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Microwave-Assisted Copper-Catalyzed Preparation of Diaryl Chalcogenides

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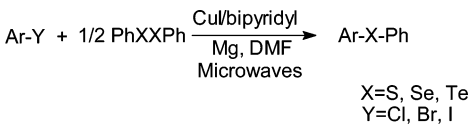

Diaryl chalcogenide synthesis employing diaryl dichalcogenides and aryl halides as starting materials in the presence of excess magnesium and a catalytic amount of CuI/bipyridyl is significantly improved by microwave heating. Reaction times can be reduced from 2 to 3 days to 6−8 h. Both aryl bromides and aryl chlorides can be used as substrates in the substitution reaction. The procedure is useful not only for diaryl sulfide and diaryl selenide synthesis but also for the preparation of unsymmetrical diaryl tellurides. Starting from suitable aryl halides, the novel microwave-assisted procedure was used for the facile preparation of novel chalcogen analogues (PhS-, PhSe-, and PhTe-) of various antioxidants (ethoxyquin and 3-pyridinol). Attempts to use dialkyl dichalcogenides for the coupling of alkylchalcogeno moieties to aryl halides were only successful in the case of long-chain (such as *n*-octyl) disulfides and diselenides.

Introduction

Aryl chalcogenide structural motifs are commonly found in a variety of molecules of biological/pharmaceutical[1] and materials[2] interest. We study the antioxidative properties[3] of organosulfur, organoselenium, and organotellurium compounds with the perspective to find compounds which could act in a catalytic fashion to decompose both hydroperoxides (peroxide decomposing antioxidants) and peroxyl radicals (chain-breaking donating antioxidants). Because of their stability also at elevated temperatures, aryl chalcogenides are often our target molecules. For evaluating the effect of the chalcogen in a structure selected, it is desirable to have easy access to all three arylchalcogenide analogues[4] (sulfide, selenide, and telluride) starting from a common precursor. Out of the many methods available for aryl-chalcogen bond-formation, we thought the coupling of aryl halides with thiolates, selenolates, and tellurolates would be ideally suited for our purposes. However, unless the substitution reaction is catalyzed or otherwise facilitated (e.g., by photolysis,[5] electrolysis,[6] metal-promoted electron transfer,[7] or by formation of a transition metal arene complex of the aryl halide[8]), nucleophilic substitution can only be effected under forcing conditions. Already in the 1980s, Migita and Cristau reported Pd- and Ni-catalyzed cross-coupling of aryl bromides and iodides with thiolates and selenolates.[9] Although yields were generally satisfying, long reaction times at elevated temperature were often required for nonactivated aryl halides. More recently, Itoh and Hartwig[10] have reported improved palladium-based catalyst systems for coupling of aryl halides and triflates with thiols. For diaryl selenide synthesis, phenyl tributylstannyl selenide, $PhSeSnBu_3$, was found to function as an excellent partner in the Pd- or Ni-catalyzed reaction with aryl halides and triflates.[11] Copper-based catalyst systems have proven effective for the cross-coupling of aryl iodides with both thiols and selenols.[12] Methodology for diaryl telluride synthesis by

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the substitution of unactivated aryl halides with arenetellurolate is scarce.[13] However, both diaryl ditellurides and diaryl diselenides were recently found to produce the corresponding unsymmetrical diaryl chalcogenides when reacted in DMSO at 100 °C with arylboronic acids in the presence of a catalytic amount of copper(I)-iodide.[14]

Arenethiolates, selenolates, and tellurolates are all only weakly basic, and basicity would rarely be a problem during their introduction into more complex organic molecules by aromatic nucleophilic substitution. However, the sensitivity of the chalcogenide species toward oxidation is more troublesome. This is especially true for arenetellurolates which are converted to the corresponding ditellurides unless air is rigorously excluded. Therefore, it was interesting that Taniguchi could use both arylchalcogeno moieties of easy to handle diaryl disulfides and diaryl diselenides for diaryl chalcogenide synthesis by heating in DMF for 1 to 3 days with aryl iodides in the presence of catalytic amounts of a copper catalyst, 2,2′-bipyridyl and excess magnesium metal (eq 1).[15] We were curious to see if this methodology could be extended also to diaryl telluride synthesis and if the slow cross-coupling reaction could be accelerated and induced to occur also with the much less reactive, but more readily available, aryl bromides and chlorides.

$$\mathrm{Ar'{-}I} + {}^{1}/_{2}\mathrm{ArXXAr} \xrightarrow[\text{Mg, DMF, 110 °C}]{\text{Cu(I)bipyridyl (10\%)}} \mathrm{Ar'{-}X{-}Ar} \qquad \mathrm{X = S, Se} \quad (1)$$

In the following, we report an improved, microwave-assisted method for diaryl chalcogenide synthesis which significantly widens the scope of the coupling reaction shown in eq 1.

