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240. Differences between Organic Chemistry of Silicon and some other Group IV Elements

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(30. V. 69)

The difference in physical and chemical properties of the first three members of the group IVb are mostly accounted for by the structure of the valence shell of the respective elements. The common feature of all three elements to be discussed is sp^3 hybridisation in organic compounds. Differences between carbon chemistry and the chemistry of silicon [1] and germanium are determined by

1) the availability of vacant *d*-orbitals in the valence shell,

2) electronegativity, where the most pronounced difference is between carbon and silicon (according to the PAULING scale 2.5 for C and about 1.8 for Si and Ge),

3) the covalent radius of the elements discussed – the only pronounced difference is between carbon (0.77 Å) and silicon (1.17 Å), whereas the covalent radius of germanium differs only slightly (1.22 Å) from that of silicon. This is connected with the differences in polarizability, which increases with increasing covalent radius.

How these three effects determine the properties of the corresponding organic compounds can be illustrated by typical examples.

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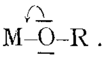
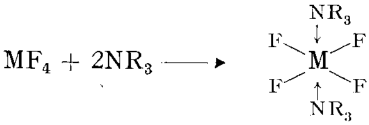
1) Eingeladener Vortrag, gehalten von Prof. V. BAŽANT an der Wintersitzung der Schweizerischen Chemischen Gesellschaft, Neuchâtel, 22. Februar 1969, veröffentlicht gemäss besonderem Beschluss des Redaktionskomitees.

1) Vacant *d*-orbitals can take part in $(p \rightarrow d)\,\pi$ bonding if they form σ-bonds with atoms containing lone electron pairs, e. g. M–N, M–O and M–X, where M = Si or Ge, and X = F, Cl:



$$\text{M–}\underline{\overline{\text{O}}}\text{–R}\,.$$

Vacant *d*-orbitals can be also utilized to the formation of $(p \rightarrow d)\,\sigma$ bonds, which can extend tetracovalency of silicon and germanium up to hexacovalency:



In the case of Si–O bonds the formation of $(p \rightarrow d)\,\pi$ bonding can be shown by
a) the relatively high acidity of silanols in comparison with alcohols [2],
b) the angle of Si-O-Si being about 145° [3],
c) the low basicity of siloxanes in comparison with that of ethers [4],
d) difference in the measured and calculated length of Si–O bond [5].

Similar facts can be found for Si-N and Si-halogen bonds, where also NMR. studies are conclusive.

In the case of germanium the $(p \rightarrow d)\,\pi$ character of the Ge-O bond is less developed, which leads to the increasing basicity of germoxanes and alkoxygermanes, and to the decrease of the Ge-O-Ge angle, the value of which being probably comparable with that of the C-O-C angle (111°).

In cases where M-phenyl and M-vinyl bonds are involved, interactions between π-system and *d*-orbitals can occur. This idea can be substantiated by the values of σ constants for trimethylsilyl (–0.07) and trimethylgermyl (–0.06) groups in comparison with the *t*-butyl group (–0.20), resulting both in a relatively high acidity of silylbenzoic acids and even for instance in the increased acidity of silyl-substituted phenols and decreased basicity of trimethylsilylaniline.

The ability for $(p \rightarrow d)\,\sigma$ bond formation is well established for both silicon and germanium, it being more enhanced for the latter element. This can be demonstrated by the ability of germanium tetrafluoride to form complexes with ethers and ketones, which is not known for silicon tetrafluoride.

2) Owing to the differences in electronegativity, the positive inductive effect is decreasing in the series $(CH_3)_3Ge > (CH_3)_3Si \gg (CH_3)_3C$ group. From this it can be seen that in all cases, where $(p \rightarrow d)\,\pi$ dative bonding is not possible, trimethylgermyl and trimethylsilyl groups behave as strong electron-donors.

3) The polarizability of Si-X and Ge-X (where X = O, N or halogen) is at least, according to SOMMER [6], one of the main reasons for higher reactivity of organosilicon and organogermanium compounds in nucleophilic substitution.

We can arrive at the same conclusion using the idea of availability of *d*-orbitals for $(p \rightarrow d)\,\sigma$ bonds with nucleophilic species.

For some time now we are concerned with the study of different chemical and physical properties of organosilicon and organogermanium compounds. This paper is to be an account of our contribution to the problems of the metal-oxygen and metal-phenyl bonds. There are two possible approaches: the study of changes between the ground and transition states, the latter being connected with kinetics, and the study of suitable series of model compounds in the ground state.

An example of the first kind of approach is offered by the results of chlorination of the series of phenylmethylchlorogermanes and phenylmethylchlorosilanes in comparison with some carbon analogues.

Relatively few quantitative data exist concerning the chlorination of silyl-substituted aromatic compounds. In the series of phenylchlorosilanes the greatest attention has been devoted so far to phenyltrichlorosilane. Several authors have already determined the percentages of *o*-, *p*-, *m*-isomers of this derivative [7]. From their findings it follows that the results of individual measurements differ substantially from one another, even if it is clear that, in agreement with the theoretical assumption, the trichlorosilyl group is strongly *meta*-orientating. The orientation effects have not yet been studied systematically with other silyl groups. The effects of variously substituted germyl groups remain quite unknown. The present work is devoted to a systematic study of the orientation effects of methyl-chloro-substituted silyl groups (*i. e.* from Cl_3Si to $(CH_3)_3Si$) and of methyl-chloro-substituted germyl groups (hence again from Cl_3Ge to $(CH_3)_3Ge$). To facilitate interpretation, especially to assess whether and to what extent the $(p \rightarrow d)\pi$ character of the bond of silicon with the phenyl group might be effective in these reactions, we decided to determine the relative reactivities of phenylchlorosilanes with respect to known organic standards. To estimate whether the $(p \rightarrow d)\pi$ bond between silicon and the phenyl group plays a role in this case, we have also determined orientation effects in a series of benzylmethylchlorosilanes.

The obtained results [8] indicate that a substantial effect on the orientation of the electrophilic chlorination of phenylchlorosilanes may be displayed by the catalyst used or even by the solvent. For this reason, in our work also these two factors were taken into account. The catalyst used was first of all ferric chloride; it was applied instead of aluminium chloride though it was found to be less active, but it caused less cleavage of the phenyl-silicon bond, giving rise to chlorobenzene. Other catalysts of the FRIEDEL-CRAFTS type, such as chlorides of antimony and boron, were relatively still less active. The second catalyst used here was iodine. In view of the fact that some authors assumed, even in the case of ferric chloride, the possible role of interactions between ferric chloride and the silyl group, we thought it prudent to compare the effect of this catalyst with one of a completely different type.

The orientation effects in the chlorination were studied in all cases at 60 °C, using 3-molar percent catalysts. The reaction was always carried to conversions of some 5% in order to prevent chlorination to the second stage. The reaction mixture was then methylated with methylmagnesium chloride, excess GRIGNARD reagent was destroyed by hydrolysis and, after distilling off the excess ether, the ratio of the *o*-, *p*- and *m*-chloroaryl-trimethylsilanes was determined chromatographically. Of the results obtained, let us first mention the data for the model series of benzylmethylchlorosilanes.

