

NOTE

Some phenylantimony and -bismuth dithiocarbamates

As a supplement to our previous report on phenyltin, -lead, and -antimony dithiocarbamates¹, we wish to report that phenylantimony dithiocarbamates and phenylbismuth dithiocarbamates can be prepared by allowing stoichiometric quantities of phenylantimony dichloride² or phenylbismuth dibromide³ to react with the appropriate sodium dithiocarbamate [ammonium phenyldithiocarbamate⁴ in the case of (I)] in chloroform at 25° (Table 1).

Phenylantimony bis(benzylidithiocarbamate) (I) was prepared also (86%) by allowing phenylantimony oxide⁶ (0.005 mole) to react with benzylamine (0.01 mole) and carbon disulfide (50 ml) in chloroform (20 ml) for 15 h at 25°. The reaction of diphenylantimony chloride⁷ (0.0064 mole) with sodium benzylidithiocarbamate¹ (0.0064 mole) in chloroform (50 ml) for 24 h at 25° also gave (I) (17%) rather than the expected diphenylantimony benzylidithiocarbamate. The other products of this reaction were benzyl isothiocyanate (51% yield based on the 1-benzyl-2-thiobiurea derivative⁸) and bis(diphenylantimony) sulfide (29%). The addition of benzylamine (0.0093 mole) in chloroform (20 ml) to a carbon disulfide (25 ml) solution of bis(diphenylantimony) oxide⁹ (0.004 mole) followed by stirring for 4 h at 25° also gave (I) (36%). The other products were benzyl isothiocyanate (43% yield based on the 1-benzyl-2-thiobiurea derivative), bis(diphenylantimony) sulfide (39%), and a trace amount of benzylammonium benzylidithiocarbamate. In an attempt to prepare diphenylantimony phenyldithiocarbamate, diphenylantimony chloride (0.01 mole) was allowed to react with ammonium phenyldithiocarbamate (0.01 mole) in chloroform (50 ml) for 1 h at 25°. The products were phenylantimony bis(phenyldithiocarbamate) (II) (11%), phenyl isothiocyanate (71% based on the 1-phenyl-2-thiobiurea derivative¹⁰), and bis(diphenylantimony) sulfide (62%).

The reaction of diphenylbismuth chloride¹¹ (0.01 mole) with sodium dimethyldithiocarbamate dihydrate (0.01 mole) in chloroform (50 ml) for 1 h at 25° gave (IX) (84%) instead of the expected diphenylbismuth dimethyldithiocarbamate; the other product was triphenylbismuth (64%). In the preparation of phenylbismuth bis(diethyldithiocarbamate) (X) there was also isolated bismuth tris(diethyldithiocarbamate) (60%), m.p. 185–186° (lit.¹² m.p. 186°), no depression on admixture with a sample, m.p. 188–191°, prepared by allowing bismuth trichloride to react with sodium diethyldithiocarbamate trihydrate. (Found: C, 28.41; H, 4.46; N, 6.45; S, 29.36; mol. wt., 662. C₁₅H₃₀BiN₃S₆ calcd.: C, 27.56; H, 4.62; N, 6.43; S, 29.43%; mol. wt., 654.) IR: 1490 cm⁻¹(CN). Far IR: 566, 503, 496, 399, 357, and 316 cm⁻¹. UV: λ_{max} 260 mμ (ε 7.06 × 10⁴). The reaction of diphenylbismuth chloride (0.01 mole) with sodium diethyldithiocarbamate trihydrate (0.01 mole) in chloroform (50 ml) for 1 h at 25° gave (X) (38%), triphenylbismuth (46%), and bismuth tris(diethyldithiocarbamate) (11%). The formation of (I) and (II) from diphenylantimony chloride and of (IX) and (X) from diphenylbismuth chloride illustrates the ease of cleavage

