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HALOMETHYL-METAL COMPOUNDS
XV*. CONCERNING THE MECHANISM OF THE REACTION OF DIAZOMETHANE WITH ARYLTRICHLOROGERMANES

DIETMAR SEYFERTH** AND JIŘÍ HETFLEJŠ***
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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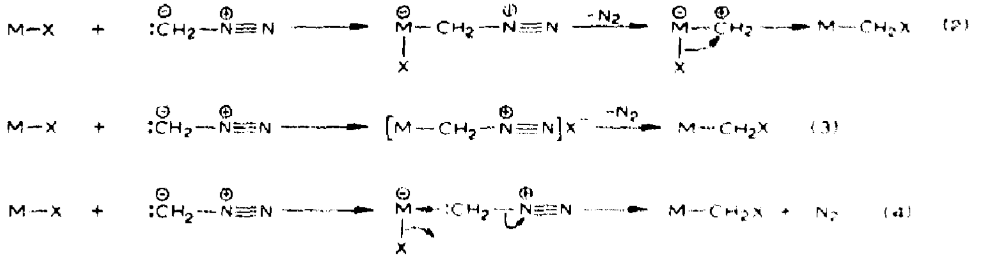
INTRODUCTION

The methylenation of metal- and metalloid-halogen bonds with diazomethane to form halomethyl derivatives of the respective elements is a well-known, general reaction of preparative utility[2] (eqn. 1). Two fundamentally different mechanisms

$$M\text{-}X + CH_2N_2 \rightarrow M\text{-}CH_2\text{-}X + N_2 \qquad (1)$$

have been proposed for this CH_2 insertion into the metal(loid)-halogen linkage: (1) nucleophilic attack of the diazomethane molecule at the metal(loid) center, with



$$M\text{—}X + :\overset{\ominus}{C}H_2\text{—}\overset{\oplus}{N}{\equiv}N \longrightarrow \underset{X}{\underset{|}{\overset{\ominus}{M}}}\text{—}CH_2\text{—}\overset{\oplus}{N}{\equiv}N \xrightarrow{-N_2} \underset{X}{\underset{|}{\overset{\ominus}{M}}}\text{—}\overset{\oplus}{C}H_2 \longrightarrow M\text{—}CH_2X \qquad (2)$$

$$M\text{—}X + :\overset{\ominus}{C}H_2\text{—}\overset{\oplus}{N}{\equiv}N \longrightarrow [M\text{—}CH_2\text{—}\overset{\oplus}{N}{\equiv}N]X^- \xrightarrow{-N_2} M\text{—}CH_2X \qquad (3)$$

$$M\text{—}X + :\overset{\ominus}{C}H_2\text{—}\overset{\oplus}{N}{\equiv}N \longrightarrow \underset{X}{\underset{|}{\overset{\ominus}{M}}}\leftarrow :CH_2\text{—}\overset{\oplus}{N}{\equiv}N \longrightarrow M\text{—}CH_2X + N_2 \qquad (4)$$

displacement of halide ion, either in a stepwise or concerted manner (eqn. 2, 3 or 4)[2-6], and (2) insertion of free methylene derived from diazomethane into the M–X bond (eqn. 5 and 6), with a biradical intermediate (*i.e.*, CH_2 in the triplet state) being favored[7].

$$CH_2N_2 \xrightarrow{-N_2} CH_2 \qquad (5)$$

$$M\text{-}X + CH_2 \rightarrow M\text{-}CH_2X \qquad (6)$$

The body of evidence concerning the mechanism of this reaction that had been available, while only indirect in nature, appeared to favor nucleophilic attack by diazomethane rather than a process involving methylene either in the triplet or singlet state. Thus, for instance, such methylenations proceed more readily in diethyl

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* For Part XIV see ref. 1.
** Alfred P. Sloan Foundation Fellow, 1962–1966.
*** Postdoctoral Research Associate, 1966–1967, on leave from the Institute for Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Praha-Suchdol.

