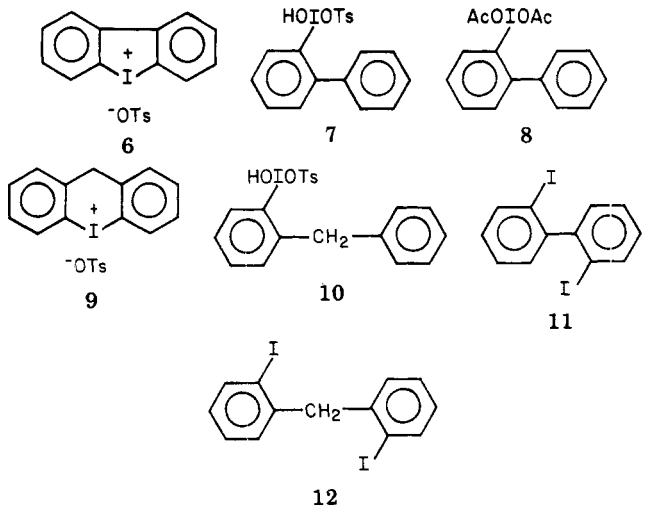
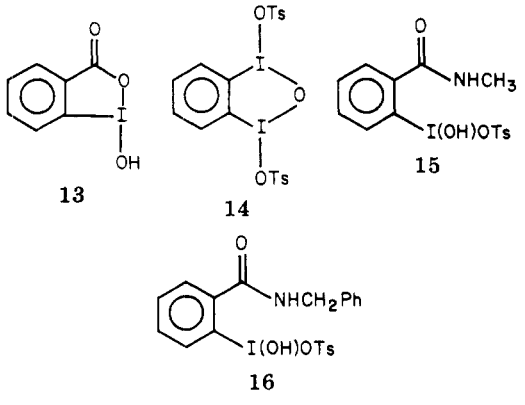


uct whose elemental composition (C, H, I, N) and NMR spectrum are consistent with structure **15** (91% before recrystallization). 2-Iodo-*N*-benzylbenzamide was similarly oxidized to a compound whose elemental composition (C, H, I) and NMR spectrum are consistent with structure **16** (64% after recrystallization).



[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.

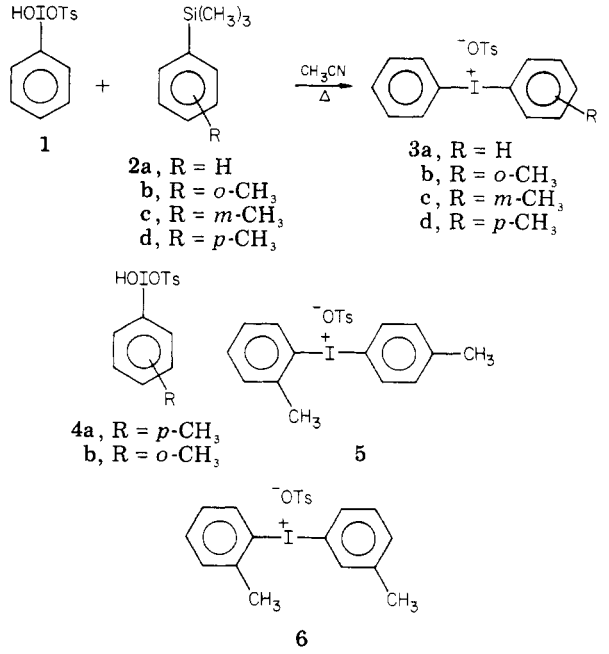
Registry No. **1**, 27126-76-7; **2a**, 73178-07-1; **2b**, 73178-08-2; **2c**, 73178-09-3; **2d**, 73177-96-5; **2e**, 73178-10-6; **2f**, 73178-11-7; **3**, 73178-12-8; **4**, 73178-14-0; **5**, 625-88-7; **6**, 73178-15-1; **8**, 41018-58-0; **9**, 73178-16-2; **10**, 73178-17-3; **11**, 2236-52-4; **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 (Ar-$SiMe_3$) 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_3CN. 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).