TABLE I
PRESHYNTHTIC AND -BISMUTH DITHIO ARBAMATES

No.	R	R	Recrystd. from	M.p. ^a (°C)	Yield (%)	Calcd. (%)			Found (%) ^b			Mol. wt. calcd. (found) ^c	CN str. freq. ^d (cm ⁻¹)	λ_{max} ^e (m μ)	10 ⁻⁴ ϵ_{max}
						C	H	N	C	H	N				
C₅H₅Sh(SCSNR)₂															
(I)	H	CH ₂ C ₆ H ₄	Methylene chloride	135-136	83	46.90	3.76	4.97	46.80	3.56	5.03	563(506)	1490	245	9.01
(II)	H	C ₆ H ₅	f	142-144	57	44.87	3.20	5.23	45.11	3.16	5.36	535 ^g	1495	257	4.39
(III)	CH ₃	CH ₃	Acetonitrile	237-239	95	32.81	3.90	6.38	33.09	3.97	6.38	439(482)	1508	256	4.37
(IV)	C ₂ H ₅	C ₂ H ₅	Acetonitrile	148-150	97	38.79	5.09	5.65	38.56	5.02	5.59	495(475)	1488	257	5.45
(V)	C ₆ H ₅	C ₆ H ₅	Tetrahydrofuran	241-244	80	55.90	3.66	4.07	55.83	3.52	4.32	688(746)	1488	262	6.65
C₆H₅(Cf)ShSCSNR₂															
(VI)	CH ₃		Acetonitrile	172-175	96	30.49	3.13	3.95	31.14	3.18	4.05	355(372)	1531	244	4.30
(VII)	C ₂ H ₅		Ethyl acetate	90-93	97	34.53	3.95	3.66	34.81	3.99	3.74	388(396)	1504	245	3.68
(VIII)	C ₆ H ₅		Acetonitrile	176-178	84	47.68	3.16	2.93	47.40	3.14	3.24	479(444)	1488	245	5.31
C₆H₅Bij(SCSNR)₂															
(IX)	CH ₃		Acetonitrile	210-211	98	27.32	3.44	5.31	27.79	3.42	5.05	528(679) ^h	1502	259	5.93
(X)	C ₂ H ₅		Ethanol	131-133	21	32.98	4.33	4.81	32.98	4.37	4.59	583(601) ⁱ	1490	262	6.21

^a Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. ^b Performed by Dr. G. Weiler and Dr. F. B. Strauss, Microanalytical Laboratory, Oxford, England. ^c Performed by Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y. using the method of Tomlinson⁷ at 37°. Unless otherwise noted, the solvent was benzene. ^d Determined with a Beckman IR8 infrared spectrophotometer using KBr pellets. ^e Determined with a Bausch and Lomb Spectronic 505 spectrophotometer using chloroform as solvent. ^f Washed with diethyl ether and benzene. ^g Not determined because of insolubility. ^h Determined in chlorobenzene. ⁱ 629, determined in chlorobenzene; 662 and 681, determined by the Rast method.

of a phenyl group from antimony or bismuth in these reactions.

As has been recently observed for dialkyldithiocarbamate complexes of metal carbonyls¹³, gold dithiocarbamates¹⁴, and dialkyldithiocarbamate complexes of molybdenum(V) and molybdenum(VI)¹⁵, the compounds in Table 1 contain a strong band in the 1488–1531 cm^{-1} region assignable^{16,17} to the partial C=N bond of the canonical form $[\bar{S}_2C=\bar{N}R_2]^-$. The dithiocarbamate group, as in esters of dithiocarbamic acids, shows strong ultraviolet bands in the regions 275–290 $m\mu$ and 245–260 $m\mu$, and weaker absorption in the region 325–360 $m\mu$ ¹⁸. All of the compounds in Table 1 were observed to have a strong absorption in the region 245–262 $m\mu$.

