ORGANOSILICON COMPOUNDS. XCIII.*

THE AROMATIC BROMINATION AND BROMODESILYLATION
OF PHENYLHALOGENOSILANES

J.Včelák and V.Chvalovský

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague - Suchdol*

Isomer distribution and relative rate constants of the iron- and iodine-catalysed bromination of compounds of the type $C_6H_5(CH_3)_{3-n}SiX_n$ (X = Cl, F; $n = 0—3$) were determined. Bromination of all the compounds proceeds to the *ortho* and *para* positions, most extensively with compounds containing two chlorine atoms bonded to silicon. In the iodine-catalysed bromination the reactivity of the members of both series decreases with increasing number of halogens in the silyl group monotonously, whereas in the iron-catalysed bromination phenylmethyldichlorosilane was found to be the most reactive. Phenyl-substituted silanes all suffer bromodesilylation. Its extent decreases with increasing —I effect of the silyl group. With the exception of phenyltrihalogenosilanes, bromodesilylation is always faster than bromination. Relative rate constants of bromodesilylation of the series of *p*- and m-$BrC_6H_4(CH_3)_{3-n}SiCl_n$ ($n = 0—2$) were also determined. With iodine as catalyst, iododesilylation completes with bromination. The relative rates of this reaction, with respect to the aromatic bromination, were also determined. The factors responsible for observed phenomena are discussed.

In previous works we studied directing effects of methylchlorosilyl and methylfluorosilyl groups and their effect on the overall reactivity of the substance in chlorination[1,2]. The trimethylsilyl group directs the substitution of the phenyl group weakly to *ortho* and *para* positions in the iron-catalysed reaction; with increasing number of halogens on silicon the *meta* position becomes increasingly preferred. In the iodine catalysed reaction the *ortho* position is significantly favoured in the expense of the *para* position. Of both series of phenylmethylchlorosilanes and phenyl-methylfluorosilanes, only phenyltrimethylsilane is the more reactive than benzene; the rate of chlorination decreases with increasing number of halogens bonded to silicon. From comparison of these reaction rates with the rates of chlorination of benzylmethylhalogenosilanes[3,4] it can be concluded that in the chlorination, similarly as in other reactions[5,6], the reactivity of phenylmethyl-halogenosilanes is influenced by the $(p \rightarrow d)\pi$ character of the Si—C_{ar} bond.

Among brominations of silyl-substituted aromatic compounds, the reaction of phenyltrichlorosilane was most studied[7]. A study by Stoffey[8] showed that while the iron-catalysed bromination gives 31% *ortho*, 28% *meta*, and 41% *para* isomer, the chlorination yields 35% *ortho*, 60% *meta*, and 5% *para* isomer. Weakly *ortho*, *para* directing in the iodine-catalysed bromination is also the methyldichlorosilyl group (35% *ortho*: 25% *meta*: 40% *para*)[9]. The selectivity of halogenation depends also on the solvent[10,11], already from its comparatively low concentrations (around

$5\%^{12}$, while the catalyst concentration does not change appreciably the selectivity of this reaction[1,3,13,14].

Halogenation of silyl-substituted benzenes is accompanied by cleavage reactions, by which the silyl group on the aromatic ring is replaced by hydrogen or halogen.

$$C_6H_5SiR_3 + XY \rightarrow C_6H_5X + YSiR_3 \quad X = H, Br, I \quad Y = Br, I \quad (A)$$

Desilylation reactions are also electrophilic[15,16] and are less selective than halogenation of the aromatic ring[17]. Protodesilylation as the side reaction in the halogenation can be strongly limited by the use of a solvent which dissolves poorly the hydrogen halogenide formed during halogenation[8]. The extent of halodesilylation is strongly dependent on the kind of halogen. As an example, chlorodesilylation of phenyltrimethylsilane is eight times slower than its iododesilylation[18]. The proportion of the cleavage decreases with increasing electronegativity of the substituted silyl group[1,2,19] and strongly depends on the sort of the catalyst. The most active in cleavage are aluminium halogenides[20−22]; the salts of iron and antimony are less effective[23]. With iodine as the catalyst, chlorination of phenyltrichlorosilane has not been observed to be accompanied by chlorodesilylation[20,22]; in our study of chlorination of phenylmethylchlorosilane we have observed, however, that in several cases the chlorodesilylation was more extensive in the iodine-than in the iron-catalysed reaction. In a study of protodesilylation of bromo-substituted phenyltrimethylsilanes[24−26] the relative rates of individual isomers were found to be: p-Br 0·096, o-Br 0·025, and m-Br 0·010 (1·00 for unsubstituted phenyl).

The aim of the present work was to obtain a systematic information concerning directing effects of silyl groups in bromination of the series of phenylmethylchlorosilanes and phenylmethylfluorosilanes and to determine the effect of structure on the overall reactivity of the compounds, both in the proper bromination and in the reactions in which the Si—C_{ar} bond is cleaved. We chose n-heptane as the solvent, because its low solubility of hydrogen bromide would limit protodesilylation reaction. In addition, the sufficient amount of the solvent (70%) would further compensate the changes in basicity, which could otherwise affect the selectivity of the reaction.

EXPERIMENTAL

Starting Compounds

Phenylmethylchlorosilanes were prepared in the usual manner with the use of Grignard reagents[1], *i.e.* phenyltrimethylsilane by complete methylation of commercial phenyltrichlorosilane, phenylmethyldichlorosilane by a partial methylation of phenyltrichlorosilane, and phenyldimethylchlorosilane by a reaction of phenylmagnesium bromide with dimethyldichlorosilane. Phenylmethylfluorosilanes were obtained by replacement of the chlorine in phenylmethylchlorosilanes with fluorine by means of antimony trifluoride[2]. Into a phenylmethylchlorosilane was added with stirring antimony trifluoride in 20% excess, then the mixture was refluxed for about 3 hours, the liquid portion distilled and rectified. p-Bromophenyldimethylchlorosilane and p-bromophenylmethyldichlorosilane were prepared in a previous study[27]. These were rectified prior to use. p-Bromophenyltrimethylsilane was prepared by methylation of p-bromophenyltrichlorosilane with the methylmagnesium bromide.[27] m-Bromophenylmethyldichlorosilane was obtained by adding the Grignard reagent prepared from 0·87 mol of m-dibromobenzene, 0·9 mol of magne-

sium, and 0·8 l of ether to an ethereal solution of 2·5 mol of methyltrichlorosilane. After decantation of the formed salts, distillation, and rectification, the desired product was obtained in 35% yield (based on *m*-dibromobenzene). *m*-Bromophenyldimethylchlorosilane was prepared in the same manner and with the same amounts of the reactants, except that 2 mol of dimethyldichlorosilane were used in place of methyltrichlorosilane. *m*-Bromophenyltrimethylsilane was prepared by methylation of *m*-bromophenyldimethylchlorosilane (without isolation) with excess methylmagnesium bromide in 15% yield. The purity of the prepared compounds was checked by g.l.c. Their properties are given in Table I.

