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Synthesis of 2-Germatranylmethylsuccinimides

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ABSTRACT

The title compounds were prepared by two methods: one by the reaction of 2-methylenesuccinimides with trichlorogermane and the other by the reaction of 2-methylenesuccinamic acids with trichlorogermane. The X-ray analyses showed that the geometry about the germanium atom was a slightly distorted trigonal bipyramid. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Derivatives of itaconic acid (2-methylenesuccinic acid) have been known as good plant hormones for a long time [1]. Germatranes have also been reported to have remarkable bioactivities [2], but the bioassays of them as plant-growth regulaters have not been investigated. To introduce germatranes to the structural skeleton of itaconic acid derivatives may give a new type of compound with interesting biologically active properties.

As a part of our investigation on this work, two convenient synthetic routes to 2-germatranylmethylsuccinimides are reported.

RESULTS AND DISCUSSION

The reactions of 2-methylenesuccinimides **2** [3] with trichlorogermane were followed by the hydrolysis of compounds **3** with water and dehydration of compounds **4** with triethanolamine (Scheme 1).

We have tried to prepare compounds **5** by the reaction of 2-methylenesuccinamic acids [3] with trichlorogermane, but compounds **1** were obtained instead of **5** (Scheme 2).

Compounds **6** can be converted into compounds **2** by the action of acetic anhydride with sodium acetate as the catalyst [3]. However, as herein reported, trichlorogermane acts as a dehydrating agent to cause compounds **6** or **7** to lose water before or after the addition reaction of $HGeCl_3$ to **6** (Scheme 3).

Both of the reaction sequences shown in Schemes 1 and 3 took place under mild conditions, and the easy workup make the methods practical. The products **1** were easily purified by recrystallization and were stable in air. There are no obvious differences between the two methods. The structures of all products were confirmed by spectroscopic studies (Tables 1 through 3) and elemental analyses (Table 4).

Crystallographic analysis of $\mathbf{1}_c$ (Figure 1) has shown that the geometry about the germanium atom is a slightly distorted trigonal bipyramid. Important bond lengths and angles are given in Table 5.

EXPERIMENTAL

^1H NMR spectra were taken on a JEOL FX-90Q spectrometer. ^1H chemical shifts are reported in parts per million relative to internal tetramethylsilane. The nuclei that are deshielded relative to their respective standards are assigned a positive chemical shift. IR spectra were taken on a DS-301 spectrometer. Quan-

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Dedicated to Prof. Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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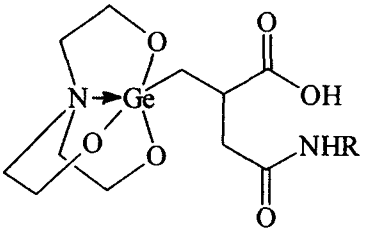
TABLE 1 ^{1}H NMR Data of Compounds **1**[a,b]



R= C_6H_5; 4-$CH_3C_6H_4$; 4-ClC_6H_4; 2-ClC_6H_4.

5

Compound	R	1-H and 2-H	3-H	4-H	5-H
$\mathbf{1}_a$	7.27–7.60 (C_6H_5)	1.00–1.21	*	2.81(*t*)	3.75(*t*)
$\mathbf{1}_b$	7.30 (d, 4-ClC_6H_4(o)) 7.54 (d, 4-ClC_6 H_4(m))	1.05–1.31	2.49–2.82	2.79(*t*)	3.58(*t*)
$\mathbf{1}_c$	7.20–7.49 (2-ClC_6H_4)	1.10–1.38	2.50–2.72	3.13(*t*)	3.85(*t*)
$\mathbf{1}_d$	7.15–7.53 (3-ClC_6H_4)	1.09–1.36	2.62–2.91	2.98(*t*)	3.90(*t*)
$\mathbf{1}_e$	7.12 (d, 4-$Ch_3C_6H_4$(o)) 7.24 (d, 4-$CH_3C_6H_4$(m))	1.02–1.20	3.29–3.33	2.80(*t*)	3.59(*t*)
$\mathbf{1}_f$	6.90–7.32 (2-$CH_3C_6H_4$) 2.06 (s, 2-CH_3 C_6H_4)	1.00–1.40	3.00–3.40	2.79(*t*)	3.62(*t*)
$\mathbf{1}_g$	7.11–7.42 (3-$CH_3C_6H_4$) 2.18 (s, 3-$CH_3C_6H_4$)	1.11–1.34	*	3.17(*t*)	3.70(*t*)
$\mathbf{1}_h$	7.41 (d, 4-NO_2-C_6H_4(m)) 7.50 (d, 4-NO_2-C_6H_4(o))	1.25–1.46	•	3.00(*t*)	3.42(*t*)
$\mathbf{1}_i$	7.59–8.60 (3-NO_2-C_6H_4)	1.20–1.41	3.19–3.41	2.88(*t*)	3.72(*t*)

[a] Unresolved multiplets.
[b] All solvents are DMSO-d_6.
*Overlapping with position 4-H.

