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The use of aminoiminomethanesulfinic acid (thiourea dioxide) under phase transfer conditions for generating organochalcogenate anions. Synthesis of sulfides, selenides and tellurides

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Abstract

A procedure is described which allows for the in situ synthesis of arylalkyl, diaryl and dialkylchalcogenides under phase transfer conditions starting from the corresponding diorganodichalcognides. The dichalcogenides are reduced by aminoiminomethanesulfinic acid (thiourea dioxide) in alkaline medium and catalyzed by a quaternary ammonium salt. The reduction proceeds easily for diaryl disulfides and diaryl diselenides at a sodium hydroxide concentration of 13%; diaryl ditellurides require a 50% sodium hydroxide solution to give the aryl tellurolate anion. The dialkyl diselenides and dialkyl ditellurides are more difficult to reduce. The intermediate arylthiolates and arylselenolates are quenched by alkyl and activated aryl halides to give the corresponding sulfides and selenides in high yield (77–97%). The aryltellurolates react with alkyl halides giving the aryl alkyl tellurides in 81–96% yield. The procedure could not be successfully used for the synthesis of dialkylselenides and dialkyl tellurides; low yields and mixture of products were formed.

Introduction

Aminoiminomethanesulfinic acid (thiourea dioxide) (I) has been widely used as a strong reducing agent for inorganic metal ions.

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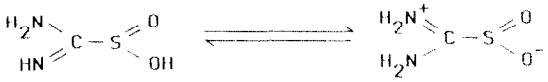

(I)

Its use in organic chemistry is limited and to our knowledge, very few synthetic transformations have been done with this reagent. The reduction of aromatic nitro compounds by thiourea dioxide (I) has been described by Gore [1]. Drabowicz and Mikolajczyk have used the same reagent in the presence of iodine to reduce sulfoxides to sulfides [2]. Ketones have been reduced with this reagent to the corresponding secondary alcohols [3–5]. Borgogno, et al. [6] have utilized thiourea dioxide to reduce sulfimines to sulfides and disulfides to thiols in a two phase system in the presence of hexadecyltributylphosphonium bromide. In this paper we report the synthesis of sulfides, selenides and tellurides using I to reduce the corresponding dichalcogenides.

In previous papers we have reported the synthesis of arylalkyl sulfides, selenides and tellurides under phase transfer conditions (P.T.C.). In these reactions the nucleophilic arylthiolate [7] selenolate [8] or tellurolate [9] anions were generated by phase transfer catalysed cleavage of the corresponding dichalcogenides with concentrated sodium hydroxide solution in a two-phase system (eq. 1).

$$ArXXAr \xrightarrow[P.T.C.]{50\%\ NaOH/THF} 3/4\ ArX + 1/4\ ArXO_2 \qquad (1)$$

X = S, Se, Te

The great advantage of this methodology is the use of disulfides and diselenides which are easier and more pleasant to work with instead of the evil smelling thiophenol or selenophenol. In addition, the reactions were carried out in tetrahydrofuran/water and at low temperature which avoids the use of carcinogenic hexamethylphosphoric triamide (HMPA). The use of complex metal hydrides and anhydrous conditions is also eliminated. The disadvantage of this method is that only 3/4 of the starting diaryl dichalcogenide is incorporated into the desired product as shown in eq. 1.

When we tried to apply this methodology to the synthesis of diarylsulfides, the main product was the corresponding phenol formed from the direct aromatic substitution of the halide by the hydroxide ion under the strong alkaline conditions required to promote the disproportionation reaction of the disulfide.

The use of aminoiminomethanesulfinic acid (I) allowed us to overcome this problem. The reduction of disulfides using this reagent in alkaline medium occurs at lower sodium hydroxide concentration and it was possible to develop a very efficient method for the synthesis of diaryl sulfides and diaryl selenides. Preliminary results have been recently reported [10].

In this paper we give a full account of the synthesis of sulfides, selenides and tellurides based on the reduction of disulfides, diselenides and ditellurides with thiourea dioxide in alkaline medium under phase transfer conditions in the presence of an alkyl of aryl halide.

