

Synthesis, Structures, and Some Reactions of [(Thioacyl)thio]- and (Acylseleno)antimony and -bismuth Derivatives ((RCSS)_xMR_{3-x}¹ and (RCOSe)_xMR_{3-x}¹ with M = Sb, Bi and x = 1–3)

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A series of [(thioacyl)thio]- and (acylseleno)antimony and [(thioacyl)thio]- and (acylseleno)bismuth, *i.e.*, (RCSS)_xMR_{3-x}¹ and (RCOSe)_xMR_{3-x}¹ (M = Sb, Bi, R¹ = aryl, x = 1–3), were synthesized in moderate to good yields by treating piperidinium or sodium carbodithioates and -selenoates with antimony and bismuth halides. Crystal structures of (4-MeC₆H₄CSS)₂Sb(4-MeC₆H₄) (**9b'**), (4-MeOC₆H₄COSe)₂Sb(4-MeC₆H₄) (**12c'**), (4-MeOC₆H₄COS)₂Bi(4-MeC₆H₄) (**15c'**), and (4-MeOC₆H₄CSS)₂BiPh (**18c**) along with (4-MeC₆H₄COS)₂SbPh (**6b**) and (4-MeC₆H₄COS)₃Sb (**7b**) were determined (*Figs. 1* and *2*). These compounds have a distorted square pyramidal structure, where the aryl or carbothioato (= acylthio) ligand at the central Sb- or Bi-atom is perpendicular to the plane that includes the two carbodithioato (= (thioacyl)thio), carboselenato (= acylseleno), or carbothioato ligand and exist as an enantiomorph pair. Despite the large atomic radii, the C=S⋯Sb distances in (RCSS)₂MR¹ (M = As, Sb, Bi; R¹ = aryl) and the C=O⋯Sb distances in (RCOS)_xMR_{3-x}¹ (M = As, Sb, Bi; x = 2, 3) are comparable to or shorter than those of the corresponding arsenic derivatives (*Tables 2* and *3*). A molecular-orbital calculation performed on the model compounds (MeC(E)E¹)_{3-x}MMe_x (M = As, Sb, Bi; E = O, S; E¹ = S, Se; x = 1, 2) at the RHF/LANL2DZ level supported this shortening of C=E⋯Sb distances (*Table 4*). Natural-bond-orbital (NBO) analyses of the model compounds also revealed that two types of orbital interactions n_S → σ_{MC}^{*} and n_S → σ_{MS(1)}^{*} play a role in the (thioacyl)thio derivatives (MeCSS)_{3-x}MMe_x (x = 1, 2) (*Table 5*). In the acylthio-MeCOSMMe₂ (M = As, Sb, Bi), n_O → σ_{MC}^{*} contributes predominantly to the orbital interactions, but in MeCOSeSbMe₂, none of n_O → σ_{MC}^{*} and n_O → σ_{MSe}^{*} contributes to the orbital interactions. The n_S → σ_{MC}^{*} and n_S → σ_{MS(1)}^{*} orbital interactions in the (thioacyl)thio derivatives are greater than those of n_O → σ_{MC}^{*} and n_O → σ_{ME}^{*} in the acylthio and acylseleno derivatives (MeCOE)_{3-x}MMe_x (E = S, Se; M = As, Sb, Bi; x = 1, 2).

The reactions of RCOSeSbPh₂ (R = 4-MeC₆H₄) with piperidine led to the formation of piperidinium diphenylselenoantimonate(1-) (= piperidinium diphenylstibinoselenoite) (H₂NC₅H₁₀)⁺Ph₂SbSe⁻, along with the corresponding *N*-acylpiperidine (*Table 6*). Similar reactions of the bis-derivatives (RCOSe)₂SbR¹ (R, R¹ = 4-MeC₆H₄) with piperidine gave the novel di(piperidinium) phenyldiselenoantimonate(2-) (= di(piperidinium) phenylstibonodiselenoite), [(H₂NC₅H₁₀)⁺]₂(PhSbSe₂)²⁻, in which the negative charges are delocalized on the SbSe₂ moiety (*Table 6*). Treatment of RCOSeSbR₂¹ (R, R¹ = 4-MeC₆H₄) with *N*-halosuccinimides indicated the formation of *Se*-(halocyclohexyl) arenecarboselesenoates (*Table 8*). Pyrolysis of bis(acylseleno)arylantimony at 150° gave *Se*-aryl carboselenoates in moderate to good yields (*Table 9*).

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1. Introduction. – The chemistry of antimony and bismuth compounds with carbo-dithioato (R_2NCSS^-) and carbonodithioato ligands ($ROCSS^-$) has been extensively investigated (see reviews [1]). In contrast, the preparation of antimony and bismuth compounds with carbothioato (=acylthio; $RCOS^-$) and carbodithioato (= (thioacyl)-thio; $RCSS^-$) ligands was limited to only seven carbothioato²⁾ and two carbodithioatoantimony³⁾ and $(PhCSS)_3Bi$ [3a] when our study began in 1976 [4]. No carboselenoato (=acylselene; $RCOSe^-$) derivative had been described. This lack seems to have been due to the difficulty of preparing and purifying the starting compounds such as alkali metal and ammonium carbodithioates and carboselenoates, and diorganoantimony and -bismuth halides such as R_2MX ($M = Sb, Bi; X = Cl, Br, I$).

We previously developed convenient syntheses of ammonium and alkali metal carbochalcogenoates and their main group element derivatives [1g]. In addition, (acylthio)- and [(thioacyl)thio]diphenylarsenics, $RCOSAsPh_2$ and $RCSSAsPh_2$ have been found to be effective precursors for the synthesis of ammonium diphenylarsinochalcogenoites, $R_2NH_2^+Ph_2AsX^-$ ($X = O, S$) salts [5]. The antimony and bismuth compounds with carbodithioato and carboselenoato ligands are considered to be effective precursors for the synthesis of organoantimony and -bismuth species with a thiolato and selenolato ligand such as R_2ME^- ($M = Sb, Bi; E = S, Se$) which can be used to easily introduce the $Sb-S$ or $Bi-S$ framework into a molecule⁴⁾.

During our research on carbochalcogenoic acid group-14-element derivatives, we found that the $C=O \cdots Sn$ distance in $RCOSSnPh_3$ is shorter than the $C=O \cdots Ge$ distance in $RCOSGePh_3$ ($R = 4-MeC_6H_4$) [6]. To the best of our knowledge, there has been no report with such a short $C=E \cdots Sb$ distance ($E = O, S$) compared with the corresponding $C=E \cdots As$ distance. This prompted us to reveal our results concerning heavier Group-15-element derivatives of carbochalcogenoic acids.

We describe here the synthesis and structural analyses of a series of [(thioacyl)-thio]antimony and -bismuth $(RCSS)_xMR_{3-x}^1$ ($M = Sb, Bi; x = 1-3$) and (acylselene)antimony and -bismuth $(RCOSe)_xMR_{3-x}^1$ ($M = Sb, Bi; x = 1-3$), and show that the $C=E \cdots Sb$ distances in $(RCEE^1)_{3-x}SbR_x^1$ ($E = O, S; E^1 = S, Se; x = 1-3$) are shorter than the $C=E \cdots As$ distances in $(RCEE^1)_{3-x}AsR_x^1$ ($E = O, S; E^1 = S, Se; x = 1-3$). Moreover, a new facile synthetic method of *Se*-aryl arenecarboselenoates from such compounds is described, along with reactions with piperidine and sodium ethoxide.

2. Synthesis of Complexes. – Considering the conditions used for the synthesis of (carbodithioato)arsenic derivatives, the syntheses of diphenyl[(thioacyl)thio]-, phenyl-bis[(thioacyl)thio]-, and tris[(thioacyl)thio]antimony **8**, **9**, and **10**, respectively, were examined starting from piperidinium 4-methylbenzenecarbodithioate **2b** ($R = 4-MeC_6H_4$) and an antimony halide **4**. Since it appeared to be difficult to obtain Ar_2SbX ($X = Cl, Br, I$) in high purity by the disproportionation reaction of Ar_3Sb and SbX_3 , a

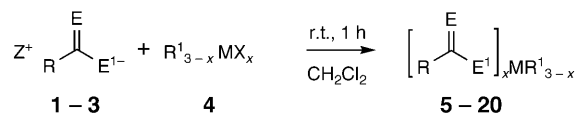
²⁾ $(PhCOS)_3Sb$ [2a, b], $(MeCOS)_3Sb$ [2c], $(MeCOS)_2PhSb$ [2d], and $(RCOS)_3SbR'_2$ [2e].

³⁾ $(PhCSS)_3Sb$ [3b], $(1-naphCSS)_3Sb$ [3c], and $(pyrol-3-CSS)_3Sb$ and $(indol-3-CSS)_3Sb$ [3d].

⁴⁾ To the best of our knowledge, R_2SbE^- and R_2BiE^- species ($E = S, Se, Te$) have not been reported. In our research, the preparation of $R_2ME^- (M^1)^+$ ($E = S, Se; M = Sb, Bi; M^1 = \text{alkali metal}$) by the reaction of alkali metal diorganoantimony and -bismuth with elemental sulfur appeared to be impractical due to low yields.

reaction mixture that included ArSbX_2 , Ar_2SbX , and SbX_3 was used for the synthesis of **8**. The syntheses of carboselenoic acid derivatives **11–13** were carried out with sodium carboselenoates **3a** ($\text{R}=4\text{-MeC}_6\text{H}_4$) [7] instead of **2b** ($\text{R}=4\text{-MeC}_6\text{H}_4$) [8]. Under the mild conditions shown in *Scheme 1*, these compounds were obtained in 25–90% yield (*Table 1*).

Scheme 1



No.	E	E ¹	Z ^{a)}	No.	M	E	E ¹	x
1a	O	S	K	5	Sb	O	S	1
1b	O	S	H-pip.	6	Sb	O	S	2
2a	S	S	Na	7	Sb	O	S	3
2b	S	S	H-pip.	8	Sb	S	S	1
3a	O	Se	Na	9	Sb	S	S	2
3b	O	Se	H-pip.	10	Sb	S	S	3
				11	Sb	O	Se	1
				12	Sb	O	Se	2
				13	Sb	O	Se	3
				14	Bi	O	S	1
				15	Bi	O	S	2
				16	Bi	O	S	3
				17^{b)}	Bi	S	S	1
				18	Bi	S	S	2
				19	Bi	S	S	3
				20	Bi	O	Se	1

^{a)} H-pip. = H-piperidine

^{b)} Not formed

No.	R	R ¹
1a, 1b – 3a, 3b, 5 – 20a	C_6H_5	C_6H_5
b	4-MeC ₆ H ₄	C_6H_5
c	4-MeOC ₆ H ₄	C_6H_5
d	4-ClC ₆ H ₄	C_6H_5
e	1-Naph	C_6H_5
f	Me	C_6H_5
g	Me ₂ CH	C_6H_5
h	tert-C ₄ H ₉	C_6H_5
5 – 20a'	C_6H_5	4-MeC ₆ H ₄
b'	4-MeC ₆ H ₄	4-MeC ₆ H ₄
c'	4-MeOC ₆ H ₄	4-MeC ₆ H ₄
d'	3-Cl,2,6-(MeO) ₂ C ₆ H ₂	4-MeC ₆ H ₄
e'	4-BrC ₆ H ₄	4-MeC ₆ H ₄
f'	tert-C ₄ H ₉	4-MeC ₆ H ₄
g'	n-C ₁₇ H ₃₅	4-MeC ₆ H ₄

To compare the structure and spectral data, a series of (acylthio)diphenyl-, bis-(acylthio)phenyl- and tris(acylthio)antimony **5**, **6**, and **7**, respectively, were synthesized under similar reaction conditions with potassium and piperidinium carboselenoates **1a** and **1b**. The low yields of some compounds such as **5c**, **6c**, **9c**, **9e**, **19a–d**, and **20f** are due to loss during purification. Their formation proceeded quantitatively.

Table 1. Yields of Carbochalcogenoantimony and -bismuth **5–13** and **14–20**, respectively

	$(\text{RCOS})_x\text{SbR}_{3-x}^1$		$(\text{RCSS})_x\text{SbR}_{3-x}^1$		$(\text{RCOSe})_x\text{SbR}_{3-x}^1$		$(\text{RCOS})_x\text{BiR}_{3-x}^1$		$(\text{RCSS})_x\text{BiR}_{3-x}^1$		$(\text{RCOSe})_x\text{BiR}_{3-x}^1$	
	yield [%]		yield [%]		yield [%]		yield [%]		yield [%]		yield [%]	
$x=1$ (mono)	5a	90	8a	90	11a	81	14a	54	17a	–	20a'	68
	5b	94	8b	83	11b	89	14b	98	17b	–	20b'	72
	5c	62	8c	82	11c	75	14c	81	17c	–	20c'	85
	5d	82	8d	55	11d	68	14d	61	17d	–	20d'	73
	5b'	93	8e	83	11f	85	14c'	66			20e'	96
	5c'	92	8f	62	11g	79					20f'	53
			8b'	80	11h	90					20g'	78
			8c'	83								
$x=2$ (bis)	6a	61	9a	61	12a	89	15a	90	18a	61		
	6b	57	9b	71	12b	73	15b	86	18b	77		
	6c	88	9c	77	12c	92	15c	63	18c	61		
	6d	74	9e	56	12d	67	15d	78	18d	50		
	6a'	95	9a'	96	12f	62						
	6b'	95	9b'	86	12g	75	15c'	63				
	6c'	96	9c'	91	12h	89						
	6d'	91	9d'	89	12a'	96						
					12b'	96						
					12c'	90						
$x=3$ (tris)	7a	91	10a	97	13a	71	16a	50	19a	51		
	7b	96	10b	98	13b	94	16b	90	19b	42		
	7c	93	10c	96	13c	91	16c	94	19c	50		
	7d	94	10d	95	13d	61	16d	87	19d	34		
			10e	90								

Similarly, bis[(thioacyl)thio]phenyl- and tris[(thioacyl)thio]bismuth **18** and **19**, respectively, were obtained in good yields by reacting **2a** or **2b** with PhBiI_2 or BiI_3 , respectively. The reactions of carbodithioic acids with Ph_2BiCl or of piperidinium carbodithioate **2b** with Ph_2BiI gave a mixture of **17b** and **18b**, from which the isolation of **17b** by fractional crystallization and column chromatography failed. In contrast, mono-, bis- and tris(acylthio)bismuth **14–16** were readily synthesized by treating **1a** or **1b** with the corresponding bismuth halide. Although isolation of the selenium derivatives RCOSeBiPh_2 and $(\text{RCOSe})_2\text{BiPh}$ was difficult due to their instability, we succeeded in isolating $\text{RCOSeBi}(4\text{-MeC}_6\text{H}_4)_2$ **20** by using $(4\text{-MeC}_6\text{H}_4)_2\text{BiI}$ instead of Ph_2BiI .

The obtained [(thioacyl)thio]antimony and -bismuth are stable both thermally and toward O_2 and H_2O . Upon exposure to air, they did not show any appreciable change for three months. However, carboselenoatos bismuth compounds are labile toward O_2 and decomposed in air with the liberation of a black solid (bismuth). Under O_2 -free conditions at room temperature, a ligand coupling reaction between aryl and RCOSe groups of **20** occurred mainly to give the corresponding *Se*-aryl carboselenoate and tri-aryl bismuth.

3. Crystal Structures. – *Structures.* The ORTEP drawings of the (thioacyl)thio derivative (4-MeC₆H₄CSS)₂Sb(4-MeC₆H₄) **9b'** and acylseleno derivative (4-MeOC₆H₄COSe)₂Sb(4-MeC₆H₄) **12c'** are shown in Fig. 1 along with those of the acylthio derivatives (4-MeC₆H₄COS)₂SbPh **6b** and (4-MeC₆H₄COS)₃Sb **7b**. Those of the corresponding bismuth isologues (4-MeOC₆H₄CSS)₂BiPh **18c** and (4-MeOC₆H₄COS)₂Bi(4-MeC₆H₄) **15c'** are shown in Fig. 2. Selected bond distances and angles are listed in Table 2 together with those of the corresponding phosphorus and arsenic complexes for comparison (for more detailed data, see Table 11 in the *Exper. Part*).

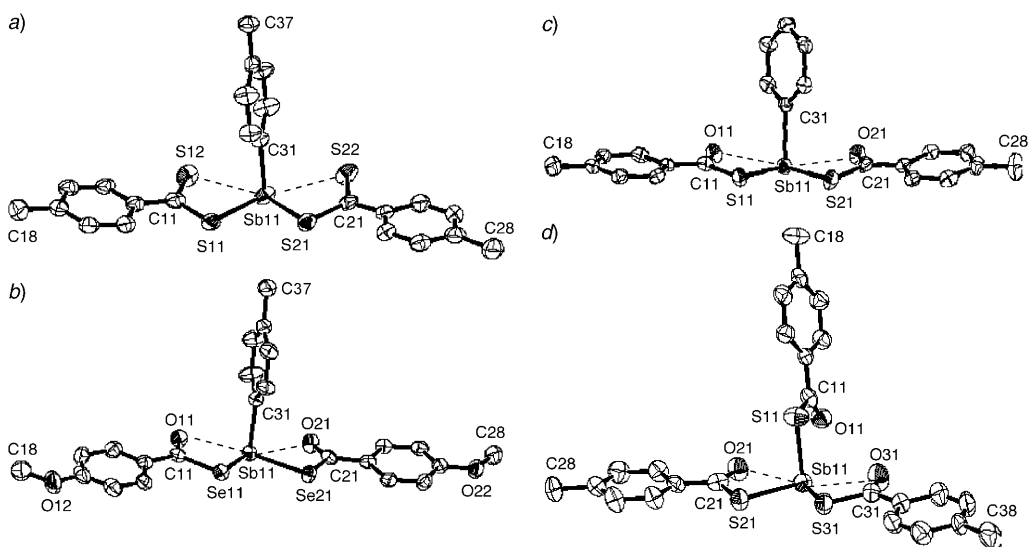


Fig. 1. Molecular structure of a) (4-MeC₆H₄CSS)₂Sb(4-MeC₆H₄) **9b'**, b) (4-MeOC₆H₄COSe)₂Sb(4-MeC₆H₄) **12c'**, c) (4-MeC₆H₄COS)₂SbPh **6b**, and d) (4-MeC₆H₄COS)₃Sb **7b**. The thermal ellipsoid plots represent 50% probability. H-atoms are omitted for clarity.

