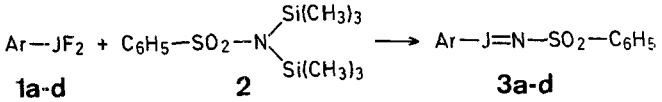
Bis[phenylsulphonylimino]iodoarenes: A New Type of Pentavalent Iodine Compound

I. I. MALETINA, A. A. MIRONOVA, V. V. ORDA, L. M. YAGUPOLSKII

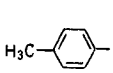
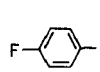
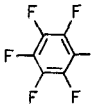
Institute of Organic Chemistry of Ukrainian SSR Academy of Sciences, 252094 Kiev, U.S.S.R.

Ylids of trivalent iodine with a J—C bond have been known since 1957 and studied sufficiently[1,2,3]. Recently, iodonium ylids with a J—N bond were obtained[4] by the interaction of diacetoxyiodoarenes with *p*-toluenesulphonamide in methanol in the presence of potassium hydroxide. These tosyliminoiodoarenes proved to be rather stable compounds which may be used in reylidation reactions for the synthesis of sulphur and phosphorus ylids[4] as well as other iodonium ylids[5].

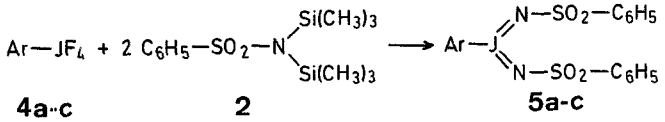
We have now synthesised sulphonyliminoiodoarenes **3a–d** (Table) from difluoroiodoarenes **1** and *N,N*-bis[trimethylsilyl]benzenesulphonamide (**2**)[6] in a mixture of anhydrous ether and dichloromethane at room temperature (Method A). Initial attempts to prepare compounds **3** from diacetoxyiodoarenes and benzenesulphonamide under the conditions of Ref.[4] were unsuccessful; however, we have now found that this reaction is possible under carefully controlled conditions (Method B).



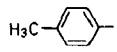
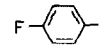
1a-d **2** **3a-d**

1,3	a	b	c	d
Ar				

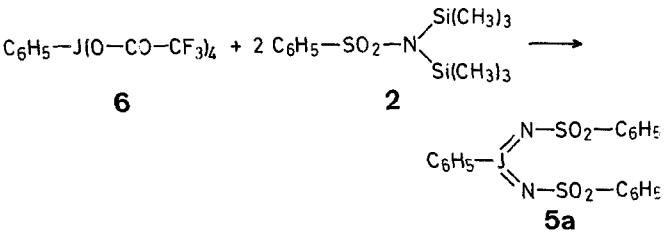
We also investigated the reaction of tetrafluoroiodoarenes **4a–c**[7,8] with **2** and found that they react with two equivalents of **2** to form the bis[phenylsulphonylimino]iodoarenes **5** (Table).



4a-c **2** **5a-c**

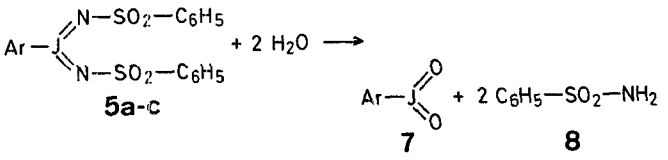
4,5	a	b	c
Ar			

In place of **4** for synthesis of **5**, it is possible to use tetrakis[trifluoroacetoxy]iodobenzene **6**[9] which reacts with **2** under the same conditions.



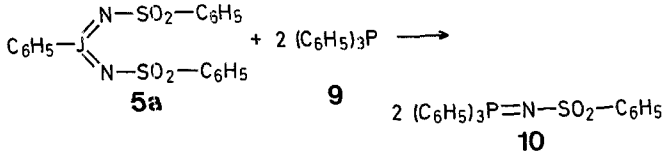
6 **2** **5a**

Compounds **5a–c** are colourless or slightly yellowish crystalline substances which are slightly soluble in ordinary organic solvents. They are hydrolysed by atmospheric moisture and are unstable during storage especially in the light. When boiled with water, they are transformed quantitatively into the corresponding iodylarene (**7**) and benzenesulphonamide (**8**).



