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ORGANOGERMANIUM COMPOUNDS; SPECTROSCOPIC STUDY ON THE INFLUENCE OF ARYL GROUPS IN THE ORGANOGERMANIUM ARYL COMPOUNDS ON THE (P-d)π INTERACTION

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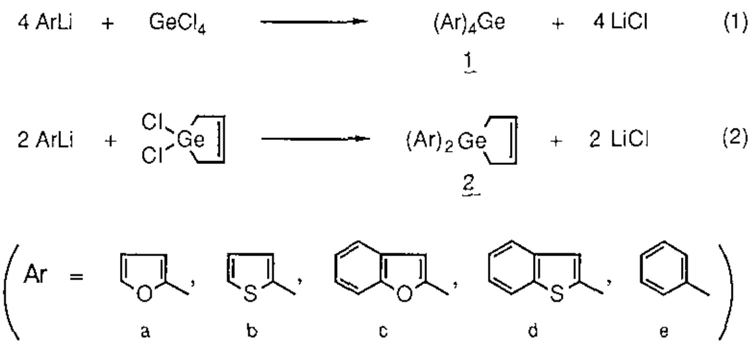
Abstract——The synthesis and properties of arylgermanium compounds through the reactions of aryllithium with germanium halides were investigated. ^{1}H-Nmr spectroscopic analysis showed the (p-d)π interaction between the germanium atom and the double bond of the aryl group to diminish in the following group order: 2-benzofuranyl > 2-furanyl > 2-benzothiophenyl > 2-thiophenyl > phenyl group.

A study of the physical properties of compounds of the type R_3M-CH=CH-R' (M=Si, Ge, Sn, and Pb) indicated that the interactions of the p-orbitals of π-electrons in multiple bonds with the d-orbitals of M atoms can be characterized by ir, Raman and nmr studies.[1] Lukevits et al.[2] recently succeeded for the first time in synthesizing furylgermanes with functional substituents as organometallic furan derivatives; they examined the influence of substituents in the furan ring on (p-d)π interactions. In the present study, the synthesis of arylgermanium compounds (phenyl, thiophenyl, furanyl, benzothiophenyl, and benzofuranyl groups) was carried out so as to make a comparison of the (p-d)π interactions involved in these compounds. Reactions of alkyl and aryl halides with germanium halide in the presence of a suitable catalyst,[3] usually copper, provide a direct route for the synthesis of alkyl or aryl germanium compounds. However, for general laboratory purpose, the reactions of organolithium or magnesium with alkyl and aryl halides have been used on a broad scale.[4] We prepared arylgermanium compounds (1) and (2) using organolithium reagents, as shown by equations (1) and (2). Germanium tetrachloride and 1,1-dichlorogerma-3-cyclopentene[5] were also used as germanium halides so that the effects of aryl groups on the germanium atom could be compared with those of the alkenyl groups.



Representative results are presented in Table I and ^{1}H-nmr and uv spectral data in Table II.

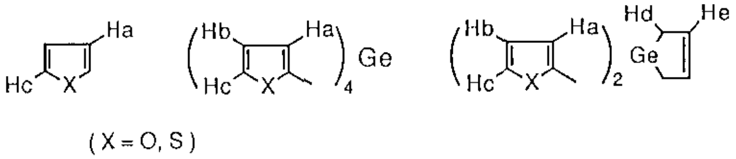
Table I. Reactions of Organolithium Reagents with Germanium halides

entry	lithium reagent	germanium[a] halide	product	mp(°C)	yield(%)
1	2-furanyl Li	A	1a	93	50
2	2-thiophenyl Li	A	1b	141	40
3	2-furanyl Li	B	2a	oil	40
4	2-thiophenyl Li	B	2b	oil	37
5	2-benzofuranyl Li	B	2c	86	25
6	2-benzothiophenyl Li	B	2d	124-126	42
7	phenyl Li	B	2e	oil	45
8	1-lithio-1,3-dithiane	B	2f	117-118	50

[a] A stands for tetrachlorogermane and B for 1,1-dichloro-1-germa-3-cyclopentene.

Uv spectra of arylgermanium compounds 1 and 2 showed bathocromic shifts with respect to the aryl compounds; these shifts resulted from (p-d)π interactions, as indicated by ^{1}H-nmr spectroscopic data. The differences, Δ , between the chemical shifts of the aryl proton of arylgermanium compounds 1-2,

Table II. ¹H-Nmr and Uv Spectral Data of Arylgermanium Compounds (1 and 2).



