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Activation of Iodosylbenzene with One Equivalent of Triflic (Trifluoromethanesulphonic) Anhydride. Novel Preparation of (*p*-Phenylene)bisiodonium Triflates

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A reagent prepared from PhIO and triflic anhydride (1:1 molar ratio) in dichloromethane gave aryl(vinyl)(*p*-phenylene)bisiodonium triflates **2** on reaction with alk-1-ynes and diaryl(*p*-phenylene)bisiodonium triflates **3** on treatment with aromatics.

Hypervalent iodine(III) reagents are useful in organic synthesis.[1] Recently much attention has been paid to functionalized iodonium salts,[1,2] including aryl, alkenyl and alkynyliodonium salts because of their unique properties and synthetic utility.

Very recently μ-oxybis[(trifluoromethanesulphonato)(phenyl)iodine], Zefirov's reagent,[3] was prepared by the combination of 2 equiv. of PhIO with 1 equiv. of triflic anhydride[4] and was used for the preparation of 1,2-ditriflates[3,4] and the parent alkynyliodonium salt.[2b] However, when 1 equiv. of PhIO was activated by 1 equiv. of triflic anhydride, a drastic change in the reaction was observed. In this communication, we report the novel preparation of diaryl- and aryl(vinyl)-(*p*-phenylene)bisiodonium triflates.

To a suspension of PhIO (5 mmol) in dichloromethane (5 ml) was added 5 mmol of triflic anhydride and the mixture was stirred for 3 h at room temperature. Then, pent-1-yne (5 mmol) was added, and the white crystals that precipitated after a few minutes were filtered, washed with dichloromethane and water, and finally dried *in vacuo*. The crystals had characteristic ^{1}H and ^{13}C NMR spectra consistent with the bisiodonium triflate structure **2a**.†‡ The *ortho* aromatic protons of the iodine(III) atoms appeared at relatively low-field positions, δ 8.23–8.32 (m, 4 H) and 8.40–8.43 (m, 2 H) in [$^2H_6$]dimethylsulphoxide (DMSO). The vinylic proton absorbed at δ 7.84 (s). The signals of the three aromatic carbons attached to the iodine(III) atoms showed high-filed shifts at δ 117.0, 120.0 and 120.6. The vinylic carbons absorbed at δ 99.2 and 160.4. Analogous chemical shifts of vinylic carbons have been observed in β-(trifluoromethanesulphonyloxy)vinyliodonium triflates.[5] The IR spectrum showed absorption at 1632 cm^{-1} due to the carbon–carbon double bond. Hex-1-yne and oct-1-yne reacted in a similar manner to give bisiodonium triflates **2b** and **2c**,† respectively, in high yields (Scheme 1).

The reagent prepared from PhIO and triflic anydride as above is electrophilic and provides diarylbisiodonium triflates **3**§ on treatment with aromatics such as toluene, benzene and bromobenzene.

Reaction with cyclohexene was conducted to obtain further evidence for the formation of the proposed bisiodine(III) reagent. The reagent prepared from PhIO (5 mmol) and triflic anydride (5 mmol) was treated with cyclohexene (5 mmol) and *p*-iodophenyl(phenyl)iodonium triflate¶ was obtained in 70% yield, together with 1,2-cyclohexanediyl ditriflate which was also obtained in the case of the use of Zefirov's reagent, [3,4] Therefore, the present result suggests that the hypervalent

† *Characterisation data* for **2a**: m.p. 208–215 °C (decomp.); NMR δ_H (250 MHz, [$^2H_6$] DMSO) 0.79 (t, *J* 7 Hz, Me, 3 H), 1.36–1.45 (m, CH_2, 2 H), 2.83 (t, *J* 7 Hz, CH_2, 2 H), 7.51–7.57 (m, ArH, 2 H), 7.65–7.71 (m, ArH, 1 H), 7.84 (s,=CH, 1 H), 8.23–8.32 (m, ArH, 4 H) 8.40–8.43 (m, ArH, 2 H); δ_C ([$^2H_6$] DMSO) 12.6, 18.9, 35.2, 99.2, 117.0, 120.0, 120.6, 131.8, 132.3, 135.2, 137.6, 137.7, 160.4; IR ν_{max}/cm^{-1} 1632 (C=C).

2b: m.p. 182–188 °C (decomp.); NMR δ_H (250 MHz, [$^2H_6$] DMSO) 0.80 (t, *J* 7 Hz, Me, 3 H), 1.20–1.42 (m, CH_2CH_2, 4 H), 2.84 (t, *J* 7 Hz, CH_2, 2 H), 7.50–7.56 (m, ArH, 2 H), 7.65–7.71 (m, ArH, 1 H), 7.82 (s,=CH, 1 H), 8.23–8.29 (m, ArH, 4 H), 8.38–8.42 (m, ArH, 2 H); δ_C ([$^2H_6$] DMSO) 13.6, 21.4, 27.7, 33.7, 99.1, 117.1, 120.1, 120.6, 132.0, 132.4, 135.5, 137.7, 137.9, 160.7; IR ν_{max}/cm^{-1} 1634 (C=C).

