ORGANOGERMANIUM COMPOUNDS. XIV.*

THE CATALYSED BROMINATION OF PHENYLMETHYLCHLOROGERMANES

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Directing effects of substituted germyl groups have been studied and relative rates of the iron- and the iodine-catalysed bromination of the phenylmethylchlorogermanes $C_6H_5(CH_3)_{3-n}GeCl_n$ ($n = 0-3$) been determined by the method of competition reactions. The germyl groups are mainly o,p-directing, methyldichlorogermyl group exhibiting the strongest effect. The reactivity of the compounds decreases with increasing number of halogens in the germyl group. The bromination is accompanied by the bromodegermylation which with all members of the series proceeds at a faster rate than the bromination, its extent decreasing with increasing electronegativity of the germyl group. Also the iododegermylation, taking place in the iodine-catalysed bromination, is always faster than the bromination.

Directing effects of germyl groups in bromination have not yet been studied. Only distribution of isomers and the reactivity of phenylmethylchlorogermanes in their chlorination catalysed by ferric chloride or by iodine in the absence of a solvent have been reported[1]. Germyl groups in this series changed from o,p-directing to m-directing with increasing number of chlorines in the germyl group. The only compound which was found to be more reactive than benzene was phenyltrimethylgermane. When compared with the chlorination of the series of silicon analogues, germanium appears to be more electropositive than silicon[2] and also it shows lesser ability to form $(p \rightarrow d)$ π bonds, both of the Ge—C_{ar} and of the Ge—Hal type[3,4].

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Side reactions taking place in electrophilic bromination of phenylgermanes are cleavage reactions of the Ge—C_{ar} bond. Demetalation reactions are electrophilic in nature and are assumed to proceed by the commonly accepted S_E2 mechanism, *via* the formation of benzenium ion of the same character as in other electrophilic reactions[5]. Some authors have suggested for the cleavage of M—C_{ar} bonds a mechanism which involves, however, a four-center transition state, *e.g.* of type[6] I, or the coordination of type[7] II. Eaborn and Pande[8] reported that the rate of protodegermylation

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by perchloric acid is in aqueous-ethanolic solution 36-times faster than the rate of protodesilylation.

In the brominations catalysed by iodine the formation of iodobromine in the reaction mixture is assumed to occur in some cases, since in tetrachloromethane at 25°C the equilibrium is shifted in favour of this compound ($\Delta G = -1\,746$ cal/mol)[9]. Iodobromine is more active species than iodine or bromine molecules. The iodine-catalysed bromination of benzene[10] and of alkylbenzenes[11] has been described by kinetic equation including iodobromine term. In a nonpolar solvent bromination can be effected directly by iodobromine, while iodination[12,13] is the only reaction occuring under the same conditions in polar solvents.

We believed that a study of the bromination of the series of phenylmethylchlorogermanes carried out at the same conditions as was the bromination of phenylmethylchlorosilanes and phenylmethylfluorosilanes[14] should contribute to the explanation of the difference between the properties of the same silyl or germyl groups in bromination and chlorination, as well as to further comparison of the properties of the compounds of germanium and silicon.

EXPERIMENTAL

Phenylmethylchlorogermanes for kinetic measurements were prepared by Grignard syntheses. Phenyltrimethylgermane[1] was obtained in 54% yield by methylation of phenyltrichlorogermane with methylmagnesium chloride in excess, followed by usual work-up of the formed mixture and by fractional distillation at reduced pressure. Phenyldimethylchlorogermane[1] was prepared from dimethyldichlorogermane and phenylmagnesium bromide. After the extraction of the salts, rectification yielded the product in 60% yield (relative to dimethyldichlorogermane).

