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BUTYLGERMANETHIOLATES

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A few ethylgermanethiolates were synthesized by Anderson[1] in 1956 by the reaction of the corresponding acetate with thiols of boiling points higher than acetic acid. The preparation of a few phenylgermanethiolates was reported by Henry *et al.*[2,3] in 1962–63 employing the reaction of alkyl and aryl halides with $Ph_2Ge(SNa)_2$ and Ph_3GeSNa. Recently (1964) some phenylgermanethiolates have been synthesised by the reaction of thiol with the corresponding halide in the presence of tertiary organic bases[4,5]. While this work was in progress, Abel and coworkers[6] described the preparation of some methylgermanethiolates by a number of new metathetical reactions.

In the present communication, a number of di- and tributylgermanethiolates have been prepared (*i*) by passing ammonia into or (*ii*) by adding triethylamine to a mixture of butylgermanium chloride and thiol in benzene:

$$Bu_{4-n}GeCl_n + n\ RSH + n\ NH_3\ (\text{or}\ n\ NEt_3) \rightarrow Bu_{4-n}Ge(SR)_n + n\ NH_4Cl\ (\text{or}\ n\ NEt_3 \cdot HCl) \quad (n = 1 \text{ and } 2)$$

All the products are viscous liquids, soluble in benzene and could be purified by distillation *in vacuo*. Molecular weight determinations in boiling benzene showed them to be monomeric.

Reactions of di- and tributylgermanium oxides with excess butanethiol were found to be slow and could be completed only in the presence of *p*-toluenesulfonic acid as catalyst:

$$Bu_2GeO + 2\ BuSH \rightarrow Bu_2Ge(SBu)_2 + H_2O$$

$$(Bu_3Ge)_2O + 2\ BuSH \rightarrow 2\ Bu_3GeSBu + H_2O$$

In view of hydrolytically stable nature of the Ge–S bond in such derivatives, the removal of water was not found to be necessary. Analogous reactions of $Bu_2Ge(OEt)_2$ with dodecanethiol was found to be sluggish and required a catalyst:

$$Bu_2Ge(OEt)_2 + 2\ C_{12}H_{25}SH \xrightarrow{C_6H_6} Bu_2Ge(SC_{12}H_{25})_2 + 2\ EtOH \uparrow$$

The progress of this reaction was followed by estimating ethanol in the azeotrope. It is interesting to compare that similar thiolysis in the case of alkyltin ethoxide has been found to be very facile[7]. This may be presumably due to lower stability of Ge–S bond which appears to be substantiated by carrying out the reverse reaction of $Bu_2Ge(SC_3H_7)_2$ with excess ethanol. The reaction was slow but was found to be faster than the corresponding reaction in the case of tin[7]. For this interchange

TABLE 1

PREPARATION, ANALYSIS AND PROPERTIES OF $Bu_2Ge(SR)_2$[a]

No.	Bu_2GeCl_2	Thiol	Yield	Found (%)			Calcd. (%)			B.p.	Mol. wt. in benzene		
	(g)	(g)	(%)	C	H	SR	C	H	SR	(°C/mm)	wt. (g/15 ml)	Found	Calcd.
1	1.708	Ethanethiol 1.28 (3 moles)	84	46.78	9.15	38.72	46.62	9.128	39.55	120–122/1.0	0.3643	303, 312, 326, 319,	309.06
2	2.166	n-Propanethiol 1.348	80	49.94	9.59	44.16	49.87	9.572	44.60	115/0.2	0.2730	332, 359, 316, 349,	337.11
3	1.523	Iso-propanethiol 1.00	94	49.60	9.55	43.44	49.87	9.572	44.60	114–115/0.5	0.2883	311, 316, 348, 328	337.11
4	2.357	n-Butanethiol 1.66	97	52.98	10.01	48.72	52.61	9.938	48.84	140–143/0.5	0.3392	361, 355, 353, 369	365.16
5	1.260	Iso-butanethiol 0.916	89	52.97	9.96	46.78	52.61	9.938	48.84	141/0.7	0.2380	329, 379, 358, 356	365.16
6	1.402	tert-Butanethiol 1.40	75	52.19	9.88	49.09	52.61	9.938	48.84	145/1.5	0.2161	359, 330, 356, 353	365.16
7	1.529	n-Dodecanethiol 2.414	99	65.29	11.58	65.77	65.18	11.62	68.31	238/0.6	0.2504	585, 562, 549, 543	589.58
8	1.575	Toluene-α-thiol 1.52	89	61.01	7.54	54.62	60.98	7.447	56.85	233–235/1.7	0.2449	416, 422, 425, 402	433.18
9	1.560	Thiophenol 1.42	80	59.18	6.95	51.92	59.29	6.965	53.89	204–206/1.2	0.2985	416, 404, 358, 390	405.14

