– CH_2Ph^+), 133 (M – $C_6H_5CO^+$), 120 ($OC_6H_4CO^+$), 105 ($C_6H_5CO^+$), 91 (CH_2Ph^+). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.67; H, 5.88. (b) 4-Chromanone (**32**) (32%).

Cyclization of 1-[(*E*)-4-Phenylbut-3-en-1-yl]-5-thioxopyrrolidin-2-one (23). The reaction was performed according to procedure F and stopped after 40 min. Flash chromatography (ethyl acetate–hexane, 3/1) of the crude obtained after evaporation of the solvent afforded starting material (**23**) (14%) and 1-aza-4-benzylbicyclo[3.3.0]oct-4-en-8-one (**33**) (54%): IR (CH_2Cl_2) 1681 cm^{-1}; ^1H NMR δ 2.34–2.44 and 2.7 (2 m, 4 H, 6-CH_2 and 7-CH_2), 2.8 (m, 2 H, 3-CH_2), 3.33 (s, 2 H, $PhCH_2$), 3.61 (t, J = 8.7 Hz, 2 H, 2-CH_2), 7.15–7.33 (m, Ph); ^{13}C NMR (270 MHz) δ 17.81, 33.50, 34.68, 39.88, 110.34, 126.33, 128.51, 128.64, 139.18, 140.3, and 170.33; HRMS m/e M^+ 213.1169 (calcd for $C_{14}H_{15}NO$ 213.1149.1286), 136 (M^+ – Ph), 122 (M^+ – $PhCH_2$).

Cyclization of 1-((*E*)-4-Phenylbut-3-en-1-yl)thiosaccharin (24). The reaction was performed according to procedure E for 30 min, flash chromatography (ethyl acetate–hexane, 1/6) of the crude obtained after evaporation of the solvent afforded the tributyltin derivative **34** (54%): mp 118–120 °C (methylene chloride/hexane); IR (CH_2Cl_2) 1171, 1247 cm^{-1}; ^1H NMR δ 0.81–1.41 (m, 27 H, *n*-Bu_3Sn), 2.1–2.3 (m, 2 H), 2.3–2.45 (m, 1 H), 2.92–3.15 (m, 2 H), 3.31–3.39 (m, 1 H), 3.71–3.81 (m, 1 H), 7.05–7.25 (m, Ph), 7.75–7.73 (m, 4 H, Ar). Anal. Calcd for $C_{29}H_{43}NO_2S_2Sn$: C, 56.1; H, 7.0; N, 2.3; S, 10.3. Found: C, 55.8; H, 6.6; N, 2.4; S, 10.1.

Pyrrolinodihydrobenzisothiazole, 35. Conversion of **34** into **35** with TFA is quantitative, and the reaction can be performed using the crude reaction mixture from the cyclization of **24**. Thus, when cyclization of **24** (1 mmol) was completed (TLC), the reaction mixture was cooled to room temperature and stirred with TFA (2 mL) for 4 h. The reaction mixture was then neutralized with a saturated $NaHCO_3$ solution. Flash chromatography (ethyl acetate–hexane, 1/6) of the crude obtained after standard workup afforded the pyrrolinodihydrobenzisothiazole (**35**) (60%): mp 140 °C; IR (CH_2Cl_2) 1161, 1263 cm^{-1}; ^1H NMR δ 2.93 (t, J = 8.5 Hz, 2 H), 3.69 (t, J = 8.4 Hz, 2 H), 3.84 (s, 2 H, $PhCH_2$), 7.20–7.51 (m, Ph), 7.53–7.85 (m, 4 H, Ar). Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.7; H, 5.1; N, 4.7; S, 10.8. Found: C, 68.6; H, 5.0; N, 4.7; S, 10.7.

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Preparation of (*p*-Phenylene)bis(aryliodonium) Ditriflates and Their Double Substitution by Some Nucleophiles

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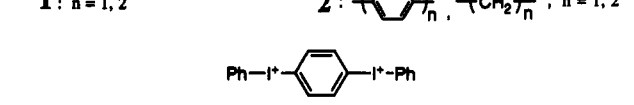
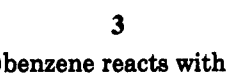
A reagent prepared from a 1:1 molar mixture of PhIO and Tf_2O or from a 1:2 molar mixture of PhIO and TfOH shows high reactivity toward aromatic substrates and gives (*p*-phenylene)bis(aryliodonium) ditriflates (**8**). Interaction of the reagent [PhIO–Tf_2O] with cyclohexene suggests that it has a *p*-[phenyl[(trifluoromethanesulfonyl)-oxy]iodo]phenyliodine(III) structure. Reactions of (*p*-phenylene)bis(aryliodonium) ditriflates with pyridine, triphenylphosphine, or diphenyl sulfide give doubly para-substituted benzene derivatives in good to high yields.