Results

Many methods have been described for the synthesis of diaryl, arylalkyl and dialkyl sulfides. However all of these methods require special conditions such as

high temperature [11], strong basic conditions [12], dipolar aprotic solvents [13–15] or catalysis by transition metal complexes [16,17].

Using the method described in this paper the generation of the arylthiolate anion occurs almost instantaneously and can be followed by observing the discoloration of the diaryl disulfide solution. The reaction time for nucleophilic aromatic substitution using activated aryl halides and phenyl thiolate was four hours. However, aryl thiolate anions deactivated by electron-withdrawing groups did not react within this time. When we tried to carry out the reaction of 4-nitrophenylthiolate with 2-nitrophenyl chloride and 4-nitrophenyl bromide, the starting diaryl disulfide and the aryl halide were recovered unchanged. Under the same conditions phenylthiolate gave the corresponding sulfides in 97% and 85% yield, respectively. Less-activated aryl halides such as 3-bromochlorobenzene and 1,2,4,5-tetrabromobenzene failed to react. Cetyltrimethylammonium bromide (CTAB) was used as a catalyst for the preparation of diaryl disulfides. A comparative blank experiment (in the absence of the catalyst) was conducted using 2,4-dinitrochlorobenzene as substrate and diphenyl disulfide as the source of thiolate. The reaction time was four times longer and the desired diaryl sulfide was obtained in only 24% yield.

Arylalkyl sulfides were obtained by the reaction of arylthiolates and alkyl halides. As one can see in Table 1 activated alkyl halides such as benzyl chloride (entry 7) and allyl bromide (entries 8 and 9) react almost instantaneously leading to the benzyl or allyl aryl sulfides in good yields. The reaction with primary alkyl halides occurred in a relatively short time and in good yields. Secondary alkyl halides did not react, and this makes it possible to achieve good regioselectivity in cases where the substrate has both primary and secondary reactive sites (entry 17).

Unsymmetrical dialkyl sulfides were also obtained by allowing dialkyl disulfides to react with alkyl halides (Table 1, entries 18–22).

For the synthesis of aryl alkyl and dialkyl sulfides the phase transfer catalyst used was cetyltrimethylammonium chloride (CTACl). It was observed that increasing the base concentration increases the reaction rate. The yields, however, decrease. The best compromise between reaction time and yield in the case of aryl alkyl and dialkyl sulfides was achieved by using 6% aqueous sodium hydroxide solution (eq. 2).

$$\mathrm{RSSR} \xrightarrow[2\ \mathrm{R^1X,\ P.T.C.}]{\mathrm{(I),\ 6\%\ NaOH,\ THF}} 2\ \mathrm{RSR^1} \qquad (2)$$

R = Alkyl, Aryl
R^1 = Alkyl, Aryl
P.T.C. = CTACl, CTAB

Several methods are available for the synthesis of dialkyl [18,19], arylalkyl [18,20,21], and diaryl selenides [18,25–27]. The methodology described above for the synthesis of sulfides could be advantageously applied for the synthesis of diaryl and arylalkyl selenides avoiding some of the problems encountered in the described methods (Eq. 3).

$$\mathrm{RSeSeR} \xrightarrow[\mathrm{P.T.C.,\ 2R^1X}]{\mathrm{(I),\ 6\%\ NaOH,\ THF}} \mathrm{RSe\ R^1} \qquad (3)$$

R = Alkyl, Aryl
R^1 = Alkyl, Aryl
P.T.C. = CTACl

(Continued on p. 334)

Table 1

Synthesis of diaryl, arylalkyl and dialkyl sulfides under phase transfer conditions