As may be seen from Table I, the results were interesting for two reasons. First of all, even benzyltrichlorosilane is chlorinated, almost fully with iron and completely with iodine, practically exclusively in the *o*- and *p*-positions. Theoretically, one would have assumed that the negative inductive effect of the trichlorosilyl group would play a greater role than the positive inductive effect of the methylene group, and hence

Table I. *Chlorination of benzylmethylchlorosilanes*
(3-molar % catalyst, 60°C, max. 5% conversion; yields: % ± relative error)

Compound	$FeCl_3$			I_2		
	p- %	*m*- %	*o*- %	*p*- %	*m*- %	*o*- %
$(CH_3)_3SiCH_2C_6H_5$	65.9 ± 1.1	0	34.1 ± 2.3	71.9 ± 1.9	0	28.1 ± 5.0
$(CH_3)_2ClSiCH_2C_6H_5$	62.4 ± 0.4	0	37.6 ± 0.7	62.7 ± 1.4	0	37.3 ± 2.3
$(CH_3)Cl_2SiCH_2C_6H_5$	53.2 ± 1.8	5 ± 25	41.8 ± 2.3	58.5 ± 1.5	0	41.5 ± 2.2
$Cl_3SiCH_2C_6H_5$	52.2 ± 0.9	5 ± 25	42.8 ± 1.1	60.8 ± 2.1	0	39.2 ± 3.3

that the trichlorosilylmethyl group would be weakly *m*-orientating. The second interesting result is the systematically rising relative amount of the *o*-derivatives, on going from the trimethylsilyl group to the trichlorosilyl group.

Very interesting results were obtained on studying the relative reactivity of these derivatives. For their estimation, we chlorinated the corresponding benzylsilane mixed with an organic standard (*t*-butylbenzene in all cases, and also diisopropylbenzene in the case of the trimethyl derivative, and benzene in the case of the trichloromethyl derivative, and benzene in the case of the trichloro derivative). The molar ratio of both aromatic derivatives was selected in such a way that approximately indentical amounts of monochloro derivatives were formed. Halogenosilanes contained in the mixture were converted by methylation into trimethylbenzyl derivatives and, after hydrolysis, drying and separation of the ether, the mixture was evaluated chromatographically. From the results of the study of benzylchlorosilanes with both catalysts, which are summarized in Table II, it can be seen that the relative reactivities of benzylsilanes referred to benzene are generally higher with iodine than with ferric chloride catalysts. The difference is constant in the whole series, as follows from Fig. 1. The additivity of the inductive effect is not satisfactory, particularly between the last two members of the series, but that is known even for the σ constants of the chlorinated methyl group (Fig. 2), so that the relationship between the logarithms of the relative rate constants of methylchlorobenzylsilanes and the σ constants of the chloromethyl groups with a corresponding number of chlorine atoms is roughly linear.

Let us now proceed to the study of phenylmethylchlorosilanes. In this connection we estimated the effect of the amount of catalyst (from 0.1 to 10%) and of temperature (from 30 to 90 °C). In both cases we found that within the above limits the effect of the various factors does not exceed the experimental error. The experiments themselves were still carried out under constant conditions, *i. e.* using 3-molar % catalysts and a temperature of 60 °C. The results of the study of the orientation effects and of chlorodesilylation during chlorination under catalysis with ferric chloride are listed in Table III. As can be seen, passing from the trimethyl group with weak *o*-, *p*-orientating effects *via* the dimethylchlorosilyl groups with a weakly *m*-directing effect to the trichlorosilyl derivative, the percentage of the *m*-derivative formed increases.

Table II. *Chlorination of benzylmethylchlorosilanes*
(yields: % ± relative error)

Compound	I_2			$FeCl_3$		
	$k/k_{t\text{-BB}}$	k/k_B	$\log k/k_B$	$k/k_{t\text{-BB}}$	k/k_B	$\log k/k_B$
$(CH_3)_3SiCH_2C_6H_5$	130 ±4.8	3870	3.588	171 ±15.3	1803	3.256
$(CH_3)_2ClSiCH_2C_6H_5$	9.26 ±0.5	275.5	2.440	9.47 ±18.9	99.8	1.999
$CH_3Cl_2SiCH_2C_6H_5$	0.685 ±5.3	20.4	1.310	0.571 ±10	6.02	0.782
$Cl_3SiCH_2C_6H_5$	0.132 ±1.1	3.93	0.594	0.127 ±9.8	1.39	0.143

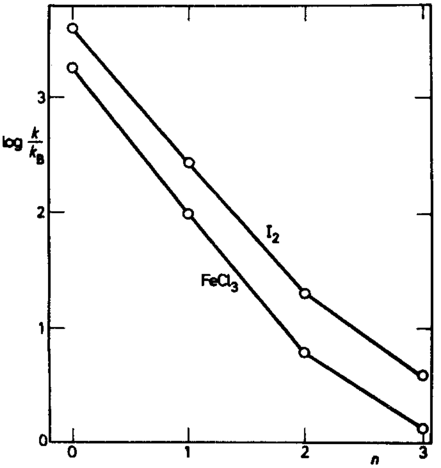


Fig. 1. *The dependence of* $\log k_{rel}$ *of benzylmethylchlorosilane chlorination* ($C_6H_5CH_2Si(CH_3)_{3-n}Cl_n$) *on the number of chloro substituents* (n)
3 molar % of Fe or I_2 used as catalyst; benzene taken as standard

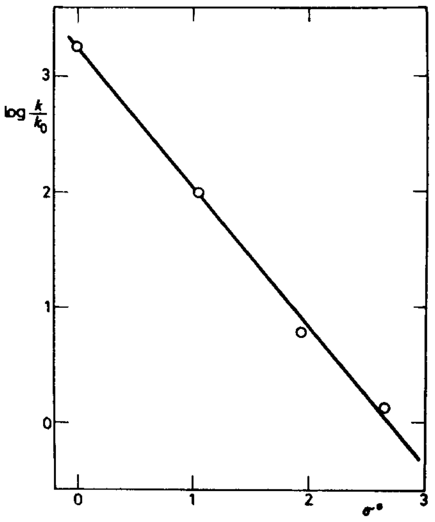


Fig. 2. *The dependence of* $\log k_{rel}$ *of benzylmethylchlorosilane chlorination* ($C_6H_5CH_2Si(CH_3)_{3-n}Cl_n$) *on the* TAFT's σ^* *values for* $-CH_{3-n}Cl_n$

Concomitant with this, the role of the competitive chloro-desilylation reaction to chlorobenzene sharply decreases. The two trends are even more apparent in the series of phenylmethylchlorogermanes [9] (Table IV). Whereas the trimethyl derivative is chlorinated still more markedly in *ortho* and *para* positions, the trichlorogermyl group directs to the *meta* position more markedly than does the trichlorosilyl group. The relatively greater differences between individual members of the germyl-substituted series can probably be ascribed to the ready polarizability of the germanium atom as compared with that of silicon. In the phenylgermane series, the role of the chloro-degermylation reaction decreases from the trimethyl to the trichloro derivatives more rapidly than in the phenylsilane series. It should also be mentioned that in all the members of the phenylsilane and phenylgermane series the percentage of the *o*-derivative is less than twice the amount of the *p*-derivative formed.