[a] All products are colourless, viscous liquids except $Bu_2Ge(SPh)_2$ (No 9) which is pale yellow.

TABLE 2

PREPARATION, ANALYSIS AND PROPERTIES OF Bu_3GeSR^a

No.	*Bu_3GeCl*	*Thiol*	*Yield*	*Found (%)*			*Calcd. (%)*			*B.p.*	*Mol. wt. in benzene*		
	(g)	*(g)*	*(%)*	*C*	*H*	*SR*	*C*	*H*	*SR*	*(°C/mm)*	*wt. (g/ml)*	*Found*	*Calcd.*
1	1.503	Ethanethiol 0.50	90	55.12	10.62	20.00	55.09	10.58	20.04	103/0.8	0.2290	292, 317 292, 280	305.04
2	2.101	n-Propanethiol 0.604	95	56.26	10.65	23.29	56.48	10.74	23.56	115–116/0.5	0.3538	316, 319, 314, 325	319.07
3	1.353	Isopropanethiol 0.446	90	56.40	10.87	22.22	56.48	10.74	23.56	120/1.0	0.2840	324, 316, 310, 303	319.07
4	2.25	n-Butanethiol 0.80	93	57.66	10.94	27.79	57.71	10.90	26.77	130–132/2.0	0.2810	340, 331, 304, 340	333.09
5	1.53	Isobutanethiol 0.80	98	57.50	10.81	25.80	57.71	10.90	26.77	136–138/2.0	0.3064	325, 337, 324, 330	333.09
6	1.588	tert-Butanethiol 0.60	92	57.52	10.93	27.39	57.71	10.90	26.77	125/1.0	0.2055	317, 347, 328, 348	333.09
7	1.810	n-Dodecanethiol 1.314	90	64.72	11.89	43.89	64.71	11.77	45.21	192–193/0.4	0.2297	430, 439, 470, 438	445.3
8	1.887	Toluene-α-thiol 0.855	84	61.97	9.39	33.39	62.16	9.335	33.56	171–174/1.2	0.1778	350, 342, 376, 345	367.1
9	1.626	Thiophenol 0.655	90	61.08	9.13	30.84	61.24	9.137	30.89	143/0.5	0.2784	339, 382, 341, 367	353.08

[a] All products are colourless, viscous liquids.

reaction, n-propanethiol derivative was especially chosen as it forms a convenient azeotrope with ethanol; the progress of the reaction was followed by estimating the thiol content in the azeotrope.

Displacement reaction of $Bu_2Ge(SC_3H_7)_2$ with thiophenol in cyclohexane also required a catalyst for completion; the liberated thiol could be removed azeotropically and estimated:

$$Bu_2Ge(SC_3H_7)_2 + 2\ C_6H_5SH \rightarrow Bu_2Ge(SC_6H_5)_2 + 2\ C_3H_7SH \uparrow$$

Infra-red spectra of these butylthiogermanes have been recorded in the range 4000–400 cm^{-1}. Where present the following modes have been assigned on the basis of previous measurements[8–11]: (A) asymmetric C–H stretching of butyl group, (B) symmetric C–H stretching of butyl group (split into two in some cases due to resonance effect), (C) Ge–C asymmetric stretching, (D) Ge–C symmetric stretching, (E) Ge–Bu characteristic vibration, (F) =C–H stretching of aromatic system, (G) phenyl overtone and combination bands, (H) vibrations characteristic of aromatic ring.

EXPERIMENTAL

Butylgermanium halides (obtained from the Institute for Organic Chemistry TNO, Utrecht, The Netherlands) were purified by distillation. Other experimental and analytical details have been reported earlier[7,12]. The infrared spectra were recorded by Perkin–Elmer 337 model employing capillary film technique in cell filled with KBr windows.