Results and Discussion

Microwave dielectric heating causes an extremely rapid and uniform energy transfer to the reactants of chemical reactions.[16] This will minimize byproduct formation and increase product yields. In pressurized systems, it is also possible to use temperatures far above the boiling point of the solvent. We therefore thought it would be interesting to study the effect of microwave heating on the reaction of aryl halides with diaryl dichalcogenides in the presence of a copper(I)-catalyst, 2,2′-bipyridyl, and magnesium. Initially, to find proper reaction conditions, diphenyl ditelluride, diphenyl diselenide, or diphenyl disulfide was allowed to react with either chloro- or bromobenzene at various temperatures in solvents suitable for microwave heating (THF, NMP, or DMF). It was indeed possible to successfully perform all the coupling reactions attempted, but temperatures in the range of 160−200 °C and reaction times in the order of 6 to 7 h were required for complete conversion of the starting materials (Table 1). Under the best conditions found (DMF as a solvent; 10−20% of CuI as a catalyst[17]), moderate to good (40−65%) yields of diphenyl chalcogenides could be obtained (Table 1). Isolated yields of the three diaryl chalcogenides under similar conditions using iodobenzene as a starting material turned out to be in the same range (60−62%). Out of the three diphenyl chalcogenides, the telluride was the most readily prepared (usually at 160 °C using 10 mol-% of catalyst[18]). For preparation of the selenide and sulfide, heating at 200 °C in the presence of 15 and 20 mol-%, respectively, of catalyst was required. It is noteworthy that ordinary magnesium turnings could be used in these experiments instead of magnesium powder.[15]

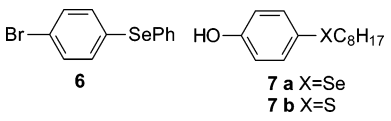
TABLE 1. Preparation of Diphenyl Chalcogenides from Diphenyl Dichalcogenides and Halobenzenes

$$\mathrm{Ph{-}Y} + {}^{1}/_{2}\mathrm{PhXXPh} \xrightarrow[\substack{\text{Mg, DMF}\\ \text{microwaves}}]{\text{CuI/bipyridyl}^{a}} \mathrm{Ph{-}X{-}Ph}$$

Y	X	reaction time (h)	temperature (°C)	product (% yield)[b]
Cl	Te	6	200	Ph_2Te (40)
Br	Te	6	160	Ph_2Te (65)
I	Te	6	160	Ph_2Te (60)
Cl	Se	6	200	Ph_2Se (48)
Br	Se	6	200	Ph_2Se (60)
I	Se	6	200	Ph_2Se (62)
Cl	S	6	200	Ph_2S (58)
Br	S	6	200	Ph_2S (64)
I	S	6	200	Ph_2S (60)

[a] An amount of 10, 15, and 20 mol-%, respectively, for diphenyl telluride, diphenyl selenide and diphenyl sulfide synthesis. [b] Isolated yield.

By using the conditions in Table 1, we next turned to explore the generality of the substitution reaction for diaryl chalcogenide synthesis and the possibility to prepare aryl alkyl chalcogenides by a similar protocol using dialkyl dichalcogenides as starting materials. In Table 2 it is shown that phenylchalcogeno groups could be coupled to both haloaromatics and haloheteroaromatics (4-bromotoluene, 1-bromonaphthalene, 4-chloro- and 4-bromophenol, *N*,*N*-dimethyl-4-bromoaniline, and 3-bromopyridine) containing various functional groups in fair to good yields (42−90%). However, attempted coupling with 4-bromoanisole produced a complex mixture of products where the *O*-methyl group was no longer present. We speculate that copper(I)-phenylchalcogenenolate under the harsh reaction conditions is causing demethylation by nucleophilic attack at the methyl. This type of reactivity was not a problem when 4-iodoanisole was used as a starting material and the reaction subjected to ordinary heating at 110 °C in DMF.[15] To show that the microwave-assisted reaction is not restricted to the coupling of diphenyl dichalcogenides with haloaromatics, di-1-naphthyl ditelluride, di-1-naphthyl diselenide, and di-1-naphthyl disulfide were reacted with bromobenzene under the usual catalyzed conditions to provide compounds **2a**−**c** in an alternative way (55, 68, and 78% yields, respectively; for structures see Table 2). Some attempts were also made to introduce more than one arylchalcogeno group into polyhalogenated aromatics. However, when 1,4-dibromobenzene was subjected to microwave-assisted, copper-catalyzed substitution using a stoichiometric amount of diphenyl diselenide, only the monosubstitution product **6** was



