SYNTHESIS OF NOVEL GERMANIUM COMPOUNDS BY INTRAMOLECULAR CATALYTICAL MANNICH-TYPE REACTIONS

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ABSTRACT A series of organogermanium sesquioxides containing dialkyl phosphonyl groups were synthesized by the Mannich-type reaction of β-trichlorogermylbutanal with dialkyl phosphite and different amines. The mechanism was considered to be the intramolecular catalytical process. The structures of all products were determined by ^{1}H, ^{31}P NMR, IR spectra, and elemental analyses.

INTRODUCTION

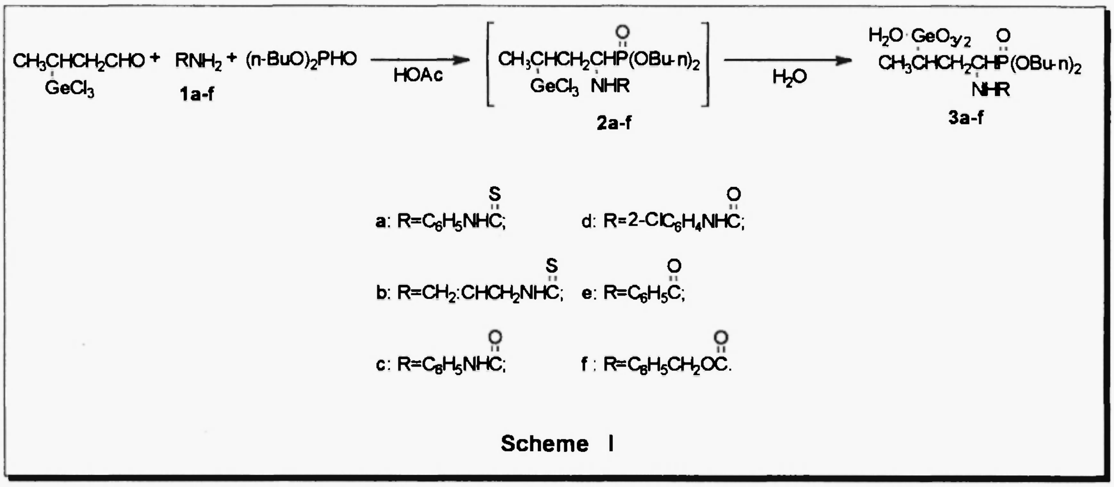
The Mannich-type reaction has been studied for many years. Different phosphorus agents, amines, aldehydes or ketones lead to different reacting conditions and results. It has been known that the Mannich-type reaction involving the amines bonded to strong electron-withdrawing groups, or alphatic aldehydes or ketones, are more difficult to be carried out than those involving the amines without electron-withdrawing groups, aromatic aldehydes or ketones, respectively[1-2]. High temperature, strong protonic solvent, and catalyst are the efficient factors to make those inert Mannich-type reaction easily carried out. Some Lewis acids, e.g. $BF_3 \cdot Et_2O$, $TiCl_4$, $AlCl_3$, $ZnCl_2$, etc., are usually used as catalysts to make the carbonyl group more reactive and easily attacked by amines[3-4]. The Mannich-type reaction involving an intramolecular catalysis by an organogermanium group was firstly evidenced when β-trichlorogermylbutanal reacted with triaryl phosphite and different amines.[5]

RESULTS AND DISCUSSION

This paper investigates the same reaction with dibutyl phosphite (Scheme I), that can also be carried out easily(reaction time: 40-150 min.) and smoothly under mild conditions (14-16 ℃), yielding the reaction products with good yields and purities(determined by ^{31}P NMR, Table I).

The end-point of the formation of the germanium compounds 2a-f was followed by the disappearance of the dibutyl phosphite and amine(^{31}P NMR and TLC). These intermediate compounds 2a-f cannot be isolated in pure form and were hydrolyzed in situ to yield germasesquioxides when dried under vacuum. The structures of all products were determined by ^{1}H, ^{31}P NMR, IR spetra, and elemental analyses(Tables II, III, IV).

The ^{31}P NMR spectra of compounds 2a-f and 3a-f exhibit two resonances due to the existence of chiral center at α-position of phosphorus atom. The products 3a-f can easily absorb water molecules in the air to relieve the positivity on germanium atom resulting in the formation of a aquous solution.



Scheme I

Table I. Reaction conditions for the preparation of compounds 2a-f, and their ^{31}P chemical shifts

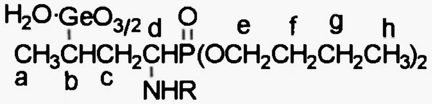
Compds.	T(°C)	t(min.)	Yields by ^{31}PNMR(%)	δ_p
2a	14	40	98.4	23.55
2b	14	40	100	23.55
2c	14	35	100	23.55
2d	14	40	100	23.69, 24.23
2e	16	150	100	23.89, 24.16
2f	16	150	100	23.77, 24.01

Table II. Yields, melting points, ^{31}P chemical shifts and elemental analyses of compounds 3a-f