Much attention has recently been paid to the utilization of iodine(III) compounds for organic synthesis.[1] Iodine(III) compounds containing aryl, alkenyl, alkynyl, and fluoroalkyl ligands are most conveniently prepared from reagents bearing the phenyliodonio [PhI(III)] group. The phenyliodonio group is highly sensitive to replacement by nucleophiles and useful for the introduction of functional groups. If polyphenyliodinated compounds are employed, one can introduce polyfunctionality into the substrate. Recently, Stang and co-workers[2] have prepared bis-iodonium compounds of types **1** and **2** which can be used for the introduction of bifunctionality. *p*-Phenylene bis-iodonium salts **3** are also known,[3] having been prepared by the oxidation of 1,4-diiodobenzene to 1,4-bis(diacetoxyiodo)benzene and subsequent condensation of the latter with benzene in the presence of concentrated H_2SO_4. However, little attention has been paid to the synthesis and reactions of these compounds.



1: n = 1, 2

2: n = 1, 2



3

(Diacetoxyiodo)benzene reacts with triflic acid to give μ-oxybis[(trifluoromethanesulfonyl)oxy](phenyl)iodine] (**4**)[4] known as Zefirov's reagent. Zefirov's reagent can also

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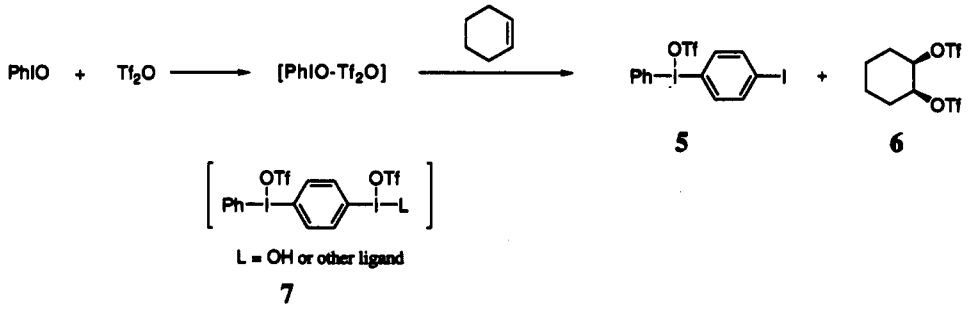
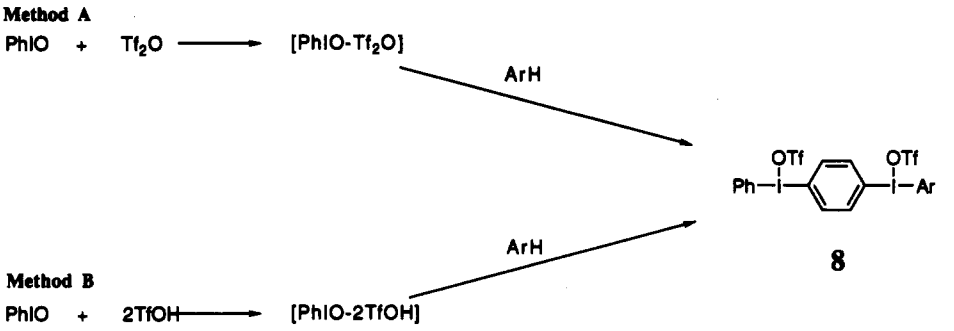
Scheme I



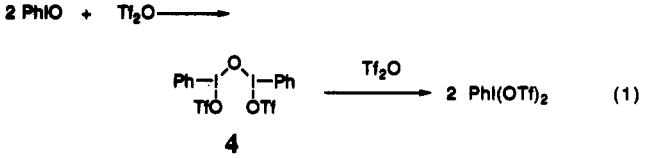
Scheme II



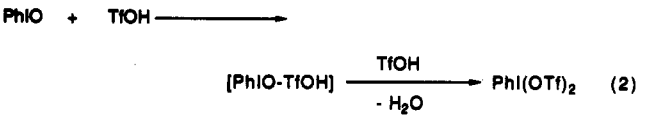
be prepared by the combination of 2 equiv of iodosylbenzene (PhIO) with an equimolar amount of triflic anhydride[5] and has been employed for preparation of 1,2-ditriflates[4,5] and the parent alkynyliodonium triflate.[6] We have recently found that a reagent [PhIO–TfOH] made from equimolar amounts of PhIO and triflic acid reacts with alkynes and aromatic substrates to give aryl(vinyl)-[7] and diaryliodonium triflates.[8] However, when 1 equiv of PhIO was treated with 1 equiv of triflic anhydride, a drastic change in the reaction was observed.[9] A similar change of the reaction was found when 1 equiv of PhIO was treated with 2 equiv of triflic acid. We now report that (*p*-phenylene)bis(aryliodonium) ditriflates can be prepared directly by the reactions of [PhIO–Tf_2O] or [PhIO–2TfOH] with aromatic substrates. The (*p*-phenylene)bis(aryliodonium) ditriflates undergo double substitution reactions with selected nucleophiles to give novel (*p*-phenylene)-*bisonium* salts.