6 **7 a** X=Se **7 b** X=S

formed (55% yield). To see if the microwave-assisted reaction would be suitable for the coupling of alkylchalcogeno groups

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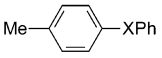
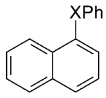
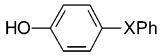
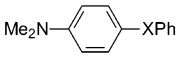
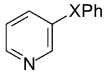
(17) It was found that Cu_2O was a much poorer catalyst than CuI in these coupling reactions.

TABLE 2. Preparation of Aryl Phenyl Chalcogenides from Haloaromatics and Diphenyl Dichalcogenides

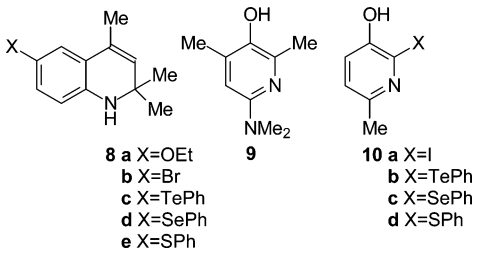
$$Ar{-}Y + {}^{1}/_{2}PhXXPh \xrightarrow[\text{Mg, DMF}\\ \text{microwaves}]{\text{CuI/bipyridyl}^{a}} Ar{-}X{-}Ph$$

Ar-Y	X	Reaction time (h)	Temperature (°C)	Product (% yield[b])
				
4-bromotoluene	Te	6	160	**1a** X=Te (58)
4-bromotoluene	Se	6	200	**1b** X=Se (70)
4-bromotoluene	S	7	200	**1c** X=S (72)
				
1-bromonaphthalene	Te	6	160	**2a** X=Te (68)
1-bromonaphthalene	Se	6	200	**2b** X=Se (72)
1-bromonaphthalene	S	7	200	**2c** X=S (88)
				
4-bromophenol	Te	6	160	**3a** X=Te (45)
4-chlorophenol	Se	8	200	**3b** X=Se (45)
4-bromophenol	Se	7	200	**3b** X=Se (60)
4-bromophenol	S	8	200	**3c** X=S (68)
				
N,N-dimethyl-4-bromoaniline	Te	6	160	**4a** X=Te (42)
N,N-dimethyl-4-bromoaniline	Se	6	200	**4b** X=Se (61)
N,N-dimethyl-4-bromoaniline	S	6	200	**4c** X=S (65)
				
3-bromopyridine	Te	6	160	**5a** X=Te (62)
3-bromopyridine	Se	6	200	**5b** X=Se (70)
3-bromopyridine	S	7	200	**5c** X=S (90)

[a] 10, 15, and 20 mol-%, respectively, for telluride, selenide and sulfide synthesis. [b] isolated yield.

to aryl bromides, 4-bromophenol was allowed to react with di-*n*-propyl disulfide and di-*n*-butyl diselenide, respectively, under the usual catalyzed conditions. Although the desired substitution products were formed, most of the bromophenol remained unreacted. Surprisingly, conversion was much better when di-*n*-octyl disulfide or di-*n*-octyl diselenide were employed as dichalcogenide starting materials. Thus, compounds **7a** and **7b** were isolated in 79 and 94% yields, respectively. Attempts to use di-*n*-octyl ditelluride for coupling an octyltelluro moiety to 4-bromophenol and other haloaromatics were met with failure. Dehalogenation seems to become a major competing process in these reactions. Thus, naphthalene was isolated in 42% yield when 1-bromonaphthalene was used as a substrate. In a control experiment in the absence of ditelluride, the bromonaphthalene was recovered.