Let us now proceed to an examination of the relative reactivities of phenylmethylchlorosilanes [10]. Table V shows the experimentally obtained relative reactivities of

Table III. *Chlorination of phenylmethylchlorosilanes*
($t = 60° \pm 2°C$; 3-molar % catalyst)

Compound	% *o*-		% *m*-		% *p*-		*o*-/*p*-		(*o*+*p*)/*m*		% products of desilylation	
	Fe	I	Fe	I	Fe	I	Fe	I	Fe	I	Fe	I
$C_6H_5Si(CH_3)_3$	46.9	45.8	30.5	24.5	22.6	29.7	2.12	1.54	2.28	3.08	46.3	98.1
$C_6H_5Si(CH_3)_2Cl$	40.9	53.0	48.6	18.7	10.5	28.3	3.90	1.87	1.06	4.35	30.8	78.0
$C_6H_5Si(CH_3)Cl_2$	38.9	65.0	53.5	19.6	7.6	15.4	5.12	4.22	0.87	4.10	23.9	9.2
$C_6H_5SiCl_3$	37.5	67.4	55.8	29.1	6.7	4.5	5.60	19.26	0.79	2.44	5.3	2.6

Table IV. *Chlorination of phenylmethylchlorogermanes*
($t = 60 \pm 2°C$; 3-molar % catalyst)

Compound	% *o*-		% *m*-		% *p*-		*o*-/*p*-		(*o*+*p*)/*m*		% products of desilylation	
	Fe	I	Fe	I	Fe	I	Fe	I	Fe	I	Fe	I
$C_6H_5Ge(CH_3)_2$	53.2	53.5	27.5	28.2	19.3	18.1	2.75	2.96	2.64	2.55	57.2	85.2
$C_6H_5Ge(CH_3)_2Cl$	35.3	54.2	49.8	29.0	14.9	16.8	2.37	3.22	1.01	2.45	39.2	68.0
$C_6H_5Ge(CH_3)Cl_2$	37.5	52.9	52.4	32.9	10.1	14.2	3.71	3.73	0.91	2.04	22.0	45.0
$C_6H_5GeCl_3$	26.5	53.3	64.6	35.1	8.9	11.6	2.98	4.60	0.55	1.85	1.5	3.1

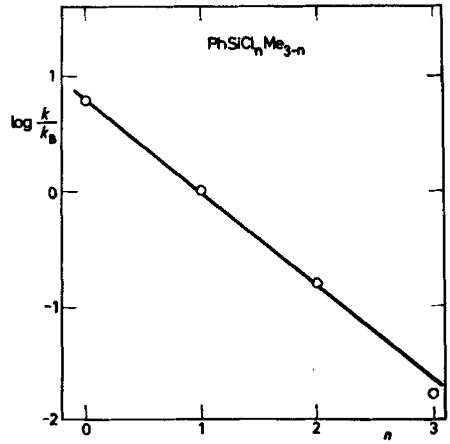


Fig. 3. *The dependence of* $\log k_{rel}$ *of phenylmethylchlorosilane chlorination* ($C_6H_5Si(CH_3)_{3-n}Cl_n$) *on the number of chloro substituents* (n)
3 molar % of Fe used as catalyst; benzene taken as standard

phenylsilanes referred to the organic standards used, cumene and bromobenzene. In Fig. 3 is shown a plot of the relationship between the relative reaction rate of chlorination of phenylsilanes catalysed by ferric chloride and the number of chlorine atoms in the silyl group. It can be seen that in this case the difference in $\log k/k_B$ between the various derivatives is roughly constant and the dependence of $\log k/k_B$ on the substitution is thus approximately linear. Analogous relationships between reactivity and the number of halogen atoms were obtained also in the chlorination of phenylmethylchlorogermanes [9] (Table VI).

Table V. *Chlorination of phenylchlorosilanes*
(3-molar % $FeCl_3$, 60°C)

	$(CH_3)_3SiC_6H_5$	$(CH_3)_2ClSiC_6H_5$	$(CH_3)Cl_2SiC_6H_5$	$Cl_3SiC_6H_5$
k/k_{cumene}	0.54	0.09	0.014	–
$k/k_{bromobenzene}$	–	2.75	0.53	0.06

Table VI. *Relative chlorination rates of phenylmethylchlorogermanes*
(60° ± 2°C, 3-molar % Fe)

Compound	$k/k_{Standard}$	$k/k_{benzene}$	reactivity of position		
			ortho	*meta*	*para*
$C_6H_5Ge(CH_3)_3$	2.37 [a]	26.40	42.15	43.60	15.25
$C_6H_5Ge(CH_3)_2Cl$	0.048 [a]	0.536	0.568	1.604	0.238
$C_6H_5Ge(CH_3)Cl_2$	0.163 [b]	0.0342	0.0384	0.1074	0.0105
$C_6H_5GeCl_3$	0.034 [b]	0.0071	0.0056	0.0276	0.0019

[a] cumene used as standard [b] bromobenzene used as standard

However, on the basis of our results, the separation of inductive effects of silyl or germyl substituents from their ability to form $(p \rightarrow d)\,\pi$ dative bonds between a central atom and the phenyl group (or even chlorine atoms) can be effected only with difficulty. A detailed discussion of the orientation on substitution and the relative reaction rates is not possible without perfect understanding of the character of the complexe formed by phenylmethylchlorosilanes and the corresponding germanes with the catalysts used. Whereas the formation of the complexes with ferric chloride can be proved only indirectly (on the basis of an abnormally high proportion of *ortho*-substitution), the formation of molecular complexes of phenylmethylchlorosilanes with iodine has been proved by measuring their UV. spectra and dipole moments. The ability for the formation of the above complexes is markedly higher as compared with the carbon analogous (for $(CH_3)_3SiC_6H_5$ $k_c = 0.72$, for $(CH_3)_3CC_6H_5$ $k_c = 0.39$), there being no doubt again, however, about its dependence on the number of chlorine atoms attached to the silicon atom (see *e. g.* Table VII). The formation of these complexes may, indeed, considerably change the original character of substituted compounds and, therefore, the discussion of structure effects on the reactivity of the non-complex compounds considered is not fully justified. The interpretation of the results obtained is further complicated by the fact that the basicity of the medium affords significant changes in the evaluation of the relative reactivities of the various pairs. We have found in our earlier work that the basicity of the medium plays an important role in the selectivity of the reactions of electrophilic agents. Also in this case of electrophilic aromatic chlorination, the differences between the reactivities of both components in a competitive reaction are increased in a more basic medium.

Table VII. *Dipole moments of phenylmethylchlorosilanes complexes with iodine*

Compound	$C_6H_5Si(CH_3)_3$	$C_6H_5Si(CH_3)_2Cl$	$C_6H_5Si(CH_3)Cl_2$	$C_6H_5SiCl_3$
μ complex (D)	8.2	6.6	1.5	–

To obtain, by employing another independent method, additional data concerning the significance of the formation of $(p \rightarrow d)\,\pi$ dative bonds in the compounds possessing the M-C_6H_5 bond, as well as of the polarizability of these compounds, we measured dipole moments of both series of compounds, *i. e.* of phenylmethylchlorosilanes [11] and of analogous germanes [12].

In applying dipole moments for an estimation of the $(p \rightarrow d)\,\pi$ nature of the silicon bonds, it is usual to proceed from a simple comparison of experimental values of dipole moments of analogous silicon and carbon derivatives. In view of the higher electropositivity of silicon, the organosilicon compounds will be expected to possess higher dipole moments. It is a common observation, however, that the silicon derivatives possess lower dipole moments than their carbon analogues. These anomalies are attributed to the possible contribution of structures of the type $\overset{-}{Si}{=}\overset{+}{X}$, the polarization of which decreases the overall dipole moment.

The magnitude of interaction of two groups linked to the silicon atom can be determined by comparing the experimental values of dipole moments of two compounds, in each of which only a single functional group represents the substituent, with the dipole moment of the bifunctional derivative. This comparison will show to what extent the polarity of one substituent is affected by the other.

To determine the extent of interaction between the atom of silicon and the phenyl group, we proceeded from a comparison of dipole moments of two series of compounds: $(CH_3)_{4-n}SiCl_n$ (I) [12] and $C_6H_5(CH_3)_{3-n}SiCl_n$ (II) (Table VIII).