Results and Discussion

The combination of equimolar quantities of PhIO and triflic anhydride might be expected to generate $PhI(OTf)_2$, a compound known to be formed by the treatment of the Zefirov's reagent with triflic anhydride[10] (eq 1). The



formation of $PhI(OTf)_2$ is also expected from the reaction of PhIO with 2 molar equiv of triflic acid (eq 2). Zefirov



et al. have prepared $PhI(OTf)_2$ by the addition of TMSOTf to PhIO in dichloromethane, and this reagent exhibits high reactivity toward unsaturated substrates.[10]

However, the reagent prepared by the treatment of PhIO with equimolar triflic anhydride exhibited different behavior from $PhI(OTf)_2$. When the reagent [PhIO–Tf_2O], generated in situ, was allowed to react with cyclohexene, (*p*-iodophenyl)phenyliodonium triflate (**5**) and cyclohexane-1,2-diyl ditriflate (**6**) were produced (Scheme I). The formation of cyclohexane-1,2-diyl ditriflate in the reaction of Zefirov's reagent with cyclohexene is known,[4,5] the byproducts being iodobenzene and iodosylbenzene. The formation of (*p*-iodophenyl)phenyliodonium triflate **5** in the present study is noteworthy and suggests that the reagent [PhIO–Tf_2O] has the *p*-[(phenyl)[(trifluoromethanesulfonyl)oxy]iodo]phenyliodine(III) structure (**7**). As described later, this structure of [PhIO–Tf_2O] is supported by the reactions of [PhIO–Tf_2O] with aromatic substrates which provide (*p*-phenylene)bis(aryliodonium) ditriflates (**8**).

Preparation of (*p*-Phenylene)bis(aryliodonium) Ditriflates (8). Iodosylbenzene was treated with equimolar triflic anhydride in dichloromethane, and the resulting reagent [PhIO–Tf_2O] was allowed to react with aromatic substrates. Within a few minutes, white crystalline solids separated and exhibited characteristic ^1H and ^{13}C NMR spectra consistent with (*p*-phenylene)bisiodonium structures. The aromatic protons ortho to the iodine(III) atoms appear at relatively low field, δ 8.20–8.40. The ^{13}C signals of the four aromatic carbons attached to the iodine(III) atoms showed high-field shifts around δ

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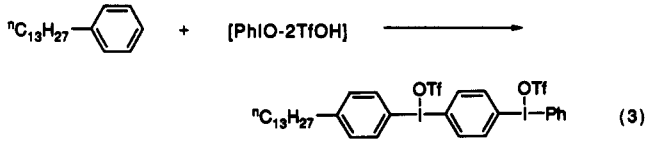
Table I. Preparation of Aryl(phenyl)(*p*-phenylene)bisiodonium Ditriflates 8

entry	aromatic substrate	reagent	product	isolated yield, %
1	benzene	[PhIO–Tf_2O]	8a	73
2		[PhIO–2TfOH]		92
3	toluene	[PhIO–Tf_2O]	8b	76
4		[PhIO–2TfOH]		98
5	*tert*-butylbenzene	[PhIO–2TfOH]	8c	76
6	*p*-xylene	[PhIO–2TfOH]	8d	74
7	indane	[PhIO–2TfOH]	8e	96
8	anisole	[PhIO–2TfOH]	8f	76
9	benzyl methyl ether	[PhIO–2TfOH]	8g	78
10	benzylcyanide	[PhIO–2TfOH]	8h	78
11	chlorobenzene	[PhIO–Tf_2O]	8i	65
12	bromobenzene	[PhIO–Tf_2O]	8j	71
13	*n*-tridecylbenzene	[PhIO–2TfOH]	8k	75

100–120. The combustion analyses are well in accord with calculated values. The results are given in Table I. Thus, arylation at the iodine(III) atom of the prepared reagent proceeds readily to provide (*p*-phenylene)bis(aryliodonium) ditriflates (8) (Scheme II). Furthermore, when benzene and toluene were mixed with the reagent [PhIO–2TfOH] prepared in situ from PhIO and triflic acid, the products were the same as those obtained from [PhIO–Tf_2O] (entries 2 and 4). Accordingly, it is suggested that the reagents [PhIO–Tf_2O] and [PhIO–2TfOH] have either the same or very similar structures such as **7**. Arylation occurs with benzene derivatives containing electron-donating to weakly electron-withdrawing substituents but did not occur with strongly deactivated aromatic compounds such as nitrobenzene.