Determination of Isomers for Bromination

The procedure used in bromination and the work-up of the reaction mixture was described in a previous work[34]; in the case of the phenylsilanes a greater amount of bromine was added, which was partly consumed in bromodesilylation reaction. When iodine was used as a catalyst, it was weighed to the reaction mixture after previous addition on n-heptane, shortly before warming the mixture. The addition of iodine as the solution in n-heptane to the reaction mixture warmed to the reaction temperature was not possible due to low solubility of iodine in n-heptane. As checked by gas chromatographic analysis, the iododesilylation of phenyltrimethylsilane, which is the most rapid in the phenylsilane series, during warming the reaction mixture and its cooling (in total 6 minutes) is negligible (only 0·04% conversion).

TABLE I

Preparation of Model Silicon Compounds

Compound	Yield %	B.p., °C/Torr found/lit.	Calculated/Found	
			% Cl	% Br
p-BrC$_6$H$_4$(CH$_3$)$_3$Si[a]	80	115/16 75—77/4[28]	-- 	34·87 33·72
m-BrC$_6$H$_4$(CH$_3$)$_3$Si[b]	15	115—116/23 96—97/5[31]	-- 	34·87 33·58
p-BrC$_6$H$_4$(CH$_3$)$_2$SiCl	--	111/9 127/12[27]	14·20 14·59	32·01 32·27
m-BrC$_6$H$_4$(CH$_3$)$_2$SiCl	31	92—93/3 121/7[33]	14·20 14·19	32·01 30·07
p-BrC$_6$H$_4$(CH$_3$)SiCl$_2$	--	102/6 128/12[27]	26·26 25·55	29·59 29·49
m-BrC$_6$H$_4$(CH$_3$)SiCl$_2$	35	95/2 115—116/7[9]	26·26 25·83	29·59 28·42

[a] For C$_9$H$_{13}$Br$_1$Si$_1$ (229·2) calculated: 47·16% C; 5·72% H; found: 46·90% C; 5·55% H; n_D^{20} 1·5294 (lit.[29] 1·5285); d_4^{22} 1·2161 (lit[30] d_4^{25} 1·2010). [b] For C$_9$H$_{13}$Br$_1$Si$_1$ (229·2) calculated: 47·16% C; 5·72% H; found: 46·98% C; 5·44% H; n_D^{20} 1·5295 (lit.[32] 1·5282); d_4^{22} 1·2582 (lit.[32] d_4^{20} 1·219).

The worked-up reaction mixture was analysed chromatographically. A partial separation of isomeric *p*- and *m*-bromophenyltrimethylsilanes was achieved by the use of 15% Fluoro Silicone FS-16 on Chromosorb as the stationary phase; a mixed phase consisting of 2·5% Bentone B-34 and 7·5% FS-16 on grinded unglazed tiles enabled to separate all the isomers. The best separation was obtained with a mixture of 1·25% Bentone B-34 and 3·75% silicone elastomer E-302 on grinded unglazed tiles (0·1—0·2 mm), with the use of a steel spiral column which was 300 cm long and 0·6 cm across. The measurements were carried out on Chrom 31 instrument (supplied by Laboratorní přístroje, Prague) provided with flame-ionization detector. The oven temperature was 105°C and the nitrogen and hydrogen flow rates were 25 ml per min and 70 ml per min, respectively. It is worthy of note that under the conditions suitable for the separation of bromophenyltrimethylsilane this phase does not separate bromobenzene from phenyltrimethyl-silane. It was found by calibration that the ratio of the areas of chromatographic peaks corresponds to the weight ratio within the errors usual for analyses of this type.

Determination of Relative Rate Constants of Bromination

Relative rate constants were determined by the method of competition reactions. The rate constants for all the compounds were related to benzene, which, however, could not be directly used as the standard, since bromodesilylation gives rise to bromobenzene. As experimental standard we used chlorobenzene, the reactivity of which was determined with respect to benzene under the same conditions. Experimental procedure used in the competitive bromination and the work-up of the analysed sample was analogous to the procedure used in determination of isomer distribution[34]. The sample was analysed on Chrom 3 chromatograph on 15% silicone elastomer E-302 on Chromosorb (100—120 mesh) (the oven temperature 110°C, the column was 240 cm long and 0·6 cm across; the nitrogen and hydrogen flow rates were 30 ml/min and 70 ml/min, respectively). Quantitative response of the instrument to individual substances was calibrated by test mixtures in the used concentration range.

Calculation of the relative rate constant for halogenation of the phenylsilanes is complicated by the present cleavage reactions, *i.e.* by bromodesilylation and, in case that iodine is used as a catalyst, also by iododesilylation. It was therefore necessary to derive the formula which would include these parallel reactions. The reaction scheme involving simultaneously proceeding bromodesilylation can be written as follows:

$$A + n\,V \xrightarrow{\;k_1\;} B + (n-1)\,V + HV_{0.5}\,, \tag{B}$$

$$A + n\,V \xrightarrow{\;k_2\;} C + (n-1)\,V + R_3MV_{0.5}\,, \tag{C}$$

$$X + n\,V \xrightarrow{\;k_3\;} Y + (n-1)\,V + HV_{0.5}\,, \tag{D}$$
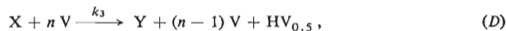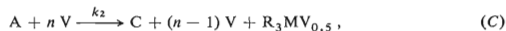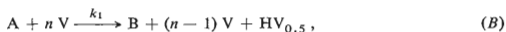
where reaction (*B*) is the bromination of the compound to be determined, (*C*) is bromodesilylation reaction, and (*D*) is the bromination of the standard. The other symbols denote the concentrations of the compounds to be determined (*A*), its monobromo derivative (*B*), bromobenzene (*C*), the standard (*X*), and the monobromo derivative thereof (*Y*), the reagent bromine (*V*), and *n* is the order of the reaction in the reagent. The following assumption were made in the calculation: all the reactions are first-order in the substrate and are of the same order in the reagent. Kinetic equations describing the given reaction scheme can be written in the following form:

$$dB/dt = k_1 A V^n\,,\quad dC/dt = k_2 A V^n\,,\quad dY/dt = k_3 X V^n\,. \tag{1), (2), (3}$$

The searched relative rate constant is then defined by the relation:

$$k_{rel} = k_1/k_3 = (dB/dY)(X/A). \tag{4}$$

Upon substitution $Y = X_0 - X$ and $A = A_0 - B - C$ and with the use of the equation

$$dC = k_2/k_1 . dB \tag{5}$$

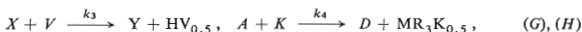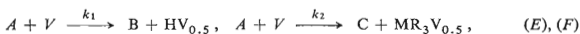the integration from the initial (0) to the final concentration (k) gives the relation for

$$k_{rel} = [k_1/(k_1 + k_2)] \log (A_0/A_k)/\log (X_0/X_k), \tag{6}$$

which for the calculation from experimental data can be rewritten to the form

$$k_{rel} = \frac{B_k}{B_k + C_k} \cdot \frac{\log [A_0/(A_0 - B_k - C_k)]}{\log [X_0/(X_0 - Y_k)]}, \tag{7}$$

where concentrations were obtained by mass balance of the initial and the final mixture.

