a chemical shift difference of the diastereotopic protons.

Reactions of Dimethyl Sulfite with Methyl Triflate. These reactions were mostly done in NMR tubes, and the products were identified by proton chemical shifts and volatile products by GC/MS. In addition to dimethyl sulfite, methyl triflate, and dimethyl ether, a small peak identified as the trimethyloxonium ion, expected from dimethyl ether and methyl triflate, was also sometimes observed. The peaks for methyl methanesulfonate, especially those of the sulfur bound methyl, are well-resolved from any others and were not detectable in this system.

Reaction of Dimethyl Sulfite and Methyl 2,4,6-Trinitrobenzenesulfonate. With excess dimethyl sulfite, dimethyl ether and sulfur dioxide were detected by GC/MS, the peaks of the

methylating agent disappeared, and a solid was formed, identified by its melting point as trimethyloxonium 2,4,6-trinitrobenzenesulfonate, mp 181 °C.

Regiospecific Synthesis of Aryl(2-furyl)iodonium Tosylates, a New Class of Iodonium Salts, from [Hydroxy(tosyloxy)iodo]arenes and 2-(Trimethylsilyl)furans in Organic Solvents

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The treatment of 2,5-bis(trimethylsilyl)furan with various [hydroxy(tosyloxy)iodo]arenes (ArI(OH)OTs) in acetonitrile/methanol has been found to give aryl[5-(trimethylsilyl)-2-furyl]iodonium tosylates in yields ranging from 62% to 80%. With 2-methyl-5-(trimethylsilyl)furan as the substrate, aryl(5-methyl-2-furyl)iodonium tosylates are likewise obtained in yields ranging from 61% to 74%. The reactions of [hydroxy(tosyloxy)iodo]arenes with 2-(trimethylsilyl)furan in methanol give aryl(2-furyl)iodonium tosylates in much lower yield (9–23%) and are accompanied by the reductive decomposition of the hypervalent organoiodine component. To our knowledge, these are the first reported examples of aryl(furyl)iodonium salts.

Aryl(thienyl)iodonium salts of general structure 1 are
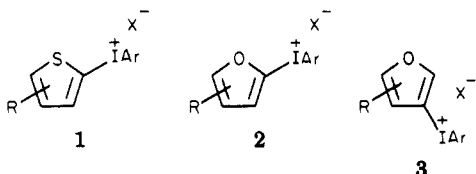
moderately well-known[1,2] and are active microbicides.[3] On the other hand, both the aryl(2-furyl)iodonium salts (2) and aryl(3-furyl)iodonium salts (3) are unknown. This is not a surprising fact in the context of classical methodology for iodonium salt synthesis. For example, one general approach to diaryliodonium salts involves the condensation of an iodosoarene with an iodoxyarene in the presence of base (eq 1).[4,5] This procedure is not amenable to the

$$ArIO + Ar'IO_2 \xrightarrow[\text{H}_2\text{O}]{\text{OH}^- \text{ or Ag}_2\text{O}} (ArI^+Ar')X^- \qquad (1)$$
$$X^- = HO^-, IO_3^-$$
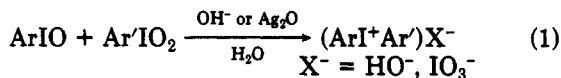
preparation of aryl(furyl)iodonium analogues since iodosofurans and iodoxy furans have not, to our knowledge, been synthesized. Another general approach to diaryliodonium salts entails the condensation of either an iodosoarene or a (diacyloxyiodo)arene with an aromatic substrate in the presence of a strong acid, typically sulfuric

acid (eq 2).[6] This method and those related to it such as

$$ArIO \text{ or } ArI(OOCR)_2 + Ar'H \xrightarrow{\text{H}_2\text{SO}_4} (ArI^+Ar')HSO_4^- \qquad (2)$$
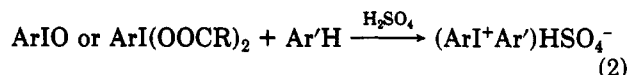
the condensation of $(IO)_2SO_4$ with arenes in the presence of sulfuric acid[6] may likewise preclude the synthesis of aryl(furyl)iodonium salts owing to the sensitivity of the furan nucleus to acid-induced decomposition reactions.

The di-2-furyl- and di-3-furyliodonium ions 4 and 5 have
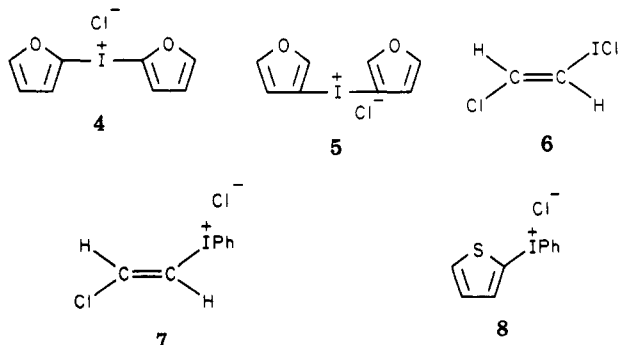
been prepared as their chloride salts by the condensations of 2-furyllithium and 3-furyllithium with (E)-1-(dichloroiodo)-2-chloroethene (6).[7,8] However, while a similar reaction of (*trans-β*-chlorovinyl)phenyliodonium chloride (7) with 2-thienyllithium has been reported to give phenyl(2-thienyl)iodonium chloride (8), the analogous treatment

(1) Beringer, F. M.; Bachofner, H. E.; Falk, R. A.; Leff, M. *J. Am. Chem. Soc.* 1958, *80*, 4279.
(2) Yamada, Y.; Okawara, M. *Bull. Chem. Soc. Jpn.* 1972, *45*, 2515.
(3) For example, see: Moyle, C. L. U.S. Patent 3 994 498, Mar 16, 1976; *Chem. Abstr.* 1976, *84*, P189912b.
(4) Willgerodt, C. "Die Organischen Verbindungen mit Mehrwertigem Jod"; Enke: Stuttgart, West Germany, 1914.
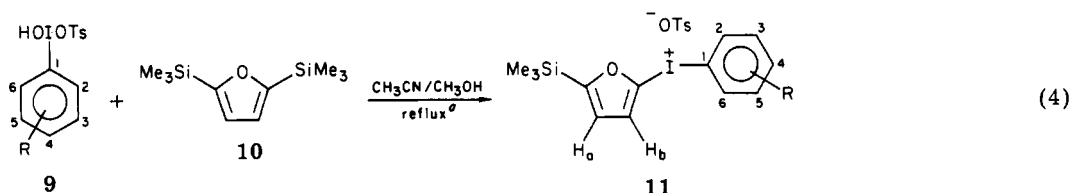(5) Lucas, H. J.; Kennedy, E. R. "Organic syntheses"; Wiley; New York, 1955; Collect. Vol. III, p 355.

