Chemistry

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1964

SovietRxiv

Abstract

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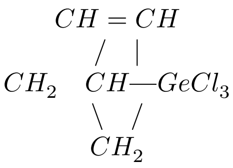
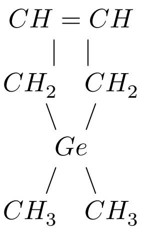
MANIFESTATION OF σ, π-CONJUGATION IN THE SPECTRA OF β-ALKENYLGERMANES AS A FUNCTION OF SPATIAL FACTORS

(Presented by Academician A. N. Nesmeyanov on 8 April 1964)

It was shown earlier ($^{1-6}$) that, among the members of the homologous series $R_3Si(CH_2)_{nCH} = CH_2$ and $R_3Si(CH_2)_n$-phenyl-X, compounds with $n = 1$, i.e., with the Si atom in the β-position relative to the multiple bond, occupy an exceptional position. They possess maximum reactivity in ionic addition reactions and minimum reactivity in radical reactions, considerable exaltation of MR_D, a bathochromic shift in the UV spectra, and an anomalously high intensity of the line corresponding to the vibration of the multiple bond in Raman spectra. As is known, precisely the same phenomena are characteristic of compounds possessing conjugated multiple bonds. The listed exceptional physical and chemical features of allyl- and benzylsilanes were explained by interaction between the Si atom and the multiple bond situated in the β-position to it (the "β-effect"), which in its manifestations is formally analogous to conjugation of multiple bonds. We subsequently showed (^{6,7}) that the "β-effect" is not specific to silicon compounds and increases as the Si atom in the molecule R_3SiCH_2—$CH = CH_2$ is replaced by Ge and Sn.

In the present work we continued the study of one aspect of this phenomenon—the intensities of lines in Raman spectra—using as examples various alkenylgermanes with the Ge atom in the β-position relative to the $C = C$ bond. For this purpose the following compounds were synthesized:


(I)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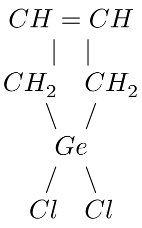
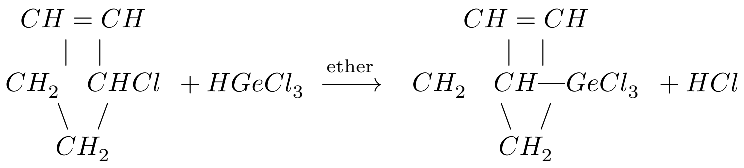

(III)

$Cl_3GeCH_2CH = CHCH_2GeCl_3$ $(CH_3)_3GeCH_2C$

IV

and their spectra were recorded. The synthesis and spectra of II and III were published earlier (8,9). Compounds I, IV, and V were obtained by a new condensation reaction recently discovered by us (10):



(I)

$$ClCH_2—CH = CH—CH_2Cl + 2HGeCl_3 \xrightarrow{\text{ether}} Cl_3Ge—CH_2—CH = CH—CH_2—GeCl_3 \quad \text{(IV)}$$

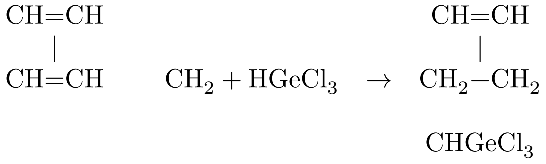
$$\xrightarrow{CH_3MgX} (CH_3)_3GeCH_2—CH = CH—CH_2Ge(CH_3)_3 \quad \text{(V)}$$

It is curious to note that the formation of I proceeded well even in the absence of ether, although in the case of other chlorides of the allylic type, in the absence of ether the condensation reaction was always replaced by the addition reaction of $HGeCl_3$ at the multiple bond (10).

$$\mathrm{CH_2{=}CHCH_2Cl + HGeCl_3 \xrightarrow{ether} Cl_3GeCH_2CH{=}CH_2}$$

$$\mathrm{CH_2{=}CHCH_2Cl + HGeCl_3 \longrightarrow Cl_3GeCH_2CH_2CH_2Cl}$$

In addition, the synthesis of compound I has now allowed us to show rigorously that, upon addition of $HGeCl_3$ to cyclopentadiene, it is precisely compound I that is formed (11)



Study of the intensity of the Raman line corresponding to the vibration in which the C=C bond is predominantly changed led to the following results (see Table 1).