The reaction scheme for bromination and parallel iododesilylation has the form

$$A + V \xrightarrow{k_1} B + HV_{0.5}, \quad A + V \xrightarrow{k_2} C + MR_3V_{0.5}, \qquad (E), (F)$$

$$X + V \xrightarrow{k_3} Y + HV_{0.5}, \quad A + K \xrightarrow{k_4} D + MR_3K_{0.5}, \qquad (G), (H)$$

where reaction (H) is iododesilylation. The other symbols are: K the molar concentration of the catalyst iodine and D the concentration of iodobenzene; the scheme is described by the following kinetic equations

$$dB/dt = k_1 AV, \tag{8}$$

$$dC/dt = k_2 AV, \tag{9}$$

$$dY/dt = k_3 XV, \tag{10}$$

$$dD/dt = k_4 AK. \tag{11}$$

This set of the equations was solved uder the assumption that all the reactions are first order in both reagents, conversions of reactions (E) and (G) are low, the catalyst operates in reaction (H) in the concentration which equals to its initial concentration, the brominating agent is active in its simple form and is not consumed otherwise than by bromination during the reaction. The solution leads to the expression

$$k_{rel} = (X_0/Y_k)(B_k/a)[1 - 1/2a(2V_0 - C_k) + 1/3a^2(3V_0^2 - 3V_0C_k + C_k^2)] \tag{12}$$

where $a = A_0 - K_0 - V_0$.

This equation is not a general solution for the given system, since with a certain experimental arrangement $(a < 0)$ it gives negative relative rate constants. The case where $a < 0$ occurs when the compound to be determined is extensively bromodesilylated and its initial concentration is lower than that of the standard. In such a case it is necessary to increase the concentration V_0 and the expression $(A_0 - V_0 - K_0)$ will become negative. Also the assumption on the functioning of the catalyst and of the brominating reagent can hardly be regarded as fully justified. For that reason we used another method, based on an approximative solution.

The approximative calculation of relative rate constant for the bromination parallel iodo-desilylation was made under the following assumptions: *I*) If the assumption on infinitesimal course of reaction (*H*) is introduced, one arrive at a problem which can be generally solved, similarly to the reactions where only bromodesilylation is taking place:

$$k_{rel}^- = \frac{B_k}{B_k + C_k} \frac{\log [A_0/(A_0 - B_k - C_k)]}{\log [X_0/(X_0 - Y_k)]} .$$ (13)

2) Contrarily, the assumption that iododesilylation reaction is very fast leads again to the system consisting of only parallel reaction. In this case, however, the initial concentration A_0 is decreased to the value $A_0 - D_k$. This system has a general solution, and the so obtained relative rate constant is denoted as

$$k_{rel}^+ = \frac{B_k}{B_k + C_k} \frac{\log [(A_0 - D_k)/(A_0 - B_k - C_k - D_k)]}{\log [X_0/(X_0 - Y_k)]} .$$ (14)

The value of the true relative rate constant will be somewhere between these values. Using similar simplifying presumptions we solved the scheme for the single bromodesilylation and resultant values of both k_{rel}^- and k_{rel}^+ were compared with exactly calculated k_{rel}. The calculations were made for many combination of k_{rel}'s and conversions of all the compounds. It was found that the exact value is very close to geometric mean of k_{rel}^- and k_{rel}^+, with the average relative error of about 1 per cent. The approximate solution leads therefore to the expression

$$k_{rel} = \sqrt{(k_{rel}^- k_{rel}^+)} .$$ (15)

Determination of Relative Rate Constants for Cleavage Reactions

The estimation of the extent of bromodesilylation reaction was made with the use of the rate constant of bromination cleavage, which was related to the simultaneously occuring bromination of the same compounds and defined as

$$k(Br) = k_2/k_3 = C_k/B_k .$$ (16)

Constants for bromodesilylation reaction were calculated from materials balance of the compounds formed in the bromination used to determine the isomer distribution. As the chromatographic phase enabling the separation of all three isomers did not separated phenyltrimethylsilane from bromobenzene, the samples had to be analysed also on the phase consisting of 7·5% Bentone B-34 and 7·5% Apiezon APL on Cellite 545 (100—120 mesh). The steel column was 360 cm long and 0·6 cm across (oven temperature was 120°C, flow rates of nitrogen and hydrogen were 30 ml/min and 70 ml/min, respectively).

Iododesilylation reaction was characterized by the rate constant related to the simultaneous bromination of the same compound

$$k(I) = D_k/B_k .$$ (17)

This quantity was dependent of initial concentrations of iodine and the brominating agent. The dependence on iodine concentration was eliminated by recalculating all the values of $k(I)$ to the initial concentration of iodine (3 mol. per cent).

The rate of the cleavage by bromine was followed also with *p*- and *m*-bromo-substituted phenylmethylchlorosilanes. For this purpose the mixture of the *para* and *meta* isomers of the same substances or of the *meta* isomer of the more reactive compound and the *para* isomer of the less reactive substance were weighed in such proportions that the areas for resulting cleavage pro-

ducts were comparable. Bromine was added, and the reaction was carried out under the same conditions as in other brominations. After similar work-up of the sample, the reaction mixture was analysed on the Bentonite B-34 — Apiezone APL mixed phase under the same conditions as in the determination of relative rate constant for bromodesilylation. The result of analysis were the areas of elution curves of p- and m-dibromobenzene and the curve of the mixture of p- and m-bromophenyltrimethylsilanes. These curves, after calibration, were used to calculate relative rate constant of bromination cleavage of a given substance with respect to m-bromophenyldimethylchlorosilane which was used as standard.

The relative rate constant of the cleavage, similarly as relative rate constants for the bromination of the benzylsilane series[34], was calculated from the expression for the relative rate constant of two competitive reactions which are first-order in the substrate:

$$k_{rel} = \log (A_0/A_k)/\log (X_0/X_k),\qquad(18)$$

where A is the molar concentration of the substance to be determined, X is the concentration of the standard, and suffices 0 and k denote the initial and the final state, respectively.

Accuracy of Calculated Values

As to the accuracy of weighing, negligible effect of changes in catalyst concentration, practical temperature independence of the quantities in the temperature range $40—60°C$ and the error caused by hand planimetring, the conclusions made in a previous work[34] hold also for bromination of the series studied in this work. Also here, the conversion to monobromo derivatives was maintained below 8% (in some cases it was less than 1 per cent), to prevent the formation of the higher-brominated compounds.

