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Arylation of Diorganochalcogen Compounds with Diaryliodonium Triflates: Metal Catalysts Are Unnecessary

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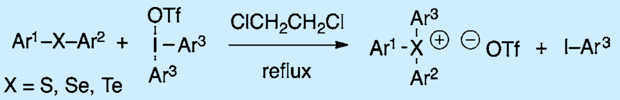
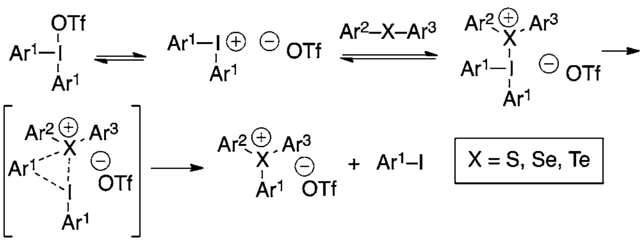
Supporting Information

ABSTRACT: Diaryliodonium triflates transfer an aryl group to the chalcogen atom of organic sulfides, selenides, and tellurides (but not ethers), in the absence of transition-metal catalyst, simply upon heating in chloroform or dichloroethane solution.



Diaryliodonium species (λ^3-iodanes)[1] *S*-arylate diaryl sulfides in the presence of a catalytic amount of Cu(II),[2] leading to the formation of triarylsulfonium salts. These materials find application in diverse areas of contemporary chemistry.[3] On the other hand, it has recently been determined that diaryliodonium triflates undergo metathesis with particular aryl iodides in the absence of any metal catalysts, seemingly by nucleophilic attack of the I atom of the incoming Ar—I onto the iodonium center, followed by reductive elimination of a nucleofugal aryl iodide from the resulting complex.[4] The *S*-atom of an organic sulfide, and indeed the chalcogen atom in a generic diorgano chalcogenide, would be anticipated to be much more nucleophilic than the I atom of an aryl iodide. The question then arises of whether diaryliodonium triflates may arylate organochalcogen centers in the absence of any metal catalyst and under mild conditions, leading to triorganochalcogenonium salts, perhaps by the mechanism of Scheme 1.[5] This process would not be of mere academic interest: a Cu-free route to triarylsulfonium triflates of technological significance[3] could be economically advantageous.

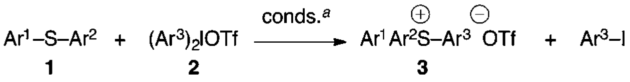
Scheme 1. Possible Metal-Free Synthesis of Triarylchalcogenium Triflates



In the past, the uncatalyzed arylation of diorganochalcogen centers with diaryl-λ^3-iodanes had been achieved only under forcing conditions. For instance, Ph_2S and Ph_2IBF_4 reacted in the absence of catalysts to form Ph_3SBF_4 but only upon prolonged heating (35 h) at temperatures above 180 °C (ca. 65% yield).[6] Such harsh conditions may not be beneficial to the survival of more sensitive sulfonium salts. Anionic chalcogen nucleophiles, such as sulfinates[7] and phenoxides,[8] are, of course, considerably more reactive and undergo uncatalyzed arylation upon reaction with diaryliodanes under much gentler conditions. Especially electrophilic λ^3-iodanes such as (alkynyl)-aryliodonium agents transfer the *alkynyl* (but not the *aryl*) ligand to diorganochalcogen substrates under mild conditions and with no need for catalysts, though probably by a mechanism that differs from the one depicted in Scheme 1.[9] Tangentially related to the reaction of interest here is the uncatalyzed arylation of anilines[10] and phosphines.[11] The latter process, however, seemingly proceeds through SET, rather than nucleophilic, mechanisms.

We now report that diaryliodonium triflates arylate diaryl chalcogenide substrates under mild conditions and without the need for metallic catalysts. Thus, Ph_3SOTf was formed in 92% yield upon heating a chloroform- or 1,2-dichloroethane (DCE) solution of Ph_2S and Ph_2IOTf to 120 °C (oil bath temperature, tube sealed with a gasketed Teflon screwcap; Table 1, entries a and b). Diverse aryl sulfides were found to undergo the reaction, regardless of whether electron-donating or electron-withdrawing groups were present on the aromatic rings (Table 1, entries d–f). In all cases, the reaction mixtures remained