1. *Preparation of butylgermanethiolates*

To a mixture of butylgermanium halide and thiol in benzene, triethylamine (10% excess) was added. After refluxing the mixture for an hour, triethylamine hydrochloride was filtered out and the product was distilled under reduced pressure after removing the excess solvent.

These butylgermanethiolates were also prepared by passing dry ammonia to a mixture of butylgermanium halide and thiol in benzene. Passage of ammonia was stopped when the reaction mixture cools down to the room temperature. After filtering the ammonium chloride, excess of solvent and ammonia was removed and the product was finally distilled under reduced pressure. The results of the above types of reactions are given in Table 1 and 2.

2. *Reaction of Bu_2GeO with n-butanethiol*

To 1.02 g of Bu_2GeO was added n-butanethiol (2.0 g, four moles) and the mixture was refluxed for 4 h after adding *p*-toluenesulfonic acid (0.005 g). After removing excess thiol, the product was distilled at 162–63°/1.5 mm. Yield (80%). (Found: C, 52.90; H, 10.01; SR, 48.19; $C_{16}H_{36}GeS_2$ calcd.: C, 52.61; H, 9.94; SR, 48.84%.)

3. *Reaction of $(Bu_3Ge)_2O$ with n-butanethiol*

A solution of 1.633 g $(Bu_3Ge)_2O$ in 1.20 g (4 moles) of n-butanethiol was refluxed for 4 h in the presence of *p*-toluenesulfonic acid (0.004 g). After removing excess thiol the product was distilled at 135°/1.5 mm. Yield (92%). (Found: C, 57.70; H, 10.90; SR, 27.27. $C_{16}H_{36}GeS$ calcd.: C, 57.71; H, 10.90; SR, 26.77%.)

4. *Reaction of $Bu_2Ge(OEt)_2$ with n-dodecanethiol in the molar ratio* 1:2

To 0.969 g of $Bu_2Ge(OEt)_2$ in benzene (60 g) was added 1.441 g of n-dodecanethiol and the mixture was refluxed under an efficient fractionating column for 6 h; the temperature of the distillating liquid remained at 80° showing that the reaction had not proceeded. The reaction was then catalysed by *p*-toluenesulfonic acid (0.002 g) and the azeotrope was collected slowly (in 16 h) and estimated. The product was distilled at 238–242°/0.2 mm. Yield (97%). Ethanol in the azeotrope 0.29 g (two moles require 0.32 g). (Found: SR, 65.04. $C_{32}H_{68}GeS_2$ calcd.: SR, 68.31%.)

5. *Reaction of $Bu_2Ge(SC_3H_7)_2$ with excess ethanol*

To 3.747 g of dibutylbis(propylthio)germane was added anhydrous ethanol (65 g) and the mixture was refluxed at 110–120°C. Propanethiol was fractionated off slowly as a binary azeotrope with ethanol. A fresh amount of ethanol was introduced to distil out completely the liberated thiol. The product was distilled at 98°/3.5 mm to yield a colourless liquid. Yield (90%). Propanethiol found in the azeotrope, 1.52 g (two moles require 1.69 g). (Found: OEt, 32.05. $C_{12}H_{28}GeO_2$ calcd.: EtO, 32.54%.)

6. *Reaction of $Bu_2Ge(SC_3H_7)_2$ with thiophenol in the molar ratio of* 1:2 *in cyclohexane*

To a cyclohexane solution (50 g) of $Bu_2Ge(SC_3H_7)_2$ (2.001 g) was added thiophenol (1.321 g) and the mixture was refluxed for 8 h. As distillation gave boiling temperature (81°) of cyclohexane, *p*-toluenesulfonic acid (0.005 g) was added and the contents were refluxed. The azeotrope of propanethiol with cyclohexane was slowly fractionated off and estimated. The reaction seems to be quite slow. After removing the excess of solvent the product was distilled at 195–200°/0.5 mm. Yield (88%). Propanethiol in the azeotrope, 0.87 g (2 moles require 0.89 g). (Found: SR, 52.44. $C_{20}H_{28}GeS_2$ calcd.: SR, 53.89%.)