Under the assumption that the bond angles of silicon are tetrahedral, that the moment of Si-CH_3 (0.2 D) is practically unaffected by other substituents at the silicon and is constant throughout, and that the moments of the $SiCl_n$ groups are constant for constant n, the dipole moment differences among compounds of series I and II for constant n are due only to the replacement of one methyl group by a phenyl group and determines qualitatively the difference between the group moments of Si-CH_3 and Si-C_6H_5. The dependence of the differences of dipole moments of the corresponding pairs from series I and II on the number of Cl atoms differs substantially from a similar relationship in series of analogously substituted allylsilanes and benzylsilanes [12].

We attempted to express quantitatively the magnitude of the group moment of Si-C_6H_5 to be able to observe directly the change of this moment in relation to the number of the X groups. Values of $\mu_{Si\text{-}C_6H_5}$ are shown in Table VIII.

The group moment of Si-C_6H_5 changes considerably with increasing n. Chlorine in phenylchlorosilanes acts on the Si-C_6H_5 bond first of all through its $-I$ effect and

Table VIII. *Experimental values of dipole moments of phenylmethylchlorosilanes and group moments Si-C_6H_5*

$C_6H_5(CH_3)_{3-n}SiCl_n$	μ D	$\mu_{\overrightarrow{\text{Si-R}}}$ D
$C_6H_5Si(CH_3)_3$	0.42	0.62
$C_6H_5(CH_3)_2SiCl$	2.11	0.14
$C_6H_5(CH_3)SiCl_2$	2.49	−0.14
$C_6H_5SiCl_3$	2.40	−0.27

supports the interaction of the π-electrons of the phenyl group with silicon. TOYODA & TANIGUCHI [13] attempted to calculate the induction effect of chlorine on the phenyl group, using the magnetic susceptibility and the dipole moments of phenylmethyldichlorosilane and diphenylmethylchlorosilane. They found a value of 0.12 D, which is in good agreement with 0.116 D calculated from the dipole moments of the phenylchlorosilane series of type $(C_6H_5)_{3-n}SiCl_n$. In view of the electrostatic interaction between chlorine atoms, their effect is not linear and the decrease of the Si-C_6H_5 moment is diminished with increasing n.

This trend toward a shift of the π-electrons of the phenyl group into the electron sphere of silicon (formation of the so-called $(p \rightarrow d)\ \pi$ dative bond) is supported also by *p*-substitution of the phenyl group with electron-releasing substituents. Different halogen atoms, a methoxy group, a methyl group, an amino and dimethylamino group and a nitro group were used by other authors for *p*-substitution. HUANG & HUI [14] measured the dipole moments of *p*-substituted trimethylphenylstannanes and found that whereas the methyl group and the methoxy group in *para* position cause the same effect as in analogous compounds of silicon, the halogen atoms show an opposite effect on the polarization of these compounds. An increase of polarity of the phenyl group with a tin atom is apparently associated with the low tendency of the tin atom toward formation of a $(p \rightarrow d)\ \pi$ bond with the phenyl group. The halogen atoms (in this case atoms of chlorine and bromine) play a role here mainly due to their $-I$ effect, while the $+M$ effect, which would support the formation of a $(p \rightarrow d)\ \pi$ bond, retreats into the background.

In connection with these facts it is of interest to establish what effect might be displayed by the chlorine atoms and by the *p*-substitution of the phenyl group in phenylmethylchlorogermanes, the central atom of which lies between silicon and tin in the periodic system of elements.

The dipole moments of all the compounds [15] examined here are shown in Tab. IX.

Phenylmethylchlorogermanes show in their entire series higher dipole moments than do phenylmethylchlorosilanes, but their changes are analogous. On comparing

Table IX. *Dipole moments of some phenyl-substituted germanes*

Compound	μ (D)	Compound	μ (D)
$C_6H_5Ge(CH_3)_3$	0.58	*p*-$CH_3C_6H_4GeCl_3$	3.71
$C_6H_5Ge(CH_3)_2Cl$	2.91	*p*-$CH_3OC_6H_4GeCl_3$	4.10
$C_6H_5Ge(CH_3)Cl_2$	3.28	*p*-$ClC_6H_4GeCl_3$	1.87
$C_6H_5GeCl_3$	3.15	*p*-$FC_6H_4GeCl_3$	1.93

them with methylchlorogermanes [16] one may see an increase of the difference in dipole moments of both the series as the number of chlorine atoms per molecule increases. For monochloro derivatives $\Delta\mu = 0.02$ D (within the limits of experimental error), for dichloro derivatives $\Delta\mu = 0.14$ D, and for trichloro derivatives $\Delta\mu = 0.45$ D. These differences may be explained only by the presence of a phenyl group in the molecule and by its interaction with the atom of germanium. The phenyl group is much more polarizable than the methyl group in methylchlorogermanes and its polarizability is markedly affected by chlorine atoms attached to germanium. The increase of dipole moments of phenylmethylchlorogermanes, as compared with values of methylchlorogermanes, corresponds to polarization of molecules as $\overrightarrow{\mathrm{PhGeCl_n}}$. The molecules of phenylmethylchlorogermanes are thus polarized thanks to the possibility of interaction of the π-electrons of the phenyl group with a germanium atom. This interaction is supported by the increasing $-I$ effect of the methylchlorogermyl groups. Therefore, the greatest deviations from the moment of the methyl analogue are shown by phenyltrichlorogermane.

If the hydrogen in the benzene ring at *para* position with respect to the trichlorogermyl group is replaced by a substituent X, the dipole moment will change. As long as the value of the dipole moment of compound C_6H_5X is known, one may calculate the moment of the rest of the molecule $C_{ar}GeCl_3$ and compare it with the moment of unsubstituted phenyltrichlorogermane. The dipole moments of different *p*-substituted derivatives are shown in Tab. IX. On substituting the *para* position with an atom of chlorine or fluorine, the dipole moment of phenyltrichlorogermane decreases, whereas substituents like the methyl or the methoxy group increase the dipole moment. This is caused both by the magnitude and by the orientation of the dipole moment of the corresponding compound C_6H_5X. Tab. X shows the differences between the experimental dipole moment of *p*-substituted phenyltrichlorogermanes and the dipole moments of C_6H_5X. For the calculation we used dipole moments of toluene (0.34 D), anisole (1.30 D), chlorobenzene (1.58 D) and fluorobenzene (1.50 D). It follows from the table that all these substituents increase the dipole moment of the rest of the molecule $C_{ar}GeCl_3$ as compared with that of unsubstituted phenyltrichlorogermane, in the sequence $CH_3 < F < Cl < OCH_3$. Whereas with the methyl group its $+I$ effect is important, the halogen atoms and the methoxy group act as electron donors, supporting the shift of the π-electrons of the phenyl group toward the central germanium atom. The methoxy group is most effective in this connection.

Table X. *Difference in the dipole moments of* p-$XC_6H_4GeCl_3$ *and* C_6H_5X

Compound	$C_6H_5GeCl_3$	*p*-$CH_3C_6H_4GeCl_3$	*p*-$OCH_3C_6H_4GeCl_3$	*p*-$ClC_6H_4GeCl_3$	*p*-$FC_6H_4GeCl_3$
$\mu_{exp}-\mu_{H_6X_5C}$	3.15	3.37	3.50	3.45	3.43

On comparing with the behaviour of the analogously substituted trimethylphenylsilanes and trimethylphenylstannanes, it may be seen, particularly for substitution with halogen atoms, that germanium as the central atom of these compounds is nearer, in its capacity to dislodge the π-electrons of the aromatic ring, to silicon than to tin.

