenyl)iodonium triflate **4** to afford mixtures of substitution products **6**, i.e. aroxyacetylenes and/or aroxy-trimethylsilylacetylenes, and also in some instances 2-aroxybenzo[*b*]furans **7**, in moderate yield. The following scheme summarizes these results (Scheme 2):



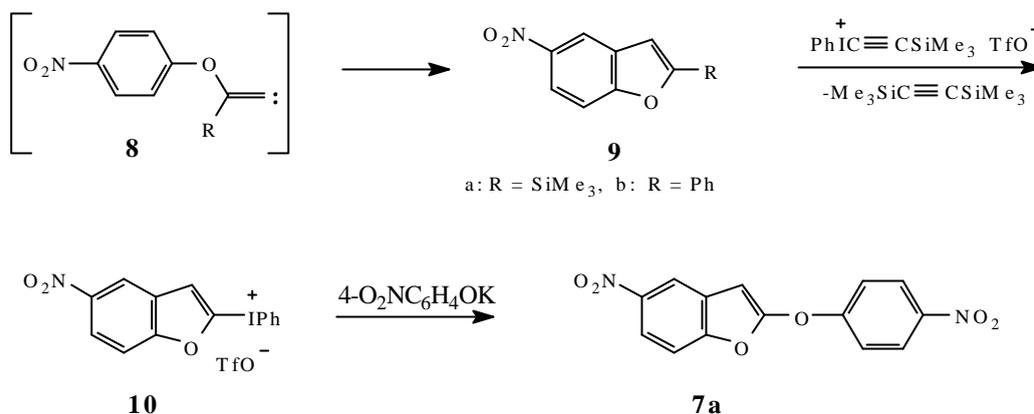
Scheme 2.

The reaction products differ, depending on the phenolate. From the reaction with potassium 4-nitrophenolate very little 4-nitrophenoxyacetylene **6a** was isolated (11%), the main product being 2-(4-nitrophenoxy)benzo[*b*]furan **7a** (38%). The salt of 2,4-dinitrophenol gave 2,4-dinitrophenoxytrimethylsilylacetylene **6b** (28%) and 2,4-dinitrophenoxyacetylene **6c** (31%). From 4-acetylphenol, 4-acetylphenoxyacetylene **6d** was obtained (17%), while 3-methyl-4-nitrophenol afforded an inseparable mixture (33%) of 2-(3-methyl-4-nitrophenoxy)-4-methyl-5-nitrobenzo[*b*]furan and 2-(3-methyl-4-nitrophenoxy)-6-methyl-5-nitrobenzo[*b*]furan **7b** and **7c** (2:1 by NMR), respectively. With the exception of **6a** [6], all products reported are new compounds.

The moderate yields of the products are due to the well-known tendency for polymerization of aroxyacetylenes [6], which are probably formed in the same way as other substitution products, via an alkylidene carbene. In order to explain the formation of the benzofurans, it is assumed that the same alkylidene carbene **8** undergoes first an aromatic C-H insertion, with formation of a trimethylsilyl-benzofuran **9a**, which may undergo two further transformations. The first transformation involves reaction with PhI⁺C≡CSiMe₃ TfO⁻ to give the triflate of 2-(phenyliodonio)benzofuran **10**. This appears to be a rare example involving transfer of the PhI⁺ group from an alkynyl(phenyl)iodonium salt; previously, some lithiated compounds derived from heterocycles have been reported to form iodonium salts by formal attack of a carbanion to the iodonium center of alkynyl(phenyl)iodonium salts [7]. In the second transformation, this iodonium salt reacts with potassium 4-nitrophenolate (or other phenolates) in an expected way.

The intermediacy of the first benzofuran was proved indirectly by reacting potassium 4-nitrophenolate with

$\text{PhI}^+\text{C}\equiv\text{CPh TfO}^-$. In this case the initially formed insertion product could not react further, so that 2-phenyl-5-nitrobenzo[*b*]furan [8] **9b** was isolated (33%) (Scheme 3).



Scheme 3.

It should be noted that some phenylated benzo[*b*]furans have been obtained from 2,4-dinitro-6-phenyliodonium phenolate and alkynes, photochemically [9]. On the other hand, it seems that only one aryloxybenzofuran has been reported in the literature from the reaction of 6-methoxy-3-methylbenzo[*b*]furan with DDQ [10].

Experimental

General

Melting points were determined on a Kofler hot stage microscope and are uncorrected. Infrared spectra were recorded in Nujol using a Perkin-Elmer 297 spectrophotometer. Mass spectra were recorded using a VG-TS 250 double focusing instrument at 70 eV. Proton NMR spectra were recorded at 300 MHz using a Bruker AM 300 spectrometer. Sample solutions were prepared in deuteriochloroform containing tetramethylsilane as an internal reference. Carbon-13 NMR spectra were recorded at 75 MHz using a Bruker AM 300 spectrometer. Deuteriochloroform was used as solvent with tetramethylsilane as an internal reference.

Typical Procedure for the preparation of **6**, **7** and **9b**

To a solution of phenol (2.2 mmol) in anhydrous CH_2Cl_2 (8mL) containing 4A molecular sieves was added *t*-BuOK (2.2 mmol) at -15°C under an argon atmosphere. The slurry was stirred at this temperature for 30 min and a solution of iodonium salt (1 mmol) in dry CH_2Cl_2 (5mL) was added. The reaction mixture was stirred at r.t. for 2 days, then diluted by the addition of CH_2Cl_2 and the insoluble materials were filtered off. The filtrate was concentrated and chromatographed on silica gel with hexane-ethyl acetate as the eluent.

