Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1992, **2(4)**, 159–160
Mendeleev Communications

1,4-Bis(iodosyl)benzene: an Efficient Reagent for the Preparation of (*p*-Phenylene)bisiodonium Salts

Peter J. Stang,*[a] Viktor V. Zhdankin[a] and Nikolai S. Zefirov[b]

[a] *Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112, USA. Fax: + 1 801 581 8433*
[b] *Department of Chemistry, Moscow State University, Moscow 119899, Russian Federation. Fax: + 7 095 939 0171*

A number of novel (*p*-phenylene)bisiodonium salts, **2–4**, have been prepared from *p*-bis(iodosyl)benzene.

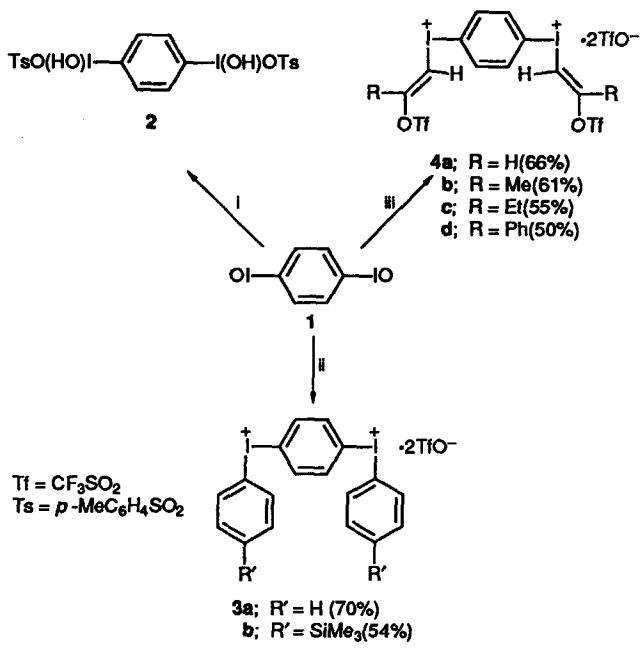
There is widespread current interest in polyvalent iodine compounds.[1] Numerous derivatives of iodosylbenzene, PhIO, such as the triflate, tosylate, mesylate, tetrafluoroborate, *etc.* have become useful reagents in organic synthesis.[1] Among the most important synthetic applications of these reagents is the preparation of various functionalised iodonium salts, some of which possess high antimicrobial activity and useful photochemical properties.[1f] The analogous derivatives of bis(iodosyl)benzene, **1**, are potentially useful as the precurors to bis- and polyiodonium salts. To our knowledge, only a single representative of a bisiodonium salt has been reported in the literature[2] and a general synthetic approach to these compounds is still unknown.

In the present communication we report the preparation of a number of (*p*-phenylene)bisiodonium salts, **2–4**, starting from bis(iodosyl)benzene **1**. Bis(iodosyl)benzene **1** has been known for one hundred years and is readily available by chlorination of *p*-diiodobenzene and subsequent hydrolysis of the intermediate tetrachloride,[3] however, to our knowledge none of its reactions have been reported.

Analogous to the mono-iodosylbenzene, compound **1** reacts with toluene-*p*-sulfonic acid in MeCN or CH_2Cl_2 with the formation of the hydroxytosylate iodonium salt **2** (Scheme 1), which is similar to the widely applied Koser's reagent, PhI(OH)OTs.[1c] The tosylate salt **2** was isolated as a white microcrystalline salt almost insoluble in the usual organic solvents and identified by elemental analysis, ^{1}H NMR and IR spectra.† In

† *Characterisation data* for **2**: m.p. 156–157°C (decomp.); ^{1}H NMR [300 MHz, $(CD_3)_2SO$], δ 2.45 (s, 6H, 2Me of 2TsO), 7.36 (d, 4H, 4CH of 2TsO, *J* 8 Hz), 7.73 (d, 4H, 4CH of 2TsO, *J* 8 Hz), 8.35 (s, 4H, C_6H_4); IR ν/cm^{-1} (CCl_4) 3141 (br, OH), 3085 (Ar), 2918 (Me), 1596, 1377, 1238, 1148, 993.