Compd.	m.p.(°C)	Yields(%)	δ_p	Elemental Analyses(%)					
				Calcd.			Found		
				C	H	N	C	H	N
3a	sticky liquid	91.5	23.82, 24.50	44.39	6.67	5.45	44.16	6.45	5.49
3b	sticky liquid	90.8	23.96, 24.23	40.20	7.17	5.86	39.87	7.11	6.09
3c	>300	88.9	24.63, 25.57	45.82	6.88	5.62	45.76	6.87	5.07
3d	>300	92.4	24.77, 25.30	42.86	6.25	5.26	42.39	6.10	4.88
3e	sticky liquid	86.4	24.50	47.25	6.89	2.90	47.11	6.83	2.37
3f	sticky liquid	93.7	24.50	46.82	6.88	2.73	46.47	6.74	2.44

In the above reaction, dibutyl phosphite cannot be added to the mixture before the reaction of the amine with β-trichlorogermylbutanal in order to avoid the unwanted reaction of dibutyl phosphite with carbonyl group of β- trichlorogermylbutanal.

Table III. ^{1}H NMR spectral data for compounds 3a-f($CDCl_3$)



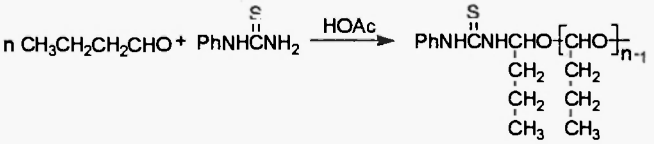
$$\underset{a}{CH_3}\underset{b}{\overset{H_2O\cdot GeO_{3/2}}{\overset{|}{C}H}}\underset{c}{CH_2}\underset{NHR}{\overset{d}{\underset{|}{C}H}}\overset{O}{\overset{\|}{P}}(O\overset{e}{CH_2}\overset{f}{CH_2}\overset{g}{CH_2}\overset{h}{CH_3})_2$$

Compds.	Positions			
	RNH	a, b, c, f, g, h	d	e
3a	(s, 9.02)$C_6H_5\underline{NH}\overset{S}{\overset{\|}{C}}NH$ (s, 6.04)$C_6H_5NH\overset{S}{\overset{\|}{C}}\underline{NH}$ (m,7.00-7.64)$\underline{C_6H_5}NH\overset{S}{\overset{\|}{C}}NH$	0.60-2.46(m)	5.16-5.28(m)	3.76-4.44(m)
3b	(s, 5.88)$\underline{CH_2}=CHCH_2NH\overset{S}{\overset{\|}{C}}NH$ (m, 4.84-5.26)$CH_2=\underline{CH}CH_2NH\overset{S}{\overset{\|}{C}}NH$ (m, 3.56-4.48)$CH_2=CH\underline{CH_2}NH\overset{S}{\overset{\|}{C}}NH$	0.58-2.66(m)	4.84-5.26(m)	3.56-4.48(m)
3c	(s, 8.20)$C_6H_5\underline{NH}\overset{O}{\overset{\|}{C}}NH$ (m, 6.60-7.80)$\underline{C_6H_5}NH\overset{O}{\overset{\|}{C}}NH$	0.56-2.60(m)	4.86-5.80(m)	3.44-4.60(m)
3d	(m, 6.76-8.40)$\underline{C_6H_5}\overset{O}{\overset{\|}{C}}NH$	0.60-2.64(m)	5.20-5.96(m)	3.60-4.68(m)
3e	(s, 8.00)$2\text{-}ClC_6H_4\underline{NH}\overset{O}{\overset{\|}{C}}NH$ (m, 6.60-7.82)$2\text{-}Cl\underline{C_6H_4}NH\overset{O}{\overset{\|}{C}}NH$	0.54-2.80(m)	4.88-5.10(m)	3.62-4.40(m)
3f	(s, 4.80)$C_6H_5\underline{CH_2}O\overset{O}{\overset{\|}{C}}NH$ (m, 7.20-7.44)$\underline{C_6H_5}CH_2O\overset{O}{\overset{\|}{C}}NH$	0.76-2.44(m)	5.00-5.20(m)	3.80-4.16(m)

Table IV. IR spectral data for compounds 3a-f

Compds.	IR(KBr cm^{-1})
3a	3269.5 3065.5 2950.5 1745.5 1672.1 1596.4 1535.9 1405.9 1452.8 1384.8 1207.5 1055.8 1018.0 983.4 873.1 753.5 707.9
3b	3268.5 2951.1 1605.8 1536.9 1504.8 1455.6 1398.3 1211.5 1056.5 1018.7 984.9 876.2 827.0 720.4
3c	3294.0 3076.0 2592.0 1665.3 1609.7 1573.3 1545.3 1497.4 1443.8 1348.4 1208.9 1054.9 1017.7 990.4 871.3 749.5 691.2
3d	3381.0-3000.0 2946.5 1699.0 1582.8 1526.3 1455.5 1394.6 1208.9 1054.2 1018.6 994.2 869.0 763.9
3e	3302.0-3000.0 2950.0 1673.6 1584.6 1529.8 1463.4 1437.6 1369.8 1299.5 1207.4 1053.4 1027.8 986.2 863.1 746.0
3f	3305.0 3059.0 2951.5 1716.9 1695.5 1603.7 1493.3 1451.5 1397.6 1338.4 1282.7 1219.6 1062.7 1019.9 970.1 873.8 728.9

In order to investigate the effect of the trichlorogermyl group in Mannich-type reaction, n-butanal was used instead of β-trichlorogermylbutanal under the same reaction conditions, but the polymeric product was formed due to the addition of the amine with many aldehyde molecules(Scheme II), which had been confirmed on a similar reaction by G.H. Birum in 1974[6].



