of least squares from the slope of a plot of $1/[ArSO_3Me]$ vs. time. The precision of this method is limited by the rather low solubility of the potassium benzenesulfonate (since doing this work we have been able to increase these concentrations by using 18-crown-6) and with some aryl groups by the poor resolution of the two methoxy groups. The problem of resolution is compounded by the fact that the spectra were taken unlocked, because tetramethylsilane is not soluble enough in sulfolane, and the sulfolane-d_4 peak is too broad to give a good lock.

Equilibrium Measurements. Equivalent concentrations of potassium benzenesulfonate and the substituted methyl benzenesulfonates with the substituents used (*o*-NO_2, 2,5-dichloro, pentafluoro) did not give any measurable amount of starting ester. Thus to measure the equilibria, a substantial measured excess of unsubstituted methyl benzenesulfonate was added to an NMR tube containing potassium benzenesulfonate and the substituted methylbenzenesulfonate. The tube was sealed and put in the thermostat until there was no further change, the concentrations of the two methyl esters were measured, and the equilibrium constant was calculated. This was successful for the first two substituents mentioned above but not for the pentafluoro-substituted compound. Hence equilibrium between the pentafluoro ester and potassium 2,5-dichlorobenzenesulfonate was measured as a relay to get the desired equilibrium constant for the pentafluoro and unsubstituted esters.

Reactions with Methylating Agents. The reactions of Table III were all done in NMR tubes, with a capillary containing tetramethylsilane as external reference. As an example, methyl 2,4,6-trinitrobenzenesulfonate (ca. 50 mg) was dissolved in methyl chlorosulfite[17] (1 mL) in an NMR tube. When solution was complete, the NMR spectrum (Varian EM390) was taken; none of the methyl group of the sulfonate ester remained; the other peaks are described in footnote *b* of Table II.

Acknowledgment. We acknowledge gratefully a grant from the National Science Foundation supporting this work. Support from a grant from the Robert A. Welch Foundation for a portion of this work is also gratefully acknowledged.

Registry No. Methyl pentafluorobenzenesulfonate, 4434-87-1; methyl 2-nitrobenzenesulfonate, 30384-53-3; methyl 2,5-dichlorobenzenesulfonate, 78150-04-6; potassium benzenesulfonate, 934-55-4; potassium 2,5-dichlorobenzenesulfonate, 46019-98-1; dimethylphenylsulfonium triflate, 85980-21-8; dimethyl sulfate, 77-78-1; potassium iodide, 7681-11-0; methyl 2,4,6-trinitrobenzenesulfonate, 53541-31-4; methyl triflate, 333-27-7.

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Methyl-Transfer Reactions. 7. System with CH_3OSO^+ Intermediate

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Methyl chlorosulfite with antimony pentachloride in thionyl chloride initially at dry ice temperature is a very powerful methylating system. It methylates sulfones, methyl chloride, and even to some extent dimethyl sulfate. The active methylating species is apparently the cation CH_3OSO^+. Dimethyl sulfite is decomposed catalytically by methyl trifluoromethanesulfonate to dimethyl ether and sulfur dioxide, and the same cation appears to be intermediate. The mechanism includes an exchange of the methyl groups between the two esters, allowing a practical synthesis of methyl-d_3 triflate. Dimethyl sulfite does not methylate detectably on sulfur.

