Polyhedron Vol. 8, No. 6, pp. 763–767, 1989
Printed in Great Britain

0277–5387/89 \$3.00+.00
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PREPARATION AND CHARACTERIZATION OF *n*- AND *i*-BUTYLINDIUM THIOLATE*

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(*Received* 25 *May* 1988 : *accepted after revision* 11 *October* 1988)

Abstract—Butylindium thiolates $Bu^n_xIn(SR)_{3-x}$ ($x = 0$, R = Pr^n, Ph ; $x = 1$, R = Pr^i, Hex^c, Ph ; $x = 2$, R = Pr^n, Pr^i, Hex^c, Ph) and $Bu^i_xIn(SR)_{3-x}$ ($x = 1$, R = Ph ; $x = 2$, R = Pr^n, Pr^i, Ph) are prepared in the reaction of Bu_3In and corresponding thiols in ether. Monothiolates can be obtained from all Bu_3In–alkanethiol combinations, but di- and trithiolates are isolated only from less hindered ones such as Bu^n_3In–Pr^nSH. While, more acidic benzenethiols can give mono-, di- and trithiolates. The mono- and dialkylthiolates, are distillable liquids and they are charactrized by means of NMR spectroscopy (^1H and ^{13}C). In contrast, the phenylthiolates are solids and have poor solubility in organic solvents. The molecular weight measurements show that the dithiolates are generally monomeric in solution.

Recent advances in the technique of OMCVD for fabricating III/V compound semiconductor materials have prompted work to investigate the nature of trialkyls of indium and their adducts with pnictogen compounds such as phosphines etc.[1–5] However, other fields of organoindium chemistry have remained insufficiently explored. Especially, only limited and non-systematic information is available for organoindium thiolates. Meanwhile, an intense interest has arisen in metal chalcogenides as photovoltaic or optoelectric device materials,[6–9] and we believe that the organometallic thiolates will be the most useful precursors for such chalcogenide materials.

Numerous research groups have reported the preparation of the organoindium thiolates since Coates and Whitecombe synthesized dimethylindium methylthiolate for the first time.[10–15] However, dithiolates were rarely obtained with the exception of dithiochelates.[16,17] In general, it has been found that the only product from the reaction of trialkyls of indium with even excess amounts of acids such as carboxylic acids, was the dialkylindium derivatives.[1] In some cases the elimination of three alkyl groups was possible under forcing conditions but monoalkylindium derivatives could not be obtained. However, the brief report from Kocheshkov *et al.*, where phenylindium derivatives were discussed, indicated that both dialkyl and monoalkylindium thiolates could be synthesized.[18] Also the organoindium thiolates already reported possessed high melting points and were sometimes insoluble in organic solvents. These properties may give rise to difficulties in purification. With the aim of obtaining soluble and/or volatile organoindium thiolates, we report the reactions of Bu^n_3In and Bu^i_3In with several thiols, carried out systematically, and analytical and spectrometric properties of the butylindium thiolates thus obtained.

EXPERIMENTAL

General

^1H and ^{13}C NMR spectra were recorded on a Hitachi R90H FT spectrometer, and the common acquisition conditions were described in the previous papers.[19,20] Coupling constants $^1J(^{13}C–^1H)$ were measured by means of the gated decoupling J-spin modulation mode of the instrument. Molecular weights were measured by cryoscopy in benzene solution. Analytical GLC was carried out with a

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* Part of this work was presented at the 52nd annual meeting of the Chemical Society of Japan in Kyoto, 1 April 1986, Abstr. No. 1K27, p. 590.

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Shimadzu GC-8A connected with a glass column (2 mm × 3 m) packed with Porapack N. All the reactions were carried out under a dry N_2 atmosphere unless otherwise noted.

Trialkylindiums

$\mathrm{Bu^n_3In}$ and $\mathrm{Bu^i_3In}$ were synthesized by the Grignard method as reported previously.[21] Yields of $\mathrm{Bu^n_3In}$ and $\mathrm{Bu^i_3In}$ were 93 and 68%, respectively. Their boiling points and NMR data are indicated in Table 1.

Butylindium thiolates

Into a solution of the indium trialkyl (5 mmol) in 30 cm^3 absolute ether was added slowly, thiol (5 or 10 mmol) in ether (5 cm^3) at −78°C with stirring. The mixture was then allowed to warm up to room temperature and was stirred for another 6–24 h. If necessary, the solution was heated under reflux for an additional 2–6 h. Solvent and unreacted thiol were removed *in vacuo* and the crude thiolates were purified by vacuum distillation or by recrystallization from ether–hexane. The alkylthiolates were obtained as colourless, viscous oils, while indium tri(phenylthiolate) appeared to be a white powder insoluble in organic solvents. In contrast, Tuck *et al.* have reported that the reaction of indium trichloride with benzenethiol,[23] or of indium with diphenyl disulphide[24] gave soluble indium tri(phenylthiolate).