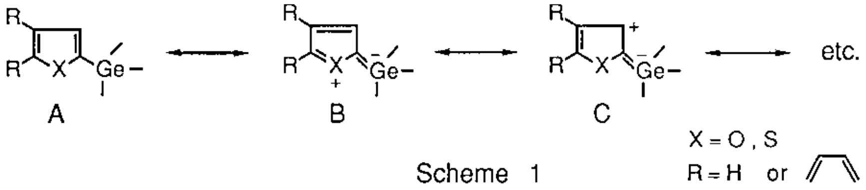
compound		¹H-nmr (CDCl$_3$) δ[ppm] [a]					uv spectra
		Ha	Hb	Hc	Hd	He	λ$_{max}$ nm (logε)
furan		6.37	6.37	7.42	-	-	218(2.15)
tetra(2-furanyl)germane	(1a)	6.78 (0.41)	6.39 (0.02)	7.65 (0.23)	-	-	226(1.21)
1,1-bis(2-furanyl)germa-3-cyclopentene	(2a)	6.74 (0.37)	6.40 (0.03)	7.66 (0.24)	2.15	6.05	226(1.27)
thiophene		7.10	7.10	7.30	-	-	230(0.70)
tetra(2-thiophenyl)germane	(1b)	7.32 (0.22)	7.16 (0.06)	7.58 (0.28)	-	-	236(1.20)
1,1-bis(2-thiophenyl)germa-3-cyclopentene	(2b)	7.22 (0.12)	7.10 (0.00)	7.50 (0.20)	2.00	6.03	236(1.55)
benzofuran		6.67	-	-	-	-	209(1.69) 244(1.18)
1,1-bis(2-benzofuranyl)germa-3-cyclopentene	(2c)	7.12 (0.45)	-	-	2.15	6.14	211(1.91) 256(1.96)
benzothiophene		7.18	-	-	2.13	6.14	226(0.33) 256(0.06)
1,1-bis(2-benzothiophenyl)-germa-3-cyclopentene	(2d)	7.56 (0.38)	-	-	-	-	205(0.49) 230(0.65) 272(0.28)
benzene		7.33	-	-	-	-	210(1.74) 255(0.44)
1,1-diphenylgerma-3-cyclopentene	(2e)	7.45 (0.08)	-	-	1.92	6.05	207(1.26)
1,1-bis[2-(1,3-dithianyl)]-germa-3-cyclopentene	(2f)	-	-	-	1.85	5.95	-

[a] Values in parenthese are defined as δ (H-Ar$_4$Ge or H-Ar$_2$Ge ) − δ (Ar-H).

δ (H-Ar_4Ge or H-Ar_2Ge) and those for corresponding aryl compounds δ (Ar-H) as defined by the following equation

$\Delta = \delta$ (H-Ar_4Ge or H-Ar_2Ge) $- \delta$ (Ar-H)

are listed in parentheses in Table II. Δ Values for Ha ranged from 0.08 - 0.45 ppm, the average being ca 0.33 ppm, though they appeared somewhat less for 2e. For Hb, they were small and for Hc, averaging a mid-range of ca 0.24 ppm. A comparison of these values for Ha indicated (p-d)π interaction between the germanium atom and the double bond of aryl groups to diminish in the following group order: 2-benzofuranyl > 2-furanyl > 2-benzothiophenyl > 2-thiophenyl > phenyl group. Substituents on the germanium atom had little influence on this order of (p-d)π interaction. Compound 2f, 1,1-bis[2-(1,3-dithianyl)]germa-3-cyclopentene, was synthesized from 2-lithio-1,3-dithiane and 1,1-dichlorogerma-3-cyclopentene and the effects of the (p-d)π interaction on the methylene (Hd) and olefin (He) protons on the germa-3-cyclopentene ring in 2a-e were examined by nmr spectroscopic analysis. The signals of the Hd and He of 2a-e generally appeared slightly more down field than that of 2f. In the (p-d)π interaction, forms B and C in particular, as shown in Scheme 1, exerted a deshielding effect on Hd and He, causing their signals in the nmr spectrum to shift down field. However, this effect did not appear to be offset significantly by σ–π conjugation between the Ge-C bond and the double bond in the germacyclopentene ring.



Scheme 1

In recent years, certain organogermanium compounds have come to attract considerable attention in consideration of the clinical application as anti-cancer drugs.[6] The biological activities of the germanium compounds described in the present paper are now being studied and the results will be presented in a future paper.

EXPERIMENTAL

All the melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Uv spectra were recorded with a Hitachi 557. ^{1}H-Nmr spectra were determined with a Varian EM-390 spectrometer using tetramethylsilane as an internal standard. Mass spectra were measured with a Hitachi M-80 mass spectrometer.

General procedure for tetraarylgermane (1a-b) and 1,1-diarylgerma-3-cyclopentene (2a-e).

To a solution of aryllithium (0.11 mol) in THF (100 ml) was gradually added a solution of tetrachlorogermane (0.025 mol) or 1,1-dichlorogerma-3-cyclopentene[5] (0.05 mol) in THF (50 ml) -30°C under nitrogen atmosphere with stirring. The reaction mixture was subsequently warmed to room temperature, poured into ice-water and extracted with ether (50 ml). The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness in vacuo. The residue was recrystallized from EtOH or purified by silica gel on column using ethyl acetate-hexane (80:20) as eluant. The results are shown in Table I and II.

1a: ms, m/z 541 (M^+); Anal. Calcd for $C_{32}H_{20}O_4Ge$: C, 70.97, H, 3.69 Found: C, 70.86, H, 3.52. 1b: ms, m/z 604 (M^+); Anal. Calcd for $C_{32}H_{20}S_4Ge$: C, 63.51; H, 3.31. found: C, 63.50; H, 3.33. 2a: ms, m/z 260(M^+). 2b: ms, m/z 292 (M^+). 2c: ms, m/z 360 (M^+). 2d: ms, m/z 392 (M^+). 2e: ms, m/z 280 (M^+).

1,1-Bis[2-(1,3-dithianyl)]germa-3-cyclopentene (2f).

To a solution containing 1.47 g of 1,3-dithiane in 25 ml of THF was added 7.5 ml of a 1.6 M n-butyllithium solution at -30°C under a nitrogen atmosphere. After the mixture was stirred at -30°C for 3h, the solution was added to a solution containing 1.2 g of 1,1-dichlorogerma-3-cyclopentene in 50 ml of THF at -30°C. The mixture was stirred for 4 h at -30°C and then allowed to warm to room temperature, poured into ice-water, and extracted with ether. The ether layer was separated, washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness in vacuo. The resulting solid was recrystallized from ethanol to give 2.2 g (50%) of 1,1-bis[2-(1,3-dithianyl)]germa-3-cyclopentene (2f): ms, m/z 364 (M^+).

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