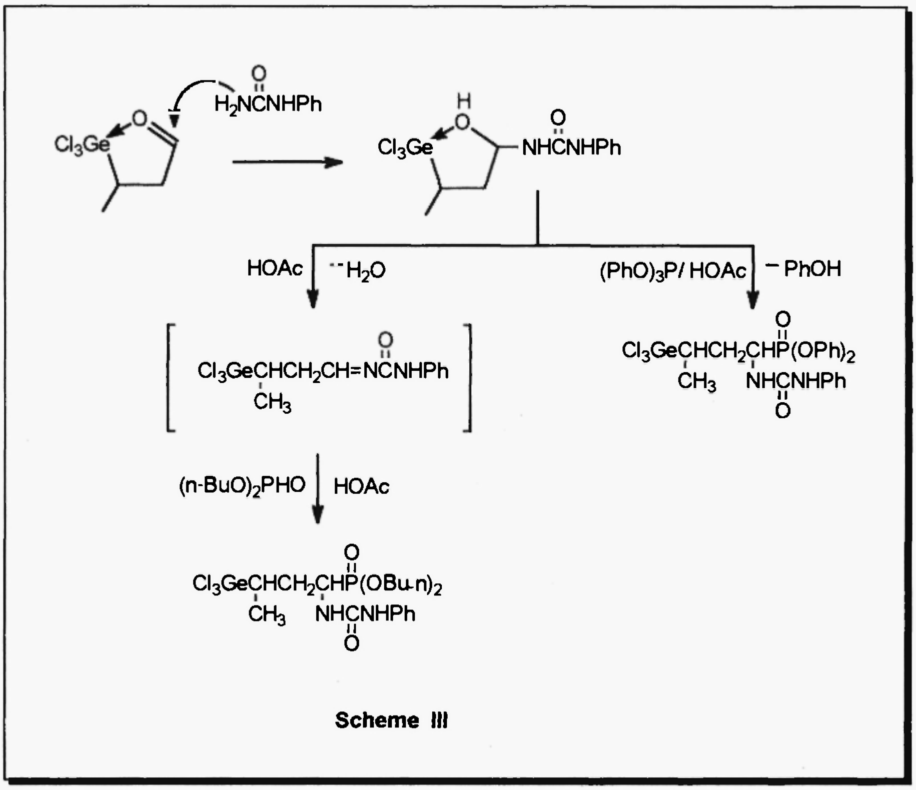
$$n\,CH_3CH_2CH_2CHO + PhNH\overset{S}{\overset{\|}{C}}NH_2 \xrightarrow{HOAc} PhNH\overset{S}{\overset{\|}{C}}NH\underset{CH_2CH_2CH_3}{CH}O\left[\underset{CH_2CH_2CH_3}{CH}O\right]_{n-1}$$

Scheme II

In contrast to triphenyl phosphite, as determined by ^{31}P NMR, the signal of dibutyl phosphite did not disappear when dichloromethane was used as a solvent instead of acetic acid. In the mechanism of the reaction with dibutyl phosphite as a reactant, a transesterification may be involved. As for dibutyl phosphite, the formation of imine may be important. Imine intermediates can not be formed in non-protonic media, which led to the following results(Scheme III).

EXPERIMENTAL SECTION

^{1}H and ^{31}P NMR spectra were run on a JEOL-90Q spectrometer. ^{1}H chemical shifts are reported in ppm relative to internal tetramethylsilane. All ^{31}P NMR chemical shifts are reported in ppm relative to external 85% phosphoric acid. In all cases the nuclei which are deshielded relative to their respective standards are assigned a positive chemical shift. ^{31}PNMR spectra were obtained by using a full proton coupling. IR spectra were run on a DS-301 spectrometer. Quantitative elemental analyses were run on a Yana MT-3. The wave length of UV light used in TLC was 253.7 nm, and the eluent was petroleum ether-acetone(4:1).



Scheme III

The reaction of β-trichlorogermylbutanal with amine and dibutyl phosphite.

To a solution of β-trichlorogermylbutanal(5mmol) in gl. acetic acid(25mL), the amine(5mmol) was added. The reaction mixture was stirred at room temperature untill the solid was completely dissolved. Then dibutyl phosphite(5mmol) was added. The reaction was examined by TLC and ^{31}P NMR every ten minutes.

General procedure for the preparation of compounds 3a-f.

The above reaction mixture was concentrated by evaporation under vacuum. The residue was hydrolysed with water to give a white solid which was recrystallized from dichloromethane/acetone to give compounds 3a-f.

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