The most important source of systematic errors in the determination of isomer distribution was the subsequent bromodesilylation of formed bromo derivatives; iododesilylation reaction did not practically take place.

The *para* and *ortho* isomers obviously reacts the most easily in this way. Allowance for this error cannot be made, since the products, dibromobenzenes, are formed also by consecutive bromination of the present bromobenzene. This error will affect most the values expressing the distribution of isomers for phenyltrimethylsilane, where the real ratio of the isomers will be shifted in favour of the meta isomer.

Cleavage reactions affect at least in part also the values of relative rate constants of bromination. Although the direct effect of the cleavage reaction was already eliminated by the use of modified expressions for the relative rate constant, the extensive cleavage reaction leads to low conversion to the monobromo derivatives of the studied compounds, which, with a given sensitivity of the instrument used for analysis, results in a greater scattering of the data. Bromodesilylation reaction proceeds also as consecutive reaction with the bromo derivatives of the compounds to be determined and, as the result, the easier the compound is cleaved, the greater is the decrease in the real values of relative rate constants.

The amount of bromobenzene necessary for the calculation of bromodesilylation constants is in the case of the compounds which most easily undergo cleavage reactions influenced by subsequent bromination of bromobenzene to the second stage, but the loss of bromobenzene by this reaction is at worst 1 per cent, which does not practically affect the value of bromodesilylation constant. Iododesilylation constants are not influenced by consecutive bromination of iodobenzene, since if the iodine would completely react to give iodobenzene, its amount would not exceed 6 per cent. In the study of bromodesilylation of individual isomers the side reaction, bromination of bromo-substituted phenylmethylchlorosilanes, was neglected, since it processeed

to a very small extent (bromodesilylation of these compounds proceeds several times faster than their bromination, and the cleavage reaction was allowed to proceed to maximum 10 per cent conversion). Further parallel reaction the cleavage of bromophenylmethylchlorosilanes by hydrogen bromide, in the employed solvent and under the conditions used, was observed only with phenyltrimethylsilane, where the reaction proceeded, however, to a negligible extent. Every sample was analysed 2—5 times and the accuracy of the analysis was tested by the variation range, the standard deviation, and by the coefficient of variation for arithmetic mean, calculated from the expressions

$$s = (k_n / \sqrt{n}) R ; \quad v = (s/\bar{x}) 100 , \qquad (19), (20)$$

where s is the standard deviation of the mean, k_n is the coefficient according to Dean-Dixon[35], R the maximum variation range, n is the number of analyses, $\bar{x}$ is the arithmetic mean, and v is the coefficient of variation in per cent.

The average value of the coefficient of variation was 4% for the isomer distribution, 9% for the relative constants of bromination, and 10% for the rate constants of bromodesilylation and iododesilylation. The standard deviation of the mean (s_y) for the resultant values of k_b and the reactivity of individual positions (y) was calculated according to the formulae[36]

$$y = f x_1 x_2 ; \quad s_y = f \sqrt{(x_1^2 s_{x_2}^2 + x_2^2 s_{x_1}^2)} , \qquad (21), (22)$$

where f is the numerical constant, x_1 and x_2 are the respective rate constants or percentual proportion of the isomers.

RESULTS AND DISCUSSION

Distribution of isomers for bromination of the phenylmethylchlorosilanes is given in Table II, along with the standard deviations and the coefficients of variation of the arithmetic mean, which were calculated from at least three parallel bromination experiments. From the value for phenylmethyldichlorosilane for the reaction temperature 60°C (this Table) it is evident that such change in temperature does not affect the directing effect of the silyl group. The table presents also the data for uncatalysed bromination of phenylmethylchlorosilanes. Phenylmethyldichlorosilane and phenyltrichlorosilane were not brominated under these conditions, in the absence of catalyst; they are not therefore included in the table. Distribution of isomers for bromination of the phenylmethylfluorosilanes is given in Table III. It is obvious that in the bromination of both phenyl-substituted series the silyl groups all exhibit a weak *ortho, para* directing effect, while chlorination of these substances[1,2] shows indistinct *meta* orientation, except for the catalysis with iodine. Stoffey[8] explained this change in the directing effect of the trichlorosilyl group upon change of the electrophilic particle by assuming that the iron trichloride-catalysed chlorination proceeds *via* a complex with the catalyst of type (*I*), which desactivates *para* and *ortho* positions, while in the bromination a resonance structure *II* is more important, since the structure *I* cannot be so favoured with a weaker Lewis acid, iron tribromide, relative to iron trichloride. The explanation by Stoffey does not account for all the reasons for the different behaviour of the same silyl group in bromination and chlorination.

Table II

Distribution of Isomers in Bromination of Phenylmethylchlorosilanes (70% n-heptane, 40°C, 3 mol.% catalyst)

Compound	ortho %	s	v %	meta %	s	v %	para %	s	v %	$\dfrac{o + p}{m}$	$\dfrac{p}{o}$
Catalyst iron											
$C_6H_5(CH_3)_3Si$	18	2	8·3	25	1	2·2	57	1	1·6	3·06	3·22
$C_6H_5(CH_3)_2SiCl$	21·6	0·5	2·3	19·7	0·6	3·1	58·7	0·5	0·8	4·08	2·72
$C_6H_5(CH_3)SiCl_2$	15·7	0·4	2·2	14·9	0·1	0·9	69·4	0·5	0·7	5·73	4·44
$C_6H_5(CH_3)SiCl_2{}^a$	18·4	0·7	3·6	16·5	0·7	4·4	65·1	0·9	1·3	5·06	3·53
$C_6H_5SiCl_3$	64·5	0·2	0·3	20·7	0·8	4·0	14·9	0·6	4·3	3·83	0·23
Catalyst iodine											
$C_6H_5(CH_3)_3Si$	21·5	0·3	1·5	26·7	0·3	1·2	51·8	0·5	1·0	2·75	2·41
$C_6H_5(CH_3)_2SiCl$	32	1	3·0	18	1	2·7	50	2	2·9	4·47	1·60
$C_6H_5(CH_3)SiCl_2$	33	1	4·3	17	1	6·5	50	2	4·8	4·98	1·50
$C_6H_5SiCl_3$	17	2	9·5	19	1	5·7	64	2	3·1	4·30	3·88
Without catalyst											
$C_6H_5(CH_3)_3Si$	19	1	2·9	24	1	4·9	57	1	1·2	3·14	3·10
$C_6H_5(CH_3)_2SiCl$	21·8	0·3	1·5	15·6	1·5	3·2	62·6	0·8	1·3	5·42	2·87

[a] Bromination was carried out at 60°C.

