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CLEAVAGE OF α-HALO-SUBSTITUTED ALKYL GROUPS FROM SILICON. THE MECHANISM OF CATALYSIS BY AMMONIA BUFFER

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Summary

Kinetic studies have been made of the base-catalysed cleavage of α-dihalo-substituted alkyl groups from silicon in n-propanol—water in the presence of ammonia buffer. The separate rate constants for the concurrent base-catalysed and base-plus-nucleophile-catalysed processes have been determined for the compounds $XC_6H_4(Me_2)SiCHCl_2$ with X = H, *p*-MeO, *p*-Me, *p*-Cl, *m*-Cl, *m*-CF_3 and a good correlation with σ-constants found for both types of catalysis. Solvent isotope effects and steric effects of substituents have also been studied. Possible mechanisms are discussed.

Introduction

The cleavage of α-dihalo-substituted alkyl groups from silicon in alcohol—water mixtures in the presence of an ammonia buffer was recently shown to proceed according to the following rate law [1]:

$$\frac{-d[\equiv SiCHX_2]}{dt} = \frac{d[CH_2X_2]}{dt} = \{k_1 + k_2[NH_3]\}\frac{[NH_3]}{[NH_4Cl]}[\equiv SiCHX_2]$$

This was interpreted in terms of two competitive mechanisms of catalysis: simple base and combined base—nucleophile catalysis. The former involves nucleophilic attack by alkoxide or hydroxide ion OR^- (R = n-Pr or H), on silicon, and the latter involves base-catalysed ammonolysis of the Si—C bond followed by fast solvolysis of the resulting silylamine.

The OR^--catalysed ammonolysis represents an unusual type of Si—C bond cleavage in alcohol—water systems. If as usual amide ion is assumed not to be present in kinetically significant concentration, the mechanism must either include a termolecular elementary reaction or involve the formation of a 5-coordinated silicon intermediate. Structural variation in the leaving group is known to exert a pronounced influence on the rate of reaction [1], and the main purpose of the present study was to obtain information about the type and degree of the charge developed on the silicon atom in the transition state and to provide more information about steric effects. Secondary aim was to see whether solvent-isotope effect measurements could give any evidence for proton transfer in the rate-determining step.

Results and discussion

a. General considerations

The results previously obtained are best rationalized in terms of the general mechanism previously proposed [1] comprising the sequence of reactions 2-6.

Simple catalysis:

$$OR^- + Me_3SiCHX_2 \xrightarrow{slow} Me_3SiOR + CHX_2^- \tag{2}$$

$$CHX_2^- + ROH \xrightarrow{fast} CH_2X_2 + RO^- \tag{3}$$

Combined catalysis:

$$OR^- + NH_3 + Me_3SiCHX_2 \xrightarrow{slow} Me_3SiNH_2 + CHX_2^- + ROH \tag{4}$$

$$CHX_2^- + ROH \xrightarrow{fast} CH_2X_2 + OR^- \tag{5}$$

$$Me_3SiNH_2 + ROH \xrightarrow{fast} Me_3SiOR + NH_3 \tag{6}$$

Step 3 may be also synchronous with step 2, just as step 5 may be synchronous with step 4, there then being electrophilic assitance to the leaving group.

(continued on p. 363)

TABLE 1

KINETIC RESULTS

n-PrOH/H_2O system 8/2 v/v, μ = 0.4, temp. 25°C.

Silane	[silane] (*M*)	[NH_3] (*M*)	[NH_4Cl]^a × 10^2 (*M*)	k_{obs} × 10^4 (s^{-1})	k_1 × 10^7 (s^{-1})	k_2 × 10^6 (l mol^{-1} s^{-1})
$XC_6H_4Si(Me)_2(CHCl_2)$						
X = H	0.39	0.099	0.13	0.27		
	0.39	0.197	0.26	0.43		
	0.39	0.494	0.65	0.62		
	0.39	0.691	0.91	0.80	2 1 ± 0.5	1.31 ± 0.04
	0.39	0.987	1.30	1.06		
	0.39	1.480	1.95	1.73		
	0.39	1.974	2.60	2.18		
	0.39	2.961	3.90	3.09		
X = *p*-Meo	0.19	0.099	0.13	0.10		
	0.19	0.197	0.26	0.16		
	0.19	0.494	0.65	0.23		
	0.19	0.691	0.91	0.27	0.84 ± 0.33	0.40 ± 0.03
	0.19	0 987	1.30	0.29		

(Table continued)

TABLE 1 (continued)

