Exchange of Carbon Ligands at Iodine in Iodonium Salts. A Direct Synthesis of Aryl(2-furyl)iodonium Tosylates from Aryl(*tert*-butylethynyl)iodonium Tosylates

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Various [hydroxy(tosyloxy)iodo]arenes ($RC_6H_4I(OH)OTs$, R = H, 2-Me, 3-Me, 4-Me, 2-F, 3-F, 4-F, 2-Cl, 3-Cl) have been found to react with *tert*-butylacetylene in chloroform under reflux to give the corresponding aryl(*tert*-butylethynyl)iodonium tosylates ($Me_3CC{\equiv}CI^+C_6H_4R^-OTs$) in yields ranging from 56% to 80%. When the arylethynyl salts (R = 2-Me, 3-Me, 4-Me, 2-F, 3-F 4-F, 3-Cl) were mixed with 2-lithiofuran in ether–hexane and treated subsequently with p-$TsOH{\cdot}H_2O$ in ether, the corresponding aryl(2-furyl)iodonium tosylates were obtained in yields ranging from 21% to 74%. 2-Lithiofuran reacted similarly with phenyl(phenylethynyl)iodonium tosylate to give a 60% yield of (2-furyl)phenyliodonium iodide (after HCl quenching and KI treatment). The exchange reaction is not limited to 2-lithiofuran. Thus, (*tert*-butylethynyl)(2-methylphenyl)iodonium tosylate reacted with 2-lithiothiophene and with 2-lithio-5-methylthiophene to give the corresponding (2-methylphenyl)(2-thienyl)iodonium tosylates in 62% and 64% yields, respectively. (*tert*-Butylethynyl)phenyliodonium tosylate reacted similarly with 2-lithiothianaphthene to give a 70% yield of phenyl(2-thianaphthenyl)iodonium tosylate.

We report herein the preparation of a series of aryl(*tert*-butylethynyl)iodonium tosylates **1** and their application in a direct synthesis of aryl(2-furyl)iodonium tosylates **2** (R′ = H). There are three aspects of this study that warrant emphasis. (1) Iodonium salts in which the iodine(III) atom bears an alkynyl ligand are rare. Apart from our own work in this area, we know of only two alkynyliodonium salts (i.e., **3** and **4**) in the chemical literature.[1,2] (2) The common classical methods of iodonium salt synthesis preclude the preparation of aryl(2-furyl)iodonium salts, compounds of interest as potential microbicides.[3] We recently synthesized the first examples of **2** by the condensation of various [hydroxy(tosyloxy)iodo]arenes **5** with 5-R′-2-(trimethylsilyl)furans **6** in either MeOH/MeCN (R′ = Me_3Si, Me) or MeOH (R′ = H); eq 1.[3] When R′ was Me_3Si or Me, the furyl salts were isolated in good yield, but when R′ was H, product yields were low (9–23%). The choice of the aryl(2-furyl)iodonium tosylates (R′ = H) as synthetic targets in the present study serves to illustrate the effectiveness of the carbon ligand exchange method. (3) The reaction that has been developed is an unusual one involving the direct replacement of the *tert*-butylethynyl group in **1** with the 2-furyl group, this being accomplished by the treatment of 2-lithiofuran (**7**) in Et_2O/hexane with **1**; eq 2.

The concept of a "carbanion" exchange at iodine in **1** was inspired by an earlier study of Beringer and Chang who described the preparation of diphenyliodonium iodide from bis(4-chlorophenyl)iodonium chloride and phenyllithium and the preparation of bis[4-(dimethylamino)phenyl]iodonium iodide from diphenyliodonium chloride and [4-(dimethylamino)phenyl]lithium,[4] eq 3. Evidence for the intermediacy of tetraaryliodate ions in these reactions was presented. As a working hypothesis, we reasoned that the formal displacement of one "carbanion" by another at iodine would be facilitated if the basicity of the incoming species significantly exceeded that of the departing species; i.e., the displacement of (*tert*-butylethynyl)lithium by 2-buryllithium should be thermodynamically favorable, but the displacement of aryllithium by 2-furyllithium should be much less so.