So, for example, the chlorination of the phenylmethylfluorosilanes would have produced the greater amount of the *ortho* and *para* isomers than the chlorination of phenylmethylchlorosilanes, since the $-I$ effect of fluorine is only slightly greater than that of chlorine, but these compounds can hardly be expected to form complexes of the type *I*, des activating *ortho* and *para* positions. However, the opposite was found experimentally[1,2] (the $(o + p)/m$ ratio for $C_6H_5SiF_3$ is 0·39 for the FeCl$_3$- and 0·83 for the iodine-catalysed reaction; for $C_6H_5SiCl_3$ it is 0·79 and 2·44 respectively). Similarly, structure *II* cannot be solely responsible for the directing effect of the silyl groups in the bromination since if the proportion of the $(p \rightarrow d)\pi$ bonding in M—Hal bonds is regarded to decrease in the order Si—F > Si—Cl > Ge—Cl, as suggested by many authors[4,37−39], then for the compounds with two halogens bonded to the central atom (*i.e.* those which would favour the structure *II*) the proportion of *ortho*, *para* substitution should decrease in the same order. It was found experimentally that with iron as catalyst the $(o + p)/m$ ratio for phenylmethyldifluorosilane was 3·91, for phenylmethyldichlorosilane 5·73, and for phenylmethyldichlorogermane 9·00[40].

In both series the proportion of the *ortho, para* isomers increases with increasing number of halogens towards dihalogeno derivatives; and decreases for trihalogeno derivatives. With the chlorosilanes, the directing effects of the silyl groups are similar for both catalysts, while with the fluorosilanes the stronger *ortho, para* orientation is observed for the iodine-catalysed reaction. With purely inductive action of the groups the proportion of the *ortho, para* direction should, of course, decrease with increasing number of halogens in the group. The observed course (Tables II and III) can hardly be explained on the basis of current knowledge of this system.

In contrast to the chlorination, in the bromination of these compounds a dominant role is obviously played by the formation of charge-transfer complexes of the studied compounds with the brominating agent and probably also with the catalyst, which affects both the directing properties of the groups, and the overall reactivity of the compounds. In a study of the ultraviolet spectra and dipole moments of these systems[41] it was established that the studied compounds act in these complexes as electron donors and that mainly by their benzene rings. The strength of these complexes with bromine and iodine decreases with increasing number of halogens in a silyl group. Phenylmethylchlorosilanes form stronger complexes with bromine than with iodine.

Apart from the aromatic part, also the silyl group of the compound brominated can take part in the formation of the complex. The formation of the complexes with reacting compounds is obviously more important with iodine than with iron tribromide. So, for example, the distribution of isomers in uncatalysed brominations of phenyltrimethylsilane and phenyldimethylchlorosilane is very similar to the distribution of the monobromo derivatives in the reaction catalysed with iron.

In order to estimate the participation of methylchlorosilyl groups in the formation of charge-transfer complexes with bromide and iodine the ultraviolet spectra of the systems of the methylchlorosilanes with bromine and iodine were measured in various solvents[41]. Of this series, weak charge-transfer complexes were found to be formed only by dimethyldichlorosilane and by trimethylchlorosilane, a number of anomalies in the spectra of both the pure compounds and their systems with halogens being observed for the compounds having two halogens on the silicon. The formation and stability of charge-transfer complexes with halogens can be influenced also by methylhalogenosilyl groups, and this influence may be especially important in the compounds containing two halogen atoms on the silicon. The trimethylsilyl group and trichlorosilyl group do not form the complex with bromine or with iodine[41]. This might account for the fact that the last members of both series show weaker *ortho, para* direction than the medium members. A relatively weak *ortho, para* directing of the trimethylsilyl group indicates that the inductive effect of this group is at least in part weakened by $(p \rightarrow d)\pi$ dative character of the $Si-C_{ar}$ bond.

The p/o ratio is for the phenylmethylchlorosilanes (except phenyltrichlorosilane) in the iron-catalysed reaction higher than statistical, while for the phenylmethyl-

fluorosilanes it is nearly statistical for all the members containing fluorine, or lesser. From comparison of both series it is obvious that in the fluorosilanes the *ortho* position is more favoured and that the extent of the *ortho* substitution increases with increasing number of fluorine atoms bonded to the silicon. This can be the result of the operation of steric effects, since in the series of the chlorosilanes, where the substitution of the methyl group for chlorine does not affect so much the size of the silyl group, the p/o ratio varies in a nonsystematic fashion. In the case of studied fluorosilanes the substitution of the methyl group for the smaller fluorine atom results in a decreased shielding of the *ortho* positions. For that reason the proportion of the *ortho* substitution is the greatest with the trifluorosilyl group.

From comparison of the results of the studies of the chlorination and bromination of both series of phenylhalogenosilanes it can be concluded that the important factor is also the size of the electrophilic particle, since chlorination leads in both series to the greater ortho substitution, relative to bromination. The relative proportion of the isomers in bromination is influenced by subsequent bromination cleavage of the already formed monobromo derivatives. Eaborn and coworkers[24-26] determined the relative rate constants of protodesilylation of bromophenyltrimethylsilanes, relative to phenyltrimethylsilanes: the *para* 0·096, the *meta* 0·010, and the *ortho* derivative 0·025.

In the case of bromodesilylation it can be expected that bromo-substituted derivatives by comparison with phenyltrimethylsilane will be cleaved more reluctantly

TABLE III

Distribution of Isomers in Bromination of Phenylmethylfluorosilanes (70% n-heptane, 40°C, 3 mol.% catalyst)

Compound	ortho %	s	v %	meta %	s	v %	para %	s	v %	$\dfrac{o+p}{m}$	$\dfrac{p}{o}$
				Catalyst iron							
$C_6H_5(CH_3)_3Si$	18	1	8·3	25	1	2·2	57	1	1·6	3·06	3·22
$C_6H_5(CH_3)_2SiF$	46·4	0·5	1·0	20·7	0·6	2·8	32·9	1·0	3·2	3·83	0·71
$C_6H_5(CH_3)SiF_2$	42	1	2·5	20	1	3·4	38	2	4·1	3·91	0·90
$C_6H_5SiF_3$	30	3	9·7	67	3	3·9	3	0·3	9·7	0·49	0·09
				Catalyst iodine							
$C_6H_5(CH_3)_3Si$	21·5	0·3	1·5	26·7	0·3	1·2	51·8	0·5	1·0	2·75	2·41
$C_6H_5(CH_3)_2SiF$	53	1	2·6	18	0	2·7	29	1	3·0	4·53	0·56
$C_6H_5(CH_3)SiF_2$	76·3	0·9	1·2	7·5	0·7	9·1	16·2	0·8	4·8	12·4	0·21
$C_6H_5SiF_3$	68	3	5·0	25	3	14	7	1	8·2	2·92	0·10

than are in protodesilylation, since the former reaction is more selective (the selectivity factor for the bromodesilylation is 1·226, while for protodesilylation[42] 0·964). The relative rate constants of bromodesilylation of the *meta* and *para* isomers for three different cleaved silyl groups, determined under the experimental conditions used in brominations, are presented in Table IV. The cleavage reaction decreases above all the amount of the *para* isomer. The least difference in cleavage rates of the *para* and *meta* isomers has been found for bromophenyltrimethylsilane, which, in the view of the accuracy achieved in this work, is of advantage: at the low conversions used in the brominations the change of the isomer distribution can be observed practically only with phenyltrimethylsilane. Despite of this fact, the cleavage reaction can aid in weakening of the otherwise relatively weak *ortho, para* substitution in the case of the bromination of the trimethylsilyl groups. A similar influencing of the direction in the compounds with methylchlorosilyl groups will be much lesser.

