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AROMATIC BROMINATION OF BENZYL METHYLCHLOROSILANES

J. VČELÁK and V. CHVALOVSKÝ

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

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Directing effects of substituted silylmethyl groups were studied in the catalysed aromatic bromination of silanes of the type $C_6H_5CH_2(CH_3)_{3-n}SiCl_n$ ($n = 0-3$). The effect of the catalysts, iron powder and iodine, on distribution of isomers in this series was also determined. The reactivity of the above compounds with respect to benzene was determined by the method of competitions. The silylmethyl groups all are very strongly *o,p*-directing, with prevailing direction to the *para* position. As the number of chlorine atoms in the molecule increases the ratio of the *para* to the *ortho* isomer decreases (being, however, always higher than statistic), the amount of the *meta* isomer increases, this being accompanied by decreasing gross reactivity. These phenomena were explained by positive inductive action of the silylmethyl groups, enhanced by hyperconjugative contribution from Si—C or C—H bonds.

Electronic effects of silylmethyl groups were studied most often with trimethylsilylmethyl group, which, as expected, has been found to be more electropositive than the analogous carbon group¹⁻⁴. Electrophilic substitution on the aromatic ring of benzylsilanes proceeds very easily, benzyltrichlorosilane⁵ and benzyltrifluorosilane⁶ being almost as reactive as benzene. Analogous phenylsilanes react at the same conditions in two to three orders slower rates^{7,8}. Similar increase in the rate of aromatic substitution on going from the Si—C_{ar} to the Si—CH₂—C_{ar} grouping has already been observed in nitration⁹, bromination¹⁰ and acylation¹¹ of the silanes $C_6H_5.(CH_2)_nSi(CH_3)_3$, the reactivity of which decreased in the order $n = 1 \gg 3 > 2 > 0$. This sequence does not correspond to the pure inductive effect of the silylmethyl groups but it suggests that this effect is further enhanced by hyperconjugative contribution. In benzyltrimethylsilane this contribution comes from the Si—C bond (Scheme 1), as indicated by the results of the analysis of Hammett and Brown constants of the $[(CH_3)_3Si]_nCH_3$ groups, which were obtained, respectively, from dissociation constants of corresponding benzoic acids, rates of solvolysis of tert-cumyl chlorides¹², as well as from ¹⁹F-NMR spectra of a series of substituted fluorobenzenes¹³. The rate of the cleavage of the Si—C bond in $[(CH_3)_3Si]_nCH_3$ — C_6H_4 —Si(CH₃)₃ was found to increase in the order¹⁴ $n = 0 < 3 < 1 < 2$, which parallels the increase in dissociation constants of (trimethylsilylmethyl)benzoic acids¹⁵. These results indicate that the properties of the compounds possessing different number of Si—C bonds in the position α with respect to the aromatic ring are strongly influenced by hyperconjugative contribution from Si—C bonds, which, from steric reasons, is greatest in the case of two Si—C bonds. The effect of hyperconjugation in benzyltrimethylsilane has been calculated by SCF-LCAO-MO method by Nagy¹⁶. When interpreting

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ionisation potentials of series of silyl- and germyl-substituted indanes, the compounds which have both M-phenyl and M-benzyl bonds, Pitt¹⁷ has assigned the different behaviour of these two types solely to the hyperconjugation contribution in the latter compounds, not taking into account possible influence of a ($p \rightarrow d$) π character of the silicon to phenyl bond. So far, the complete series of benzylmethylchlorosilanes⁵ and benzylmethylfluorosilanes⁶ have only been studied by means of electrophilic chlorination, which proceeds in these compounds to positions *ortho* and *para*. The reactivity of all the compounds was found to be higher than or comparable with that of benzene. The reactivity of benzylmethylfluorosilanes is affected in part by ($p \rightarrow d$) π bonding in the Si—F bond. The iron-catalysed bromination was carried out with benzyltrichlorosilane (to the high degree of substitution, where pentabromo derivatives were formed)¹⁸ and with benzyltrimethylsilane¹⁹. In both cases only the *para* isomer was isolated. The Si—C bond in the benzyl compounds is not cleaved during bromination^{18,20} or chlorination^{5,6}, in contrast to the Si—C_{ar} bond in phenyl-substituted compounds.

