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Synthesis of Pentacoordinated Germanium Compounds Containing a Phosphonyl Group

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ABSTRACT

The title compounds were prepared by the reaction of germanium sesquioxides with diethyl N,N-bis(2-hydroxyethyl)aminomethylphosphonate in good yields (72–94%). The X-ray analyses showed that the geometry about the germanium atom was a distorted trigonal bipyramid. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

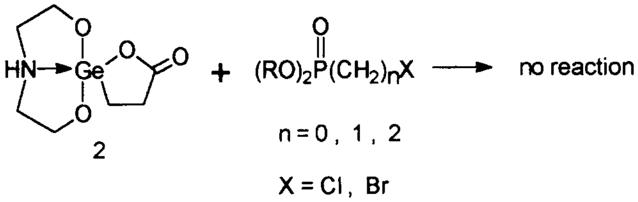
Derivatives of germanium sesquioxide have recently attracted a great deal of attention due to their remarkable bioactivities [1]. *a*-Aminophosphonates also are reported to exhibit diverse biological activities [2]. It is conceivable that the incorporation of the two moieties into one structural unit might produce a synergistic effect on the activity of such a compound, and that studies of this type of novel structure would provide some interesting information of biological importance.

As a part of our investigations on pentacoordinated germanium compounds containing the phosphonyl group, we wish to report a new synthetic route to these compounds.

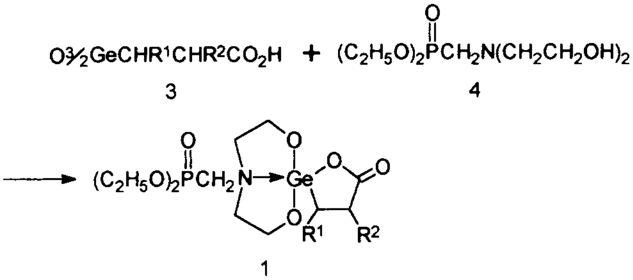
RESULTS AND DISCUSSION

A common route for the preparation of the title compounds would be the reaction of 2 [3] with phosphonylation reagents. Unexpectedly, even under vigorous conditions, such reactions did not take place (Scheme 1).

It may be shown that the nitrogen atom of compound 2 exhibits remarkably reduced nucleophilicity because of formation of an N → Ge bond. It was



SCHEME 1



a: $R^1 = R^2 = H$; b: $R^1 = H$, $R^2 = CH_3$; c: $R^2 = H$, $R^1 = C_6H_5$;
d: $R^2 = H$, $R^1 = 4\text{-}CH_3C_6H_4$; e: $R^2 = H$, $R^1 = 2\text{-}ClC_6H_4$;
f: $R^2 = H$, $R^1 = 4\text{-}ClC_6H_4$; g: $R^2 = H$, $R^1 = 4\text{-}CH_3OC_6H_4$;
h: $R^2 = H$, $R^1 = 3,4\text{-}Cl_2C_6H_3$; i: $R^2 = H$, $R^1 = 2\text{-}CH_3OC_6H_4$;
j: $R^2 = H$, $R^1 = 2\text{-}CH_3C_6H_4$; k: $R^2 = H$, $R^1 = 4\text{-}NO_2C_6H_4$;
l: $R^2 = H$, $R^1 = 2\text{-}BrC_6H_4$; m: $R^2 = H$, $R^1 = 3\text{-}BrC_6H_4$;
n: $R^2 = H$, $R^1 = 4\text{-}BrC_6H_4$; o: $R^2 = H$, $R^1 = 4\text{-}FC_4H_4$;

SCHEME 2

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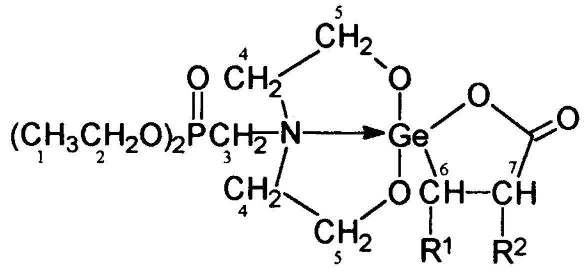
TABLE 1 ^1H and ^{31}P NMR data of Compounds $1^{a,b}$