Table IV

Relative Rate Constants of Bromodesilylation of *p*- and *m*-Bromophenylmethylchlorosilanes (70% n-heptane, 40°C, 3 mol.% iron)

Compound	Experimental standard	$\bar{k}_{rel}$	v, %	k_{rel}^F	s	v, %
p-BrC$_6$H$_4$(CH$_3$)$_3$Si	*m*-BrC$_6$H$_4$(CH$_3$)$_3$Si	2·2	7·1	69	7	9·6
m-BrC$_6$H$_4$(CH$_3$)$_3$Si	*p*-BrC$_6$H$_4$(CH$_3$)$_2$SiCl	2·0	5·0	31	2	6·5
p-BrC$_6$H$_4$(CH$_3$)$_2$SiCl	*m*-BrC$_6$H$_4$(CH$_3$)$_2$SiCl	15·2	4·1	15·2	0·6	4·1
p-BrC$_6$H$_4$(CH$_3$)SiCl$_2$	*m*-BrC$_6$H$_4$(CH$_3$)$_2$SiCl	0·88	11	0·88	0·10	11
m-BrC$_6$H$_4$(CH$_3$)SiCl$_2$	*p*-BrC$_6$H$_4$(CH$_3$)SiCl$_2$	0·039	7·0	0·034	0·005	13

k_{rel}^F is the relative rate constant of bromodesilylation with respect to *m*-BrC$_6$H$_4$(CH$_3$)$_2$SiCl.

Bromodesilylation reactions of the phenylsilanes. Relative rate constants of bromodesilylation, related to the simultaneous bromination, are given in Table V. With phenylmethyldichlorosilane as an example, temperature independence of the rate constant of bromodesilylation was tested over the temperature range of 40—60°C. The activation energies of both reactions do not obviously differ so much as to change the value of the relative rate constant in the given temperature region. As obvious from the dependence of the relative rate constants of bromodesilylation on the number of halogens in the silyl group, the extent of bromination cleavage markedly decreases with the increasing electronegativity of the silyl group. In both series, the bromination to the benzene ring prevails over the bromodesilylation reaction only in the case of phenyltrihalogenosilanes. In Table V are also given the logarithms

of relative rate constants of bromodesilylation with respect to the bromination of benzene $(k_B(Br))$. In both series the cleavage is faster in the presence of iodine than in the presence of iron. On chlorination of these compounds, the chlorodesilylation catalysed by iodine was faster than the iron-catalysed reaction only with phenyltrimethylsilane and phenyldimethylchlorosilane[1]. This finding is at variance with the commonly accepted assumption that halogenations catalysed with iodine proceed less destructively than in the presence of Lewis acids as catalysts[20,22]. From comparison of the cleavage reactions it can be concluded that the relative rate of bromodesilylation, relative to the bromination, is for both series about two orders faster than the relative rate of chlorodesilylation, related to the chlorination. This is obviously connected with the easier polarizability of bromine molecule (when compared with the chlorine one) in the course of the reaction process. A more extensive cleavage in the fluorosilane than in the chlorosilane series might be due to the fact that the electron withdrawal by the fluoro-substituted groups is reduced by the back donation of electrons in the silicon-fluorine bond.

Iododesilylation reactions. Rates of the cleavage by iodine, expressed as the relative constants calculated with respect to the rate of the bromination of the same com-

TABLE V

Relative Rate Constants of Bromodesilylation of Phenylmethylchlorosilanes and Phenylmethylfluorosilanes (70% n-heptane, 40°C, 3 mol% catalyst)

	Chlorosilane				Fluorosilane			
n^a	$k(Br)^b$	s	v, %	$\log k_B(Br)^c$	$k(Br)$	s	v, %	$\log k_B(Br)$
				Catalyst iron				
0	146	7	4·7	2·22	—	—	—	—
1	55	6	11	0·68	156	5	3·0	+1·51
2	3·22	0·01	0·4	0·68	9·1	0·6	6·6	−0·29
2^d	3·22	0·03	1·0	—	—	—	—	—
3	0·041	0·007	16	−3·48	0·054	0·006	11	−4·08
				Catalyst iodine				
0	106	7	6·5	3·06	—	—	—	—
1	17	1	7·4	1·65	67	4	6·3	+2·52
2	16	1	7·1	0·85	1·35	0·07	5·2	−0·20
3	0·035	0·008	22	−3·19	0·5	0·1	25	−3·30

^{a} Number of halogens in the compound, ^{b} bromodesilylation constant expressing the relative rate of bromodesilylation with respect to simultaneous bromination, ^{c} bromodesilylation constant recalculated to the bromination of benzene, ^{d} determined at 60°C.

pound, are given in Table VI. The values for phenyltrihalogenosilanes could not be determined, since the extent of the cleavage was so small, that the amount of the iodobenzene formed could not be estimated. The rate of the desilylation decreases again with increasing number of halogens in the silyl group, *i.e.* with the increasing $-I$ effect of the group. Iododesilylation is faster than bromination only with phenyltrimethylsilane and phenyldimethylfluorosilane. On calculating the conversion of starting compounds to iodobenzene, we have found that for phenyltrimethylsilanes the amount of the iodobenzene is greater than 3 per cent, *i.e.* the value corresponding to the complete consumption of the added molecular iodine. As the conversion to iodobenzene was max. 6%, it seems likely that the cleavage of the $Si—C_{ar}$ bond does not proceed *via* the attack by iodine molecule, but rather *via* the attack by iodinebromine molecule, which is formed in the reaction mixture from iodine and bromine. The equilibrium reaction $1/2\ Br_2(CCl_4) + 1/2\ J_2(CCl_4) \rightleftarrows JBr(CCl_4)$ is at 25°C shifted to the right $(\Delta G^0 = -1746\ cal/mol)^{43}$. The iodine atom as the more positive part of iodinebromine attacks the carbon of the aromatic ring, while the bromine attacks the silicon, so that both iodine atoms are utilized for the formation of iodobenzene. Because of the less extensive cleavage, this phenomenon is not observed with the chloro-substituted derivatives. The relative rate of the iododesilylation proceeding during chlorination, which was studied earlier, is about one order slower that the same reaction in the bromination (both estimates were made to the respective halogenation to the ring). The difference in the importance of iododesilylation in the chlorination and the bromination will be in fact even greater, since the extent of iododesilylation during bromination will further increase upon increase of the reaction temperature to 60°C, used to study the chlorination.