With the aim to maintain constant basicity of the medium in the whole series of measured compounds, in the present work we have used the inert solvent, n-heptane, in order to eliminate the effect of the change of reaction medium on the selectivity of occurring reactions²¹. As the catalysts, ferric bromide and iodine were used. In analogy with the results of our previous study of chlorination of similar compounds we expected that also here catalyst concentration would not greatly influence the course of the reaction^{5,7,22}. For this reason all the measurements were carried out only with one concentration of the catalysts.

EXPERIMENTAL

Benzyltrichlorosilane was prepared by Grignard reaction from silicon tetrachloride and benzyl chloride, by adding several ml of benzyl chloride to a mixture containing the appropriate amount of magnesium and a part of the total volume of ether, then adding the total amount of silicon chloride, followed by dropwise addition of the remaining benzyl chloride at such a rate as to ensure refluxing. After extraction of the salts and fractional distillation, benzyltrichlorosilane was obtained in 35% yield. B.p. 107–107.5°C/17 Torr (recorded²³ b.p. 106.5–107.5°C/18 Torr). The preparation and physical properties of the other members of the series were reported elsewhere⁵. *p*- and *m*-*Bromobenzyltrimethylsilanes*, used as standards in chromatographic analysis, were prepared by Grignard reaction from the corresponding bromobenzyl bromide and dimethyldichlorosilane (used in 65% excess), using the procedure described in the preparation of benzyltrichlorosilane. After methylation with excess methylmagnesium bromide, *p*- and *m*-bromobenzyltrimethylsilanes were obtained in 19% and 21% yield (based on bromobenzyl bromides), respectively. The *meta* derivative had b.p. 132°C/21 Torr, n_D^{20} 1.5198, d_4^{22} 1.0460 (lit.²⁴ b.p. 79°C/2 Torr, n_D^{25} 1.5250). The *para* derivative had b.p. 147–148°C/34 Torr, n_D^{20} 1.5295, d_4^{22} 1.1093 (lit.¹⁹ b.p. 88–89°C/3 Torr, n_D^{20} 1.5303). The purity of all the compounds was checked by gas chromatography.

Distribution of Isomers in Bromination

To a 5 ml flask were weighed 3% mol of the catalyst (with respect to the substrate). Then the substrate and a portion of n-heptane were successively added and weighed. The flask was then protected from light by jacket and provided with reflux condenser topped with calcium chloride tube. The flask was then fitted to the vibrator, placed in the 40°C bath, and the bromine solution

(2.5 ml of Br₂ in 10 ml of n-heptane) was added. The amount of bromine corresponded to 8% conversion of brominated silane and the resultant concentration of n-heptane was 70% mol. The mixture was then heated to constant temperature with shaking for the period which depended on the reactivity of the brominated compound (10–50 min). After the reaction was completed, the flask was allowed to cool for 3 min, and then the contents were added to the flask containing ethereal solution of methylmagnesium bromide (in 50% excess, c. 1.5 mol/l). Even when compounds did not contain hydrolysable chlorine, at least minimum amount (10 ml) of methylmagnesium bromide was added. The methylation was finished after efficient stirring and standing for 12 h at room temperature by hydrolysis with dilute HCl (c. 1 : 10). The ether layer was washed successively with sodium bicarbonate solution and water and dried over magnesium sulphate. The major portion of the ether was removed by distillation from water bath through a 6 TP column at the temperatures inside the reaction flask up to 60°C. The residual mixture was analysed by gas chromatography, using 4% poly(ethylene glycol)adipate on grinded unglazed tiles at 105°C. As found by calibration, the weight ratio of isomers corresponded within experimental error to the ratio of the area of their chromatographic peaks.