(6) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Masullo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* 1959, *81*, 342.
(7) Beringer, F. M.; Nathan, R. A. *J. Org. Chem.* 1970, *35*, 2095.
(8) Gronowitz, S.; Holm, B. *J. Heterocycl. Chem.* 1977, *14*, 281.

Chart I

(4)

R	g (mmol)		vol, mL		yield of 11,
	9	10	CH₃CN	CH₃OH	g (%)
H	7.85 (20)	4.25 (20)	25	25	8.17 (79)
2-Me	8.12 (20)	4.25 (20)	25	25	8.23 (78)
3-Me	8.13 (20)	4.46 (21)	25	25	8.10 (77)
4-Me	8.12 (20)	4.25 (20)	25	25	8.21 (78)
4-F	6.16 (15)	3.19 (15)	25	6	5.58 (70)
4-Cl	8.53 (20)	4.27 (20.1)	25	25	6.79 (62)
4-Br	6.80 (14.4)	3.02 (14.2)	25	25	6.78 (80)
4pI	8.65 (16.7)	3.55 (16.7)	30	27	7.45 (70)
4-Ph	3.31 (7.07)	1.50 (7.06)	25	10	2.67 (64)

a Solutions were brought to reflux and maintained at reflux for 2 h (2.2 h for R = 4-CH₃).

of 7 with 2-furyllithium did not yield the corresponding furyl salt.[7]

We have recently described a regiospecific synthesis of diaryliodonium tosylates from [hydroxy(tosyloxy)iodo]-arenes (9)[9] and (trimethylsilyl)arenes in organic solvents under mild conditions (eq 3).[10] The most notable features

(3)
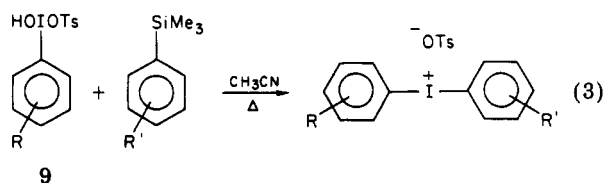
of this reaction are that (1) aryliodination occurs at the site of attachment of the silicon atom in the arylsilane and (2) no added acids are required to promote condensation.

We now report the application of this method to the synthesis of aryl(2-furyl)iodonium salts (2) wherein X⁻ = OTs⁻ and R = 5-SiMe₃, 5-Me, and 5-H.

Results and Discussion

When [hydroxy(tosyloxy)iodo]-*o*-toluene (9, R = 2-Me) was allowed to react with 2,5-bis(trimethylsilyl)furan (10) in 1:1 (v/v) acetonitrile–methanol (2 h at reflux), (*o*-tolyl)[5-(trimethylsilyl-2-furyl]iodonium tosylate (11, R = 2-Me) was obtained in 78% yield (eq 4, Chart I). The workup consisted simply of concentrating the reaction mixture to ca. one-half volume and pouring it into ether whereupon the product precipitated from solution. The ¹H NMR spectrum of 11 (R = 2-Me) in CDCl₃ exhibits a 9 H singlet at δ 0.19 (-SiMe₃), a 3 H singlet at δ 2.28 (Me of OTs group), a 3 H singlet at δ 2.63 (Me of *o*-tolyl group), a 1 H doublet at δ 6.47 (Hₐ), an *apparent* 1 H doublet at δ 8.05 (H₆), and a complex 8 H pattern between δ 6.8 and 7.5 (aromatic hydrogens and H_b). The elemental composition (C, H, I) of 11 (R = 2-Me) is also consistent with the assigned structure.

The reactions of 10 with other [hydroxy(tosyloxy)-iodo]arenes (9) proceeded similarly to give the corresponding aryl [5-(trimethylsilyl)-2-furyl]iodonium tosylates (11) in good yield; the results are summarized in Chart I. A characteristic feature of the ¹H NMR spectra of all of these iodonium salts (in CDCl₃ or CDCl₃/CD₃OD) is the

Chart II

(5)
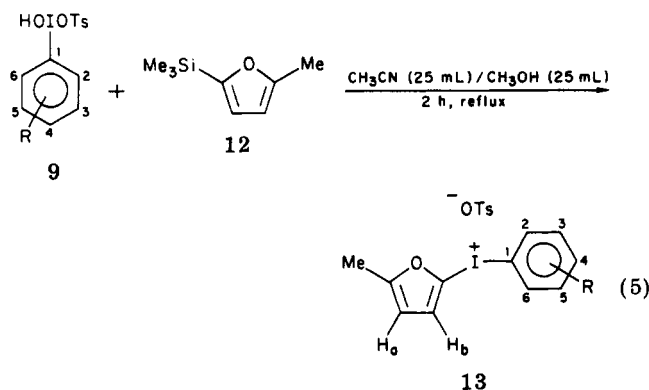
R	g (mmol)		yield of 13,
	9	10	g (%)
2-Me	6.09 (15)	2.31 (15)	4.98 (71)
3-Me	6.09 (15)	1.82 (11.8)	3.41 (61)
4-Me	6.15 (15)	2.31 (15)	4.85 (69)
4-F	6.15 (15)	2.31 (15)	4.90 (69)
4-Cl	6.40 (15)	2.34 (15.2)	4.95 (67)
4-Br	7.08 (15)	2.31 (15)	5.91 (74)
4-I	7.77 (15)	2.31 (15)	5.43 (62)

appearance of the Hₐ doublet upfield from the aromatic region (i.e., δ 6.46–6.76 ppm). The H_b resonance, on the other hand, is located in the aromatic region and, in a few cases, can be distinguished (as a doublet) from the surrounding multiplets; see Table I. The shielding of Hₐ relative to H_b is consistent with the NMR behavior of other furans bearing electron-withdrawing substituents (e.g., CN, CHO, COMe, COOMe) at one of the α-positions.[11]