Aryl(*tert*-butylethynyl)iodonium Tosylates. Alkynylaryliodonium tosylates can be obtained from the direct reactions of [hydroxy(tosyloxy)iodo]arenes **5** with terminal alkylacetylenes if the alkyl group of the acetylene is sterically comparable to or larger than isopropyl.[5,6] Various

(1) Beringer, F. M.; Galton, S. A. *J. Org. Chem.* **1965**, *30*, 1930.
(2) Merkushev, E. B.; Karpitskaya, L. G.; Novosel'tseva, G. I. *Dokl. Akad. Nauk SSSR* **1979**, *245*, 607.
(3) Carman, C. S.; Koser, G. F. *J. Org. Chem.* **1983**, *48*, 2534 and references cited therein.
(4) Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1972**, *37*, 1516.
(5) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1981**, *46*, 4324.
(6) Rebrovic, L. Ph.D. Thesis, The University of Akron, Jan 1984.

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Table I. Aryl(*tert*-butylethynyl)iodonium Tosylates from Reactions of [Hydroxy(tosyloxy)iodo]arenes with *tert*-Butylacetylene (5 + 8 → 1; eq 4)

5	8/5[a]	conditions,[b] time in h	1, % yield[c]
R			
H[d]	2.81	5.0	73
2-Me	2.80	5.75	80
3-Me	6.65	5.0	79
4-Me	3.66	24.0	56
2-F	3.11	4.5	64
3-F	3.16	4.5	65.5
4-F	4.26	5.0	76
3-Cl	4.06	4.0	69
4-Cl	3.16	17.0	63

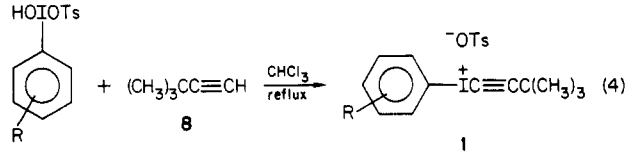
[a] Initial concentrations of 5 ranged from 0.25 to 0.43 mmol of 5/mL $CHCl_3$. [b] $CHCl_3$ at reflux. [c] Rounded off to nearest percent. [d] Previously prepared and characterized by L. Rebrovic.[6]

Table II. Aryl(2-furyl)iodonium Tosylates from Reactions of Aryl(*tert*-butylethynyl)iodonium Tosylates with 2-Lithiofuran (1 + 7 → 2; eq 2)[a]

1, R =	2, % yield[b,c]	1, R =	2, % yield[b,c]
2-Me	74	3-F[d]	21
3-Me	72	4-F	32.5
4-Me	65	3-Cl[d]	21
2-F[d]	45		

[a] 7/1 ca. 20 mmol/8 mmol except for R = 4-Me where 7/1 = 10 mmol/2 mmol. [b] Rounded off to nearest percent. [c] The aryl(2-furyl)iodonium tosylates melt with decomposition. The known furyl and thienyl salts isolated in the present study all exhibited lower decomposition points than the same compounds previously prepared by Carman, Margida, and Koser.[3,8] This is not surprising since the decomposition points of iodonium salts can change significantly upon their recrystallization. [d] Previously unreported compounds.

[hydroxy(tosyloxy)iodo]arenes have been found to react with *tert*-butylacetylene (8) in chloroform at reflux to give good yields of the corresponding aryl(*tert*-butylethynyl)-iodonium tosylates; eq 4, Table I. Workup was

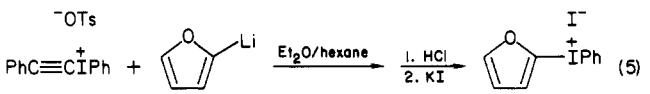


straightforward. After the reaction mixtures were washed with H_2O, dried ($MgSO_4$), and reduced in volume, the alkynyl salts were precipitated with Et_2O and characterized by elemental (C, H, I) and ^1H NMR analyses. For example, the ^1H NMR spectrum ($CDCl_3$) of (*tert*-butylethynyl)(4-methylphenyl)iodonium tosylate (1, R = 4-Me) exhibits a 9-H singlet at δ 1.19 (Me_3C), overlapping singlets at δ 2.31 and 2.35 (6 H, Me's of $^-$OTS and *p*-tolyl), and a complex pattern ranging ca. from δ 6.85 to 8.0 (8 H, aromatic hydrogens).