In order to assess the reactivity of the reagent prepared in this work, the arylation reactions are qualitatively compared with those effected with other hypervalent iodine(III) reagents, Koser's reagent [PhI(OH)OTs], [PhIO–H_2SO_4], and [PhIO–TfOH]. Koser's reagent reacts with anisole but does not react with benzene or toluene.[11] [PhIO–H_2SO_4] reacts with benzene but not with bromobenzene.[12] [PhIO–TfOH] reacts with halobenzenes only in refluxing dichloromethane.[8] Accordingly, the relative reactivities of these hypervalent iodine(III) reagents appear to conform to the trend [PhI(OH)OTs] < [PhIO–H_2SO_4] < [PhIO–TfOH] < [PhIO–Tf_2O] or [PhIO–2TfOH]. The high reactivity of [PhIO–Tf_2O] or [PhIO–2TfOH] may derive from the nucleofugacity of the TfO group[13] and the electron-withdrawing nature of the phenyliodonio group at the para position.[14]

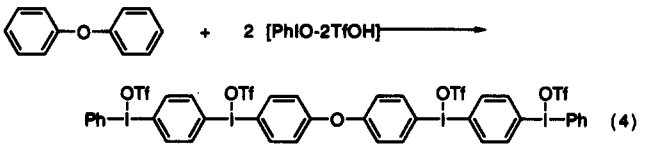
Reactions were also conducted with an alkylbenzene bearing a long alkyl chain and with diphenyl ether. Tridecylbenzene gave a good yield of the bisiodonium ditriflate **8k** which is expected to have ambiphilic character (eq 3). In the reaction with diphenyl ether, the bis-



(3)

8k

iodonium functionality was introduced into two phenyl groups, and the novel tetrakisiodonium salt **9** was obtained quantitatively (eq 4).



(4)

9

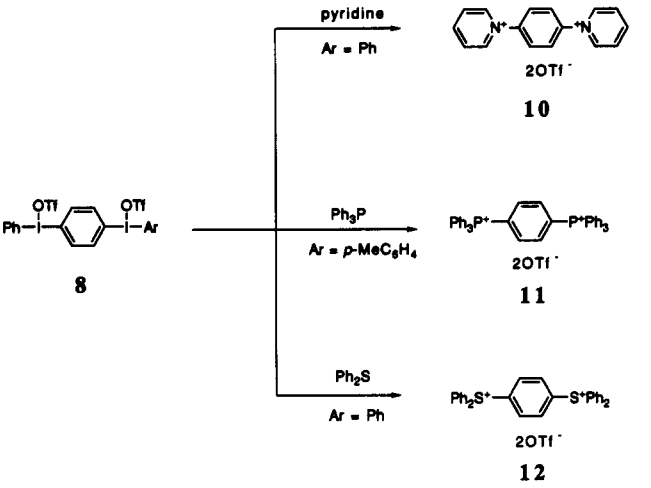
Double Substitution of (*p*-Phenylene)bis(aryliodonium) Ditriflates (8). The phenyliodine(III) group is a good leaving group and diaryliodonium salts have been used for the arylations of a variety of nucleophilic substrates.[1] It is noteworthy that (*p*-phenylene)bis(aryliodonium) triflates (8) have *two phenyliodine(III) groups* on a single aromatic ring, and the aromatic ring of the *p*-phenylene moiety is *activated by two iodine(III) atoms*. This unique structural feature of the (*p*-phenylene)bis(aryliodonium) salts prompted us to study substitution reactions as a new method for the introduction of the *p*-phenylene moiety.

Good to high yields of doubly substituted benzene derivatives were obtained by using (*p*-phenylene)bisiodonium ditriflates (8) (Scheme III). When (*p*-phenylene)bis(phenyliodonium) ditriflate (**8a**) was allowed to react with pyridine under reflux, (*p*-phenylene)bispyridinium ditriflate (**10**) was obtained in 37% yield. The treatment of bisiodonium ditriflate **8b** with triphenylphosphine in ethanol under reflux gave (*p*-phenylene)bis(triphenylphosphonium) ditriflate (**11**) quantitatively (Scheme III). The double substitution by pyridine is interesting since diphenyliodonium salts do not yield N-arylated pyridines with pyridine but give a mixture of 2-, 3-, and 4-phenylpyridines.[3]

Finally, when a mixture of (*p*-phenylene)bisiodonium ditriflate (**8a**) and diphenyl sulfide (4–8 equiv) in the presence of a catalytic amount of copper(II) acetate was heated (120–130 °C), (*p*-phenylene)bis(diphenylsulfonium) ditriflate (**12**) was obtained in quantitative yield (Scheme III).

In summary, we have prepared directly (*p*-phenylene)bis(aryliodonium) ditriflates (8) by using the reaction of [PhIO–Tf_2O] or [PhIO–2TfOH] with aromatic substrates. This method is convenient and versatile because of the high reactivity of the reagent [PhIO–Tf_2O] or [PhIO–2TfOH] and the high yields of the products 8. The reactions with some nucleophiles indicate a potent synthetic application to 1,4-disubstituted benzene derivatives.