Phenylmethyldichlorogermane, prepared previously[1], was freshly redistilled prior to measurements. Phenyltrichlorogermane[1] was prepared by adding dropwise an ethereal solution of phenylmagnesium bromide to germanium tetrachloride, followed by extraction of the salts formed.

m-*Bromophenyltrimethylgermane* was obtained by the reaction of ethereal solution of m-bromophenylmagnesium bromide, prepared from 0·4 mol (94 g) of m-dibromobenzene and 0·4 mol (9·8) of magnesium turnings, with 0·53 mol (113 g) of germanium tetrachloride. The reaction mixture was directly methylated by 3 mol of methylmagnesium chloride and worked-up in the usual manner. Distillation through the column filled with kanthal wire rings afforded 14 g (13%, with respect to the starting m-dibromobenzene) of m-bromophenyltrimethylgermane. The p-bromo derivative was prepared similarly from 0·5 mol (118 g) of p-dibromobenzene, 0·5 mol (12·2 g) of magnesium, 0·6 mol (129 g) of germanium tetrachloride and 3·5 mol of methylmagnesium chloride in 6% yield (8 g; calculated with respect to p-dibromobenzene). The purity of all the compounds was checked chromatographically[16]. The analyses and physical constants of the prepared compounds are presented in Table I.

Bromination was carried out at 40°C in 70% n-heptane as solvent, using 3 mol % catalyst (iron powder or iodine). The procedure used in bromination and the work-up of samples for chromatographic analysis were described in detail elsewhere[14,16]. The distribution of isomers was analysed with the use of the same stationary phase as in the case of phenylchlorosilanes[14] (a Benton B-34-silicon elastomer E-302 mixed phase) at identical conditions. In the case of the germanium compounds the separation of phenyltrimethylgermane from bromobenzene occurred on this phase, which made it possible to determine the areas of both compounds, needed for calculations of bromodegermylation constants, from one analysis. Competitive bromination of the phenylmethylchlorogermanes (with the use of chlorobenzene as experimental standard), the analy-

ses of reaction mixtures and the calculations of relative rate constants of bromination were also carried out in the same way as in the case of phenylmethylhalogenosilanes[14]. Relative rate constants of bromodegermylation and iododegermylation were defined as $k(Br) = C/B$, and $k(I) = D/B$, respectively, both constants being related to simultaneously occurring bromination of the same compound. B stands for the molar concentration of bromophenyltrimethylgermanes, C for bromobenzene and D is the molar concentration of iodobenzene, all in the resultant reaction mixture. From experimental relative rate constants of bromination of the phenylmethyl-chlorogermanes, relative to chlorobenzene, the rate constants with respect to benzene were calculated, along with the reactivity of individual positions in the aromatic nucleus.

The accuracy of the calculated values of k was expressed by the standard deviation of the averaged value (s) and by the coefficient of variation (v)[16,19]. The mean values of the coefficient of variation were 5% for isomer distribution analysis, 8% for determination of relative rate constants of bromination, and 7% for the values of the constants characterizing cleavage reactions.

RESULTS AND DISCUSSION

Determination of directing effects of germyl groups. Average distribution of isomers in bromination of the phenylchlorogermanes, calculated from at least three parallel determinations, is given in Table II, along with the quantities characterizing the error in their determination. In the bromination catalysed by both catalysts the germyl groups are strongly *o,p*-directing, most strongly methyldichlorogermyl group (similarly as methyldichlorosilyl and methyldifluorosilyl groups[14]). In the chlorination of these compounds it has been observed that weak *o,p*-directing effect of germyl groups changed to *m*-directing effect with increasing number of chlorine atoms in the germyl group[1]. *o,p*-Directing effect of germyl groups is more pronounced

TABLE I
Physical Constants of Prepared Germanes

Compound	n_D^{20}	d_4^{22}	B.p. (°C/Torr) found	B.p. (°C/Torr) lit.	Halogen found	Halogen calc.
$C_6H_5(CH_3)_3Ge^a$	1.5071^b	1.1180^c	82/29	$77.5-78/22.5^{17}$	—	—
$C_6H_5(CH_3)_2GeCl$	—	—	132.5/30	$99/6^1$	16.32	16.47
$C_6H_5(CH_3)GeCl_2$	—	—	$102-102.5/5$	$113/7^1$	29.92	30.09
$C_6H_5GeCl_3$	—	—	102/11	$118-119/24^{18}$	41.29	41.54
$p\text{-}BrC_6H_4(CH_3)_3Ge^d$	1.5454	1.4308	131/23	$118/20^{15}$	29.14	29.20
$m\text{-}BrC_6H_4(CH_3)_3Ge^e$	1.5450	1.4330	127.5/25	—	28.95	29.20