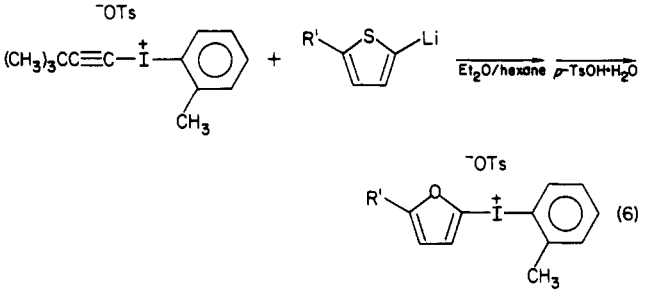
Aryl(2-furyl)iodonium Tosylates. The aryl(2-furyl)iodonium tosylates were prepared by the addition of *solid* aryl(*tert*-butylethynyl)iodonium tosylates to an excess of 2-lithiofuran in Et_2O/hexane and subsequent treatment of the reaction mixtures with a saturated solution (~0.22 M) of *p*-TsOH·H_2O in Et_2O; eq 2, Table II.

Previously unreported aryl(2-furyl)iodonium tosylates (2, R = H) were characterized by elemental (C, H, I) and ^1H NMR analyses while previously reported compounds[3] were identified from their ^1H NMR spectra, and, in most cases, by elemental analysis.

Preliminary efforts have been made to extend the general methodology to other systems. The phenylethynyl group is also subject to exchange. Phenyl(phenylethynyl)iodonium tosylate[5] was mixed with 2-lithiofuran in Et_2O/hexane. Subsequent acidificiation of the reaction mixture with HCl/Et_2O and treatment of the resulting chloride salt with aqueous potassium iodide gave (2-furyl)phenyliodonium iodide (C, H, I; ^1H NMR) in 60% yield; eq 5.

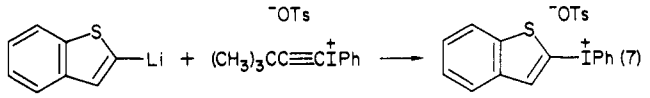


The reactions of (*tert*-butylethynyl)(2-methylphenyl)-iodonium tosylate with 2-lithiothiophene and with 5-methyl-2-lithiothiophene gave the corresponding (2-methylphenyl)(2-thienyl)iodonium tosylates in 62% and 64% yields, respectively; eq 6. 2-Lithiothianaphthene

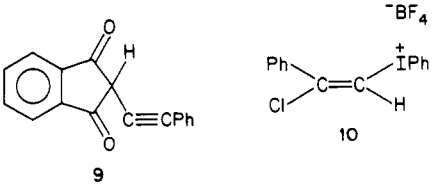


R' = H, Me

reacted similarly with (*tert*-butylethynyl)phenyliodonium tosylate to give a 70% yield of phenyl(2-thianaphthenyl)iodonium tosylate; eq 7.



The replacement of the phenylethynyl ligand with the 2-furyl ligand (eq 6) reveals a third mode of reactivity for the phenyl(phenylethynyl)iodonium ion toward nucleophilic species. Phenyl(phenylethynyl)iodonium chloride has previously been employed by Beringer and Galton as an alkynylating reagent for the 2-phenyl-1,3-indandionate ion in *tert*-butyl alcohol, the product being 2-phenyl-2-(phenylethynyl)-1,3-indandione (9) in 73% yield.[7] Finally an attempt by the same investigators to metathesize the chloride salt to the corresponding tetrafluoroborate salt led instead to phenyl(2-phenyl-2-chloroethenyl)iodonium tetrafluoroborate (10), presumably via Michael addition of the chloride ion to the carbon–carbon triple bond of the alkynyliodonium ion.[7]



Experimental Section

General Methods. The ^1H NMR spectra reported herein were recorded on a Varian Model EM-360 NMR spectrometer. Chemical shifts are given relative to internal tetramethylsilane. The number of "protons" reported for a given multiplet is based on the combined integration of all resonances in the spectrum (except for those of minor impurities) divided by the total number of "protons" in the molecule under consideration. For NMR descriptions; s = singlet, d = doublet, t = triplet, dd = doublet

(7) Beringer, F. M.; Galton, S. A. *J. Org. Chem.* **1965**, *30*, 1930.

of doublets, m = multiplet. The resonances of the aromatic region are referred to collectively as m, and the range of chemical shifts is given. Elemental compositions were determined at Galbraith Labs in Knoxville, TN. Decomposition points are uncorrected.