Bis[(thioacyl)thio]arylantimony **9b'** has a structure that is essentially similarly distorted pyramidal as those of the corresponding P [9a] and As isologues [5]. Thus, the aryl group at the central Sb atom is perpendicular to the plane that includes the two carbodithioato groups where in the two C=S moieties point to the same direction. The structure of the corresponding carboselenoato derivative **12c'** is also similar to those of **6b** and **9b'**. The space group of tris(4-methylbenzoylthio)antimony **7b** is $P2_{1/2}$, and it adopts a similar structure: two carbthioato ligands are located in the same plane, while the third one is located perpendicular to this plane. The space group of (2-MeC₆H₄COS)₃Sb which was reported by *Nöth* and coworkers is $R3c$ [10] which differs from that observed for **7b**. This difference of the crystal forms may depend on the manner in which the single crystals were obtained. The structures of bis[(thioacyl)thio]- and bis(acylthio)arylbismuth **18c** and **15c'** closely resemble those of the corresponding antimony isologues **9b'** and **6b**, respectively, where the aryl group at the Sb-atom is located perpendicularly. For **9b'** and **18c**, each of the four C–S bond distances of the carbodithioato ligands are different and can be roughly divided into shorter (1.66–1.67 Å) and longer (1.72–1.73 Å) bonds, which are close to C=S double and

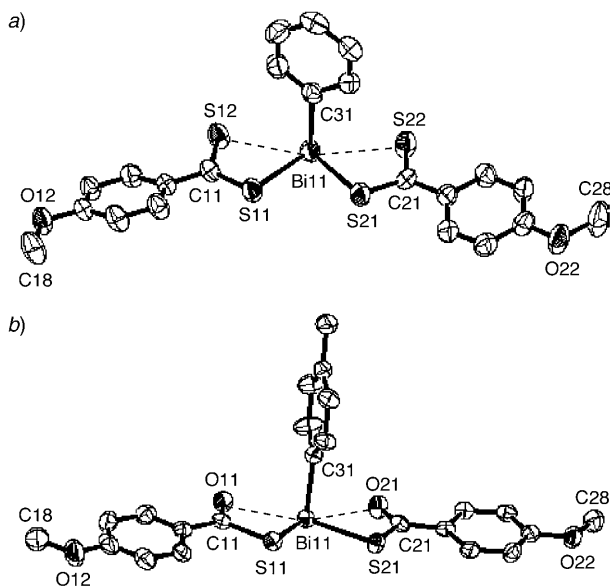


Fig. 2. Molecular structure of a) $(4\text{-MeOC}_6\text{H}_4\text{CSS})_2\text{BiPh}$ **18c** and b) $(4\text{-MeOC}_6\text{H}_4\text{COS})_2\text{Bi}(4\text{-MeC}_6\text{H}_4)$ **15c'**. The thermal ellipsoid plots represent 50% probability. H-atoms are omitted for clarity.

C–S single bonds in dithioesters, respectively [11]. Previously, we found that the distances between the carbonyl O-atom or the thiocarbonyl S-atom and Sn-atom in $(\text{RCOS})_x\text{SnPh}_{4-x}$ and $(\text{RCSS})_x\text{SnPh}_{4-x}$ ($x=1$ or 2) are shorter than those in the corresponding germanium analogues $(\text{RCOS})_x\text{GePh}_{4-x}$ [6] and $(\text{RCSS})_x\text{GePh}_{4-x}$ ($x=1$ or 2) [12], which reflects the magnitude of the affinities of the O- and S-atom for a group-14 element. The average distances between the thiocarbonyl S-atom and the central Sb- or Bi-metal are 2.936(3) Å for **9b'** and 2.989(2) Å for **18c**, which are significantly shorter than the sum (Sb–S 4.05 Å, Bi–S 4.25 Å [13]) of the *van der Waals* radii of both atoms. This suggests the presence of intramolecular interactions between these atoms, due to interactions between the nonbonding orbital (n_s) of the lone-pair electrons of the thiocarbonyl S-atom and the antibonding orbital (σ_{MS}^*) of the Sb–S or the Bi–S bond. Similarly, the C=O (1.21–1.22 Å), C–Se (1.94–1.95 Å), and Se–Sb distances (2.59–2.60 Å) in carboselenoate **12c'** are normal, and are close to the typical C=O double and C–Se or Se–Sb single bonds, respectively. However, the two C=O...Sb distances are 2.768(4) and 2.807(5) Å, which are significantly shorter than the sum (3.66 Å) of the *van der Waals* radii of both atoms [14] ($\text{C}(\text{sp}^2)=\text{O}$ 1.21–1.23 Å, $\text{C}(\text{sp}^2)-\text{S}$ 1.66–1.68 Å) [15]. In the corresponding carbothioates, the distances C=O...Sb (average 2.694(3) Å for **6b** and average 2.67(1) Å for $(\text{C}_6\text{H}_5\text{COS})_2\text{SbPh}$ **14**) and C=O...Bi (average 2.67(3) Å for **15c'**) are significantly shorter than the sum (O–Sb 3.66 Å [14][15], O–Bi 3.99 Å [14][15]) of the *van der Waals* radii of the corresponding atoms. These results suggest that there are interactions between the nonbonding orbital (n_o) of the lone-pair electrons on the carbonyl O-atom and the antibonding orbital (σ_{MS}^*) of the Sb–S or the Bi–S bond. Despite the large atomic radius of Sb, the C=E...Sb distances (E = O or S)

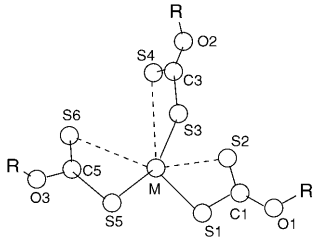
Table 2. Selected Bond Distances in Compounds **6b**, **7b**, **9b**, **12c**, **15c**, and **18c**

		Space Distance [Å]		Ref.		Space Distance [Å]		Ref.								
R	R ¹	M	M...S	M-S	C=S	C-S ¹	R	M	M...O	M-Se	C=O	C-Se				
4-MeC ₆ H ₄	Ph	P	<i>P</i> _{2,ln}	2.965(3)	2.170(3)	1.630(6)	1.75(1)	[9a] 12c	4-MeOC ₆ H ₄	Sb	<i>P</i> _{2,ln}	2.768(4)	2.5904(6)	1.217(3)	1.945(5)	
4-MeC ₆ H ₄	Ph	As	<i>P</i> _{2,ln}	2.975(3)	2.150(3)	1.634(6)	1.74(1)	[5]				2.807(5)	2.5973(7)	1.212(3)	1.940(5)	
9b	4-MeC ₆ H ₄	4-MeC ₆ H ₄	Sb	<i>P</i> _{2,ln}	2.956(4)	2.299(4)	1.65(1)	1.75(1)								
	4-MeC ₆ H ₄	4-MeC ₆ H ₄	Sb	<i>P</i> _{2,ln}	2.957(4)	2.316(4)	1.64(1)	1.74(1)								
	4-MeC ₆ H ₄	4-MeC ₆ H ₄	Sb	<i>P</i> _{2,ln}	2.933(2)	2.542(2)	1.666(6)	1.723(7)								
	4-MeOC ₆ H ₄	Ph	Bi	<i>P</i> ₁	2.940(2)	2.537(2)	1.672(7)	1.732(7)								
	4-MeOC ₆ H ₄	Ph	Bi	<i>P</i> ₁	2.974(2)	2.676(2)	1.658(7)	1.741(7)								
					3.003(2)	2.673(2)	1.652(7)	1.727(6)								
		Space Distance [Å]		Ref.		Space Distance [Å]		Ref.								
R	R ¹	M	M...O	M-S	C=O	C-S ¹	R	M	M...O	M-S	C=O	C-S				
4-MeC ₆ H ₄	Ph	P	<i>P</i> _{2,lc}	2.747(3)	2.144(2)	1.211(5)	1.75(1)	[9a]	4-MeC ₆ H ₄	P	<i>R</i> _{3c}	2.82(1)	2.142(5)	1.222(2)	1.79(2)	
4-MeOC ₆ H ₄	Ph	As	<i>P</i> _{2,ln}	2.784(3)	2.146(3)	1.214(5)	1.74(1)	[5]	4-MeC ₆ H ₄	As	<i>R</i> _{3c}	2.81(1)	2.264(6)	1.18(2)	1.80(1)	
6b	4-MeC ₆ H ₄	Ph	Sb	<i>P</i> _{2,ln}	2.708(3)	2.286(1)	1.223(4)	1.777(4)								
	4-MeC ₆ H ₄	Ph	Sb	<i>P</i> _{2,ln}	2.731(3)	2.280(1)	1.216(4)	1.797(4)	7b	4-MeC ₆ H ₄	Sb	<i>P</i> _{2,ln}	2.74(3)	2.44(1)	1.22(1)	1.76(1)
	4-MeOC ₆ H ₄	4-MeC ₆ H ₄	Bi	<i>P</i> ₁	2.673(3)	2.486(1)	1.233(4)	1.772(4)								
	4-MeOC ₆ H ₄	4-MeC ₆ H ₄	Bi	<i>P</i> ₁	2.714(3)	2.489(1)	1.230(4)	1.765(4)								
	4-MeOC ₆ H ₄	4-MeC ₆ H ₄	Bi	<i>P</i> ₁	2.63(1)	2.644(4)	1.25(2)	1.76(2)								
					2.71(1)	2.614(4)	1.22(2)	1.77(2)								
					3.01*(1) ^{a)}											
					3.426*(15) ^{b)}											

^{a)} M...O=C (neighboring molecule). ^{b)} M...O (O of MeO of neighboring molecule).

in **6b** and **9b'** are shorter than the corresponding C=E...As distances (E = O or S) in [4-MeC₆H₄C(E)S]₂AsPh (*Table 2*). To the best of our knowledge, no reports have been published in which such short intramolecular distances between Sb and a C=O O-atom or C=S S-atoms were pointed out, although a number of X-ray structure analyses of carbamochoalcogenoic, carbonochalcogenoic, and diorganophosphinochoalcogenoic acid derivatives have been reported. This stimulated us to search for other examples within these known derivatives. In fact, we found that a similar shortening of the C=S...Sb distances compared to those of the corresponding arsenic compounds could be observed in tris(*O*-alkyl carbonodithioato)pnictogen(III) (ROCS₂)₃M (M = As, Sb, Bi; R = Me [16], iso-C₃H₇ [13]) (*Table 3*).

Table 3. The C=S...M Distances in (ROCS₂)₃M (M = As, Sb, Bi)



R	C=S...M	Distance [Å]			Ref.
		(ROCS ₂) ₃ As	(ROCS ₂) ₃ Sb	(ROCS ₂) ₃ Bi	
Me	S(2)...M	2.999(2)	2.966(1)	2.933(4)	[16]
Me	S(4)...M	3.026(2)	3.079(1)	2.988(4)	[16]
Me	S(6)...M	2.991(2)	2.930(1)	2.961(4)	[16]
iso-C ₃ H ₇	S(2)...M	2.978(2)	3.006(1)	2.926(2)	[13]
iso-C ₃ H ₇	S(4)...M	3.026(2)	3.079(1)	3.175(2)	[13]
iso-C ₃ H ₇	S(6)...M	2.991(2)	2.930(1)	2.842(4)	[13]

The bond angles around the Sb-atom are within the range of 83–97° (see *Table 11* in the *Exper. Part*), indicating that the complexes show a distorted tetrahedral structure with one lone pair at the apex. To maintain the tetrahedral structure, two carbothioato, carboselenoato, or carbodithioato ligands in these bis or tris derivatives should be located such that their C=O or C=S moieties point to the same direction. Moreover, the donation of the lone-pair electrons of the carbonyl O-atom or thiocarbonyl S-atom to the antibonding orbital of the M–E¹ bond in (RCEE¹)_{3–x}MR_x¹ (E = O, S; E¹ = S, Se; x = 0, 1; M = P, As, Sb, Bi) may be favorable for such a location with the two carbonyl O-atoms or thiocarbonyl S-atoms, pointing in the same direction.

Packing. Compounds **6b**, **7b**, **9b'**, **12c'**, **15c'**, and **18c** exist as two or four molecules in a unit cell, where two molecules form an enantiomorph pair in a discrete manner, *e.g.*, as shown in *Fig. 3, b*, for **9b'** [17]. Although there are no significant intermolecular interactions between Sb- and S-atoms, the distances between the benzene-ring C-atoms (C(33)) and the CH H-atoms (H–C(14)* = H33*) of the opposite molecule are relatively short (*Fig. 3, b*). The corresponding acylthio derivative **6b** is also discrete (*Fig. 4, a*). However, the distances between the benzene-ring C-atom and the ring CH H-atom (H–C(34) = H33) or the carbonyl O-atoms (O(21)*) of the opposite molecule

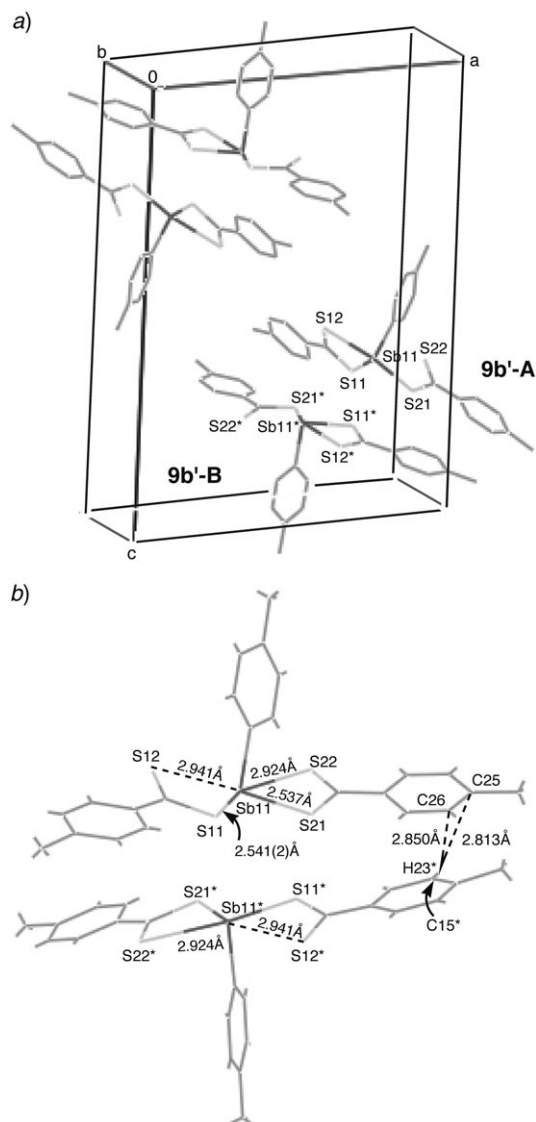


Fig. 3. a) Packing and b) molecular arrangement of bis[(4-methylthiobenzoyl)thio](4-methylphenyl)antimony (**9b'**). Drawn with the program Mercury 1.3. For a), H-atoms are omitted for clarity. Molecules **9b'-A** and **9b'-B** are enantiomorphic to each other.

are relatively short, 2.669 Å and 2.632 Å, respectively (Fig. 4, b). The central Sb-atoms are five-coordinated. Such intermolecular interactions are not observed for the $^i\text{PrC}(\text{E})\text{E}^1$ -coordinated phosphorus [9a] and arsenic isologues [5] $(\text{RC}(\text{E})\text{E}^1)_x\text{MR}_{3-x}^1$; M = P, As; E, E¹ = O or S; x = 1–3).

Bis(acylseleno)(4-methylphenyl)antimony **12c'** exists as four molecules in the unit cell (Fig. 5, a) and the structures **12c'-A** and **12c'-B** are an enantiomorph pair. One of

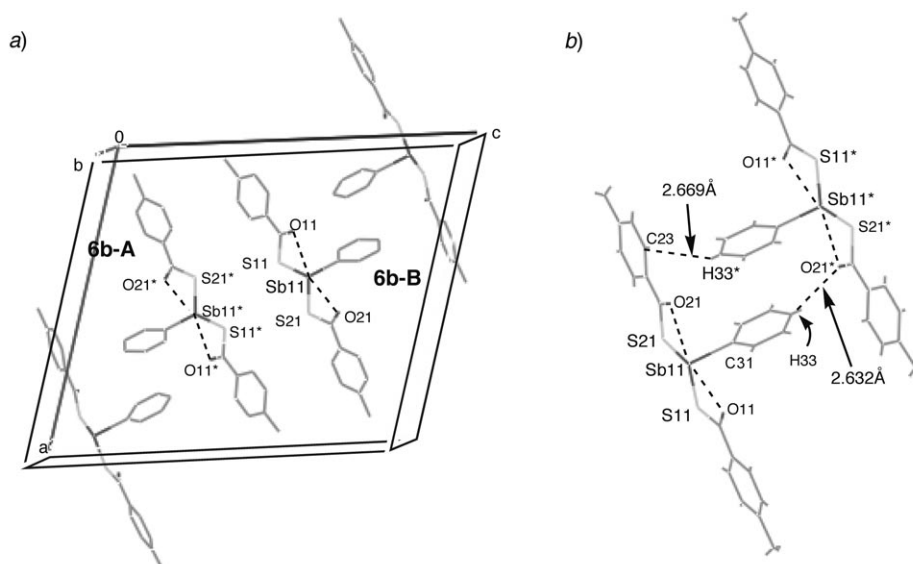


Fig 4. a) Packing and b) molecular arrangement of bis[(4-methylbenzoyl)thio]phenylantimony (**6b**). Drawn with the program Mercury 1.3. For a), H-atoms are omitted for clarity. Molecules **6b-A** and **6b-B** are enantiomorphic to each other.

the two Se-atoms in the molecule interacts with the Sb-atom of the neighboring molecule (average Se(11) ... Sb(11) distance of 3.874 Å), resulting in the formation of a novel Se ... Sb linear chain, where the coordination of both central atoms are six (Fig. 5, b). Such a linear ... Sb–Se ... Sb–Se ... chain has never been reported, although a zig-zag ... Sb–Se ... Sb–Se ... chain has been observed for a solid compound (MeSe)₃Sb [18]. In the case of tris(acylthio) antimony **7b**, there are four molecules in the unit cell (Fig. 6, a), where two molecules pair through associations between the Sb-atom and the S-atom of the opposite molecule (Fig. 6, b) (average S(11) ... Sb(11)* distance of 3.761 Å; sum of the *van der Waals* radii of both atoms 4.15 Å [14]). The central Sb-atom is seven-coordinated.

In contrast to the Sb-derivatives, the bismuth carbothioate **15c'** has two molecules in the unit cell, where the central Bi-atom associates with the carbonyl O-atom of the opposite molecule to form a square unit, *i.e.* a dioxadibismethane ring (average C=O ... Bi distances 3.01(1) Å), and the two molecules **15c'-A** and **15c'-B** are enantiomorphic (Fig. 7, a). In addition, the *para*-methoxy O-atom of the neighboring molecule associates with the Bi-atom (average O ... Bi distance 3.43(1) Å), forming a polymeric network. In the case of the (thioacyl)thio derivative **18c**, two molecules are present in the unit cell (Fig. 8, a) and **18c-A** and **18c-B** are enantiomorphic (Fig. 8, b). Though no intermolecular interactions were observed between the Bi-atoms and the MeO groups or between Bi- and S-atoms, the central Bi-atom (Bi(11) or Bi(11)*) interacts with two benzene-ring C-atoms (C(32)* and C(33)* or C(32) and C(33), resp.) of the opposite molecule (Fig. 8, b). The Bi-atoms of **15c'** and **18c** are seven-coordinated.