Infrared spectra (in cm^{-1}):

1. $Bu_2Ge(SC_2H_5)_2$: 2970s (A), 2937s (A), 2879w (B), 1462w, 1384vw, 1273w, 1261w, 1084vw, 1054vw, 1003vw, 970vw, 888vw (E), 870vw, 690vw (C), 656vw (D), 565vw, 427vw.
2. $Bu_2Ge(SC_3H_7)_2$: 2973vs (A), 2939s (A), 2880s (B), 1468m, 1384w, 1298vw, 1241w, 1084vw, 1054vw, 1004vw, 967vw, 888w (E), 840vw, 788vw, 722vw, 690w (C), 655w (D), 565vw, 425vw.
3. $Bu_2Ge(S\text{-iso-}C_3H_7)_2$: 2963vs (A), 2927vs (A), 2866vs (B), 1470vs, 1385vs, 1370vs, 1297vw, 1255s, 1249s, 1155vs, 1085s, 1051vs, 1004w, 965w, 927vw, 885m (E), 687m (C), 655vw (D), 628vs, 565w, 454vs.
4. $Bu_2Ge(SC_4H_9)_2$: 2975vs (A), 2940vs (A), 2880s (B), 1480s, 1393w, 1275w, 1275vw, 1228s, 1085vw, 1051vw, 1005vw, 966vw, 920vw, 880vw (E), 850vw, 780vw, 748vw, 690w (C), 655vw (D), 565vw.
5. $Bu_2Ge(S\text{-iso-}C_4H_9)_2$: 2960vs (A), 2932vs (A), 2878vs (B), 1475vs, 1386vs, 1372vs, 1325s, 1247vs, 1174s, 1087s, 1006w, 967vw, 950vw, 926vw, 888vw (E), 855m, 736w, 725w, 693s (C), 655w (D), 570vw, 520vw, 446vw.
6. $Bu_2Ge(S\text{-tert-}C_4H_9)_2$: 3086w, 3070w, 2972vs (A), 2939vs (A), 2882s (B), 1595vs, 1494vs, 1478m, 1425vw, 1390w, 1305w, 1275vw, 1177vw, 1088s, 1072w, 1028vs, 1006w, 967vw, 914vw, 886vw (E), 855vw, 845vw, 746vs, 700vs, 694vs (C), 660w (D), 490w, 430m.

