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# An Efficient Ligand Exchange Reaction of (E)-[ $\beta$ -(Trifluoromethanesulfonyloxy)ethenyl](phenyl)iodonium Triflates with Aryl- and Alkynyllithium Reagents Leading to Diaryl- and Alkynyliodonium Triflates

Namig Sh. Pirguliyev,<sup>a</sup> Valery K. Brel,<sup>b\*</sup> Navruz G. Akhmedov,<sup>a</sup> Nikolai S. Zefirov<sup>a,b</sup>

<sup>a</sup>Department of Chemistry, Moscow State University, Moscow 119899, Russia

Fax +7(095)9390290

<sup>b</sup>Institute of Physiologically Active Compounds of Russian Academy of Sciences, 142432 Moscow Region, Chernogolovka, Russia

FAX: +7(095)9132113; E-mail: brel@ipac.ac.ru

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**Abstract**: Reaction of (E)-[ $\beta$ -(trifluoromethanesulfonyloxy)-ethenyl](phenyl)iodonium triflates with aryl- and alkynyllithium reagents gave aryl(phenyl)- and alkynyl(phenyl)iodonium triflates in high yields and selectively. These reactions indicate that ligand exchange takes place efficiently at the hypervalent iodine atom and provides another approach to diaryl- and alkynyliodonium salts.

Key words: alkynes, aryl halides, hypervalent elements, iodine

Recently much attention has been paid to polyvalent iodine(III) compounds in organic synthesis.<sup>1</sup> Symmetric and asymmetric diaryliodonium salts, Ar<sub>2</sub>I<sup>+</sup>X<sup>-</sup> and [ArI-Ar']<sup>+</sup>X<sup>-</sup>, and alkynyliodonium salts, RC=CI<sup>+</sup>Ar X<sup>-</sup>,<sup>2,3</sup> with a large diversity of inorganic and organic counterions, X<sup>-</sup>, represent the most important classes of polyvalent iodine(III) compounds.<sup>2</sup> Diaryliodonium salts are widely used in organic synthesis as efficient arylating reagents for a great variety of nucleophiles, some of them display biological (e.g. antimicrobial) activity and photochemical properties, and they are also suggested to be efficient catalysts for radiation-initiated polymerization.<sup>1,2</sup> The application of alkynyliodonium salts in organic synthesis cannot be overemphasized.<sup>2,3</sup> Thus, new or important preparations are being sought in many laboratories.<sup>4</sup> Especially, considering the useful properties of salts and other derivatives of triflic acids,<sup>5</sup> the development of a simple and efficient procedure for the preparation of diaryl- and alkynyliodonium triflates is a desirable goal.

Our approach to the synthesis of diaryliodonium salts involved the following steps: (a) preparation of a compound X-Z-IArX such that Z represents a masking group inert to R'Li under the reaction conditions, X, the nucleofugal group; (b) reaction of X-Z-IArX with 2 equivalents of R'Li forming X-Z-IArR' (R' = Ar' or  $RC \equiv C$ ); and (c) removal of Z to form  $[ArIAr']^+X^-$  or RC=CI<sup>+</sup>ArX<sup>-</sup>. Several considerations lead to the selection of the-CH=CHgroup as Z and the triflate group as X. There were several reasons for believing in the possibility of the final ionic elimination: (a) the analogous compounds, namely ( $\beta$ chlorovinyl(iodonium chloride with the base yields acetylenes;<sup>6</sup> (b) the large size of the IArR' group might favor elimination; (c) the third carbon-iodine bond should be weak;<sup>2</sup> (d) the ( $\beta$ -triflyloxy)vinyliodonium triflates have a good leaving group, OTf, with the geometry trans to aryliodonio group; and (e) the high nucleofugacity of OTf is very suitable to induce elimination at the stage of ligand exchange.

There are only a few successful examples of application of the ligand exchange reaction<sup>7</sup> using vinyliodonium salts for synthesis of diaryliodonium salts.<sup>7,8</sup> Due to the reasons given above, we considered that ( $\beta$ -trifluoromethanesulfonyloxyvinyl)iodonium triflates would undergo ligand exchange effectively. In this paper we report a direct convenient preparation of diaryl- and alkynyliodonium triflates using (*E*)- $\beta$ -triflylvinyliodonium triflates.



