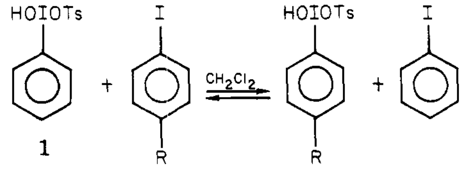
[Hydroxy(tosyloxy)iodo]benzene, a Versatile Reagent for the Mild Oxidation of Aryl Iodides at the Iodine Atom by Ligand Transfer

Summary: Treatment of a variety of aryl iodides with [hydroxy(tosyloxy)iodo]benzene (1) under mild conditions resulted in ligand transfer, and new [hydroxy(tosyloxy)iodo]arenes were obtained. However, with some substrates containing proximate functional groups cyclic iodonium salts and iodinanes resulted. The reaction between 1 and 2-iodothiophene took a distinctly different course.

Sir: [Hydroxy(tosyloxy)iodo]benzene (**1**) undergoes ligand-transfer reactions with a variety of aryl iodides, some eventuating in new [hydroxy(tosyloxy)iodo]arenes and some in iodine heterocycles. Whereas the iodoylarenes (ArIO), the (dichloroiodo)arenes ($ArICl_2$), and the (diacetoxyiodo)arenes ($ArI(OAc)_2$) have been known for nearly a century,[1] **1** is a relative newcomer to the iodoso family, having been first reported in 1970.[2] The benzenesulfonate, *p*-chlorobenzenesulfonate, and *p*-nitrobenzenesulfonate analogues of **1** have also been reported,[3] but no derivatives of **1** with substituents on the phenyl moiety have, to our knowledge, yet appeared in the chemical literature.

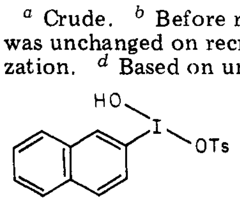
When a solution of *p*-chloroiodobenzene (0.61 g) in dichloromethane (10 mL) was mixed with **1** (1.00 g) and allowed to stand at room temperature (3 days), the hydroxy tosylate **2a** was obtained (90% crude yield). *p*-Bromo-, *p*-iodo-, *p*-methyl-, *p*-nitro-, and *p*-phenyliodobenzenes and *β*-iodonaphthalene were oxidized by **1** under similar conditions to give [hydroxy(tosyloxy)iodo]arenes **2b-f** and **3** (eq 1).



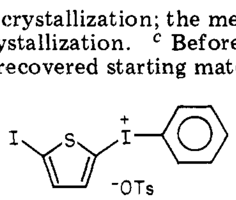
1 2 (1)

compd	R	% yield
2a	Cl	90[a]
2b	Br	85[b]
2c	I	62
2d	CH_3	~85[c]
2e	NO_2	26[d]
2f	Ph	71[d]
3		74[b]

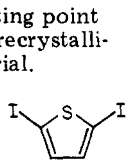
[a] Crude. [b] Before recrystallization; the melting point was unchanged on recrystallization. [c] Before recrystallization. [d] Based on unrecovered starting material.



3



4



5

The [hydroxy(tosyloxy)iodo]arenes are only slightly soluble in CH_2Cl_2. For example, **1** and **2a** are soluble to the extent of about 5.3 and 2.5 mg/mL at room temperature (~22 °C). Thus, the aryl iodide oxidations could be monitored by the gradual visible replacement of solid PhI(OH)OTs with solid ArI(OH)OTs, a change in physical appearance and/or crystal density being noted. Products "contaminated" with unreacted **1** were purified by recrystallization either from CH_3CN or CH_3CN/CH_3OH and characterized by elemental (C, H, I)[4] and NMR analysis. Product **2d** was contaminated with **1** even after recrystallization and was unequivocally identified by NMR comparison with authentic **2d** prepared from *p*-methyl(diacetoxyiodo)benzene (p-$CH_3C_6H_4I(OAc)_2$) and toluenesulfonic acid.