Bromodesilylation cleavage of bromo-substituted phenylmethylchlorosilanes. The dependence of logarithms of the rate constants of bromodesilylation reaction

TABLE VI

Relative Rate Constants of Iododesilylation of Phenylmethylchlorosilanes and Phenylmethylfluorosilanes (70% n-heptane, 40°C, 3 mol.% iodine)

Compound	$k(I)^a$	s	$v, \%$
$C_6H_5(CH_3)_3Si$	3·9	0·2	6·0
$C_6H_5(CH_3)_2SiCl$	0·19	0·02	7·9
$C_6H_5(CH_3)SiCl_2$	0·12	0·02	13
$C_6H_5(CH_3)_2SiF$	2·9	0·4	12
$C_6H_5(CH_3)SiF_2$	0·033	0·005	15

^{a} $k(I)$ is the relative rate constants of iododesilylation with respect to simultaneous bromination.

on the number of the chlorine atoms on the silicon (Table IV) shows a monotonous decrease of the reactivity of the *meta* derivatives, indicating purely inductive action of silyl groups. This is accompanied by increasing difference between the reactivities of the *meta* and *para* derivatives, which corresponds to the increasing selectivity of bromodesilylation reaction with decreasing rate of the reaction, the latter being caused by increasing electronegativity of the silyl group. A different curve for the para isomers could be explained by assuming that the reactivity is influenced by the back donation of electrons in the Si—C_{ar} bond which is here more important than in the case of the *meta* derivatives. This interaction may be strengthened in the *para* isomers by the positive mesomeric effect of the *para* bromine, which is stimulated by the negative inductive effect of the chlorine atoms. Rates of bromodesilylation of isomeric bromophenyltrichlorosilanes were not determined, since in this case parallel bromination to the ring proceeded to a greater extent.

Reactivity of the phenylsilanes. Relative rate constants, determined by the method of competitive reactions, for both series are given in Table VII. With phenylmethyldichlorosilane, the effect of temperature on the value of the relative rate constant was also studied. It was found that the change of the temperature from 40°C to 60°C does not exert any appreciable effect. With the use of data on isomer distribution (Tables II and III) we calculated the reactivities of individual positions in the aromatic ring (the reactivity of one position in the benzene ring was regarded as being equal to one). The relative rate constants of the bromination of the phenylhalogenosilanes are about two orders smaller than the corresponding values for the benzylchlorosilanes. Such a difference is obviously due to both an increased positive inductive action of the silylmethyl groups by hyperconjugation in the case of the benzylmethylchlorosilanes, and by a decreased +I effect of the silyl groups due to the $(p \rightarrow d)\pi$ character of the Si—C_{ar} bond in the case of the phenylmethylchlorosilanes.

Most members of both series are more reactive in the iodine than in the iron-catalysed reaction, which, similarly as in the chlorination of these compounds[1,2] (and the chlorination[3,4] and bromination[34,43] of benzylmethylchlorosilanes) shows that the iodine-catalysed halogenation is more selective that the halogenation catalysed with iron. The course of the dependence of log k_B on the number of halogens in molecule is monotonous for the iodine-catalysed halogenation of the phenylmethylchlorosilanes. It can be thus said that the reactivity of these compounds is influenced above all by the inductive effect of the methylchlorosilyl groups. With the phenylmethylfluorosilanes, the difference between the reactivity of the first and the last member of the series is greater than with the chlorosilanes, in agreement with the more negative inductive effect of the fluorine relative to the chlorine. Phenyldimethylfluorosilane is however the more reactive than phenyldimethylchlorosilane. These facts indicate that the polarity of the Si—F bonds is influenced by the $(p \rightarrow d)\pi$ bond contribution which decreases their polarity in the case of one or two in the molecule, while the third Si—F bond acts already purely inductively.

Table VII

Relative Rate Constants and Reactivities of Aromatic Ring Positions in Bromination of Phenylmethylchlorosilanes and Phenylmethylfluorosilanes Catalysed by 3 mol.% Iron or Iodine (40°C, 70% n-heptane)

Compound	$\bar{k}_{rel}^{\,a}$	$v, \%$	$k_B^{\,b}$	s	$v, \%$	ortho	$v, \%$	meta	$v, \%$	para	$v, \%$
								Reactivity of position			
Catalyst iron											
$C_6H_5(CH_3)_3Si$	5·8	2·8	1·13	0·07	6·3	0·61	10	0·84	6·7	3·9	6·5
$C_6H_5(CH_3)_2SiCl$	0·44	6·2	0·087	0·007	8·3	0·056	8·6	0·051	8·9	0·31	8·4
$C_6H_5(CH_3)SiCl_2{}^{c}$	7·7	2·9	1·50	0·9	6·3	0·70	6·7	0·67	6·3	6·2	6·3
$C_6H_5SiCl_3$	0·0418	1·2	0·0082	0·0005	5·7	0·0158	5·7	0·0051	7	0·0073	7·2
$C_6H_5(CH_3)_2SiF$	1·06	9·0	0·21	0·02	10	0·29	11	0·13	11	0·41	11
$C_6H_5(CH_3)SiF_2$	0·29	10	0·056	0·007	12	0·071	12	0·034	12	0·13	12
$C_6H_5SiF_3$	0·0080	12	0·0016	0·0002	13	0·0014	16	0·0032	14	0·00027	16
C_6H_5Cl	—	—	0·20	0·01	5·6	—	—	—	—	—	—
Catalyst iodine											
$C_6H_5(CH_3)_3Si$	65	6·8	10·9	0·9	8·6	7·0	8·8	8·7	8·7	34	8·7
$C_6H_5(CH_3)_2SiCl$	16	14	2·7	0·4	15	2·5	15	1·5	15	8	15
$C_6H_5(CH_3)SiCl_2$	2·7	13	0·45	0·07	14	0·46	15	0·23	16	1·4	15
$C_6H_5SiCl_3$	0·11	19	0·019	0·004	20	0·009	22	0·010	21	0·07	20
$C_6H_5(CH_3)_2SiF$	29	12	4·9	0·6	13	7·7	13	2·7	13	8·6	13
$C_6H_5(CH_3)SiF_2$	2·8	10	0·47	0·05	11	1·1	12	0·11	15	0·46	12
$C_6H_5SiF_3$	0·006	21	0·0010	0·0002	22	0·0020	22	0·0008	26	0·00040	23
C_6H_5Cl	—	—	0·168	0·009	5·3	—	—	—	—	—	—

[a] Average value of the relative rate constant with respect to chlorobenzene, [b] the relative rate constant with respect to benzene, [c] $\bar{k}_{rel}$ at 60°C was 6·5 (v 2·9%).