The (*E*)- $\beta$ -triflylvinyliodonium triflates were prepared by the reaction of [ArI<sup>+</sup>F <sup>-</sup>OTf] with acetylene in dichloromethane at -78 °C in 57–91% yield.<sup>9</sup> Ligand exchange reaction of these compounds with R'Li provided the corresponding diaryl- and alkynyliodonium triflates in good yields.

In general, the best yields of iodonium salts were obtained by the dropwise addition of a solution of the aryl- or alkynyllithium in hexane to a solution of the corresponding alkenyliodonium salts under argon at dry-ice-acetone temperature. This temperature was then maintained for 1-3 hours before the reaction mixture was allowed to rise slowly to room temperature. Stirring of the resulting suspension was then continued for approximately 1-5 hours. The availability of low-temperature solvent systems, unreactive toward aryl and alkynyllithium reagents is limited, however, we have compared the reaction in diethyl ether, toluene, tetrahydrofuran and pentane. Low yields (20-27%) of iodonium salts could be isolated from the reactions ran in tetrahydrofuran, but the yields from the reactions done in toluene or  $Et_2O$  were frequently over 60%. When dry pentane was used as solvent the yields were erratic and usually below 30%. The lithium reagents with activated aryl residues such as 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-EtOC<sub>6</sub>H<sub>4</sub> and 4-AlkC<sub>6</sub>H<sub>4</sub> reacted completely within 1-2 hours. Weakly deactivated aryllithium reagents such as HalC<sub>6</sub>H<sub>4</sub>Li needed a prolonged reaction time to produce reasonable yields of the diaryliodonium triflates. However, the alkenyliodonium triflates with strongly deactivated aromatics such as 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> did not give the corresponding diaryliodonium triflates. As far as alkynyliodonium salts are concerned, this method is clearly general for the formation of any alkynyliodonium salt, being limited only by the possibility of preparation of the alkynyllithium reagents.

In summary, we have found that ligand exchange reaction of (E)- $\beta$ -triflylvinyliodonium triflates with aryl- and alky-nyllithium reagents is a mild and efficient method for the preparation of diaryl- and alkynyliodonium salts. The

present method is an example of transfer from one class of hypervalent iodine compounds to another.

All reactions were conducted under a dry Ar atmosphere. NMRspectra were recorded on a Varian VXR-400 spectrometer. <sup>1</sup>H NMR spectra were recorded at 400 MHz, and all chemical shifts ( $\delta$ ) are reported in ppm relative to the solvent peaks (CDCl<sub>3</sub>: 7.21 ppm or CD<sub>3</sub>OD: 3.31 ppm). <sup>13</sup>C NMR spectra were recorded at 100 MHz, and all chemical shifts ( $\delta$ ) are reported in ppm relative to the solvent peaks (CD<sub>3</sub>OD: 49.0 ppm or CDCl<sub>3</sub>: 77.0 ppm). Mps are uncorrected. Et<sub>2</sub>O and THF were purified by literature procedures<sup>12</sup> and were distilled over Na/benzophenone.

### **Diaryliodonium Triflates; General Procedure**

A 100 mL flask was charged with toluene (25 mL) or  $Et_2O$  (25 mL) and the desired bromoarene or alkyne (8.8 mmol). The mixture was cooled to -78 °C using a dry ice-acetone bath. A 2.5 M solution of BuLi in hexanes (4,0 mL, 10,0 mmol) was added with a syringe and the mixture was stirred at -78 °C for 15 min. Alkenyliodonium triflate **1** (7.5 mmol) was then added all at once and the mixture was stirred at -78 °C for additional 1-3 h, then the temperature was allowed to warm gradually to r.t. during 1-1.5 h. After stirring at r.t. for an additional 1-5 h, the reaction mixture was filtered using an aspirator pump under an Ar stream. After evaporation of the solvent,  $Et_2O$  was added to crystallize the residue. The solid was filtered, washed with  $Et_2O$ , and dried in vacuo. Spectral data for newly prepared diaryliodonium triflates are as follows.