The aryliodination reaction extends nicely to 2-methyl-5-(trimethylsilyl)furan (12) as the substrate. For example, when 12 was allowed to react with 9 (R = 2-Me) in 1:1 (v/v) acetonitrile–methanol (2 h at reflux), (5-methyl-2-furyl)(*o*-tolyl)iodonium tosylate (13, R = 2-Me) was obtained in 71% yield (eq 5, Chart II). The workup was straightforward: after most of the reaction solvent had been removed, the residual material was taken up in methanol and poured into ether whereupon 13 separated from solution. The structure of 13 follows from its elemental composition (C, H, I), and its ¹H NMR spectrum

(9) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 1542.

(10) Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, *45*, 1543.

(11) Gronowitz, S.; Sorlin, G.; Gestblom, B.; Hoffman, R. A. *Ark. Kemi.* **1962**, *19*, 483.

Table I. 60-MHz ^{1}H NMR Spectra of Aryl[5-(trimethylsilyl)-2-furyl]iodonium Tosylates (11)

	chemical shift δ (ppm),[a] multiplicity			
R	SiMe$_3$	Me	H$_a$	aromatic,[b] H$_b$ (no. of hydrogens)
H	0.22, s	2.27, s	6.50, d	6.8-7.55 (m, 8 H); 7.92 (m, 2 H)
2-Me	0.19, s	2.28, s	6.47, d	6.8-7.5 (m, 9 H; includes d at 7.09)
		2.63, s		8.05 (apparent br d, 2 H)
3-Me	0.23, s	2.26, s	6.46, d	6.75-7.75 (m, 9 H)
		2.21, s		
4-Me	0.22, s	2.28, s[c]	6.49, d	6.8-7.9 (m, 9 H)
4-F	0.21, s	2.28, s	6.47, d	6.7-7.55 (m, 7 H; includes d at 7.20)
				7.90 (four line m with further splitting, 2 H)
4-Cl	0.22, s	2.30, s	6.52, d	6.8-8.0 (m, 9 H; includes overlapping AA'BB' m and d at 7.24)
4-Br	0.23, s	2.30, s	6.51, d	6.8-7.95 (m, 9 H)
4-I	0.28, s	2.35, s	6.64, d	6.9-7.75 (m, 9 H; includes apparent sharp s at 7.68 and d at 7.25)
4-Ph	0.22, s	2.21, s	6.52, d	6.8-8.2 (m, 14 H, lower half of AA'XX' m apparent)

[a] In CDCl$_3$ relative to Me$_4$Si except for compounds with R = 4-Br and 4-I, which were dissolved in CDCl$_3$/CD$_3$OD. [b] The aromatic hydrogen patterns are complex and are referred to as multiplets; chemical shifts are given as a range that includes all multiplets. [c] The two methyl absorptions are coincident, and the singlet at δ 2.29 integrates for 6 H.

Table II. 60-MHz ^{1}H NMR Spectra of Aryl(5-methyl-2-furyl)iodonium Tosylates (13)

	chemical shift δ (ppm),[a] multiplicity[b]		
R	Me	H$_a$[c]	aromatic hydrogens and H$_b$[d]
2-Me	2.29, s; 2.34, s (overlapping); 2.64, s	6.29 "d"	6.9-7.75 (m, 8 H); 8.35 (apparent d, 1 H)
3-Me	2.29, s; 2.32, s; 2.35, s (all overlapping)	6.30 "d"	6.95-7.7 (m, 7 H); 7.8-8.2 (m, 2 H)
4-Me	2.31 (br resonance with "peaks" at 2.28 and 2.32, 9 H)	6.28 "d"	6.95-7.7 (m, 7 H); 7.96 and 8.10 (low-field peaks of an AA'XX' m, 2 H)
4-F	2.30, s (coincident methyl resonances, 6 H)	6.00 "d"	6.75-7.6 (m, 7 H; H$_b$ d is obvious at 7.20); 7.8-8.2 (four-line m with added splitting, 2 H)
4-Cl	2.31, s (coincident methyl resonances, 6 H)	6.00 "d"	6.85-7.6 (m, 7 H); 7.83 and 7.97 (low-field peaks of an AA'XX' m, 2 H)
4-Br	2.30, s; 2.37, s (overlapping)	6.33 "d"	7.0-7.85 (m, 7 H); 8.06 and 8.21 (low-field peaks of AA'XX' m, 2 H)
4-I	2.30, s; 2.37, s (some overlap)	6.33 "d"	6.95-7.65 (m, 5 H); 7.90 (apparent s, 4 H; p-iodophenyl nucleus)

[a] Relative to internal Me$_4$Si; solvent, Me$_2$SO-d$_6$ (R = 4-Br, 4-I, 2-Me, 3-Me, 4-Me), CDCl$_3$ (R = 4-F, 4-Cl). [b] Singlet = s, doublet = d, multiplet = m. [c] The H$_a$ "doublet" (H$_a$ is coupled with H$_b$) exhibits fine structure or broadening due to long-range coupling with the methyl group on the furan ring. [d] The various overlapping multiplets spread over the indicated range are referred to simply as m; the number of hydrogen atoms is also specified.