Table 1

Frequency and intensity of the line corresponding to the C=C vibration in the Raman spectra of alkenylgermanes

	R–CH=CH$_2$ (according to (^{12}))*	Me$_3$GeCH$_2$CH=CH$_2$	Me$_3$GeCH=CH$_2$	I	()–CH$_3$ (according to (^{12}))	II	III
ν, cm^{-1}	1640	1630	1650	1606	1614	1613	1605
I^*_∞	~400	1170	4520	1790	370	290	270

* I_∞ is the integral intensity of the line on the cyclohexane scale, recalculated to an equal number of molecules in the scattering volume.

The data of Table 1 make it possible to shed some light on the nature of the "β-effect." It was previously believed ($^{1,5-7}$) that the "β-effect" in β-alkenylsilanes (germanes) is brought about as a consequence of their pseudocyclic state, i.e., the geometrical approach of atom M and the multiple bond, with polarization of the multiple bond occurring through interaction of its π-electrons with the vacant d-orbitals of atom M.

However, this hypothesis is refuted by the fact that in the spectrum of I, in which geometrical approach of the Ge atom and the C=C bond is impossible, $I_{C=C}$ is 1790 units, i.e., 1.5 times higher than in $CH_2{=}CHCH_2Ge(CH_3)_3$, and almost 5 times higher than in 3-methylcyclopentene-1.

Investigation of $I_{C=C}$ in the Raman spectra of allylic compounds of the type $CH_2{=}CH{-}CH_2{-}X$, containing elements of other groups of the periodic system –Br, J, Hg–which will be the subject of a subsequent communication, shows that the "β-effect" is not specific for compounds of Group IV elements: Si, Ge, Sn, but is a particular case of the well-known exceptional nature, in organic chemistry, of allylic and benzylic systems.

The very high reactivity of these systems in ionic addition reactions, their stability in radical reactions, the ability of allylic hydrogen to be readily exchanged for deuterium, etc., were explained by Nesmeyanov (^{13,14}) as σ–π conjugation of bonds 1-2 and 3-4 in the system

$$\overset{1}{C}{=}\overset{2}{C}{-}\overset{3}{C}{-}\overset{4}{M}.$$

The determining factor for σ–π conjugation is the dynamic electromeric effect, which increases with increasing polarizability of the system.

Obviously, the "β-effect" observed by us, which increases upon replacement of Si by Ge and Sn, i.e., with increasing polarizability of the M–C bond, also belongs to this class of phenomena.

If the "β-effect" is a special case of σ–π conjugation according to Nesmeyanov, then it should depend on the mutual arrangement of the conjugating σ- and

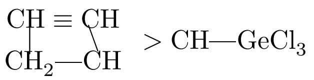
π-clouds. In particular, their perpendicularity should lead to "switching off" of $\sigma-\pi$ conjugation.

Indeed, from the data of Table 1 it is seen that in the Raman spectra of the planar rings II and III (where the C–C bond is also located in the β-position to the Ge atom, but the σ-cloud of the C–Ge bond and the π-clouds of the C=C bond are mutually perpendicular), $I_{C=C}$ is not only not increased, but is even somewhat smaller than in methylcyclopentene*. Comparison of $I_{C=C}$ in the spectra of both rings also shows that the induction effect (replacement of the electropositive group $(CH_3)_2Ge <$ by the electronegative $Cl_2Ge <$) has no substantial influence on $I_{C=C}$, as was noted earlier in (^{16}).

The very high $I_{C=C}$ in the Raman spectrum of $(CH_3)_3GeCH_2—CH = CH—CH_2—Ge(CH_3)_3$, 4520 units, is noteworthy: on going from the system $Ge\overset{\sigma}{—}C—C \overset{\pi}{=} C$ to the system $Ge\overset{\sigma}{—}C—C \overset{\pi}{=} C—C\overset{\sigma}{—}Ge$, $I_{C=C}$ increases by approximately a factor of 3, probably because of lengthening of the conjugated chain.