Entry	Disulfide	Halide	Reaction Time (h)	Yield [a] (%)	m.p. (°C) or b.p. (°C/mmHg)	Anal. (Found (calc))(%)			^{1}H NMR, δ (ppm), J in Hz CCl_4/TMS internal standard
						C	H	N	
1	$(C_6H_5S)_2$	1-Cl-2,4-$NO_2C_6H_3$	4.0	95	118–121 (119–120) [38]				6.80 (d, J 9,1H); 7.35 (m, 5H); 7.86 (dd, J 9.3, 1H); 8.77 (d, J 3, 1H) [b]
2	$(C_6H_5S)_2$	1-F-2,4-$NO_2C_6H_3$	4.0	89	118–121				
3	$(C_6H_5S)_2$	1-Cl-2-$NO_2C_6H_4$	4.0	97	78–81 (78–79) [39]				6.60 (dd, J 9.3, 1H); 6.7–7.5 (m, 7H); 7.80 (dd, J 9.3, 1H) [b]
4	$(C_6H_5S)_2$	1-Br-4-$NO_2C_4H_4$	4.0	85	58–60 (52–53) [40]				6.81 (d, J 9, 2H); 7.15 (br s, 5H) 7.7 (d, J 9, 2H) [b]
5	$[4\text{-}(CH_3)_2NC_6H_4S]_2$	1-Br-4-$NO_2C_6H_4$	4.0	80	185–187 (180) [41]				2.85 (s, 6H); 5.00 (d, J 9.2 H); 6.90 (d, J 9.2H); 7.10 (d, J 9, 2H); 7.70 (d, J 9 2H) [b]
6	$[4\text{-}(CH_3)_2NC_6H_4S]_2$	1-Cl-2-$NO_2C_6H_4$	4.0	82	190–192	61.13 (61.29)	5.05 (5.14)	10.2 (10.28)	3.00 (s, 6H); 6.73 (d, J 9, 2H); 6.8–7.2 (m, 3H); 7.33 (d, J 9, 2H); 8.13 (dd, J 8.2, 1H) [b]
7	$(4\text{-}NO_2C_6H_4S)_2$	$C_6H_5CH_2Br$	0.2	92	121 (123) [42]				4.28 (s, 2H); 7.33 (d, J 9, 2H); 7.35 (br s, 5H); 8.10 (d, J 9, 2H) [b]
8	$(4\text{-}NO_2C_6H_4S)_2$	$C_6H_5CH_2Br$	0.25	82	121				4.28 (s, 2H); 7.2–7.6 (m, 5H); 7.35 (d, J 9, 2H); 8.16 (d, J 9, 2H) [b]
9	$(4\text{-}NO_2C_6H_4S)_2$	$CH_2{=}CHCH_2Br$	0.25	82	38 (40–41) [43]				3.66 (d, J 6, 2H); 5.0–6.3 (m, 3H); 7.3 (d, J 9, 2H); 8.08 (d, J 9, 2H) [b]
10	$(4\text{-}NO_2C_6H_4S)_2$	C_4H_9Br	0.9	82	69–70 (73) [44]				1.00 (t, J 9, 3H); 1.2–2.1 (m, 4H); 3.03 (t, J 7, 2H); 7.3 (d, J 9, 2H); 8.12 (d, J 9, 2H) [b]