Relative Rate Constants of Bromination

Relative rate constants of bromination were determined by the method of competition reactions and related to benzene. This compound has however been directly used only in measuring the reactivity of benzyltrichlorosilane. In the other cases, where the reactivity of the compounds was not comparable with that of benzene, tert-butylbenzene was chosen as auxiliary standard, and its reactivity was determined at the same conditions by carrying out the competition reaction with benzene. The procedure used in competition bromination and the work-up of the reaction mixture was the same as in the determination of distribution of isomers at maximum 8% conversion to monobromo derivatives. Standard and brominated compound were weighed in amounts which ensured that chromatographic peaks of the bromo derivatives were, as far as possible, of approximately equal heights. Weighed amounts of the catalyst and the amount of n-heptane were calculated with respect to the total amount of brominated substances. In all the measurements the catalysts were used in c. 3% mol, the reaction temperature was 40°C and the amount of the solvent was 70% mol. The relative rate constants were calculated according to the equation

$$k_{rel} = \log [A_0/(A_0 - B)] / \log [X_0/(X_0 - Y)], \quad (1)$$

where the symbols for molar concentrations designate A brominated compound, B its monobromo derivative, X standard, Y the monobromo derivative of the standard and suffix the initial concentrations. A₀ and X₀ are the quantities known from weighed amounts, B and Y were obtained by weight balance on the basis of the chromatogram of the analysed mixture, for which analysis of peak areas of both monobromo derivatives and of at least one of the unreacted starting compounds had to be known. The area corresponding to the unreacted silane was used in calculations, since there was lesser danger of its loss during work-up of the analysed sample, because of higher boiling point of the substance, relative to the standard. The reaction mixture after competitive bromination was analysed with 15% silicone elastomer E-302 on Chromosorb.

Precision of Quantities Measured

The samples were weighed with the accuracy ±0.3 mg at the weighed amounts 80–1500 mg, the catalyst with the accuracy ±0.2 mg, *i.e.* at the worst case 6% rel. at the weighed amount 6–55 mg. The changes in reaction temperature have not essential effect on the distribution

of isomers, as well as on relative rate constants, since, as checked in the bromination of phenylmethylchlorosilane under otherwise identical conditions at 60°C, the so obtained values do not differ from those determined at the temperature²⁵ 40°C; the temperature was maintained constant within $\pm 2^\circ\text{C}$. The areas of corresponding chromatographic peaks were planimetrically measured at least five times and their average was taken as the resultant value. The error in planimetry amounted to 2–3%. Each sample was analysed from two to five times and the arithmetic mean of calculated values was further used. The accuracy of the analysis (including the error in planimetry) was tested by determining limits of variation, standard deviation and variation coefficient of arithmetic mean²⁶. The standard deviation was estimated according to Dean and Dixon²⁷ with the use of the formula for small set of data, $s = (k_n/\sqrt{n}) R$, and the variation coefficient in per cent was calculated according to the formula $v = (s/\bar{x}) \cdot 100$, where s is the standard deviation of the average, k_n is Dean–Dixon coefficient (different values for different n), R limits of variation, n is the number of analyses, \bar{x} is the arithmetic mean and v is the variation coefficient in per cent. The average value of variation coefficient in the determination of isomer distributions was c. 3–4%, in the determination of relative rate constants it amounted to 5–6%. The standard deviation of the average for k_B and for the reactivity of individual positions was calculated from the corresponding standard deviations s_1 and s_2 and the values of the appropriate constants according to the relation

$$s = f \sqrt{(s_1^2 x_2^2 + s_2^2 x_1^2)},$$

where f is the constant corresponding to the number of positions, x_1 and x_2 are corresponding rate constants or percentual amounts of isomers.

RESULTS AND DISCUSSION

Directing Effects of Silylmethyl Groups

Distribution of the isomers formed in the catalytic bromination of benzylmethylchlorosilanes is presented in Table I. For the *meta* isomer, formed in very small amounts, only upper limits of its amount are given. The silylmethyl groups all are strongly *ortho*, *para*-directing and with benzyltrimethylsilane and benzyldimethylchlorosilane the *meta* isomer has not been found at all. From Table I it is obvious that the *p/o* ratio varies over broad range and that the *para* position is preferred more when iodine, instead of iron, is used as catalyst. In all the cases this ratio is higher than that corresponding to purely statistical occurrence and it is also higher than the ratio found in a study of analogous chlorination⁵. The fact that the *para* position is preferred more in bromination than in chlorination can probably be accounted for by greater steric requirements of the bulkier electrophilic species in the course of the bromination.