As for the iron-catalysed reaction, the situation is complicated by irregular dependence of k_{rel} on the substitution, which shows maximum for phenylmethyldichlorosilane. In spite of this, these is a certain similarity with the analogous dependence for the iodine-catalysed bromination, namely the smaller difference in the reactivities of the phenylmethylchlorosilanes compared with the phenylmethylfluorosilanes, and the higher reactivity of phenyldimethylfluorosilane, in comparison with phenyldimethylchlorosilane. The maximum in the reactivity observed for phenylmethyldichlorosilane is obviously caused by a specific complex formation of this compound in the presence of iron tribromide as a catalyst. The structure of a methylhalogenosilyl group plays an important role, too: if the silyl group contains fluorine, which is known to form intramolecular complexes less radily, the break in the reactivity is significantly smaller. These assumption agree also with similar anomalies on the curves representing the dependence of the $(o + p)/m$ ratio on the number of halogens, where in the iron-catalysed reaction phenylmethyldichlorosilane shows the highest $(o + p)/m$ ratio of all the compounds, which is even higher than in the iodine-catalysed reaction, similarly also the reactivity. On the other hand, with phenylmethyldifluorosilane the maximum in the $(o + p)/m$ ratio is in distinct in their iron-catalysed reaction and the ratio is substantially smaller than in the iodine-catalysed reaction (similarly also the course of reactivities).

The relative rate constant of bromination of phenyltrimethylsilane may be in fact somewhat greater than that found experimentally, since, of the series, the bromophenyltrimethylsilane formed is the most readily cleaved by bromodesilylation (Table V). Because of low conversions to the monobromoderivatives, this influencing is however small and does not affect therefore the course of the dependence of reactivities.

From Table VII it is evident that the use of different catalysts has a marked effect on the reactivity of the same compound. So, for example, the *para* position in phenyldimethylchlorosilane, relative to that in benzene is in the iodine-catalysed reaction eight times more reactive, while in the iron-catalysed reaction it is three times less reactive. The formation of different complexes in the course of bromination thus makes the determination of Brown σ^+ constants of methylhalogenosilyl groups impossible.

REFERENCES

1. Lepeška B., Chvalovský V.: This Journal **34**, 3553 (1969).
2. Lepeška B., Bažant V., Chvalovský V.: J. Organometal. Chem. **23**, 41 (1970).
3. Včelák J., Bažant V., Chvalovský V.: This Journal **35**, 136 (1970).
4. Včelák J., Chvalovský V.: J. Organometal. Chem. **23**, 47 (1970).
5. Bott R. V., Eaborn C., Grealey P. M.: J. Chem. Soc. **1964**, 4804.
6. Černyšev E. A., Zeleneckaja A. A., Krasnova T. L.: Izv. Akad. Nauk SSR, Otd. Chim. Nauk **1966**, 1118.
7. Jakubovič A. Ja., Mocarev G. V.: Ž. Obšč. Chim. **29**, 2395 (1959).

8. Stoffey D. G.: Univ. Microfilms, Ann Arbor, Michigan, U.S.A. 59—1648, *Thesis.* Purdue Univ., Lafayette; Chem. Abstr. *53*, 14921 (1959).

9. Mocarev G. V., Rozenberg V. R., Tarasova T. T.: Ž. Obšč. Chim. *34*, 2911 (1964).

10. Lebedev N. N., Baltadzhi I. I.: Kinetika i Katal. *5*, 305 (1964).

11. Lebedev N. N., Baltadzhi I. I.: Izvest. Vysš. Učeb. Zaved. Chim. i Chim. Technol. *12*, 1522 (1969).

12. Dolanský J.: Unpublished results.

13. Kropanev Ju. S., Pljusnin V. G., Plotkina N. I., Uljanova L. P.: Neftechimija *9*, 591 (1969).

14. Kropanev Ju. S., Pljusnin V. G., Plotkina N. I.: Neftechimija *7*, 398 (1967).

15. Eaborn C., Pande K. C.: J. Chem. Soc. *1960*, 1566.

16. Eaborn C.: J. Chem. Soc. *1956*, 4858.

17. Stock L. M., Brown H. C.: J. Am. Chem. Soc. *84*, 1668 (1962).

18. Stock L. M., Spector A. R.: J. Org. Chem. *28*, 3272 (1963).

19. Ponomarenko V. A., Snegova A. D., Egorov Ju. P.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk *1960*, 244.

20. Jakubovič A. Ja., Mocarev G. V.: Ž. Obšč. Chim. *26*, 568 (1956).

21. Jakubovič A. Ja., Mocarev G. V.: Ž. Obšč. Chim. *23*, 412 (1953).

22. Jakubovič A. Ja., Mocarev G. V.: Dokl. Akad. Nauk SSSR *91*, 277 (1953).

23. Jakubovič A. Ja., Mocarev G. V.: Ž. Obšč. Chim. *25*, 1748 (1955).

24. Deans F. B., Eaborn C., Webster D. E.: J. Chem. Soc. *1959*, 3031.

25. Eaborn C., Pande K. C.: J. Chem. Soc. *1961*, 5082.

26. Eaborn C., Walton D. R. M., Young D. J.: J. Chem. Soc. B *1969*, 15.

27. Mareš F., Neudörfl P., Plzák Z., Chvalovský V.: This Journal *35*, 2324 (1970).

28. Brown H. C., Okamoto Y., Inukai T.: J. Am. Chem. Soc. *80*, 4964 (1958).

29. Gilman H., Melvin H. W., Goodman J. J.: J. Am. Chem. Soc. *76*, 3219 (1954).

30. Campagna P. J.: Univ. Microfilms Publ. No 5117, Dissertations Abstr. *13*, 312 (1953).

31. Benkeser R. A., Krysiak H. R.: J. Am. Chem. Soc. *76*, 599 (1954).

32. Benkeser R. A., Hickner R. A., Hoke D. I., Thomas O. H.: J. Am. Chem. Soc. *80*, 5289 (1958).

33. Kriegsmann H.: *Thesis.* Technische Hochschule, Dresden 1960.

34. Včelák J., Chvalovský V.: This Journal *37*, 3623 (1972).

35. Dean R. B., Dixon W. J.: Anal. Chim. *23*, 636 (1951).

36. Eckschlager K.: *Chyby chemických rozborů.* Published by SNTL, Prague 1961.

37. Gordy W.: Discussions Faraday Soc. *18*, 14 (1955).

38. Hradil J., Chvalovský V.: This Journal *32*, 171 (1967).

39. Cradock S., Ebsworth E. A. V.: Chem. Commun. *1971*, 57.

40. Včelák J., Chvalovský V.: This Journal *37*, 3615 (1972).

41. Véle I., Hetflejš J., Vaisalová V., Chvalovský V.: This Journal *36*, 4111 (1971).

42. Stock L. M., Brown H. C.: *Advances in Physical Organic Chemistry* (V. Gold, Ed.), Vol. 1, p. 35. Academic Press, London 1963.

43. Yost D. M., Anderson T. F., Skoog F.: J. Am. Chem. Soc. *55*, 552 (1933).

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