Scheme III



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Experimental Section

General. Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. ^1H NMR spectra were obtained with a HITACHI R-600 (60 MHz), a Bruker AC-250P (250 MHz), or a JEOL GSX-400 (400 MHz) spectrometer, and ^{13}C NMR spectra with a Bruker AC-250P (62.9 MHz) or a JEOL GSX-400 (100.5 MHz) spectrometer. Chemical shifts are given in ppm. IR spectra were recorded with a HITACHI 270-30 spectrometer. Microanalyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. Iodosylbenzene was prepared from (diacetoxy)iodobenzene (Aldrich Chemical Co.) according to the reported procedure.[15]

Preparation of [PhIO–Tf_2O] in Situ and the Reaction with Cyclohexene. To a stirred suspension of PhIO (0.66 g, 3 mmol) in CH_2Cl_2 (5 mL) was added dropwise Tf_2O (0.55 mL, 3.3 mmol) at room temperature. After the mixture was stirred for 15 h at room temperature, cyclohexene (0.3 mL, 3 mmol) was added and the resulting mixture was stirred for 4 h. The solvent was evaporated and the residue was treated with ether, giving crystals. The crystals were filtered and dried in vacuo, yielding 0.584 g of **(p-iodophenyl)(phenyl)iodonium triflate (5)** (70%): mp 126–129 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.35–7.46 (m, 2 H, ArH), 7.57–7.64 (m, 1 H, ArH), 7.72 (s, 4 H, ArH), 7.96–8.03 (m, 2 H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$–DMSO-d_6) δ 98.22, 113.73, 114.63, 130.55, 130.87, 133.76, 135.17, 139.28. Anal. Calcd for $C_{13}H_9F_3I_2O_3S$: C, 28.08; H, 1.63. Found: C, 28.33, H, 1.68. The filtrate was evaporated and the ^1H NMR (400 MHz) of the residue showed the presence of **cyclohexane-1,2-diyl ditriflate (6)**[4,5] in $CDCl_3$ [δ 1.40–1.60 (m, 2 H), 1.65–1.80 (m, 2 H), 1.80–1.90 (m, 2 H), 2.10–2.20 (m, 2 H), 5.05–5.13 (m, 2 H)].

Preparation of (p-Phenylene)bis(aryliodonium) Ditriflates (8). Method A. To a stirred suspension of PhIO (0.44 g, 2 mmol) in CH_2Cl_2 (5 mL) was added dropwise Tf_2O (0.34 mL, 2 mmol) at room temperature. After the mixture was stirred for 3 h, an aromatic substrate (2 mmol) was added, generating crystals in a few minutes. The mixture was stirred for 2 h, and the crystals were filtered, washed with ether, and dried in vacuo.

Method B. The same procedure as method A was adapted except for use of TfOH (0.35 mL, 4 mmol) instead of Tf_2O.

1,4-Bis[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8a): mp 304–306 °C; ^1H NMR (250 MHz, DMSO-d_6) δ 7.50–7.56 (m, 4 H, ArH), 7.64–7.70 (m, 2 H, ArH), 8.24–8.33 (m, 8 H, ArH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 116.62, 120.33, 132.01, 132.48, 135.50, 137.76. Anal. Calcd for $C_{20}H_{14}F_6I_2O_6S_2$: C, 30.71; H, 1.81. Found: C, 30.60; H, 1.78.

1-[(4-Methylphenyl)[(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8b): mp 283–285 °C; ^1H NMR (400 MHz, CD_3OD) δ 2.39 (s, 3 H, Me), 7.33–7.35 (m, 2 H, ArH), 7.51–7.55 (m, 2 H, ArH), 7.68–7.72 (m, 1 H, ArH), 8.06–8.08 (m, 2 H, ArH), 8.20–8.27 (m, 6 H, ArH); ^{13}C NMR (100 MHz, CD_3OD) δ 21.40, 112.36, 116.15, 119.78, 120.01, 133.42, 134.11, 134.15, 136.89, 138.95, 139.10, 145.69. Anal. Calcd for $C_{21}H_{16}F_6I_2O_6S_2$: C, 31.67; H, 2.03. Found: C, 31.53; H, 1.95.

1-[(4-*tert*-Butylphenyl)[(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8c): mp 283–286 °C; ^1H NMR (250 MHz, CD_3OD) δ 1.30 (s, 9 H, Me), 7.50–7.60 (m, 4 H, ArH), 7.68–7.74 (m, 1 H, ArH), 8.10–8.13 (m, 2 H, ArH), 8.23–8.24 (m, 6 H, ArH); ^{13}C NMR (62.9 MHz, CD_3OD) δ 31.32, 36.21, 112.63, 116.19, 119.86, 119.97, 130.77, 133.43, 134.12, 136.71, 136.92, 139.06, 139.13, 158.40. Anal. Calcd for $C_{24}H_{22}F_6I_2O_6S_2$: C, 34.38; H, 2.65. Found: C, 34.25; H, 2.65.