The [hydroxy(tosyloxy)iodo]arenes utilized in this study were prepared by procedures similar to those already described in the literature.[3]

Detailed experimental procedures for the preparation of (*tert*-butylethynyl)(3-methylphenyl)iodonium tosylate and (2-furyl)(3-methylphenyl)iodonium tosylate are given as examples. For other alkynyl- and furyliodonium salts and for two of the thienyliodonium salts, the experimentals are confined primarily to characterization data. The reactions of phenyl(phenylethynyl)iodonium tosylate with 2-lithiofuran and of (*tert*-butylethynyl)phenyliodonium tosylate with 2-lithiothianaphthene are described in full. In general, the quantities (mmol) of lithiofuran and lithiothiophenes are assumed to be equal to those of the starting furan and thiophenes.

(*tert*-Butylethynyl)(3-methylphenyl)iodonium Tosylate. A mixture of 3,3-dimethyl-1-butyne (8.20 g, 99.8 mmol), [hydroxy(tosyloxy)iodo]-*m*-toluene (6.09 g, 15.0 mmol), and $CHCl_3$ (50 mL) was stirred and heated under reflux for 5 h. The resulting golden solution was allowed to cool to room temperature, washed with H_2O (2 × 50 mL), dried ($MgSO_4$), and concentrated on a rotary evaporator to a volume of 5 mL. The concentrate was then warmed in a water bath (70 °C), and warm Et_2O (100 mL) was added with swirling. White crystals of (*tert*-butylethynyl)(3-methylphenyl)iodonium tosylate separated as the mixture cooled to room temperature. The mixture was kept overnight at −10 °C, and the product was subsequently isolated, washed with Et_2O and dried in air: yield, 5.54 g (79%); mp 127–128 °C dec; ^1H NMR ($CDCl_3$) δ 1.21 (s, 8.8 H), 2.32 (s, 5.9 H), 6.87–8.00 (m, 8.3 H).

Anal. Calcd for $C_{20}H_{23}ISO_3$: C, 51.07; H, 4.93; I, 26.98. Found: C, 51.12; H, 5.06; I, 27.18.

(*tert*-Butylethynyl)(2-methylphenyl)iodonium tosylate: from 3,3-dimethyl-1-butyne (6.95 g, 84.6 mmol) and [hydroxy(tosyloxy)iodo]-*o*-toluene (12.27 g, 30.2 mmol) in $CHCl_3$ (70 mL); yield, 11.40 g (80%); mp 139–141 °C dec; ^1H NMR ($CDCl_3$) δ 1.16 (s, 8.7 H), 2.30 (s, 3.0 H), 2.63 (s, 2.9 H), 6.83–7.67 (m, 7.3 H), 8.03 (d, 1.1 H).

Anal. Calcd for $C_{20}H_{23}ISO_3$: C, 51.07; H, 4.93; I, 26.98. Found: C, 51.03; H, 5.15; I, 26.80.

(*tert*-Butylethynyl)(4-methylphenyl)iodonium tosylate: from 3,3-dimethyl-1-butyne (2.97 g, 36.2 mmol) and [hydroxy(tosyloxy)iodo]-*p*-toluene (4.02 g, 9.90 mmol) in $CHCl_3$ (25 mL); yield, 2.60 g (56%); mp 152–155 °C dec; ^1H NMR ($CDCl_3$) δ 1.19 (s, 9.0 H), 2.31 and 2.35 (singlets, 6.0 H), 6.88–8.01 (m, 8.0 H).

Anal. Calcd for $C_{20}H_{23}ISO_3$: C, 51.07; H, 4.93; I, 26.98. Found: C, 51.23; H, 5.12; I, 26.73.

(*tert*-Butylethynyl)(2-fluorophenyl)iodonium tosylate: from 3,3-dimethyl-1-butyne (5.10 g, 62.1 mmol) and [hydroxy(tosyloxy)iodo]-2-fluorobenzene (8.20 g, 20.0 mmol) in $CHCl_3$ (50 mL); yield, 6.03 g (63.6%); mp 130–131 °C dec; ^1H NMR ($CDCl_3$) δ 1.12 (s, 8.9 H), 2.30 (s, 3.0 H), 6.83–8.23 (m, 8.1 H, includes br "t" at 8.01 (1.1 H)).

Anal. Calcd for $C_{19}H_{20}IFSO_3$: C, 48.11; H, 4.25; I, 26.75. Found: C, 48.25; H, 4.21; I, 26.79.