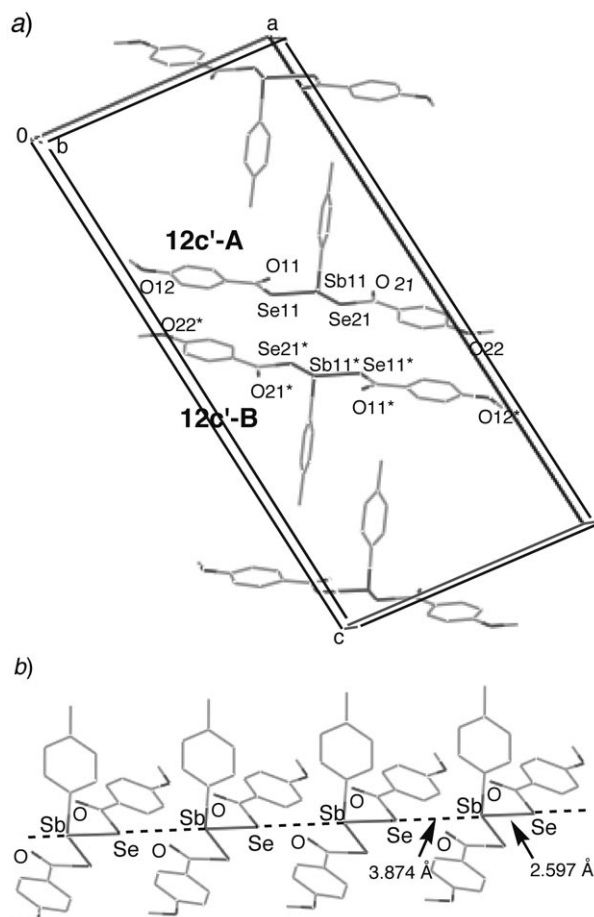


Fig. 5. a) Packing and b) molecular arrangement of bis[(4-methoxybenzoyl)seleno](4-methylphenyl)antimony (**12c'**). Drawn with the program Mercury 1.3. H-Atoms are omitted for clarity. Molecules **12c'-A** and **12c'-B** are enantiomorphic to each other.

4. *Ab initio* Calculations. – To elucidate the nature of these nonbonding attractions, *ab initio* geometry optimizations at the RHF/LANL2DZ level⁵⁾ were performed with the Gaussian 98 program [20] on the model compounds dimethyl[(thioacetyl)thio]antimony **3'** and -bismuth **4'** and (acetylseleno)(dimethyl)antimony **5'** and -bismuth **6'** for $RC(E)E^1MAr_2$ ($E = O, S; E^1 = S, Se; M = Sb, Bi$), and methylbis[(thioacetyl)thio]antimony **3''** and -bismuth **4''**, and methylbis(acetylseleno)antimony **5''** and -bismuth **6''** for $RC(E)E^1_2MPh$ ($E = O, S; E^1 = S, Se; M = Sb, Bi$). Selected bond distances and

⁵⁾ The effective core potentials (ECPs) LANL2DZ were used for heavy atoms S, Se, As, Sb, and Bi [19a–d]. Except for H, the d polarization function for the ECP basis set of all atoms are taken from [19e].

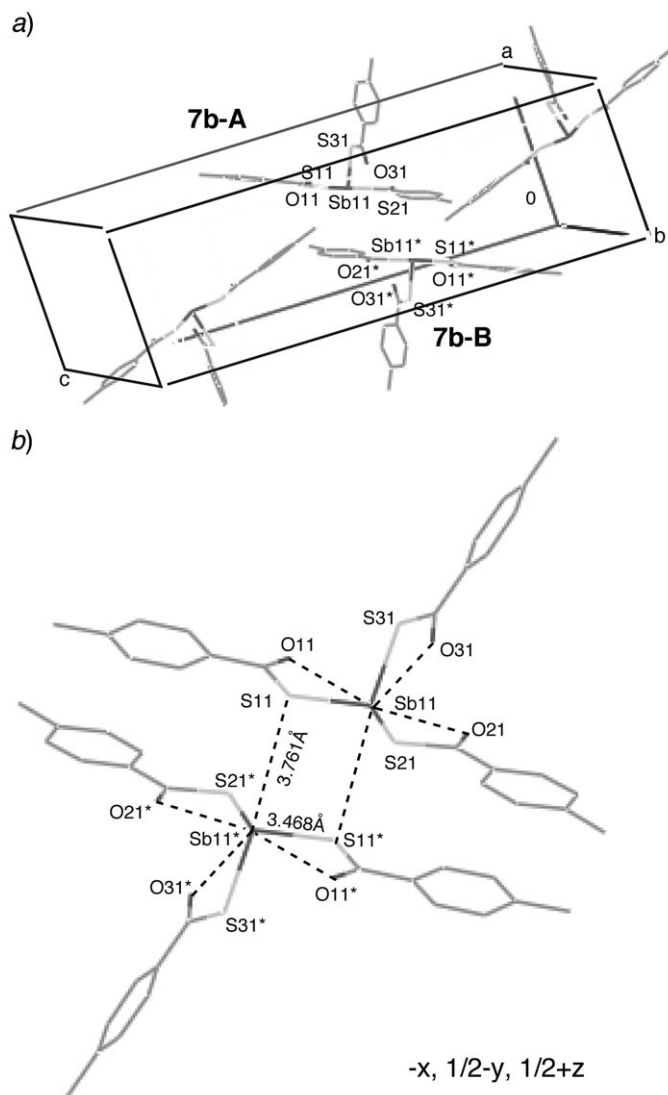


Fig. 6. a) Packing and b) molecular arrangement of tris[(4-methylbenzoyl)thio]antimony (**7b**). Drawn with the program Mercury 1.3. H-Atoms are omitted for clarity. Molecules **7b-A** and **7b-B** are enantiomeric to each other.

angles are shown in Table 4 along with those of the corresponding arsenic compounds **A'**, **B'**, **A''** and **B''** and carbothioic acid derivatives **1'**, **2'**, **1''**, and **2''**.

The C=E...M distances and angles in the optimized structures were similar to those obtained by crystal-structure analysis.

The natural-bond-orbital (NBO) analysis of the mono derivatives **1'**–**6'** showed two types of nonbonding orbital interactions, $n_E \rightarrow \sigma_{MC}^*$ (E = O, S; M = Sb, Bi) and $n_E \rightarrow$

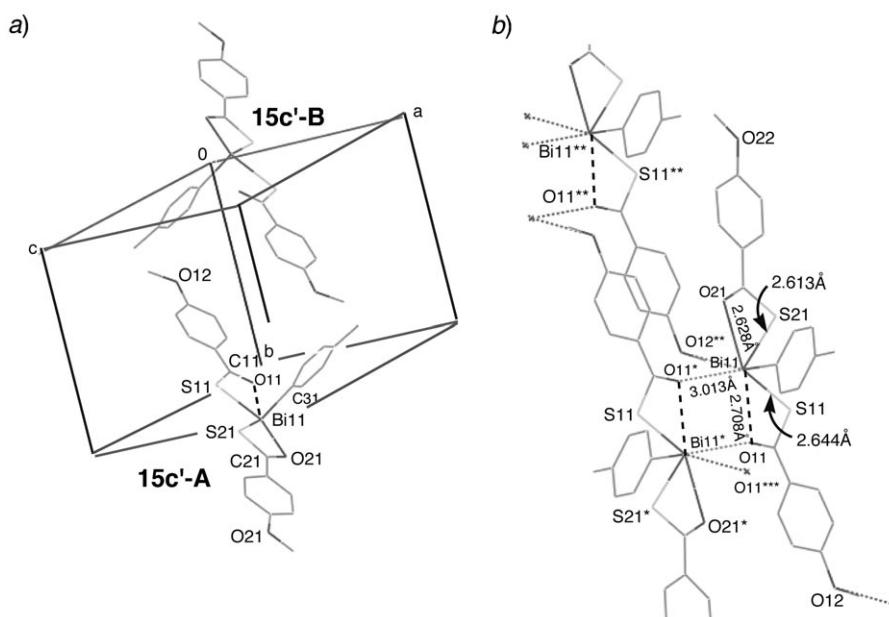


Fig. 7. a) Packing and b) short contacts between Bi and aryl-ring C-atoms of bis[(4-methoxybenzoyl)thio](4-methylphenyl)bitmuth (**15c**). Drawn with the program Mercury 1.3. H-atoms are omitted for clarity. Molecules **15c'-A** and **15c'-B** are enantiomorphic to each other.

$\sigma_{ME^1}^*$ ($E^1 = S, Se; M = Sb, Bi$) (see Table 5), except for the carboselenoantimony **5'** which has an Sb–Se–C=O torsion angle of 49.16° (Table 4). These contribute to the shortening of the C=E...M distance but the contribution of $n_E \rightarrow \sigma_{MC}^*$ is larger than that of $n_E \rightarrow \sigma_{ME^1}^*$. In carbodithioantimony **A'**, two orbital interactions, $n_S \rightarrow \sigma_{BiC(2)}^*$ and $n_S \rightarrow \sigma_{BiC(3)}^*$, along with the $n_S \rightarrow \sigma_{BiS(1)}^*$ orbital interactions contribute to the shortness of the C=S...Bi distances. In the case of carbodithioantimony **B'**, both nonbonding orbital interactions $n_S \rightarrow \sigma_{AsC}^*$ and $n_S \rightarrow \sigma_{AsS(1)}^*$ contribute to the shortening of C=E...As ($E = O, S$), while carbodithioantimony **A'** lacks $n_O \rightarrow \sigma_{AsS}^*$ interactions. In carboselenoantimony **5'**, neither $n_O \rightarrow \sigma_{SbC}^*$ nor $n_O \rightarrow \sigma_{SbSe}^*$ contribute to the shortening of C=O...Sb distances. The magnitude of $n_E \rightarrow \sigma_{MC}^*$ and $n_E \rightarrow \sigma_{ME^1}^*$ interactions in these mono derivatives increases in the order $M = As < Sb < Bi$.

In the case of the bis derivatives **1''–6''**, both $n_{E^1} \rightarrow \sigma_{ME^3}^*$ and $n_{E^1} \rightarrow \sigma_{ME^2}^*$ nonbonding orbital interactions play a dominant role in the shortening of C=E...M distances ($E = O, S; M = Sb, Bi$), and $n_E \rightarrow \sigma_{MC}^*$ makes little, if any, contribution. Carbodithioantimony **A''** and carbodithioantimony **B''** lack $n_E \rightarrow \sigma_{AsC}^*$ interactions. The contributions of both the $n_{E^1} \rightarrow \sigma_{ME^3}^*$ and $n_{E^4} \rightarrow \sigma_{ME^2}^*$ interaction ($E^1, E^4 = O, S; E^2, E^3 = S, Se; M = As, Sb, Bi$) in the bis derivatives (MeC(E^1)E²)(MeC(E^4)E³)MMe increase upon going from As to Sb and to Bi. The magnitudes of the $n_O \rightarrow \sigma_{MSe(1)}^*$ and $n_O \rightarrow \sigma_{MSe(2)}^*$ orbital interactions in carboselenoantimony derivatives **5', 5'', 6', 6''** are close to those of the corresponding carbodithioantimony derivatives **1', 1'', 2', 2''**, respectively. The large stabilization energy (orbital interactions) of the carbodithioantimony derivatives **3', 3'', 4', 4'', B', and B''** compared to those of the corresponding carbodithioantimony derivatives

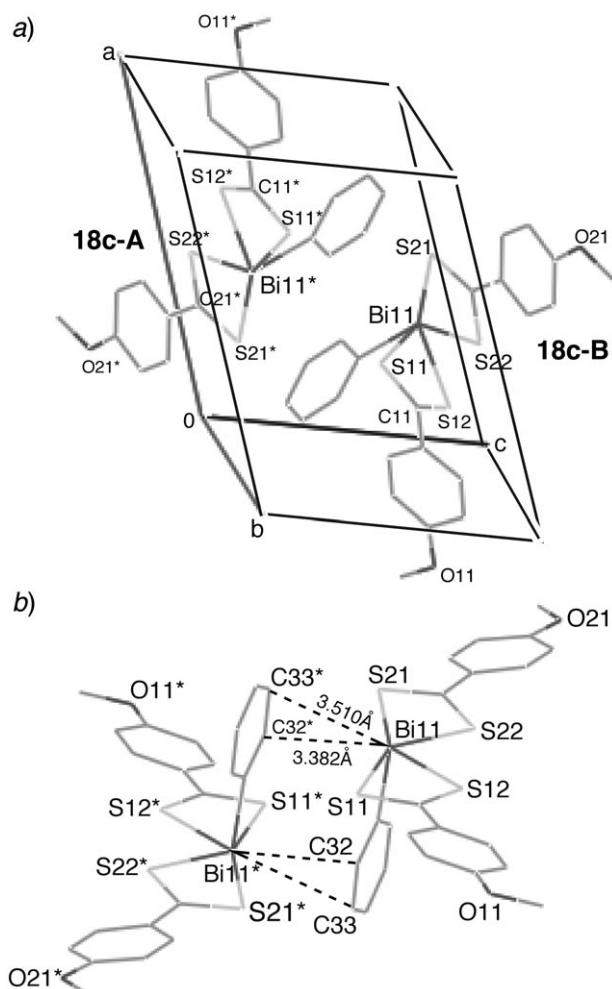
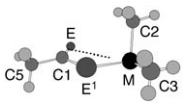


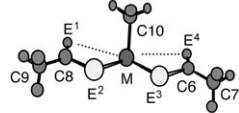
Fig. 8. a) Packing and b) short contacts between Bi and aryl-ring C-atoms of bis[(4-methoxythiobenzoyl)thio]phenylbismuth (**18c**). Drawn with the program Mercury 1.3. H-atoms are omitted for clarity. Molecules **18c-A** and **18c-B** are enantiomeric to each other.

1', **1''**, **2'**, **2''**, **A'**, and **A''** and carboselenoato derivatives **5'**, **5''**, **6'**, and **6''** may be understood in terms of the lower energy level of the n_o orbitals of **1'** and **1''** ($n_o = -0.93299$, -0.48048 au for **1'**, $n_o = -0.94827$, -0.53976 au for **1''**) compared to that of the n_s orbitals of **3'** and **3''** ($n_s = -0.66256$, -0.48689 au for **3'**, $n_s = -0.89756$, -0.54252 au for **3''**), of the n_o orbitals of **2'** and **2''** ($n_o = -0.93066$, -0.56778 au for **2'**, $n_o = -0.95143$, -0.52221 au for **2''**) compared to that of the n_s orbitals of **4'** and **4''** ($n_s = -0.65830$, -0.57517 au for **4'**, $n_s = -0.65043$, -0.51704 au for **4''**); cf. also the n_o levels of **5'**, **5''**, **6'**, and **6''** ($n_o = -0.93057$, -0.47003 au for **5'**, $n_o = -0.94822$, -0.48697 au for **5''**, $n_o = -0.46864$, -0.56576 au for **6'**, $n_o = -0.93250$, -0.51156 au for **6''**). Moreover,

Table 4. Calculated Geometrical Parameters for $\text{MeC(E)E}^1\text{MMe}_2$ ($\text{E}=\text{O}, \text{S}; \text{E}^1=\text{S}, \text{Se}; \text{M}=\text{As}, \text{Sb}, \text{Bi}$) and $(\text{MeC(E}^1\text{)E}^2\text{)-}(\text{MeC(E}^4\text{)E}^3)\text{MMe}$ ($\text{E}^1, \text{E}^4=\text{O}, \text{S}; \text{E}^2, \text{E}^3=\text{S}, \text{Se}; \text{M}=\text{As}, \text{Sb}, \text{Bi}$) at RHF/LANL2DZ Levels of Theory



$\text{MeC(E)E}^1\text{MMe}_2$			Distance [\AA]					Angle [$^\circ$]		Ref.
T	E^1	M	$\text{C(1)=E}\cdots\text{M}$	M-E(1)	M-C(3) M-C(2)	C(1)=E	C(1)-E^1	$\text{E}^1\text{C-}\angle\text{M-C(2)}$ $\text{E}^1\text{-M-C(3)}$	$\text{C(1)-E}^1\text{-M-C(3)}$ $\text{M-E}^1\text{-C(1)-E}$	
A'	O	As	3.386	2.491	2.068	1.219	1.810	99.47 99.46	178.64 2.55	[5]
1'	O	Sb	3.281	2.557	2.159 2.154	1.221	1.825	95.74 90.91	170.57 5.43	
2'	O	Bi	3.231	2.261	2.226 2.219	1.224	1.820	95.20 90.80	171.06 6.50	
B'	S	As	3.732	2.442	2.077	1.678	1.812	91.51 97.75	176.32 4.42	[5]
3'	S	Sb	3.641	2.564	2.160 2.155	1.675	1.790	96.16 89.50	177.18 3.67	
4'	S	Bi	3.616	2.672	2.228 2.220	1.680	1.786	94.43 91.12	177.09 4.78	
5'	O	Se	3.651	2.661	2.157 2.157	1.221	1.985	98.41 91.83	49.16 0.02	
6'	O	Bi	3.266	2.734	2.231 2.222	1.222	1.976	95.23 90.54	171.4 4.25	



$\text{MeC(E}^1\text{)E}^2\text{-(MeC(E}^4\text{)E}^3)\text{MMe}$				Distance [\AA]					Angle [$^\circ$]	Ref.
E^1 or E^4	E^2 or E^3	M		$\text{C(8)=E}^1\cdots\text{M}$ $\text{C(6)=E}^4\cdots\text{M}$	M-E^2 M-E^3	C(8)=E^1 C(6)=E^4	C(8)-E^2 C(6)-E^3	$\text{E}^2\text{-M-C(10)}$	$\text{C(8)-E}^2\text{-M-E}^3$ $\text{M-E}^2\text{-C(8)-E}^1$	
A''	O	As		3.162 3.162	2.498 2.497	1.220 1.219	1.811 1.812	96.47	177.83 2.43	[5]
1''	O	Sb		3.003 3.003	2.574 2.575	1.223 1.227	1.820 1.820	95.19	172.81 4.26	
2''	O	Bi		2.768 2.768	2.767 2.767	1.237 1.237	1.806 1.806	93.83	174.68 2.88	
B''	S	As		3.452 3.451	2.473 2.474	1.665 1.664	1.805 1.805	96.28	176.94 3.34	[5]
3''	S	Sb		3.386 3.385	2.591 2.591	1.683 1.683	1.784 1.784	94.60	179.78 5.88	
4''	S	Bi		3.287 3.289	2.674 2.674	1.693 1.694	1.770 1.770	93.33	179.29 4.45	
5''	O	Se		3.081 3.081	2.695 2.695	1.23 1.23	1.968 1.968	95.82	172.88 4.88	
6''	O	Bi		2.835 2.835	2.784 2.784	1.23 1.23	1.967 1.967	94.55	174.91 3.16	

the tendency of increasing interaction in the order $\text{As} < \text{Sb} < \text{Bi}$ can also be understood in terms of similar energy levels, *i.e.*, the energy level of the σ_{ME^1} orbitals decreases in the order $\text{M} = \text{As} > \text{Sb} > \text{Bi}$.