5a-c **7** **8**

Compounds **5a–c**, similar to the *p*-tosyliminoiodoarenes[4], may be used in reylidation reactions. For instance, from the reaction of **5a** and triphenylphosphine (**9**), *N*-phenylsulphonyl-triphenylphosphinimine (**10**) is isolated in high yield.



5a **9** **10**

In the I.R. spectra of compounds **3a–d** and **5a–c** the bands for the SO_2-group stretching vibrations are within the frequency range of 1240–1280 cm^{-1} and 1130–1140 cm^{-1}. In both types of compounds, as compared to benzenesulphonamide [I.R. (Nujol): ν_{SO_2}-asym. = 1340, ν_{SO_2}-sym = 1160 cm^{-1}], there is a shift of these characteristic frequencies to the lower wavenumber region.

Table. Compounds **3a–d** and **5a–c** prepared

Product	Yield [%] by Method A	Method B	m.p. (dec) [°C]	Molecular formula[a]	
3a	87	76	119–120°	$C_{12}H_{10}JNO_2S$	(359.2)
3b	90	81	115–116°	$C_{13}H_{12}JNO_2S$	(373.2)
3c	81	78	113–114°	$C_{12}H_9FJNO_2S$	(377.2)
3d	96	—	134–135°	$C_{12}H_5F_5JNO_2S$	(449.1)
5a	63	69	121–122°	$C_{18}H_{15}JN_2O_4S_2$	(514.4)
5b	71	—	106–107°	$C_{19}H_{17}JN_2O_4S_2$	(528.4)
5c	78	—	115–116°	$C_{18}H_{14}FJN_2O_4S_2$	(532.3)

[a] Satisfactory microanalyses obtained: C ±0.23, H ±0.13, N ±0.07, J ±0.30.

All melting points were measured in closed capillary tubes and are uncorrected. The I.R. spectra were obtained with a UR-20 spectrometer.

Phenylsulphonyliminoiodoarenes (3a–d); General Procedure:

Method A from difluoroiodoarenes **1** and *N,N*-bis[trimethylsilyl]benzenesulphonamide (**2**): To a solution of difluoroiodoarene **1a–d** (5 mmol) in anhydrous dichloromethane (30 ml) at 20 °C, a solution of *N,N*-bis[trimethylsilyl]benzenesulphonamide (**2**; 1.51 g, 5 mmol) in anhydrous ether (30 ml) is added. The colourless product precipitates.

The reaction mixture is maintained at 20 °C for 0.5 h and then evaporated in vacuo to dryness. The precipitate is washed by decantation with anhydrous ether (3 × 50 ml) and then dried in vacuo.

Method B from diacetoxyiodoarenes and benzenesulphonamide by a modification of the procedure of Ref.[4]: To a stirred mixture of benzenesulphonamide (0.79 g, 5 mmol), potassium hydroxide (0.70 g, 12.5 mmol), and methanol (25 ml) at −30 °C, the diacetoxyiodoarene (5 mmol) is added. The resulting solution is stirred at 20 °C for 3 h. The reaction mixture is poured into water (70 ml) to precipitate a colourless or slightly yellowish solid on standing overnight at 0 °C. The dry solid is recrystallised from methanol. Mixture m.p. with the corresponding sample prepared by Method A is not depressed.

Bis[phenylsulphonylimino]iodoarenes (5a–c); General Procedure:

Method A: Tetrafluoroiodoarene **4a–c** (5 mmol) is dissolved in anhydrous ether (40 ml) and filtered in a dry chamber via an anhydrous KF-filled filter. To the filtrate at 20 °C, a solution of *N,N*-bis[trimethylsilyl]benzenesulphonamide (**2**; 3.01 g, 10 mmol) in anhydrous ether (40 ml) is added. The mixture is maintained for 0.5 h at 20 °C and then evaporated in vacuo to dryness. The residue is washed by decantation with anhydrous ether (3 × 70 ml) and dried in vacuo.