1-[(2,5-Dimethylphenyl)[(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8d): mp 218–226 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 2.29 (s, 3 H, Me), 2.53 (s, 3 H, Me), 7.39–7.45 (m, 2 H, ArH), 7.51–7.55 (m, 2 H, ArH), 7.66–7.70 (m, 1 H, ArH), 8.22–8.31 (m, 7 H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.93, 24.38, 116.59, 119.22, 119.99, 121.10, 131.13, 131.84, 132.33, 133.70, 135.33, 137.07, 137.43, 137.58, 139.23. Anal. Calcd for $C_{22}H_{18}F_6I_2O_6S_2$: C, 32.61; H, 2.24. Found: C, 32.40; H, 2.23.

1-[(5-Indanyl)[(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8e): mp 264–274 °C; ^1H NMR (250 MHz, DMSO-d_6) δ 1.93–2.05 (m, 2 H, CH_2), 2.86–2.92 (m, 4 H, CH_2), 7.36–7.70 (m, 4 H, ArH), 7.87–8.40 (m, 8 H, ArH). Anal. Calcd for $C_{23}H_{19}F_6I_2O_6S_2$: C, 33.59; H, 2.21. Found: C, 33.50; H, 2.28.

1-[(4-Methoxyphenyl)[(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8f): mp 276–279 °C; ^1H NMR (250 MHz, DMSO-d_6) δ 3.79 (s, 3 H, OMe), 7.05–7.09 (m, 2 H, ArH), 7.50–7.56 (m, 2 H, ArH), 7.65–7.71 (m, 1 H, ArH), 8.16–8.19 (m, 2 H, ArH), 8.25–8.34 (m, 6 H, ArH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 55.66, 105.29, 116.69, 117.57, 119.95, 120.54, 131.85, 132.32, 135.31, 137.22, 137.42, 137.50, 162.15. Anal. Calcd for $C_{21}H_{16}F_6I_2O_7S_2$: C, 31.05; H, 1.99. Found: C, 30.94; H, 1.99.

1-[[4-(Methoxymethyl)phenyl][(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8g): mp 248–250 °C; ^1H NMR (250 MHz, DMSO-d_6) δ 3.29 (s, 3 H, OMe), 4.45 (s, 2 H, CH_2), 7.44–7.56 (m, 4 H, ArH), 7.65–7.70 (m, 1 H, ArH), 8.21–8.40 (m, 8 H, ArH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 57.83, 72.35, 114.92, 116.65, 120.12, 120.24, 130.29, 131.84, 132.31, 135.31, 137.53, 143.62. Anal. Calcd for $C_{22}H_{18}F_6I_2O_7S_2$: C, 31.98; H, 2.20. Found: C, 32.49; H, 2.20.

1-[[4-(Cyanomethyl)phenyl][(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8h): mp 276–279 °C; ^1H NMR (250 MHz, CD_3OD) δ 4.01 (s, 2 H, CH_2), 7.50–7.56 (m, 4 H, ArH), 7.68–7.74 (m, 1 H, ArH), 8.20–8.30 (m, 8 H, ArH); ^{13}C NMR (62.9 MHz, CD_3OD) δ 23.46, 115.13, 116.19, 118.57, 119.25, 120.00, 120.09, 133.05, 133.43, 134.12, 136.90, 137.51, 138.40, 139.19. Anal. Calcd for $C_{22}H_{15}F_6I_2NO_6S_2$: C, 32.17; H, 1.84. Found: C, 31.91; H, 1.86.

1-[(4-Chlorophenyl)[(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8i): mp 278–283 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 7.52–7.55 (m, 2 H, ArH), 7.61–7.63 (m, 2 H, ArH), 7.66–7.68 (m, 1 H, ArH), 8.25–8.27 (m, 4 H, ArH), 8.32 (s, 4 H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 114.37, 116.62, 120.21, 120.37, 131.84, 132.31, 135.31, 137.14, 137.54, 137.62, 137.69. Anal. Calcd for $C_{20}H_{13}ClF_6I_2O_6S_2$: C, 29.41; H, 1.61. Found: C, 29.35; H, 1.61.

1-[(4-Bromophenyl)[(trifluoromethanesulfonyl)oxy]iodo]-4-[phenyl[(trifluoromethanesulfonyl)oxy]iodo]benzene (8j): mp 258–267 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 7.52–7.56 (m, 2 H, ArH), 7.66–7.68 (m, 1 H, ArH), 7.74–7.77 (m, 2 H, ArH), 8.18–8.20 (m, 4 H, ArH), 8.26–8.28 (m, 4 H, ArH), 8.33 (s, 4 H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 115.09, 116.62, 120.21, 120.32, 126.55, 131.86, 132.31, 134.73, 135.31, 137.23, 137.56, 137.62. Anal. Calcd for $C_{20}H_{13}BrF_6I_2O_6S_2$: C, 27.89; H, 1.52. Found: C, 27.92; H, 1.48.