Silane	[silane] (*M*)	[NH$_3$] (*M*)	[NH$_4$Cl]^a × 10^2 (*M*)	k_{obs} × 10^4 (s^{-1})	k_1 × 10^7 (s^{-1})	k_2 × 10^6 (l mol^{-1} s^{-1})
	0.19	1.480	1.95	0.53		
	0.19	1.974	2.60	0.70		
X = *p*-Me	0.19	0.099	0.13	0.12		
	0.19	0.197	0.26	0.15		
	0.19	0.494	0.65	0.27		
	0.19	0.691	0.91	0.38	0.92 ± 0.27	0.59 ± 0.02
	0.19	0.987	1.30	0.42		
	0.19	1.480	1.95	0.58		
	0.19	1.974	2.60	0.92		
X = *p*-Cl	0.19	0.099	0.13	1.08		
	0.19	0.197	0.26	1.38		
	0.19	0.494	0.65	2.73		
	0.19	0.691	0.91	3.42	6.0 ± 1.5	5.97 ± 0.14
	0.19	0.987	1.30	4.80		
	0.19	1.480	1.95	6.97		
	0.19	1.974	2.60	9.67		
X = *m*-Cl	0.19	0.099	0.13	1.08		
	0.19	0.197	0.26	2.00		
	0.19	0.494	0.65	3.67		
	0.19	0.691	0.91	4.75	9.5 ± 1 8	8.6 ± 1.7
	0.19	0.987	1.30	6.50		
	0.19	1.480	1.95	11.67		
	0.19	1.974	2.60	14.00		
X = *m*-CF$_3$	0.18	0.099	0.13	2.50		
	0.18	0.197	0.26	2.83		
	0.18	0.494	0.65	4.83		
	0.18	0.691	0.91	6.58	11.4 ± 1.1	13.2 ± 0.9
	0.18	0.987	1.30	12.90		
	0.18	1.480	1.95	15.05		
	0.18	1.974	2.60	20.67		
Et$_3$SiCHBr$_2$	0.22	0.099	0.13	0 20		
	0.22	0.197	0.26	0 23		
	0.22	0.494	0.65	0.33	2.08 ± 0.04	0.468 ± 0.004
	0.22	0.987	1.30	0.52		
	0.22	1.974	2.60	0.86		
Me$_3$SiCHBr$_2$ in deuterated system	0.30	0.046	0.39	1.83		
	0.30	0.092	0.78	2.25		
	0.30	0.184	1.56	2.40	159 ± 11	19.5 ± 2.9
	0.30	0.461	3.90	2.75		
	0.30	0.645	5.46	3.47		
		[MeNH$_2$]	[MeNH$_2$ · HCl]			
Me$_3$SiCHBr$_2$	0.29	0.092	0.78	6.65		
	0.29	0.184	1.56	6.57	570 ± 9	<1.7
	0.29	0.461	3.90	6.67		
	0.29	0.922	7.80	6.83		

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[a] $k_{obs.} = (k_1 + k_2[NH_3])\dfrac{[NH_3]}{[NH_4Cl]}$.

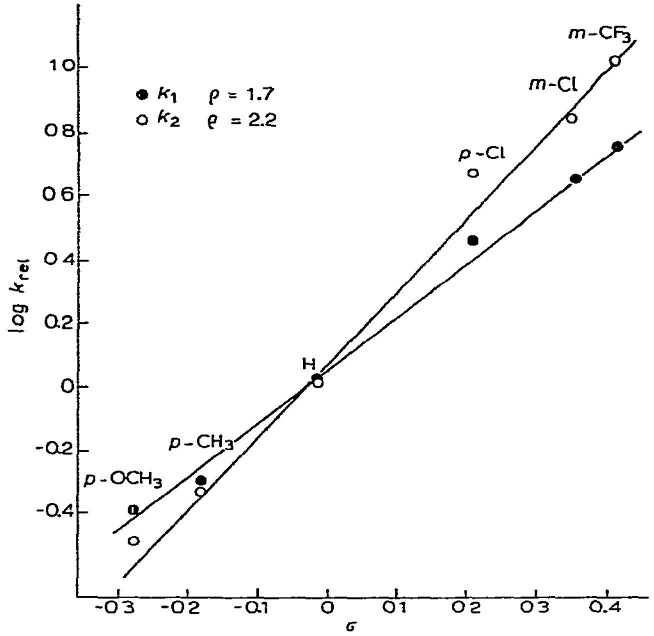

Fig. 1. Hammett plot for solvolysis of $XC_6H_4Si(Me_2)(CHCl_2)$ compounds ($PrOH/H_2O$ 8/2 v/v system, NH_3/NH_4Cl buffer, $\mu = 0.4$, 25°C).