Compound	^1H NMR									^{31}P NMR
	1-H	2-H	3-H	4-H	5-H	6-H	7-H	R^1	R^2	
1_a	1.34(t)	4.05–4.29	3.02(d)	3.14–3.35	3.74–4.13	1.76(t)	2.77(t)	**	*	19.92
1_b	1.20–1.29	4.05–4.12	3.34(d)	2.95–3.30	3.80(t)	1.41–1.56	2.00–2.17	**	1.14(d)	21.53
1_c	1.22–1.36	3.88–4.22	3.08–3.18	3.23–3.50	3.56–4.00	2.41–2.59	2.57–2.74	7.21–7.39(C_6H_5)	*	19.65
1_d	1.21–1.46	3.83–4.20	3.08–3.15	3.20–3.51	3.60–4.00	2.48–2.61	2.60–2.82	2.34(s, CH_3), 7.13–7.32(C_6H_4)	*	19.51
1_e	1.12–1.50	3.70–4.28	2.95–3.04	3.05–3.40	3.51–4.00	2.26–2.55	2.56–2.92	7.20–751(C_6H_5)	*	19.11
1_f	1.04–1.44	3.83–4.20	3.89–3.08	3.02–3.41	3.63–3.97	2.38–2.46	2.56–2.70	7.11–7.39(C_6H_5)	*	19.78
1_g	1.12–1.56	3.80–4.36	3.03–3.10	2.91–3.40	3.51–3.85	2.44–2.56	2.61–2.81	3.75(s, CH_3), 6.71–7.36(C_6H_4)	*	19.51
1_h	1.08–1.46	3.81–4.30	3.12–3.22	2.83–3.33	3.57–3.96	2.23–2.40	2.40–2.56	7.17–7.56(C_6H_4)	*	18.98
1_i	1.10–1.45	3.84–4.28	2.92–3.00	3.01–3.27	3.48–3.88	2.29–2.55	2.56–2.81	3.80(s, CH_3), 6.74–7.35(C_6H_4)	*	20.19
1_j	1.07–1.41	3.68–4.14	3.00–3.10	2.92–3.38	3.40–3.89	2.20–2.46	2.54–2.78	2.34(s, CH_3), 7.04–7.56(C_6H_4)	*	19.25
1_k	1.08–1.38	3.80–4.24	3.04–3.16	3.20–3.55	3.61–3.92	2.18–2.34	2.64–3.00	7.40–8.09(C_6H_4)	*	20.05
1_l	1.06–1.46	3.70–4.20	2.85–2.99	2.98–3.29	3.70–4.20	2.05–2.65	2.05–2.65	6.92–7.60(C_6H_4)	*	18.98
1_m	1.12–1.32	3.74–4.26	2.87–3.01	3.01–3.31	3.31–3.40	2.36–2.53	2.53–2.80	7.00–7.42(C_6H_4)	*	18.71
1_n	1.10–1.44	3.72–4.30	2.92–3.08	3.00–3.29	3.30–3.88	2.36–2.48	2.49–2.74	6.94–7.48(C_6H_4)	*	19.11
1_o	1.08–1.47	3.70–4.29	2.84–3.12	3.01–3.56	3.64–4.00	2.28–2.46	2.47–2.70	6.76–7.32 (C_6H_4)	*	19.25

[a] Unresolved multiplets.
[b] All solvents are $CDCl_3$ except for 1_b, 1_k (solvent is DMSO-d_6).
*Same with position 7-H.
**Same with position 6-H.

TABLE 2 IR Spectral Data of Compounds 1

Compound	IR cm^{-1} (KBr)
1_a	3371, 3073–2918, 1669, 1292–1234, 1154, 1082–1031, 954–934, 892
1_c	2960, 1689, 1296–1259, 1157, 1086–1018, 964–936, 899
1_d	2969, 1652, 1307–1245, 1085–1019, 964–939, 900
1_e	3400, 2970–2869, 1679, 1470, 1293–1225, 1088–1018, 968–938, 898
1_i	3403, 3055–2923, 1675, 1492–1456, 1295–1238, 1089–1013, 971, 896

TABLE 3 Mass Spectral Data of Compounds 1

Compound	1_a	1_c	1_d	1_e	1_f	1_i
$M.^{+a}$	399 (4)	475 (18)	489 (8)	509 (8)	509 (10)	505 (2)

[a] Relative intensity in parentheses.

found that germanium sesquioxides 3 reacted with diethyl N,N-bis(2-hydroxyethyl)aminomethylphosphonate 4 to afford products 1 (Scheme 2).