As an example of another approach we shall present the results of basicity measurements of Si-O-C, Si-O-Si, Ge-O-C, Ge-O-Ge bonds. We have studied with the aid of infrared spectroscopy the relative basicities of oxygen atoms in model series of hexaalkyl-disiloxanes, hexaalkyl-digermoxanes, propylethoxysilanes, methyl-trimethylsiloxy-silanes, methylethoxygermanes, and propylethoxygermanes. The compounds studied are listed in Table XI.

As the relative measure of basicity we used the strength of hydrogen bonds. The strength of this bond was expressed as the difference in wave numbers $\Delta\nu$ of infrared absorption bands of the X–H bond of the non-associated proton donor (where X = O, N, C) and of the bond X–H---Y (where Y = O).

Table XI. *Compounds measured*

$Si(OC_2H_5)_4$	$Ge(OC_2H_5)_4$
n-$C_3H_7Si(OC_2H_5)_3$	$CH_3Ge(OC_2H_5)_3$
$(n$-$C_3H_7)_2Si(OC_2H_5)_2$	$(CH_3)_2Ge(OC_2H_5)_2$
$(n$-$C_3H_7)_3SiOC_2H_5$	$(CH_3)_3GeOC_2H_5$
$Si[OSi(CH_3)_3]_4$	
$CH_3Si[OSi(CH_3)_3]_3$	n-$C_3H_7Ge(OC_2H_5)_3$
$(CH_3)_2Si[OSi(CH_3)_3]_2$	$(n$-$C_3H_7)_2Ge(OC_2H_5)_2$
$(CH_3)_3SiOSi(CH_3)_3$	$(n$-$C_3H_7)_3GeOC_2H_5$
$[(CH_3)_3Ge]_2O$	$[(n$-$C_3H_7)_3Ge]_2O$
$[(C_2H_5)_3Ge]_2O$	$[(n$-$C_4H_9)_3Ge]_2O$

The proton acceptors of this bond were the oxygen containing compounds studied. As proton donors we employed the following compounds: phenol, 2,6-xylenol, methanol, ethanol, pyrrole, deuterochloroform and phenylacetylene. In Fig. 4 is shown summarily the shape of the absorption bands of hydrogen bonds of the listed proton donors with hexaethyl-digermoxane [17]. It was found that the relative basicities of the different series can be compared by employing pyrrole. For organosilicon compounds, phenol also was suitable. Phenol has a more acid hydrogen atom and small steric requirements. As can be seen from Fig. 5, the sterically more demanding 2,6-xylenol (curve 3) also forms hydrogen bonds with alkoxysilanes, but as is to be expected, the values of $\Delta\nu$ are much lower than those for phenol [18] (curve 1). Also the intensity of the associated band is much reduced, which is apparently the result of steric hindrance of the hydroxyl group. For silicon-containing compounds it was found that deuterochloroform is not suitable, nor phenylacetylene whose only slightly acid hydrogen is a negligibly weak donor for these compounds. However, phenylacetylene is suitable with alkylethoxygermanes. The formation of hydrogen bonds with phenylacetylene has also been confirmed with all the hexaalkyl-digermoxanes studied, although their associated bands have a considerable half-width and a very low intensity. When phenol was employed as the proton donor for tetraethoxygermane, re-esterification of the proton acceptor with the proton donor occured, with the formation of ethyl alcohol which acted as a further proton donor. The effect of the concentration of proton acceptors on the value of $\Delta\nu$ was investigated with tetraethoxygermane and tetraethoxysilane. In Fig. 6 is shown the concentration dependence for tetraethoxysilane with 0.02 M phenol. The differences in $\Delta\nu$ amount to 4 cm^{-1} at the most.

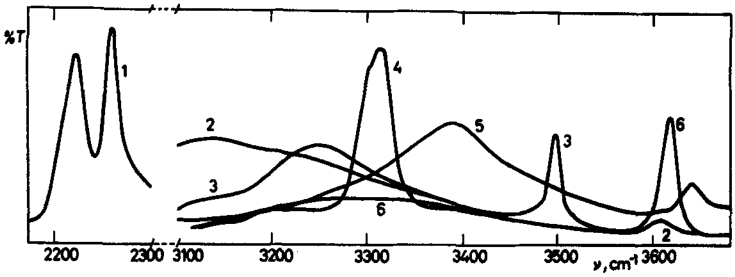


Fig. 4. *Infrared spectra of hydrogen bridges of hexaethyl-digermoxane with various proton donors in carbon tetrachloride*

1: Deuterochloroform; 2: Phenol; 3: Pyrrole; 4: Phenylacetylene; 5: Methanol; 6: 2.6-Xylenol

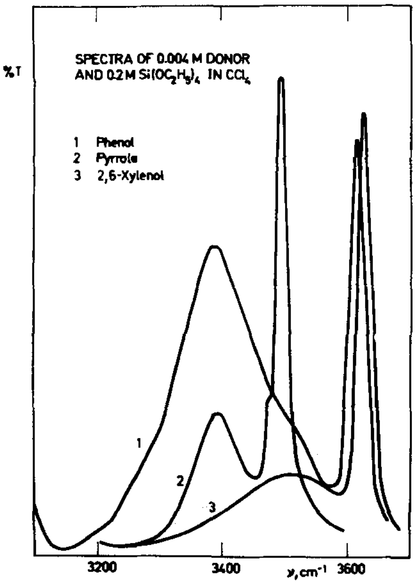


Fig. 5. *Infrared spectrum of the hydrogen bond in systems containing tetraethoxysilane as proton donor* Determined in 1 cm Infrasil cells in tetrachloromethane solution. Tetraethoxysilane was 0.2 mol/l the proton donor was 0.004 mol/l. 1: Tetraethoxysilane-phenol; 2: tetraethoxysilane-pyrrole; 3: tetraethoxysilane-2.6-xylenol

It is interesting to note that, in contrast to organosilicon compounds and alkylethoxygermanes, all the hexaalkyl-digermoxanes form hydrogen bonds also with the weakly acid and sterically demanding deuterochloroform (curve 1, Fig. 4). The reason for this is apparently the smaller angle of the Ge-O-Ge bond as compared with that of the Si-O-Si bond, as a result of which the electron pair in the former bond is more accessible. In accordance with our desire to use several proton donors with each proton acceptor, we employed in the case of germanium acceptors also alkyl alcohols in place of the unsuitable phenol. It seems that, compared to compounds with the Ge-O-C bond, the more stable germoxanes do not undergo re-esterification with phenol. However, the strongly diffuse associated band of this hydrogen bond has its flat maximum in the immediate neighbourhood of the stretching vibrations of C-H bonds, and this makes the estimate of $\Delta\nu$ very inaccurate. The situation is similar with 2.6-xylenol (curve 6, Fig. 4).

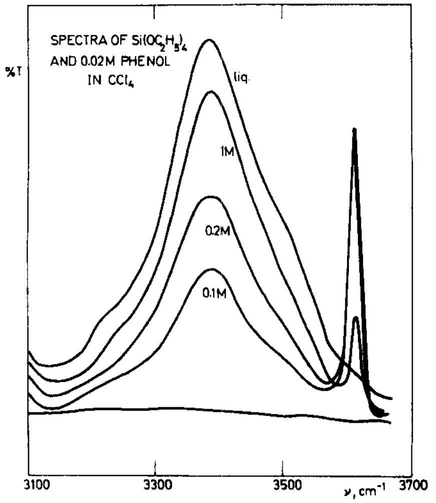


Fig. 6. *Spectra of tetraethoxysilane and 0.02* M *phenol in carbon tetrachloride*

The comparison of the values of $\Delta\nu$ (Fig. 7), obtained in the manner described above, confirms that the relative basicity of oxygen decreases in going from ethers *via* alkoxysilanes to siloxanes [4]. This can be interpreted as being due to the withdrawal of the oxygen electron as a result of its π-bond with silicon. This is also supported by the marked decrease of the basicities of siloxanes as compared with those of ethers and germoxanes.