TABLE 2

COMPARISON OF SOLVOLYSIS REACTIONS OF (DIHALOALKYL)TRIORGANOSILANES SHOWING SIMPLE AND COMBINED CATALYSIS

n-$PrOH/H_2O$ system 8/2 v/v, NH_3—NH_4Cl buffer, temp 25°C, $\mu = 0.4$.

Feature	Simple catalysis	Combined catalysis
Reactivites in the series $k(Cl)/k(Br)/k(I)$ [a] (Me_3SiCHX_2)	1/116/246	1/24/49
$\Delta H^{\neq}$ in the series Cl/Br/I [a] (Me_3SiCHX_2)	-/15.9/13.0	19.5/12.7/11.3
$\Delta S^{\neq}$ in the series Cl/Br/I [a] (Me_3SiCHX_2)	-/(—27.9)/(—36.1)	(—21.1)/(—37.7)/(—41.0)
Polar effects of substituents $\rho(XC_6H_4SiMe_2CHCl_2)$	1.7	2.20
Steric effects in the leaving group [a] $k(Me_3SiCCl_2Me)/k(Me_3SiCHCl_2)$	0.19	0.048
Steric effects of substituents $k(Et_3SiCHBr_2)/k(Me_3SiCHBr_2)$	0.0194	0.0277
Solvent isotope effect ($Me_3SiCHBr_2$, $PrOD/D_2O$) $k(H)/k(D)$	0.67	0.87
Buffer effect ($Me_3SiCHBr_2$) $k(MeNH_2—MeNH_2 \cdot HCl)/k(NH_3—NH_4Cl)$	5.3	<0.1
Contribution of OH^- and OPr^- ions $Me_3SiCHBr_2$ $k(\equiv SiOH)/k(\equiv SiOPr)$	2.60	—

[a] From ref. 1.

We think it reasonable to interpret the ammonolysis 4 as formally composed of three steps as follows:

$$NH_3 + Me_3SiCHX_2 \rightleftharpoons \underset{(I)}{[Me_3Si(NH_3)(CHX_2)]} \qquad (a)$$

$$OR^- + I \rightleftharpoons \underset{(II)}{[Me_3Si(NH_2)(CHX_2)]^-} + ROH \qquad (b)$$

$$II \rightarrow Me_3SiNH_2 + CHX_2^- \qquad (c)$$

The choice of mechanisms is as follows: (1) A one-step synchronous mechanism, with steps a, b and c simultaneous. (2A) A two-step mechanism involving the formation of intermediate I, with b and c synchronous. (2B) A two-step mechanism involving the formation of intermediate II, with a and b synchronous, (3) A three-step mechanism with a, and b and c all separate. Since stabilisation of the leaving carbanion markedly increases the reactivity [1], the Si—C bond breaking must take place in the rate-determining step. Mechanisms 1 and 2A correspond to the general base catalysis and mechanisms 2B and 3 to specific base catalysis.

Formally we could write an analogous mechanism for the slow step (2) in simple catalysis using a solvent molecule in the place of ammonia. However, though additional driving force seems to be necessary to form the NH_2^--like species, direct attack of OR^- on silicon is more feasible in simple solvolysis, and the process can be represented in two steps:

$$OR^- + MeSiCHX_2 \rightleftharpoons \underset{(II')}{[Me_3Si(OR)(CHX_2)]^-} \qquad (b')$$

$$II' \rightarrow Me_3SiOR + CHX_2^- \qquad (c')$$

The formation of the intermediate II in ammonolysis seems more probable than that of II′ in simple solvolysis. First ammonia and amines are known to be better ligands for pentacovalent silicon than water or alcohol, and the same should apply to their conjugate bases. Secondly, NH_2^- is a much poorer leaving group than OR^-, thus the intermediate II would be much more likely to break down to product than the intermediate II′. The latter, if formed should always break down to give starting materials, because the extremely bad leaving group CHX_2^-, is not likely to be able to compete with OR^- as a leaving group.