It is gratifying to note that the yields are fairly good, 72% being the lowest. The products 1 were easily isolated in pure form by recrystallization and were stable in the air. Their structures were confirmed by spectroscopic criteria (Tables 1, 2, and 3) and quantitative elemental analyses (Table 4).

The synthetic route shown previously takes place under mild conditions, and the easy workup, and also convenient handling, make the method practical.

Surprisingly, attempts to conduct the reaction of 3 with diethoxy N,N-bis(2-hydroxyethyl)phosphamide 5 [4] have not been successful. This may be due to the strong electron withdrawing effect of the phosphoryl group which, directly bonded to the nitrogen atom, limited the formation of the N → Ge bond.

TABLE 4 Quantitative Elemental Analyses Data of Compounds 1

			Elemental Analyses (%)					
			Calculated			Found		
Compound	*Yield* (%)[a]	*M.P.* (°C)	C	H	N	C	H	N
1_a	78.11	164–6	36.23	6.08	3.54	36.20	6.14	3.70
1_b	72.84	144–8	37.91	6.36	3.42	38.08	6.15	3.17
1_c	86.00	198–9	45.62	5.95	2.97	45.52	5.98	3.06
1_d	94.15	195–7	46.77	6.20	2.88	46.67	6.61	2.82
1_e	93.87	201–2	42.53	5.35	2.77	42.45	5.53	2.90
1_f	92.49	219–21	42.53	5.35	2.77	42.30	5.33	2.56
1_g	90.87	200–1	45.28	6.00	2.79	45.39	6.12	2.52
1_h	93.06	189–90	39.82	4.83	2.59	39.53	4.73	2.11
1_i	90.27	156–9	45.28	6.00	2.79	45.31	6.29	2.80
1_k	94.00	199–202	41.82	4.87	5.44	41.90	4.78	5.31

[a] Yield determined by isolation.

TABLE 5 Important Molecular Parameters of Compound 1_b

Atoms	*Ge–O(4)*	*Ge–O(5)*	*Ge–O(6)*	*Ge–C(33)*	*Ge–N*	*C(33)–Ge–O(4)*	*C(33)–Ge–O(5)*	*O(4)–Ge–O(5)*	*O(6)–Ge–N*
Bond lengths[a] (Å)	1.765(4)	1.778(4)	1.891(4)	1.930(6)	2.288(4)				
Bond angles[a] (degrees)						123.0(2)	123.0(2)	113.9(2)	171.4(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

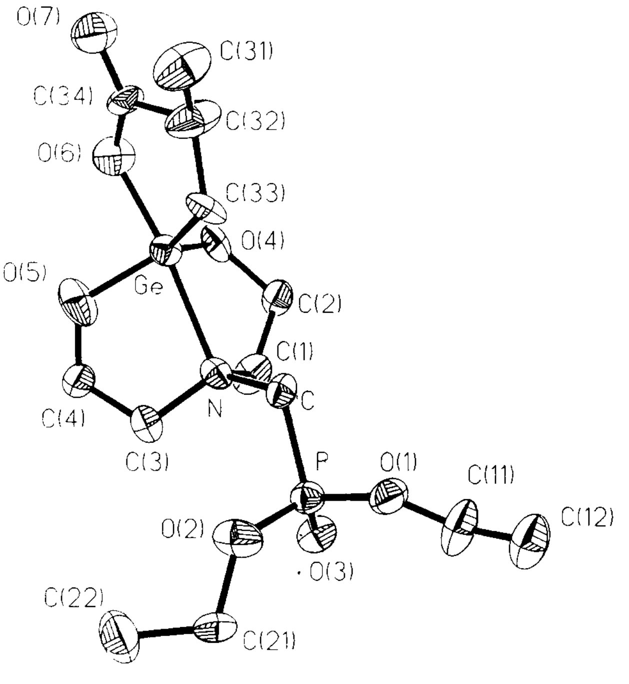
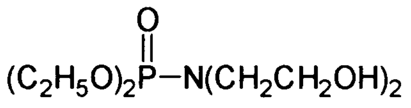


FIGURE 1



$(C_2H_5O)_2P(=O)–N(CH_2CH_2OH)_2$

5

We have performed an X-ray single-crystal study on compound 1_b (Figure 1). Crystallographic analysis has shown that the geometry about the germanium atom is a distorted trigonal bipyramid. Important bond lengths and angles are given in Table 5.