The reaction between **1** and 2-iodothiophene took a markedly different course, and the thienyliodonium tosylate **4** was obtained in 80% yield. The structure of **4** was deduced from its elemental composition (C, H, I), by NMR analysis, and by its metathesis (99%) to the iodonium iodide and pyrolysis of the iodide in the solid state to 2,5-diiodothiophene (**5**) [90% yield before recrystallization, mp 39.5-40.5 °C (lit.[5] mp 40 °C)].

The oxidations of aryl iodides with proximate functional groups were sometimes accompanied by cyclization reactions. For example, 2-iodobiphenyl reacted with **1** in acetonitrile to give dibenziodolium tosylate (**6**) directly in 55% yield. It seems likely that 2-[hydroxy(tosyloxy)iodo]biphenyl (**7**) is an intermediate in this reaction, but it was not isolated, and an attempt to synthesize it by treatment of 2-(diacetoxyiodo)biphenyl (**8**) with toluenesulfonic acid also yielded **6** (60%). While the above reaction (CH_3CN, room temperature) was complete within 4 days, the cyclization of (2-iodophenyl)phenylmethane occurred much more slowly. Thus, treatment of (2-iodophenyl)phenylmethane (3.0 g) in CH_2Cl_2 (25 mL) with **1** (4 g) (coupled with a very patient investigator) gave, after 3 months at room temperature, 1.63 g of dibenziodinium tosylate (**9**) (87% yield based on 1.81 g of recovered iodide). [2-[Hydroxy(tosyloxy)iodo]phenyl]phenylmethane (**10**) was isolated when the corresponding iodo diacetate was treated with toluenesulfonic acid (23% yield). In refluxing acetonitrile, **10** cyclized to **9** (42% yield).

The structures of iodonium tosylates **6** and **9** were confirmed by their metathesis to the known iodide salts [**6**, 95% yield, mp 225-226 °C dec (lit.[6] mp 215 °C); **9**, 96% yield, mp 194-196 °C (lit.[7] mp 184.5-185.5 °C)] and subsequent pyrolysis of the iodides to 2,2'-diiodobiphenyl (**11**) [79% crude yield, mp 112-114 °C (after recrystallization) (lit.[6] mp 108 °C)] and 2,2'-diiododiphenylmethane (**12**) (85% yield), respectively.

The oxidation of 2-iodobenzoic acid with **1** gave the known 1,3-dihydro-1-hydroxy-3-oxo-1,2-benziodoxole (**13**) [(76%, mp 222 °C dec (lit.[8] mp 223-225 °C)] while treatment of *o*-diiodobenzene with 2 equiv of **1** gave, after 3 weeks at room temperature, a yellow crystalline solid to which we assign structure **14** (42% yield),[9] on the basis of elemental (C, H, I) and NMR analysis. The diacetate analogue of **14** has been reported by Wolf and co-workers.[10]

o-Iodobenzamides are also oxidized smoothly by **1**. Thus 2-iodo-*N*-methylbenzamide reacted with **1** to give a prod-

---

[1] C. Willgerodt, "Die Organischen Verbindungen mit Mehrwertigen Jod", F. Enke, Stuttgart, 1914.

[2] O. Neiland and B. Karele, *J. Org. Chem. USSR* (*Engl. Transl.*), **6**, 889 (1970).

[3] G. F. Koser and R. H. Wettach, *J. Org. Chem.*, **42**, 1476 (1977).

[4] **2a-f**, **3**, **4**, **10**, and **14-16** were sent out for combustion analysis and the percentage composition of C, H, and I was determined. The experimental values were within 0.4% of the calculated values with two exceptions. For **2c**, the C and H analyses were within the 0.4% tolerance, but the I analysis was off by 0.79%; for **2f**, the H and I values were within the 0.4% tolerance, but the C analysis was off by 0.62%. The yields reported herein are rounded off to the nearest percent, and melting points are uncorrected.

[5] *Beilstein IV Aufbage*, Systematic No. 2306.

[6] L. Mascarelli and G. Benati, *Gazz. Chim. Ital.*, **38**, 619-29 (1908).