Mendeleev Commun., 1992, 2(4), 159–160



Scheme 1 *Reagents and conditions*: i, *p*-TsOH·H_2O (2 mol equiv.), MeCN, 25°C; 15 h; ii, Me_3SiOTf (3 mol equiv.), *p*-R'$C_6H_4SiMe_3$ (3 mol equiv.), CH_2Cl_2, −40 to 25°C, 10 h; iii, Me_3SiOTf (4 mol equiv.), RC≡CH or RC≡C$SiMe_3$ (3–5 mol equiv.), CH_2Cl_2, −40 to 25°C, 10 h

contrast to Koser's reagent, compound **2** is not reactive toward silylated arenes and acetylenes, probably owing to its low solubility in the usual organic solvents (methylene chloride or chloroform) used in these reactions.[1c] However, we were able to prepare several bis(iodonium) salts **3**,**4** by the reaction of bis(iodosyl)benzene **1** with terminal acetylenes or silylated organic substrates in the presence of trimethylsilyltriflate (Scheme 1).

Bis(iodosyl)benzene reacts with silylated aromatic compounds and trimethylsilyltriflate at room temperature in dichloromethane with the formation of tris(aryl) bis(iodonium) salts **3a**,**b** in 60–70% yield.‡ Interestingly, the trimethylsilyl groups in the iodonium salt **3b** are deactivated towards further reaction with **1** even under forcing conditions, and this reaction does not yield any of the tris- or poly-iodonium salts.

Reactions of bis(iodosyl)benzene with acetylenes or monotrimethylsilylated acetylenes under similar conditions give novel vinylic bis(iodonium) triflates **4**§ in moderate yield (Scheme 1). These products have characteristic ^1H, ^{19}F and ^{13}C NMR spectra. Specifically, the fluorine spectrum displays two different types of CF_3 signals at δ −74 and −79 with 1:1 intensities, which correspond to the covalent and ionic triflate groups, respectively. The *trans*-configuration of the double bond in **4a** is assigned from the value of the ^2J constant of 13 Hz in the proton spectrum. Further evidence for the structure of **4** is given by the high-resolution mass spectra. The formation of compounds **4** can be explained by the electrophilic addition of the Me_3SiOTf-activated bis(iodosyl)benzene to the triple bond of the alkyne under reaction conditions analogous to those in the previously reported reactions of mono-iodosobenzene triflate.[2]

In summary, bis(iodosyl)benzene **1** can be used as a reagent for the preparation of interesting (*p*-phenylene)bisiodonium salts of various types.

Financial support by the NSF (CHE9101767) is gratefully acknowledged.

References

1 For reviews, see [a] P. J. Stang, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 274; [b] R. M.Moriarty and R. K. Vaid, *Synthesis*, 1990, 431; [c] R. M. Moriarty, R. K. Vaid and G. F. Koser, *Synlett*, 1990, 365; [d] E. B. Merkushev, *Russ. Chem. Rev.*, 1987, **56**, 826; [e] A. Varvoglis, *Synthesis*, 1984, 7099; [f] G. F. Koser, in *The Chemistry of Functional Groups*, Suppl. D. S. Patai and Z. Rappoport, ed., Wiley–Interscience, New York, 1983, pp. 721–811 and 1265–1351; [g] A. Varvoglis, *Chem. Soc. Rev.*, 1982, **10**, 377.

2 T. Kitamura, R. Furuki, H. Taniguchi and P. J.Stang, *Mendeleev Commun.*, 1991, 148.

3 C. Willgerodt, *Ber.*, 1892, **27**, 1790.

Received: Cambridge, 28th April 1992; Com. 2/02209E
Moscow, 8th May 1992

‡ **3a**: m.p. and spectral data for this compound are identical to that previously reported.[2]