11	$(4\text{-}NO_2C_6H_4S)_2$	$C_6H_5(CH_2)_2Br$	2.1	96	43	64.55 (64.89)	4.98 (5.02)	5.29 (5.40)	2.8–3.4 (m, 4H); 7.0–7.4 (m, 5H); 7.2 (d, *J* 9, 2H); 8.06 (d, *J* 9, 2H) [b]
12	$(4\text{-}NO_2C_6H_4S)_2$	$C_{12}H_{25}Br$	3.3	96	30 (29–30) [45]				0.6–2 (m, 23H); 3.0 (t, *J* 6, 2H); 7.3 (d, *J* 9, 2H); 8.12 (d, *J* 9, 2H) [b]
13	$(C_6H_5S)_2$	C_4H_9Br	3.0	95	130/15 (116–117/16) [46]				0.93 (t, *J* 7, 3H); 1.1–1.9 (m, 4H); 2.87 (t, *J* 7, 2H); 6.7–7.4 (m, 5H)
14	$(C_6H_5S)_2$	$C_6H_5CH_2Br$	4.5	94	41–43 (41–42) [47]				3.95 (s, 2H); 6.8–7.5 (m, 10H)
15	$(C_6H_5S)_2$	$C_{12}H_{25}Br$	8.5	90	31 (33–34) [48]				0.9–2 (m, 23H); 2.83 (t, *J* 7, 2H); 7.0–7.4 (m, 5H)
16	$[4\text{-}(CH_3)_2NC_6H_4S]_2$	$C_{12}H_{25}Br$	2.0	87		74.17 (74.70)	11.07 (10.97)	4.01 (4.36)	0.8–1.7 (m, 23H); 2.63 (t, *J* 7, 2H); 2.86 (s, 6H); 6.45 (d, *J* 9, 2H); 7.10 (d, *J* 9, 2H)
17	$(4\text{-}NO_2C_6H_4S)_2$	$BrCH_2CH_2$ $CHBrCH_3$	1.1	87	140–150/0.25	41.36 (41.38)	4.22 (4.16)	4.75 (4.82)	1.78 (d, *J* 7, 3H); 2.25 (q, *J* 7, 2H); 3.25 (m, 2H); 4.20 (sext., *J* 7, 2H); 7.4 (d, *J* 9, 2H); 8.1 (d, *J* 9, 2H)
18	$(CH_3S)_2$	$C_8H_{17}Br$	4.0	90	100/17 [49]				0.6–1.8 (m, 15H); 2.00 (m, 3H); 2.40 (t, *J* 7, 2H)
19	$(CH_3S)_2$	$C_6H_5CH_2Br$	4.0	86	80/25 195–198/760 [50]				1.90 (s, 3H); 3.60 (s, 2H); 7.26 (br s, 5H)
20	$(CH_3S)_2$	$C_{12}H_{25}Br$	3.3	83	90/5 135/760 [51]				0.7–1.8 (m, 20H); 2.00 (s, 3H); 2.40 (t, *J* 7, 2H)
21	$(C_4H_9S)_2$	$1\text{-}Cl\text{-}4\text{-}NO_2C_6H_4$	4.0	89	see entry 10				
22	$(C_4H_9S)_2$	$C_8H_{17}Br$	4.0	40	85/0.25 110/2 [52]				0.6–1.1 (m, 6H); 1.1–1.8 (m, 16H); 2.63 (t, 4H, *J* 7)
23	$(C_6H_5S)_2$	$(CH_3O)_2$ $CH(CH_2)_2Br$	4.0	71		62.36 (62.23)	7.2 (7.6)		1.6–2.1 (m, 2H); 2.88 (t, *J* 7, 2H); 3.23 (s, 6H); 4.43 (t, *J* 7, 1H); 7.0–7.3 (m, 5H)

[a] Yield of the chromatographed product. [b] ^{1}HNMR spectra in $CDCl_3$. [c] Purified by column chromatography on silica gel eluting with atyl acetate.

The reaction time for the preparation of diaryl selenides was 4 h. In the case of the aryl alkyl selenides the reaction time was monitored by TLC and it was observed that the secondary alkyl halides react very slowly and the reaction is quite selective for one of the two sites present in the substrate (Table 2, entries 7, 8). The catalyst used in the preparation of selenides was CTACl and the sodium hydroxide concentration was also 6%.

Recently tellurium compounds have found considerable use in organic synthesis [28]. In view of these recent developments convenient high yield methods for the introduction of tellurium into organic molecules are desirable. So we have applied the above methodology to the synthesis of tellurides. The reaction of diaryl ditellurides with alkyl halides under these reaction conditions did not lead to the corresponding tellurides. It was necessary to increase the sodium hydroxide solution concentration to 50% in order to obtain aryl alkyl tellurides in good yield (eq. 4, Table 3).

$$ArTeTeAr \xrightarrow[P.T.C., 2RX]{(1),\ 50\%\ NaOH,\ THF} ArTeR \qquad (4)$$

The synthesis of diaryl tellurides was not possible since at this base concentration the main product was the phenol. Reduction of the base concentration resulted in the formation of only small amounts of the diaryl tellurides after prolonged reaction time. In the case of dialkyl tellurides the alkanetellurolate anion probably deactivates the catalyst by dealkylation; a mixture of the dialkyltelluride and the starting dialkyl ditelluride was obtained. In comparison with these results the reaction of divinyl ditellurides with alkyl halides under the standard conditions employed for the synthesis of aryl alkyl tellurides leads to the formation as vinyl alkyl tellurides in up to 73% yield [29].