Table 1. Metal-Free *S*-Arylation of Diaryl Sulfides



entry	Ar^1	Ar^2	Ar^3	yield of 3^b (%)
a	Ph	Ph	Ph	92
b	Ph	Ph	Ph	92^c
c	Ph	Ph	4-BrC_6H_4–	96
d	4-$MeOC_6H_4$-	4-$MeOC_6H_4$–	Ph	87
e	4-BrC_6H_4–	4–BrC_6H_4–	4-BrC_6H_4–	79
f	Ph	4-$O_2NC_6H_4$–	Ph	85

[a] Conditions: 0.1 M solution of Ar_2IOTf (1.0 equiv) in $(CH_2Cl)_2$, 1.5 equiv of diaryl sulfide, thick-walled glass tube sealed with a Teflon screwcap and immersed in an oil bath maintained at 120 °C, 15 h. [b] Percent yield after silica gel column chromatography (gradient 10% → 40% acetone–CH_2Cl_2) to remove nonpolar byproducts. [c] This reaction was run in $CHCl_3$ as the solvent.

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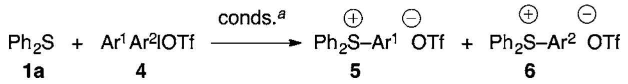
colorless throughout the course of the reaction, indicating that the intervention of charge-transfer complexes, and possibly of SET events, is unlikely, i.e., that the reaction probably occurs by a nucleophilic mechanism.

As observed earlier in the iodonium metathesis case,[4] attempts to carry out the reaction in alternative solvents, such as MeCN, THF, or CH_2Cl_2, were uniformly unsuccessful. Furthermore, no *S*-arylation of Ph_2S occurred when Ph_2IOTf was replaced with diphenyliodonium tetrafluoroborate, hexafluorophosphate, tosylate, or chloride (no reaction with the BF_4^- or PF_6^- salts; thermal degradation of the iodonium species with the TsO^- or Cl^- salts).

Experiments aiming to probe the aryl group transfer preference from mixed diaryliodonium species to diphenyl sulfide revealed a diminished selectivity relative to analogous iodonium metathesis reactions (Table 2). Still, the triaryl sulfonium triflates arising from displacement of the more nucleofugal aryl iodide[4] were the dominant products. The lower degree of selectivity observed in these reactions may be due to the fact that a portion of the diaryl sulfide reacts with the iodonium species by an S_NAr mechanism, on account of the increased nucleophilic character of divalent sulfur relative to monovalent iodine. As detailed elsewhere,[4] the S_NAr mechanism and the metathesis mechanism depicted in Scheme 1 promote opposite aryl group transfer selectivity.

Table 2. Aryl Group Transfer Selectivity



$$\underset{\mathbf{1a}}{Ph_2S} + \underset{\mathbf{4}}{Ar^1Ar^2IOTf} \xrightarrow{\text{conds.}^a} \underset{\mathbf{5}}{Ph_2S^{\oplus}\text{–}Ar^1\ OTf^{\ominus}} + \underset{\mathbf{6}}{Ph_2S^{\oplus}\text{–}Ar^2\ OTf^{\ominus}}$$

entry	Ar^1	Ar^2	ratio **5**:**6**[b]	yield of **5** + **6**[c] (%)
a	$4\text{-}O_2NC_6H_4\text{–}$	Ph	1:2.3	98
b	$4\text{-}MeO_2CC_6H_4\text{–}$	Ph	1:1.9	94
c	$4\text{-}O_2NC_6H_4\text{–}$	$4\text{-}MeOC_6H_4\text{–}$	1:1.3	92
d	2-thienyl	Ph	1:3.8	82
e	2-thienyl	$4\text{-}MeO_2CC_6H_4\text{–}$	1:3.9	85

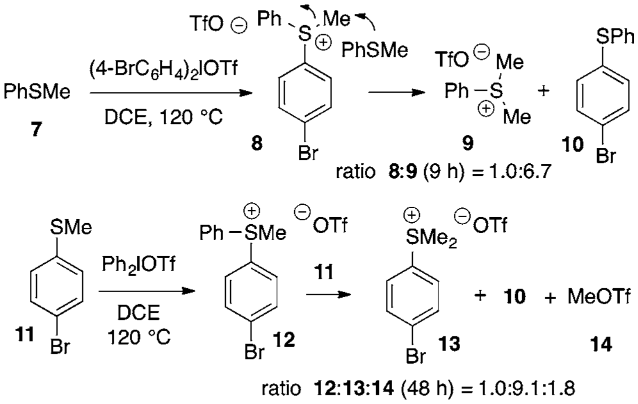
[a] 0.1 M solution of Ar_2IOTf (1.0 equiv) in $(CH_2Cl)_2$, 1.5 equiv of diphenyl sulfide, thick-walled glass tube sealed with a Teflon screwcap and immersed in an oil bath maintained at 120 °C, 15 h. [b] Molar ratios calculated by integration of ^1H NMR spectra of the crude reaction mixtures. [c] Percent yield after silica gel column chromatography (gradient 10% → 40% acetone–CH_2Cl_2) to remove nonpolar byproducts. The stated value is the sum of the yields of individual compounds present in the product mixture. A comparison of ^1H NMR spectra of crude and purified reaction mixtures indicated that insignificant changes in the ratio of sulfonium triflate products had occurred upon chromatography.