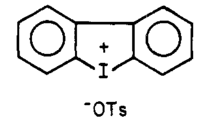
[7] J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Am. Chem. Soc.*, **78**, 3819 (1956).

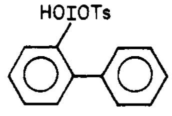
[8] E. Shefter and W. Wolf, *J. Pharm. Sci.*, **54**, 104 (1965).

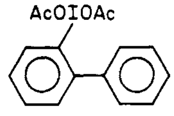
[9] **1** was the limiting reagent here.

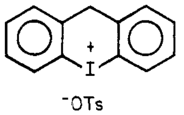
[10] W. Wolf, E. Chalekson, and D. Kobata, *J. Org. Chem.*, **32**, 3239 (1967).

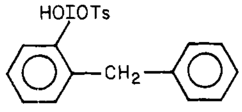
0022-3263/80/1945-1542$01.00/0

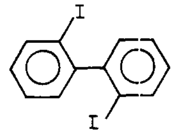

6

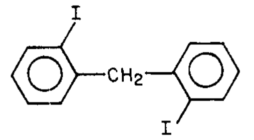

7


8

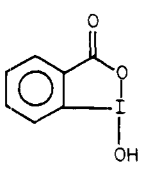

9

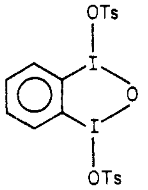

10

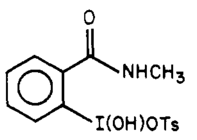

11

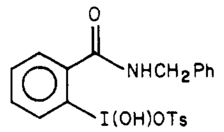

12

uct whose elemental composition (C, H, I, N) and NMR spectrum are consistent with structure **15** (91% before recrystallization). 2-Iodo-*N*-benzylbenzamide was similarly oxidized to a compound whose elemental composition (C, H, I) and NMR spectrum are consistent with structure **16** (64% after recrystallization).


13


14


15


16

[Hydroxy(tosyloxy)iodo]benzene (**1**) is a useful reagent for aryl iodide oxidations for more reasons than its versatility. It is easy to prepare from (diacetoxyiodo)benzene and *p*-toluenesulfonic acid[2,3] and is a relatively stable crystalline solid which may be viewed conveniently as "stabilized" pertoluenesulfonic acid. It also exhibits moderate solubility in water (~1 g/42 mL). To our knowledge, similar metathetical redox reactions between either (diacetoxyiodo)benzene or iodosylbenzene and aryl iodides have not been reported.

Registry No. 1, 27126-76-7; **2a**, 73178-07-1; **2b**, 73178-08-2; **2c**, 73178-09-3; **2d**, 73177-96-5; **2e**, 73178-10-6; **2f**, 73178-11-7; **3**, 73178-12-8; **4**, 73178-14-0; **5**, 625-88-7; **6**, 73178-15-1; **8**, 41018-58-0; **9**, 73178-16-2; **10**, 73178-17-3; **11**, 2236-52-4; **12**, 38059-15-3; **13**, 131-62-4; **14**, 73178-18-4; **15**, 73178-19-5; **16**, 73178-20-8; *p*-chloroiodobenzene, 637-87-6; *p*-bromoiodobenzene, 589-87-7; *p*-diiodobenzene, 624-38-4; *p*-methyliodobenzene, 624-31-7; *p*-nitroiodobenzene, 636-98-6; *p*-phenyliodobenzene, 1591-31-7; *β*-iodonaphthalene, 612-55-5; 2-iodothiophene, 3437-95-4; 5-iodo-2-(phenyliodonium)thiophene iodide, 73178-21-9; 2-iodobiphenyl, 2113-51-1; (2-iodophenyl)phenylmethane, 35444-93-0; [2-(diacetoxyiodo)phenyl]phenylmethane, 73178-22-0; dibenziodolium iodide, 1010-76-0; dibenziodinium iodide, 41634-35-9; 2-iodobenzoic acid, 88-67-5; *o*-diiodobenzene, 615-42-9; 2-iodo-*N*-methylbenzamide, 58084-22-3; 2-iodo-*N*-benzylbenzamide, 73178-23-1.