Table 5. *NBO Analysis of MeC(E)E¹MMe₂ (E=O, S; E¹=S, Se; M=As, Sb, Bi) and (MeC(E¹E²)-MeC(E⁴E³))MMe (E¹, E⁴=O, S; E², E³=S, Se; M=As, Sb, Bi) at RHF/LANL2DZ Levels of Theory*

MeC(E)E ¹ MMe ₂				ΔE^a [kcal mol ⁻¹]		Ref.
	E	E ¹	M	$n_E \rightarrow \sigma_{MC}^*$	$n_E \rightarrow \sigma_{ME^1}^*$	
A'	O	S	As	0.77 (C(3))	–	[5]
1'	O	S	Sb	1.51 (C(3))	0.84	
2'	O	S	Bi	2.17 (C(3))	1.57	
B'	S	S	As	2.22 (C(3))	0.84	[5]
3'	S	S	Sb	3.53 (C(3))	0.62	
4'	S	S	Bi	4.82 (C(3))	3.07	
				3.37 (C(2))		
5'	O	Se	Sb	–	–	
6'	O	Se	Bi	2.23 (C(3))	0.77	

MeC(E ¹ E ²)-MeC(E ⁴ E ³))MMe				ΔE^b [kcal mol ⁻¹]			Ref.
	E ¹	E ²	M	$n_{E^1} \rightarrow \sigma_{MC(10)}^*$	$n_{E^1} \rightarrow \sigma_{ME^3}^*$	$n_{E^1} \rightarrow \sigma_{ME^2}^*$	
A''	O	S	As	–	2.84 (E ³)	0.64 (E ²)	[5]
1''	O	S	Sb	–	6.12 (E ²)	3.18 (E ¹)	
2''	O	S	Bi	0.64 (E ¹)	15.51 (E ²)	6.53 (E ¹)	
B''	S	S	As	–	8.25 (E ²)	2.50 (E ¹)	
3''	S	S	Sb	–	14.47 (E ²)	6.18 (E ¹)	
4''	S	S	Bi	0.58 (E ¹)	23.88 (E ²)	8.16 (E ¹)	[5]
5''	O	Se	Sb	0.51 (E ¹)	5.12 (E ²)	2.11 (E ¹)	
6''	O	Se	Bi	–	13.69 (E ²)	4.60 (E ¹)	

^{a)} Stabilization energy associated with delocalization. ^{b)} The values of the contributions of $n_{E^4} \rightarrow \sigma_{ME^2}^*$ and $n_{E^4} \rightarrow \sigma_{ME^3}^*$ are omitted since they have the same values as those of $n_{E^1} \rightarrow \sigma_{ME^2}^*$ and $n_{E^1} \rightarrow \sigma_{ME^3}^*$.

These nonbonding orbital interactions between n_E and $\sigma_{ME^1}^*$ in the bis derivatives **1''–6''** may facilitate the same orientation for the two carbothioato, carbodithioato, or carboselenoato ligands with respect to each other (see *Figs. 1* and *2*).

5. Spectra. – The thiocarbonyl stretching frequencies for **8–10** and **17–19** appear at 1230–1244 cm⁻¹, while the carbonyl stretching frequencies for the corresponding carboselenoato derivatives **11–13** and **20** and carbothioato derivatives **5–7** and **14–16**

are observed at 1550–1682 cm^{-1} and show a low frequency shift in the order tris > mono > bis (see electronic supplementary information⁶): *ESI-Table 1*). The carbonyl stretching frequencies of the carbothioato derivatives of group-15 elements RCOSMPh_2 (M = group-15 elements), except for the bismuth derivative **14**, are shifted to the lower-frequency region in going from N to Sb.

In the ^{13}C -NMR spectra, the thiocarbonyl shifts of **8–10** are observed in the region $\delta(\text{C})$ 235–238, and those of **8** show upfield shifts of 2–6 ppm relative to those of **9** and **10**. The carbonyl shifts of the carboselenoates appear in a relatively narrow range of $\delta(\text{C})$ 192–196 for both the antimony derivatives **11–13** and bismuth derivatives **20**. In the ^{77}Se -NMR spectra, the $\delta(\text{Se})$ are at 488–491 for the Sb derivatives and at δ 530 for the Bi derivatives, and move downfield in the order mono-, bis-, and trisacyl derivatives.

The tentative MS fragmentation patterns of carbodithioatodiphenylantimony **8b** and carboselenoatodiphenylantimony **11b** and selected ions, along with those of the corresponding carbothioatoantimony **5b** and carbothioato bismuth **14b** are summarized in the electronic supplementary information⁶) (*ESI-Schemes 1* and *2*, *ESI-Table 2*). The molecular-ion and $[M+2]^+$ peaks of these compounds are observed at the ratio of the natural isotope abundance. For example, the carbodithioatoantimony **8b** shows these peaks at the ratio 0.57:0.43. The base peak at m/z 135 is due to $[\text{MeC}_6\text{H}_4\text{CS}]^+$, and the second highest one is due to $[\text{MeC}_6\text{H}_4\text{C}(\text{S})\text{SSbPh}]^+$. Although the carboselenoatoantimony **11b** shows the three characteristic molecular-ion isotope peaks at m/e 472, 474, and 476, its fragment pattern resembles that of the corresponding carbothioatoantimony **5b**, where the base peak is at m/z 119 ($[\text{MeC}_6\text{H}_4\text{CO}]^+$) and the second highest peak at m/z 91 ($[\text{MeC}_6\text{H}_4]^+$) (*ESI-Scheme 2*). In the case of the carbothioato bismuth **14b**, the second highest peak is the $[\text{PhBi}]^+$ ion. The $[\text{MeC}_6\text{H}_4\text{CS}]^+$ or $[\text{MeC}_6\text{H}_4\text{CSe}]^+$ ion is observed for **5b**, **11b**, and **14b**, which suggests that Ph_2M (M = Sb, Bi) groups are rearranged to the carbonyl O-atom to form carbothioato- κO and carboselenoato- κO derivatives 4- $\text{MeC}_6\text{H}_4\text{C}(\text{E})\text{OMPh}_2$ (E = S, Se; M = Sb, Bi). Moreover, the detection of $[\text{Ph}_3\text{Bi}]^+$ and $[\text{MeC}_6\text{H}_4\text{C}(\text{O})\text{SPh}]^+$ ions, albeit at a very low intensity of < 1%, suggests an easy cleavage of the Ph–Bi bond in **11b**. In fact, heating of **14b** led to the preparative synthesis of Se-aryl carboselenoates, as mentioned below (see *Sect. 7*).

6. Reactions. – 6.1. *Reactions of 5–20 with Piperidine.* To the best of our knowledge, there has been no previous report on the reactions of carbochalcogenoatoantimony and -bismuth derivatives. Previously, we found that (acylthio-, [(thioacyl)thio]- and (acylseleno)arsenic derivatives react with piperidine to afford piperidinium (phenylthio) [21] and (phenylseleno)arsenate(III) $(\text{H}_2\text{NC}_5\text{H}_{10})^+ \text{Ph}_2\text{AsE}^-$ (E = S or Se) [5] [21], (diphenyldithio)- [5] and (diphenyldiseleno)arsinate(V) $[(\text{H}_2\text{NC}_5\text{H}_{10})^+]_2(\text{Ph}_2\text{AsE}_2)^{2-}$ (E = S, Se) [5], and diphenyl trithioarsenate(V) $[(\text{H}_2\text{NC}_5\text{H}_{10})^+]_2(\text{Ph}_2\text{AsS}_3)^{2-}$ [5].

Expecting to obtain the antimony and bismuth isologues of these salts, we treated the (carbochalcogenato)antimony derivatives **5b–13b** and the (carbochalcogenato)-bismuth derivatives **20b'** and **20c'** with piperidine (*Table 6* and *Table 7*). The reactions

⁶) Electronic supplementary information is available upon request from the author (S. K.).

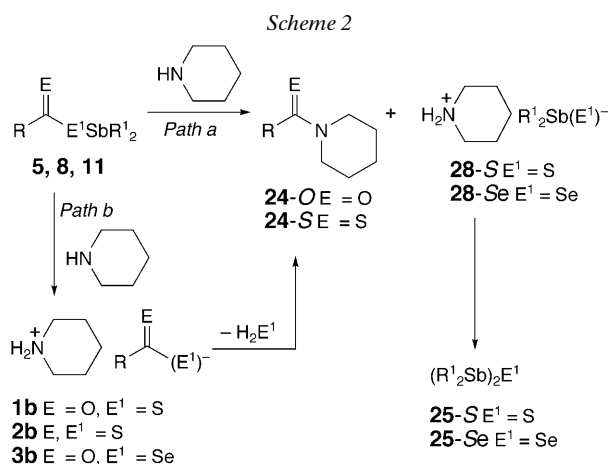
Table 6. Reactions of (Acylthio)-, [(Thioacyl)thio]-, and (Acylseleno)antimony **5b–7b**, **8b–10b**, and **11b–13b**, respectively, with Piperidine

						$\left(\text{R} \begin{array}{c} \text{E} \\ \parallel \\ \text{C} \\ \parallel \\ \text{E}^1 \end{array} \right)_x \text{SbPh}_{3-x} \xrightarrow{\text{HN} \begin{array}{c} \diagup \\ \text{C}_5\text{H}_{10} \\ \diagdown \end{array}} \text{H}_2\text{N} \begin{array}{c} \diagup \\ \text{C}_5\text{H}_{10} \\ \diagdown \end{array} \text{R} \begin{array}{c} \text{E} \\ \parallel \\ \text{C} \\ \parallel \\ \text{E}^1 \end{array} + \text{R} \begin{array}{c} \text{E} \\ \parallel \\ \text{C} \\ \parallel \\ \text{N} \end{array} \begin{array}{c} \diagup \\ \text{C}_5\text{H}_{10} \\ \diagdown \end{array} + (\text{Ph}_2\text{Sb})_2\text{E}^1 + \text{PhSb} \begin{array}{c} \diagup \\ \text{E}^1 \\ \diagdown \\ \text{SbPh} \\ \diagup \\ \text{E}^1 \\ \diagdown \end{array}$			
R = 4-MeC ₆ H ₄						1b E = O, E ¹ = S	24-O E = O	25-S E ¹ = S	26-S E ¹ = S
						2b E = S, E ¹ = S	24-S E = S	25-Se E ¹ = Se	26-Se E ¹ = Se
5b–7b E = O, E ¹ = S						3b E = O, E ¹ = Se			
8b–9b E = S, E ¹ = S									
11b–13b E = O, E ¹ = Se									
						+ Sb ₂ E ¹ ₃	+ $\left(\text{H}_2\text{N} \begin{array}{c} \diagup \\ \text{C}_5\text{H}_{10} \\ \diagdown \end{array} \right)^+ \text{Ph}_2\text{Sb}(\text{E}^1)^-$	+ $\left(\text{H}_2\text{N} \begin{array}{c} \diagup \\ \text{C}_5\text{H}_{10} \\ \diagdown \end{array} \right)_2^+ \text{PhSb} \begin{array}{c} (\text{E}^1)^- \\ \diagdown \\ (\text{E}^1)^- \end{array}$	
						27-S E ¹ = S	28-S E ¹ = S	29-S E ¹ = S	
						27-Se E ¹ = Se	28-Se E ¹ = Se	29-Se E ¹ = Se	
X	piperidine ^{a)}	Time [h]	Temp. [°]	Solvent	Yield ^{b)} [%]				
					24	25, 26, or 27	28 or 29	1b, 2b, or 3b	
5b	1	1:1	6	r.t.	CH ₂ Cl ₂	46 (24-O)	55 (25-S)		–
6b	2	1:2	4	r.t.	CH ₂ Cl ₂	73 (24-O)	46 (26-S)		trace (1b)
7b	3	1:1	3	r.t.	CH ₂ Cl ₂	67 (24-O)	99 (27-S)		22 (1b)
8b	1	1:2	5	r.t.	CH ₂ Cl ₂	38 (24-S)	46 (25-S)		–
9b	2	1:2	5	r.t.	CH ₂ Cl ₂	74 (24-S)	18 (26-S)		29 (2b)
10b	3	1:2	22	r.t.	Et ₂ O	58 (24-S)	74 (27-S)		31 (2b)
11b	1	1:1	1	0	Et ₂ O	80 (24-O)	46 (25-Se)	80 (28-Se)	trace (3b)
12b	2	1:2	1	0	Et ₂ O	87 (24-O)	18 (26-Se)	84 (29-Se)	trace (3b)
13b	3	1:2	1	r.t.	Et ₂ O	52 (24-O)	74 (27-Se)	–	–

^{a)} Mol ratio. ^{b)} Isolated yield.

of (acylthio)diphenylantimony **5b** or diphenyl[(thioacyl)thio]antimony **8b** with piperidine took place at room temperature and gave *N*-(4-methylbenzoyl)piperidine (**24-O**) or *N*-[(4-methyl(thiobenzoyl)]piperidine (**24-S**) in 46 and 38% yield, respectively, along with bis(diphenylstibino) sulfide (**25-S**) in 46–55% yields. A similar reaction of the selenium isologue **11b** gave piperidinium diphenylstibinoselenoite (**28-Se**) along with **24-O** and a trace of bis(diphenylstibino) selenide (**25-Se**). Similarly, the reactions of bis derivatives **6b** or **12b** with piperidine gave the amides (**24-O** or **24-S**), cyclic compounds (**26-S** or **26-Se**) and antimony chalcogenides (**27-S** and **27-Se**), or salt **29-Se** as a yellow solid along with piperidinium carbothioate **1b** or carboselenoate **3b**. In these reactions, however, piperidinium diphenylstibinothioite **28-S** and di(piperidinium) phenylstibonodithioite **29-S** were not detected, and unstable **3b** only in trace amounts. In the reactions of the tris derivatives **7b** and **10b** with piperidine, the yields of the salts **1b** and **2b** were 22 and 31%, respectively, isolated along with the corresponding amide (**24-O** or **24-S**) and antimony chalcogenide (**27-S**).

A plausible reaction pathway for the formation of **1–3** and **24, 25**, and **28** is shown in *Scheme 2*, where piperidine initially attacks the carbonyl or thiocarbonyl C-atom to



give amide **24-O** or thioamide **24-S** and piperidinium diphenylstibinochalcogenoite **28-S** or **28-Se** which lead to diphenylstibinochalcogenides **25-S** and **25-Se** (*Path a*) or attacks the S- or Se-atom of the carbothioato, carbodithioato, or carboselenoato ligands to give the corresponding piperidinium carbochalcogenoate **1b**, **2b**, or **3b** (*Path b*). In the case of the reactions of the bis derivatives **11** and **12**, dipiperidinium salt **29-Se** is formed *via* intermediate **30** (*Path a* in Scheme 3), while the cyclic dichalcogenadistibetane **26** is formed *via* intermediates **31** (*Path b*).

The reactions of the carboselenoato bismuth **20b'** and **20c'** with piperidine gave **24-O**, bis(diarylbismuthino) selenide **32** and triarylbismuthine **33** in 93–98%, 18–41%,

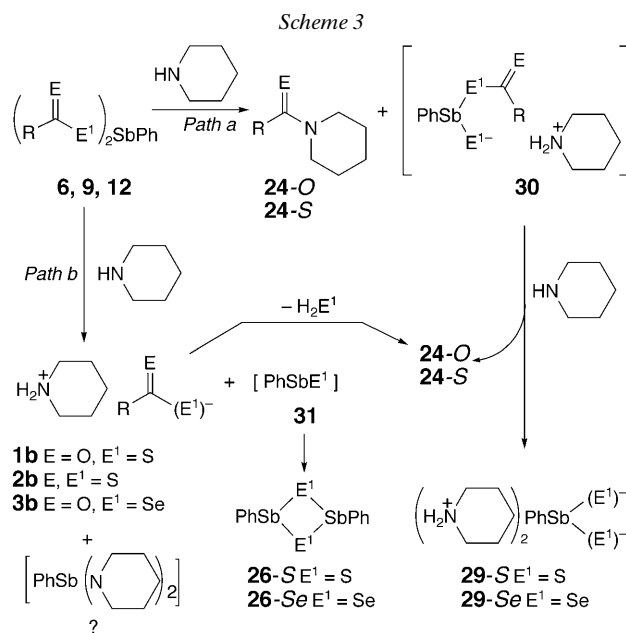


Table 7. Reactions of (Acylseleno)diarylbi-muth **20** with Piperidine

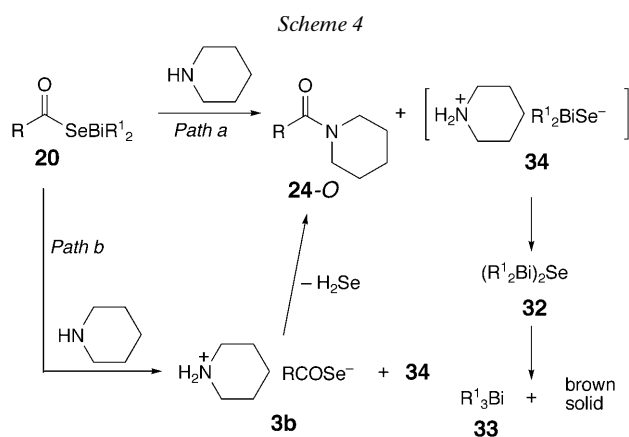
R	R ¹	20 piperidine ^{a)}	Time [h]	Temp. [°]	Solvent	Yield ^{b)} [%]			
						24-O	32	33	
20b'	4-MeC ₆ H ₄	4-MeC ₆ H ₄	1:2.2	1	0	CH ₂ Cl ₂	93	20 (32b)	51 (33b)
			1:2.2	1	0	THF	95	18 (32b)	50 (33b)
			1:2.2	1	-70	Et ₂ O	–	–	–
			1:2.2	1	0	Et ₂ O	98	41 (32b)	–
			1:5	1	0	Et ₂ O	93	33 (32b)	26 (33b)
20c'	4-MeOC ₆ H ₄	1:2.2	1	0	Et ₂ O	93	26 (32b)	39 (33b)	

^{a)} Mol ratio. ^{b)} Isolated yield.