The very strong *ortho*, *para*-direction with prevailing *para* position and simultaneous desactivation of position *meta* (even with trichlorosilylmethyl group, Table III, in which case reactivity is comparable with the reactivity of benzene) can above all be explained by hyperconjugation contribution, which is made possible by methylene bridge. In benzyltrimethylsilane we deal here obviously with hyperconjugation shift of Si—C bond electrons in the sense of formula I. It seems likely that in this com-

pound the contribution from the Si—C bond, which is more polar than the C—H one, is prevailing. The ability of the Si—C bond to share electrons with the aromatic nucleus decreases with decreasing electropositivity of the silyl group bonded to the methylene bridge. So, *e.g.* while in the bromination of the series $C_6H_5(CH_2)_n \cdot Si(CH_3)_3$ the reactivity of the compounds decreases in the order $n = 1 \gg 3 > 2 > 0$, in the bromination of the series $C_6H_5(CH_2)_nSiCl_3$ the reaction rate parallels the order corresponding to the pure inductive effect of trichlorosilylmethyl groups¹⁰, *i.e.* $n = 0 < 1 < 2$.

Hyperconjugation contributions from C—H bonds of the methylene bridge (formula II) also decrease with increasing electronegativity of the group bonded to the methyl groups²⁸. The decrease of electron density on the C—H bond upon substitution of the methyl group on silicon for chlorine radical can be expected to be smaller (transfer of electron density through more bonds) than the decrease of electron density on the Si—C bond. In the series of benzylmethylchlorosilanes under study, where the nature of the group bonded *via* methylene bridge varies from strongly electropositive (SiMe₃—) to strongly electronegative (SiCl₃—), it is difficult to decide which type of hyperconjugation is operating. In the case of trimethylsilylmethyl group hyperconjugative action of the Si—C bond is probably more important than that of the C—H bond. On the other hand, it is possible that in trichlorosilylmethyl group weak hyperconjugation influencing of direction is caused rather by hyperconjugation from C—H bonds.

TABLE I

Distribution of Isomers in Bromination of Benzylmethylchlorosilanes
Temperature 40°C, 70% n-heptane, 3 mol% catalyst.

| Compounds | <i>ortho</i> % | <i>s</i> | <i>v</i> % | <i>meta</i> % | <i>para</i> % | <i>s</i> | <i>v</i> % | <i>p/o</i> |
|--------------------------|-------------------|----------|---------------|------------------|------------------|----------|---------------|------------|
| Catalyst Fe | | | | | | | | |
| $C_6H_5CH_2(CH_3)_3Si$ | 3.4 | 0.4 | 11 | 0 | 96.6 | 0.4 | 0.4 | 28.5 |
| $C_6H_5CH_2(CH_3)_2SiCl$ | 7.6 | 0.3 | 4.2 | 0 | 92.4 | 0.3 | 0.4 | 12.1 |
| $C_6H_5CH_2(CH_3)SiCl_2$ | 19.8 | 0.8 | 4.1 | < 0.2 | 80.2 | 0.8 | 1.0 | 4.0 |
| $C_6H_5CH_2SiCl_3$ | 26.7 | 0.6 | 2.1 | < 0.9 | 73.3 | 0.6 | 0.8 | 2.8 |
| Catalyst I ₂ | | | | | | | | |
| $C_6H_5CH_2(CH_3)_3Si$ | 3.0 | 0.2 | 7.5 | 0 | 97.0 | 0.2 | 0.2 | 32.4 |
| $C_6H_5CH_2(CH_3)_2SiCl$ | 4.3 | 0.4 | 9.2 | 0 | 95.7 | 0.4 | 0.4 | 22.1 |
| $C_6H_5CH_2(CH_3)SiCl_2$ | 6.9 | 0.2 | 2.4 | < 0.1 | 93.1 | 0.2 | 0.2 | 13.6 |
| $C_6H_5CH_2SiCl_3$ | 10.6 | 0.5 | 5.0 | < 0.3 | 89.4 | 0.5 | 0.6 | 8.5 |

