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A GENERAL PROCEDURE FOR THE SYNTHESIS OF METHYLTHIO-, METHYLSELENO- AND METHYLTELLURO-SUBSTITUTED AROMATIC COMPOUNDS

LARS ENGMAN* and JONAS S.E. HELLBERG

Royal Institute of Technology, Department of Organic Chemistry, S-100 44 Stockholm (Sweden)

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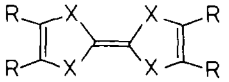
Summary

A one-pot procedure is described which allows the facile introduction of one or two methylchalcogeno groups into a variety of monobromo or dibromo aromatics. The bromo compounds were converted to their corresponding lithio derivatives by treatment with t-butyllithium in tetrahydrofuran at −78°C, and these derivatives were then treated, at ambient temperature with elemental sulfur, selenium, or tellurium. The resulting lithium thiolates, selenolates and tellurolates were finally methylated with methyl iodide to afford good yields (typically 50–80%) of the various methylchalcogeno-substituted aromatic compounds. The procedure could not be used for the synthesis of *ortho*-disubstituted compounds, or for the simultaneous introduction of three methylchalcogeno groups.

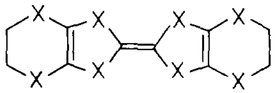
Introduction

The discovery of highly conductive organic ion-radical salts has aroused considerable interest in the synthesis of new electron donors. Since the preparation of the first superconducting salt from tetramethyltetraselenafulvalene (**1a**) [1], interest has primarily focused on the tetraheterofulvalene family of donors.

As a result of early interest in the effects of alkylthio substitution (compound **1b**) [2,3], a second superconducting organic material, based on bis(ethylendithiolo)tetrathiafulvalene (**2a**), was recently prepared [4]. Its seleno-analogue, **2b**, has also been synthesized [5].



1 a R=Me; X=Se
b R=SMe; X=S



2 a X=S
b X=Se

0022-328X/85/$03.30

We have been involved for some time in a programme directed towards the synthesis of new electron donors containing sulfur, selenium, or tellurium [6]. In connection with this program we were faced with the general problem of introducing one or several methylthio, methylseleno or methyltelluro groups into rather simple aromatic compounds.

A great variety of methods are available for the introduction of methylthio groups into organic molecules. Most involve methylation of a thiophenol [7], which in turn is available from precursors such as aromatic phenols (Newman–Kwart [8] or Schönberg [9] rearrangement), aromatic amines (diazotization and conversion to a xanthate [10], thiocyanate [11] or chlorosulfonate [12]), non-functional aromatic compounds (chlorosulfonation [13], thiocyanation [14], or reaction with 2,4-dinitrobenzenesulfenyl chloride [15]) or arylmagnesium compounds (reaction with elemental sulfur [16]). Direct introduction of an alkylthio group has also been successfully accomplished. Aromatic Grignard compounds form aryl methyl sulfides with dimethyl disulfide [17]. Cuprous mercaptides are known to convert haloaromatics into aryl alkyl sulfides [18]. However, the most general method for the introduction of one or several methylthio groups seems to be the recently developed nucleophilic aromatic substitution of halo aromatics by sodium methanethiolate [19].

A general method for the introduction of methylseleno groups into aromatic compounds involves methylation of aromatic selenols [20]. The selenols are most conveniently prepared from arylmagnesium halides (reaction with elemental selenium [21]) or aromatic amines (diazotization, selenocyanation and hydrolysis/reduction [22]). Another useful method involves aromatic nucleophilic substitution of haloaromatics with lithium methaneselenolates [23].

Only a very few methods are available for the introduction of methyltelluro groups into aromatic compounds [24]. The most general method involves reduction of a diaryl ditelluride to an aryl tellurolate followed by methylation [25]. The required diaryl ditellurides can be prepared from aryllithium or arylmagnesium compounds [26].

