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Microwave-assisted reaction of aryl diazonium fluoroborate and diaryl dichalcogenides in dimethyl carbonate: a general procedure for the synthesis of unsymmetrical diaryl chalcogenides[†]

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A convenient, general and efficient procedure for the synthesis of unsymmetrical diaryl chalcogenides has been developed by the reaction of aryl diazonium fluoroborates and diaryl dichalcogenides in the presence of zinc dust in dimethyl carbonate under microwave irradiation. The reactions of a wide range of substituted aryl diazonium fluoroborates and diaryl dichalcogenides have been addressed. The zinc dust is required for the cleavage of diaryl dichalcogenides. The products are obtained in high purity after fast column chromatography of the crude residue after evaporation of dimethyl carbonate.

1. Introduction

The organochalcogenides, particularly selenium and tellurium as structural motifs are found in a variety of molecules of biological, pharmaceutical and material interest.¹ They have useful applications as intermediates in organic synthesis.² Thus, a number of methods have been developed for their synthesis.³ Transition metal catalyzed aryl-chalcogen bond formation is one of the most common practices for the synthesis of aryl chalcogenides.³ Several metals including palladium,⁴ nickel⁵ and copper,⁶ have been employed to catalyze the reaction of aryl halides with thiol and selenol/PhSeNa under basic conditions for the synthesis of diaryl sulphides and selenidies although synthesis of diayl tellurides by this protocol is not very successful. However, due to the foul smell of thiols, instability of selenols and toxicity of sodium selenolates, synthesis using stable and easily accessible diaryl dichalcogenides is prefered.⁷ Recently, a few greener procedures involving the reaction of diaryl dichalcogenides/arylselenium halides/potassium aryltrifluoroborates and aryl boronic acids catalyzed by benign metals such as Cu and Fe or ionic liquid have been reported.8 In general, reaction with diaryl dichalcogenides and aryl halides/boronic acids requires a reductant for the generation of a chalcogenide anion and a metal for a subsequent reaction. Usually, a metal such as Zn or In is used as reducing agent or a strong base like NaOH is used for the cleavage of dichalcogenides and a transition metal initiates the reaction thereafter.⁷

We report here a transition metal free synthesis of unsymmetrical diaryl chalcogenides by a simple one-pot reaction of aryl diazonium fluoroborate and diaryl dichalcogenide in presence of Zn

Ar¹-N₂BF₄ + Ar²₂X₂
$$\xrightarrow{Zn, DMC, MW}$$
 Ar¹-X-Ar²
80 °C, 30 min.
X = S, Se, Te
Scheme 1 Synthesis of diaryl chalcogenide.

dust in dimethyl carbonate (Scheme 1) under microwave irradiation.

The involvement of diazonium salts for the synthesis of diaryl chalcogenides was reported earlier too.⁹ However these processes used lithium, sodium or potassium salts of arene thiolate/selenolate/tellurolate which are highly toxic.¹⁰ In addition, hazardous solvents such as acetonitrile and DMSO have been employed. Thus, these methods, although metal free, are not appreciated from an industrial and environmental standpoint. This prompted us to consider stable and nontoxic diaryl dichalcogenides in place of arene chalcogenates and Zn has been employed for their cleavage to generate chalcogenide anion *in situ.* The use of a strong base such as KOH for the cleavage of dichalcogenides leads to the formation of a considerable amount of phenol from diazonium fluoroborates and thus Zn remained as an obvious choice.

2. Results and discussion

To standardise the reaction conditions a series of experiments were performed under varying reaction parameters such as solvent, temperature and time for a representative reaction of 4-methoxyphenyl diazonium fluoroborate and diphenyl ditelluride in presence of zinc. Among a variety of solvents studied dimethyl carbonate furnished the best results in terms of reaction time and yield. Under microwave irradiation the reaction was complete after 30 min, whereas conventional heating at 80 °C

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Table 1 Optimization of reaction cond