Table Yields of Iodonium Triflates Prepared

Product <sup>c</sup>	Ar	R′	Isolated Yields <sup>a</sup> (%)	Mp <sup>b</sup> (°C) (Lit)
2a	Ph	Ph	84	177–180 (178–180) <sup>4</sup> c
2b	Ph	$4-CH_3C_6H_4$	76	123–125 (122–125) <sup>4b</sup>
2c	Ph	$4-\text{MeOC}_6\text{H}_4$	69	110–112 (109–111) <sup>4b</sup>
2d	Ph	$2,5-Me_2C_6H_4$	63	138–139 (136–138) <sup>4b</sup>
2e	Ph	$4-IC_6H_4$	82	143–147 (144–148) <sup>4b</sup>
2f	Ph	$4-ClC_6H_4$	71	110–112 (110–111) <sup>4b</sup>
2g	Ph	4- <i>tert</i> -BuC <sub>6</sub> H <sub>4</sub>	87	161–164
2h	Ph	$4\text{-EtOC}_6\text{H}_4$	66	74-76 (73-75) <sup>4b</sup>
2i	$4-CH_3C_6H_4$	$4-CH_3C_6H_4$	64	185–186 (185–187) <sup>4</sup> c
2j	$4-CH_3C_6H_4$	Ph	78	124–126 (122–125) <sup>4b</sup>
2k	Ph	$4-EtC_6H_4$	75	136–140
21	Ph	$4-Pr^{i}-C_{6}H_{4}$	68	144–148
2m	Ph	quinolin-3-yl	56	176–184
2n	Ph	MeOCH <sub>2</sub> C≡C	76	73-74 (72-72)10
20	Ph	PhC≡C	69	82-84 (83) <sup>11</sup>
2p	Ph	<i>n</i> -BuC≡C	71	67-69 (67-68) <sup>11</sup>

<sup>a</sup> Based on ethenyliodonium salts.

<sup>b</sup> Uncorrected, measured on a micro melting point apparatus.

<sup>c</sup> Satisfactory microanalyses obtained (C, 0.4%; H, 0.25%).

# (4-tert-Butylphenyl)(phenyl)iodonium Triflate (2g)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.28 (s, 9H, Me), 7.35–7.63 (m, 4H, ArH), 7.87–8.10 (m, 5H, ArH).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 30.97, 35.30, 109.63, 113.76, 129.55, 132.12, 132.35, 135.14, 135.23, 156.65.

# (4-Ethylphenyl)(phenyl)iodonium Triflate (2k)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.12 (t, 3H, Me), 2,08 (q, 2H, CH<sub>2</sub>), 7,25–7,62 (m, 4H, ArH), 7,92–8,03 (m, 5H, ArH).

 $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.40, 35.40, 106.10, 118.20, 119.50, 131.61, 131.98, 135.11, 136.62, 141.84.

### (4-Isopropylphenyl)(phenyl)iodonium Triflate (2l)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.4 (m, 6H, Me), 2.65 (m, 1H, CH), 7.11–7.67 (m, 4H, ArH), 8.01–8.31 (m, 5H, ArH).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 17.85, 29.20, 114.67, 121.65, 129.80, 131.50, 132.04, 132.26, 134.60, 134.95, 142.23, 143.85.

#### (Quinolin-3-yl)(phenyl)iodonium Triflate (2m)

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.35–7.56 (m, 5H, ArH), 7.79 (t, 1H, *J* = 5.5 Hz, H-6), 7.96 (t, 1H, *J* = 6.9 Hz, H-7), 8.01–8.04 (m, ArH), 8.10 (d, 1H, *J* = 8.0 Hz, H-5), 8.16 (d, 1H, *J* = 8.0 Hz, H-8), 9.43 (d, 1H, *J* = 2.0 Hz, H-4), 9.49 (d, 1H, *J* = 2.0 Hz, H-2).

<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD): δ = 111.40, 115.20, 129.90, 130.1, 130.24, 130.70, 131.95, 132.19, 134.4, 143.87, 145.90, 152.80.

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