(in Me$_2$SO-d$_6$), which exhibits overlapping methyl singlets at δ 2.29 and 2.34 (6 H, Me's of furyl and tosyloxy groups), a 3 H singlet at δ 2.64 (Me of o-tolyl group), a 1 H multiplet at δ 6.29 (H$_a$), an *apparent* 1 H doublet at δ 8.35 (H$_b$), and a complex 8 H pattern between δ 6.95 and 8.33 (aromatic hydrogens and H$_b$). The H$_a$ resonance appears as a doublet ($J_{ab} \sim$ 3-4 Hz) with superimposed fine structure due to long-range coupling of H$_a$ with the methyl substituent on the furan ring. The reactions of 12 with other [hydroxy-(tosyloxy)iodo]arenes (9) proceeded similarly to give the corresponding aryl (5-methyl-2-furyl)iodonium tosylates (13) in yields ranging from 61% to 74%; the results are summarized in Chart II.

As with the silyl series of iodonium salts, the ^{1}H NMR spectra of the 5-methyl-2-furyl analogues characteristically exhibit the H$_a$ multiplet at higher field than the aromatic hydrogen and H$_b$ resonances (see Table II). In the case of 13 (R = 4-F), the H$_b$ doublet can be seen distinctly at δ 7.20. The aromatic region of the *iodide* salt of the (p-chlorophenyl)(5-methyl-2-furyl)iodonium ion (in Me$_2$SO-d$_6$) is unambiguous, and a complete assignment of all resonances can be made; H$_a$ (m, δ 6.29), H$_b$ (d, δ 7.34), Me (s, δ 2.36), aromatic (AA'BB' m, δ 7.86). Several of the salts of this series are rather unstable to decomposition in the solid state at room temperature.

Application of the general methodology to 2-(trimethylsilyl)furan (14) as reactant provides access to aryl(2-furyl)iodonium tosylates (15) although the reactions proceed in much lower yield. For example, the reaction of 14 with 9 (R = 3-Me) in methanol (1 day, room tem-

perature) gave, after workup, a 14% yield of 2-furyl(m-tolyl)iodonium tosylate (15, R = 3-Me); see eq 6, Chart III). The ^{1}H NMR spectrum (CDCl$_3$) of 15 (R = 3-Me) features two overlapping methyl singlets at δ 2.23 and 2.28, a 1 H multiplet consisting of four sharp lines at δ 6.34 (H$_a$), and a complex 10 H pattern between δ 6.90 and 7.75. The reactions of 14 with other [hydroxy(tosyloxy)iodo]arenes proceeded similarly to give aryl(2-furyl)iodonium tosylates (15) in yields ranging from 9% to 23%; the results are summarized in Chart III. The four-line H$_a$ multiplet upfield from the remaining aromatic and furyl hydrogen resonances is a common NMR spectral feature of all compounds of this series; see Table III).

The reason(s) why the yields of iodonium salts derived from 14 are so much lower than the yields of iodonium salts derived from 10 and 12 have not been firmly ascertained. It has been observed, however, that some [hydroxy(to-syloxy)iodo]arenes (9) suffer reductive decomposition when they are mixed with 14 in methanol. For example, p-iodobiphenyl and p-diiodobenzene were isolated in 50% and 73% yields, respectively, from the reactions of 9 (R = p-Ph) and 9 (R = p-I) with 14. In a second study of the reaction of 9 (R = p-I) with 14, the yields of p-diiodo-benzene and 15 (R = 4-I) were determined to be 72% and 15%, and the yield of p-toluenesulfonic acid, based on NaOH titration of the aqueous extract of the crude product mixture, was found to be 76%. It seems likely that some reductive decomposition of all [hydroxy(tosyloxy)iodo]-arenes occurs when they are mixed with 14 in methanol. However, no other measurements of iodoarene yields have

Chart III

(6)
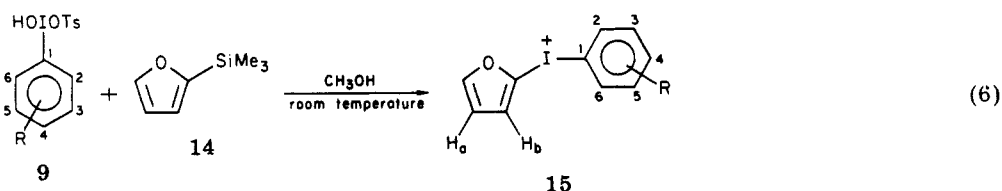
	g (mmol)		vol CH$_3$OH,	time,	yield of 15,
R	9	14	mL	days	g (%)
H	7.84 (20.5)	2.80 (20)	75	2	1.80 (20)
2-Me	8.12 (20)	2.80 (20)	75	4.92	1.81 (20)
3-Me	20.31 (50)	7.36 (52.5)	100	1	3.28 (14)
4-Me	8.24 (20.3)	2.80 (20)	50	1	0.86 (9)
4-F	8.20 (20)	2.95 (21)	100	1.07	2.10 (23)
4-Cl	8.56 (20.1)	3.00 (21.4)	100	1.09	1.72 (18)
4-Br	9.43 (20)	2.80 (20)	120	1	1.39 (13)
4-I	9.10 (17.6)	2.58 (18.4)	100	1	1.83 (18)

Table III. 60-MHz ^{1}H NMR Spectra of Aryl(2-furyl)iodonium Tosylates (15)

		chemical shift δ (ppm),^{a} multiplicity ^{b}	
R	Me	H$_a$^{c}	aromatic hydrogens,^{d} H$_b$ and H$_c$
H	2.31, s	6.47, dd	6.95-7.8 (m, 8 H); 8.00 (m, 2 H; appears almost as a dd)
2-Me	2.24, s; 2.57, s	6.26, dd	6.75-7.45 (m, 8 H); m with lines at 7.80 and 8.04 (1 H, apparent d)
3-Me	2.23, s; 2.28, s (overlapping)	6.34, dd	6.90-7.75 (m, 10 H)
4-Me	2.33, s (coincident methyl singlets)	6.55, dd	7.0-8.1 (m, 10 H; H$_b$ d is obvious at 7.42)
4-F	2.33, s	6.44, dd	6.8-7.7 (m, 8 H; H$_b$ d is obvious at 7.30); 7.8-8.25 (four-line m with added "splitting", 2 H)
4-Cl	2.33, s	6.44, dd	6.8-8.0 (m, 10 H; H$_b$ d is obvious at 7.20 and low-field peaks of an AA'XX' m are obvious at 7.78 and 7.93)
4-Br	2.30, s	6.64, dd	6.95-8.35 (m, 10 H; high-field half of an AA'XX' m is obvious at 7.02 and 7.15)
4-I	2.36, s	6.60, dd	7.0-8.0 (m, 10 H; includes H$_b$ d at 7.48, an AA'XX' m, and an *apparent* s at 7.82)