1-[Phenyl[(trifluoromethanesulfonyl)oxy]iodo]-4-[(4-*n*-tridecylphenyl)[(trifluoromethanesulfonyl)oxy]iodo]benzene (8k): mp 221–223 °C; ^1H NMR (250 MHz, DMSO-d_6) δ 0.85 (t, J = 6.3 Hz, 3 H, Me), 1.23 (bs, 20 H, CH_2), 1.52 (bs, 2 H, CH_2), 2.59 (t, J = 7.5 Hz, 2 H, CH_2), 7.34–7.37 (m, 2 H, ArH), 7.50–7.56 (m, 2 H, ArH), 7.56–7.71 (m, 1 H, ArH), 8.13–8.16 (m, 2 H, ArH), 8.25–8.32 (m, 6 H, ArH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 13.86, 22.02, 28.55, 28.63, 28.69, 28.95, 30.49, 31.22, 34.69, 113.13, 116.67, 120.08, 131.84, 132.30, 135.33, 137.50, 147.57. Anal. Calcd for $C_{33}H_{40}F_6I_2O_6S_2$: C, 41.08; H, 4.19. Found: C, 41.18; H, 4.24.

Reaction of (p-Phenylene)bis(aryliodonium) Ditriflate 8a with Pyridine. A mixture of **8a** (784 mg, 1 mmol) and pyridine (4.5 mL, 56 mmol) was refluxed with stirring for 2 h. After removal of pyridine in vacuo the resulting crystals were filtered, washed, and dried in vacuo, yielding 198 mg of **(p-phenylene)bispyridinium ditriflate (10)** (37%): mp 305–323 °C; ^1H NMR (250 MHz, DMSO-d_6) δ 8.30 (s, 4 H, ArH), 8.36–8.41 (m, 4 H, pyr-H), 8.84–8.90 (m, 2 H, pyr-H), 9.41–9.43 (m, 4 H, pyr-H); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 126.72, 128.18, 144.21, 145.03, 147.33. Anal. Calcd for $C_{18}H_{14}F_6N_2O_6S_2$: C, 40.60; H, 2.66; N, 5.26. Found: C, 40.68; H, 2.67; N, 5.29.

Reaction of (p-Phenylene)bis(aryliodonium) Ditriflate 8b with Triphenylphosphine. A mixture of **8b** (804 mg, 1 mmol), triphenylphosphine (2.63 g, 10 mmol), and EtOH (13 mL) was placed in a Pyrex flask and exposed to sunlight for 3 days. After evaporation of the solvent ether was added to dissolve the unreacted triphenylphosphine and the residual crystals were filtered and washed with ether and methanol, giving white crystals of **(p-phenylene)bis(triphenylphosphonium) ditriflate (11)** (1.026 g, 100%): mp 325–336 °C; ^1H NMR (250 MHz, DMSO-d_6)

δ 7.77–7.84 (m, 24 H, ArH), 7.97–8.02 (m, 6 H, ArH), 8.09–8.15 (m, 4 H, ArH). Anal. Calcd for $C_{44}H_{34}F_6O_6P_2S_2$: C, 58.79; H, 3.82. Found: C, 58.93; H, 3.89.

Reaction of (*p*-Phenylene)bis(aryliodonium) Ditriflate 8a with Diphenyl Sulfide. A mixture of **8a** (789 mg, 1 mmol), $Cu(OAc)_2$ (9 mg, 0.05 mmol), and diphenyl sulfide (1.36 mL, 8.2 mmol) was gradually heated with stirring to 200 °C. After being stirred for 30 min at 200 °C the mixture was cooled to room temperature and was triturated with ether to give 771 mg of **(*p*-phenylene)bis(diphenylsulfonium) ditriflate (12)** (100%) as white crystals: mp 103–125 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72–7.75 (m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.26, 131.12, 131.75, 132.45, 134.81, 140.83. Anal. Calcd for $C_{44}H_{34}F_6O_6S_4$: C, 51.46; H, 3.25. Found: C, 51.32; H, 3.35.