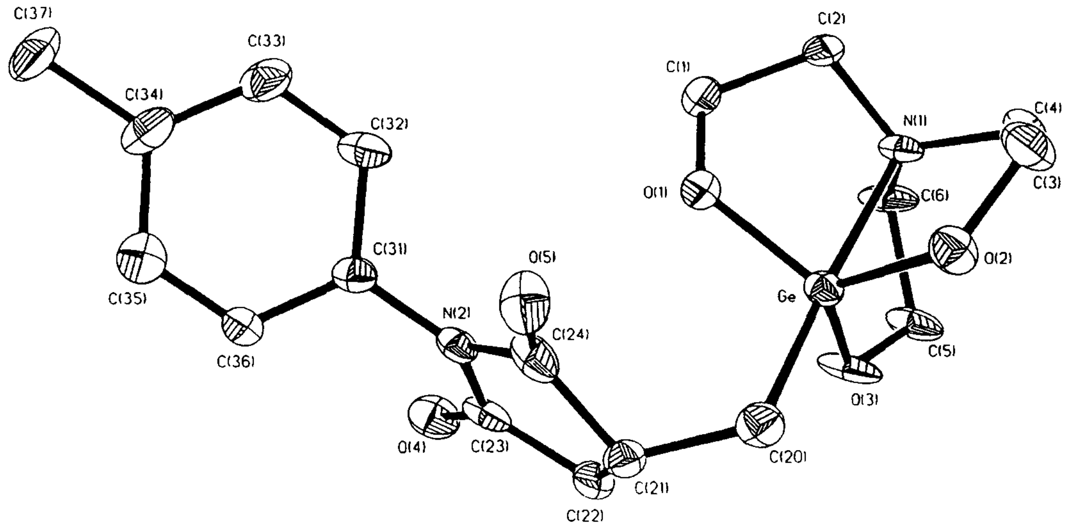
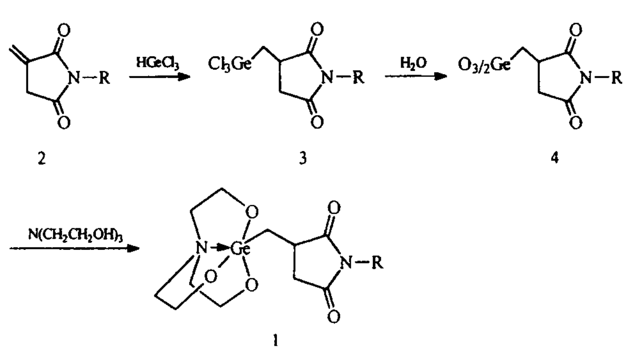


FIGURE 1 The molecular structure of compound $\mathbf{1}_e$.



a: R=C_6H_5; b: R=4-ClC_6H_4; c: R=2-ClC_6H_4; d: R=3-ClC_6H_4;

e: R=4-$CH_3C_6H_4$; f: R=2-$CH_3C_6H_4$; g: R=3-$CH_3C_6H_4$;

h: R=4-$NO_2C_6H_4$; i: R=3-$NO_2C_6H_4$.

SCHEME 1

TABLE 2 IR Spectral Data of Compounds 1

Compound	*IR cm⁻¹* (KBr)				
1_a	3402.0	3189.0	2957.0	1731.8	1669.5
	1495.6	1397.2	1254.0	1186.2	1091.4
	1067.8	1031.8	925.1	900.4	872.7
1_b	3412.0	3142.0	2960.5	1776.8	1702.9
	1489.6	1400.7	1272.3	1184.5	1100.8
	1070.1	1021.1	928.3	901.2	868.8
1_e	3412.0	3112.0	2950.0	1771.7	1700.0
	1511.8	1447.2	1403.7	1274.4	1186.6
	1100.9	1071.0	1021.0	929.1	902.2
	873.4				
1_f	3390.5	3109.0	2951.5	1768.9	1700.0
	1489.9	1449.0	1381.9	1270.7	1186.9
	1099.9	1067.6	1019.8	928.4	900.5
	873.1				

TABLE 3 Mass Spectral Data of Compounds 1[a]

Compound	M^+	M_1(**$N(CH_2CH_2O)_3Ge^+$)	M_2(M_1–CH_2O)	M_3(M_2–CH_2O)	**GeOH
1_a	408(28)	220(100)	190(74)	160(98)	91(19)
1_b	442(16)	220(76)	190(53)	160(78)	91(19)
1_e	422(26)	220(76)	190(87)	160(100)	91(22)
1_f	422(21)	220(100)	190(56)	160(94)	91(42)

[a] Relative intensity in parentheses.