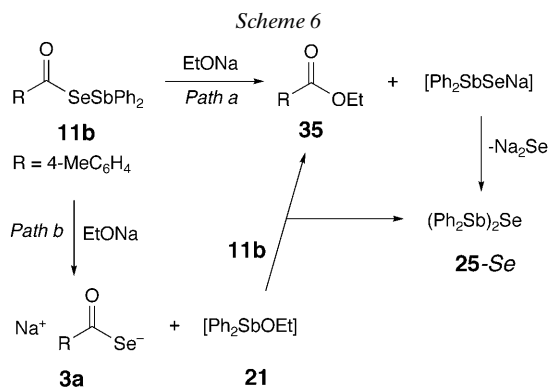
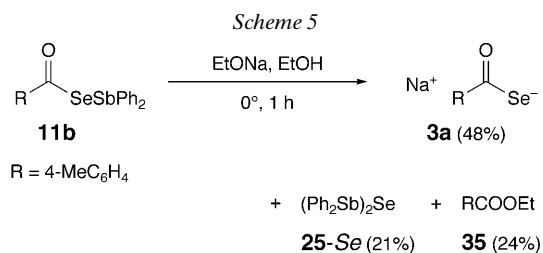
and 26–51% yields, respectively, along with traces of an unidentified black solid (Table 7).

One plausible mechanism for the formation of these products *via* an intermediate piperidinium diphenylbismuthinoselenoite **34** is shown in Scheme 4, where the carbonyl C-atom (Path a) or Se-atom of **20** (Path b) is attacked by piperidine. Compound **24-O** would also be formed by the decomposition of piperidinium carboselenoate **3b** (R = 4-MeC₆H₄) and by the disproportionation of **20** or **30**. We observed that the piperidinium salt **3b** gradually decomposed at room temperature with the liberation of hydrogen selenide to give the corresponding amide [22]. In addition, bis(diarylbi-muthino) chalcogenides **32** ((Ar₂Bi)₂E; E = S, Se) undergo disproportionation at room temperature to give trisarylbi-muth **33** in quantitative yields [23].

6.2 Reaction of **11b** with Sodium Ethoxide. Next, NaOEt was used as a nucleophile. The reaction of carboselenoantimony **11b** with NaOEt readily proceeded in EtOH

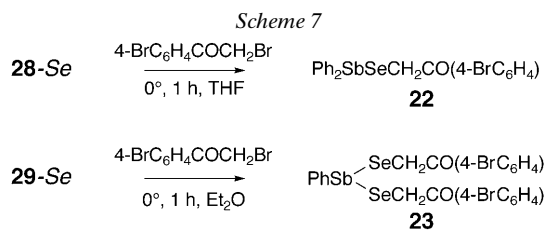


at 0° to give sodium carbo-selenoate **3a**, ester **35** (R = 4-MeC₆H₄) and selenide **25-Se** in 48, 24, and 21% yield, respectively (*Scheme 5*), suggesting that both the carbonyl C-atom (*Path a* in *Scheme 6*) and Sb-atom (*Path b*) are attacked by the ethoxide anion.



Reaction conditions: 0°, 1 h, in EtOH.

6.3 Identification of Products. The structures of compounds **25**, **26**, **28-Se**, **29-Se** and **32** were determined by ¹H- and ¹³C-NMR spectroscopy and elemental analysis. Compounds **28-Se** and **29-Se** were converted into *Se*-(4-bromophenacyl) stibinoselenoite **22** and stibonodiselenoite **23**, respectively (*Scheme 7*).



6.4. Reactions of **11 and **20** with N-Halosuccinimides.** Previously, we found that treatment of (carbo-selenoato)diphenylarsenic derivatives RCOSeAsPh₂ with *N*-chloro- (NCS) and *N*-bromosuccinimides (NBS) generated acylseleno halides [24]. Expecting the formation of acylseleno halides, we treated some antimony and bismuth analogues **11** and **20** with NCS and NBS in the presence of cyclohexene under various con-

Table 8. Reactions of (Acylseleno)diarylantimony **11b** and -bismuth **20** with N-Halosuccinimides (NXS)

$\text{R-C(=O)-SeMR}^1_2 + \text{Cyclohexene} + \text{NXS} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{M = Sb, } -70^\circ, 2 \text{ h}}$ $\text{R-C(=O)-Se(X)-Cyclohexene} + (\text{R-C(=O)-Se})_2$
36 X = Cl **37** X = Br **38**

$\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{M = Bi, } 0^\circ, 1 \text{ h}}$ **36 or 37** + **38** + R^1_3M **33**

11 M = Sb **20** M = Bi
X = Cl, Br

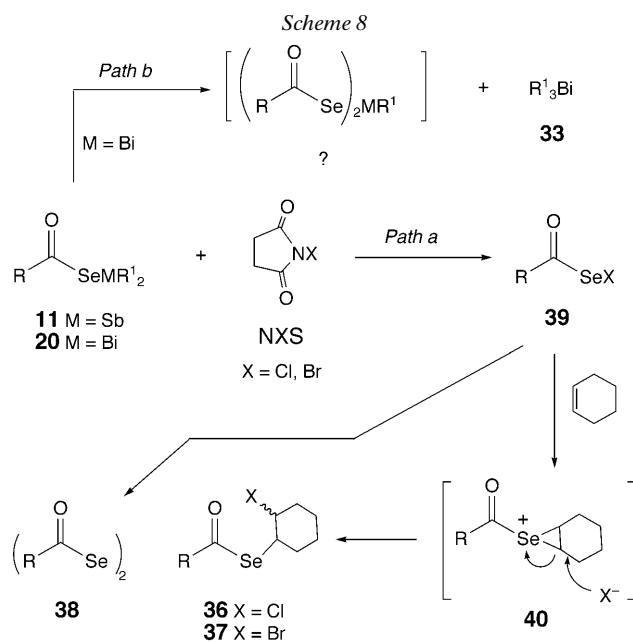
R	R ¹	M X	11 or 20 /Cyclo- hexene	Time [h]	Temp. [°]	Yield ^{a)} [%]			
						36	37	38	33
11b	4-MeC ₆ H ₄	C ₆ H ₅	Sb Br 1:5	1	0	< 3	74	82	
						(37b)	(38b)	(33a)	
20b'	4-MeC ₆ H ₄	4-MeC ₆ H ₄	Bi Cl 1:5	1	0	10		83	72
			Cl 1:10	1	0	(36b)		(38b)	(33b)
			Br 1:5	3	-30	(36b)	trace	83	70
			Br 1:5	5	-50		(37b)	(38b)	(33b)
			Br 1:10	1	0		trace	89	81
						(37b)	(38b)	(33b)	
						(37b)	(38b)	(33b)	
20c'	4-MeOC ₆ H ₄	4-MeC ₆ H ₄	Bi Br 1:5	1	-30		20 ^{b)}	53	63
			Br 1:2	1	1		(37c)	(38c)	(33b)
						(37c)	(38c)	(33b)	

^{a)} Isolated yield. ^{b)} Single isomer.

ditions (Table 8). The reactions of **11b** and **20b'** with NBS afforded the desired trapping product **37** in low yields of 10–20% in almost exclusively *trans* configuration, along with the corresponding diacyl diselenides **38**. In the reaction of **20b'** with NCS, the trapping product **36b** was obtained in only 10–12% yield as a stereoisomer mixture (*cis/trans* 1:1), along with **33b** and **38b** [24⁷⁾].

One plausible reaction mechanism is shown in Scheme 8, where acylseleno bromide **39** (X = Br) reacts with cyclohexene to form the seleniranium intermediate **40**, followed by a bromide attack from the opposite side (Path a), while triarylbismuthines **33** are formed by disproportionation of the starting compounds **20** (Path b). Diacyl diselenide **38** may be derived from the decomposition of **39**.

7) In the reaction of (acylseleno)diphenylarsenic with NCS in cyclohexene, adduct **36** is also obtained as a (*E*)/(*Z*)-stereomer mixture 1:1.



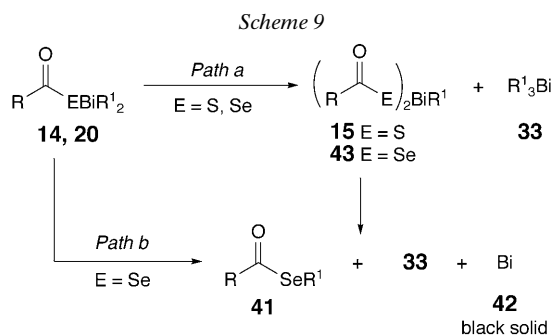
7. Pyrolysis of Compounds 20 leading to *Se*-Aryl Carboselenoates 41. – As mentioned above, (acylseleno)diarylbismuth **20** were gradually decomposed at room temperature to give *Se*-aryl carboselenoates with precipitates of black solid (bismuth). Expecting a high-yield synthesis of the carboselenoates, we performed pyrolysis of **20** under several conditions. As shown in *Table 9*, heating of **20** at 150° for 2 h under Ar gave the desired *Se*-aryl carboselenoates **41** in 80–90% yield along with the corresponding triarylbismuthine **33** ($\text{R}^1 = 4\text{-MeC}_6\text{H}_4$) and a black solid precipitate **42** of elemental bismuth. In contrast, heating of bis(4-methylphenyl)(4-methylbenzoylthio)bismuth **14b'** at 150° for 2 h afforded bis[(4-methylbenzoylthio)(4-methylphenyl)bismuth **15b'** and **33b'** in 50 and 38% yield, respectively. One plausible mechanism for the formation of **33** and carboselenoates **41** is shown in *Scheme 9*, where the formed bis(acylseleno)arylbismuth **43** undergoes disproportionation (*Path a*) and/or **20** undergoes direct ligand coupling (*Path b*). The formation of **41** and **42** by heating of **43** has been observed [23].

8. Conclusions. – A series of [(thioacyl)thio]- and (acylseleno)antimony and -bismuth $(\text{RC}(\text{E})\text{E}^1)_x\text{MR}^1_{3-x}$, ($\text{E} = \text{O}$ or S , $\text{E}^1 = \text{S}$ or Se ; $\text{M} = \text{Sb}$, Bi ; $x = 2$ or 3) could be synthesized in moderate to good yields by reacting piperidinium or alkali-metal carbodithioates and carboselenoates with the corresponding arylantimony and arylbismuth halides. Crystal structure analyses revealed that their structures are essentially similar to those of the corresponding phosphorus and arsenic derivatives, and thus the environment around the metal atom is a distorted tetrahedron with one lone pair at the apex where the thiocarbonyl S-atom or carbonyl O-atom is coordinated to the central As- or Sb-metal. Despite the large atomic radii, the $\text{C}=\text{O} \cdots \text{Sb}$ distances in $(\text{RCOS})_x\text{MR}^1_{3-x}$

Table 9. Pyrolysis of (Acylthio)diarylbi-muth- **14c'** and (Acylseleno)diarylbi-muth **20**

R	R ¹	E	Time [h]	Temp. [°]	Yield ^{a)} [%]			
					41	33b	42	
20a'	C ₆ H ₅	4-MeC ₆ H ₄	Se	2	150	81 (41a')	90	traces
20b'	4-MeC ₆ H ₄	4-MeC ₆ H ₄	Se	2	150	78 (41b')	93	traces
20c'	4-MeC ₆ H ₄	4-MeC ₆ H ₄	Se	2	150	85 (41c')	92	traces
20d'	3-Cl-2,6-(MeO) ₂ C ₆ H ₂	4-MeC ₆ H ₄	Se	12	150	63 (41d')	70	traces
20e'	4-BrC ₆ H ₄	4-MeC ₆ H ₄	Se	2	150	82 (41e')	95	traces

^{a)} Isolated yield.



(E = O, S; M = Sb, x = 2, 3) and the C=S...Sb distances in (RCSS)₂MAR (E = O, S; M = Sb) are shorter than those of the corresponding arsenic derivatives. This tendency for shortening is consistent with the results of NBO (natural bond orbital) analyses of the model compounds MeCEE¹MMe₂ and (MeCEE)₂MMe (E = O, S; E¹ = S, Se; M = Sb, Bi) at the RHF/LANL2DZ level. NBO Analyses also indicated that two types of nonbonding orbital interactions n_E → σ_{MC}^{*} (E = O, S; M = Sb, Bi) and n_E → σ_{ME¹}^{*} (E¹ = S, Se; M = Sb, Bi) play an important role in this shortening of C=E...Sb (E = O, S), except in MeCOSeMMe₂, which has Sb-Se-C=O torsion angle of 49.16°. n_E → σ_{ME¹}^{*} interactions make their greatest contribution in the bis derivatives, and n_E → σ_{MC}^{*} interactions play a dominant role in mono derivatives (see Table 5). On the other hand, the n_S orbitals of the C=S groups in the carbodithioato derivatives MeCSSMMe₂ and (MeCSS)₂MMe (M = As, Sb, Bi) extend more deeply to the σ_{MC}^{*} and σ_{MS}^{*} nonbonding orbitals than those of n_O → σ_{MS}^{*} in the corresponding carbothioato derivatives.

The reactions of RCOSeSbPh_2 ($\text{R} = 4\text{-MeC}_6\text{H}_4$) with piperidine lead to the formation of piperidinium diphenylstibinoselenoite $(\text{H}_2\text{NC}_5\text{H}_{10})^+\text{Ph}_2\text{SbSe}^-$ along with the corresponding *N*-(thioacyl)- or *N*-acylpiperidine, whereas the similar reactions of the bis derivatives $(\text{RCOSe})_2\text{SbR}^1$ ($\text{R}, \text{R}^1 = 4\text{-MeC}_6\text{H}_4$) with piperidine give the novel di(piperidinium) phenylstibonodiselenoite, $[(\text{H}_2\text{NC}_5\text{H}_{10})^+]_2(\text{PhSbSe}_2)^{2-}$, in which the negative charges are delocalized on the SbSe_2 moiety. On the other hand, pyrolysis of diaryl-(acylseleno)bismuth at 150° led to the formation of *Se*-aryl carboselenoates in moderate to good yields.

These results shed some light not only on the structures of group-15 element carboselenoates but also on the chemistry of pnictogens and chalcogen atoms.

This research was supported by a *Grant-in-Aid for Scientific Research on Priority Areas* from the Ministry of Education, Science, Sports and Culture of Japan. We thank Prof. *Takashi Kawamura* and Associate Prof. *Masahiro Ebihara* of Gifu University for their invaluable assistance with X-ray crystallography, Associate Prof. *Mao Minoura* of Kitasato University for X-ray structure analysis, and also Drs. *T. Kanda* and *K. Tani* for running the X-ray analyses. We also thank Associate Professor *Osamu Sakurada* for the measurement of bismuth by ICP-AES analysis and Professors *Hideharu Ishihara* and *Toshiaki Murai* for the measurement of mass spectra.

Experimental Part

1. *General.* All solvents were dried with P_2O_5 or Na metal and distilled under Ar prior to use. All manipulations were carried out under Ar. Antimony(III) chloride and bromide and bismuth(III) iodide were obtained from *Aldrich*. Piperidine and 4-bromophenacyl bromide were of commercial grade and obtained from *Nacalai Tesque Inc.* Column chromatography (CC): silica gel 60 of *Kanto Chemical Co., Ltd.* M.p.: *Yanagimoto* micro-melting point apparatus; uncorrected. UV/VIS Spectra: *Hitachi-124* and *-330* spectrophotometers; λ_{max} in nm. IR Spectra: *JASCO-grating-IR-G* and *Perkin-Elmer-FT-IR-1640* spectrophotometers; KBr disc unless stated otherwise; in cm^{-1} . ^1H -, ^{13}C -, and ^{77}Se -NMR Spectra: at 400, 100, and 76 MHz, resp.; *Jeol-JNM- α 400* spectrometers; CDCl_3 solns. containing Me_4Si and Me_2Se as an internal standard, resp., unless stated otherwise; the ^1H -NMR spectra (60 MHz) of **17–19** were measured on a *Hitachi R-24*. Mass spectra: *Hitachi-RMU-6M* (for high resolution) and *Shimadzu-GC-MS-QP-1000* (EI mode) spectrometer; in m/z (rel. %). Elemental analyses were performed by the Elemental Analysis Center of Kyoto University and the *Bernhardt Analytisches Laboratorium*. Inductively coupled plasma atomic emission spectra (ICP-AES): *JICP-PS-1000UVAT* spectrometer (*Leeman Laboratories, Inc.*) in the sequential mode; power input 1.1 kW; coolant (Ar): 19 l/min^{-1} ; nebulizer: 3.0 kg/cm^{-2} , the anal. lines for the analysis of bismuth and selenium by the ICP technique (their limits of detection) are 223.061 nm ($34 \mu\text{g/l}^{-1}$) and 196.090 nm ($75 \mu\text{g/l}^{-1}$) [25].

Standard Solutions and Starting Materials. Bismuth standard solns. of 0.63 and 1.25 ppm were prepared by dilution of the *Nacalai Tesque* bismuth standard soln. (10^3 ppm, $\text{Bi}(\text{NO}_3)_3$ in 0.75M aq. HNO_3 (anal. grade; *Nacalai Tesque Inc.*)) with deionized H_2O .

2. *Starting Materials 1–3 and Compounds 5–20.* The following compounds were prepared according to the literature: sodium [8] and piperidinium carbodithioates **2a** and **2b** [26], resp., piperidinium [27] and potassium carbodithioates **1b** and **1a** [28][29], resp., and sodium [7] and piperidinium carboselenoates **3a** and **3b** [22], resp., triphenyl [30] and tris(4-methylphenyl)antimony [31] and triphenyl- [31] and tris(4-methylphenyl)bismuth [32][33], chloro- [33] and bromodiphenylantimony [34], dichloro- [33] and dibromophenylantimony [35], diphenylbromo- [36] and phenyldibromobismuth [31], diphenyliodo- [36] and bis(4-methylphenyl)iodobismuth [36], and phenyl- [37] and (4-methylphenyl)diiodobismuth [36]. The detailed preparation and purification procedures of these organopnictogen halides are given in the electronic supplementary information^a) (*ESI-Experimental*).

X-Ray Crystallography. Measurements were carried out on a *Rigaku-AFC7R* four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.71069 Å). All the structures were solved and

refined with the TEXSAN crystallographic software package. All crystal samples were cut from the grown crystals, mounted on a glass fiber, and coated with an epoxy resin. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections (Ψ -scans [38] (**6b**, **7b**, **9b'**, **12c'**) and DIFABS [39] (**15c'** or **18c**)) were also applied. The structures were solved by the direct method with SHELXS 86 [38] and expanded with DIRDIF 94 [40]. Scattering factors for neutral atoms were from Cromer and Waber [41], and anomalous dispersion [42] was used. A full-matrix least-squares refinement was performed, with non-H-atoms being anisotropic for **6b**, **9b'**, **12c'**, **15c'**, and **18c**, and by means of SHELXL 93 for **7b** [43]. The final least-square cycle included fixed H-atoms at calculated positions, for which each isotropic thermal parameter was set to 1.2 times that of the connecting atoms. Crystal data and data collection parameters are summarized in Table 10. Selected bond lengths, bond angles, and torsion angles are given in Table 11. CCDC-602742 to -602747 (**6b**, **7b**, **9b'**, **12c'**, **15c'**, and **18c**, resp.) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.com.ac.uk/data_request/cif.