Method B: To a solution of tetrakis[trifluoroacetoxy]iodobenzene (**6**; 1.32 g, 2 mmol) in anhydrous ether (30 ml) at 20 °C, a solution of *N,N*-bis[trimethylsilyl]benzenesulphonamide (**2**; 0.60 g, 2 mmol) in anhydrous ether (15 ml) is added. The reaction mixture is treated in the same way as described in Method A to give **5a**; yield: 0.71 g (69%); m.p. 119 °C (dec); mixture m.p. with sample prepared by Method A is not depressed.

$C_{18}H_{15}JN_2O_4S_2$	calc.	C 42.03	H 2.94	N 5.45	J 24.67
(514.4)	found	41.70	3.12	5.37	24.75

Hydrolysis of Bis[phenylsulphonylimino]iodobenzene (5a):

To bis[phenylsulphonylimino]iodobenzene (**5a**; 1.03 g, 2 mmol) water (50 ml) is added, the mixture is brought to boiling, and then filtered. The filtrate is evaporated to dryness in vacuo. The residue is washed with ether, filtered, and dried to leave *iodylbenzene* **(7a)**; yield: 0.47 g (~100%); m.p. 230 °C (explosive decomposition).

The ether extract is evaporated to give *benzenesulphonamide* **(8)**; yield: 0.63 g (~100%); m.p. 153 °C; mixture m.p. with authentic sample is not depressed.

Compounds **5b** and **5c** are hydrolysed analogously.

Reaction of Bis[phenylsulphonylimino]iodobenzene (5a) with Triphenylphosphine (9):

To a suspension of bis[phenylsulphonylimino]iodobenzene (**5a**; 1.03 g, 2 mmol) in anhydrous dichloromethane (20 ml) at 20 °C a solution of triphenylphosphine (**9**; 1.05 g, 4 mmol) in anhydrous dichloromethane (20 ml) is added. The reaction mixture is allowed to warm slightly and becomes brown, and the precipitate dissolves. The mixture is maintained at 20 °C for 1 h, then is evaporated to dryness, and the residue is crystallised from benzene to give N-*phenylsulphonyltriphenylphosphinimine* **(10)**; yield: 1.27 g (76%); m.p. 158–159 °C (Ref.[10], m.p. 157–158 °C).

$C_{24}H_{20}NO_2SP$	calc.	P 7.42
(417.4)	found	7.30

Received: August 31, 1982
(Revised form: January 4, 1983)

[1] E. Gudriniece, O. Y. Neiland, G. Vanag, *Zh. Obshch. Khim.* **27**, 2737 (1957); *C. A.* **52**, 7177 (1958).
[2] O. Y. Neiland, *Thesis*, Riga, 1970.
[3] G. A. Olah, *Halonium Ions*, John Wiley & Sons, New York, London, Sydney, Toronto, 1975, Chap. 6.
[4] Y. Yamada, T. Yamamoto, M. Okawara, *Chem. Lett.* **1975**, 361.
[5] B. Ya. Adamsone, D. E. Prikule, O. Ya. Neiland, *Zh. Org. Khim.* **14**, 2625 (1978); *C. A.* **90**, 137416 (1979).
[6] N. Ya. Derkach, N. P. Smetankina, *Zh. Obshch. Khim.* **34**, 3613 (1965); *C. A.* **62**, 9164 (1965).
[7] L. M. Yagupolskii, V. V. Lyalin, V. V. Orda, L. A. Alekseeva, *Zh. Obshch. Khim.* **38**, 2813 (1968); *C. A.* **70**, 77464 (1969).
[8] V. V. Lyalin, G. P. Syrova, V. V. Orda, L. A. Alekseeva, L. M. Yagupolskii, *Zh. Org. Khim.* **6**, 1420 (1970); *C. A.* **73**, 87298 (1970).
[9] L. M. Yagupolskii, I. I. Maletina, N. V. Kondratenko, V. V. Orda, *Synthesis* **1977**, 574.
[10] A. V. Kirsanov, Z. D. Nekrasova, *Zh. Obshch. Khim.* **26**, 903 (1956); *C. A.* **51**, 3486 (1957).