^{a} Relative to internal Me$_4$Si; solvent CD$_3$OD (R = H, 4-Me, 4-I, 4-Ph), Me$_2$SO-d_6 (R = 3-Me, 4-Br), CDCl$_3$/CD$_3$OD (R = 4-F, 4-Cl, 2-Me). ^{b} s = singlet, dd = doublet of doublets, m = multiplet. ^{c} Four-line m assigned as dd. ^{d} The various overlapping multiplets spread over the indicated range are referred to collectively as m; the number of hydrogens is also specified.

been made nor has the ultimate fate of 14 been determined.

One salt from each series of aryl(furyl)iodonium tosylates reported herein was metathesized to the correponding iodide and heated to decomposition in the solid state; eq 7, Chart IV). In each case, ^{1}H NMR analysis of the crude pyrolysate revealed that a reasonably clean conversion of the iodide salt to an ca. 1:1 mole mixture of the expected iodofuran and iodoarene had occurred. For identification purposes, authentic iodofurans were prepared by the direct iodination of the corresponding lithiofurans, and product ratios were determined by integration of appropriate proton resonances. Although absolute product yields were not determined, the ^{1}H NMR spectra of the crude pyrolysates were nearly identical with those of authentic product mixtures.

Experimental Section

General Methods. The ^{1}H NMR spectra reported herein were recorded on a Varian EM-360 NMR spectrometer. Chemical shifts are given relative to internal tetramethylsilane, and integrations are rounded off to the nearest whole number. Elemental compositions were determined at Galbraith Labs. in Knoxville, TN. All 24 furyl(aryl)iodonium tosylates reported herein are previously unreported compounds and were subjected to carbon, hydrogen, and iodine analysis. The experimental percentage compositions were generally within 0.4% of the calculated values, although this was not necessarily achieved on the first attempt. In the case of 15 (R = 4-F), the Δ%I was 0.41% (see supplementary material). Melting points, decompositions points, and boiling points are uncorrected.

Chart IV

(7)
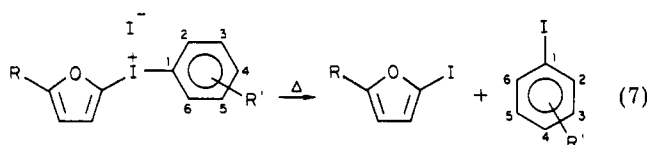
R	R'	mp of iodide, °C	temp, °C	mole ratio (ArI:FurI)
H	3-Me	126-128	130-140	0.99
Me	4-Cl	101.5-103	105	1.04
SiMe$_3$	4-Br	115.5-116	115-124	1.07

Starting Materials. The silylfurans utilized in this study were prepared by procedures similar to those already reported in the literature.[12-14]

2,5-Bis(trimethylsilyl)furan (10). To a solution of furan in ether was added a solution of n-butyllithium (ca. 2 molar equiv) in hexane. The 2,5-dilithiofuran thus produced was treated with trimethylsilyl chloride. After an aqueous workup, crude 10 was isolated and distilled: bp 45-47 °C (~0.6-0.8 mm) [lit.[13] bp 64 °C (7 mm)]; ^{1}H NMR (CDCl$_3$) δ 0.26 (s, 18 H), 6.54 (s, 2 H) [lit.[15] ^{1}H NMR (c-C$_6$H$_{12}$, "infinite" dilution) δ 0.21, 6.51].

2-(Trimethylsilyl)furan (14). To a solution of furan in ether was added a solution of n-butyllithium (ca. 1 molar equiv) in

(12) Benkeser, R. A.; Currie, R. B. *J. Am. Chem. Soc.* **1948**, *70*, 1780.
(13) Lukevits, E. Ya.; Voronkov, M. G. *Khim. Geterotsikl. Soedin.* **1965**, *1*, 19.
(14) Lukevits, E. Ya.; Voronkov, M. G. *Khim. Geterotsikl. Soedin.* **1966**, *2*, 235.
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hexane. The 2-lithiofuran thus produced was treated with trimethylsilyl chloride. After an aqueous workup, crude 14 was isolated and distilled: bp 115–134 °C [lit. bp 125–126 °C (760 mm),[13] 124–125 °C (750 mm)[12]]; ^{1}H NMR (CDCl$_3$) δ 0.27 (s, 9 H), 6.31 (dd, 1H), 6.57 (d, 1 H), 7.59 (d, 1 H) [lit.[15] ^{1}H NMR (c-C$_6$H$_{12}$, "infinite" dilution) δ 0.22, 6.25, 6.58, 7.51].

2-Methyl-5-(trimethylsilyl)furan (12)[14] was prepared in similar fashion and purification by distillation: ^{1}H NMR (CDCl$_3$) δ 0.24 (s, 9 H), 2.30 (s, 3 H), 5.92 (m, 1 H), 6.47 (d, 1 H) [lit.[15] ^{1}H NMR (c-C$_6$H$_{12}$, "infinite" dilution) δ 0.20, 2.24, 5.83, 6.44].