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

(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.

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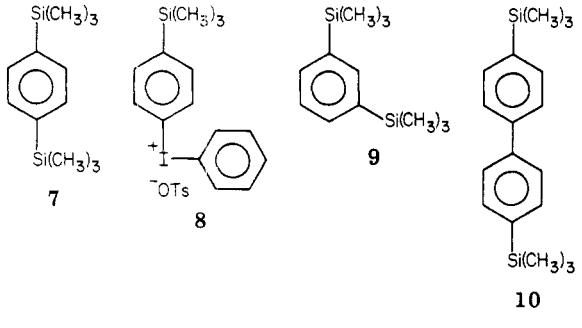
NMR spectrum of **3b** exhibits methyl singlets at δ 2.28 (OTs) and 2.57 (*o*-tolyl) and a complex, two-part aromatic pattern, the hydrogens ortho to positive iodine being sufficiently deshielded to generate a multiplet downfield from the remaining aromatic resonances. In the ^1H NMR spectrum of **3c**, the tolyl and tosylate methyl singlets exhibit the same chemical shift; a similar situation exists in the spectrum of **3d**.

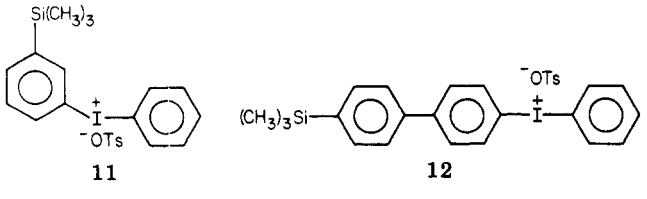
Other [hydroxy(tosyloxy)iodo]arenes behave similarly. Thus, the reaction of [hydroxy(tosyloxy)iodo]-*p*-toluene (**4a**) with (trimethylsilyl)benzene (**2a**) (CH_3CN, Δ) gave **3d** (30%) and with *o*-methyl(trimethylsilyl)benzene (**2b**) (CH_3CN, Δ) gave 2,4′-dimethyldiphenyliodonium tosylate (**5**) in 59% yield. When [hydroxy(tosyloxy)iodo]-*o*-toluene (**4b**) was allowed to react with *m*-methyl(trimethylsilyl)-benzene (**2c**), 2,3′-dimethyldiphenyliodonium tosylate (**6**) was obtained (58% yield).

Dichloromethane has also been employed successfully as a solvent in the preparation of **3d** (17%) from **4a** and **2a**, of **3c** (63%) from **1** and **2c**, and of **3a** (48%) from **1** and **2a**, although longer reaction times are required.

When *p*-bis(trimethylsilyl)benzene (**7**) was allowed to react with **1** in acetonitrile, phenyl[*p*-(trimethylsilyl)-phenyl]iodonium tosylate (**8**) was obtained in 49% yield (after recrystallization). Thus far, we have been unsuccessful in attempts to obtain a bis(iodonium) salt by replacement of the trimethylsilyl group in **8** by the action of **1**. The ^1H NMR spectrum of **8** ($CDCl_3$, Me_4Si) exhibits singlets at δ 0.23 ($SiMe_3$) and δ 2.23 (CH_3 of OTs) and a complex multiplet in the aromatic region. The four hydrogens ortho to positive iodine give rise to a multiplet distinctly downfield from the rest of the aromatic peaks. Iodonium salt **8** also has the expected elemental composition.



Similar results were obtained with *m*-bis(trimethylsilyl)benzene (**9**) and 4,4′-bis(trimethylsilyl)biphenyl (**10**). Thus, reaction of **9** with **1** in acetonitrile gave the monoiodonium tosylate **11** (24%, after recrystallization), and reaction of **10** with **1** gave the monoiodonium tosylate **12** (27%).