(*tert*-Butylethynyl)(3-fluorophenyl)iodonium tosylate: from 3,3-dimethyl-1-butyne (5.18 g, 63.1 mmol) and [hydroxy(tosyloxy)iodo]-3-fluorobenzene (8.20 g, 20.0 mmol) in $CHCl_3$ (50 mL); yield, 6.21 g (65.5%); mp 126–128 °C dec; ^1H NMR ($CDCl_3$) δ 1.20 (s, 8.8 H), 2.33 (s, 2.9 H), 6.90–8.07 (m, 8.3 H).

Anal. Calcd for $C_{19}H_{20}IFSO_3$: C, 48.11; H, 4.25; I, 26.75. Found: C, 48.21; H, 4.47; I, 26.92.

(*tert*-Butylethynyl)(4-fluorophenyl)iodonium tosylate: from 3,3-dimethyl-1-butyne (5.25 g, 63.9 mmol) and [hydroxy(tosyloxy)iodo]-4-fluorobenzene (6.16 g, 15.0 mmol) in $CHCl_3$ (60 mL); yield, 5.40 g (76%); mp 140–142 °C dec, ^1H NMR ($CDCl_3$) δ 1.18 (s, 9.0 H), 2.33 (s, 2.9 H), 6.80–8.26 (m, 8.1 H).

Anal. Calcd for $C_{19}H_{20}IFSO_3$: C, 48.11; H, 4.25; I, 26.75. Found: C, 48.32; H, 4.27; I, 26.81.

(*tert*-Butylethynyl)(3-chlorophenyl)iodonium tosylate: from 3,3-dimethyl-1-butyne (5.00 g, 60.9 mmol) and [hydroxy(tosyloxy)iodo]-3-chlorobenzene (6.41 g, 15.0 mmol) in $CHCl_3$ (50 mL); yield, 5.12 g (69%); mp 122–124 °C dec; ^1H NMR ($CDCl_3$) δ 1.20 (s, 8.9 H), 2.32 (s, 3.0 H), 6.90–8.13 (m, 8.1 H).

Anal. Calcd for $C_{19}H_{20}IClSO_3$: C, 46.50; H, 4.11; I, 25.86. Found: C, 46.30; H, 4.14; I, 25.82.

(*tert*-Butylethynyl)(4-chlorophenyl)iodonium tosylate: from 3,3-dimethyl-1-butyne (5.18 g, 63.1 mmol) and [hydroxy(tosyloxy)iodo]-4-chlorobenzene (8.51 g, 20.0 mmol) in $CHCl_3$ (85 mL); yield, 6.16 g (63%); mp 157–159 °C dec; ^1H NMR ($CDCl_3$) δ 1.18 (s, 8.9 H), 2.33 (s, 3.0 H), 6.91–8.18 (m, 8.1 H).

Anal. Calcd for $C_{19}H_{20}IClSO_3$: C, 46.50; H, 4.11; I, 25.86. Found: C, 46.21; H, 4.16; I, 25.62.

(*tert*-Butylethynyl)phenyliodonium tosylate: from 3,3-dimethyl-1-butyne (7.00 g, 85.2 mmol) and [hydroxy(tosyloxy)iodo]benzene (11.87 g, 30.3 mmol) in $CHCl_3$ (85 mL); yield, 10.02 g (73%); mp 136–137 °C dec [lit.[6] mp 137.5–139 °C]; ^1H NMR ($CDCl_3$) δ 1.21 (s, 8.9 H), 2.31 (s, 3.0 H), 6.88–8.21 (m, 9.1 H, includes d of m at 7.99 (2.1 H)).

Phenyl(phenylethynyl)iodonium Tosylate. A mixture of phenylacetylene (8.90 g, 87.1 mmol), [hydroxy(tosyloxy)iodo]benzene (12.05 g, 30.7 mmol), and $CHCl_3$ (70 mL) was stirred and heated under reflux for 45 min. The resulting brown solution was allowed to cool to room temperature, washed with H_2O (65 mL), dried ($MgSO_4$), and concentrated to a volume of 10 mL. The concentrate was warmed (water bath, 70 °C), and warm Et_2O (50 mL) was added with stirring. Crystals of phenyl(phenylethynyl)iodonium tosylate separated upon cooling. The mixture was kept overnight at 4 °C, and the product was subsequently isolated, washed with Et_2O, and dried in air: yield, 9.61 g (66%); mp 109–112 °C dec. [lit.[6] mp 119–122 °C dec]; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3.4 H), 6.72–8.28 (m, 13.6 H, includes d of m at δ 8.03).