In conclusion, the methodologies described in this work allow the synthesis of aryl alkyl sulfides, selenides and tellurides under very attractive conditions and in high yield. Diaryl and dialkyl sulfides as well as diaryl selenides were also efficiently prepared by this method, although dialkyl selenides, dialkyl tellurides and diaryl tellurides were obtained only in low yield.

At this point it must be mentioned that hydroxymethyl sulfoxylate (Rongalite), an inexpensive reagent which works under conditions similar to those used for thiourea dioxide, has been used to transform diphenyl diselenide into phenylselenolate [30]. However, to our knowledge no extensive systematic work was done to generalize the use of Rongalite to prepare organic chalcogenides from the corresponding organo dichalcogenides.

Experimental

General. Melting points were measured with a Kofler hot plate and are uncorrected. The infrared spectra were recorded on a Perkin–Elmer-735 spectrophotometer and the ^1H NMR spectra were determined at 60 MHz on a Varian T-60 and a Perkin–Elmer Hitachi R-24A spectrometers, and a 80 HMz on a Varian FT-80A spectrometer using TMS as internal reference, CCl_4 was used as the solvent when not otherwise specified. Mass spectra were determined with a Hewlett–Packard 5995 GC-MS spectrometer operating at an ionising potential of 70 eV. Silica gel 60 (Merck) was used for column chromatography. Pre-coated aluminum sheets (0.2

(Continued on p. 338)

Table 2. Synthesis of diaryl-, arylalkyl- and dialkyl selenides under phase transfer conditions