Christiaens and co-workers [27] have recently developed a general method for the introduction of alkylthio, alkylseleno and alkyltelluro groups into aromatic compounds. This synthesis is based on the reaction of dialkyl dichalcogenides with

$$(1) \qquad \mathrm{ArN_2^{\oplus}BF_4^{\ominus}} + \mathrm{RXXR} \xrightarrow{\text{18-Crown-6}} \underset{\mathrm{X=S,\,Se,\,Te}}{\mathrm{ArXR}}$$

arenediazonium tetrafluoroborates (eq. 1). Although the preparation allows the introduction of one or several methylchalcogeno groups, the low yields (typically 30–50%) and the need to handle odorous dialkyl dichalcogenides make it less attractive.

We describe below a general procedure for the introduction of methylchalcogeno groups based on the ready insertion of elemental sulfur, selenium and tellurium, respectively, into the carbon–lithium bond of mono- or di-lithiated aromatic compounds.

Results and discussion

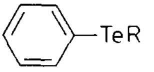
The chalcogenides sulfur [28], selenium [29] and tellurium [30] have long been known to insert into the carbon–lithium bond of various aryllithium compounds.

but this reaction has found very limited use for the preparation (via alkylation) of aryl alkyl chalcogenides (eq. 2).

Some early work in the tellurium [25] and selenium [31] series emphasized the need to generate the organolithium compound in an appropriate way. When

$$(2) \quad \mathrm{ArLi} \xrightarrow{X} \mathrm{ArXLi} \xrightarrow{RI} \mathrm{ArXR}$$

$$\mathrm{X = S, Se, Te}$$



3 a R = Bu
b R = Me

phenyllithium made from bromobenzene and n-butyllithium was treated with elemental tellurium, an undesired alkylation product, butyl phenyl telluride (**3a**), was formed before addition of the external alkylating agent [25]. On the other hand, phenyllithium made by metal–halogen exchange from lithium and bromobenzene reacted with elemental tellurium to afford methyl phenyl telluride (**3b**) on treatment with methyl iodide.

The availability of t-butyllithium has offered another possibility for generating aryllithium compounds free from any alkylating agent. Two moles of t-butyllithium are then required per mole of the aryl halide, the second equivalent serving to eliminate HBr from the initially formed t-butyl halide (eq. 3). This technique was recently applied to the introduction of both selenium [32,33] and tellurium [34] into organic molecules. Furthermore, the successful, although low-yield, introduction of two chalcogen atoms into 1,8-dilithionaphthalene [35] and 5,6-dilithioacenaphthylene [36] (both generated from n-butyllithium and the corresponding dibromide) by Meinwald and co-workers lends some support to the idea of a simultaneous introduction of more than one chalcogen atom into di- or poly-lithiated (t-butyllithium) aromatic compounds.

Table 1 shows a series of methylthio-, methylseleno- and methyltelluro-substituted aromatic compounds prepared from the corresponding bromo aromatics by lithiation, chalcogen insertion, and methylation. The mono- or di-bromo compounds were treated with t-butyllithium (two and four equivalents, respectively) in tetrahydrofuran at −78°C. After formation of the aryllithium reagent, the respective elemental chalcogen was added at ambient temperature. Elemental sulfur and selenium were usually consumed within a few minutes, whereas elemental tellurium required more time. Methylation was effected by the addition of a slight excess of methyl iodide. This alkylation process was practically instantaneous with tellurolates and selenolates, but slower with thiolates as judged by the colour changes (bleaching of colour) observed during the addition of the alkylating agent.

(3)