Satisfactory explanation of the higher p/o ratio in the brominations catalysed by iodine and iron cannot at present be offered. Substitution to the *ortho*-positions in the catalysis by iodine might be in part sterically unfavoured by the presence of bulky agglomerates formed in the course of polarization of bromine molecule by iodine molecules. The formation of charge-transfer complexes between brominated substance and bromine or iodine molecules, which are being studied by UV spectroscopy²⁹, may play a role, too.

The Effect of Structure on the Reactivity of Benzylmethylchlorosilanes

Relative rate constants of the bromination of benzylmethylchlorosilanes with respect to *tert*-butylbenzene were determined by the *Method of Competition Reactions* (Table II). For purposes of comparison, relative rate constant of benzyltrichlorosilane was determined also with respect to benzene. The value of the so obtained constant did not differ much from the value determined with the aid of *tert*-butylbenzene. In order to ensure consistency of the results throughout the series, calculations were made only with the values obtained with the aid of *tert*-butylbenzene. Using the values presented in Tables I and II, the reactivities of individual positions in aromatic ring have been calculated (Table III). From Table III it is evident that benzylmethyl-

TABLE II

Average Relative Rate Constants of the Bromination
40°C, 70% *n*-heptane, 3 mol.% catalyst.

| Compound | Standard | \bar{k}_{rel} | s | $v, \%$ |
|--------------------------|-------------------|-----------------|-------|---------|
| Catalyst Fe | | | | |
| $C_6H_5CH_2(CH_3)_3Si$ | $(CH_3)_3CC_6H_5$ | 31 | 1 | 3.8 |
| $C_6H_5CH_2(CH_3)_2SiCl$ | $(CH_3)_3CC_6H_5$ | 16 | 1 | 8.5 |
| $C_6H_5CH_2(CH_3)SiCl_2$ | $(CH_3)_3CC_6H_5$ | 1.08 | 0.05 | 4.3 |
| $C_6H_5CH_2SiCl_3$ | $(CH_3)_3CC_6H_5$ | 0.42 | 0.03 | 7.6 |
| $C_6H_5CH_2SiCl_3$ | C_6H_6 | 0.71 | 0.05 | 7.5 |
| $(CH_3)_3CC_6H_5$ | C_6H_6 | 2.21 | 0.07 | 3.3 |
| Catalyst I ₂ | | | | |
| $C_6H_5CH_2(CH_3)_3Si$ | $(CH_3)_3CC_6H_5$ | 181 | 13 | 7.2 |
| $C_6H_5CH_2(CH_3)_2SiCl$ | $(CH_3)_3CC_6H_5$ | 34 | 2 | 6.3 |
| $C_6H_5CH_2(CH_3)SiCl_2$ | $(CH_3)_3CC_6H_5$ | 0.98 | 0.01 | 1.2 |
| $C_6H_5CH_2SiCl_3$ | $(CH_3)_3CC_6H_5$ | 0.065 | 0.003 | 5.3 |
| $C_6H_5CH_2SiCl_3$ | C_6H_6 | 2.52 | 0.04 | 1.7 |
| $(CH_3)_3CC_6H_5$ | C_6H_6 | 29 | 2 | 6.1 |

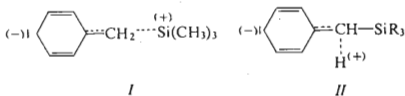
TABLE III
 Reactivity of Individual Positions in Bromination of Benzylmethylchlorosilanes
 Temperature 40°C, 70% n-heptane, 3 mol.% catalyst.