Preparation of Single Crystals. The slow evaporation of a CH_2Cl_2 /hexane soln. of compound at 18–20° yielded crystals of **6b**, **7b**, **9b'**, **12c'**, **15c'**, and **18c** suitable for X-ray diffraction studies: **6b** (0.080 g) from CH_2Cl_2 (10 ml)/hexane (35 ml) for 2 days, **7b** (0.075 g) from CH_2Cl_2 (15 ml)/hexane (45 ml) for 1 day, **9b'** (0.050 g) from CH_2Cl_2 (2.0 ml)/hexane (2.0 ml) for 7 days, **12c'** (0.050 g) from CH_2Cl_2 (2.0 ml)/hexane (2.0 ml) for 7 days, **15c'** (0.038 g) from CH_2Cl_2 (4 ml)/hexane (3 ml) for 13 days, and **18c** (0.047 g) from CH_2Cl_2 (5 ml)/hexane (5 ml) for 10 days.

Table 10. Crystal Data and Refinement Parameters for Compounds **6b**, **7b**, **9b'**, **12c'**, **15c'**, and **18c**

Compound	6b	7b	9b'	12c'	15c'	18c
Formula	$\text{C}_{22}\text{H}_{19}\text{O}_2\text{S}_2\text{Sb}$	$\text{C}_{24}\text{H}_{21}\text{O}_3\text{S}_3\text{Sb}$	$\text{C}_{23}\text{H}_{21}\text{S}_4\text{Sb}$	$\text{C}_{23}\text{H}_{21}\text{O}_4\text{SbSe}_2$	$\text{C}_{23}\text{H}_{21}\text{BiO}_4\text{S}_2$	$\text{C}_{22}\text{H}_{19}\text{BiO}_2\text{S}_4$
M_r	501.26	575.36	547.41	641.09	634.53	652.61
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P1$ (No. 2)	$P1$ (No. 2)
a [Å]	17.8704(9)	7.920(2)	16.259(3)	12.961(2)	10.886(3)	10.703(1)
b [Å]	5.757(1)	24.340(3)	6.121(4)	6.161(3)	11.348(2)	13.675(1)
c [Å]	20.9801(7)	12.798(2)	22.505(3)	28.871(2)	10.392(2)	8.8159(8)
α [°]					102.50(2)	102.255(7)
β [°]	106.34(3)	103.31(2)	91.38(1)	99.77(1)	91.86(2)	104.570(8)
γ [°]					107.56(2)	109.601(6)
V [Å ³]	2071.3(3)	2400.9(7)	2239(1)	2272(1)	1188.3(5)	1112.5(2)
Z	4	4	4	4	2	2
F_{000}	1000.00	1152.00	1096.00	1240.00	536.00	628.00
D_{calc} [g cm ⁻³]	1.607	1.592	1.624	1.874	1.561	1.948
μ (Mo- $K\alpha$) [cm ⁻¹]	15.46	14.31	16.10	44.44	75.04	83.02
T [K]	193	193	193	193	193	193
Total reflections	6082	5930	5805	5928	5718	5448
Unique reflections	5250	5544	5127	5195	5538	5116
No. observations	3201	2755	3041	3518	4349	3191
No. variables	245	275	253	271	272	262
R_{int}	0.027	0.026	0.045	0.030	0.030	0.025
Residuals: R	0.029	0.083	0.046	0.034	0.072	0.035
R_w	0.030	0.100	0.150	0.097	0.106	0.023
Goodness of fit	1.54	1.97	1.34	0.95	2.23	0.79

Table 11. Selected Bond Distances [Å], Angles [°] and Torsion Angles [°] of Compounds **6b**, **7b**, **9b**, **12c**, **15c**, and **18c**

Bis[(4-methylbenzoyl)thio]phenylantimony (6b)							
Bond length [Å]		Angle [°]					
Sb(11)–S(11)	2.486(1)	S(11)–C(11)	1.772(4)	Sb(1)–S(11)–C(11)	88.9(1)	S(11)–Sb(11)–S(21)	84.03(3)
Sb(11)–S(22)	2.489(1)	C(11)–O(11)	1.233(4)	Sb(1)–S(21)–C(21)	87.7(1)	O(11)–Sb(11)–O(21)	153.1(8)
Sb(11)–O(11)	2.714(3)	S(21)–C(21)	1.765(4)	C(11)–O(11)–Sb(1)	92.3(2)	S(21)–Sb(11)–O(11)	142.96(6)
Sb(11)–O(21)	2.673(3)	C(21)–O(21)	1.230(4)	O(11)–Sb(11)–S(11)	92.6(3)	S(11)–Sb(11)–C(31)	96.57(10)
Sb(11)–C(31)	2.140(4)			O(21)–Sb(11)–S(21)	59.87(6)	S(21)–Sb(11)–C(31)	96.16(9)
				O(21)–Sb(11)–S(21)	60.34(6)	O(11)–Sb(11)–C(31)	81.2(1)
				S(11)–C(11)–O(11)	118.9(3)	O(21)–Sb(11)–C(31)	82.7(1)
Torsion angle [°]							
Sb(11)–S(11)–C(11)–O(11)	0.2(2)	Sb(11)–S(21)–C(21)–O(21)	2.3(5)	S(21)–Sb(11)–C(31)–C(32)	76.5(2)		
S(11)–Sb(11)–S(21)–O(21)	175.0(1)	S(21)–Sb(11)–S(11)–C(11)	171.4(1)				
Tris[(4-methylbenzoyl)thio]antimony (7b)							
Bond length [Å]		Angle [°]					
Sb(11)–S(11)	2.468(4)	S(11)–C(11)	1.76(1)	O(11)–Sb(11)–S(11)	59.4(2)	Sb(11)–S(11)–C(11)	89.5(5)
Sb(11)–S(22)	2.436(4)	C(11)–O(11)	1.22(1)	O(21)–Sb(11)–S(21)	57.1(2)	Sb(11)–S(21)–C(21)	94.5(4)
Sb(11)–S(31)	2.484(4)	S(21)–C(21)	1.77(1)	O(31)–Sb(11)–S(31)	58.5(2)	Sb(11)–S(31)–C(31)	94.5(4)
Sb(11)–O(11)	2.943(9)	C(21)–O(21)	1.20(2)	Sb(11)–O(11)–C(11)	90.9(5)	S(11)–C(11)–O(11)	120.1(1)
Sb(11)–O(21)	2.740(10)	S(31)–C(31)	1.76(1)	Sb(11)–O(21)–C(21)	86.4(7)	S(21)–C(21)–O(21)	121.3(10)
Sb(11)–O(31)	2.80(1)	O(31)–C(31)	1.22(1)	Sb(11)–O(31)–C(31)	90.5(9)	S(31)–C(31)–O(31)	120.1(1)
Sb(11)–C(31)	2.140(4)			S(21)–Sb(11)–S(31)	82.4(1)	S(21)–Sb(11)–S(11)	92.9(1)
Torsion angle [°]							
Sb(11)–S(11)–C(11)–O(11)	5.8(1)	Sb(11)–S(21)–C(21)–O(21)	1.1(1)	Sb(11)–S(31)–C(31)–O(31)	8.4(1)		
S(11)–Sb(11)–S(21)–O(21)	174.5(1)	S(21)–Sb(11)–S(11)–C(11)	178.94(1)	S(11)–Sb(11)–S(31)–C(31)	147.6(2)		
Bis[(4-methylthiobenzoyl)thio]-(4-methylphenyl)antimony (9b)							
Bond length [Å]		Angle [°]					
Sb(11)–S(11)	2.540(2)	S(11)–C(11)	1.723(7)	Sb(11)–S(11)–C(11)	93.3(2)	S(22)–Sb(11)–S(21)	64.77(6)
Sb(11)–S(21)	2.537(2)	C(11)–S(12)	1.666(6)	S(11)–C(11)–S(12)	120.7(4)	S(11)–Sb(11)–S(21)	83.06(6)
Sb(11)–S(12)	2.940(2)	S(21)–C(21)	1.732(7)	C(11)–S(12)–Sb(11)	81.2(2)	S(11)–Sb(11)–S(22)	147.09(6)
Sb(11)–S(22)	2.923(2)	C(21)–S(22)	1.672(7)	S(12)–Sb(11)–S(11)	64.52(5)	S(21)–Sb(11)–S(12)	146.45(6)

Table 11 (cont.)

Bis[(4-methylthiobenzoyl)thio](4-methylphenyl)antimony (9b)			
Bond length [Å]		Angle [°]	
Sb(11)–C(31)	2.155(6)	Sb(11)–S(21)–C(21)	93.5(3)
		S(21)–C(21)–S(22)	119.7(4)
		C(21)–S(22)–Sb(11)	81.9(2)
Torsion angle [°]			
Sb(11)–S(11)–C(11)–S(11)	5.84(2)	Sb(11)–S(21)–C(21)–S(21)	3.67(5)
S(11)–Sb(11)–S(21)–C(21)	170.82(1)	S(21)–Sb(11)–S(11)–C(11)	173.95(4)
Bis[(4-methoxybenzoyl)seleno](4-methylphenyl)antimony (12c')			
Bond length [Å]		Angle [°]	
Sb(11)–Se(11)	2.5904(6)	Se(21)–C(11)	1.945(5)
Sb(11)–Se(21)	2.5973(7)	C(11)–O(11)	1.217(6)
Sb(11)–O(11)	2.768(4)	Se(21)–C(21)	1.940(5)
Sb(11)–O(21)	2.807(4)	C(21)–O(21)	1.212(6)
Sb(11)–C(31)	2.149(5)	O(11)–Sb(11)–Se(11)	59.87(6)
		O(21)–Sb(11)–Se(21)	60.34(6)
		Se(11)–C(11)–O(11)	118.9(3)
		Se(11)–Sb(11)–Se(21)	88.9(1)
		O(11)–Sb(11)–O(21)	87.7(1)
		C(11)–O(11)–Sb(11)	92.3(2)
		C(21)–O(21)–Sb(11)	92.6(3)
		O(11)–Sb(11)–C(31)	96.57(10)
		O(21)–Sb(11)–C(31)	96.16(9)
		O(11)–Sb(11)–C(31)	81.2(1)
		O(21)–Sb(11)–C(31)	82.7(1)
Torsion angle [°]			
Sb(11)–Se(11)–C(11)–O(11)	10.21(2)	Sb(11)–Se(21)–C(21)–O(21)	2.84(2)
Se(11)–Sb(11)–Se(21)–C(21)	177.48(3)	Se(21)–Sb(11)–Se(11)–C(11)	178.02(4)
Bis[(4-methoxybenzoyl)thio](4-methylphenyl)bismuth (15c')			
Bond length [Å]		Angle [°]	
Bi(11)–S(11)	2.644(4)	Bi(11)–C(31)	2.25(1)
Bi(11)–S(21)	2.614(4)	S(11)–C(11)	1.76(1)
Bi(11)–O(11)	2.71(1)	C(11)–O(11)	1.25(2)
Bi(11)–O(21)	2.63(1)	S(21)–C(21)	1.77(2)
		O(11)–Bi(11)–S(11)	87.5(1)
		O(21)–Bi(11)–S(21)	85.1(5)
		S(11)–Bi(11)–S(21)	118(1)
		S(11)–Bi(11)–O*(11)	118(1)
		O(11)–Bi(11)–S(11)	57.9(2)
		O(21)–Bi(11)–S(21)	59.0(3)
		S(11)–Bi(11)–S(21)	82.2(1)
		S(11)–Bi(11)–O*(11)	137.9(2)

Table 11 (cont.)

Bis[(4-methoxybenzoyl)thio](4-methylphenyl)bismuth (15c)							
Bond length [Å]		Angle [°]					
Bi(11)–O*(11)	3.01(1)	C(21)–O(21)	1.22(2)	O(11)–Bi(11)–O(11)	80.4(4)	S(21)–Bi(11)–O(11)	139.9(3)
Bi(11)–O*(12)	3.426(15)			O(21)–Bi(11)–O(11)	80.8(3)	S(11)–Bi(11)–C(31)	96.5(4)
				O(21)–Bi(11)–O*(11)	160.4(4)	S(21)–Bi(11)–C(31)	95.8(4)
Torsion angle [°]							
Bi(11)–S(11)–C(11)–O(11)	8.63(2)	Bi(11)–S(21)–C(21)–O(21)	8.14(2)	S(21)–Bi(11)–C(31)–C(32)	73.62(2)		
S(11)–Bi(11)–S(21)–O(21)	176.85(4)	S(21)–Bi(11)–S(11)–C(11)	174.58(3)				
Bis[(4-methoxythiobenzoyl)thio]phenylbismuth (18c)							
Bond length [Å]		Angle [°]					
Bi(11)–S(11)	3.003(2)	S(11)–C(11)	1.652(7)	Bi(11)–S(11)–C(11)	83.5(3)	S(12)–Bi(11)–S(22)	78.33(6)
Bi(11)–S(21)	2.974(2)	S(12)–C(11)	1.741(7)	Bi(11)–S(21)–C(21)	84.5(3)	S(11)–Bi(11)–S(22)	140.55(6)
Bi(11)–S(11)	2.676(2)	S(21)–C(21)	1.658(7)	S(11)–C(11)–S(12)	120.1(4)	S(21)–Bi(11)–S(12)	156.95(5)
Bi(11)–S(21)	2.673(2)	S(21)–C(21)	1.727(8)	Bi(11)–S(12)–C(11)	121.8(2)	S(11)–Bi(11)–C(31)	89.3(2)
Bi(11)–C(31)	2.254(7)			C(11)–S(12)–Bi(11)	92.7(2)	S(21)–Bi(11)–C(31)	91.8(2)
				S(11)–Bi(11)–S(12)	62.47(6)	S(12)–Bi(11)–C(31)	92.3(2)
				S(21)–Bi(11)–S(22)	62.25(5)	S(22)–Bi(11)–C(31)	92.4(2)
Torsion angle [°]							
Bi(11)–S(11)–C(11)–S(11)	4.80(2)	Bi(11)–S(21)–C(21)–S(21)	4.87(3)	S(21)–Bi(11)–C(31)–C(32)	58.86(3)		
S(11)–Bi(11)–S(21)–C(21)	176.87(3)	S(21)–Bi(11)–S(11)–C(11)	175.83(3)				

(*Acylthio*)antimony **5–7**, [(*Thioacyl*)thio]antimony **8–10**, (*Acylseleno*)antimony **11–13**, (*Acylthio*)-bismuth **14–16**, [(*Thioacyl*)thio]bismuth **17–19**, and (*Acylseleno*)bismuth **20**. Typical procedures are described in detail below for **5b**, **6b**, **7b**, **8b'**, **9b'**, **10b**, **11b**, **12c'**, **13b**, **14b**, **15b**, **15c'**, **16b**, **18c**, **19c**, and **20a'**. The spectroscopic data of other derivatives **5–20** are given in the electronic supplementary information⁶).

[(*4-Methylbenzoyl*)thio]diphenylantimony (**5b**) and Bis[(*4-methylbenzoyl*)thio]phenylantimony (**6b**). The reaction of Ph₂SbBr (0.312 g, 0.88 mmol) containing PhSbBr₂ 0.210 g (0.59 mmol) with potassium 4-methylbenzenecarbothioate **1a** (R=4-MeC₆H₄; 0.390 g, 2.05 mmol) gave 0.354 g (94%) of **5b** as colorless crystals and 0.168 g (57%) of **6b** as colorless needles.

Data of 5b: M.p. 90–92°. IR: 1624 (C=O), 1603, 1573, 1480, 1428, 1230, 1210, 1075, 1063, 1023, 1000, 928, 824, 796, 740, 732, 717, 696, 642, 620. ¹H-NMR: 2.30 (*s*, Me); 7.12–7.91 (*m*, 14 arom. H). ¹³C-NMR: 21.6 (Me); 128.9, 129.1, 129.2, 129.3, 134.8, 135.9, 139.4, 144.3 (arom. C); 194.2 (C=O). EI-MS: 426 (*M*⁺).

Data of 6b: M.p. 184–186°. IR: 1590 (C=O). ¹H-NMR: 2.40 (*s*, 2 Me); 7.21–7.97 (*m*, 13 arom. H). ¹³C-NMR: 21.8 (Me); 128.9, 129.0, 129.1, 129.2, 129.8, 134.4, 134.5, 145.0 (arom. C); 198.3 (C=O). EI-MS: 500 (*M*⁺). Anal. calc. for C₂₂H₁₉O₂S₂Sb: C 52.71, H 3.82; found: C 52.98, H 3.59.

Tris[(*4-methylbenzoyl*)thio]antimony (**7b**). To a suspension of **1a** (R=4-MeC₆H₄; 0.241 g, 1.27 mmol) in CH₂Cl₂ (10 ml) was added a soln. of SbCl₃ (0.095 g, 0.41 mmol) in CH₂Cl₂ (5 ml) at r.t., and the mixture was stirred at r.t. for 1 h. CH₂Cl₂ (50 ml) was added, and the insoluble parts were filtered off. The filtrate was evaporated at 23°/2.7 kPa and the residue was recrystallized from CH₂Cl₂ (10 ml)/hexane (30 ml) (–20° for 24 h): 0.230 g (96%) of **7b**. Colorless crystals. M.p. 172–174°. IR: 3056, 3027, 2978, 2944, 2918, 1628 (C=O), 1598, 1569, 1504, 1442, 1406, 1376, 1308, 1293, 1208, 1173, 1113, 1035, 990, 907, 818, 790, 714, 645, 626. ¹H-NMR: 2.41 (*s*, 3 Me); 7.23 (*d*, *J*=8.3, 6 arom. H); 7.95 (*d*, *J*=8.3, 6 arom. H). ¹³C-NMR: 21.8 (Me); 129.0, 129.2, 134.3, 145.3 (arom.); 198.4 (C=O). Anal. calc. for C₂₄H₂₁O₃S₃Sb: C 50.10, H 3.68; found: C 49.84, H 3.78.