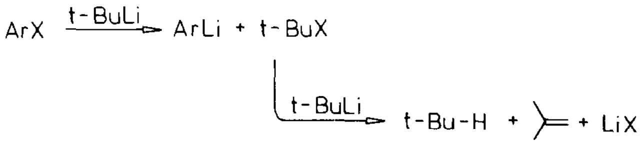


TABLE 1

METHYLTHIO-, METHYLSELENO- AND METHYLTELLURO-SUBSTITUTED COMPOUNDS PREPARED FROM THE CORRESPONDING BROMO AROMATICS

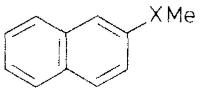
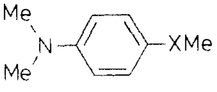
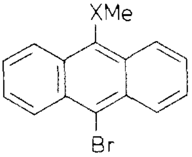
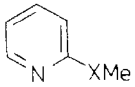
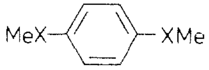
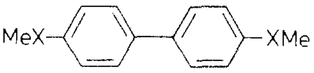
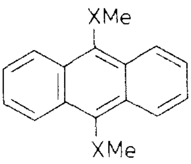
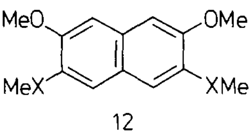
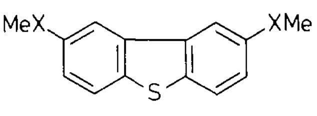
Compound		X	Yield (%)	m.p. (°C)/b.p. (°C/mmHg)	lit.	Analysis (Found (calcd.)(%)) C	H
 4	**a**	S	77	59–60	59–60 [39]		
	b	Se	87	52	52–53 [23]		
	c	Te	58	57–58		49.23 (48.98)	3.66 (3.74)
 5	**a**	S	89	23–24	22–23 [40]		
	b	Se	86	64–66/0.1	68–70/0.4 [22]		
	c	Te	46	165–167	—	30.09 (29.96) [a]	3.12 (3.14)
 6	**a**	S	60	140–142/11	152–154/15 [41]		
	b	Se	98	88–90/15	—	[b]	
	c	Te	64	25–26	—	[b]	
 7	**a**	S	69	136–137	136–138 [42]		
	b	Se	70	137–138		[b]	
	c	Te	52	110–112	—	45.23 (45.18)	2.73 (2.78)
 8	**a**	Se	51	44/0.3	43–44/0.25 [43]		
 9	**a**	S	78	79–80	80–82 [44]		
	b	Se	80	79–80	81 [45]		
	c	Te	67	70–71	—	26.69 (26.59)	2.83 (2.79)
 10	**a**	S	73	184	185–186 [39]		
	b	Se	84	180	178 [46]		
	c	Te	86	153–155	—	38.47 (38.44)	3.22 (3.23)
 11	**a**	S	66	163	161–162 [39]		
	b	Se	74	174–175	—	53.22 (52.77)	3.84 (3.87)
	c	Te	55	134–135	—	41.89 (41.64)	3.05 (3.06)

TABLE 1 (continued)

Compound		X	Yield (%)	m.p. (°C)/b.p. (°C/mmHg) lit.		Analysis (Found (calcd.)(%))	
						C	H
 12	**a**	S	70	198–200	–	60.08 (59.97)	5.84 (5.75)
	b	Se	79	210	–	44.85 (44.94) [g]	4.21 (4.31)
	c	Te	15	210–212	–	35.72 (35.67)	3.37 (3.42)
 13	**a**	S	92	144.5 [d]	–	60.70 (60.82) [e]	4.31 (4.38)
	b	Se	84	107–107.5	–	45.47 (45.41) [f]	3.16 (3.27)
	c	Te	27	124–124.5	–	36.09 (35.96)	2.45 (2.59)

[a] The product was isolated and characterized as its tellurium dichloride: methyl-4-methoxyphenyltellurium dichloride. [b] Not analysed. [c] Calcd: Se, 22.82; Found: Se, 22.46. [d] The crude product (92% yield) melted at 136–140°C. The analytical sample was obtained by sublimation. [e] Calcd: S, 34.80; Found: S, 34.56%. [f] Calcd: Se, 42.65; Found Se, 42.67%. [g] Calcd: Se, 42.20; Found Se, 42.32%.

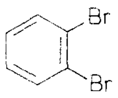
As can be seen from Table 1, the introduction of one (compounds **4**–**8**) or two (compounds **9**–**13**) methylchalcogeno groups proceeds equally well (50–90% yield), with a few exceptions. Within the different chalcogen series the selenium compounds tend to give the best results.

Our attempts to introduce two methylchalcogeno groups into *ortho*-disubstituted bromoaromatics met with failure. Thus, 1,2-dibromobenzene (**14**) yielded a foul-smelling mixture of many products (not identified) when treated with t-butyllithium, selenium, and methyl iodide in the usual way.