Introduction

Powerful methylating agents are in principle compounds or ions with methyl attached to good leaving groups. Anionic leaving groups of exceptional stability are ClO_4^-, FSO_3^-, $F_3CSO_3^-$, 2,4,6-$(NO_2)_3C_6H_2SO_3^-$, listed in order of apparent increasing methylating power.[1-3] However, still more powerful cationic methylating agents may be designed with neutral leaving groups; thus trimethyloxonium ion is more powerful than methyl triflate, although less so than methyl 2,4,6-trinitrobenzenesulfonate.[3] Dimethylhalonium ions are presumably more powerful than trimethyloxonium ion, but even less nucleophilic leaving groups than methyl halides are known, notably N_2 from $CH_3N_2^+$, the leaving group in the system diazomethane + acid, as well as in perceptibly stable diazonium salts. The system $CH_3F + SbF_5$ is perhaps as powerful as any well-characterized system, but one can conceive of other stable neutral molecule leaving groups, some of which may show reactions other than methylation, such as the known mass spectrometric species $CH_3^+H_2(CH_5^+)$ and CH_3Ar^+, and in the gas-phase limit, CH_3^+. In solution, however, the solvent will always be attached to methyl if there is not a better nucleophile in solution. Thus in the solvent S, no better methylating agent than CH_3S^+ will exist at equilibrium, although (in contrast to the leveling effect of solvents on proton acidity) more powerful methylating agents than CH_3S^+ may have transient stability, since the methyl-transfer reactions are often perceptibly slow. Thus it is possible to do alkylations in aqueous solution with cyclic halonium salts[4] or with methyl triflate.[5] In this paper we shall be concerned with the species CH_3OS^+O (*1*), which is formally the ultimate methylating agent in liquid SO_2 and can be made from SO_2 and a more powerful methylating agent. This has been realized, by the mixture of $CH_3F + SbF_5 + SO_2$, and the ion CH_3OS^+O has been well identified in solution[6] and as a crystalline salt with the counter ion $Sb_2F_{11}^-$.[7] The use of CH_3F, SbF_5, or CH_2N_2 + acid are possible but expensive, inconvenient, and hazardous methods. Our approach has been to use the

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0022-3263/83/1948-2531$01.50/0

cheap and readily available methyl chlorosulfite and antimony pentachloride as a possible source of this cation and to study its methylating power and other reactions. The same cation is implicated as an intermediate in the decomposition of dimethyl sulfite initiated by methylation.

We were also interested in dimethyl sulfite as a possible ambident nucleophile; methylation on sulfur has parallels in lower oxidation states[8] and would be the first step in a potential rearrangement to methyl methanesulfonate, a sulfur analogue of the Arbuzov reaction.

Results

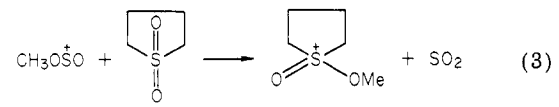
Methyl chlorosulfite, MeOS(=O)Cl, is readily prepared from methanol and thionyl chloride; it is thus a cheap and very accessible reagent. Antimony pentachloride is an easily handled substance compatible with glass and about a tenth the price per mole of antimony pentafluoride. When methyl chlorosulfite is treated with antimony pentachloride at room temperature, a violent reaction giving methyl chloride and sulfur dioxide takes place, which can be modified by cooling and by dilution with thionyl chloride, which is very resistant to methylation.[3] In this solvent at −78 °C the combination is reasonably stable, yet we believe the species CH_3OS^+O $SbCl_6$ is already formed. On warming, CH_3Cl and SO_2 are produced, corresponding to a catalysis by $SbCl_5$ of the decomposition of the chlorosulfite. We postulate a mechanism comprising reactions 1 and 2. Thus we

$$CH_3OS(=O)Cl + SbCl_5 \rightarrow CH_3OS^+O + SbCl_6^- \quad (1)$$

$$Cl_5SbCl^- + CH_3OS^+O \rightarrow Cl_5Sb + ClCH_3 + SO_2 \quad (2)$$

add an electrophilic catalysis to the uncatalyzed[9] and chloride-catalyzed[10] decomposition of chlorosulfates.

Reaction 2 attracted our attention because $SbCl_6^-$ is not expected to be a very nucleophilic species; hence $CH_3OS^+ = O$ must be an extremely powerful methylating agent. In the treatment of methyl chlorosulfite with SbF_5SO_2, Olah[11] observed the formation of the dimethylchloronium ion on warming. This indicates a very powerfully methylating intermediate, which he also assumed to be CH_3OS^+O. Hence, if we were to add a nucleophile competitive with $SbCl_6^-$, we could expect the methylation to compete with this catalytic decomposition. This has proven to be the case, and the conversions given in eq 3–6 take place in this system.