Ethoxyquin (**8a**) possesses remarkable antioxidant capacity.[19] It is used as an antioxidant in fish meal and animal feed and as an additive to rubber. With the perspective to obtain catalytic and multifunctional (chain-breaking and peroxide decomposing) antioxidants, we were interested in the synthesis of ethoxyquin analogues carrying phenylchalcogeno groups in the 6-position of the dihydroquinoline backbone. The corresponding bromide, **8b,** is readily available by condensation of 4-bromoaniline with 2 equiv of acetone. We were pleased to find that the microwave-assisted copper-catalyzed methodology developed was well suited for preparation of the desired organochalcogen antioxidants. Thus, under the standard conditions for coupling, compounds **8c**, **8d**, and **8e** were obtained in 32, 63, and 70% yield, respectively.



8 a X=OEt
b X=Br
c X=TePh
d X=SePh
e X=SPh

9

10 a X=I
b X=TePh
c X=SePh
d X=SPh

Electron-rich 3-pyridinols have recently been introduced as new antioxidant scaffolds. Thus, compounds such as **9** are the fastest chain-breaking antioxidants ever reported.[20] We were curious to see if introduction of arylchalcogeno groups into this class of compounds would improve the antioxidant capacity even further, for example, by imposing a peroxide decomposing capacity and a catalytic mode of action in the presence of a suitable stoichiometric reducing agent. As a model compound, we therefore subjected the commercially available iodopyridinol **10a** to the usual conditions for microwave-assisted introduction of phenylchalcogeno groups. Although the yield of the tellurium compound was only modest (compounds **10b**, **10c**, and **10d** were obtained in 30, 63, and 70% yields, respectively) all chalcogen derivatives could be readily prepared. The novel organochalcogen antioxidants **8** and **10** are presently being evaluated in our laboratories.

In summary, we have shown that the CuI-catalyzed coupling of arylchalcogeno-moieties to aryl halides is significantly improved by microwave heating. Thus, reaction times can be reduced from 2 to 3 days to 6−8 h. Both aryl bromides and aryl chlorides can be used as substrates in the substitution reaction. The procedure is useful not only for diaryl sulfide and diaryl selenide synthesis but also for the preparation of diaryl tellurides. The usefulness of the microwave-procedure was demonstrated in the preparation of novel chalcogen containing antioxidants (ethoxyquins and 3-pyridinols).

Experimental Section

Typical Procedure for Microwave-Assisted Synthesis of Diaryl Chalcogenides. 4-Hydroxyphenyl Phenyl Selenide (3b). 4-Bromophenol (519 mg, 3.0 mmol) and diphenyl diselenide (469 mg, 1.5 mmol) were added to a stirred mixture of CuI (86 mg, 0.45 mmol), Mg turnings (144 mg, 6.0 mmol), and 2,2-bipyridyl (bpy) (69 mg, 0.45 mmol) in DMF (5 mL). This reaction mixture was heated at 200 °C in a sealed tube in a microwave reactor (300 W) for 7 h. The reaction mixture was poured into water (15 mL) and extracted with with Et_2O (20 × 4 mL). The organic phase was washed with brine (50 mL), dried ($MgSO_4$), filtered, and evaporated in vacuo. The crude product was purified by flash chromatography on silica, eluting with ethyl acetate and pentane (1:19) to give the title compound **3b** as a white solid (448 mg, 60%), mp 52−53 °C. ^{1}H and ^{13}C NMR data were in accordance with the literature.[11a]

(18) A control experiment showed that microwave heating of diphenyl ditelluride in DMF at 160 °C for 6 h in the presence of 10 mol-% CuI/bipy and magnesium did not produce diphenyl telluride (diphenyl ditelluride was recovered in 86% yield).

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Compounds **1**−**5**, **7**, **8**, and **10** were similarly prepared. For reaction times and temperatures, see Table 2. Amounts of 10, 15, and 20 mol-%, respectively, of CuI/2,2′-bipyridyl were used for telluride, selenide, and sulfide synthesis.

Phenyl 6-(2,2,4-Trimethyl-1,2-dihydroquinolinyl) Telluride (8c). The crude product was purified by flash chromatography on silica, eluting with Et_2O and pentane (5:95) to give the title compound **8c** (121 mg, 32%) as a red liquid. ^{1}H NMR δ 7.57−7.49 (several peaks, 4H), 7.19−7.16 (several peaks, 3H), 6.34 (d, J = 8.0, 1H), 5.33 (b s, 1H), 3.82 (s, 1H), 1.98 (s, 3H), 1.30 (s, 6H). ^{13}C NMR δ 18.7, 31.6, 52.2, 97.8, 114.3, 117.2, 122.8, 126.9, 128.1, 128.7, 129.3, 135.3, 136.4, 141.3, 143.9. MS: *m*/*z* 380 ($M+1^+$, 18), 173 (100).