It also proved difficult to introduce three methylchalcogeno groups simultaneously. 1,3,5-Tribromobenzene (**15**) yielded a complex reaction product when treated with six equivalents of t-butyllithium, three equivalents of elemental selenium, and then methyl iodide. Tribromomesitylene (**16**) gave a similarly disappointing result. 2,4,6-Tribromo-1,3,5-trimethoxybenzene (**17**) gave a low yield (7%) of the methylthio-substituted compound **18**. It even proved difficult to introduce two methylcalcogeno groups into the tribromosubstituted compound **17**. Attempts with elemental sulfur and elemental selenium resulted in low yields of compounds **19a** and **19b**, respectively (6% isolated yields for both compounds).

An attempted preparation of compound **13b** from 2,8-diiododibenzothiophene (**20**) led to a lower yield (36%) and a more complex reaction compared with that starting from 2,8-dibromodibenzothiophene.

We have described a general one-pot procedure for the introduction of one or two methylchalcogeno groups into a variety of bromo-substituted aromatic compounds. Unfortunately the method is unsuitable when *ortho*-disubstituted derivatives are required. This is apparently due to problems associated with the formation of the *ortho*-dilithio compounds (competing benzyne formation). A similar problem has been overcome in the thiophene [33] and selenophene [37] series by the use of two



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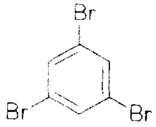

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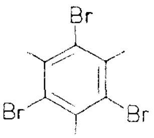

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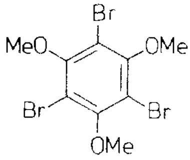

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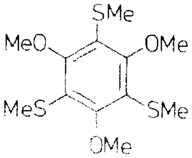

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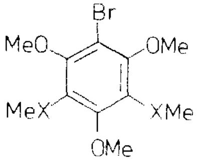
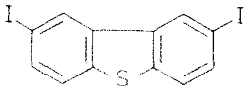


19 a X = S
b X = Se



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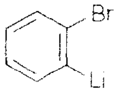

21

consecutive stepwise treatments of the 3,4-dibromo compounds with alkyllithium and elemental chalcogen. A recent study [38] of the monolithiation of *ortho*-dibromobenzene (**14**) indicated that the monolithio compound **21** is stable only at very low temperatures (−110°C). Although the aryllithium compound is not likely to give a good yield of all three chalcogen insertion products at this temperature, the sequential technique might prove useful in special cases also for the preparation of *ortho*-disubstituted methylchalcogenobenzenes.

Experimental

All melting points were uncorrected. NMR spectra were obtained with a Bruker WP 200 instrument at 200 MHz. They were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ units. Mass spectra were recorded with an LKB 9000 mass spectrometer. Mass spectral data (*m/e*, relative intensity, only five largest peaks above *m/e* = 100) were reported for the following isotopes only: ^{32}S, ^{80}Se, ^{130}Te, ^{81}Br. Tetrahydrofuran was distilled from K/benzophenone. Elemental tellurium was finely crushed in a mortar immediately before use. Elemental analyses were performed by Novo Microanalytical Laboratory, Bagsvaerd, Denmark and Institut für Organische Chemie der Universität Hamburg.

2,8-Dibromodibenzothiophene [47] and 3,6-dibromo-2,7-dimethoxynaphthalene [48] were synthesized according to literature methods. 2,8-Diiododibenzothiophene was synthesized in analogy with a literature procedure [49].

General procedure for the synthesis of methylthio-, methylseleno- and methyltelluro-substituted aromatic compounds.