If we compare the relative basicities of hexaalkyl-disiloxanes (Fig. 8, curve with ●) given by ENGELHARDT [19] with the values for the analogous hexaalkylgermoxanes

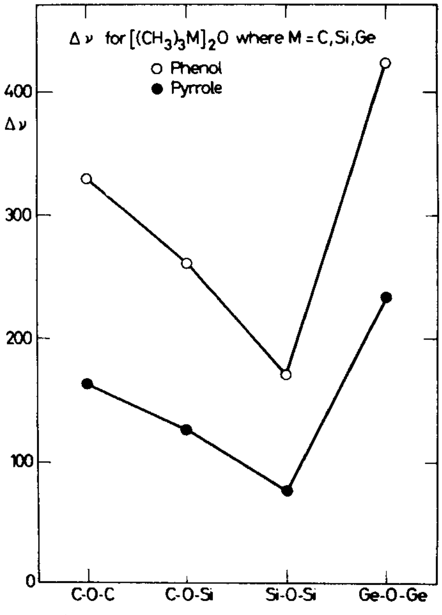


Fig. 7. *$\Delta\nu$ for $[(CH_3)_3M]_2O$, where M = C, Si, Ge*

prepared by us, we find that in both series they decrease from the butyl derivative to the methyl derivative; this is due to the positive inductive effect of the alkyl groups. The largest difference, as expected, is between the methyl derivatives and ethyl derivatives. Although the differences between ethyl, propyl and butyl derivatives are practically within the experimental error, our explanation is fully confirmed by the fact that the changes are systematic, which has been determined by measuring the $\Delta\nu$ values of germoxanes with several proton donors (phenol, 2.6-xylenol, pyrrole, methanol, deuterochloroform and phenylacetylene).

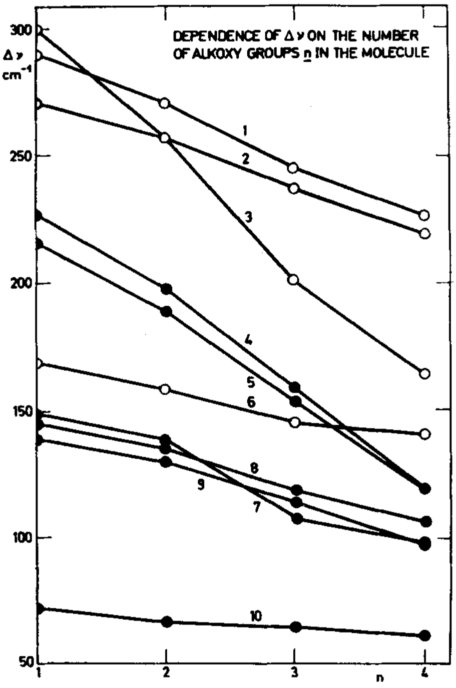


Fig. 8. *Comparison of basicities of some hexaalkyl-disiloxanes and hexaalkyl-digermoxanes*

The plot in Fig. 9 represents the dependence of some values of $\Delta\nu$ on the number of alkoxy groups in the molecules of alkylethoxysilanes and their germanium and carbon analogues, and of methyl-trimethylsiloxy-silanes. Analogously to alkylsiloxanes and alkylgermoxanes [20], also propylethoxysilanes (curve 1 and 8) and propylethoxygermanes (curve 4) display higher basicities with phenol (●) and pyrrole (○) than the corresponding derivatives (curves 2, 9, 5). The values of $\Delta\nu$ for methylethoxysilanes (curves 2, 9) and their carbon analogues (curves 3, 7) were taken over from WEST and coworkers [21].

In all the series investigated, we observed a systematic decrease in basicity with the increasing number of alkoxy groups; this is undoubtedly due to their $-I$ effect.

The basicity of the individual members in each series decreases approximately linearly, which is in accordance with the additivity of the inductive effects of the substituents. Deviations from linearity are largest for the series with a central carbon atom, they are smaller for silicon compounds and smallest for germanium derivatives. This indicates that the deviations are apparently the result of steric hindrance of the substituents. This is also supported by the fact that within the carbon series the deviation from linearity is less when phenol is used as the proton donor than when the sterically substantially more demanding pyrrole is employed (curve 7).

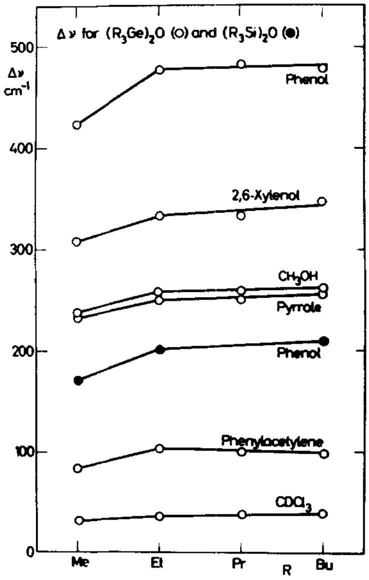


Fig. 9. *Dependence of Δν on the number n of alkoxy groups in the molecule*

As proton donors we used phenol (●) and pyrrole (⊙). 1: $(C_3H_7)_{4-n}Si(OC_2H_5)_n$; 2: $(CH_3)_{4-n}Si(OC_2H_5)_n$ [18]; 3: $(CH_3)_{4-n}C(OC_2H_5)_n$ [18]; 4: $(C_3H_7)_{4-n}\cdot Ge(OC_2H_5)_n$; 5: $(CH_3)_{4-n}Ge(OC_2H_5)_n$; 6: $(CH_3)_{4-n}Si[OSi(CH_3)_3]_n$; 7: $(CH_3)_{4-n}C(OC_2H_5)_n$ [18]; 8: $(C_3H_7)_{4-n_n}Si(OC_2H_5)_n$; 9: $(CH_3)_{4-n}Si(OC_2H_5)_n$ [18]; 10: $(CH_3)_{4-n}Si[OSi(CH_3)_3]_n$

It is also of interest to compare the differences in the slopes of the curves representing the dependence of the basicity on the degree of substitution. The curves are steepest for carbon derivatives (curve 3) and for germanium derivatives (curves 4, 5). This indicates that in all the members of these series practically only the $-I$ effect of alkoxy groups plays a role.

In organosilicon ethoxy derivatives this effect is reduced by the interaction in the opposite sense of the electron pair shared by oxygen and silicon. For monoethoxysilicon compounds this $(p \rightarrow d)\,\pi$ dative nature of the Si-O bond reduces the basicity of oxygen below the value found for *t*-butyl ethyl ether, which is in agreement with previously obtained results.

With alkyltriethoxysilanes and tetraethoxysilanes it is probably not possible to obtain such a significant interaction with all the oxygen atoms; therefore the basicity decreases relatively slowly with the increasing number of ethoxy groups. Hence, it attains higher values than with the analogous carbon compounds, in accordance with the fact that the electronegativity of carbon is higher than that of silicon.

The significance of the electronegativity of the central atom is most distinctly apparent from the high basicities found for all the ethoxygermanes investigated: in these compounds the high basicity due to the significant electron enrichment of oxygen by the germyl group is practically unaffected by any of the π-interactions between oxygen and germanium.