^{a} For $C_9H_{14}Ge_1$ found: 55.33% C, 7.21% H; calculated: 55.49% C, 7.24% H. ^{b} Lit.[1] 1.5070. ^{c} Lit.[1] d_4^{20} 1.1174. ^{d} For $C_9H_{13}Br_1Ge_1$ found: 39.76% C, 4.76% H; calculated: 39.49% C, 4.79% H. ^{e} For $C_9H_{13}Br_1Ge_1$ found: 39.65% C, 4.76% H; calculated: 39.49% C, 4.79% H.

in the bromination catalysed with iodine. Methyldichlorogermyl group directs in the presence of both catalysts more to positions *ortho* and *para* than does the silyl group containing the same number of halogen atoms[14]. The explanation offerred by Stoffey[20] of the different directing effects of silyl groups in bromination, compared with chlorination, is not obviously correct also in the case of germyl groups[14]. This is clearly seen when a lower ability of germanium, relative to silicon, to form $(p \to d)\pi$ bonds with halogens is compared with the higher extent of o,p-direction induced by germyl groups. The greater amount of o,p-isomers in the case of germyl groups can probably be accounted for by a more distinct positive inductive action of germyl groups, compared to silyl groups. The directing effect of germyl groups is influenced predominantly by the formation of specific complexes, obviously of charge-transfer type[21], with bromine and catalysts, which change the character of the group so much that *e.g.* trichlorogermyl group, which — with respect to its purely inductive effect — should have been m-directing, is in the iodine-catalysed reaction still strongly o,p-directing. The nature of the complex cannot be, of course, only the result of electron-donor action of the aromatic nucleus in the formation of a charge-transfer complex, but it is probably affected also by the coordination ability of a germyl group, which could play a role only during polarisation of the molecule in the formation of the complex. A comparatively small o,p-directing effect of trimethylgermyl group (even smaller than that of trimethylsilyl group) may not be real. The found $o + p/m$ ratio can probably be influenced by subsequent cleavage of bromophenyltrimethylgermanes which is more extensive than in the case of bromo-

TABLE II

Directing Effects of Germyl Groups in Bromination of Phenylmethylchlorogermanes (40°C, 3 mol% catalyst, 70% n-heptane)

Compound	o, %	s	v, %	m, %	s	v, %	p, %	s	v, %	$o + p/m$	p/o
					Catalyst iron						
$C_6H_5(CH_3)_3Ge$	44·5	0·3	0·7	29·4	0·2	0·8	26·1	0·3	1·0	2·40	0·59
$C_6H_5(CH_3)_2GeCl$	62·1	0·4	0·6	21·7	0·6	2·9	16·2	0·4	2·2	3·60	0·26
$C_6H_5(CH_3)GeCl_2$	56	1	1·3	10	2	17	34	2	7·1	9·00	0·62
$C_6H_5GeCl_3$	19	3	14	71	3	4·6	10	1	7·1	0·40	0·51
					Catalyst iodine						
$C_6H_5(CH_3)_3Ge$	47	1	2·4	29	2	7·2	24	2	8·1	2·39	0·51
$C_6H_5(CH_3)_2GeCl$	59	1	1·6	20	1	3·7	21	2	8·1	4·00	0·36
$C_6H_5(CH_3)GeCl_2$	45	3	6·3	6	0	3·9	49	3	5·3	15·2	1·10
$C_6H_5GeCl_3$	60	3	5·0	9	1	7·9	31	3	8·4	10·2	0·52

phenyltrimethylsilanes and which increases apparently the amount of *m*-isomer in the resulting reaction mixture, relative to that of *p*- and *o*-isomers, in analogy with silicon compounds[14]. This effect would be much smaller with the other members of the series, since the rate of the cleavage reaction falls down more rapidly than the rate of bromination[14]. The p/o ratio obtained with both catalysts is approximately statistic or higher. It is further higher than in the chlorination of these compounds[1], but lower than in the bromination of phenylmethylchlorosilanes[14]. It seems probable that both greater steric demands of electrophilic species in the bromination and the greater Ge—C bond length, relative to that of the Si—C bond, are responsible for the fact that *o*-substitution proceeds to a greater extent in phenylgermanes than in phenylsilanes.