t-Butyllithium (2 or 4 equivalents, respectively, 1.6 *M* in pentane) was added dropwise under nitrogen to a stirred solution of the appropriate monobromo or dibromo compound in dry tetrahydrofuran (≈ 5 mmol/40 ml) at −78°C. After 30 min the temperature was allowed to rise to ambient and an equivalent amount of the appropriate chalcogen (finely crushed) was added while a brisk stream of nitrogen was passed through the open system to exclude air. Elemental sulfur and selenium were consumed rapidly (less than 30 min), whereas elemental tellurium required longer (≈ 2 h). Small amounts of tellurium usually remained even after this period. The solutions of the lithium thiolates, selenolates and tellurolates were purple to orange coloured. This colour faded considerably as a slight excess of a solution of methyl iodide in a few ml of tetrahydrofuran was added. In the case of thiolates a 50% excess could be used without problems. However, in the preparation of organotellurium compounds the excess must be kept to a minimum to avoid formation of telluronium salts. After the completion of the alkylation process (≈ 10 min for Se or Te compounds, ≈ 1 h for S compounds), the solvent was evaporated and the residue dissolved in CH_2Cl_2 and washed with water. The organic phase was separated, dried, and evaporated, and the residue either chromatographed on silica and distilled (compounds **5b**, **6a**, **6b**, **8**), submitted to gradient chromatography [50] (compounds **13a**–**13c**, **18**, **19a**, **19b**) or recrystallized from CH_2Cl_2/EtOH (all others).

The tellurides **4c** and **5c** were red because of contamination with diaryl ditellurides. The crude products were therefore dissolved in EtOH and treated under N_2 with $NaBH_4$ (10% aq.) until the red colour disappeared (ditellurides converted into sodium arenetellurolates). After addition of a few drops of methyl iodide the solutions did not turn red on exposure to air and the products were extracted into ether and washed several times with water. The reported yields in Table 1 are those obtained after this purification procedure. A similar purification was also necessary in the preparation of selenide **5b**.

Compound **5c** was precipitated as its crystalline tellurium dichloride by addition of 0.50 g SO_2Cl_2 to a solution of the telluride in CCl_4.

In the preparation of compounds **12a** and **12b** the reaction mixture was stirred with the respective chalcogen for 1 h before methylation.

Much unreacted tellurium remained even after stirring for 15 h in the preparation of compound **12c**. After methylation and chromatographic purification a pure material was obtained in 15% yield by crystallization from CH_3CN.

9,10-Dilithioanthracene was stirred for 4 h with elemental tellurium before the methyl iodide was added (compound **11c**).

Compounds **18** (m.p. 36–37.5°C) and **19a** (m.p. 44–45°C) were obtained as solids. Compound **19b** was an oil.

2,4,6-Tribromomesitylene (16). To a boiling solution of mesitylene (12.0 g, 0.1 mol) in 1,2-dichloroethane (125 ml) containing a catalytic amount of $FeCl_3$ a solution of bromine (48.0 g, 0.3 mol) in 1,2-dichloroethane (25 ml) was added during 0.5 h. After 2 h at reflux temperature the solution was cooled and the crystalline material filtered off and washed with MeOH. The product was then dissolved in CH_2Cl_2 and washed with $Na_2S_2O_3$ (aq.), water, and brine. After evaporation 22.9 g (64%) of compound **16**, m.p. 225.5–226.5°C (lit. 224–225°C [51]) was obtained.

2,4,6-Tribromo-1,3,5-trimethoxybenzene (17). To a boiling solution of 1,3,5-trimethoxybenzene (8.41 g, 0.050 mol) in 1,2-dichloroethane (120 ml) containing a catalytic amount of $FeCl_3$ a solution of bromine (25.0 g, 0.156 mmol) in 1.2-dichloroethane (20 ml) was added during 0.5 h. The solution was heated under reflux overnight, cooled, diluted with CH_2Cl_2 and washed with $Na_2S_2O_3$ (aq.), water and brine. Drying, evaporation and gradient chromatography (light petroleum b.p. 40–60°C/toluene/CH_2Cl_2) afforded 14.1 g (70%) of compound **17**, m.p. 144°C. ^1H NMR δ 3.89 (s). Mass spectrum: 408 (21), [404 (100)], 363 (6), 312 (4), 297 (16), 269 (9). Analysis Found: C, 26.70; H, 2.25. $C_9H_9Br_3O_3$ calcd.: C, 26.70; H, 2.11%.

NMR data for new compounds (δ, ppm)

4c: 2.28 (s, 3H), 7.43–7.53 (several peaks, 2H), 7.68–7.88 (several peaks, 4H), 8.13 (s, 1H).