[Hydroxy(tosyloxy)iodo]arenes (9).[9,16-18] The [hydroxy(tosyloxy)iodo]arenes utilized in this study were prepared either by treatment of iodoarenes with [hydroxy(tosyloxy)iodo]-*o*-toluene (9, R = 2-Me) or by the action of *p*-toluenesulfonic acid on the corresponding (diacetoxyiodo)arenes. One example of each method is included herein.

[Hydroxy(tosyloxy)iodo]-*o*-toluene. (Diacetoxyiodo)-*o*-toluene was prepared by the oxidation of *o*-iodotoluene with 40% peracetic acid according to a literature procedure.[19]

To 21.82 g (0.100 mol) of stirred *o*-iodotoluene was added 36.62 g (ca. 31 mL, 0.244 mol) of 40% peracetic acid in dropwise fashion over a period of 1 h and 41 min. Stirring was continued for 23 min more, during which time the product solidified. The reaction mixture was then chilled in an ice bath, and the (diacetoxyiodo)-*o*-toluene was isolated, washed with cold water, and allowed to dry overnight: yield 31.32 g (93%); mp 141.5–143.5 °C [lit.[20] mp 138 °C]; ^{1}H NMR (CDCl$_3$) δ 1.96 (s, 6 H), 2.70 (s, 3 H), 7.04–7.53 (m, 3 H), 8.13 (b d, 1 H).

A hot solution of *p*-TsOH·H$_2$O (15.51 g, 0.082 mol) in CH$_3$CN (50–51 mL) was poured into a hot, light yellow solution of (diacetoxyiodo)-*o*-toluene (24.71 g, 0.074 mol) in CH$_3$CN (ca. 100 mL). The reaction solution, deep yellow in color, was heated briefly, filtered, and cooled at ca. –20 °C overnight whereupon a solid precipitated. The white solid was then isolated, purified by trituration with Et$_2$O, and dried in air to give 25.16 g (84.3%) of [hydroxy(tosyloxy)iodo]-*o*-toluene; white, fluffy, fine needles: mp 108–110 °C dec to a yellow liquid; ^{1}H NMR (CDCl$_3$) δ 2.26 (s, 3 H), 2.43 (s, 3 H), 6.87–7.42 (m, 7 H), 7.65 (br s), 7.90 (br d, 1 H).

[Hydroxy(tosyloxy)iodo]-*p*-chlorobenzene.[9] A solution of [hydroxy(tosyloxy)iodo]-*o*-toluene (20.31 g, 0.05 mol) and *p*-chloroiodobenzene (11.93 g, 0.05 mol) in CH$_2$Cl$_2$ (120 mL) was stirred for 3 days at room temperature, during which time a fluffy, white solid precipitated from solution. The product was isolated, washed with Et$_2$O, and dried, (yield 13.13 g). After 8 more days, a second fraction was obtained from the filtrate, (yield 3.23 g), and, after 5 more days, a third fraction was obtained, (yield 1.19 g). The combined yield of [hydroxy(tosyloxy)iodo]-*p*-chlorobenzene was 17.55 g (82.3%); mp 159–161 °C dec to a yellow liquid; ^{1}H NMR (Me$_2$SO-*d*$_6$) δ 2.29 (s, 3 H), 6.47 (very br s, 1 H), 7.33 (AA'BB' m, 4 H), 7.90 (AA'BB' m, 4 H), the two multiplets overlap.

Aryl(furyl)iodonium Tosylates. An example preparation of one iodonium salt from each of the series 11, 13, and 15 follows. We emphasize, however, that workups vary for the individual compounds of each series.

(*m*-Tolyl)[5-(trimethylsilyl)-2-furyl]iodonium Tosylate (11, R = 3-Me). A yellow solution of [hydroxy(tosyloxy)iodo]-*m*-toluene (8.13 g, 0.020 mol) and 2,5-bis(trimethylsilyl)furan (4.46 g, 0.021 mol) in CH$_3$CN (25 mL) and CH$_3$OH (25 mL) was refluxed for 2 h. The reaction mixture was then cooled to room temperature and filtered (in order to remove trace insolubles) into a beaker, a few milliliters of CH$_3$OH being utilized in the transfer process. The volume was reduced by evaporation of the solvent (i.e., weight change from 51.52 to 13.52 g) whereupon some crystal formation occurred. The concentrated mixture was then poured into ca. 300 mL of Et$_2$O with the precipitation of (*m*-tolyl)[5-(trimethylsilyl)-2-furyl]iodonium tosylate; filtration and drying

gave fluffy shiny white crystals: yield, 8.10 g (76.6%); mp 142–144 °C dec to dark brown liquid; ^{1}H NMR (CDCl$_3$) δ 0.22 (s, 9 H), 2.23 (s, 3 H), 2.27 (s, 3 H), 6.53 (d, 1 H), 6.87–7.80 (complex m, 9 H).

Anal. Calcd for C$_{21}$H$_{25}$IO$_4$SSi: C, 47.73; H, 4.77; I, 24.01. Found: C, 47.18, 47.44; H, 5.09, 5.04; I, 23.86.

(*p*-Chlorophenyl)(5-methyl-2-furyl)iodonium Tosylate. A solution of [hydroxy(tosyloxy)iodo]-*p*-chlorobenzene (6.40 g, 0.015 mol) and 2-methyl-5-(trimethylsilyl)furan (2.34 g, 0.0152 mol) in CH$_3$OH (25 mL) and CH$_3$CN (25 mL) was heated at reflux for 2 h, filtered (gravity, CH$_3$OH added to aid transfer), and concentrated in vacuo to a clear, brown liquid (9.53 g). The residual liquid was taken up in CH$_3$OH (6 mL), and the resulting solution was poured into Et$_2$O (ca. 300 mL), whereupon (*p*-chlorophenyl)(5-methyl-2-furyl)iodonium tosylate precipitated as a white, flocculent mass. The product was isolated, washed with Et$_2$O, and dried in air: yield 4.87 g; mp 114.5–116.5 °C dec to black liquid. The filtrate, when stored at ca. –20 °C, gave 0.08 g more of product: mp 116–117 °C dec; combined yield 4.95 g (67.2%); ^{1}H NMR (CDCl$_3$) δ 2.31 (s, 6 H) coincident CH$_3$ singlets), 6.00 (appears as d with fine structure at 10-ppm width but as a d of d at expanded sweep width, 1H, H$_4$ of furan ring), 6.93–7.50 (complex m, 7 H aromatic protons, H$_3$ of furan ring), 7.90 (apparent d, 2 H, protons ortho to iodine in *p*-chlorophenyl nucleus); UV (CH$_3$OH, 1.88 × 10^{-5} M) λ_{max} 202.7 μm (ϵ 25 500), 221.6 (24 000), 248–250 (10 800).