The prepared alkylindium thiolates are relatively stable in air, compared with the trialkylindiums and alkylindium alkoxides, but have some disagreeable odour. They became glassy in appearance along with a decrease of C and H contents after weeks under moist air.

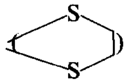
RESULTS AND DISCUSSION

The reactions of $\mathrm{Bu^n_3In}$ and $\mathrm{Bu^i_3In}$ with several thiols were carried out as described above and the products and their yields are summarized in Table 2. Additionally, the spectral and analytical data of the isolated thiolates are also displayed in Tables 1 and 3, respectively.

$$\mathrm{R_3In} + n\mathrm{R'SH} \longrightarrow \mathrm{R_{3-n}In(SR')_n}.$$

A dropwise addition of equimolar amounts of thiols into the ether solutions of the trialkyls of indium resulted in a gradual evolution of the corresponding butane isomer which was checked by GLC analysis and dialkylindium thiolates were

Table 1. B.p. (m.p.) and NMR data of butylindium thiolates

		δ ^{1}H					δ ^{13}C				
		Bu					Bu				
Compounds[a]	B.p., °C/mmHg (m.p., °C)[b]	α	β	γ	δ	In—S—CH	α	β	γ	δ	In—S—C
$\mathrm{Bu^nIn}$	81/1[c]	0.92	1.39	1.72	0.92		22.5	30.1	28.7	13.8	
$\mathrm{Bu^n_2InSPr^n}$	$70/10^{-3}$	0.97	1.1–1.8		0.92	2.73	16.6	30.0	28.4	13.8	29.7
$\mathrm{In(SPr^n)_3}$	(167)										
$\mathrm{Bu^n_2InSPr^i}$	$78/10^{-3}$	0.95	1.1–1.8		0.85	3.28	17.5	30.0	28.6	13.8	33.8
$\mathrm{Bu^nIn(SPr^i)_2}$	$148/10^{-3}$	1.00	165	1.40	0.93	3.46	17.9	29.9	28.3	13.7	34.1
$\mathrm{Bu^n_2In(SHex^c)}$	78/0.02		1.0–1.9		0.93	3.10	16.6	29.9	28.2	13.8	41.9
$\mathrm{Bu^nIn(SHex^c)_2}$	91/0.04		1.3–2.2		0.94	3.17	19.2	26.7	25.3	13.7	42.6
$\mathrm{Bu^n_2InSPh}$	(160 dec)	0.98	1.54	1.21	0.83		19.5	29.6	28.2	13.6	[d]
$\mathrm{Bu^nIn(SPh)_2}$	(150 dec)	[e]					[e]				
$\mathrm{Bu^nIn}$ 	(117–118)	1.41	1.69	1.33	0.93	3.16	19.6	29.8	28.2	13.8	34.8
$\mathrm{Bu^i_3In}$	81/7	1.14	2.40	1.14			24.7	37.6	27.9		
$\mathrm{Bu^i_2InSPr^n}$	$132/10^{-3}$	1.03	2.14	0.99		2.75	26.1	29.8	27.8		29.8
$\mathrm{Bu^i_2InSPr^i}$	$100/10^{-3}$	0.95	2.08	0.93		3.25	30.5	28.0	27.8		33.7
$\mathrm{Bu^i_2InSPh}$	$> 190/10^{-3}$	1.01	2.00	0.86			32.7	27.6	27.0		154.2

[a] $\mathrm{Hex^c}$ means cyclohexyl.

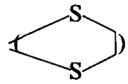
[b] Melting points were measured by TG.

[c] Ref. 22, 86–87°C/0.4 mmHg.

[d] Signals for *ipso* carbon were fairly broadened and the accurate chemical shifts of them could not be read.

[e] The solubility of this thiolate was too low to record a NMR spectrum.