Phenyl 6-(2,2,4-Trimethyl-1,2-dihydroquinolinyl) Selenide (8d). The crude product was purified by flash chromatography on silica, eluting with CH_2Cl_2 and pentane (1:9) to give the title compound **8d** as a light yellow liquid. ^{1}H NMR δ 7.33−7.10 (several peaks, 7H), 6.39 (d, J = 8.0, 1H), 5.32 (s, 1H), 3.85 (b s, 1H), 1.95 (s, 3H), 1.29 (s, 6H). ^{13}C NMR δ 18.6, 31.5, 52.2, 113.9, 114.0, 122.4, 125.8, 128.0, 128.8, 129.1, 129.9, 131.9, 134.8, 136.7, 143.8. The crystalline hydrochloride of the material was obtained by addition of HCl in ether to an ethereal solution of the selenide. Anal. Calcd for $C_{18}H_{19}NSe\cdot HCl\cdot 0.25Et_2O$: C, 59.87; H, 5.63. Found: C, 59.84; H, 5.67.

Phenyl 6-(2,2,4-Trimethyl-1,2-dihydroquinolinyl) Sulfide (8e). The crude product was purified by flash chromatography on silica, eluting with CH_2Cl_2 and pentane (1:9) to give the title compound **8e** as a colorless liquid. ^{1}H NMR δ 7.25−7.12 (several peaks, 7H), 6.45 (d, J = 8.0, 1H), 5.36 (s, 1H), 3.91 (b s, 1H), 2.00 (s, 3H), 1.35 (s, 6H). ^{13}C NMR δ 18.7, 31.6, 52.3, 113.8, 117.8, 122.3, 125.0, 126.7, 128.1, 128.8, 128.9, 131.0, 135.8, 140.5, 144.0. The crystalline hydrochloride of the material was obtained by addition of HCl in ether to an ethereal solution of the sulfide. Anal. Calcd for $C_{18}H_{19}NS\cdot HCl\cdot 0.25Et_2O$: C, 68.01; H, 6.41. Found: C, 68.10; H, 6.47.

3-Hydroxy-6-methyl-2-pyridyl Phenyl Telluride (10b). The reaction mixture was heated in the microwave reactor at 140 °C for 10 h. The residue was then concentrated under vacuo, extracted with $CHCl_3$, washed with water, and dried over Na_2SO_4. The crude product was purified by flash chromatography using ethyl acetate and pentane (20:80) to give the title compound **10b** as white solid, mp 150−51 °C. ^{1}H NMR δ 7.68 (d, J = 8.1, 2H), 7.28−7.17 (several peaks, 4H), 7.05 (d, J = 8.3, 1H), 6.07 (b s, 1H), 2.51 (s, 3H). ^{13}C NMR δ 23.5, 113.3, 121.2, 125.2, 128.3, 129.8, 130.6, 137.2, 152.3, 153.0. Anal. Calcd for $C_{12}H_{11}NOTe$: C, 46.07; H, 3.54. Found: C, 45.88; H, 3.47.

3-Hydroxy-6-methyl-2-pyridyl Phenyl Selenide (10c). The reaction mixture was extracted with ethyl acetate, and purification was carried out by flash chromatography using CH_2Cl_2 and MeOH (99:1) as eluent. Selenide **10c** was obtained as a white solid, mp 126−127 °C. ^{1}H NMR δ 7.41−7.37 (several peaks, 2H), 7.26−7.20 (several peaks, 4H), 7.10 (d, J = 8.2, 1H), 6.14 (s, 1H), 2.51 (s, 3H). ^{13}C NMR d 23.6, 122.9, 125.7, 127.6, 129.5, 131.4, 138.4, 151.6, 151.7. MS: *m*/*z* 266 ($M+1^+$, 100), 204 (18), 102 (41).

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Supporting Information Available: General synthetic details, experimental and spectral data for compounds **5a** and **7a**,**b** and copies of ^{1}H and ^{13}C NMR spectra of compounds **5a**, **7a**,**b**, **8c**−**e**, and **10b**−**d in pdf format**. This material is available free of charge via the Internet at http://pubs.acs.org.

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