2c: m.p. 206–210 °C (decomp.); NMR δ_H (250 MHz; [$^2H_6$] DMSO) 0.80–0.83 (m, Me, 3 H), 1.19–1.41 (m, $CH_2CH_2CH_2CH_2$, 8 H) 2.85 (t, *J* 7 Hz, CH_2, 2 H), 7.51–7.57 (m, ArH, 2 H), 7.66–7.72 (m, ArH, 1 H), 7.84 (s,=CH, 1 H), 8.24–8.32 (m, ArH, 4 H), 8.39–8.43 (m, ArH, 2 H); δ_C ([$^2H_6$] DMSO) 13.7, 21.7, 25.3, 27.5, 30.6, 33.6, 98.9, 116.9, 119.9, 120.5, 131.8, 132.3, 135.3, 137.5, 137.7, 160.6; IR ν_{max}/cm^{-1} 1632 (C=C).

‡ Satisfactory elemental analyses were obtained for all new compounds.

§ *Characterisation data* for **3a**: m.p. 254–259 °C (decomp.); NMR δ_H (250 MHz, [$^2H_4$]MeOH) 2.39 (s, CH_3, 3 H), 7.33–7.35 (m, ArH, 2 H), 7.51–7.55 (m, ArH, 2 H), 7.68–7.72 (m, ArH, 1 H), 8.06–8.08 (m, ArH, 2 H) 8.20–8.27 (m, ArH, 6 H); δ_C ([$^2H_4$]MeOH) 21.4, 112.4, 116.2, 119.8, 120.0, 133.4, 134.1, 134.2, 136.9, 138.9, 139.1, 145.7.

3b: m.p. 277–287 °C (decomp.); NMR δ_H (250 MHz, [$^2H_6$]DMSO) 7.50–7.56 (m, ArH, 4 H), 7.64–7.70 (m, ArH, 2 H), 8.24–8.33 (m, ArH, 8 H); δ_C ([$^2H_6$]DMSO) 116.6, 120.3, 132.0, 132.5, 135.5, 137.8.

3c: m.p. 258–267 °C (decomp.); NMR δ_H (250 MHz, [$^2H_6$]DMSO) 7.52–7.56 (m, ArH, 2 H), 7.66–7.68 (m, ArH, 1 H), 7.74–7.77 (m, ArH, 2H), 8.18–8.20 (m, ArH, 2 H), 8.26–8.28 (m, ArH, 2 H), 8.33 (br s, ArH, 4 H); δ_H ([$^2H_6$]DMSO) 115.1, 116.6, 120.2, 120.3, 126.6, 131.9, 132.3, 134.7, 135.3, 137.2, 137.56, 137.62.

¶ M.p. 126–129 °C (decomp.); NMR δ_H (250 MHz, [$^2H_6$]DMSO) 7.35–7.46 (m, ArH, 2 H), 7.57–7.64 (m, ArH, 1 H), 7.72 (s, ArH, 4 H), 7.96–8.03 (m, ArH, 2 H); δ_C ($CDCl_3$–[$^2H_6$]DMSO) 98.2, 113.7, 114.6, 130.5, 130.9, 133.8, 135.2, 139.3.

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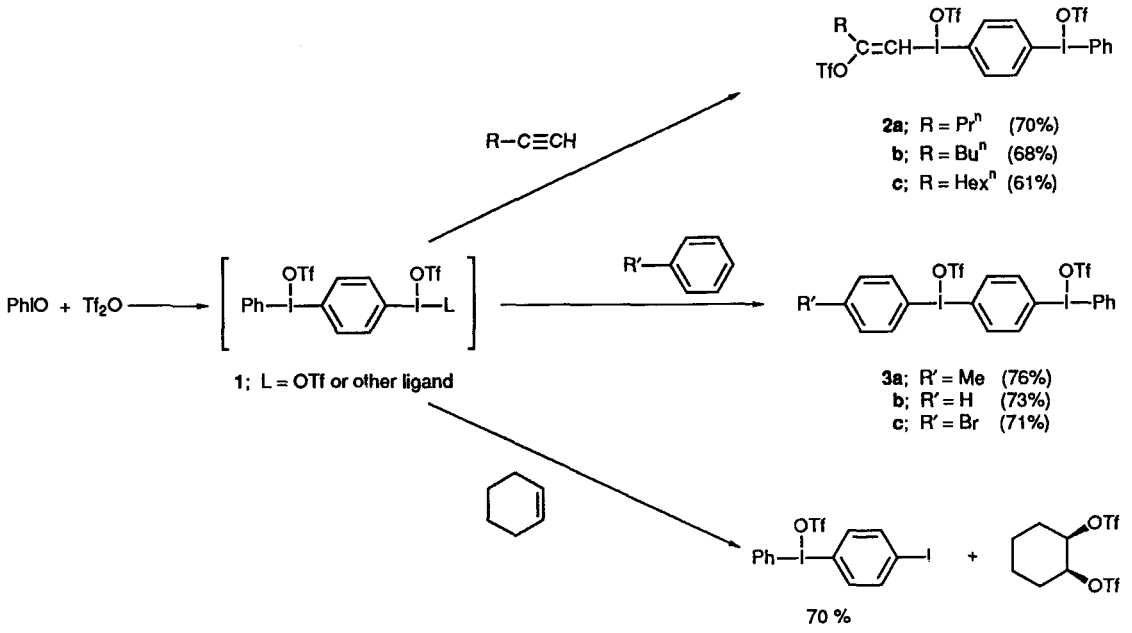

Scheme 1

iodine reagent generated has a bisiodine(III)-containing skeleton **1** as described in Scheme 1.

The present work provides a direct preparation of diaryl- and aryl(vinyl)-*p*-(phenylene)bisiodonium salts and suggests that a type of bisiodine(III) reagent **1** is the intermediate in the formation of *p*-iodophenyliodonium bisulphate by the reaction of PhIO and H_2SO_4.[6]

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