(*4-Methylphenyl*)bis[(*4-methylphenyl*)thioxomethyl]thioantimony (**8b'**). To a suspension of piperidinium 4-methylbenzenecarbodithioate **2b** (R=4-MeC₆H₄; 0.150 g, 0.59 mmol) in CH₂Cl₂ (5 ml) was added a soln. of chlorobis(4-methylphenyl)antimony (0.060 g, 0.18 mmol) containing dichloro(4-methylphenyl)antimony (0.038 g) and tris(4-methylphenyl)antimony (0.052 g) in CH₂Cl₂ (5 ml) under Ar, and the mixture was stirred at r.t. for 1 h. CH₂Cl₂ (100 ml) was added, the org. layer washed with H₂O (*ca.* 3 × 100 ml), dried (MgSO₄), and evaporated at 30°/2.7 kPa, and the residue subjected to CC (silica gel): 0.067 g (80%) of **8b'**. Red oil. *R*_f (CH₂Cl₂/hexane 1:4) 0.70. IR (neat): 3060, 3026, 3007, 2960, 2917, 2861, 1598, 1490, 1444, 1389, 1308, 1225, 1177, 1114, 1059, 1035, 886, 818, 794, 637, 577. ¹H-NMR: 2.34 (*s*, 2 Me); 2.36 (*s*, Me); 7.14 (*d*, *J*=8.3, 2 arom. H); 7.18 (*d*, *J*=7.6, 4 arom. H); 7.54 (*d*, *J*=7.6, 4 arom. H); 8.16 (*d*, *J*=8.3, 2 arom. H). ¹³C-NMR: 21.5 (Me); 21.6 (Me); 127.7, 128.7, 129.9, 135.9, 136.8, 139.3, 142.0, 143.9 (arom.); 231.6 (C=S).

(*4-Methylphenyl*)bis[(*4-methylphenyl*)thioxomethyl]thioantimony (**9b'**). To a suspension of **2b** (R=4-MeC₆H₄; 0.506 g, 2.00 mmol) in CH₂Cl₂ (5 ml) was added a soln. of dichloro(4-methylphenyl)antimony (0.300 g, 1.06 mmol) in CH₂Cl₂ (5 ml) at 20° under Ar, and the mixture was stirred at 20° for 1 h. CH₂Cl₂ (100 ml) was added followed by stirring for 1 h. The org. layer was washed with H₂O (*ca.* 3 × 100 ml), dried (MgSO₄), and evaporated at 30°/2.7 kPa and the residue recrystallized from CH₂Cl₂ (2 ml)/hexane (2 ml) (–20° for 24 h): 0.477 g (86%) of **9b'**. Orange crystals. M.p. 169–171°. IR: 3058, 3020, 2977, 2945, 2912, 1596, 1487, 1440, 1401, 1387, 1307, 1226 (C=S), 1176, 1113, 1060, 1019, 1009, 981, 902, 841, 822, 789, 710, 635, 589, 580. ¹H-NMR: 2.27 (*s*, 1 Me); 2.36 (*s*, 2 Me); 7.15 (*d*, *J*=8.1, 6 arom. H); 7.85 (*d*, *J*=7.8, 2 arom. H); 8.16 (*d*, *J*=8.1, 4 arom. H). ¹³C-NMR: 21.5 (Me); 21.7 (Me); 127.0, 128.8, 129.7, 135.3, 139.3, 142.1, 142.4, 144.9 (arom.); 235.3 (C=S). Anal. calc. for C₂₃H₂₁S₄Sb · 0.5 H₂O: C 50.46, H 3.87; found: C 50.11, H 3.81.

Tris[(*4-methylphenyl*)thioxomethyl]thioantimony (**10b**). To a suspension of **2b** (R=4-MeC₆H₄; 0.455 g, 1.80 mmol) in CH₂Cl₂ (10 ml) was added a soln. of SbCl₃ (0.137 g, 0.60 mmol) in CH₂Cl₂ (5 ml), and the mixture was stirred at r.t. for 1 h. CH₂Cl₂ (50 ml) was added, the org. layer washed with H₂O (3 × 30 ml), dried (Na₂SO₄), and evaporated at 15–20°/2.7 kPa, and the residue recrystallized from CH₂Cl₂ and hexane (10 ml) (–20°): 0.203 g (97%) of **10b**. Orange crystals. M.p. 219–221°. IR: 3050, 3034, 3020, 2983, 2913, 1597, 1402, 1306, 1241, 1225 (C=S), 1176, 1025, 1002, 974, 909, 838, 819,

787, 710, 635, 592, 581. $^1\text{H-NMR}$ ($\text{CDCl}_3/\text{CS}_2$): 2.39 (*s*, 3 Me); 7.15 (*d*, $J=8.0$, 6 arom. H); 8.12 (*d*, $J=8.0$, 6 arom. H). $^{13}\text{C-NMR}$ ($\text{CDCl}_3/\text{CS}_2$): 21.8 (Me); 127.1, 128.6, 141.6, 144.8 (arom. C); 237.6 (C=S). Anal. calc. for $\text{C}_{24}\text{H}_{21}\text{S}_6\text{Sb}$: C 46.23, H 3.39; found: C 46.26, H 3.25.

[(4-Methylbenzoyl)seleno]diphenylantimony (11b). To a suspension of sodium 4-methylbenzenecarboxoselenoate **3a** ($\text{R}=4\text{-MeC}_6\text{H}_4$; 10.325 g, 1.47 mmol) in Et_2O (10 ml) was added soln. of chlorodiphenylantimony (0.270 g, 0.87 mmol) containing phenyldichloroantimony (0.077 g) and triphenylantimony (0.104 g) in Et_2O (5 ml) at 0° under Ar. The mixture was stirred at 0° for 1 h. The insoluble parts were filtered off, and the filtrate was evaporated at $15\text{--}20^\circ/3.0$ kPa and the residue purified by CC (silica gel, hexane/ CH_2Cl_2 1:1): 0.367 g (89%) of **11b**. Colorless needles. M.p. $84\text{--}85^\circ$ (dec.). IR: 3050, 1643 (C=O), 1601, 1570, 1477, 1429, 1202, 1173, 880, 816, 784, 726, 693, 633, 615. $^1\text{H-NMR}$: 2.37 (*s*, Me); 7.20–7.88 (*m*, 14 arom. H). $^{13}\text{C-NMR}$: 21.7 (Me); 128.9, 129.1, 129.4, 129.5, 136.3, 136.4, 137.7, 145.2 (arom.); 194.2 (C=O). $^{77}\text{Se-NMR}$: 488.6. Anal. calc. for $\text{C}_{20}\text{H}_{17}\text{OSbSe}$: C 50.67, H 3.61; found: C 50.48, H 3.66.

Bis[(4-methoxybenzoyl)seleno](4-methylphenyl)antimony (12c'). To a suspension of sodium 4-methoxybenzenecarboxoselenoate **3a** ($\text{R}=4\text{-MeOC}_6\text{H}_4$; 0.627 g, 2.65 mmol) in Et_2O (10 ml) was added a soln. of dichloro(4-methylphenyl)antimony (0.361 g, 1.27 mmol) in Et_2O (5 ml) at 0° under Ar, and the mixture was stirred at 0° for 1 h. The insoluble parts were filtered off. The filtrate was evaporated and the residue recrystallized from CH_2Cl_2 (5 ml)/hexane (5 ml) (-20° for 2 days): 0.664 g (89%) of **12c'**. Pale yellow needles. M.p. $118\text{--}120^\circ$ (dec.). IR: 3055, 3035, 2962, 2941, 1614 (C=O), 1595, 1576, 1487, 1446, 1387, 1344, 1308, 1252, 1205, 1174, 891, 793, 769, 685, 675, 625. $^1\text{H-NMR}$: 2.32 (*s*, Me); 3.85 (*s*, 2 MeO); 6.89 (*d*, $J=8.8$, 4 arom. H); 7.17 (*d*, $J=7.8$, 2 arom. H); 7.85 (*d*, $J=7.8$, 2 arom. H); 7.94 (*d*, $J=8.8$, 4 arom. H). $^{13}\text{C-NMR}$: 21.5 (Me); 55.6 (MeO); 113.8, 129.8, 131.2, 131.9, 134.3, 135.6, 139.6, 164.4 (arom. C); 195.2 (C=O). $^{77}\text{Se-NMR}$ (CDCl_3): 456.9. Anal. calc. for $\text{C}_{23}\text{H}_{21}\text{O}_4\text{SbSe}_2$: C 43.09, H 3.30; found: C 43.10, H 3.36.

Tris[(4-methylbenzoyl)seleno]antimony (13b). To a suspension of **3a** ($\text{R}=4\text{-MeC}_6\text{H}_4$; 0.220 g, 1.00 mmol) in Et_2O (10 ml) was added a soln. of SbCl_3 (0.076 g, 0.33 mmol) in Et_2O (5 ml) at 0° , and the mixture was stirred at 0° for 1 h. CH_2Cl_2 (30 ml) was added and the insoluble parts were filtered off. The filtrate was evaporated and the residue recrystallized from CH_2Cl_2 (20 ml)/hexane (10 ml) (-20° for 24 h): 0.222 g (94%) of **13b**. Colorless crystals. M.p. $123\text{--}124^\circ$ (dec.). IR: 3105, 3082, 3058, 3024, 2957, 2915, 1667, 1622 (C=O), 1600, 1571, 1445, 1404, 1307, 1259, 1202, 1170, 1119, 1015, 886, 816, 784, 708, 640, 615. $^1\text{H-NMR}$: 2.39 (*s*, 3 Me); 7.22 (*d*, $J=8.1$, 6 arom. H); 7.87 (*d*, $J=8.1$, 6 arom. H). $^{13}\text{C-NMR}$ (CDCl_3): 21.8 (Me); 129.1, 129.3, 136.2, 145.3 (arom. C); 196.9 (C=O). $^{77}\text{Se-NMR}$: 477.7.

[(4-Methylbenzoyl)thio]diphenylbismuth (14b). To a suspension of **1a** ($\text{R}=4\text{-MeC}_6\text{H}_4$; 0.105 g, 0.55 mmol) in CH_2Cl_2 (10 ml) was added a soln. of iododiphenylbismuth (0.250 g, 0.47 mmol) in CH_2Cl_2 (5 ml), and the mixture was stirred at 18° for 30 min. CH_2Cl_2 (50 ml) was added and stirred for 1 h. The org. layer was washed with H_2O (3×30 ml), dried (Na_2SO_4), and evaporated and the residue recrystallized from CH_2Cl_2 (2 ml) (-20° for 48 h): 0.237 g (98%) of **14b**. Colorless crystals. M.p. $115\text{--}118^\circ$. IR: 3028, 2960, 1624 (C=O) 1600, 1575, 1550, 1540, 1470, 1420, 1250, 1235, 1215, 1200, 1185, 1165, 1110, 1050, 1010, 995, 920, 820, 800, 720, 690, 650, 625. $^1\text{H-NMR}$: 2.40 (*s*, Me); 7.20–8.13 (*m*, 14 arom. H). $^{13}\text{C-NMR}$: 21.6 (Me); 128.4, 129.0, 129.1, 129.2, 131.5, 135.2, 138.2, 144.0 (arom. C); 196.5 (C=O). EIMS: 514 (M^+). Anal. calc. for $\text{C}_{20}\text{H}_{17}\text{BiOS}$: C 46.70, H 3.33; found: C 46.42, H 3.38.

Bis[(4-methylbenzoyl)thio]phenylbismuth (15b). To a suspension of **1a** ($\text{R}=4\text{-MeC}_6\text{H}_4$; 0.202 g, 1.06 mmol) in CH_2Cl_2 (10 ml) was added a soln. of PhBiI_2 (0.288 g, 0.53 mmol) in CH_2Cl_2 (5 ml), and the mixture was stirred at r.t. for 30 min. CH_2Cl_2 (50 ml) was added, followed by stirring for 30 min. The org. layer was washed with H_2O (3×30 ml), dried (Na_2SO_4), and evaporated and the residue recrystallized from CH_2Cl_2 (5 ml) (-20° for 5 days): 0.385 g (86%) of **15b**. Colorless crystals. M.p. $212\text{--}214^\circ$. IR: 1620 (C=O), 1600, 1580, 1550, 1515, 1470, 1430, 1300, 1215, 1205, 1170, 1115, 995, 925, 825, 795, 725, 715, 690, 645, 625. $^1\text{H-NMR}$: 2.40 (*s*, 2 Me); 7.23–8.57 (*m*, 13 arom. H). $^{13}\text{C-NMR}$: 21.7 (Me); 128.8, 128.9, 129.0, 132.5, 136.3 137.5, 137.6, 144.9 (arom. C); 202.1 (C=O). Anal. calc. for $\text{C}_{22}\text{H}_{19}\text{BiO}_2\text{S}_2$: C 44.90, H 3.25; found: C 44.41, H 3.06.

Bis[(4-methoxybenzoyl)thio](4-methylphenyl)bismuth (15c'). Piperidinium 4-methoxybenzenecarbothioate **1b** ($\text{R}=4\text{-MeOC}_6\text{H}_4$; 0.540 g, 2.01 mmol) was added to soln. of $4\text{-MeC}_6\text{H}_4\text{BiI}_2$ (0.553 g, 1.00 mmol; prepared by the disproportionation reaction of $(4\text{-MeC}_6\text{H}_4)_3\text{Bi}$ with BiI_3 in Et_2O (50 ml) and stir-

red at 10° for 5 h under N₂. CH₂Cl₂ (50 ml) was added and the mixture washed with H₂O (3 × 20 ml). After evaporation, the residue was recrystallized from CH₂Cl₂/Et₂O/petroleum ether: 0.379 g (63%) of **15c'**. Colorless crystals. M.p. 163–166°. IR: 1558 (C=O), 1505, 1482, 1445. ¹H-NMR: 2.32 (s, Me); 3.59 (s, 2 MeO); 6.90–8.03 (dd, 12 arom. H). ¹³C-NMR: 21.7 (Me); 56.2 (MeO); 196.6 (C=O). Anal. calc. for C₂₃H₂₁BiO₄S₂: C 45.85, H 3.51; found: C 45.64, H 3.61.

Tris[(4-methylbenzoyl)thio]bismuth (**16b**). To a suspension of **1a** (R=4-MeC₆H₄; 3.691 g, 19.40 mmol) in CH₂Cl₂ (10 ml) was added a soln. of BiCl₃ (1.999 g, 6.34 mmol) in CH₂Cl₂ (5 ml), and the mixture was stirred at r.t. for 1 h. CH₂Cl₂ (50 ml) was added, followed by stirring for 1 h. The organic layer was washed with H₂O (3 × 30 ml), dried (Na₂SO₄), and evaporated and the residue recrystallized from CH₂Cl₂ (20 ml) (–20°): 2.332 g (90%) of **16b**. Colorless crystals. M.p. 158–162°. IR: 1600, 1585, 1560, 1300, 1215, 1170, 920, 825, 785, 715, 640, 625. ¹H-NMR: 2.41 (s, 3 Me); 7.23–7.99 (m, 12 arom. H). ¹³C-NMR (CDCl₃): 21.8 (Me); 129.0, 129.1, 136.1, 145.2 (arom. C); 201.5 (C=O). Anal. calc. for C₂₄H₂₁BiO₃S₃ (662.6): C 43.50; H 3.19; found: C 43.51, H 3.39.

Bis[(4-methoxyphenyl)thioxomethyl]thio]phenylbismuth (**18c**). To a suspension of piperidinium 4-methoxybenzenecarbothioate **2b** (R=4-MeOC₆H₄; 0.270 g, 1.00 mmol) in CH₂Cl₂ (50 ml) was added a soln. of PhBiI₂ (0.270 g, 1.00 mmol) in CH₂Cl₂ (5 ml), and the mixture was stirred at r.t. for 1 h. CH₂Cl₂ (50 ml) was added, followed by stirring for 1 h. The org. layer was washed with H₂O (3 × 30 ml), dried (Na₂SO₄), and evaporated and the residue recrystallized from CH₂Cl₂ (2 ml)/hexane (2 ml) (–20° for 24 h): 0.199 g (61%) of **18c**. Red needles. M.p. 175–177°. IR: 1585, 1555, 1495, 1450, 1430, 1420, 1315, 1255, 1230, 1180, 1155, 1115, 1015, 1030, 1020, 950, 900, 835, 730, 690, 630. ¹H-NMR: 3.89 (s, 2 MeO); 6.92–8.85 (m, 13 arom. H). ¹³C-NMR: 55.9 (MeO); 114.4, 129.5, 129.6, 139.2, 141.5, 141.8, 154.2, 164.8 (arom. C); 233.5 (C=S). Anal. calc. for C₂₂H₁₀BiO₂S₄ (652.6): C 40.49, H 2.93; found: C 40.51, H 3.05).

Tris[(4-methoxyphenyl)thioxomethyl]thio]bismuth (**19c**). To a suspension of **2b** (R=4-MeOC₆H₄; 6.201 g, 23.00 mmol) in CH₂Cl₂ (10 ml) was added a soln. of BiCl₃ (2.403 g, 7.60 mmol) in CH₂Cl₂ (5 ml) and the mixture was stirred at 21° for 1 h. CH₂Cl₂ (150 ml) was added and the mixture stirred for 30 min. The org. layer was washed with H₂O (3 × 30 ml), dried (Na₂SO₄), and evaporated and the residue recrystallized from CH₂Cl₂ (200 ml)/hexane (200 ml) (–20° for 48 h): 2.888 g (50%) of **19c**. Orange crystals. M.p. 180–182°. IR: 1590, 1500, 1310, 1265, 1240, 1165, 1025, 980, 910, 835, 635. ¹H-NMR: 3.88 (s, 3 MeO); 6.86–8.29 (m, 12 arom. H). ¹³C-NMR: 21.8 (Me); 127.4–145.7 (arom. C); 232.8 (C=S). Anal. calc. for C₂₄H₂₁BiO₃S₆: C 37.99, H 2.79; found: C 37.93, H 2.71.

(Benzoylseleno)bis(4-methylphenyl)bismuth (**20a'**). To a suspension of sodium benzenecarboseleonoate **3a** (R=Ph; 0.311 g, 1.50 mmol) in CH₂Cl₂ (30 ml) was added a soln. of (4-MeC₆H₄)₂BiI (0.682 g, 1.32 mmol) in CH₂Cl₂ (5 ml) at 0° under Ar, and the mixture was stirred at 0° for 1 h. Hexane (5 ml) was added, and the insoluble parts were filtered off. The filtrate was allowed to stand in the refrigerator (–20°) for 4 h, followed by concentration to ca. 15 ml. Filtration of the resulting crystals gave 0.471 g (68%) of **20a'**. Pale yellow needles. M.p. 92–93°. IR: 1635 (C=O), 1577, 1486, 1443, 1309, 1202, 1168, 1052, 1101, 929, 885, 844, 791, 770, 686, 671, 625. ¹H-NMR: 2.32 (s, 2 Me); 7.33 (d, J=7.6, 4 arom. H); 7.40 (t, J=7.6, 2 arom. H); 7.54 (t, J=7.6 Hz, 1 arom. H); 8.01 (d, J=7.6, 6 arom. H). ¹³C-NMR: 21.6 (Me); 128.5, 129.1, 132.3, 133.4, 138.1, 138.1, 138.7, 139.7, 159.3 (arom. C); 196.7 (C=O). ⁷⁷Se-NMR: 534.2. Anal. calc. for C₂₁H₁₀BiOSe: C 43.84, H 3.33; found: C 43.55, H 3.34.