   Cleavage reactions in the bromination of phenylmethylchlorogermanes. Cleavage reactions, in which Ge—C_{ar} bond is cleaved under the formation of Ge—Hal and C_{ar}—Hal bonds, compete with the bromination of aromatic nucleus. Relative rate constants of bromodegermylation related to the simultaneously proceeding bromination of the same compounds are presented in Table III. The rate of bromodegermylations reaction rapidly decreases with increasing number of halogens in the germyl group, being always faster, however, than bromination. Analogous organosilicon compounds suffer bromodesilylation to a lesser extent and the difference between the

TABLE III

Relative Rate Constants of Bromodegermylation and Iododegermylation of Phenylmethylchlorogermanes (40°C, 3 mol.% catalyst, 70% n-heptane)

Compound	$k(Br)^a$	s	$v, \%$	$k(I)^b$	s	$v, \%$
		Catalyst iron				
$C_6H_5Ge(CH_3)_3Ge$	401	7	1·6	—	—	—
$C_6H_5(CH_3)_3GeCl$	622	20	3·2	—	—	—
$C_6H_5(CH_3)GeCl_2$	34	3	7·4	—	—	—
$C_6H_5GeCl_3$	10	1	14	—	—	—
		Catalyst iodine				
$C_6H_5(CH_3)_3Ge$	780	54	7·0	52	5	9·2
$C_6H_5(CH_3)_2GeCl$	626	22	3·5	50	4	8·4
$C_6H_5(CH_3)GeCl_2$	7·7	0·6	7·2	1·4	0·2	14
$C_6H_5GeCl_3$	99	5	5·5	—	—	—

^{a} $k(Br)$ is the relative rate constant of bromodegermylation related to the simultaneously proceeding bromination. ^{b} $k(I)$ is the relative rate constant of iododegermylation related to bromination.

rates of bromodesilylation of the first and the last member of the series is greater than in the case of germanium analogous[14]. According to selectivity principle, bromodegermylation is thus less selective than bromodesilylation. The greater electropositivity and the lower ability of germanium, relative to silicon, to form π-bonds of the M—C_{ar} type increases electron density of Ge—C_{ar} bond, which results in its easier electrophilic cleavage. Comparison of the rates of the cleavage of the Ge—C_{ar} bond in chlorination[1] and in bromination indicates that the cleavage by bromine is approximately by two orders of magnitude greater. Some irregularities in the dependence of relative rate constants of bromodegermylation on the number of halogens (the higher relative rate constant of bromodegermylation of phenyldimethylchlorogermane, compared with phenyltrimethylgermane, in the iron-catalysed reaction and comparatively high rate of the cleavage of phenyltrichlorogermane in the case of the iodine-catalysed bromination) are probably due to insufficiently known formation of specific complexes by the compounds mentioned. Different course of the dependence of relative rate constants of bromodegermylation and bromodesilylation[14] on the number of halogens and the dependence of the $o + p/m$ ratio and of relative rate constants of bromination on the number of chlorine atoms n indicates that the same complex intermediate is not formed in the cleavage and in the bromination reaction. Table III presents also the values of relative rate constants of iododegermylation reaction, related to the bromination of the same substance. The constants for phenyltrichlorogermane were not determined since the extent of the cleavage was so small that the iodobenzene formed could not be determined chromatographicaly. With all three members of the series iododegermylation was faster than bromination (iododesilylation reaction in the silicon series proceeds faster only with phenyltrimethylsilane[14]) and nearly by one order faster than iododesilylation. When compared with the chlorination[1], iododegermylation in the bromination is by c. one order faster. Nearly equal rates of iododegermylation of phenyltrimethylgermane and phenyldimethylchlorogermane are obviously due to the fact that the reaction mixture contained only 3% of iodine which were almost completely consumed by phenyltrimethylgermane, so that this compound could not be further cleaved. With phenyltrimethylgermane and phenyldimethylchlorogermane (similarly as with phenyltrimethylsilane[14]) on the basis of calculations of the conversion of the starting compound to iodobenzene it was also proved that the cleavage is probably caused by iodobromine and not by iodine itself, and that in such a way that iodine attacks the aromatic nucleus and bromine approaches the germanium.