Especially significant interference from the S_NAr mechanism would be anticipated with nitro-substituted iodonium salts. Indeed, unusually poor selectivity was observed in the reaction of (4-anisyl)-4-nitrophenyliodonium triflate with diphenyl sulfide (Table 2, entry c).

The separation of products **5** and **6** proved to be less than straightforward due to their very similar chromatographic mobilities. Some separation was achieved for entries a–c but not for the thienyl sulfonium salts (entries d and e). Therefore, the yields reported in the table are those of the mixture of **5** and **6** obtained after chromatographic removal of nonpolar byproducts.

The reaction of bis(4-bromophenyl)iodonium triflate with thioanisole, **7**, initially yielded sulfonium salt **8**, which rapidly transferred a methyl group to unreacted thioanisole to produce phenyl dimethylsulfonium triflate **9** and diaryl sulfide **10** (Scheme 2). After 9 h at 120 °C, compounds **8** and **9** were present in a ratio of 1.0:6.7. Analogous methyl group transfer steps have been observed during the alkynylation of thioanisole[9] and are attributable to a thermodynamically favorable displacement of a less nucleophilic diorganosulfur species (**10**) by a more nucleophilic one (**7**). While nonpolar materials such as **7** and **10** were easily separated from the mixture of sulfonium salts, the latter was not as readily resolved into the components and was therefore characterized as such. In a like manner, 4-bromothioanisole, **11**, reacted with Ph_2IOTf to produce sulfonium salt **12**, which transferred a methyl group to unreacted **11** to furnish **13**. The rate of this second reaction was noticeably slower than that of **8** with **7** and prolonged heating was required to attain a significant degree of conversion of **12** into **13**. After 31 h at 120 °C, MeOTf, **14**, also became apparent in the reaction mixture [^1H NMR ($CDCl_3$): δ = 4.2 ppm]. After 48 h at 120 °C, compounds **12**, **13**, and **14** were present in a ratio of 1.0:9.1:1.8. We note that the formation of MeOTf by reaction of triflate ion with a methyl diarylsulfonium species is documented.[2b] The foregoing methyl group transfer reactions are interesting from a physical organic standpoint,[12] but in the present context they constitute a complication, which dissuaded us from carrying out more work with thioanisole or other aryl alkyl sulfides.

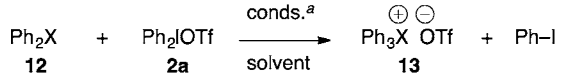
Scheme 2. Reactions of Thioanisole Substrates



Diphenyl sulfoxide failed to react with Ph_2IOTf. Likewise, all attempts to induce the *O*-arylation of diphenyl ether, leading to triaryloxonium salts, met with failure. However, the arylation reactions of diphenyl selenide and telluride were successful (Table 3). The reaction of Ph_2Se with Ph_2IOTf occurred at a rate comparable to that of Ph_2S and produced Ph_3SeOTf in 94% yield. In the past, this selenonium species had been obtained in lower yield from the same starting materials in the presence of a catalytic amount of copper benzoate.[13] This suggests that Cu salts may actually constitute a liability in the present case.

Curiously, the arylation of Ph_2Te proceeded at an abnormally slow rate compared to that of other diphenyl chalcogenides. Only a 36% conversion (^1H NMR) was achieved after 48 h at 120 °C (bath temperature, sealed tube) in DCE, leading to the isolation of Ph_3TeOTf (ca. 30% yield) contaminated with a byproduct of uncertain structure but seemingly arising through the reaction of Ph_2Te with the solvent.[14] While this byproduct was difficult to separate from Ph_3TeOTf, its formation could be