(2-Furyl)(3-methylphenyl)iodonium Tosylate. A solution of furan (1.36 g, 20.0 mmol) and *n*-butyllithium (8.33 mL of a 2.4 M solution in hexane, 20 mmol) in Et_2O (40 mL), kept under nitrogen, was stirred overnight at room temperature. The resulting heterogeneous mixture of 2-lithiofuran and solvent was cooled in an ice/salt bath (ca. 0 °C), and *solid* (*tert*-butylethynyl)(3-methylphenyl)iodonium tosylate (3.80 g, 8.08 mmol) was introduced under a positive nitrogen pressure. The resulting mixture was stirred for 1 h at ca. 0 °C, during which time it became less heterogeneous and slightly darker, and was then treated with a saturated solution (125 mL, ca. 0.22 M) of *p*-TsOH·H_2O in Et_2O whereupon additional white solids separated. The mixture was allowed to warm to room temperature, and the solids were isolated and triturated for 15 min with CH_2Cl_2 (225 mL). The insoluble material was separated, and the CH_2Cl_2 solution was treated with decolorizing carbon, dried ($MgSO_4$), and concentrated to a volume of 20 mL. The concentrate was then warmed (water bath) and treated with warm Et_2O (20 mL). White crystals of (2-furyl)(3-methylphenyl)iodonium tosylate separated as the mixture cooled to room temperature. The mixture was kept at −10 °C for 1 h and the product was isolated, washed with Et_2O, and dried in air: yield, 2.66 g (72%); mp 129–131 °C dec; ^1H NMR (CD_3OD) δ 2.32 (s, 6 H), 6.53 (dd, 1 H), 6.92–8.08 (m, 10 H).

Anal. Calcd for $C_{18}H_{17}ISO_4$: C, 47.38; H, 3.76; I, 27.81. Found: C, 47.51; H, 3.89; I, 28.04.

(2-Furyl)(2-methylphenyl)iodonium tosylate: from 2-lithiofuran (20 mmol) and (*tert*-butylethynyl)(2-methylphenyl)iodonium tosylate (3.81 g, 8.10 mmol); yield, 2.73 g (74%); mp 131–133 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.25 (s, 2.8 H), 2.61 (s, 3.1 H), 6.57 (dd, 1.1 H), 6.88–7.74 (m, 7.9 H), 7.95 (m, 1.1 H), 8.31 (d, 1.1 H).

Anal. Calcd for $C_{18}H_{17}ISO_4$: C, 47.38; H, 3.76; I, 27.81. Found: C, 47.13; H, 3.84; I, 28.09.

(2-Furyl)(4-methylphenyl)iodonium tosylate: from 2-lithiofuran (10 mmol) and (*tert*-butylethynyl)(4-methylphenyl)iodonium tosylate (0.94 g, 2.0 mmol); yield, 0.59 g (65%); mp 109–111 °C dec; ^1H NMR (CD_3OD) δ 2.33 (s, 5.7 H), 6.50 (dd, 1.2 H), 6.93–8.10 (m, 10.1 H).

(2-Fluorophenyl)(2-furyl)iodonium tosylate: from 2-lithiofuran (20 mmol) and (*tert*-butylethynyl)(2-fluorophenyl)-iodonium tosylate (3.80 g, 8.01 mmol); yield, 1.66 g (45%); mp 131–133 °C dec; ^1H NMR (CD_3OD) δ 2.30 (s, 2.9 H), 6.53 (m, 1.0 H), 6.97–8.43 (m, 10.0 H, includes br t at δ 8.20 (1.1 H)).

Anal. Calcd for $C_{17}H_{14}FISO_4$: C, 44.36; H, 3.07; I, 27.57. Found: C, 44.57; H, 3.30; I, 27.63.

(3-Fluorophenyl)(2-furyl)iodonium tosylate: from 2-lithiofuran (20 mmol) and (*tert*-butylethynyl)(3-fluorophenyl)-iodonium tosylate (3.80 g, 8.01 mmol); yield, 0.76 g (21%); mp

126–129 °C dec; ^{1}H NMR (CD_3OD) δ 2.30 (s, 2.8 H), 6.57 (dd, 1.1 H), 6.97–8.13 (m, 10.1 H).