Reactivity of phenylgermanes. Relative rate constants of bromination of phenylmethylchlorogermanes determined by the method of competition brominations are presented in Table IV, along with reactivities of individual positions (the reactivity of one position in benzene was taken as being equal to one). The value of relative rate constant of the iodine-catalysed bromination of phenyltrichlorogermane could not be determined, because the reactivity of this compound was so low that at the

long time necessary for attaining at least minimum conversion to bromophenyltrichlorogermanes, side reactions were taking place, *e.g.* bromination of bromochlorobenzenes, which made the determination of this constant impossible. All the compounds of this series are less reactive than benzene, and with both catalysts the dependence of log k_B on the number of halogens is irregular. When compared with the series of analogous silanes[14], the germanium compounds, as a rule, are less reactive. The obtained values of the reactivity of phenyltrimethylgermane are probably decreased, however, by consecutive bromodegermylation cleavage of bromophenyltrimethylgermanes, which, judging from the difference between the values of $k(Br)$ of the bromodesilylation and bromodegermylation of phenylmethylchlorosilanes and of phenylmethylchlorogermanes, is by about one order faster than in the silicon analogues.

This fact could account for the lower value of relative rate constant of bromination of phenyltrimethylgermane (log $k_{rel} = -0.41$) in the reaction catalysed with iron, in comparison with that found for phenyltrimethylsilane (1.13). With respect to nearly double value of relative rate constant of the bromodegermylation of phenyltrimethylgermane in the presence of iodine, relative to the value obtained in the iron-catalysed bromination (Table III), also the obtained ratio of relative rate constants of bromination changes with both catalysts. The value of k_B in the iron-catalysed reaction is

TABLE IV

Relative Rate Constants of Bromination of Phenylchlorogermanes and Reactivities of Individual Positions in Aromatic Ring (40°C, 3 mol% catalyst, 70% n-heptane)

Compound	k_{rel}^a	v, %	$k_B^b . 10^2$	$s . 10^2$	v, %	Reactivity of positions . 10^2					
						ortho	v, %	meta	v, %	para	v, %
				Catalyst iron							
$C_6H_5(CH_3)_3Ge$	2·11	0·4	41	2	5·6	55	5·6	36	5·6	64	5·7
$C_6H_5(CH_3)_2GeCl$	0·85	2·7	17	1	6·2	31	6·3	10·9	6·9	16	6·6
$C_6H_5(CH_3)GeCl_2$	1·2	11	24	3	12	40	12	7	21	49	14
$C_6H_5GeCl_3$	0·010	17	0·20	0·04	18	0·11	22	0·44	18	0·12	19
				Catalyst iodine							
$C_6H_5(CH_3)_3Ge$	1·47	0·7	25	1	5·4	35	5·9	22	8·9	35	9·7
$C_6H_5(CH_3)_2GeCl$	5·8	9·1	97	10	10	170	11	58	11	120	13
$C_6H_5(CH_3)GeCl_2$	0·47	15	8	1	16	11	17	1·5	17	23	17

^{a} k_{rel} is the average value of relative rate constant of bromination with respect to chlorobenzene, ^{b} k_B is the constant converted to benzene as standard (the reactivity of chlorobenzene was determined earlier[14]).

again higher for phenylmethyldichlorogermane than for phenyldimethylchlorogermane; the difference in the values of log k_B (0·16) is substantially smaller than in the series of the chlorosilanes[14] (1·25), but it is still greater than that obtained with analogous fluorosilanes[14] (−0·57). The order of the differences in log k parallels that of o,p-directing effects of methyldihalogenosilyl and -germyl groups in the reactions catalysed with iodine and iron; when from the value of the $o + p/m$ ratio for the iodine-catalysed reaction that for the iron-catalysed one is substracted, the following values, in the given order, are obtained[14]: 4·2, −0·75, and 8·49. The effect of the formation of specific complexes by the studied compounds in the course of reaction process on the reactivity and directing ability is greater with iodine as catalyst than with iron, while the complex formation in the iron-catalysed reaction is more dependent on the number and kind of halogens attached to the central atom.

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