Stepwise mechanisms for α-dihaloalkylsilane ammonolysis can thus be expected. They show some analogy to the mechanisms of base-catalysed ester aminolysis, which involve the formation of tetrahedral intermediates [2-4].

b. Variation in the nature of the nucleophile

GLC analysis shows that the contribution of OH^- and OR^- to the simple solvolysis reaction of (dibromomethyl)trimethylsilane is $\dfrac{k_1(\equiv Si—OH)}{k_1(\equiv Si—OPr)} = 2.60$

(25°C). The molar concentrations of water and alcohol are almost equal, and the basicity can be eliminated as a factor affecting the ratio. Propoxide ion, being a softer base than hydroxide ion [5], should be a more efficient nucleophile, so steric requirements are probably responsible for the larger contribution from OH^-.

Methylamine proved to be a stronger base than ammonia in propanol—water 8/2 v/v, and the apparent rate constant for simple solvolysis was more than five times larger with methylamine buffer. However, methylamine buffer was found to be much less effective than ammonia buffer in combined catalysis. In view of the fact that OPr^- is an effective nucleophile in simple solvolysis of (dihalomethyl)trimethylsilanes, the small reactivity in methylaminolysis may not be due only to steric effects*, but may result also from the smaller tendency of methylamine or methylamine-substrate complex to donate a proton to the base.

c. Solvent isotope effects

Experiments in deuterated solvent, PrOD + D_2O, gave small values of solvent isotope effect for both types of catalysis ($k(H)/k(D)$ was 0.67 and 0.87 for simple and combined catalysis, respectively). The contribution of secondary solvent effects is dominant in both cases. In deuterated media the OR^- species are less effectively solvated and their concentration, as governed by the equilibrium $ROL + NL_3 \rightleftharpoons RO^- + NL_4^+$ (L = H or D) is lower. From values of fractionation factors, and assuming that the situation in propanol—water mixture is similar as in water, this would tend to increase $k(H)/k(D)$ by a factor of about 1.7-1.8 [6]. Thus the true isotope effect for the simple solvolysis may be as low as 0.4, which would be close to the expected value of about 0.4-0.5 for secondary isotope effects resulting from OR^- transfer from its solvation shell to silicon atom, (e.g. changing from OR^- to ROSi)**. The low value of the solvent isotope effects is consistent with a structure for the transition state*** in which the Si—O bond is fully or almost fully formed. It indicates also that no substantial proton transfer to the leaving carbanion takes place in the rate-determining step of simply solvolysis.

If the mechanism of ammonolysis involved specific base-catalysis mechanisms (2B and 3) a secondary solvent-isotope effect close to unity could be expected since the factor associated with the smaller concentration of OR^- in deuterated medium should be outweighed by its higher basicity in reaction with the intermediate I (mechansim 3), or with ammonia and substrate (mechanism 2B). Calculation based on aqueous systems using available values of fractiona-

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* See the discussion of steric effects of substituents.

** The CH_3OH molecule is preferred over CH_3OD in the methoxide ion solvation shell by a factor of 1.32 [7]. The reaction of this ion to form a transition state in which its solvation shell consisting of 3 solvent molecules is dispersed will proceed more slowly in CH_3OH than in CH_3OD by a factor of 0.43. A similar effect may be expected for other alkoxide ions and for hydroxide ion. The experimentally determined factor for OH^- in water was about 0.5 [8] and the base solvolysis of benzylsilanes was found to give the same value of about 0.5 in alcohol and in alcohol—water systems [9]. It seems unlikely that the behaviour of OR^- in a water—propanol mixture differs significantly in this respect.

*** In the case of a stepwise mechanism the highest energy transition state must be considered.

tion factors [6] and assuming that the nitrogen atom in the intermediate I carries the same charge as in NH_4^+, and in II the same as in NH_3, gives 0.95 for the secondary effect contribution to $k(H)/k(D)$*, which is close to experimental value of $k(H)/k(D)$ 0.87. Again the isotope effects give no indication of proton transfer to the leaving group in the rate-determining step.

d. Steric effects of substituents

Steric effects of substituents at silicon play a rather substantial influence in both the ammonolysis and the simple solvolysis, as is indicated by a marked decrease in reactivity on going from trimethyl to triethyl derivatives (Table 2). The factors are 36 for ammonolysis and 52 for simple solvolysis.