In this way the following compounds have been obtained:

6a: mp = $161\text{--}162^\circ\text{C}$ (lit.[6]: $158\text{--}161^\circ\text{C}$); IR (Nujol) 2160 cm^{-1} ($\text{C}\equiv\text{C}$); $^1\text{H-NMR}$ (CDCl_3): (δ) 8.30 (d, $J = 9.2\text{ Hz}$, 2H), 7.44 (d, $J = 9.2\text{ Hz}$, 2H), 2.29 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3): (δ) 159.7 (C-1), 144.6 (C-4), 125.9 (C-3, C-5), 115.7 (C-2, C-6), 82.7 (C_α), 35.9(C_β); MS m/z (%): 164 ($[\text{M}+\text{H}]^+$, 21), 148(43), 89(100).

6b: mp = 80 °C; IR (Nujol): 2163 cm⁻¹ (C≡C); ¹H-NMR (CDCl₃): (δ) 8.88 (d, J = 2.7 Hz, 1H), 8.57 (dd, J = 9.2 Hz, J = 2.7 Hz, 1H), 7.98 (d, J = 9.2 Hz, 1H), 0.27 (s, 9H); ¹³C-NMR (CDCl₃): (δ) 152.7 (C-1), 143.4 (C-4), 137.7 (C-2), 129.4 (C-5), 122.

1 (C-3), 117.8 (C-6), 97.9 (C_a), 51.0 (C_a), 0.10 (CSiMe₃); MS *m/z* (%): 267(10), 237(8), 190(14), 99(100);

6c: mp = 55 °C; IR (Nujol): 2160 cm⁻¹ (C≡C); ¹H-NMR (CDCl₃): (δ) 8.89 (d, J = 2.7 Hz, 1H), 8.57 (dd, J = 9.2 Hz, J = 2.7 Hz, 1H), 8.03 (d, J = 9.2 Hz, 1H), 2.5 (s, 1H); ¹³C-NMR (CDCl₃): (δ) 152.5 (C-1), 143.6 (C-4), 137.8 (C-2), 129.4 (C-5), 122.1 (C-3), 117.8 (C-6), 80.6 (C_a), 39.1 (C_a); MS *m/z* (%): 209 ([M+H]⁺, 17), 192(23), 167(52), 79(100);

6d: mp = 43 °C; IR (Nujol): 2165 cm⁻¹ (C≡C); ¹H-NMR (CDCl₃): (δ) 8.0 (d, J = 8.7 Hz, 2H), 7.4 (d, J = 8.7 Hz, 2H), 2.6 (s, 3H), 2.2 (s, 1H); ¹³C-NMR (CDCl₃): (δ) 196.4 (C=O), 155.9 (C-1), 134.0 (C-4), 130.5 (C-3, C-5), 115.1 (C-2, C-6), 83.4 (C_a), 34.9 (C_a), 29.7 (CH₃); MS *m/z* (%): 161 ([M+H]⁺, 2), 160(M⁺, 15), 145(39), 136(69), 121(100);

7a: mp = 162-163 °C; IR (KBr): 3125, 1604, 1573, 1508, 1480, 1442, 1345 cm⁻¹; ¹H-NMR (CDCl₃): (δ) 8.44 (d, J = 2.3 Hz, 1H), 8.32 (d, J = 9.3 Hz, 2H), 8.22 (dd, J = 9 Hz, J = 2.3 Hz, 1H), 7.52 (dd as d, J = 9 Hz, 1H), 7.30 (d, J = 9.3 Hz, 2H), 6.24 (d, J = 0.8 Hz, 1H); ¹³C-NMR (CDCl₃): (δ) 159.7 (m, C-7_a), 159.5 (d, ²J = 5.6 Hz, C-2), 152.6 (m, C-1'), 144.7 (m, C-4', C-5), 128.8 (m, C-3_a), 126.1 (dd, ¹J = 170.0, ³J = 5.2 Hz, C-3', C-5'), 119.7 (dd, ¹J = 167.0, ³J = 5.0 Hz, C-6), 118.0 (dd, ¹J = 170.0, ³J = 4.6 Hz, C-2', C-6'), 116.9 (dd, ¹J = 170.0, ³J = 5.0 Hz, C-4), 111.4 (dd, ¹J = 169.0, ³J = 1.2 Hz, C-7), 87.4 (dd, ¹J = 184.0, ³J = 3.3 Hz, C-3); MS *m/z* (%): 300(M⁺, 100), 284(6), 270(4), 254(26);

Mixture of **7b**, **7c**: mp = 136-137 °C; IR (Nujol): 3110, 1598, 1565, 1506, 1333 cm⁻¹; ¹H-NMR (CDCl₃): (δ) 8.17 (s, 1H), 8.13-8.06 (m, 2H), 7.96 (d, J = 9 Hz, 1H), 7.36-7.31 (m, 2H), 7.15-7.05 (m, 4H), 6.20 (d, J = 0.9 Hz, 1H), 6.13 (d, J = 0.8 Hz, 1H), 2.71 (s, 3H), 2.68 (s, 3H), 2.645 (s, 3H), 2.639 (s, 3H); ¹³C-NMR (CDCl₃): (δ) 159.29, 159.07, 158.13, 158.11 (C-1', C-2), 151.57, 150.65 (C-7_a), 146.14, 145.67, 145.59, 145.39 (C-5, C-4'), 137.19, 137.17 (C-3'), 130.06, 129.98 (C-3_a), 127.46, 127.43, 127.40, 126.71 (C-6, C-5', C-4), 121.21, 121.11, 121.00 (C-2', C-6), 117.72, 115.73, 115.64 (C-4, C-6'), 114.13, 109.25 (C-7), 86.68, 86.29 (C-3), 21.11, 21.02, 16.75 (4-CH₃); MS *m/z* (%) 328 (M⁺, 100), 311(43), 308(11), 283(27).

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Sample Availability: Not available.

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