3. Reactions of Some Compounds **5–20** with Pyridine. 3.1. Reaction of **5b** with Piperidine. To a suspension of [(4-methylbenzoyl)thio]diphenylantimony (**5b**; 0.483 g, 1.13 mmol) in CH₂Cl₂ (10 ml) was added a soln. of piperidine (0.100 g, 1.18 mmol) in CH₂Cl₂ (5 ml) at r.t., and the mixture was stirred at 0° for 6 h. After evaporation, the residue was extracted with Et₂O (20 ml). The insoluble parts were recrystallized from CH₂Cl₂/hexane 1:3 (3 ml): 0.067 g, (25%) of piperidinium 4-methylbenzenecarbothioate (**1b**, R=4-MeC₆H₄) as colorless crystals. The Et₂O extract was evaporated and the residue purified by CC (silica gel, hexane/CH₂Cl₂ 6:1): 0.181 g (55%) of bis(diphenylstibino) sulfide (=thiobis[diphenylstibine]; **25-S**, R¹=Ph) and 0.052 g (23%) of N-(4-methylbenzoyl)piperidine (**24-O**, R=4-MeC₆H₄) as colorless solid.

3.2. Reaction of **6b** with Piperidine. According to 3.1, with bis[(4-methylbenzoyl)thio]phenylantimony (**6b**; 0.210 g, 0.42 mmol), CH₂Cl₂ (10 ml), piperidine (0.090 g, 1.06 mmol), and CH₂Cl₂ (5 ml) for 5 h. Filtration of the mixture gave 0.045 g (46%) of 2,4-diphenyl-1,3,2,4-dithiadistibetane (**26-S**) as a

brown solid. After evaporation of the filtrate, the residue was extracted with Et₂O (20 ml). The insoluble parts were recrystallized from CH₂Cl₂/hexane 2:5 (0.7 ml) to give 0.006 g (3%) of *piperidinium 4-methylbenzenecarbothioate* (**1b**, R = 4-MeC₆H₄) as colorless crystals. The Et₂O extract was evaporated and the residue purified by CC (silica gel, hexane/CH₂Cl₂ 6:1): 0.145 g (85%) of *N-(4-methylbenzoyl)piperidine* (**24-O**, R = 4-MeC₆H₄) as colorless solid.

3.3. *Reaction of 7b with Piperidine.* According to 3.1, with tris[(4-methylbenzoyl)thio]antimony (**7b**; 0.286 g, 0.50 mmol), CH₂Cl₂ (10 ml), piperidine (0.128 g, 1.50 mmol), and CH₂Cl₂ (5 ml) for 3 h. Filtration of the mixture gave a brown solid (0.083 g, 98% as Sb₂S₃). After evaporation of the filtrate, the residue was extracted with Et₂O (20 ml). The insoluble parts were recrystallized from CH₂Cl₂/hexane 1:2 (1.5 ml) to give 0.078 g (22%) of *piperidinium 4-methylbenzenecarbothioate* (**1b**, R = 4-MeC₆H₄) as colorless crystals. The Et₂O extract was evaporated, and the residue purified by CC (silica gel, hexane/CH₂Cl₂ 6:1): 0.204 g (67%) of *N-(4-methylbenzoyl)-piperidine* (**24-O**, R = 4-MeC₆H₄) as colorless solid.

3.4. *Reaction of 8b with Piperidine.* – According to 3.1., with [(4-methylphenyl)thioxomethyl]thio-diphenylantimony (**8b**; 0.208 g, 0.47 mmol), Et₂O (10 ml) piperidine (0.040 g, 0.47 mmol), and Et₂O (5 ml) for 6 h. After evaporation, the residue was extracted with hexane (20 ml). The insoluble parts were filtered off, and hexane extract was evaporated and the residue purified by CC (silica gel, hexane/CH₂Cl₂ 6:1): 0.063 g (46%) of *bis(diphenylstibino) sulfide* (**25-S**) as colorless solid and 0.039 g (38%) of *N-[(4-methylphenyl)thioxomethyl]piperidine* (**24-S**, R = 4-MeC₆H₄) as yellow solid.

3.5. *Reaction of 9b with Piperidine.* According to 3.1, with bis[(4-methylphenyl)thioxomethyl]thio-phenylantimony (**9b**; 0.267 g, 0.50 mmol), Et₂O (10 ml), piperidine (0.085 g, 1.00 mmol), and Et₂O (5 ml) for 5 h. Filtration of the mixture gave a brown solid. The filtrate was evaporated and the residue purified by CC (silica gel, hexane/CH₂Cl₂ 6:1): 0.162 g (74%) of *N-[(4-methylphenyl)thioxomethyl]piperidine* (**24-S**, R = 4-MeC₆H₄) as yellow crystals. To the insoluble part (brown solid) was added CH₂Cl₂ (5 ml), and filtration of the resulting precipitate gave 0.018 g (8%) of *2,4-diphenyl-1,3,2,4-dithiadistibetane* (**26-S**) as brown solid. The filtrate was evaporated and the residue recrystallized from CH₂Cl₂/hexane 1:1 (2.0 ml): 0.073 g (29%) of *piperidinium 4-methylbenzenecarbothioate* (**2b**, R = 4-MeC₆H₄) as red crystals.

3.6. *Reaction of 10b with Piperidine.* According to 3.1, with tris[(4-methylphenyl)thioxomethyl]thioantimony (**10b**; 0.312 g, 0.50 mmol), Et₂O (10 ml) piperidine (0.128 g, 1.50 mmol), and Et₂O (5 ml) for 22 h. Filtration of the mixture gave 0.243 g of brown solid. The filtrate was evaporated and the residue purified by CC (silica gel, hexane/CH₂Cl₂ 6:1): 0.189 g (58%) of *N-(4-methylphenyl)thioxomethyl]piperidine* (**24-S**, R = 4-MeC₆H₄) as yellow crystals. To the insoluble parts (brown solid) was added CH₂Cl₂ (5 ml), and filtration of the resulting precipitate gave brown solid (Sb₂S₃ 0.063 g, 74%). The filtrate was evaporated and the residue recrystallized from CH₂Cl₂/hexane 1:1 (2.0 ml): 0.118 g (31%) of *piperidinium 4-methylbenzenecarbothioate* (**2b**, R = 4-MeC₆H₄) as red crystals.

3.7. *Reactions of 11b with Piperidine.* According to 3.1, with [(4-methylbenzoyl)seleno]diphenylantimony (**11b**; 0.219 g, 0.46 mmol), Et₂O (10 ml) (→ soln.), piperidine (0.079 g, 0.93 mmol), and Et₂O (5 ml) at 0° for 1 h. Filtration of the yellow precipitates gave 0.162 g (80%) of *piperidinium diphenylstibinoselenoite* (**28-Se**) as yellow crystals. After evaporation of the filtrate, the residue was purified by CC (silica gel, Et₂O): 0.076 g (81%) of *N-(4-methylbenzoyl)piperidine* (**24-O**, R = 4-MeC₆H₄) as colorless oil and a trace of *bis(diphenylstibino) selenide* (**25-Se**).

Data of 28-Se: M.p. 79–95°. IR: 2908, 2671, 2471, 2379, 1560, 1475, 1427, 1059, 1036, 996, 789, 726, 695. ¹H-NMR: 1.42–1.57 (*m*, 3 CH₂); 2.32–2.81 (*m*, CH₂NCH₂); 7.24–7.92 (*m*, 10 arom. H); 9.5 (br., ⁺NH₂). ¹³C-NMR: 22.6, 23.2, 44.2 (CH₂); 128.0, 128.4, 128.7, 134.7 (arom. C). ⁷⁷Se-NMR: 205.3.

Data of 24-O: IR (neat): 2936, 2875, 1631 (C=O), 1610, 1444, 1375, 1276, 1110, 1003, 830, 753. DEIMS: 203 (*M*⁺).

Reaction of Compound 28-Se with 4-Bromophenacyl Bromide (=2-Bromo-1-(4-bromophenyl)ethanone). To a soln. of piperidinium diphenylstibinoselenoite (**28-Se**; 0.088 g, 0.20 mmol) in THF (10 ml) was added a soln. of 4-bromophenacyl bromide (0.056 g, 0.20 mmol) in THF (5 ml) at 0° under argon. The mixture was stirred at 0° for 1 h. Insoluble parts were filtered off, and the filtrate was evaporated. The resulting residue was recrystallized from Et₂O/hexane 1:1 (2.0 ml): 0.043 g (39%) of *Se-2-oxo-2-*

(4-bromophenyl)ethyl diphenylstibinoselenoite **22**. Yellow solid. M.p. 157–160°. IR: 1665 (C=O), 1585, 1567, 1484, 1397, 1273, 1261, 1071, 1008, 992, 809. ¹H-NMR: 3.93 (s, CH₂); 7.26–7.83 (m, 14 arom. H). ¹³C-NMR: 29.5 (CH₂); 129.6, 130.2, 130.3, 132.1, 132.3 (arom. C); 196.4 (C=O).

3.8. *Reaction of 12b with Piperidine*. According to 3.1, with bis[(4-methylbenzoyl)seleno]phenylantimony (**12b**; 0.329 g, 0.55 mmol), Et₂O (10 ml), piperidine (0.188 g, 2.21 mmol), and Et₂O (5 ml) at 0° for 1 h. Filtration of the yellow precipitate gave 0.245 g (84%) of di(piperidinium) phenylstibonodiselenoite (**29-Se**) as yellow crystals. After evaporation of the filtrate, the residue was purified by CC (silica gel, Et₂O): 0.196 g (87%) of N-(4-methylbenzoyl)piperidine (**24-O**) as colorless oil.

Data of 29-Se: M.p. 67–82°. IR: 2950, 2842, 2731, 2527, 2428, 1593, 1571, 1463, 1431, 1302, 1162, 1081, 1038, 1032, 943, 862, 734, 694, 556. ¹H-NMR ((D₆)DMSO/CDCl₃): 1.40–1.68 (m, 6 CH₂); 2.92–3.08 (m, 2 CH₂NCH₂); 7.22–7.89 (m, 5 arom. H); 8.5 (br., 2 ⁺NH₂).

Reaction of 29-Se with 4-Bromophenacyl Bromide. As described in 3.7 for **22**, with di(piperidinium) phenylstibonodiselenoite (**29-Se**; 0.106 g, 0.20 mmol), THF (10 ml), 4-bromophenacyl bromide (0.111 g, 0.40 mmol), and THF (5 ml): 0.075 g (97.3%) of bis[2-oxo-2-(4-bromophenyl)ethyl] phenylstibonodiselenoite (**23**). Yellow crystals. M.p. 104–105°. IR: 1687 (C=O). ¹H-NMR: 4.40 (s, 2 CH₂); 7.26–7.87 (m, 13 arom. H). ¹³C-NMR: (CDCl₃): 30.3 (CH₂); 129.3, 130.3, 130.4, 132.3, 132.7 (arom. C); 190.4 (C=O). Anal. calc. for C₂₂H₁₇Br₂O₂SbSe₂: C 35.10, H 2.28; found: C 34.81, H 2.02.

3.9. *Reaction of 13b with Piperidine*. According to 3.1, with tris[(4-methylbenzoyl)seleno]antimony (**13b**; 0.206 g, 0.29 mmol), Et₂O (10 ml), piperidine (0.073 g, 0.86 mmol), and Et₂O (5 ml) for 1 h. Filtration of the precipitate gave a black solid (0.069 g). After evaporation of the filtrate, the residue was purified by CC (silica gel, Et₂O): 0.092 g (52%) of N-(4-methylbenzoyl)piperidine (**24-O**) as colorless oil.

3.10. *Reaction of 20b' with Piperidine*. According to [(4-methylbenzoyl)seleno]bis(4-methylphenyl)bismuth (**20b'**; 0.589 g, 1.0 mmol), CH₂Cl₂ (10 ml), piperidine (0.168 g, 2.2 mmol), and CH₂Cl₂ (5 ml) at 0° for 2 h (addition within 10 min). After evaporation of the mixture, Et₂O (10 ml) was added. Recrystallization of the resulting solid from AcOEt/hexane 2:1 (15 ml), followed by filtration of the insoluble material and by evaporation, gave 0.086 g (20%) of bis[bis(4-methylphenyl)bismuthino] selenide (= selenobis[bis(4-methylphenyl)bismuthine]; **32**) as colorless crystals. Evaporation of the filtrate gave a mixture of 1-(4-methylbenzoyl)piperidine (**24-O**; 0.189 g, 93%) and tris(4-methylphenyl)bismuth (**33b**; 0.246 g, 51%).

Data of 32: M.p. 131–132°. IR: 2919, 1484, 1385, 1207, 1186, 1050, 1010, 790. ¹H-NMR: 2.32 (s, 2 Me); 7.18 (d, J=7.6, 4 arom. H); 7.38 (d, J=7.6, 2 arom. H). ¹³C-NMR: 21.6 (Me); 131.8, 137.7, 137.9, 157.6 (arom. C).

4. *Reaction of 11b with Sodium Ethoxide*. To a soln. of [(4-methylbenzoyl)seleno]diphenylantimony (**11b**; 0.455 g, 0.96 mmol) in Et₂O (10 ml) was added NaOEt (0.069 g, 0.90 mmol) at 0° under Ar, and the mixture was stirred at 0° for 1 h. Filtration of the resulting precipitates gave sodium 4-methylbenzenecarboxylate (**3a**, R=4-MeC₆H₄; 0.096 g, 48%) as yellow crystals. After evaporation of the filtrate, the residue was purified by CC (silica gel): 0.035 g (24%) of ethyl 4-methylbenzenoate (**35**) and 0.065 g (21%) of bis(diphenylstibino) selenide (= selenobis[diphenylstibine]; **25-Se**) as colorless crystals. M.p. 123–125° (dec.). IR: 3020, 1572, 1476, 1429, 1330, 1183, 1062, 1017, 997, 727, 693, 460. ¹H-NMR: 7.23–7.60 (m, arom. H). ¹³C-NMR: 128.86, 128.94, 135.8, 139.3 (arom. C). ⁷⁷Se-NMR: –154.3.

Reaction of Sodium Selenide with Diphenylchloroantimony. Diphenylchloroantimony (682 mg, 2.19 mmol) was added to a suspension of sodium selenide (273 mg, 2.19 mmol), and the mixture was stirred at 22° for 4 h. Filtration of the resulting precipitate and evaporation of the filtrate gave 498 mg (66%) of bis(diphenylstibino) selenide (**25-Se**) as colorless crystals.

5. *Reaction of 20 with N-Halosuccinimides*. 5.1. *Reaction of 20c' with N-Bromosuccinimide* (Table 8). To a suspension of [(4-methoxybenzoyl)seleno]bis(4-methylphenyl)bismuth (**20c'**; 0.303 g, 0.5 mmol) in CH₂Cl₂ (10 ml) containing cyclohexene (0.205 g, 2.5 mmol), a soln. of N-bromosuccinimide (0.358 g, 4.0 mmol) in CH₂Cl₂ (5 ml) was added at –70° under Ar (yellow → pale yellow). The mixture was stirred for 2 h at –70°, for 3 h at –20°, and then for 1 h at 0°. Evaporation at 60°/3 kPa gave an oily residue (0.214 g) which was subjected to CC (silica gel, hexane/CH₂Cl₂ 2:5): traces of Se-(2-bromocyclohexyl) 4-methoxybenzenecarboxylate (**37c**), bis(4-methoxybenzoyl) diselenide (**38c**; 0.079 g, 80%; R_f 0.3) [44], and tris(4-methylphenyl)bismuth (**33b**; 0.125 g, 78%; R_f=0.4) [17]. IR, ¹H- and ¹³C-NMR of **38c** and **33b**: identical with those of authentic samples [44].

5.2. *Reaction of 20b' with N-Chlorosuccinimide (Table 8)*. According to 5.1, with [(4-methylbenzoyl)-seleno]bis(4-methylphenyl)bismuth (**20b'**; 0.589 g, 1.0 mmol), CH₂Cl₂ (10 ml), cyclohexene (0.408 g, 5.0 mmol), N-chlorosuccinimide (0.536 g, 4.0 mmol), and CH₂Cl₂ (5 ml). The mixture was stirred at –70° for 2 h and then at 0° for 1 h. CC (silica gel, hexane/CH₂Cl₂ 5:1) gave 0.205 g (10%) of Se-(2-chlorocyclohexyl) 4-methylbenzenecarboselenoate (**36b**), 0.166 g (83%) of bis(4-methylbenzoyl) diselenide (**38b**; R_f=0.2) [44], and 0.245 g (72%) of tris(4-methylphenyl)bismuth (**33b**; R_f 0.4) [44]. ¹H- and ¹³C-NMR of **36b**: identical with those of the authentic sample [26].

5.3. *Reaction of 20b' with N-Bromosuccinimide (Table 8)*. According to 5.1, with [(4-methylbenzoyl)-seleno]bis(4-methylphenyl)bismuth (**20b'**; 0.589 g, 1.0 mmol), CH₂Cl₂ (10 ml), cyclohexene (0.82 g, 10.0 mmol), N-bromosuccinimide (0.190 g, 1.1 mmol), and CH₂Cl₂. The mixture was stirred at –60 to –70° for 2 h and then at 0° for 1 h. CC (silica gel, hexane/CH₂Cl₂ 1:5) gave traces of Se-(2-bromocyclohexyl)-4-methylbenzenecarboselenoate (**37b**), 0.136 g (86%) of **38b** (R_f 0.2) [44], and 0.222 g (93%) of **33b** (R_f 0.8) [30]. IR and ¹³C-NMR of: **37b** identical with those of the authentic sample [23].

6. *Pyrolysis of 20c' (Table 9)*. [(4-Methoxybenzoyl)seleno]bis(4-methylphenyl)bismuth (**20c'**; 0.605 g, 1.0 mmol) under N₂ in an ampoule was heated at 150° for 2 h. The resulting black precipitate (0.0240 g) was washed with Et₂O (20 ml) and CH₂Cl₂ and dried at 60°/3 kPa for 3 h. The dried black precipitate **42** was dissolved in 13M nitric acid (14.0 ml) and soln. diluted with purified H₂O (2486.0 ml) until the concentration of Bi³⁺ was 0.98 ppm. The ICP-AES analysis of the resulting Bi³⁺ soln. showed that the calibration line (223.061 nm for bismuth; emission intensity vs. concentration of Bi³⁺) was consistent with those of the two standard solns. (0.63 and 1.25 ppm of Bi³⁺). The ether/CH₂Cl₂ washing solns. (see above) were evaporated, and the residue was subjected to CC (silica gel, hexane/Et₂O 8:2): 0.257 g (85%) of Se-(4-methylphenyl) 4-methoxybenzenecarboselenoate (**41c'**; R_f 0.3) and 0.146 g (92%) of (4-MeC₆H₄)₃Bi (**33b**; R_f 0.4). IR and ¹H-NMR of **41c'**: identical with those of an authentic sample, prepared from 4-methoxybenzoyl chloride and sodium 4-methylbenzeneselenolate.

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