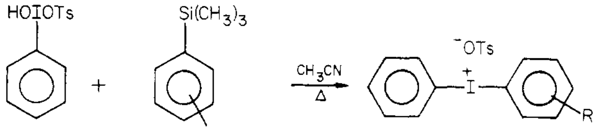
Gerald F. Koser,* Richard H. Wettach
Department of Chemistry
The University of Akron
Akron, Ohio 44325

Received November 1, 1979

New Methodology in Iodonium Salt Synthesis. Reactions of [Hydroxy(tosyloxy)iodo]arenes with Aryltrimethylsilanes

Summary: [Hydroxy(tosyloxy)iodo]arenes react with aryltrimethylsilanes in acetonitrile to give diaryliodonium tosylates. The phenyliodinations proceed with silicon–carbon bond cleavage, thus allowing control of substituent placement in both rings. With bis(trimethylsilyl)arenes, monoiodonium salts were obtained.

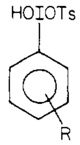
Sir: We report that the action of [hydroxy(tosyloxy)iodo]arenes (ArI(OH)OTs) on aryltrimethylsilanes (ArSiMe$_3$) allows the directed synthesis of diaryliodonium tosylates ($Ar_2I^{+-}OTs$) in *neutral, nonhydroxylic solvents.* To our knowledge, aryltrimethylsilanes have not previously been employed in iodonium salt synthesis. The [hydroxy(tosyloxy)iodo]arenes are moderately stable crystalline solids which can be stored and used when needed. The parent compound **1** (Ar = Ph), first reported in 1970 by Neiland and Karele,[1] may be viewed conveniently as the tosylate salt of the phenylhydroxyiodonium ion (PhI$^+$OH), a conclusion supported by X-ray analysis of a single crystal.[2] Although **1** reacts directly with anisole to give phenyl(*p*-methoxyphenyl)iodonium tosylate,[1] it does not react similarly with nonactivated arenes (i.e., PhH, PhCH$_3$, and PhBr)[3] in CH$_3$CN. However, when **1** was heated with (trimethylsilyl)benzene (**2a**) in acetonitrile (near reflux, 4 h), diphenyliodonium tosylate (**3a**) was obtained in 46% yield after workup. Similar treatment of *o*-, *m*-, and *p*-methyl(trimethylsilyl)benzenes **2b–d** with **1** in acetonitrile afforded phenyl-*o*-tolyliodonium tosylate (**3b**) (42% yield), phenyl-*m*-tolyliodonium tosylate (**3c**) (63% yield), and phenyl-*p*-tolyliodonium tosylate (**3d**) (29% yield).

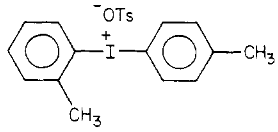


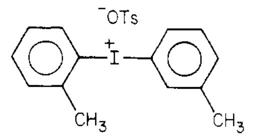
1

2a, R = H
b, R = *o*-CH$_3$
c, R = *m*-CH$_3$
d, R = *p*-CH$_3$

3a, R = H
b, R = *o*-CH$_3$
c, R = *m*-CH$_3$
d, R = *p*-CH$_3$


4a, R = *p*-CH$_3$
b, R = *o*-CH$_3$


5


6

The iodonium salts were readily characterized by elemental[4] (C, H, I) and NMR analysis. For example, the ^{1}H

---

(1) O. Neiland and B. Karele, *J. Org. Chem. USSR (Engl. Transl.)*, 6, 889 (1970).

(2) G. F. Koser, R. H. Wettach, J. M. Troup, and B. A. Frenze, *J. Org. Chem.*, 41, 3609 (1976).

(3) Neiland and Karele obtained phenyl(*p*-methoxyphenyl)iodonium tosylate from 1 and anisole in acetic acid.[1] We found that the same reaction occurred in acetonitrile, but we did not obtain iodonium salts from 1 and either PhH, PhCH$_3$, or PhBr in acetonitrile. We have not investigated the reaction of 1 with those substrates in acetic acid.

0022-3263/80/1945-1543$01.00/0