	MeO N2BF4	Ph₂Te₂ Zn ►	Te	OMe
Entr	y Solvent	Temp	Time (h)	Yield ^d (%)
1	DMF	110 °C	8	84
2	DMF	80 °C	8	86
3^a	DMF	80 °C	0.5	85
4^b	DMF	80 °C	8	Trace
5	DMSO	80 °C	12	72
6	THF	60 °C	12	20
7	Toluene	100 °C	12	Trace
8	CH ₃ CN	80 °C	35	35
9	NMP	80 °C	8	80
10	DMC	90 °C	8	87
11	DMC	80 °C	8	88
12	DMC	60 °C	15	42
13	DMC	RT	8	
14^{b}	DMC	80 °C	8	
15^c	DMC	80 °C	8	Trace
16^{a}	DMC	80 °C	0.5	87
17	H ₂ O	100 °C	8	
18	H ₂ O/TBAB	100 °C	8	40

^{*a*} Reaction is done in microwave (power = 170 W). ^{*b*} No Zn dust is used. ^{*c*} ZnSO₄ is used in presence of zinc dust. ^{*d*} Yield of isolated product (¹H and ¹³C).

required 8 hours. The reaction did not initiate at room temperature. Surprisingly the reaction did not proceed at all in water alone without any additive (Table 1, entry 17); however TBAB (tetrabutyl ammonium bromide) facilitates the reaction to some extent (Table 1, entry 18). Other polar solvents such as DMF, DMSO, and NMP mediated the reaction quite efficiently. Dimethyl carbonate (DMC) was chosen because of its environmental acceptability, moderate boiling point and costeffectiveness.¹¹

In a typical experimental procedure, a mixture of an aryl diazonium tetrafluoroborate, diphenyl ditelluride/diselenide/ disulfide in DMC in presence of Zn was heated under microwave irradiation for a required period of time (TLC). Evaporation of solvent followed by the column chromatography of the crude residue provided the pure product.

A wide range of substituted phenyl diazonium fluoroborates were reacted with diphenyl ditelluride using this procedure to provide the corresponding products. The results are summarized in Table 2. For comparison, all the reactions were performed in a conventional oil bath heating as well as under microwave irradiation. The reaction times are substantially reduced by microwave heating, however the yields are comparable in both heating modes. The substitution of electron withdrawing and electron donating groups on the phenyl ring of diazonium fluoroborates did not have any appreciable influence on the outcome of the reaction. Several functional groups such as COMe, COOMe, COOH, OMe, CN, NO₂, Br, F, OCF₃, OH are compatible with these reaction conditions. The naphthyl diazonium fluoroborate also underwent reaction without any difficulty.

The same procedure was followed for the synthesis of diaryl selenides and sulfides. Several substituted phenyl diazonium fluoroborates have been employed for these reactions. The results are reported in Table 3 for selenides and in Table 4 for sulfides. Functionalization of products with a wide range of groups such as Br, CN, NO₂, OMe, COOMe, Cl, COMe has been successfully achieved using this procedure.

In general, the reactions are clean and high yielding. Microwave heating made them faster too. The nature and position of substituents did not have any effect on the reaction rates and yields. The chalcogenides are obtained pure and are characterized properly by spectroscopic data. Several of these compounds are new. The synthesis of diaryl tellurides is less explored compared to those of other chalcogenides and a limited number of synthetic methods for tellurides are available. This procedure provides a practical alternative to the existing procedures. The dimethyl carbonate has been recovered without any appreciable loss and has been reused. Notably, dimethyl carbonate is considered one of the high priority green solvents.¹¹

A possible reaction pathway is outlined in Scheme 2. Initially Zn reacts with diphenyl dichalcogenide to form $Zn(XPh)_2^{12}$ which then interacts with diazonium fluoroborate to provide the product *via* release of N₂. The involvement of zinc metal is vital in the cleavage of diphenyl dichalcogenide. In absence of zinc dust or in presence of ZnSO₄, the progress of reaction is not more than 10%.

3. Experimental

IR spectra were recorded on a Shimadzu 8300 FTIR spectrometer. ¹H NMR and ¹³C NMR spectra were run on Bruker DPX-300 and DPX-500 instruments. HRMS were acquired on a Microtek Qtof Micro YA263 spectrometer. All commercial reagents were distilled before use. Aryl diazonium tetrafluoroborates were prepared from the corresponding anilines by diazotization by following a previously reported protocol.¹³ A monomode microwave reactor (Discover model from CEM Corporation, USA) has been used for all the reactions. Zinc dust and DMC (dimethyl carbonate) were purchased from Aldrich.