Table 2. Preparation of butylindium thiolates

Bu	R′	*n*	Reaction time (h) rt	Reflux	Product	Yield (%)
Bu^n	Pr^n	1	18		$Bu^n_2InSPr^n$	87
		2	15	2	$In(SPr^n)_3$	13
		3	20	3	$In(SPr^n)_3$	96
	Pr^i	1	20	3	$Bu^n_2InSPr^i$	81
		2	20	3	$Bu^nIn(SPr^i)_2$	44
		3	20	6	$Bu^nIn(SPr^i)_2$	58
	Hex^c	1	20		$Bu^n_2InSHex^c$	96
		2	20	2	$Bu^n_2InSHex^c$	85
		3	20	6	$Bu^nIn(SHex^c)_2$	56
	Ph	1	6		Bu^n_2InSPh	87
		2	6	2	$Bu^nIn(SPh)_2$	67
		3	6	6	$In(SPh)_3$	42
	CH_2CH_2SH	1	24		Bu^nIn 	71
	$SCNEt_2$	1	6		$In(S_2CNEt_2)_3$	33
Bu^i	Pr^n	1	20		$Bu^i_2InSPr^n$	88
		2	20	3	$Bu^i_2InSPr^n +$	47
					$Bu^iIn(SPr^n)_2$[b]	40
		3	20	5	$Bu^i_2InSPr^n +$	20
					$Bu^iIn(SPr^n)_2$[b]	50
	Pr^i	1	20		$Bu^i_2InSPr^i$	92
		2	20	3	$Bu^i_2InSPr^i$	83
		3	20	6	$Bu^i_2InSPr^i$	78
	Ph	1	20		Bu^i_2InSPh	89
		2	20		$Bu^iIn(SPh)_2$	64

[a] Hex^c means cyclohexyl.

[b] Could not be isolated by distillation and NMR yields are presented here.

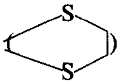
obtained in good yields. The monoalkylthiolates appeared as viscous liquids and were distillable under reduced pressures. On the other hand, the dialkylindium phenylthiolates were waxy or gummy solids at room temperature which melted as they decomposed. In contrast, more acidic diethyldithiocarbamic acid gave no butylindium derivatives, but a symmetrical indium(III) dithiocarbamate complex was formed as the sole product. It was reported that dialkylindium dithiocarbamates which were synthesized via the metathesis reaction between dialkylindium halides and sodium dithiocarbamate salts were spontaneously converted into the bis(dithiocarbamate) complex.[14] Therefore, in our case, the dialkylindium diethyldithiocarbamate is presumably formed initially and then the tris(dithiocarbamate) complex is obtained via subsequent disproportionation. However, tributylindium could not be detected as a final product as would be predicted by this scheme.

In the reactions where more than two molar equivalents of thiol were employed, the degree of substitution was found to be strongly dependent upon the isomer of the butyl group and/or those of the thiol moieties. Benzenthiol gave Bu^n_2InSPh, $Bu^nIn(SPh)_2$ and $In(SPh)_3$ in the reactions with Bu^n_3In in the molar ratios of 1 : 1, 2 : 1 and 3 : 1, respectively; and Bu^i_2InSPh, and $Bu^iIn(SPh)_2$ in the reactions with Bu^i_3In in 1 : 1 and 2 : 1 molar ratio, respectively. These phenylthiolates are solids at room temperature and poorly soluble in organic solvents.

In contrast, for some reactions with alkylthiols the product expected from reactant stoichiometry was not always obtained. For example, $Bu^n_2InSPr^n$ and $In(SPr^n)_3$ were formed in the reaction of Bu^n_3In with *n*-propanethiol in 1 : 1 and 2–3 : 1 molar ratio, respectively, but $Bu^nIn(SPr^n)_2$ could not be formed with any mole ratio of the starting materials. However, dibutylindium thiolates from the secondary alkanethiols seemed not to react with further thiol nucleophiles. Consequently, it was necessary to use more than the stoichiometric amounts of the thiols in order to prepare the dithiolates. Especially for the bulky triisobutylindium, the replacement of more than two butyl groups did not occur.

These phenomena could not be explained by the

Table 3. Analytical data and molecular weights of butylindium thiolates

Compounds[a]	Found, % (calc., %) C	H	Formula (FW)	Molecularity (concn, wt%)
$Bu^n_2InSPr^n$	42.9	8.0	$C_{11}H_{25}InS$	1.6 (0.31)
	(43.4	8.3)	(304.2)	
$In(SPr^n)_3$	31.4	6.1	$C_9H_{21}InS_3$	
	(31.8	6.2)	(340.3)	
$Bu^n_2InSPr^i$	43.2	8.2	$C_{11}H_{25}InS$	1.2 (0.30)
	(43.4	8.3)	(304.2)	
$Bu^nIn(SPr^i)_2$	41.8	8.0	$C_{10}H_{23}InS_2$	1.1 (0.50),
	(41.0	8.0)	(322.2)	1.4 (2.9)
$Bu^n_2InSHex^c$	49.5	8.5	$C_{14}H_{29}InS$	1.6 (2.9)
	(48.8	8.5)	(344.3)	
$Bu^nIn(SHex^c)_2$	47.9	8.2	$C_{16}H_{31}InS_2$	1.0 (0.35),
	(47.8	8.5)	(402.4)	1.0 (2.2)
Bu^n_2InSPh	49.7	6.4	$C_{14}H_{23}InS$	
	(49.7	6.9)	(338.2)	
$Bu^nIn(SPh)_2$	49.7	4.4	$C_{16}H_{19}InS_2$	
	(49.2	4.9)	(390.3)	
$In(SPh)_3$	48.2	3.7	$C_{18}H_{15}InS_3$	
	(48.9	3.4)	(442.3)	
Bu^nIn 	26.9	4.9	$C_6H_{13}InS_2$	2.0 (0.08)
	(27.3	5.0)	(264.1)	
$Bu^i_2InSPr^n$	42.6	8.2	$C_{11}H_{25}InS$	1.1 (0.30)
	(43.4	8.3)	(304.2)	
$Bu^i_2InSPr^i$	43.1	8.4	$C_{11}H_{25}InS$	1.0 (0.26)
	(43.4	8.3)	(304.2)	
Bu^i_2InSPh	49.7	6.9	$C_{14}H_{23}In$	
	(49.7	6.9)	(338.2)	