| Compound | k_B^a | $\log k_B$ | <i>s</i> | <i>v</i> , % | Reactivity of positions | | | | <i>v</i> , % | |
|--------------------------|---------|------------|----------|--------------|-------------------------|--------------|-------------|---------------------|--------------|--|
| | | | | | <i>ortho</i> | <i>v</i> , % | <i>meta</i> | <i>para</i> | | |
| Catalyst Fe | | | | | | | | | | |
| $C_6H_5CH_2(CH_3)_2Si$ | 68 | 1.83 | 3 | 5.1 | 6.9 | 12 | 0 | 393 | 5.1 | |
| $C_6H_5CH_2(CH_3)_2SiCl$ | 35 | 1.54 | 3 | 9.2 | 8.0 | 10 | 0 | 193 | 9.2 | |
| $C_6H_5CH_2(CH_3)SiCl_2$ | 2.4 | 0.38 | 0.1 | 5.5 | 1.4 | 6.8 | <0.01 | 12 | 5.6 | |
| $C_6H_5CH_2SiCl_3$ | 0.93 | -0.03 | 0.08 | 8.3 | 0.74 | 8.5 | <0.02 | 4.1 | 8.3 | |
| Catalyst I ₂ | | | | | | | | | | |
| $C_6H_5CH_2(CH_3)_2Si$ | 5 160 | 3.71 | 490 | 9.5 | 463 | 12 | 0 | 3 · 10 ⁴ | 9.5 | |
| $C_6H_5CH_2(CH_3)_2SiCl$ | 959 | 2.98 | 84 | 8.8 | 124 | 13 | 0 | 5 510 | 8.8 | |
| $C_6H_5CH_2(CH_3)SiCl_2$ | 28 | 1.45 | 2 | 6.2 | 5.8 | 6.7 | <0.06 | 156 | 6.2 | |
| $C_6H_5CH_2SiCl_3$ | 1.8 | 0.27 | 0.2 | 8.1 | 0.58 | 9.6 | <0.02 | 9.9 | 8.2 | |

^a k_B is the relative rate constant with respect to benzene.

chlorosilanes all are more reactive than benzene (the only exception was benzyltrichlorosilane in the iron-catalysed reaction). The dependence of logarithms of relative rate constants on the number of chlorine atoms in the silylmethyl group in the catalysis both with iron and with iodine is linear (correlation coefficients r 0.972 and 0.992, respectively). It can be thus concluded that the reactivity change in the series of benzylsilanes is caused in the main by inductive effects of silylmethyl groups, as expected, since the effect of ($p \rightarrow d$) π character of the Si—Cl bond on reactions of other substituents on silicon is not, as a rule, important⁵.

Similarly as in catalytic chlorination⁵, relative reactivity of benzylmethylchlorosilanes in the bromination catalysed by iodine is higher, relative to benzene, than in the iron-catalysed reaction. In order to achieve approximately equal conversions to monobromo derivatives, longer reaction time was required with iodine than with iron as catalyst. The difference in reactivities of the first and the last member of the series, which in the chlorination was similar for both catalysts (in the values of $\log k_B$ 2.99 for iodine and 3.11 for iron)⁵, markedly differs in the bromination (3.45 for iodine and 1.87 for iron). The bromination catalysed by iodine seems to be somewhat more selective than the chlorination of these substances, while the opposite situation arises



in the case of iron as catalyst. Also the ratio of rate constants of tert-butyl benzene to benzene in the catalysis with iodine and iron equals to 2.83 in the chlorination⁵ while it amounts to 12.9 in the bromination. The higher selectivity of bromination catalysed with iodine, relative to that catalysed with iron, is also accompanied by the lower percentual proportion of the *meta*-isomer. Differences between the two catalysts become less distinct as the reactivity of halogenated substance decreases.

Electrophilic species in the bromination catalysed with iron is thus more reactive than that in the iodine catalysed reaction. This is in full agreement with the fact that iron tribromide as Lewis acid polarizes bromine molecule better than iodine molecule. This difference in the action of both catalysts has not so far been established in the studies of chlorination, since in the absence of solvent it usually coincides with more pronounced effects of different medium.

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