It is worth pointing out that the ^{31}P chemical shifts of compounds 1 are shifted ~8 ppm upfield relative to the signal in compound 4 (δ_p 26.92). It is proposed that the electron withdrawing effect of the N → Ge interaction increased the $d\pi$-$p\pi$ back donating trend of the P=O bond and led to shielding of the phosphorus resonance.

EXPERIMENTAL

^1H and ^{31}P NMR spectra were taken on a JEOL FX-90Q spectrometer. ^1H chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{31}P chemical shifts are reported in parts per million relative to 85% phosphoric acid (external). In both cases, the nuclei that are deshielded relative to their respective standards are assigned a positive chemical shift. ^{31}P NMR spectra were obtained by using full proton coupling, a 90° tip angle, and a 2–4 s repetition rate with no pulse delay. IR spectra were taken on a DS-301 spectrometer. Quantitative elemental analyses were run on a Yana MT-3 instrument. Mass spectra were recorded on a Hewlett-Packard 5988 instrument.

Compound 3 was prepared by the method of Bai *et al.* [6].

Preparation of Compound 4

Compound 4 was prepared by the method of Petrov *et al.* [5], which was modified by us.

Diethanolamine (0.1 mol) and paraformaldehyde (0.1 mol) were mixed and stirred at 40°C for 0.5 hours to give $(HOCH_2CH_2)_2NCH_2OH$, which was then treated with diethyl phosphite (0.1 mol) in toluene (58.4 g) at 40°C for 0.5 hours. Glacial acetic acid (0.3 g) was added at 40 ~ 50°C. The reaction mixture was allowed to heat to 55°C, and it was stirred for 4 hours. Subsequently, it was concentrated at reduced pressure at 55°C to give 4 (~100% yield), ^{31}P NMR($CDCl_3$): 26.92; ^1H NMR($CDCl_3$): 1.34(t, 6H, $C\underline{H}_3CH_2O$), 2.85(t, 4H, $NC\underline{H}_2CH_2$), 3.07(d, 2H, PCH_2), 3.65(t, 4H, $NCH_2C\underline{H}_2$), 4.16(m, 4H, $CH_3C\underline{H}_2O$), 4.85(s, 2H, OH).

Preparation of Compounds 5

Compounds 5 were prepared by the method of Petrov [4], which was modified by us. To a stirred solution of diethyl phosphite (0.117 mol) in toluene (54 g) was added carbon tetrachloride (11.3 mL). Diethanolamine (0.117 mol) in triethylamine (14 mL) was added to the mixture at 0 ~ 10°C. The reaction mixture was allowed to warm to room temperature, and it was stirred for an additional 2 hours. The triethylamine hydrochloride that had formed was removed by filtration, and the filtrate was concentrated at reduced pressure to give 5 (54.4% yield), ^{31}P NMR($CDCl_3$): 11.03; ^1H NMR($CDCl_3$): 1.37(dt, 6H, $C\underline{H}_3CH_2O$), 3.28(m, 4H, $NC\underline{H}_2CH_2$), 3,74(t, 4H, $NCH_2C\underline{H}_2$), 4.09(m, 4H, $CH_3C\underline{H}_2O$), 4.60(s, 2H, OH).

General Procedure for Preparation of Compounds 1

Compounds 3 (3 mmol) and compound 4 (3 mmol) were mixed in absolute benzene (50 mL). Each mixture was heated to boiling, and the water formed was separated by azeotropic distillation. The precipitate formed was filtered off and washed with absolute benzene. The solid was recrystallized from chloroform and tetrahydrofuran to yield 1.

ACKNOWLEDGMENTS

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