The smaller degree of Si—C breaking in the activated complex in ammnolysis [1] together with the slightly higher entropy of activation could imply a more crowded structure for the transition state than in simple solvolysis. In fact, steric effects in the leaving group were found to be pronounced and more important in ammonolysis [1]. Qualitatively the same might be expected for steric effects of substituents at silicon, but in fact, the reactivities of triethyl and trimethyl derivatives show that the effects are greater for the simple solvolysis. The contribution of hydroxide ion in the simple solvolysis reaction exceeds 70%. The silicon—oxygen and silicon—nitrogen bonds have approximately the same length and the amino group and hydroxyl group have similar steric requirements. If the stereochemistry of the reaction is the same (rearside attack), the reversal of the steric effects indicates that the Si—N bond making in the transition state for ammonolysis is less advanced than the Si—O bond formation in the simple solvolysis. This is in agreement with the principle of microscopic reversibility only if the concerted mechanism 1 operates. For this mechanism the low value of solvent-isotope effects requires the species attacking silicon to have a structure close to NH_2^-, which is a much stronger nucleophile than OH^-, and thus less new bond formation is required to push out the leaving group.

However it could be argued that the observed reversal in steric effects comes from the different stereochemical paths of reactions. Substitution of hydrogen by methyl in dihalomethyl groups should make the flank attack more difficult than rearward attack. On the other hand, replacement of methyl groups at silicon by ethyl groups may markedly slow down the reaction involving backside attack as this mode of entry of the nucleophile requires three bulky ethyl groups to occupy sterically unfavourable equatorial positions in the transition state. Thus the results would be consistent with flank attack in ammonolysis and backside attack in solvolysis.

e. Polar effects of substituents

The positive ρ values indicate that a negative charge is located on silicon in the transition state and thus confirms that the mechanisms are of the associative type and that in simple and combined catalysis the formation of a new bond is in advance of bond breaking. On the other hand the variation in reactivity

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* If the charge on nitrogen in I is assumed to be the same as in ammonia the calculations give a value of 0.84.

on varying the halogens of the halomethyl groups was interpreted as indicating substantial carbanionic character at the carbon atom of the leaving group in the transition state which implies a considerable degree of Si—C bond breaking [1]. In the light of the fairly large ρ value, this means that in the activated complex the new bond is either fully formed, which is equivalent to the operation of stepwise mechanisms (2A, 2B and 3), or almost fully formed if the synchronous mechanism applies. The slightly larger values found for the ammonolysis is mainly to be associated with a smaller degree of Si—C bond breaking in the activated complex. This is consistent with the synchronous mechanism in which the attacking nucleophile has a structure close to NH_2^-, since the principle of microscopic reversibility requires less of Si—C bond breaking in the transition state, in this case. The same principle also implies that less new bond formation is also required for ammonolysis, but this only partly offsets the effect of bond breaking as far as difference between the charge on the Si atom in the activated complexes of both types of catalysis is concerned. The order of the bond between silicon and the leaving groups in the transition state is much lower than between silicon and the incoming group; thus it is reasonable that bond breaking may contribute more to the difference between the polar effects of substitients in ammonolysis and in simple solvolysis, while bond making may contribute more to the difference in the steric effects of substituents.

Conclusion

Our results do not offer a clear choice between the concerted and the stepwise mechanism as the stereochemistry of ammolysis and solvolysis is not known. However, for each of the two likely the stereochemical courses, as described below one mechanism is more probable.

1. Stereochemistry is the same for ammonolysis and simple solvolysis. The steric effects rather conclusively favour the concerted route for ammonolysis. This mechanism involves a termolecular process with a 5-centred transition state, and may seem entropically unfavourable, but the proton is almost fully transferred to OR^- and the ROH entity is only loosely bound to the rest of the activated complex and contributes little to the entropy of activation. Since formation of a pentacovalent silicon intermediate is less probable in the simple solvolysis than in the ammonolysis, the solvolysis must involve a similar concerted mechanism, and the difference between both mechanisms is only one of degree.

$[ROH \qquad RO\text{- - - - -}\,Si(CH_3)_3\text{- - - - - - -}CHX_2]^{\neq}$ (simple solvolysis)

$[RO\text{-}H\cdots\cdots\cdots NH_2\cdots\cdots\cdots Si(CH_3)_3\text{------}CHX_2]^{\neq}$ (ammonolysis)

In the view of the fact that bond-making and bond-breaking are much advanced in the transition states and that the proton is fully or almost fully transferred to the solvent conjugate base, this mechanism involves a product-like structure for the transition states very similar to those for the highest energy transition states in the stepwise mechanism.