The most pronounced differences in basicities have been found between monoethoxysilanes and monoethoxygermanes, which is in agreement with the concept that the $(p \rightarrow d)\,\pi$ nature of the Si-O bond is most marked in monoethoxysilanes. Tetraethoxygermane is only a little more basic than tetraethoxysilane; this again supports the concept that in tetraethoxysilane the contribution of the π-interaction of each oxygen atom separately is no longer very significant.

The smallest differences in basicities have been found between individual methyltrimethylsiloxy-silanes (curve 6, 10). This can also be taken as indirect evidence for the earlier given concept: whereas every oxygen atom can interact with the silicon of the trimethylsiloxy group, its interaction with the central silicon atom becomes less significant; even in tetrakis-trimethylsiloxy-silane the electropositivity of the central atom is not significant and the basicity of all the members of these series is exceptionally low.

To verify the correctness of our considerations we made an attempt to confirm the differences found between the nature of the Si-O bond and that of the Ge-O bond by measuring the dipole moments of the series of methylethoxygermanes, propylethoxygermanes and of the analogous silicon derivatives.

The experimental results and the dipole moments of all the compounds described here were summarized in Table XII.

Table XII. *Dipole moments of some organosilicon and organogermanium compounds*

Compound	μ (D)	Compound	μ (D)
n-$C_3H_7GeCl_3$	3.01	$CH_3Ge(OC_2H_5)_3$	1.76
$(n$-$C_3H_7)_2GeCl_2$	3.42	$(CH_3)_2Ge(OC_2H_5)_2$	1.51
$(n$-$C_3H_7)_3GeCl$	2.82	$(CH_3)_3GeOC_2H_5$	1.60
$(n$-$C_3H_7)_4Ge$	0	n-$C_3H_7Si(OC_2H_5)_3$	1.80
CH_3GeCl	2.70 [15]	$(n$-$C_3H_7)_2Si(OC_2H_5)_2$	1.22
$(CH_3)_2GeCl_2$	3.14 [15]	$(n$-$C_3H_7)_3SiOC_2H_5$	1.03
$(CH_3)_3GeCl$	2.89 [15]	n-$C_3H_7Si(CH_3)_3$	0.34
$Ge(OC_2H_5)_4$	1.75	$CH_3Si(OC_2H_5)_3$	1.70
n-$C_3H_7Ge(OC_2H_5)_3$	1.76	$(CH_3)_2Si(OC_2H_5)_2$	1.36
$(n$-$C_3H_7)_2Ge(OC_2H_5)_2$	1.52	$(CH_3)_3SiOC_2H_5$	1.17
$(n$-$C_3H_7)_3GeOC_2H_5$	1.45		

Using the value of 1.0 D for the bond moment of Ge-H [7] and the dipole moments of methylgermanes, the group moments of Ge-CH_3 were calculated:

$$\begin{aligned} CH_3GeH_3&:\ m(\overrightarrow{\mathrm{GeCH_3}}) = 0.36\ \mathrm{D}\\ (CH_3)_2GeH_2&:\ = 0.34\ \mathrm{D}\\ (CH_3)_3GeH&:\ = 0.33\ \mathrm{D} \end{aligned}$$

With the aid of the moments of the Ge-CH_3 groups found here the bond moments of the Ge-Cl bond were calculated for methylchlorogermanes (on the basis of the average values of the dipole moments of methylchlorogermanes determined by different authors and shown in Table XII):

$$\begin{gathered}\mathrm{CH_3GeCl_3}\colon \overrightarrow{\mathrm{m(GeCl)}} = 0.03\ \mathrm{D}\\ \mathrm{(CH_3)_2GeCl_2}\colon = 3.07\ \mathrm{D}\\ \mathrm{(CH_3)_3GeCl}\colon = 3.17\ \mathrm{D}\end{gathered}$$

These bond moments were used for calculating the group moment of the propyl group attached to the germanium atom in propylchlorogermanes, under the assumption that the replacement of the methyl groups by propyl groups has no apparent effect on the magnitude of m(GeCl):

$$\begin{gathered}n\text{-}\mathrm{C_3H_7GeCl_3}\colon \overrightarrow{\mathrm{m(GeC_3H_7)}} = 0.02\ \mathrm{D}\\ (n\text{-}\mathrm{C_3H_7)_2GeCl_2}\colon = 0.09\ \mathrm{D}\\ (n\text{-}\mathrm{C_3H_7)_3GeCl}\colon = 0.36\ \mathrm{D}\end{gathered}$$

It is understood that the moments calculated here represent only approximate values, since a tetrahedric arrangement around the germanium atom is assumed and only negligible changes of the bond moment of Ge-H in the methylgermane series are postulated. Moreover, it must be assumed that the moment of the Ge-$\mathrm{CH_3}$ group remains constant upon transition from methylgermanes to methylchlorogermanes, just as do the moments of Ge-Cl upon transition from methylchlorogermanes to propylchlorogermanes.

The calculated values still show quite clearly that the moment of the Ge-$\mathrm{C_3H_7}$ group, in contrast with that of the Ge-$\mathrm{CH_3}$ group, decreases pronouncedly with an increasing number of chlorine atoms in the molecule. This points to a greater polarizability of the propyl group attached to germanium as compared with the methyl group. In view of this fact one must exercise caution in applying the moment of the Ge-$\mathrm{C_3H_7}$ group calculated from propylchlorogermanes to propylethoxygermanes, whereas the error incurred on applying the Ge-$\mathrm{CH_3}$ group moment in methylethoxygermanes should be negligible. For the sake of comparison we have determined the moments of Ge-$\mathrm{C_3H_7}$ also in propylethoxygermanes by establishing first the contribution of the ethoxy groups to the overall dipole moment of methylethoxygermanes:

$$\begin{gathered}\mathrm{CH_3Ge(OC_2H_5)_3}\colon \mathrm{m[Ge(OC_2H_5)_3]} = 2.12\ \mathrm{D}\\ \mathrm{(CH_3)_2Ge(OC_2H_5)_2}\colon \mathrm{m[Ge(OC_2H_5)_2]} = 1.90\ \mathrm{D}\\ \mathrm{(CH_3)_3GeOC_2H_5}\colon \mathrm{m(GeOC_2H_5)} = 1.89\ \mathrm{D}\end{gathered}$$

These values and the experimental dipole moments of propylethoxygermanes were then used for calculating the values of the group moment of Ge-$\mathrm{C_3H_7}$ in relation to the number of ethoxy groups in the molecule:

$$\begin{gathered}n\text{-}\mathrm{C_3H_7Ge(OC_2H_5)_3}\colon \overrightarrow{\mathrm{m(GeC_3H_7)}} = 0.36\ \mathrm{D}\\ (n\text{-}\mathrm{C_3H_7)_2Ge(OC_2H_5)_2}\colon = 0.33\ \mathrm{D}\\ (n\text{-}\mathrm{C_3H_7)_3GeOC_2H_5}\colon = 0.56\ \mathrm{D}\end{gathered}$$

It is assumed in this connection that the contribution of the ethoxy groups in methyl- and propyl-ethoxygermanes are the same, the dipole moments of methyl- and propyl-ethoxygermanes are the same and hence the group moments of the methyl and propyl groups are identical. An exception is afforded here by tripropylethoxygermane, the dipole moment of which is slightly lower than that of the corresponding trimethyl derivative. This corresponds to a smaller contribution of the $(C_3H_7)_3GeO$ group as compared with the $(CH_3)_3GeO$ group, apparently due to mutual steric repulsion of the propyl groups. Contributions of these groups to the overall dipole moments have been estimated.