7. $Bu_2Ge(SC_{12}H_{25})_2$: 2973vs (A), 2939vs (A), 2864vs (B), 1482vs, 1478vs, 1392s, 1310w, 1268w, 1175vw, 1086m, 1028vs, 1005w, 966vw, 885vw (E), 854vw, 724s, 694m (C), 656w (D), 565vw.
8. $Bu_2Ge(SCH_2C_6H_5)_2$: 3096m (F), 3076vs (F), 3040vs (F), 2968vs (A), 2939vs (A), 2870vs (B), 1955vw (G), 1883vw (G), 1815vw (G), 1760vw (G), 1688vw (G), 1615vs (H), 1506vs (H), 1462vs, 1426m, 1390vs, 1248vs, 1210m, 1184m, 1086s, 1072vs, 1032w, 1005w, 966vw, 918s, 886vw (E), 855m, 818w, 768vs, 699vs (C), 808w, 565s, 470w.
9. $Bu_2Ge(SC_6H_5)_2$: 3088w (F), 3075w (F), 2977vs (A), 2940vs (A), 2882vs (B), 2874s (B), 1960w (G), 1887w (G), 1816w (G), 1760w (G), 1668w (G), 1598m (H), 1498w (H), 1478vs, 1452vs, 1392w, 1318vw, 1175vw, 1087s, 1072m, 1028vs, 1005w, 967w, 912vw, 886w (E), 855vw, 842vw, 746vs, 700s, 694vs (C), 660w (D), 565vw, 490m, 430m.
10. $Bu_3Ge(SC_2H_5)$: 2977vs (A), 2940vs (A), 2883vs (B), 2873vs (B), 1480vs, 1472s, 1392vs, 1356vs, 1307w, 1263vs, 1175w, 1086m, 1055w, 1030w, 1005w, 967w, 887w (E), 778vw, 695m (C), 660w (D), 560w.
11. $Bu_3Ge(SC_3H_7)$: 2975vs (A), 2942vs (A), 2884vs (B), 2873vs (B), 1480vs, 1472vs, 1433vw, 1393vs, 1357vw, 1307vw, 1253vw, 1292vw, 1240vw, 1175vw, 1085w, 1028w, 1006w, 967w, 888w (E), 792vw, 776vw, 720vw, 695m (C), 658w (D), 562vw.
12. $Bu_3Ge(S\text{-iso-}C_3H_7)$: 2975vs (A), 2941vs (A), 2885vs (B), 2873vs (B), 1480vs, 1432w, 1394vs, 1375s, 1355w, 1304vw, 1292vw, 1243m, 1175vw, 1155s, 1085vw, 1051s, 1030w, 1006w, 967w, 888s (E), 776vw, 695s (C), 657m (D), 633m, 560w, 452s.
13. $Bu_3Ge(SC_4H_9)$: 2976vs (A), 2938vs (A), 2880vs (B), 2870vs (B), 1478vs, 1430w, 1386s, 1350w, 1298w, 1275w, 1175w, 1086w, 1028w, 1006w, 967vw, 888w (E), 778vw, 750vw, 720vw, 695w (C), 657vw (D), 562w.
14. $Bu_3Ge(S\text{-iso-}C_4H_9)$: 2976vs (A), 2940vs (A), 2884vs (B), 2873vs (B), 1480vs, 1393s, 1377w, 1246vw, 1172 (VW), 1086vw, 1030vw, 1006vw, 967w, 888w (E), 776w, 720w, 695m (C), 656w (D), 563w.
15. $Bu_3Ge(S\text{-tert-}C_4H_9)$: 2975vs (A), 2940vs (A), 2884vs (B), 2874vs (B), 1480vs, 1433vw, 1392m, 1377m, 1297w, 1275w, 1215w, 1172vs, 1160vs, 1087vs, 1060w, 1030w, 1006w, 969m, 889s (E), 778w, 770vs (C), 656s (D), 590m, 560m, 445s.
16. $Bu_3Ge(SC_{12}H_{25})$: 2976vs (A), 2940vs (A), 2884vs (B), 2872vs (B), 1480m, 1432vw, 1392w, 1358w, 1297w, 1275w, 1172w, 1087w, 1030w, 1006w, 967w, 888w (E), 776w, 723w, 697w (C), 656w (D), 560w.
17. $Bu_3Ge(SCH_2C_6H_5)$: 3100m (F), 3080s (F), 3042s (F), 2974vs (A), 2940s (A), 2883vs (B), 2870vs (B), 1953w (G), 1880w (G), 1810w (G), 1760w (G), 1618m (H), 1506s (H), 1480vs, 1465vs, 1432m, 1392vs, 1297w, 1275w, 1240w, 1202w, 1175w, 1087s, 1072w, 1032w, 1006w, 967w, 915w, 888w (E), 767w, 700vs (C), 657m (D), 564w, 465w.
18. $Bu_3Ge(SC_6H_5)$: 3090sw (F), 3076w (F), 3038w (F), 2976vs (A), 2940vs (A), 2884vs (B), 2872vs (B), 1955w (G), 1882w (G), 1811w (G), 1760w (G), 1598w (H), 1495s (H), 1480s, 1453s, 1430w, 1392s, 1358w, 1308w, 1274w, 1175w, 1088m, 1070w, 1028w, 1006w, 967w, 910vw, 889m (E), 776w, 746vs, 695vs (C), 658m (D), 562w, 490vw.

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SUMMARY

A number of new, volatile butylgermanethiolates $Bu_2Ge(SR)_2$ and $Bu_3Ge(SR)$ ($R = C_2H_5$, C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9, tert-C_4H_9, n-$C_{12}H_{25}$, $CH_2C_6H_5$ and C_6H_5) have been synthesized by the reaction of the corresponding chlorogermane with thiol in the presence of a proton acceptor. The action of thiol on di- and tributylgermanium oxides could be pushed to completion in the presence of catalyst. A few typical displacement reactions of these derivatives with thiol as well as ethanol have been studied. Infrared spectra of these butylgermanethiolates have been examined.

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