Representative experimental procedure for the reaction of 4-methoxy diazonium tetrafluoroborate and diphenyl ditelluride (Table 2, entry 6)

A mixture of 4-methoxy diazonium tetreafluoroborate (272 mg, 1 mmol), diphenyl ditelluride (200 mg, 0.5 mmol) and Zn dust (32 mg, 0.5 mmol) in DMC (4 mL) was heated under microwave irradiation for 30 min (By conventional heating the mixture was stirred at 80 °C for 8 h) (TLC). The DMC was evaporated and the corresponding diaryl telluride was obtained by column chromatography as a white solid (276.35 mg, 87%), mp 60–62 °C, IR (KBr) 3062, 1880, 1585, 1488 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.76 (s, 3H), 6.78 (d, J = 8.5 Hz, 2H), 7.13–7.19 (m, 3H), 7.55 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H); ¹³ C NMR (125 MHz, CDCl₃) δ 55.2, 103.3, 115.6 (2C), 116.0, 127.4, 129.4 (2C), 136.5 (2C), 141.3 (2C), 160.1.

This procedure was followed for all the reactions in Tables 2–4. A few of these products are known compounds (see the references in Tables 2–4) and were easily identified by comparison of their spectroscopic data with those previously reported.

 Table 2
 Zn mediated reaction of diaryl ditellurides with aryl diazonium tetrafluoroborate

		⊕⊖ N ₂ BF ₄	Ph ₂ Te ₂ 50	Te Te			
		Zn, DM	C, 80 °C, 8-10 h		L TR		
			Conventional heating		Microwave heating ^b		
Entry	R	Product	Yield $(\%)^a$	Time (h)	Yield (%) ^a	Time (min)	Ref
1	4-Br	C Te C Br	90	8	92	30	7m
2	4-COMe		85	7.5	88	25	14 <i>a</i>
3	4-COOMe		88	7	90	25	7m
4	4-COOH		80	8.5	81	35	—
5	3-COMe		93	8	92	25	
6	4-OMe		88	8	87	30	7 <i>m</i>
7	4-COOEt		82	7	85	35	—
8	4-NO ₂		72	8	78	30	9 <i>a</i>
9 ^c	Naphthyl		95	7	97	25	71
10	4-CN		86	8	90	30	14 <i>b</i>
11	4-O ⁱ Pr		90	8.2	88	25	—
12	3-CN, 4-F		82	10	87	25	_
13	2-Br		80	8	83	30	—
14	4-OCF ₃		85	8	87	30	
15	4-Me		90	8.2	92	25	9 <i>a</i>
16	4-F		80	8	85	30	14 <i>c</i>

Entry		$R \xrightarrow{\mu} Zn,$	Ph ₂ Te ₂ ⁵⁰ DMC, 80 °C, 8-10 h	eating	R Microwave heating ^b		
	R	Product	Yield $(\%)^a$	Time (h)	Yield $(\%)^a$	Time (min)	Ref
17	2-ОН		74	8	78	35	
18	2-NO ₂		72	8	73	35	9 <i>a</i>

^a Yields of isolated pure products (¹H and ¹³C). ^b Microwave power = 170 W. ^c 1-Naphthyl diazonium tetrafluoroborate is used as electrophile.

The unknown compounds were fully characterized by their IR, 1 H NMR, 13 C NMR and HRMS spectra, and C, H, N-analyses. These data are given below in order of their entries in Table 2 and 3.

4-(Phenyltellanyl)benzoic acid (Table 2, entry 4)

Yellow solid; mp 160–162 °C; IR (KBr) 3300–2500 (broad), 1681, 1589, 1292, 759 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.21 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 8 Hz, 2H), 7.74–7.78 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 113.3, 125.3, 128.2, 129.0, 129.9 (2C), 130.6 (2C), 135.7 (2C), 139.9 (2C), 172.1; HRMS calcd for C₁₄H₁₄O₂Te [M + H]⁺: 328.9821; Found: 328.9816.

1-(3-(Phenyltellanyl)phenyl)ethanone (Table 2, entry 5)

Yellow liquid; IR (neat) 3053, 3014, 1685, 1573, 1253, 756 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.51 (s, 3H), 7.21–7.30 (m, 4H), 7.73 (d, J = 7 Hz, 2H), 7.81 (t, J = 8.5 Hz, 2H), 8.24 (s, 1H); ¹³C NMR (125 MHz, CDCL₃) δ 26.6, 114.1, 115.6, 127.6, 128.3, 129.6, 129.7 (2C), 137.2, 137.9, 138.6 (2C), 141.9, 197.4; anal calcd for C₁₄H₁₂OTe: C 51.92, H 3.73; found: C 51.86, H 3.69%.