Anal. Calcd for C$_{18}$H$_{16}$ClIO$_4$S: C, 44.06; H, 3.29; I, 25.86. Found: C, 44.10; H, 3.38; I, 26.08.

***p*-Iodophenyl(2-furyl)iodonium Tosylate.** A solution of [hydroxy(tosyloxy)iodo]-*p*-iodobenzene (9.10 g, 0.0176 mol) and 2-(trimethylsilyl)furan (2.58 g, 0.0184 mol) in CH$_3$OH (100 mL) was allowed to stir at room temperature. Within 28 min, *p*-diiodobenzene began separating from solution. After 1 day, the reaction mixture was concentrated to a solid/liquid residue (16.32 g) that was poured into Et$_2$O (ca. 500 mL), whereupon *p*-iodophenyl(2-furyl)iodonium tosylate precipitated and was isolated in two fractions: yield 1.79 g and 0.04 g (18.3%); mp 143–144 °C dec to a brown liquid. A 0.81-g portion was recrystallized from acetone (ca. 275 mL) and returned 0.72 g: mp 150.5–151.5 °C dec to a dark brown liquid; ^{1}H NMR (CD$_3$OD) δ 2.36 (s, 3 H), 6.60 (four-line m, 1 H), 7.11–7.86 (m, 10 H). This salt has a tendency to hold the solvent from which it crystallizes; it is removed when the sample is placed under high vacuum. It is calculated from a small Me$_3$Si singlet at δ 0.26 that the purified sample may contain an ca. 3% impurity of (*p*-iodophenyl)[5-(trimethylsilyl)-2-furyl]iodonium tosylate.

Anal. Calcd for C$_{17}$H$_{14}$I$_2$O$_4$S: C, 35.94; H, 2.48; I, 44.67. Found: C, 35.66; H, 2.56; I, 44.67, 44.49.

The Et$_2$O filtrate was subsequently concentrated to a small volume of material comprised of a yellow liquid and white crystals. This mixture was cooled (ca. –20 °C), and the crystalline material was isolated by vacuum filtration, rinsed with cold CH$_3$OH, dried in air, and identified as *p*-diiodobenzene: yield 3.88 g; mp 129–131 °C; ^{1}H NMR (CDCl$_3$) δ 7.37 (s). A second fraction weighing 0.33 g was isolated, bringing the total yield to 4.21 g (72.7%).

Thermal Decomposition Studies. One aryl(furyl)iodonium tosylate from each series, 11 (R = 4-Br), 13 (R = 4-Cl), and 15 (R = 3-Me), was converted to the corresponding iodide salt and subjected to pyrolysis. The products were determined by ^{1}H NMR analysis with reference to authentic compounds. An example procedure follows.

Preparation and Thermal Decomposition of 4-(Chlorophenyl)-2-(5-methylfuryl)iodonium Iodide. A solution of KI (3.32 g, 0.02 mol) in H$_2$O (20 mL) was mixed with a solution of (*p*-chlorophenyl)(5-methyl-2-furyl)iodonium tosylate (1.00 g, 0.002 mol) in CH$_3$OH (ca. 20 mL), whereupon the corresponding iodonium iodide precipitated as a light yellow powder (there was some warming). The iodide was isolated, washed with H$_2$O and then Et$_2$O, and dried in air: yield 0.87 g (98%); mp 101.5–103 °C dec to deep red liquid; ^{1}H NMR (Me$_2$SO-*d*$_3$) δ 2.36 (s, 3 H), 6.29 (d with fine structure, 1 H, H$_4$ of furan ring), 7.34 (d, 1 H, H$_3$ of furan ring), 7.86 (AA'XX' m, 4 H).

Anal. Calcd for C$_{11}$H$_9$ClI$_2$O: C, 29.59; H, 2.03; I, 56.85. Found: C, 29.70; H, 1.88; I, 57.25.

This compound is subject to decomposition at room temperature. A sealed glass ampoule, containing 0.13568 g of the io-

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donium iodide, was immersed in an oil bath kept at 105 °C, whereupon the yellow solid decomposed to a purplish-red liquid. An ^{1}H NMR spectrum of the decomposition mixture (in 0.5 mL of CDCl$_3$) was distinct from that of the starting iodonium salt and virtually identical with that of a mixture of authentic *p*-chloroiodobenzene and authentic 2-iodo-5-methylfuran. The decomposition was "clean", and the integration is consistent with a 1.04:1.00 molar mixture (ArI:furI) of the two components.

The iodide salt corresponding to **15** (R = 3-Me) had the expected percent iodine content ($\Delta\%$ = +0.34). The iodide salt corresponding to **11** (R = 4-Br) was not subjected to combustion analysis.