Experimental Part

β-(Trichlorogermyl)cyclopentene


(I).

To 25 g of β-chlorocyclopentene, 40 g of trichlorogermane etherate was added with stirring.

Self-heating was observed. The reaction mixture was then kept for 1 hour at 55–60° and subsequently distilled under vacuum. 28 g of I was obtained, b.p. 63.5° (5 mm). n_D^{20} 1.5280; d_4^{20} 1.5621; MR_D 48.51; calculated 47.96. Yield 76%.

Found, %: Ge 29.79; 29.90; Cl 43.11; 43.10
$C_5H_7GeCl_3$. Calculated, %: Ge 29.50; Cl 43.22

Literature data (^{11}): b.p. 76° (10 mm); n_D^{20} 1.5270; d_4^{20} 1.5574. Compound I darkened rapidly on storage. The IR and Raman spectra of I coincided completely with those published earlier (^{11}).

1,4-Bis-(trichlorogermyl)-butene-2
$Cl_3GeCH_2—CH = CH—CH_2GeCl_3$ (IV). To 19 g of 1,4-dichlorobutene-2, 75 g of trichlorogermane etherate was added. After seven hours of boiling, vacuum distillation gave 5 g of the starting dichloride and 25.5 g of IV, b.p. 146–147° (6.5 mm); m.p. 56–58°. Yield 44%. For the IR spectrum see Fig. 1.

Found, %: Ge 35.33; 35.30; Cl 51.46; 51.30
$C_4H_6Ge_2Cl_6$. Calculated, %: Ge 35.24; Cl 51.63

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

1,4-Bis-(trimethylgermyl)-butene-2
$(CH_3)_3GeCH_2$—CH = CH—$CH_2Ge(CH_3)_3$ (V). To CH_3MgBr, prepared from 42 g of magnesium in 700 ml of ether, 24 g of IV, dissolved in 70 ml of ether, was added. After five hours of boiling, the contents of the flask were decomposed with acidified water. The ether layer was dried and distilled. 14 g of V was obtained with b.p. 85° (11.5 mm), n_D^{20} 1.4713, d_4^{20} 1.1190; MR_D 72.35, calculated 71.39. Yield 83%. For the IR spectrum see Fig. 2.

Raman spectrum ($\Delta\nu$ cm^{-1}): 194(4 sh), 234(1), 281(2), 427(1), 568(10), 603(8), 643(1), 706(1), 786(1), 836(1), 957(1), 1153(8 br. dbl.), 1188(4), 1214(0), 1245(3 dbl.), 1307(2), 1410(1 sh), 1641(1), 1652(10), 2906(7 br.), 2974(5 br.).

Comparing the Raman and IR spectra of V, one may conclude that molecule V has predominantly the trans-configuration (the bright Raman line at 1652 cm^{-1}, corresponding to the C=C vibration, is absent in the IR spectrum), but pri-

* For a preliminary communication see (^{15}).

the presence of the weak line at 1641 cm^{-1} may indicate a small admixture of the *cis* isomer.

$C_{10}H_{24}Ge_2$.	Found, %:	C 41.63; 41.38;	H 8.30; 8.39;	Ge 50.28; 50.26
	Calculated, %:	C 41.49;	H 8.36;	Ge 50.15

The Raman spectra were recorded on an ISP-51 instrument with a medium chamber. The integral intensities given in Table 1 were measured by photographic photometry according to the procedure of (^{12}) and are expressed on the cyclohexane

Fig. 1

Fig. 2

scale. The coefficient for recalculating the intensity to an equal number of molecules in the scattering volume was calculated by the formula:

$$K = \frac{d_0 M_\text{v}}{M_0 d_\text{v}},$$

where d_0 and d_v, M_0 and M_v are the specific gravity of cyclohexane and of the substance, and the molecular weight of cyclohexane and of the substance, respectively. The intensities of spectrum V in the experimental part are expressed on a 10-point visual scale. The IR spectra were obtained on a double-beam UR-10 spectrograph.

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Academy of Sciences of the USSR

Received
8 IV 1964

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