Ethyl 4-(phenyltellanyl)benzoate (Table 2, entry 7)

Brown viscous liquid; IR (neat) 3018, 2983, 1712, 1280, 1215, 756 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.38 (t, J = 7.5 Hz, 3H), 4.37 (q, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.62 (d, J = 8 Hz, 2H), 7.80–7.84 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 14.4, 61.1, 113.6, 123.1, 128.7, 129.6 (2C), 129.9 (2C), 130.2 (2C), 136.1 (2C), 139.5, 166.5; anal calcd for C₁₅H₁₄O₂Te: C 50.91, H 3.99; found: C 50.88, H 3.93%.

(4-Isopropoxyphenyl)(phenyl)tellane (Table 2, entry 11)

Brown liquid; IR (neat) 3053, 2976, 1581, 1485, 1242, 731 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.21 (d, J = 6 Hz,

6H), 4.40–4.43 (m, 1H), 6.66 (d, J = 8.5 Hz, 2H), 7.03–7.09 (m, 3H), 7.46 (d, J = 7 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 12.1 (2C), 69.8, 102.9, 116.1, 117.3 (2C), 127.3 (2C), 129.4 (2C), 136.5, 141.3 (2C), 158.4; anal calcd for C₁₅H₁₆OTe: C 53.01, H 4.74; found: C 53.13, H 4.62%.

2-Fluoro-5-(phenyltellanyl)benzonitrile (Table 2, entry 12)

Yellow viscous liquid; IR (neat) 3066, 2926, 2235, 1595, 1487, 1242, 1118, 736 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.02–7.06 (m, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.36–7.39 (m, 1H), 7.76 (t, *J* = 7.5 Hz, 2H), 7.81–7.84 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 103.1, 110.2 (*J* = 5Hz), 113.3, 113.5, 117.5 (*J* = 6.25 Hz), 129.0, 130.1 (2C), 139.1 (2C), 141.8, 143.9 (*J* = 8.75 Hz), 162.0 (*J* = 258.2 Hz); anal calcd for C₁₃H₈FNTe: C 48.07, H 2.48, N 4.31; found: C 47.92, H 2.53, N 4.28%.

2-Bromophenyl)(phenyl)tellane (Table 2, entry 13)

Yellow viscous liquid; IR (neat) 3053, 2989, 1435, 1003, 746 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.92 (d, J = 7.5 Hz, 1H), 6.99–7.05 (m, 2H), 7.37 (t, J = 7 Hz, 2H), 7.46 (t, J = 7 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 114.8, 124.0, 127.1, 127.9, 128.1, 129.3, 130.1 (2C), 132.1, 134.5, 141.3 (2C); HRMS calcd for C₁₂H₉BrTe [M]⁺: 361.8950; found: 361.8918.

Phenyl(4-(trifluoromethoxy)phenyl)tellane (Table 2, entry 14)

Brown liquid; IR (neat) 3066, 2924, 1573, 1487, 1257, 1166, 732 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.95 (d, J = 8.5 Hz, 2H), 7.14 (t, J = 8Hz, 2H), 7.22 (t, J = 8 Hz, 1H), 7.56–7.64 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 112.8, 114.3, 119.6, 122.1 (2C), 128.4, 129.8 (2C), 130.6 (2C), 139.2 (2C), 149.3; anal calcd for C₁₃H₉F₃OTe: C 42.68, H 2.48; found: C 42.61, H 2.49%.