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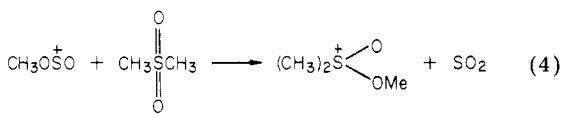
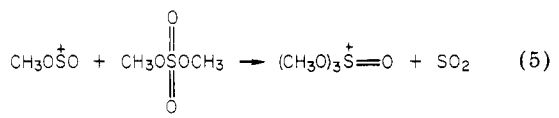
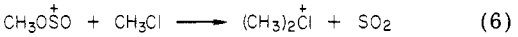


(4)



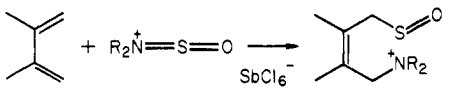
(5)



(6)

The identification of these methylated species in solution is based upon proton chemical shifts, occurring at lower field than the parent compound. The case of dimethyl sulfone, reaction 4, was the least equivocal since the product which is stable and is formed quantitatively, contained two kinds of methyl groups, one at high chemical shift (δ 4.3 (s)) and another one of twice the number of protons at δ 3.63 (s), compared to the starting sulfone (δ 3.05 (s)). The methylation of sulfolane, reaction 3, previously reported in a footnote by Jackman[12] is extensive but the product is short-lived and the ultimate decomposition products have not been identified. The dimethyl sulfate reaction (reaction 5) gave a new peak, δ 4.59 (s), but the conversion was not quantitative. The methylation of this extremely weak nucleophile, better known as a powerful methylating agent itself, is striking. We do not know if the incomplete methylation of dimethyl sulfate represents an unfavorable equilibrium with $MeOS^+O$ or merely an amount limited kinetically by competition with the weaker nucleophiles present in solution. The methylation of methyl chloride, reaction 6, differs from Olah's observation[11] only in the counterion present in this system and the deliberate addition of methyl chloride. Methylation of methyl triflate was not observed.

The identification of the ion $MeOS^+O$ was confirmed by the isolation of its deprotonated reaction product with 2-chloropropene, Peterson's[13] ene reaction, methyl 2-chloro-2-propenesulfinate, identified by proton and ^{13}C NMR, both of which were in essential agreement with the values of Peterson. Electrophilic addition to the double bond will also lead to this product. An attempt to use this ion as a dienophile, analogous to the reaction 7 reported by Kresze and Perez[14] did not give an identified low-molecular-weight product with dimethyl-1,3-butadiene.



(7)

Dimethyl sulfite is also a potential source of $MeOS^+O$, and this has indeed proven to be a likely fate when it is exposed to powerful methylating agents. We cannot study it in the thionyl chloride–methyl chlorosulfite–antimony pentachloride system because the sulfite is destroyed by conversion to chlorosulfite by thionyl chloride.[15] Most of the following work is therefore with the milder (but still very powerful) methyl triflate.

There is no very rapid or conspicuous reaction on treating dimethyl sulfite with methyl triflate. In the NMR a rather small peak at δ 4.5 appears rapidly, but further reactions are very slow. With two parts of CH_3OTf to one of $(CH_3O)_2SO$ in $CDCl_3$, there are three peaks immediately visible (all singlets). These are δ 3.58 (dimethyl sulfite), δ 4.20 (methyl triflate), and the quite weak singlet δ 4.5, which we attribute to the methylated species, the trimethoxysulfonium ion, $(MeO)_3S^+$. This structure is chosen as the one most likely given that only one peak appears. In the course of several weeks, a new peak (singlet) appears at δ 3.40. This is identified as dimethyl ether from its gas chromatographic retention time and the parent peak at m/e 46. Another new substance in the mass spectrum with m/e 64, not corresponding to any NMR signal, was identified as sulfur dioxide. Thus reaction 4 is occurring slowly, although it is not observed at these temperatures with pure dimethyl sulfite. After 10 weeks, at room temperature, the dimethyl sulfite peak at δ 3.58 had almost disappeared, but the methyl triflate peak still persisted, virtually unchanged. Thus the methyl triflate is a catalyst for the decomposition of dimethyl sulfite. We postulate the sequence of reactions 9–11.