One of the more common methods of iodonium salt synthesis employed today involves the condensation of ArIO or $ArI(OAc)_2$ with ArH in a strong acid (H_2SO_4) medium and is therefore limited to acid-insensitive functional groups. Furthermore, there is limited control on substituent placement in the iodonium salt. For example, if the 2,3′-dimethyldiphenyliodonium ion is the synthetic target, the condensation of *o*-methyl(diacetoxyiodo)-benzene with toluene in sulfuric acid would not be of much utility. However, that cation has been specifically prepared with moderate facility via the $ArSi(CH_3)_3$ route under mild conditions. This method supplements that developed by Beringer and his co-workers in which iodonium salts were synthesized from aryllithium reagents and dichloroiodoarenes ($ArICl_2$) in ether or THF at low temperatures.[5]

We shall extend these studies to a variety trimethylsilylarenes and hydroxy tosylates with the added hope of improving yields.[6] A large number of [hydroxy(tosyloxy)iodo]arenes are available from the reactions of the corresponding iodosylarenes (ArIO) or (diacetoxyiodo)-benzenes ($PhI(OAc)_2$) with toluenesulfonic acid or by direct ligand exchange of **1** with a variety of iodoarenes (see the adjoining communication). These reactions contribute something new to the elegant methodology developed by the groups of Beringer, Willgerodt,[7] and others.

(4) Iodonium tosylates **3b–d**, **5**, **6**, **8**, **11**, and **12** were all sent out for combustion analysis and the percentages of carbon, hydrogen, and iodine determined. The experimental values (24 in all) were within 0.4% of the calculated values with two exceptions. For salts **3d** and **5**, the H and I analyses were within the 0.4% tolerance, but the best carbon analyses to date were 0.58% (**3d**) and 0.60% (**5**) from the calculated values. Repeated analyses were sometimes necessary. Melting points are uncorrected.

(5) F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Am. Chem. Soc.*, **82**, 2948 (1960).

(6) Yields reported herein are rounded off to the nearest percentage point.

(7) C. Willgerodt, "Die Organischen Verbindungen mit Mehrwertigen Jod", F. Enke, Stuttgart, 1914, pp 195, 197, 198.

Gerald F. Koser,* Richard H. Wettach
Carol S. Smith
Department of Chemistry
The University of Akron
Akron, Ohio 44325
Received November 1, 1979

Total Synthesis of Erythromycins. 6. Facile Transformation of Erythronolide A into a Tricyclic Internal Ketal

Summary: Erythronolide A (**1a**), the aglycone of erythromycin A, is unusually sensitive to acid in comparison with erythronolide B (**1b**) or the erythromycins. Upon treatment with 0.02 N perchloric acid at 23 °C it is rapidly transformed into an anhydro derivative which has been shown to possess structure **2** by single-crystal X-ray diffraction analysis.

Sir: The first total synthesis of erythronolide A (**1a**), the aglycone of the medically important antibiotic erythromycin A, was recently reported from these laboratories.[1] In the course of this work, it was discovered that the acid-catalyzed hydrolysis of the 3,5-acetonide of **1a** under conditions which effected the hydrolysis of the 3,5-acetonide of erythronolide B to erythronolide B (**1b**)[2,3] did not afford erythronolide A but instead a new compound which in contrast to **1a** is very stable to acid. Erythronolide A itself (**1a**) is transformed into the same substance

(1) Corey, E. J.; Hopkins, P. B.; Kim, S.; Yoo, S.; Nambiar, K. P.; Falck, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 7131.

(2) Corey, E. J.; Nicolaou, K. C.; Melvin, L. S., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 654.

(3) Corey, E. J.; Kim, S.; Yoo, S.; Nicolaou, K. C.; Melvin, L. S., Jr.; Brunelle, D. J.; Falck, J. R.; Trybulski, E. J.; Lett, R.; Sheldrake, P. W. *J. Am. Chem. Soc.* **1978**, *100*, 4620.

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