Anal. Calcd for $C_{17}H_{14}FISO_4$: C, 44.36; H, 3.07; I, 27.57. Found: C, 44.52; H, 3.02; I, 27.70.

(4-Fluorophenyl)(2-furyl)iodonium tosylate: from 2-lithiofuran (20 mmol) and (*tert*-butylethynyl)(4-fluorophenyl)-iodonium tosylate (3.80 g, 8.01 mmol); yield, 1.20 g (32.5%); mp 136–138 °C dec; ^{1}H NMR (CD_3OD) δ 2.32 (s, 2.9 H), 6.53 (dd, 1.0 H), 6.93–8.33 (m, 10.2 H, includes obvious low field m at δ 8.12 (2.1 H)).

Anal. Calcd for $C_{17}H_{14}FISO_4$: C, 44.36; H, 3.07; I, 27.57. Found: C, 44.55; H, 3.29; I, 27.67.

(3-Chlorophenyl)(2-furyl)iodonium tosylate: from 2-lithiofuran (20 mmol) and (*tert*-butylethynyl)(3-chlorophenyl)-iodonium tosylate (3.92 g, 7.99 mmol); yield, 0.79 g (21%); mp 114–116 °C dec; ^{1}H NMR (CD_3OD) δ 2.31 (s, 2.9 H), 6.56 (dd, 1.0 H), 6.93–8.36 (m, 10.2 H).

Anal. Calcd for $C_{17}H_{14}ClISO_4$: C, 42.83; H, 2.96; I, 26.62. Found: C, 42.80; H, 2.96; I, 26.77.

(2-Methylphenyl)(2-thienyl)iodonium tosylate: from 2-lithiothiophene (10 mmol) and (*tert*-butylethynyl)(2-methylphenyl)iodonium tosylate (0.94 g, 2.0 mmol); yield, 0.59 g (62.5%); mp 116–118 °C dec [lit.[8] mp 144–148 °C]; ^{1}H NMR (CD_3OD) δ 2.28 (s, 2.8 H), 2.63 (s, 2.9 H), 6.92–8.38 (m, 11.2 H, includes d at δ 8.20 (1.0 H)).

(2-Methylphenyl)(5-methyl-2-thienyl)iodonium tosylate: from 2-lithio-5-methylthiophene (10 mmol) and (*tert*-butylethynyl)(2-methylphenyl)iodonium tosylate (0.94 g, 2.0 mmol); yield, 0.62 g (64%); mp 123–125 °C dec [lit.[8] mp 132–133 °C dec]; ^{1}H NMR (CD_3OD) δ 2.28 (s, 2.8 H), 2.48 (s, 2.7 H), 2.62 (s, 3.4 H), 6.71 (m, 1.0 H), 6.94–7.81 (m, 8.0 H), 8.18 (d, 1.0 H).

Phenyl(2-thianaphthenyl)iodonium Tosylate. To a solution of *n*-butyllithium (11.0 mmol, 2.4 M solution in hexane) in Et_2O (20 mL), kept under nitrogen and chilled in an ice/salt bath, was added, dropwise and with stirring, a solution of thianaphthene (1.34 g, 9.99 mmol) in Et_2O (5 mL). After 20 min, solid (*tert*-butylethynyl)phenyliodonium tosylate (1.82 g, 3.99 mmol) was introduced under a positive nitrogen pressure. The reaction mixture was stirred for 30 min, during which time it became less heterogeneous and turned slightly red in color, and was then treated with a solution of *p*-TsOH·H_2O in Et_2O (ca. 0.22 M, 70 mL) whereupon additional white solids separated. The mixture was allowed to warm to room temperature, and the solids were isolated, washed with Et_2O, and triturated for 15 min with H_2O (100 mL). The water insoluble, white crystals of phenyl(2-thianaphthenyl)iodonium tosylate were isolated, washed with H_2O, and dried in vacuo over P_2O_5: yield, 1.43 g (70.5%); mp 158–160 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 2.25 (s, 2.9 H), 6.87–8.57 (m, 14.1 H).

Anal. Calcd for $C_{21}H_{17}IS_2O_3$: C, 49.61; H, 3.37; I, 24.96. Found: C, 49.55; H, 3.52; I, 25.07.