Entry	Diselenide	Halide	Reaction time (h)	Yield [a] (%)	m.p. (°C) b.p. (°C/mmHg)	Anal. (found (calc)(%)) C	H	N	^{1}H NMR, δ (ppm), J Hz CCl_4/TMS Internal Standard
1	$(C_6H_5Se)_2$	1-Cl-2,4-$NO_2C_6H_3$	4.0	87	136–139 [53]				6.87 (d, J 9, 1H); 7.0–7.6 (m, 5H); 7.83 (dd, J 9, 2, 1H); 8.76 (d, J 2, 1H) [b]
2	$(C_6H_5Se)_2$	1-Cl-2-$NO_2C_6H_4$	4.0	95	86–88	51.78 (51.81)	3.41 (3.26)	5.05 (5.03)	6.6–7.6 (m, 8H); 7.9–8.1 (m, 1H) [b]
3	$(C_6H_5Se)_2$	1-Cl-4-$NO_2C_6H_4$	4.0	77	52–54	52.09 (51.81)	4.93 (5.03)	3.63 (3.26)	6.8–7.4 (m, 7H); 7.68 (d, J 9, 2H) [b]
4	$(4\text{-Cl-}C_6H_4Se)_2$	1-Cl-2-$NO_2C_6H_4$	4.0	75	106–108 [54]				6.5–7.5 (m, 7H); 7.9–8.2 (m, 1) [b]
5	$(4\text{-Cl-}C_6H_4Se)_2$	$C_6H_5CH_2Br$	0.5	96	43–45	55.78 (55.43)	4.04 3.94		3.96 (s, 2H); 6.9–7.5 (m, 9H)
6	$(4\text{-Cl-}C_6H_4Se)_2$	$C_{12}H_{25}Br$	0.5	92	100–110/0.05	59.65 (60.08)	8.17 (8.12)		0.7–1.9 (m, 23H); 2.8 (t, J 7, 2H); 7.10 (d, J 9, 2H); 7.36 (d, J 9, 2H)
7	$(4\text{-Cl-}C_6H_4Se)_2$	$CH_3CHBr(CH_2)_2Br$	1.5	87	90–100/0.05	37.09 (36.78)	3.73 (3.70)		1.63 (d, J 7, 3H); 1.7–2.3 (m, 2H); 2.95 (m, 2H); 4.10 (sext, J 7, 1H); 7.06 (d, J 9, 2H); 7.4 (d, J 9, 2H)
8	$(3\text{-}CF_3C_6H_4Se)_2$	$CH_3CHBr(CH_2)_2Br$	1.5	87	100–110/0.05	36.42 (36.68)	3.19 (3.36)		1.73 (d, J 7, 3H); 1.9–2.4 (m, 2H); 3.08 (m, 2H); 4.17 (sext., J 7, 1H); 7.1–7.9 (m, 4H)
9	$(3\text{-}CF_3C_6H_4)Se)_2$	$C_6H_5CH_2Br$	0.5	97	90–100/0.05	53.06 (53.35)	3.04 (3.52)		4.08 (s, 2H); 7.0–7.8 (m, 10H)
10	$(3\text{-}CF_3C_6H_4Se)_2$	$C_{12}H_{25}Br$	0.5	90	110–120/0.05	58.09 (58.02)	7.54 (7.43)		0.7–2.0 (m, 23H); 2.9 (t, J 7, 2H); 7.1–7.7 (m, 4H)
11	$(C_3H_7(CH_3)CHSe)_2$	$CH_3CHBr(CH_2)_2Br$	5.0	36	80/0.03	37.76 (37.78)	6.73 (6.69)		0.7–3.1 [m, 18H (the multiplet incorporates two dublets at 1.22 and at 1.76, J 6]; 4.20 (sext., 1H)
12	$(C_8H_{17}Se)_2$	$CH_3(CH_2)_2CH_2Br$	5.0	45	85–90/0.01	57.57 (57.81)	10.6 (10.51)		0.7–2.0 (m, 22H); 2.50 (t, J 7, 4H)
13	$(C_8H_{17}Se)_2$	$CH_3CHBr(CH_2)_2Br$	5.0	40	120/0.1	43.91 (43.90)	7.85 (7.68)		0.7–3.1 [m, 24H (the multiplet incorporates a singlet at 1.73]; 4.20 (sext., 1H).
14	$(C_6H_5Se)_2$	$(CH_3O)_2CH(CH_2)_2Br$	1.0	77 [c]		50.73 (50.97)	6.05 (6.22)		1.6–2.1 (m, 1H); 2.87 (t, J 7, 2H); 3.12 (s, 6H); 4.4 (t, J 7, 1H); 6.9–7.5 (m, 5H)

[a] Yield of the chromatographed product; [b] ^{1}H NMR spectra in $CDCl_3$/TMS internal standard; [c] Purified by column chromatography on silica gel eluting with ethyl acetate.