Nucleophilic Reactions of Molybdate

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Although molybdate (MoO_4^{2-}) is over 1000 times less basic than the phosphate dianion it is 35 times more nucleophilic toward *p*-nitrophenyl acetate (pNPA) and *p*-nitrophenyl thioacetate (pNPTA) at 27 °C (Wikjord, B.; Byers, L. D. *J. Am. Chem. Soc.* **1992**, *114*, 5553). Based on Bronsted relationships for the reaction of a series of phosphonate dianions with these esters (β_{nuc} = 0.3 at 37 °C), molybdate (pK_{a2} = 3.9) is as reactive as a phosphonate with pK_{a2} = 12. The activation parameters are $\Delta H^{\ddagger}$ = 15.8 (±0.1) kcal/mol and $\Delta S^{\ddagger}$ = −17.4 (±0.4) eu for the reaction with pNPA and $\Delta H^{\ddagger}$ = 16.0 (±0.2) kcal/mol and $\Delta S^{\ddagger}$ = −15.0 (±0.6) eu for the reaction with pNPTA. The second-order rate constant for the reaction of MoO_4^{2-} with a series of 13 acyl-substituted *p*-nitrophenyl esters at 27 °C shows nearly identical sensitivity to substituent effects (ρ^* = 2.8) as does the rate of alkaline hydrolysis or the equilibrium addition of hydroxide to aldehydes (Shames, S. L.; Byers, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 6170), suggesting that the transition state for the molybdenolysis reaction closely resembles the tetrahedral intermediate. In addition to the reaction with activated carboxylic esters, molybdate catalyzes the hydrolysis of a variety of electrophiles. The second-order rate constants (M^{-1} min^{-1}, 27 °C, μ = 1.5 M) for the reactions of molybdate are 0.25 (±0.01) with ethyl pyruvate, (2.10 ± 0.08) × 10^{-2} with 2,4-dinitrofluorobenzene, and (7.2 ± 0.4) × 10^{-5} with methyl iodide.

We have recently reported our observations on the remarkable nucleophilic reactivity of the molybdate dianion toward *p*-nitrophenyl acetate (pNPA) and *p*-nitrophenyl thioacetate (pNPTA).[1] Although molybdate (pK_{a2} = 4.1, 25 °C) is over 3 orders of magnitude *less basic* than the phosphate dianion it was found to be 35 times *more reactive* toward these esters than is phosphate and significantly more (20–500-fold) reactive toward pNPA than nucleophiles (e.g., aniline, acetate) of comparable basicity.[2] This study was undertaken in order to get a clearer picture of the mechanism of the molybdate-catalyzed ester hydrolysis reaction and to see if the unusual nucleophilic reactivity is a unique feature of acyl-transfer reactions.

Experimental Section

Materials. *p*-Nitrophenyl acetate, propionate, *n*-butyrate, and trimethylacetate were obtained from Aldrich Chemical Co., and *p*-nitrophenyl thioacetate was obtained from U.S. Biochemical Corp. The other *p*-nitrophenyl esters were from previous studies.[3,4] *o*-Nitrophenyl acetate, ethyl pyruvate, 2,4-dinitrofluorobenzene, bis(*p*-nitrophenyl) phosphate, HEPES[5] buffer, NADH,[5] and lactate dehydrogenase (rabbit muscle, specific activity = 860 units/mg) were obtained from Sigma Chemical Co. Sodium molybdate (dihydrate), 2,4-dinitrochlorobenzene, and methyl iodide were obtained from Matheson, Coleman, and Bell. Molybdate stock solutions (0.5 M) were prepared by dissolving Na_2MoO_4 in buffer solutions (0.01 M HEPES) and adjusting the pH to 7.5 with HCl (or DCl in D_2O). At this pH there is negligible polymerization of molybdate.[6] D_2O (99.8%) was from Sigma Chemical Co.

Methods. pH measurements were made with a Metrohm (Brinkmann) combititrator. pD values were estimated by adding 0.41 to the pH meter reading.[7] For the ester hydrolysis reactions, kinetics were followed by measuring the absorbance (λ = 400 nm for *p*-nitrophenoxide or 412 nm for *p*-nitrophenylthiolate) on a Hewlett-Packard Model 8452A diode array spectrophotometer equipped with a circulating water bath (Endocal) to maintain temperatures (±0.1°) in the sample (determined with a calibrated digitally monitored thermocouple). The reactions were initiated by adding 10 μL of the ester (10 mM in CH_3CN) to 1 mL of a thermally equilibrated buffer solution (ionic strength maintained at 1.6 M with Na_2SO_4 and, for the reactions with the esters only, 0.1 M NaCl). In general, the increase in the absorbance was typically followed for at least 4 half-lives and the data were analyzed by nonlinear regression to a first-order curve.[8] The internal standard deviations of the pseudo-first-order rate constants were consistently less than 1%. Rate constants were determined at least in triplicate for each reaction. The kinetics for the hydrolysis of ethyl pyruvate (pH = 7.5, 0.01 M HEPES, μ = 1.5 M maintained with Na_2SO_4) was obtained by coupling the reaction to the lactate dehydrogenase reaction (pyruvate + NADH → L-lactate + NAD) and monitoring the decrease in absorbance at 340 nm due to NADH. The reaction was initiated by adding 10 μL of an ethanolic solution of ethyl pyruvate (10 mM) to a 1-mL thermally equilibrated solution containing the desired concentration of molybdate, NADH (0.2 mM), and lactate dehydrogenase (25 μg/mL). The absorbance followed a single exponential decay

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