TABLE 4 Quantitative Elemental Analyses Data of Compounds 1

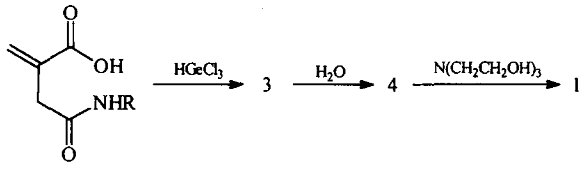
				Elemental Analyses (%)								
				Calculated			*Found (Method A)*			*Found (Method B)*		
Compd.	*Mp (°C)*	*Yield[a] (%, Method A)*	*Yield[a] (%, Method B)*	*C*	*H*	*N*	*C*	*H*	*N*	*C*	*H*	*N*
1_a	191-3	49.1	70.2	50.18	5.45	6.89	49.93	5.23	6.70	49.97	5.28	6.45
1_b	194-6	57.6		51.37	5.75	6.66	51.80	5.84	6.89			
1_c	176-7	70.5	81.3	51.37	5.75	6.66	51.12	5.67	6.51	51.69	5.83	6.18
1_d	180-2	49.7		51.37	5.75	6.66	51.24	5.56	6.58			
1_e	231-3	57.9	66.7	46.27	4.80	6.35	45.98	4.73	6.38	46.75	4.93	6.31
1_f	194-6	78.5	85.9	46.27	4.80	6.35	45.96	5.02	6.14	46.11	4.91	6.38
1_g	196-8	63.7		46.27	4.80	6.35	46.05	4.93	6.29			
1_h	166-8	62.7		45.19	4.68	9.30	45.53	4.72	8.90			
1_i	164-6	79.8		45.19	4.68	9.30	45.36	4.72	9.66			

[a] Yield determined by isolation.

TABLE 5 Important Molecular Parameters of Compound 1_e

Atoms	*Ge–O(1)*	*Ge–O(2)*	*Ge–O(3)*	*Ge–N(1)*	*Ge–C(20)*	*O(1)–Ge–O(2)*	*O(2)–Ge–O(3)*	*O(1)–Ge–O(3)*	*N(1)–Ge–C(20)*
Bond length (Å)[a]	1.808 (4)	1.819 (5)	1.797 (5)	2.241 (6)	1.978 (7)				
Bond angles (degrees)[a]						119.2 (3)	118.4 (2)	116.1 (3)	177.2 (3)

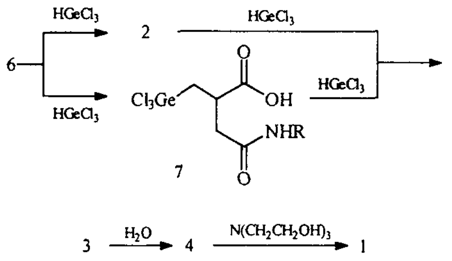
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.



6

R= C_6H_5; 4-$CH_3C_6H_4$; 4-ClC_6H_4; 2-ClC_6H_4.

SCHEME 2



SCHEME 3

titative elemental analyses were carried out on a Yana MT-3 instrument. Mass spectra were recorded on a Hewlett-Packard 5988 instrument.

General Procedure for the Preparation of Compounds 1

Method A (*from compounds* **2**). To a solution of trichlorogermane (5 mmol) in ether (50 mL) was added compounds **2** (5 mmol) at room temperature with magnetic stirring. The reaction was monitored by thin-layer chromatography (TLC). The solvent was removed under vacuum after the reaction had been completed. The residue (compounds **3**) was hydrolyzed directly with water (50 mL). A white solid that formed was filtered off, washed with water, and dried under vacuum overnight to give compounds **4**. Compounds **4** without purification reacted with triethanolamine (5 mmol) in ethanol (25 mL) by refluxing for 4 hours. The precipitate that formed was filtered off and washed with acetone. The solid was recrystallized from absolute ethanol to yield **1**.

Method B (*from compounds* **6**). To a solution of trichlorogermane (10 mmol) in ether (50 mL) was added compounds **6** (5 mmol). The procedure was the same as that of method A.

ACKNOWLEDGMENTS

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