$$CH_3OS(=O)OCH_3 \rightarrow CH_3OCH_3 + SO_2 \quad (8)$$

$$CH_3OS(=O)OCH_3 + CH_3OTf \rightleftarrows (CH_3O)_3S^+ + OTf^- \quad (9)$$

$$(CH_3O)_3S^+ \rightarrow CH_3OCH_3 + CH_3OS^+O \quad (10)$$

$$CH_3OS^+O + CH_3OS(=O)OCH_3 \rightarrow (CH_3O)_3S^+ + SO_2 \quad (11)$$

Reaction 10 may correspond to an intramolecular methyl transfer from the trimethoxysulfonium ion to give an unsymmetrical (and unseen) isomer (eq 12) followed by its unimolecular cleavage to CH_3OS^+O (eq 13). Alternatively, and kinetically indistinguishable, in addition to the observed but unfruitful reaction 9, there may be an alternative mechanism to give the unobserved isomeric cation, reaction 14, followed or occurring simultaneously with the decomposition (eq 13).

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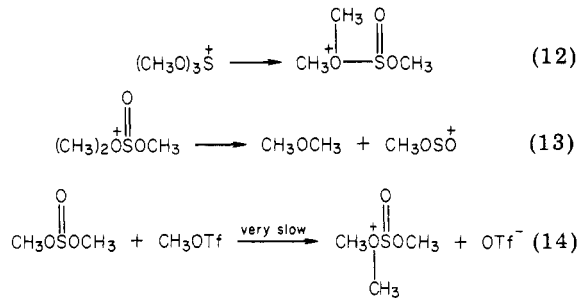

(12)

(13)

(14)

Since the direct methyl transfer (eq 12) has a rather unfavorable geometry for an intramolecular methyl transfer,[16] we prefer the separate reaction 14 as a more probable source of **1** and consider that reaction 10 as a one-step process is unlikely. The reversible methylation with a much slower rate at the methoxy oxygen is thus a more probable route, with many analogues.

The methyl triflate is catalytic because reactions 10 and 11 (or 12 and 13) constitute an ionic chain. The possible reformation of methyl triflate from CH_3OS^+O and OTf^- is discussed later.

The mechanism of reversible alkylation also accounts for the observation of methyl–ethyl exchange in the reaction of diethyl sulfite with methyl triflate, reported recently.[8] The authors of this work, however, did not notice the much slower irreversible decomposition.

When dimethyl-d_6 sulfite (easily prepared from commercial CD_3OH) is treated with methyl triflate, the NMR shows a relatively rapid exchange, the methyl triflate proton signal disappears, and a strong dimethyl sulfite signal appears. If an excess of dimethyl sulfite is used, the exchange is almost quantitative, and if the solution is then heated to accelerate the reaction described above, the dimethyl sulfite undergoes the catalytic decomposition to dimethyl ether and sulfur dioxide, leaving CD_3OTf almost uncontaminated. This constitutes an easier and cheaper synthesis than the route through CD_3I + AgOTf described earlier.[15] This is a practical synthesis of a methyl-d_3 triflate and therefore of a host of other methyl-d_3 compounds, even though much of the deuterium is lost in dimethyl ether, which is observed by GC/MS to contain CH_3OCD_3 as well as CD_3OCD_3 but little undeuterated material. There are of course other potential syntheses; a referee suggests CD_3OH + Tf_2O. We searched rather carefully and without success for the two characteristic peaks of methyl methanesulfonate in the dimethyl sulfite–methyl triflate system. Since the potential S-methylated cation would certainly lose an O-methyl group easily, we conclude that there is no perceptible S-methylation, showing that the rate of S-methylation is far less than that of the reversible O-methylation.