We previously reported that triphenylantimony dichloride converts sodium diorganodithiocarbamates into tetraorganothiuram disulfides¹. We have found that tetraorganothiuram disulfides can be obtained also in high yield by stirring a mixture of triphenylbismuth dichloride (0.005 mole), sodium diorganodithiocarbamate (0.01 mole) and chloroform (50 ml) for 2 h at 25°; the other products are triphenylbismuth and sodium chloride.

The thermal decomposition of some phenylantimony, and -tin organodithiocarbamates (Table 2) gave the corresponding phenylmetallic sulfide and the

TABLE 2

THERMAL DECOMPOSITION OF SOME PHENYLANTIMONY AND -TIN ORGANODITHIOCARBAMATES

No.	Dithiocarbamate	Conditions	Sulfide (% yield)	Thiourea (% yield)	Yield (%) ^a
(I)	$C_6H_5Sb(SCSNHCH_2C_6H_5)_2$	0.5 g CH_3CN (50 ml) Reflux 4 h	C_6H_5SbS (75)	1,3-Dibenzylthiourea (89)	
(II)	$C_6H_5Sb(SCSNHC_6H_5)_2$	1.0 g CH_3CN (50 ml) Reflux 4 h	C_6H_5SbS (70)	1,3-Diphenylthiourea (88)	
(XI)	$(C_6H_5)_3SnSCSNHCH_2C_6H_5$	2.0 g, 130°, 4 h	$[(C_6H_5)_3Sn]_2S$ (99)		69
(XII)	$(C_6H_5)_2Sn(SCSNHCH_2C_6H_5)_2$	1.0 g C_6H_6 (50 ml) Reflux 5 h	$[(C_6H_5)_2SnS]_2$ (86)	1,3-Dibenzylthiourea (85)	12
(XIII)	$(C_6H_5)_2Sn(SCSNHCH_2C_6H_5)_2$	3.2 g C_6H_6 (100 ml) Reflux 5 h	$[(C_6H_5)_2SnS]_2$ (72)	1,3-Dibenzylthiourea (35)	52

^a The yield of benzyl isothiocyanate is based on the 1-benzyl-2-thiobiurea derivative¹

corresponding 1,3-diorganothiourea and/or organo isothiocyanate. (XI) gave benzyl isothiocyanate as previously reported¹. Although (XII) and (XIII) gave benzyl isothiocyanate as previously reported¹, an additional product, 1,3-dibenzylthiourea, was found.

Attempts to prepare triphenyllead, triphenyltin, and diphenyltin phenyldithiocarbamates by allowing stoichiometric quantities of the corresponding organometallic halides to react with ammonium phenyldithiocarbamate in chloroform (50 ml) for 2 h at 25° were unsuccessful. The corresponding organometallic sulfides

[e.g. bis(triphenyltin) sulfide in the case of triphenyltin chloride] and 1,3-diphenylthiourea were obtained instead in high yield.

It was found that phenylmetallic oxides can be readily converted into sulfides by reaction with benzylammonium benzyldithiocarbamate in chloroform at 25° for 24 h (Table 3).

TABLE 3

REACTION OF PHENYLMETALLIC OXIDES WITH BENZYLAMMONIUM BENZYLDITHIOCARBAMATE

Oxide	Sulfide (% yield)	Yield (%) ^a
Bis(triphenyltin) oxide	Bis(triphenyltin) sulfide (90)	78
Diphenyltin oxide	Diphenyltin sulfide trimer (79)	82
Triphenyllead hydroxide	Bis(triphenyllead) sulfide (93)	78
Diphenyllead oxide	Diphenyllead sulfide trimer (36)	86
Bis(diphenylantimony) oxide	Bis(diphenylantimony) sulfide (96)	86
Phenylantimony oxide	Phenylantimony sulfide (36)	91 ^b

^a Yield of 1,3-dibenzylthiourea is based on the amount of benzylammonium benzyldithiocarbamate used.

^b Phenylantimony bis(benzyldithiocarbamate) was also isolated in 6% yield.

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