Table 3

Synthesis of alkyltellurides under Phase Transfer Conditions

Entry	Ditelluride	Halide	Reaction time (h)	Yield [a] (%)	m.p. (°C) or b.p. (°C/mmHg)	Anal. (Found (calc)(%))			^{1}H NMR, δ(ppm), J in Hz CCl_4/TMS internal standard
						C	H	N	
1	$(C_6H_5Te)_2$	C_4H_9Br	2.5	81	106–110/2.2 (115/7) [55]				0.86 (t, J 7, 3H); 1.0–2.0 (m, 4H); 2.83 (t, J 7, 2H); 6.9–7.3 (m, 3H); 7.4–7.8 (m, 2H)
2	$(C_6H_5Te)_2$	$C_6H_5(CH_2)_2Br$	2.5	83 [c]	[8]				3.00 (s, 4H); 6.8–7.3 (m, 8H); 7.5–7.8 (m, 2H)
3	$(C_6H_5Te)_2$	$C_{12}H_{25}Br$	3.5	95	120/0.05 [55]				0.9 (t, J 7, 3H); 1.1–2.1 (m, 20H); 2.86 (t, J 7, 2H); 7.0–7.3 (m, 3H); 7.5–7.8 (m, 2H)
4	$(C_6H_5Te)_2$	$CH_3CHBr(CH_2)_2Br$	3.0	87	130–135/0.2 [8] 108–115/0.5				1.70 (d, J 7, 3H); 1.9–2.4 (m, 2H); 2.8–3.3 (m, 2H); 4.13 (sext., J 7, 1H) 7.0–7.4 (m, 3H); 7.6–7.9 (m, 2H)
5	$(C_{10}H_7Te)_2$	C_4H_9Br	1.0	91	120–125/1 [8]				0.86 (t, J 7, 3H); 1.0–2.1 (m, 4H); 2.95 (t, J 7, 2H); 7.2–7.9 (m, 6H); 8.16 (br s, 1H)
6	$(C_{10}H_7Te)_2$	$C_6H_5(CH_2)_2Br$	1.5	92 [c]		59.79 (60.07)	4.10 (4.48)		3.10 (s, 4H); 6.8–7.8 (m, 12H); 8.06 (br s, 1H)
7	$(C_{10}H_7Te)_2$	$C_{12}H_{25}Br$	2.5	86		62.61 (62.31)	7.46 (7.60)		0.90 (t, J 7, 3H); 1.1–2.1 (m, 20H); 2.95 (t, J 7, 2H); 7.2–8.0 (m, 6H); 8.27 (br s, 1H)
8	$(C_{10}H_7Te)_2$	$CH_3CHBr(CH_2)_2Br$	2.0	96	140–150/0.05	43.11 (43.02)	3.78 (3.87)		1.56 (d, J 7, 3H); 1.8–2.4 (m, 2H); 2.7–3.2 (m, 2H); 4.06 (sext., 1H); 7.1–7.8 (m, 6H); 8.13 (br s, 1H)

9	$(4\text{-}CH_3OC_6H_4Te)_2$	C_4H_9Br	4.0	91	130–133/2 [8] 120–125/1				0.83 (t, *J* 7, 3H); 1.0–2.0 (m, 4H); 2.73 (t, *J* 7, 2H); 3.67 (m, 3H); 6.6 (d, *J* 9, 2H); 7.58 (d, *J* 9, 2H)
10	$(4\text{-}CH_3OC_6H_4Te)_2$	$C_6H_5(CH_2)_2Br$	5.0	86 [c]		52.73 (53.01)	4.73 (4.74)		2.96 (s, 4H); 3.66 (s, 3H); 6.60 (d, *J* 9, 2H); 7.06 (br s, 5H); 7.60 (d, *J* 9, 2H)
11	$(4\text{-}CH_3OC_6H_4Te)_2$	$C_{12}H_{25}Br$	6.0	96	30	56.23 (56.48)	7.97 (7.98)		0.90 (t, *J* 7, 3H); 1.1–2.0 (m, 20H); 2.76 (t, *J* 7, 2H); 3.70 (s, 3H); 6.66 (d, *J* 9, 2H); 7.63 (d, *J* 9, 2H)
12	$(4\text{-}CH_3OC_6H_4Te)_2$	$CH_3CHBr(CH_2)_2Br$	4.5	88					1.63 (d, *J* 7, 3H); 1.8–2.3 (m, 2H); 2.53–3.20 (m, 2H); 3.73 (s, 3H); 4.13 (sext., *J* 7, 1H); 6.66 (d, *J* 9, 2H); 7.63 (d, *J* 9, 2H)
13	$(3\text{-}CF_3C_6H_4Te)_2$	$CH_3CHBr(CH_2)_2Br$	3.5	87 [c]		32.66 (32.33)	2.96 (2.92)		1.73 (d, *J* 7, 3H); 2.20 (d.quart., *J* = 7, 2H); 3.10 (d, t, *J* 7.3, 2H); 4.16 (sext., *J* 7, 1H)
14	$(3\text{-}CF_3C_6H_4Te)_2$	$C_6H_5(CH_2)_2Br$	6.0	90 [c]		47.68 (47.68)	3.48 (3.47)		3.1 (s, 4H); 6.9–8.0 (m, 9H)
15	$(3\text{-}CF_3C_6H_4Te)_2$	$CH_3(CH_2)_2CH_2Br$	4.5	85 [c]		40.55 (40.06)	3.93 (3.97)		0.92 (t, *J* 7, 3H); 1.1–2.2 (m, 4H); 2.97 (t, *J* 7, 2H); 7.0–8.0 (m, 4H)
16	$(C_6H_5Te)_2$	1-Cl-2,4-$NO_2C_6H_3$	4.0	30	132–134	38.75 (38.70)	2.17 (2.16)	7.03 (7.23)	6.9–7.4 (m, 4H); 7.5–7.9 (m, 3H); 8.67 [b] (d, *J* 2, 1H)

