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A New Method for the Preparation of (Arylsulfonyliminoiodo)benzenes

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Abstract: (Arylsulfonyliminoiodo)benzenes (**3**) can be prepared in 52-92% yield via the reaction of dimethoxyiodobenzene (**1**) with the corresponding arylsulfonamide in MeOH or CH_2Cl_2 at room temperature.

(Arylsulfonyliminoiodo)benzenes, $ArSO_2N{=}IPh$ (**3**), represent a relatively new class of iodine(III) compounds.[1-4] Known reactions of (tosyliminoiodo)benzene **3a** include catalytic transfer of the tosylimino moiety to cyclohexane[5] and olefins[6,7], and methanolysis.[8] We have recently reported[9] that **3** can be catalytically carbonylated with CO to arylsulfonyl isocyanates, $ArSO_2NCO$, in moderate to good yields. The latter can be applied for the synthesis of sulfonylurea type herbicides[10]. However, the preparation of **3** may lead to undesirable ring closure if the Ar group contains an *ortho*-alkoxycarbonyl group. We initiated a search for a more versatile method for the synthesis of (arylsulfonyliminoiodo)benzenes **3**.

We have found that in suitable solvents iodobenzene dimethoxide (**1**) reacts with various sulfonamides (**2**) to give **3** in good yield (eq. 2).

$$\underset{(1)}{PhI(OMe)_2} + \underset{(2)}{ArSO_2NH_2} \xrightarrow[-2MeOH]{solvent} \underset{(3)}{ArSO_2N{=}IPh} \qquad (1)$$

The preparation of **1** was best carried out by the method described by Schardt and Hill[11]. Reaction (1) can be accomplished with **1** dissolved in methanol (Version A) or in CH_2Cl_2 (Version B). The yields and IR data of the iodoimines prepared are listed in Table 1.

Table 1. Iodimines **3** prepared via the reaction of iodobenzene dimethoxide **1** with arylsulfonamides **2**.

3	Ar	Version	Yield/%	Selected IR frequencies (KBr, cm^{-1})[14]
a	4-Methylphenyl	A	78	1266, 1132, 1081, 868, 742, 666, 547
a	4-Methylphenyl	B	78	1266, 1132, 1081, 868, 742, 666, 547
b	4-Chlorophenyl	A	76	1270, 1125, 1077, 871, 838, 748
c	4-Nitrophenyl	A	84	1528, 1345, 1276, 1123, 1077, 882, 852, 735
d	2-Nitrophenyl	A	92	1534, 1376, 1277, 1105, 885,741, 581
e	2-Chlorophenyl	B	88	1268, 1137, 1125, 1102, 1041, 890, 734, 582
f	2-Bromophenyl	B	80	1266, 1139, 1120, 1093, 1025, 886, 734, 580
g	2-Methoxycarbonylphenyl	A	58	1721, 1266, 1128,1108, 1058, 932, 592
h	2-Ethoxycarbonylphenyl	B	52	1713,1279,1112, 1059, 904, 591

Iodoimines **3** are relatively strong oxidants, with very limited solubility in most solvents, and have decomposition temperatures rather than melting points. As a consequence, their characterization by various analytical techniques may be difficult and show poor reproducibility. In order to obtain further reproducible analytical data for the new iodomimines **3g** and **3h**, we have prepared the phosphinimines $Ph_3P{=}NSO_2Ar$ by reacting equivalent amounts of Ph_3P with the corresponding iodoimine. The phosphinimines **4g** and **4h** were characterized by IR and mass spectra, which showed that derivatives of *o*-alkoxycarbonylarylsulfonamides were actually formed[13].

General Procedure

Version A. 1.1 g (5 mmol) of PhIO was stirred for 15 min with 40 cm^3 of MeOH under N_2. About 3 g of activated[12] Linde 3A was added and the suspension was stirred in a capped Schlenk tube for 2 hours. After removing the molecular sieve by filtration, the drying process was repeated with another portion of Linde 3A. Iodometric titrations indicated a 44 mg loss of PhIO. 1.0 g (4.95 mmol) of 2-nitrobenzenesulfonamide was added to the filtrate in small quantities. The solution turned yellow initially, then a white precipitate separated readily. The major part of the solvent was removed under vacuum and 5 cm^3 CH_2Cl_2 was added. The precipitate was collected on a sintered glass filter, washed with CH_2Cl_2 and dried. Yield: 1.80 g (92%). Iodometric titration showed a 98% purity.

Version B. 1.2 g (5.5 mmol) of PhIO was dissolved in 10 cm^3 of MeOH and ca. 3 g of activated Linde 3A was added. After stirring for 3 hours, the molecular sieve was filtered off and washed with 3x3 cm^3 of dry MeOH. The combined methanolic solution was evaporated to dryness. To the pale yellow precipitate 20 cm^3 of dry CH_2Cl_2 was added and the slightly disturbed liquid was stirred for 20 min. The unconverted PhIO was removed using a Schlenk filter. Iodometric analysis of a 1 cm^3 probe from the filtrate showed that the $PhI(OMe)_2$ content of the solution was 4.42 mmol (80.4%). Upon the addition of 0.75 g (4.4 mmol) of *p*-toluenesulfonamide, an intense yellow colour developed, then on standing a thick white precipitate separated from the yellow solution, which was collected on a glass filter. Yield: 1.3 g (78%).

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12. Activation of the powdered Linde 3A molecular sieve was carried out under vacuum (ca. 0.1 Torr), at 400°C for 15 hours.
13. To the iodoimine suspended in dry CH_2Cl_2, Ph_3P was added in small portions. External cooling was applied to keep the mixture at RT. Upon the addition of benzene to the evaporated reaction mixture a white precipitate separated readily, which was filtered and recrystallized from EtOH. **4g**: m/z 475 (40%); m.p. 144-5°C. IR (KBr, cm^{-1}): 1735, 1292, 1278, 1148-1100 (poorly resolved strong vibrations), 791. **4h**: m/z 489 (32%); m.p. 172-3°C. IR (KBr, cm^{-1}).1728, 1282, 1149-1099,725, 693, 603, 582, 529, 521.
14. Assignments: 1721-1713 cm^{-1} $\nu(CO)$; 1534-1528 cm^{-1} $\nu_{as}(NO_2)$; 1376-1345 $\nu_s(NO_2)$; 1270-1266 cm^{-1} $\nu_{as}(SO_2)$; 1139-1125 cm^{-1} $\nu_s(SO_2)$; 904-868 cm^{-1} iodoimine moiety.

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