2. Stereochemistry opposite: the ammonolysis involves flank- and the solvolysis backside attack by the nucleophile. A charged nucleophile should attack silicon from the opposite side of the polar dihalomethyl group, especially as dihalomethyl is a bulky group and the negative ion is strongly solvated. Thus this mode of attack is feasible for simple solvolysis and for ammonolysis involving nucleophilic attack of NH_2^--like species. Flank entry seems possible only if uncharged ammonia attacks silicon, which corresponds to a stepwise mechanism (3 or 2B). Both these mechanisms are attractive in many respects, but the three-step route for ammonolysis is preferred as it suits the small value of the solvent isotope effect better and because the partial positive charge on the NH_3-ligand in I would lead to rapid proton exchange with OR^- base.

Experimental

General

Solvents and reactants were dried by standard procedures [10]. (Dichloromethyl) methyldichlorosilane and (dichloromethyl)dimethylchlorosilane were prepared by gas-phase chlorination [11,12].

Preparation of $XC_6H_4Si(Me_2)(CHCl_2)$ compounds

(a) Except for the compounds with X = m-CF_3 and m-Cl, these were made by treating the appropriate Grignard reagent with (dichloromethyl)methyldichlorosilane, followed by methylation with MeMgBr.

(b) m-$CF_3C_6H_4Si(Me)_2(CHCl_2)$ and m-$ClC_6H_4Si(Me)_2(CHCl_2)$ were prepared from the appropriate Grignard reagent and (dichloromethyl)dimethylchlorosilane.

Analysis and some physical constants of the products are shown in Table 3.

Preparation of $R_3SiCHBr_2$ compounds

$Me_3SiCHBr_2$ and $Et_3SiCHBr_2$ were prepared by a low temperature Grignard reaction [14] of dibromomethylmagnesium bromide with trimethylchlorosilane and triethylchlorosilane.

GLC revealed no significant quantities of impurities.

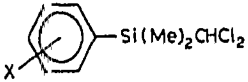
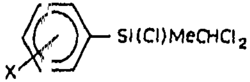
Rate measurements

The procedure has been described earlier [1,12]. Column temperatures in GLC analysis were 75°C for $XC_6H_4Si(Me)_2(CHCl_2)$ and 105°C for $R_3SiCHBr_2$ solvolysis. n-Butyl chloride and cumene, respectively, were employed as internal standards for quantitative determinations.

The hydrolysis to propanolysis rate ratio $k_1(\equiv SiOH)/k_1(\equiv SiOPr)$ for simple solvolysis of (dibromomethyl) trimethylsilane was determined by measuring the rate of formation of trimethylsilanol and trimethylpropoxysilane in the same run. Runs were performed in conditions in which the contribution from combined catalysis was negligible and consecutive propoanolysis of silanol also the hydrolysis of propoxysilane (and subsequent condensation to hexamethyldisiloxane) proceeded slowly.

TABLE 3

PHYSICAL PROPERTIES OF SYNTHESIZED COMPOUNDS

Silane	B.p. (°C/mmHg)	n_D^{25}	Analysis: found (calcd.) (%)			
			Si	H	C	Cl
						
H [a]	129-131/17	1.5327	12.71 (12.81)	5.53 (5.52)	49.23 (49.31)	32.43 (32.34)
p OCH$_3$	166/16	1.5417	11.40 (11.27)	5.81 (5.36)	48.50 (48.19)	28.20 (28.45)
p CH$_3$ [a]	146/18	1.5314	11.95 (12.04)	6.05 (6.05)	51.90 (51.50)	30.10 (30.40)
p-Cl [a]	150/11	1.5474	10.94 (11.08)	4.58 (4.37)	42.17 (42.62)	41.68 (41.94)
m Cl	120-121/4.5	1.5408	10.95 (11.08)	4.33 (4.37)	42.80 (42.62)	41.20 (41.94)
m-CF$_3$	91/2.2	1.4850	9.64 (9.78)	3.94 (3.86)	41.74 (41.82)	24.06 (24.69)
						
H	116/15	1.5435	11.58 (11.75)	3.95 (3.78)	40.40 (40.50)	43.90 (44.40)
p-CH$_3$	145/12	1.5448	10.90 (11.08)	4.58 (4.37)	42.94 (42.62)	42.10 (41.94)
p OCH$_3$	125/1	1.5226	10.61 (10.42)	4.24 (4.11)	39.98 (40.09)	39.10 (39.44)
p-Cl	126-128/3.5	1.5549	10.10 (10.22)	3.05 (2.94)	34.25 (35.05)	51.97 (51.75)
Et$_3$SiCHBr$_2$ [b]	91/6	1.5068		5.72 (5.60)	29.54 (29.18)	

[a] Prepared on other route by Seyferth et al. [13]. [b] The compound gave the expected molecular ions in the mass spectrum.

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