3b: m.p. 254–256°C (decomp.); ^1H NMR (300 MHz, CD_3CN) δ 0.2 (s, 18H, 6Me), 7.68 (d, 4H, Ar, *J* 7 Hz), 8.04 (d, 4H, 4CH, Ar, *J* 7 Hz), 8.15 (s, 4H, —IC_6H_4I—); ^{13}C NMR (75 MHz, CD_3CN, ^1H decoupled) δ_C −1.5 (Me), 121.0 (q, $CF_3SO_3^-$, J_{C-F} 319 Hz), 117.4, 133.5, 135.6, 138.0, 139.1, 148.9 (all Ar); ^{19}F NMR (282 MHz, CD_3CN) δ_F −79.01 (s, $CF_3SO_3^-$); IR ν/cm^{-1} (CCl_4) 3082 (Ar), 2957 (Me), 1562, 1469, 1378, 1259, 1170, 1028; FAB MS *m/z* 777 (20%), 479 100%), 352 (29%); HRMS *m/z* 776.947063 [M − $CF_3SO_3^-$]$^+$, calcd. for $C_{25}H_{30}F_3I_2O_3SSi_2$ 776.949338.

§ *Characterisation data* for **4a**: m.p. 227–230°C (decomp.); ^1H NMR (300 MHz, CD_3CN) δ 7.39 (d, 2H, =C*H*I$^+$, *J* 13 Hz), 7.91 (d, 2H, =C*H*OTf, *J* 13 Hz), 8.19 (s, 4H, —IC_6H_4I—); ^{13}C NMR (75 MHz, CD_3CN, ^1H decoupled) δ_C 93.6 (=CH), 121.0 (CF_3SO_3), 139.3, 139.9 (Ar), 152.2 (=CH); ^{19}F NMR (282 MHz, CD_3CN) δ_F −79.0 (s, $CF_3SO_3^-$), −73.7 (s, CF_3SO_2O); IR ν/cm^{-1} (CCl_4) 3089 (Ar, =CH), 1614 (C=C), 1442, 1288, 1239, 1135, 1027; FAB MS *m/z* 829 (24%), 505 (100%), 378 (23%); HRMS *m/z* 828.731655 [M − $CF_3SO_3^-$]$^+$, calcd. for $C_{13}H_8F_9I_2O_9S_3$ 828.727381.

4b: m.p. 210–212°C (decomp.); ^1H NMR (300 MHz, CD_3CN) δ 2.65 (s, 6H, $2CH_3$), 7.40 (s, =C*H*I$^+$), 8.18 (s, 4H, —IC_6H_4I—); ^{19}F NMR (282 MHz, CD_3CN) δ_F −79.0 (s, CF_3SO_2O); IR ν/cm^{-1} (CCl_4) 3085 (Ar, =CH), 2960 (CH_3), 1640 (C=C), 1437, 1252, 1177, 1137, 1027; FAB MS *m/z* 856 (10%), 519 (20%), 392 (10%).

4c: m.p. 213–215°C (decomp.); ^1H NMR (300 MHz, CD_3CN) δ 1.5 (t, 6H, $2CH_3$), 1.94 (q, 4H, $2CH_2$), 7.37 (s, 2H, =CHI$^+$), 8.18 (s, 4H, —IC_6H_4I—); ^{19}F NMR (282 MHz, CD_3CN) δ_F −79.2 (s, $CF_3SO_3^-$); −73.5 (s, CF_3SO_2O); IR ν/cm^{-1} (CCl_4) 3085 (Ar, =CH), 2960 (C_2H_5), 1629 (C=C), 1437, 1256, 1179, 1132, 977; FAB MS *m/z* 885 (11%), 533 (100%), 207 (16%); HRMS *m/z* 884.790363 [M − $CF_3SO_3^-$]$^+$, calcd. for $C_{17}H_{16}F_9I_2O_9S_3$ 884.789981.

4d: m.p. 227–229°C (decomp.); ^1H NMR (300 MHz, CD_3CN) δ 7.35 (s, 2H, =CHI$^+$), 7.4–7.5 (m, 10H, Ph), 8.2 (s, 4H, —IC_6H_4I—); ^{19}F NMR (282 MHz, CD_3CN) δ_F −79.0 (s, $CF_3SO_3^-$), −73.5 (s, CF_3SO_2O); IR ν/cm^{-1} (CCl_4) 3087 (Ar, =CH), 1620 (C=C), 1597 (Ar), 1288, 1217, 1181, 1132, 972; FAB MS *m/z* 885 (11%), 533 (100%), 407 (16%); HRMS *m/z* 943.790119 [M − $CF_3SO_3^-$]$^+$, calcd. for $C_{25}H_{16}F_9I_2O_9S_3$ 943.789981.