[a] Yield of the chromatographed product; [b] ^1H NMR spectra in $CDCl_3$/TMS internal standard; [c] Purified by column chromatography on silica gel eluting with ethyl acetate.

mm thickness) of silica gel 60, 60F 254 (Merck) were used for comparative thin layer chromatography. Diphenyl disulfide, bis(4-nitrophenyl) disulfide, dimethyl disulfide, di-n-butyl disulfide, cetyltrimethylammonium bromide, cetyltrimethylammonium chloride and 2HT [31] are commercially available; diphenyl diselenide [32], bis(4-chlorophenyl) diselenide [32] di-n-octyl diselenide [33], di-1-methyl-butyl diselenide [33], bis(3-trifluoromethylphenyl) diselenide [32], diphenyl ditelluride [34], di-2-naphthyl ditelluride [35], bis (4-methoxyphenyl) ditelluride [36], bis(3-trifluoromethylphenyl) ditelluride [37] and aminoiminomethanesulfinic acid (thiourea dioxide) [38] were prepared by described methods.

Typical procedure for the preparation of diarylsulfides and selenides

To a solution of the diaryl dichalcogenide (1.0 mmol) and CTAB (2.5×10^{-2} mmol) in THF (0.5 ml) under nitrogen was added a 13% aqueous solution of sodium hydroxide (1.5 ml) and aminoiminomethanesulfinic acid (0.194g, 1.8 mmol). The mixture was maintained under reflux until discoloration. Then a solution of the aryl halide (2.0 mmol) in THF (1.0 ml) was added and the mixture was vigorously stirred under reflux for 4.0 h. The reaction mixture was filtered through a pad of silica gel in a sintered funnel and chromatographed on silica gel column using diethyl ether/petroleum ether (1 : 1) as eluent. The diaryl sulfides and selenides were obtained as solids in the yields shown in Table 1.

Typical procedure for the preparation of aryl alkyl and dialkyl sulfides and selenides

To a solution of the disulfide or diselenide (1.0 mmol), aminoiminosulfinic acid (0.108 g, 1.0 mmol), CTACl (0.016 g, 5×10^{-2} mmol) and the alkyl halide (2.0 mmol) in THF (7.5 ml) under nitrogen was added a 6% aqueous solution of sodium hydroxide (7.5 ml). The two-phase system was vigorously stirred under reflux for the time indicated in Tables I and II. The phases were separated and the aqueous layer was extracted with ethyl acetate (3×20 ml). The organic phase was washed with water (3×20 ml) and dried with magnesium sulfate. The solvents were evaporated and the residue was chromatographed on a column of silica gel using ethyl acetate as the eluent. The chalcogenides were obtained in yields as shown in Tables 1 and 2.

Typical procedure for the preparation of aryl alkyl tellurides

To a solution of the diaryl ditelluride (1.0 mol), aminoiminosulfinic acid (0.108 g, 1.0 mmol), 2HT (30 mg) and the alkyl halide (2.0 mmol) in THF (7.5 ml) was added a 50% aqueous solution of sodium hydroxide (7.5 ml) and the mixture was vigorously stirred at room temperature for the time indicated in Table 3. The phases were separated and the aqueous layer was extracted with ethyl acetate (3×20 ml), washed with water and dried with magnesium sulfate. The solvent was evaporated and the residue was chromatographed on a column of silica gel eluting with ethylacetate. The aryl alkyl tellurides were obtained in the yields shown in Table 3.

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