To calculate the moments of the $(CH_3)_3GeO$ group in trimethylethoxygermane the following values were used: $m(OC_2H_5) = 1.10$ D, for the angle of GeOC 113°, the other angles being those of a tetrahedron. By a vector sum the value of 1.67 D was found. An analogous calculation for tripropylethoxygermane yields the group moment for $(n\text{-}C_3H_7)_3GeO$ equal to 1.47 D.

Since $m[(CH_3)_3GeO] = m(GeO) - m[(CH_3)_2Ge]$, one should be able to use the moment of the trimethylgermyl group (0.33 D) for calculating directly the moment of the Ge-O bond: $m(GeO) = 2.00$ D.

If this type of calculation is applied to tripropylethoxygermane, using for the $(n\text{-}C_3H_7)_3Ge$ group moment the value obtained from tripropylchlorogermane (0.35 D), one obtains the value of 1.82 D for the moment of the Ge-O bond. In view of the more pronounced $+I$ effect of the propyl group as compared with that of the methyl group, one might rather expect a greater bond moment m(GeO) in tripropylethoxygermane. It thus appears that, due to the inconstancy of the moment of the $Ge\text{-}C_3H_7$ group, one cannot use the value obtained from one compound for obtaining this value in a compound of another type.

In addition to the values of group moments, the overall dipole moments of alkylethoxygermanes are affected by the possibility of rotation of the terminal alkyl groups. For this reason the theoretical dipole moments of methylethoxygermanes and propylethoxygermanes were calculated using EYRING's formula, which is valid on the assumption that only free rotation takes place in the molecule. The values obtained (Table XIII) are in all cases higher than those experimentally found, which points to the fact that free rotation in these compounds can be very probably excluded and that the existence of certain conformations or mixtures of various conformations must be assumed.

Table XIII. *The theoretical dipole moments of alkylethoxysilanes and alkylethoxygermanes*

Compound	μ_{theor}	μ_{exp}
$CH_3Si(OC_2H_5)_3$	1.85	1.70
$(CH_3)_2Si(OC_2H_5)_2$	1.59	1.36
$CH_3Ge(OC_2H_5)_3$	2.09	1.76
$(CH_3)_2Ge(OC_2H_5)_2$	2.00	1.51
$n\text{-}C_3H_7Si(OC_2H_5)_3$	1.88	1.80
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$	1.53	1.22
$n\text{-}C_3H_7Ge(OC_2H_5)_3$	2.11	1.76
$(n\text{-}C_3H_7)_2Ge(OC_2H_5)_2$	2.03	1.52

In order to compare the polarity of the bonds of the propyl groups attached to germanium and to silicon, the moments of the $n\text{-}C_3H_7Si$ group were calculated by a procedure analogous to that described for germanium derivatives. For the calculation we used the following values: $m(C_2H_5O) = 1.10$ D, $m(SiCH_3) = 0.2$ D, the angle of SiOC being 113°, the other angles being those of a tetrahedron. The contributions of the $SiOC_2H_5$, $Si(OC_2H_5)_2$ and $Si(OC_2H_5)_3$ groups to the overall moments of methylethoxysilanes are 1.29 D, 1.59 D and 1.90 D, respectively. If it is assumed that these contributions change only negligibly on replacing methyl by propyl groups, one can calculate the moment of the propyl group attached to silicon:

$$
\begin{aligned}
n\text{-}C_3H_7Si(OC_2H_5)_3&:\ m(\overrightarrow{Si\text{-}C_3H_7}) = 0.08\ D\\
(n\text{-}C_3H_7)_2Si(OC_2H_5)_2&:\ = 0.32\ D\\
(n\text{-}C_3H_7)_3SiOC_2H_5&:\ = 0.58\ D
\end{aligned}
$$

The moment of the propyl group calculated from trimethylpropylsilane is 0.54 D. In trimethylethoxysilanes we found the value of 1.03 D for the moment of the $(CH_3)_3SiO$ group, which is in agreement with the value published for this moment in trimethylmethoxysilane [22]. Hence the moment of the Si-O bond is equal to 1.23 D. In comparison with the Ge-O bond the Si-O bond is thus much less polarized.

Similarly to alkylethoxygermanes, the moment of the $(n\text{-}C_3H_7)_3SiO$ group in alkylethoxysilanes (0.65 D) is much lower than that of $(CH_3)_3SiO$ (1.03 D). An explanation may be sought in the steric effect of the voluminous propyl groups, which is even more marked in silicon derivatives in comparison with germanium derivatives, in view of the smaller volume of the central atom.

As to the possibility of rotation of the ethyl groups in alkylethoxysilanes, one can assume, on the basis of temperature dependences found by FERENCZI-GRESZ [23], free rotation to occur only in trimethylethoxysilane. In the other methylethoxysilanes, and even more so in propylethoxysilanes, the possibility of free rotation of the ethyl groups is nil. This is indicated also by a comparison of the experimental dipole moments with the theoretical ones. The dipole moments calculated are shown in Table XIII.

The lower polarity of silicon bonds as compared with germanium bonds is evident in the moments of the Si-Cl bonds in methylchlorosilanes. These bond moments were computed from a vectorial calculation from the dipole moments of the methylchlorosilanes:

$$
\begin{aligned}
CH_3SiCl_3&:\ m(\overrightarrow{Si\text{-}Cl}) = 2.13\ D\\
(CH_3)_2SiCl_2&:\ = 2.21\ D\\
(CH_3)_3SiCl&:\ = 2.29\ D
\end{aligned}
$$

The bond moments of the Ge-Cl and Si-Cl bonds in the analogous methyl-chloro derivatives correspond to the ratio 1.38–1.42. Since the moments of the Ge-O and Si-O bonds cannot be calculated for the di- and triethoxy derivatives, they were expressed by the quotients of dipole moments of methyl- and propyl-ethoxygermanes and the corresponding methyl- and propyl-ethoxysilanes. Their values (from the mono- to the triethoxy derivatives) are the following: 1.36, 1.11 and 1.04 for the methyl derivatives, and 1.41, 1.21 and 0.98 for the propyl derivatives. In view of the fact that both the covalent radii and the electronegativities of silicon and germanium atoms are very similar, one can account for the high quotients by assuming that the $(p \rightarrow d)\,\pi$ interaction plays a much greater role in the Si-Cl and Si-O bonds than in the corresponding germanium ones. A decrease of the quotients with increasing number of the ethoxy groups in the molecule indicates that the role of the $(p \rightarrow d)\,\pi$ interaction is greatest in monoethoxysilanes and then gradually decreases.

On the basis of our results we can draw the conclusion that silicon and germanium differ from carbon by the possibility of using the vacant *d*-orbitals, and by lower electronegativity and higher polarizability. The difference between germanium and silicon is relatively small, as far as electronegativity is concerned, and it is somewhat more important in the case of polarizability. As far as the differences in ability to form bonds of the $(p \rightarrow d)\,\pi$ type are concerned, no general comparison can be made: while, from this point of view, there is no substantial difference between the Si-C_6H_5 and Ge-C_6H_5 bonds, in the case of other bond types (*e. g.* bonds with oxygen) these differences are very marked.

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241. L'hydrolyse acide des diazocétones alcoylées: formation d'ions α-acylcarbonium secondaires

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(3 X 69)

Summary. Hydrolysis of secondary diazoketones CH_3–CO–CN_2–R (R = Me, Et, isopropyl) by aqueous perchloric acid is characterized by rate-determining protonation demonstrated by solvent isotope effects k_{D_2O}/k_{H_2O} = 0,4–0,6 and by the intervention of general acid catalysis. The product determining step, yielding keto-alcohols and keto-olefines, is independent of added nucleophiles;

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[1]) Extrait de la thèse de M. BALLENEGGER, Lausanne 1967.