2-(Phenyltellanyl)phenol (Table 1, entry 17)

Yellow liquid; IR (neat) 3390, 3053, 2924, 1573, 1438 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.23 (s, 1H), 6.72 (t, *J* = 7.5 Hz, Table 3 Zn mediated reaction of diaryl diselenides with aryl diazonium tetrafluoroborate

		$R \xrightarrow{\oplus}_{N_2 BF_4}^{50} \xrightarrow{Ph_2 Se_2}_{Zn, DMC, 80 °C, 8-10 h} \square R$					
			Conventional heating		Microwave heating ^b		
Entry	R	Product	Yield ^a (%)	Time (h)	Yield ^a (%)	Time (min)	Ref
1	Н	Se	84	8	88	30	9 <i>a</i>
2	4-Br	C Se C Br	87	8	89	25	7 <i>m</i>
3	2-CN	Se C	81	9	85	30	9 <i>a</i>
4	4-COOMe	COOMe	84	8.5	83	30	7 <i>m</i>
5	4-COMe	C Se C COMe	85	8	88	25	9 <i>c</i>
6	3-Cl, 4-Me	C Se C Me	91	8	93	25	
7	3-COMe	COMe	82	8	85	35	7 <i>b</i>
8	4-OMe	C Se C OMe	90	8	94	25	7 <i>m</i>
9	3-NO ₂	Se NO ₂	80	10	82	30	7 <i>b</i>
10 ^c	4-Me	Me	86	8	90	25	7 <i>b</i>
11 ^d	Naphthyl	Se-	90	9	93	25	71
12	4-CN	C Se C CN	85	8	87	30	14 <i>d</i>
13	3-CN, 4-F	Se CN F	80	10	85	25	
14	3-Cl	C) Se C) CI	90	8	89	25	9 <i>a</i>

^{*a*} Yields of isolated pure products (1 H and 13 C). ^{*b*} Microwave power = 170 W. ^{*c*} Di(4-methoxyphenyl) diselenide is used in place of diphenyl diselenide. ^{*d*} 1-Naphthyl diazonium tetrafluoroborate is used as electrophile.

Table 4 Zn mediated reaction of diaryl disulfides with aryl diazonium tetrafluoroborate



^{*a*} Yields of isolated pure products (1 H and 13 C). ^{*b*} Microwave power = 170 W.



Scheme 2 Probable mechanism.

1H), 6.99 (d, J = 8 Hz, 1H), 7.10 (t, J = 7.5 Hz, 2H), 7.16 (d, J = 8 Hz, 1H), 7.24 (t, J = 8 Hz, 1H), 7.44 (d, J = 8 Hz, 2H), 7.68 (d, J = 7.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 103.9, 114.1, 116.3, 121.9, 127.9, 129.8 (2C), 132.3, 136.3 (2C), 141.5, 157.6; HRMS calcd for C₁₂H₁₀OTe [M + H]⁺: 300.9872; found: 300.9867.

(3-Chloro-4-methylphenyl)(phenyl)selane (Table 3, entry 6)

Yellow liquid; IR (neat) 3055, 2922, 1577, 1473, 1437, 736 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.37 (s, 3H), 7.14

(d, J = 8 Hz, 1H), 7.28–7.31 (m, 4H), 7.48–7.50 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 19.8, 127.6, 129.3, 129.5 (2C), 130.9, 131.5 131.7, 133.0, 133.3 (2C), 135.1, 135.5; anal calcd for C₁₃H₁₁ClSe: C 55.44, H 3.94; found: C 55.51, H 3.88%.

2-Fluoro-5-(phenylselanyl)benzonitrile (Table 3, entry 13)

Yellow viscous liquid; IR (neat) 3070, 2922, 2235, 1577, 1487, 1242, 1118, 740 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.10 (t, J = 8 Hz, 1H), 7.32–7.38 (m, 3H), 7.50 (d, J = 7.5 Hz, 2H), 7.60–7.64 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 113.4, 117.4, 117.5, 128.5, 128.8, 129.2, 130.0 (2C), 134.3 (2C), 136.6, 138.8 (7.5 Hz), 162.5 (258.7 Hz); anal calcd for C₁₃H₈FNSe: C 56.54, H 2.92, N 5.07; found: C 56.49, H 2.95, N 4.97%.

4. Conclusions

In conclusion, we have developed a general procedure for the synthesis of diaryl chalcogenides (sulphides, selenides and tellurides) by a reaction of aryl diazonium fluoroborates and diaryl dichalcogenides in the presence of zinc in dimethyl carbonate under microwave irradiation. The simplicity in operation, general applicability to all three chalcogenides, scope of wide functionalization, use of recyclable dimethyl carbonate as reaction medium, energy efficiency (shorter reaction time under microwave irradiation), employment of stable and readily available diaryl dichalogenide in place of foul smelling and toxic thiols/selenols/thiolate/selenoate, transition metal-free reaction and high yields of products make this procedure greener and more cost-effective.

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