5c: (Isolated as its Te,Te-dichloride) 3.27 (s, 3H), 3.88 (s, 3H), 7.06 (d, 2H, *J* 9.0 Hz), 8.05 (d, 2H, *J* 9.0 Hz).

6b: 2.27 (s, 3H), 2.94 (s, 6H), 6.66 (d, 2H, *J* 9.0 Hz), 7.41 (d, 2H, *J* 9.0 Hz).

6c: 2.11 (s, 3H), 2.95 (s, 6H), 6.59 (d, 2H, *J* 8.9 Hz), 7.61 (d, 2H, *J* 8.9 Hz).

7b: 2.25 (s, 3H), 7.60–7.65 (several peaks, 4H), 8.61 (m, 2H), 9.06 (m, 2H).

7c: 2.07 (s, 3H), 7.56–7.63 (several peaks, 4H), 8.57 (m, 2H), 8.97 (m, 2H).

9c: 2.22 (s, 6H), 7.47 (s, 4H).

10c: 2.24 (s, 6H), 7.40 (d, 4H, *J* 8.5 Hz), 7.70 (d, 4H, *J* 8.5 Hz).

11b: 2.26 (s 6H), 7.58–7.63 (several peaks, 4H), 9.03–9.08 (several peaks, 4H).

11c: 2.09 (s, 6H), 7.54–7.59 (several peaks, 4H), 8.90–8.95 (several peaks, 4H).

12a: 2.52 (s, 6H), 3.98 (s, 6H), 7.00 (s, 2H), 7.38 (s, 2H).

12b: 2.37 (s, 6H), 3.98 (s, 6H), 6.99 (s, 2H), 7.47 (s, 2H).

12c: 2.18 (s, 6H), 3.95 (s, 6H), 6.96 (s, 2H), 7.53 (s, 2H).

13a: 2.60 (s, 6H), 7.40 (dd, 2H, *J* 1.6 and 8.2 Hz), 7.74 (d, 2H, *J* 8.2 Hz), 8.02 (d, 2H, *J* 1.6 Hz).

13b: 2.46 (s, 6H), 7.55 (dd, 2H, *J* 1.7 and 8.3 Hz), 7.73 (dd, 2H, *J* 0.5 and 8.3 Hz), 8.22 (dd, 2H, *J* 0.5 and 1.7 Hz).

13c: 2.29 (s, 6H), 7.67 (dd, 2H, *J* 0.5 and 8.2 Hz), 7.75 (dd, 2H, *J* 1.4 and 8.2 Hz), 8.46 (dd, 2H, *J* 0.5 and *J* 1.4 Hz).

18: 2.45 (s, 9H), 3.94 (s, 9H).

19a: 2.45 (s, 6H), 3.92 (s, 6H), 3.93 (s, 3H).

19b: 2.36 (s, 6H), 3.89 (s, 9H).

Mass spectral data for new compounds:

4c: 272(35), 257(38), 128(16), 127(100), 126(37).

6b: 215(61), 200(100), 184(17), 134(13), 120(14).

6c: 265(62), 250(100), 249(37), 119(31), 105(34).

7b: 352(83), 337(80), 256(93), 176(100), 174(33).

7c: 402(13), 387(14), 176(100), 175(22), 174(22).

9c: 366(53), [364(100)], 351(39), 336(34), 145(30), 130(29).

10c: 442(26), 427(15), 412(15), 152(100), 151(28).

11b: 366(100), 351(98), 336(63), 256(83), 176(83).

11c: 466(15), 451(10), 436(11), 306(22), 176(100).

12a: 280(100), 218(52), 189(7), 145(7), 115(6).

12b: 376(100), 266(77), 282(45), 281(30), 115(30).

12c: 476(53), [474(100)], 317(6), 315(5), 158(5), 126(5).

13a: 276(100), 261(49), 241(14), 214(18), 170(7).

13b: 372(100), 358(58), 340(54), 262(49), 182(30).

13c: 472(41), 457(24), 312(24), 182(100), 138(43).
18: 306(100), 276(14), 263(35), 248(33), 229(9).
19a: 340(100), 310(28), 282(29), 244(27), 229(25).
19b: 436(71), [434(100)], 406(13), 378(9), 326(31), 311(19).

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