Authentic Iodofurans. 2-Iodo-5-(trimethylsilyl)furan, 2-iodo-5-methylfuran, and 2-iodofuran, being expected products from the thermal decompositions of the iodide analogues of **11** (R = 4-Br), **13** (R = 4-Cl), and **15** (R = 3-Me), were required as ^{1}H NMR standards. They were prepared by the direct lithiation of 2-(trimethylsilyl)furan, 2-methylfuran, and furan, respectively, in Et$_2$O with *n*-butyllithium in hexane and subsequent treatment of the lithiofurans thus produced with I$_2$ in Et$_2$O. The crude iodofurans were isolated after an aqueous sodium thiosulfate workup, and their ^{1}H NMR spectra (in CDCl$_3$) were recorded. 2-Iodo-5-(trimethylsilyl)furan and 2-iodi-5-methylfuran were "purified" by distillation, but they still retained dark coloration. 2-Iodofuran, also dark in color, was not further purified. Their NMR spectra revealed only minor impurities, one of which is probably *n*-octane, and were really quite clean. The ^{1}H NMR spectrum of 2-iodofuran has been described in the literature ("infinite" dilution, cyclohexane) as that of an XYZ spin system whose chemical shifts compare favorably with those measured by us.[11]

2-Iodo-5-(trimethylsilyl)furan: ^{1}H NMR (CDCl$_3$) δ 0.26 (s, 9 H), 6.48 (s, 2 H).

2-Iodo-5-methylfuran:[21] ^{1}H NMR (CDCl$_3$) δ 2.30 (d, 3 H, very close spacing at 10-ppm sweep width with one peak being more intense than the other), 5.85 (m, 1 H), 6.34 (m, 1 H, appears as a d at 10-ppm sweep width but shows evidence of fine structure at broader sweep width).

2-Iodofuran:[22] ^{1}H NMR (CDCl$_3$) δ 6.29 (m, 1 H), 6.50 (m, 1 H), 7.50 (m, 1 H) at 10-ppm sweep width; at 5-ppm sweep width, the m at δ 6.29 appears to be a pair of overlapping doublets, the m at δ 6.50 appears as a "distorted" triplet of doublets, and the m at δ 7.50 appears as a pair of closely spaced overlapping doublets [lit." ^{1}H NMR (cyclohexane) δ 6.17, 6.42, 7.37].

None of the iodofurans were subjected to C and H analysis. 2-Iodo-5-(trimethylsilyl)furan was subjected to iodine analysis; ΔI% = –4.82%.

Registry No. 9 (R = H), 27126-76-7; 9 (R = 2-Me), 73177-97-6; 9 (R = 3-Me), 84383-97-1; 9 (R = 4-Me), 73177-96-5; 9 (R = 4-F), 84383-77-7; 9 (R = 4-Cl), 73178-07-1; 9 (R = 4-Br), 73178-08-2; 9 (R = 4-I), 73178-09-3; 9 (R = 4-Ph), 73178-11-7; 10, 1578-29-6; 11 (R = H), 85925-18-4; 11 (R = 2-Me), 85925-20-8; 11 (R = 3-Me), 85925-22-0; 11 (R = 4-Me), 85925-24-2; 11 (R = 4-F), 85925-26-4; 11 (R = 4-Cl), 85925-28-6; 11 (R = 4-Br), 85925-30-0; 11 (R = 4-I), 85925-32-2; 11 (R = 4-Ph), 85925-34-4; 11·I (R = 4-Br), 85925-35-5; 12, 13271-75-5; 13 (R = 2-Me), 85925-37-7; 13 (R = 3-Me), 85925-39-9; 13 (R = 4-Me), 85925-41-3; 13 (R = 4-F), 85925-43-5; 13 (R = 4-Cl), 85925-45-7; 13 (R = 4-Br), 85925-47-9; 13 (R = 4-I), 85939-46-4; 14, 1578-33-2; 15 (R = H), 85925-49-1; 15 (R = 2-Me), 85925-51-5; 15 (R = 3-Me), 85925-53-7; 15 (R = 4-Me), 85925-55-9; 15 (R = 4-F), 85925-57-1; 15 (R = 4-Cl), 85925-59-3; 15 (R = 4-Br), 85925-61-7; 15 (R = 4-I), 85925-63-9; 15·I (R = 3-Me), 85925-64-0; furan, 110-00-9; 2-methylfuran, 534-22-5; *o*-iodotoluene, 615-37-2; *o*-(diacetoxyiodo)toluene, 31599-59-4; *p*-chloroiodobenzene, 637-87-6; (4-chlorophenyl)-2-(5-methylfuryl)iodonium iodide, 85925-65-1; 2-iodo-5-(trimethylsilyl)furan, 85939-47-5; 2-iodo-5-methylfuran, 85925-66-2; 2-iodofuran, 54829-48-0.

Supplementary Material Available: Further experimental details on the syntheses of this study (10 pages). Ordering information is given on any current masthead page.

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Homogeneous Catalytic Formation of Carbon–Nitrogen Bonds. 2. Catalytic Activation of the Silicon–Nitrogen Bond[†]

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The catalytic formation of new carbon–nitrogen single bonds can be promoted via catalytic activation of silicon–nitrogen bonds. Silazanes, compounds containing Si–N bonds, will react, in the presence of a catalyst, with compounds containing carbon–oxygen double bonds to form new C–N and Si–O bonds concurrently. Thus, CO$_2$ and phenyl isocyanate can be reacted with a number of silazane compounds to give urethane and urea derivatives in 60–90% yields. In the absence of catalysts, the identical reactions either do not proceed or go to less than 20% conversion. Aldehydes and ketones also react in a similar manner to give imines and enamines, respectively. A variety of group 8 metals have been found to activate the Si–N bond in the catalytic formation of PhCH=NPh from PhNHSiM$_3$ and PhCHO. Iron and rhodium catalysts were found to be the most active for this reaction. The catalytic activation of Si–N bonds was also found useful in the ring-opening oligomerization of –[(CH$_3$)$_2$SiNH]$_4$– in the presence of (Me$_3$Si)$_2$NH.

The chemistry that is the subject of this preliminary report arises as a result of our continuing interest in developing new catalytic methods for the formation of C–N bonds. A second directive for pursuing the following studies was the knowledge that silicon compounds are

excellent oxygenophiles, and, as such, the formation of Si–O bonds could be the driving force that promotes catalytic reactions. Consequently, our initial goal was to develop simple catalytic reactions in which C–N and Si–O bonds are formed simultaneously.

One logical approach was envisioned in which compounds containing Si–N bonds (silazanes) were reacted with compounds containing C–O multiple bonds via cat-

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