When dimethyl sulfite was treated with methyl 2,4,6-trinitrobenzenesulfonate, the reaction was more complex, in that the powerful methylating agent no longer was catalytic, and it disappeared rather rapidly. The extent of methylation to give trimethoxysulfonium ion (δ 4.5) was greater, both dimethyl ether and sulfur dioxide were formed, and the disappearance of both methyl and aryl signal in the NMR was hard to understand. The problem was resolved when a precipitate was noted, identified as trimethyloxonium trinitrobenzenesulfonate. Its formation reflects the fact that methyl trinitrobenzenesulfonate readily methylates dimethyl ether (which is present), demonstrating again[3] that it is more powerful in an equilibrium sense than the trimethyloxonium ion, and also that this trimethyloxonium salt has a very low solubility (in dimethyl sulfite as well as many other solvents).

With both methylating agents we have not been able to tell whether the further reaction 15 is important or not; we are confident that it is thermodynamically favorable with X^- = ^-OTf, but we are not sure with X^- = 2,4,6-trinitrobenzenesulfonate.

$$MeOS^+O + X^- \rightarrow MeX + SO_2 \quad (15)$$

This reaction (with X = OTf) would also cause the observed exchange of the methyl groups between sulfite and triflate, but a more quantitative kinetic treatment is required to tell if this route is necessary as well as the reverse of reaction 9. Reaction 15 would be the termination step in the ionic chain reaction. We have not looked for exchange of the sulfite and trinitrobenzenesulfonate esters.

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Experimental Section

Materials. Methyl chlorosulfite was prepared according to published procedures due to Carré and Liberman[18] and Berté.[19] It was stored over anhydrous calcium chloride. Dimethyl sulfite was prepared from 2 mol of methanol and 1 mol of thionyl chloride.

Commerically available antimony pentachloride was used without purification. Thionyl chloride (MCB) was distilled from triphenyl phosphite[20] to obtain a colorless liquid prior to use. Dimethyl-d_6 sulfite was preapred from commercial (Aldrich) CD_3OD and thionyl chloride as a colorless liquid, bp 63 °C (66 mmHg). A solution of $SbCl_5$ (1.89 M) in thionyl chloride was used. Methyl triflate was stored over molecular sieves in the refrigerator. Sulfolane was purified by a procedure described in previous papers.[21]

Proton NMR spectra were recorded from a Varian EM-390 90-MHz instrument. The chemical shift values are with reference to tetramethylsilane (Me_4Si) used as external standard (as a capillary), as well as internal standard. ^{13}C NMR spectra were recorded on a JEOL FX90Q instrument. GC/MS spectral data were obtained from a Finnigan Series 6000 data system.

Methylations Using the $CH_3OS(=O)Cl/SbCl_5/SOCl_2$ System. The following procedure for methylation of sulfolane is typical of other methylations. To about 0.5 mL of sulfolane dissolved in the antimony pentachloride–thionyl chloride solution (1.0 mL) at −73 °C was carefully added dropwise methyl chlorosulfite (1.5 mL) with magnetic stirring to keep the vigor of the reaction under control. The mixture was stirred for 15 min at this temperature and then slowly allowed to warm. Addition of an antimony pentachloride solution in thionyl chloride to a sulfolane in methyl chlorosulfite gave similar results. NMR samples were taken when the temperature reached −30 °C, but further warming to ca. 30 °C occurred before the spectra were complete.