[a] Hex^c means cyclohexyl.

reported bond energy ordering: e.g. $D_1 > D_3 > D_2$ observed for trimethylindium.[17] Perhaps such a disagreement may be related to steric crowding around the indium centre from both alkyl groups bound to the indium atom and the alkyl groups in the thiolate moieties. Therefore, the bulkiness of both alkyl groups and thiolates synergistically affects the degree of the substitution.

Generally the In—S bond is considered to have less dipolar effects than its oxygen analogue and its weak coordination ability has been reported.[1] Thus, several organoindium thio-derivatives are found to be monomeric in solutions. Therefore, we have observed the molecular weights of the following thiolates in benzene solution: $Bu^n_2InSPr^n$, $Bu^n_2InSPr^i$, $Bu^nIn(SPr^i)_2$, $Bu^n_2InSHex^c$, $Bu^nIn(SHex^c)_2$, $Bu^i_2InSPr^n$, and $Bu^i_2InSPr^i$. The observed molecularity is presented in Table 3. These data show that dithiolates are approximately monomeric in the concentration range 0.5–3.0 wt% in benzene but monothiolates of *n*-butylindium have some degree of association. In addition, it is very interesting that 1,2-ethanedithiol gave cyclic dithioindate as a sole product without the formation of the polymers consisting of a dithiol bridge. This cyclic compound was solid at room temperature and although only slightly soluble in most organic solvents, was found to be a dimer in benzene.

The degree of association seemed to depend upon the degree of branching in the indium alkyls and thiolate moieties. Therefore, among the monothiolates the molecularity decreased in the series for the following metal ligand–sulphur ligand combinations: Bu^n–Pr^n > Bu^n–Hex^c > Bu^n–Pr^i = Bu^i–Pr^n > Bu^i–Pr^i. Similarly, it has been reported that alkylzinc thiolates which have branches are liquid and almost monomeric in solution at room temperature, in comparison with the straight chain analogues which were found to be dimeric to hexameric.[25] In the indium cases, this tendency was also dependent upon the alkyl groups bound to the indium centre.

NMR spectroscopy

^{1}H and ^{13}C NMR data of the compounds are summarized in Table 1. All the measurements were obtained in chloroform-*d* solution (10 wt%). For the solid samples, it was necessary to use more diluted solutions (0.1–1 wt%) because of their low solubilities. In the ^{1}H NMR spectra, the signals due to the α-protons in the butyl groups were generally superimposed on those of terminal methyl protons in the monothiolate compounds. However, those α-proton signals were down field of the terminal signals in dithiolates.

In ^{13}C NMR spectra, the signals due to the α-carbons in the *n*-butyl groups appeared at a slightly higher field than those in the starting Bu^n_3In. While the signals of α-carbons in the *i*-butyl groups appeared at lower fields by *ca* 10 ppm compared with Bu^i_3In. In contrast, an opposite tendency was found in the signals due to the β-carbons. Since isobutylindium thiolates are believed to be monomeric in solution from the molecularity measurements, it can be said that the chemical shifts in the isobutyl group may be affected only by the covalently-bonded sulphur ligands. However, since in the *n*-butyl cases some self-association was observed, the *n*-butyl chemical shifts have been further affected. The above mentioned effect was further supported by the spectrum of thiolate moieties. In this case the signal due to the δ C1 and C2 of the thiolate ligand resembled those of sulphides, not of thiolate anions.[26] These results also indicate the less polar and more covalent nature of In—S bonding in the compounds.

CONCLUSION

In conclusion, *n*- and *i*-butylindium thiolates were easily prepared from the corresponding trialkylindium and thiols. Benzenethiol was found to give mono-, di- and trithiolates. However, it was difficult to control the stoichiometry of the reactions with some alkanethiols and not all substitution products could be isolated.

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