Phenyl(2-furyl)iodonium Iodide. To a mixture of phenyl(phenylethynyl)iodonium tosylate (0.70 g, 1.47 mmol) and Et_2O (25 mL), kept under nitrogen and cooled in a dry ice/acetone bath, was added with stirring a mixture of 2-lithiofuran (12.0 mmol) in Et_2O/hexane. After 4 h, the reaction mixture was warmed to −10 °C, kept at that temperature for 30 min, and subsequently allowed to warm to room temperature whereupon it became less heterogeneous and acquired a light red color. A saturated solution of HCl in Et_2O (10 mL) was then added, and a dark solid separated. The solids were isolated and treated with cold H_2O (150 mL), and the mixture was filtered (to remove solid impurities) into an aqueous solution of KI. Phenyl(2-furyl)iodonium iodide precipitated (yellow solid) and was isolated, washed with Et_2O, and dried in air: yield, 0.35 g (60%); mp 125–126 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 6.60 (dd, 1.1 H), 6.85–7.68 (m, 4.0 H), 7.93 and 8.15 (m and d of m, 2.9 H).

Anal. Calcd for $C_{10}H_8I_2O$: C, 30.18; H, 2.03; I, 63.77. Found: C, 30.45; H, 2.10; I, 63.84.

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Registry No. 1 (R = H), 92473-47-7; 1 (R = 2-Me), 92543-63-0; 1 (R = 3-Me), 92543-61-8; 1 (R = 4-Me), 92543-49-2; 1 (R = 2-F), 92543-51-6; 1 (R = 3-F), 92543-53-8; 1 (R = 4-F), 92543-55-0; 1 (R = 3-Cl), 92543-57-2; 1 (R = 4-Cl), 92543-59-4; 2 (R = 2-Me), 85925-51-5; 2 (R = 3-Me), 85925-53-7; 2 (R = 4-Me), 85925-55-9; 2 (R = 2-F), 92575-11-6; 2 (R = 3-F), 92543-65-2; 2 (R = 4-F), 85925-57-1; 2 (R = 3-Cl), 92543-67-4; 5 (R = H), 27126-76-7; 5 (R = 2-Me), 73177-97-6; 5 (R = 3-Me), 92543-47-0; 5 (R = 4-Me), 73177-96-5; 5 (R = 2-F), 84383-95-9; 5 (R = 3-F), 84383-96-0; 5 (R = 4-F), 84383-77-7; 5 (R = 3-Cl), 84383-84-6; 5 (R = 4-Cl), 73178-07-1; 3,3-dimethyl-1-butyne, 917-92-0; phenyl(phenylethynyl)iodonium tosylate, 79069-32-2; phenylacetylene, 536-74-3; furan, 110-00-9; (2-methylphenyl)(2-thienyl)iodonium tosylate, 91228-43-2; thiophene, 110-02-1; 2-methylthiophene, 554-14-3; (2-methylphenyl)(5-methyl-2-thienyl)iodonium tosylate, 91228-56-7; phenyl(2-thianaphthenyl)iodonium tosylate, 92543-69-6; thianaphthene, 95-15-8; phenyl(2-furyl)iodonium iodide, 92543-70-9.

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Nucleophilic Participation of Phenyl in the Ring-Opening Reactions of *cis*- and *trans*-2,3-Dibenzyloxirane

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Methanolysis reactions of both epoxides *cis*-**4** and *trans*-**5** under different conditions are completely anti stereoselective, no trace of the products arising from syn opening being found. Also the hydrolysis, the acetolysis, and the trichloroacetolysis in non-protic solvents of **4** are completely anti stereoselective, whereas the corresponding reactions of **5** yield nonnegligible amounts of syn adducts, which in some trichloroacetolysis reactions reach 21.7%. These data suggest that some of the openings of the trans epoxide **5** occur in part through nucleophilic participation of phenyl, whereas the reactions of the cis isomer **4** exhibit no such participation. The markedly lower capability of **4** to give phenyl participation may be due to the severe steric interactions which arise in the formation of the phenonium-type species from cis epoxide **4**.

It is well established that the stereochemistry of ring opening of oxiranes bearing neither aryl nor other unsaturated systems directly linked to the ring under acidic conditions is essentially anti.[1-3] However, when aryls or other unsaturated systems are present on the oxirane ring, the observed stereochemistry of the ring opening can range

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