The chemical shifts with external Me_4Si reference are as follows: sulfolane, δ 3.5 (br t, α-H), 2.6 (br t, β-H), after methylation. Methoxy protons δ 4.33 (s), α protons, δ 4.1 (br t), β protons, δ 2.8 (br t); dimethyl sulfone, (s), δ 3.05, after methylation δ 3.63 and δ 4.3 (ratio 2:1); dimethyl sulfate δ 3.94 (s); after methylation δ 4.59 (s); methyl chloride after methylation, δ 5.83 (s), intensity increase at cost of CH_3Cl signal when more of the methyl chlorosulfite is added. The CH_3Cl–$SbCl_5$ peak at δ 3.66 appeared here as well as in some other cases. No new peaks were observed in the system containing methyl triflate as a "nucleophile".

Detection of CH_3OS^+O by the Ene Reaction. The procedure is based on that of Peterson.[13] 2-Chloropropene (1.5 g) and methyl chlorosulfite (5.7 g) were cooled to −78 °C in a round-bottomed flask. A solution of antimony pentachloride (6.0 g) in dichloromethane (12 mL) cooled to −78 °C was slowly added with stirring. The system was well-mixed and then immediately poured into a solution of methanol (10 mL) containing sodium bicarbonate (0.6 g) cooled to −65 °C. After the solution was stirred and warmed to room temperature, the workup followed that of Peterson, giving a pale-yellow oil with the following ^1H NMR in $CDCl_3$ with internal Me_4Si: δ 3.76 (s, methoxy) (3.75), 3.65 (d, CH_2 S) (3.65), 5.43 (s, $=CH_2$) (5.45). Values in parentheses are from ref 6. The ^{13}C spectrum in $DCCl_3$ gave 53.85 (58.6) (CH_3O), 65.98 (68.2) (CH_2S), 118.61 (121.8) ($=CH_2$), 129.98 (131.6) ($=CCl$). The discrepancies in the ^{13}C chemical shifts are not serious and the multiplicities on off-resonance decoupling were appropriate for the structure $CH_3O(SO)CH_2CCl=CH_2$. The "doublet" reported for the CH_2S protons is probably not a coupling but represents

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(18) Carré, P.; Libermann, D. *Bull. Soc. Chim.* **1933**, *53*, 1050.
(19) Berté, G. *J. Am. Chem. Soc.* **1954**, *76*, 1213.
(20) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 1158.
(21) Lewis, E. S.; Vanderpool, S. *J. Am. Chem. Soc.* **1977**, *99*, 1946–1948.

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.

Acknowledgment. We acknowledge the support of this work by a grant from the National Science Foundation. Certain aspects were also supported by a grant from the Robert A. Welch Foundation.

Registry No. $CH_3OS(O)Cl$, 13165-72-5; dimethyl sulfite, 616-42-2; methyl triflate, 333-27-7; methyl 2,4,6-trinitrobenzenesulfonate, 53541-31-4; methyl chloride, 74-87-3; dimethyl sulfate, 77-78-1; sulfolane, 126-33-0; dimethyl sulfone, 67-71-0.

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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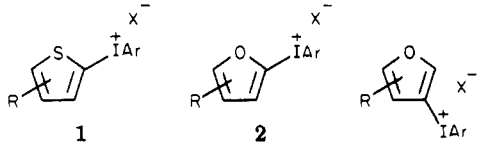
Received March 2, 1982

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



1 2 3

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

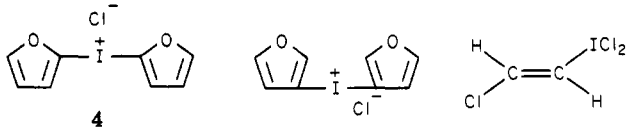
$$\mathrm{ArIO} + \mathrm{Ar'IO_2} \xrightarrow[H_2O]{OH^- \text{ or } Ag_2O} (\mathrm{ArI^+Ar'})X^- \qquad X^- = HO^-, IO_3^- \qquad (1)$$

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

$$\mathrm{ArIO \text{ or } ArI(OOCR)_2} + \mathrm{Ar'H} \xrightarrow{H_2SO_4} (\mathrm{ArI^+Ar'})HSO_4^- \qquad (2)$$

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



4 5 6

7 8

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

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