Table 3. Catalyst-Free Arylation of Ph_2Se and Ph_2Te



$$\underset{\mathbf{12}}{Ph_2X} + \underset{\mathbf{2a}}{Ph_2IOTf} \xrightarrow[\text{solvent}]{\text{conds.}^a} \underset{\mathbf{13}}{\overset{\oplus}{Ph_3X}\ \overset{\ominus}{OTf}} + Ph{-}I$$

entry	X	solvent	yield[b]
a	Se	$CHCl_3$	94
b	Se	DCE	91
c	Te	DCE	30[c]
d	Te	$CHCl_3$	14[d]

[a] Conditions: 0.1 M solution of Ph_2IOTf (1.0 equiv) in $(CH_2Cl)_2$, 1.5 equiv of diarylchalcogen, thick-walled glass tube sealed with a Teflon screwcap and immersed in an oil bath maintained at 120 °C, 24 h for selenides, 48 h for tellurides. [b] Percent yield after silica gel column chromatography (gradient 10% → 40% acetone−CH_2Cl_2) to remove nonpolar byproducts.. [c] Yield at 36% conversion (see text). [d] Yield at 15% conversion.

suppressed by carrying out the reaction in $CHCl_3$, whereupon highly pure Ph_3TeOTf was obtained. Under such conditions, however, the reaction proceeded to a modest 16% conversion (^1H NMR) after 48 h and the product was obtained in 14% yield after chromatography.

The literature seems to contain no record of this telluronium species, although two derivatives, $(C_6F_5)_3TeOTf$[15] and (4-$Ph_2NC_6H_4)_3TeOTf$,[16] have been described. Its structure was therefore ascertained by single-crystal X-ray diffractometry (Figure 1). A structural feature which is worthy of note is that, at least in the solid state, the C1−Te−C13 bond angle is significantly wider (102.6°) than the others (C1−Te−C7:95.6°; C7−Te−C13:94.0°), while all C−Te bond lengths are very similar (Te−C1:2.115 Å; Te−C7:2.133 Å; Te−C13:2.112 Å). The O−Te distances range from 2.894 to2.947 Å,[17] indicating that the interaction between the triflate oxygens and the Te atom is weak and essentially ionic in nature.[18]

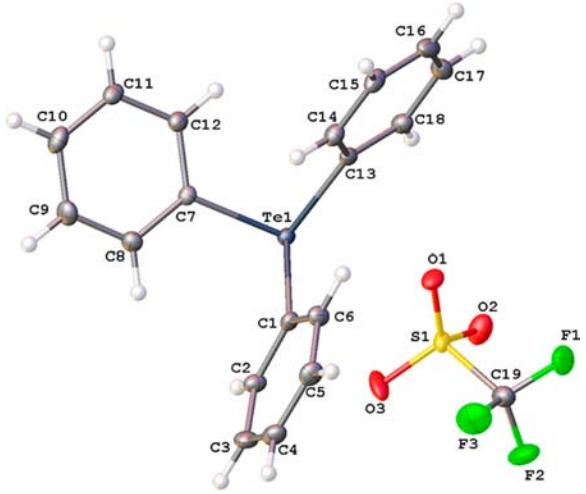


Figure 1. X-ray crystal structure of triphenyltelluronium triflate.

We also note that triaryltelluronium species, which are more commonly made by reaction of $TeCl_4$ with appropriate arylmetallic agents, may become of considerable interest in coordination and transition metal chemistry, given their recently discovered ability to function as σ-acceptor ligands.[19]

In summary, diaryliodonium triflates efficiently arylate diaryl sulfides and selenides under mild conditions, and without any need for metallic catalysts. In contrast, the uncatalyzed arylation of the same chalcogen centers with other diaryliodonium species occurs only upon vigorous thermal activation. Such harsh conditions may promote significant decomposition of the λ^3-iodanes and/or of sensitive sulfonium salts. A mild, metal-free route to triarylchalcogenonium triflates has thus been established.[20] New opportunities engendered by this development are being examined and pertinent results will be disclosed in due time.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) In addition to Ph_3TeOTf, the mass spectra of the product thus obtained revealed the presence of a cationic species of probable formula $[Ph_2TeCH_2CH_2Cl]^+$ (unknown of whether as a triflate or chloride salt), which produced the correct isotopic pattern for the presence of Te and Cl. The ^1H NMR spectrum (Supporting Information) displayed an AA′BB′ pattern centered at 4.2 ppm and a distinctive signal at 7.95 ppm. The ^{13}C NMR spectrum (Supporting Information) exhibited peaks not belonging to Ph_3TeOTf at 130, 127, 124, 120, 41, and 36 ppm.

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