ether than in hydrocarbon solvents[2,6], and for chlorosilanes the order of reactivity toward diazomethane was $SiCl_4 > ClCH_2SiCl_3 > CH_3SiCl_3 \sim (ClCH_2)_2SiCl_2 > (CH_3)_2SiCl_2 \ggg (CH_3)_3SiCl$[2,7]. It is apparent that electronegative substituents on silicon facilitate the methylenation reaction, and it is then of interest to note that electron-withdrawing substituents accelerate nucleophilic attack by diazomethane on substituted acetones[8]. Furthermore, as pointed out by Shaw[6], it is significant that in the case of trichlorosilane, $HSiCl_3$, the CH_2 moiety is inserted exclusively into the Si–Cl, not the Si–H bond[9]. On the other hand, when diazomethane is photolyzed in the presence of silanes such as $PhSiH_3$, Ph_2SiH_2, Ph_3SiH and Et_3SiH, insertion of CH_2 into the Si–H bond does occur[10], and this was viewed as a reaction of free methylene. However, such insertion into the Si–H bond did not occur in the absence of ultraviolet radiation, which is in striking contrast to the diazomethane + chlorosilane reactions. In this connection, our recent finding that dichlorocarbene (generated by $PhHgCCl_2Br$ thermolysis) inserts readily into the Si–H bond of triethylsilane and triphenylsilane[11,12], but not into the Si–Cl bond of trimethyl- and triethylchlorosilane and diethyldichlorosilane[13] may be significant. Thus, if CH_2 were indeed involved in the $CH_2N_2 + HSiCl_3$ reaction, either in the singlet or the triplet state, one might expect CH_3SiCl_3 or a mixture of CH_3SiCl_3 and $ClCH_2SiHCl_2$, rather than only $ClCH_2SiHCl_2$, to be formed.

The observations which have been cited in favor of a mechanism involving a CH_2 intermediate also have been made in the case of chlorosilane + diazomethane reactions[7]. Thus it was found that the reaction of methyltrichlorosilane with diazomethane, which is quite slow at −30°, is accelerated by addition of a catalytic quantity of copper bronze or cupric sulfate, agents which supposedly served to increase the rate of diazomethane decomposition. Also, it was noted in the tetrachlorosilane + diazomethane reaction that above −15° the formation of polymethylene became an important side reaction and that this reaction occurred at room temperature to the total exclusion of Si–Cl methylenation. The view that the mercuric halide + diazomethane reaction proceeds via intermediate CH_2 was reiterated in a recent paper by Reutov and Lovtsova[14].

More information concerning the metal(loid) halide + diazomethane reaction appeared to be required before a clear choice between the two mechanisms mentioned above could be made. We report here concerning a study of the relative rates of the reaction of a number of substituted aryltrichlorogermanes, the results of which strongly favor the mechanism involving nucleophilic attack by diazomethane at germanium.

RESULTS AND DISCUSSION

The reaction shown in eqn. (7) was chosen for study*. Its advantages are that

$$ArGeCl_3 + CH_2N_2 \xrightarrow{Et_2O,\ -78°} Ar(ClCH_2)GeCl_2 + N_2 \tag{7}$$

it uses easily prepared starting materials, that it proceeds smoothly in high yield under these conditions and that the products are stable, volatile and easily subject

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* The $PhGeCl_3 + CH_2N_2$ reaction was reported first by Kramer and Wright[15], but methylenation of the Ge–Cl bond in germanium tetrachloride and methyltrichlorogermane had been reported by us earlier[9].

to quantitative determination by means of gas–liquid partition chromatography (GLPC). A determination of the relative rates of the reactions of a number of *para*-substituted aryltrichlorogermanes, p-$ZC_6H_4GeCl_3$ (Z=H, Cl, F, Me, MeO) with diazomethane should provide important information concerning the nature of the attack by the methylenation reagent on the aryltrichlorogermane, and thus concerning the nature of the methylenation reagent itself.

The required aryltrichlorogermanes were prepared by reaction of the respective diarylmercury compound with germanium tetrachloride[16] (eqn. 8). Each aryl-

$$(p\text{-}ZC_6H_4)_2Hg + GeCl_4 \xrightarrow[150\text{-}190^\circ]{o\text{-xylene}} p\text{-}ZC_6H_4GeCl_3 + p\text{-}ZC_6H_4HgCl \qquad (8)$$

(Z=H, Cl, F, Me, OMe)

trichlorogermane was converted to the respective aryl(chloromethyl)dichlorogermane, and these were characterized by analysis and infrared and NMR spectroscopy. The relative rates of conversion of the aryltrichlorogermanes to the aryl(chloromethyl)dichlorogermanes were determined by means of experiments in which a mixture of p-$MeOC_6H_4GeCl_3$ and another aryltrichlorogermane was allowed to compete for a deficiency of diazomethane in diethyl ether at −78°. The reagent ratios (p-$MeOC_6H_4GeCl_3/ArGeCl_3/CH_2N_2$) used varied between 5 : 5 : 1 and 9 : 5 : 1. The yields of p-$MeOC_6H_4(ClCH_2)GeCl_2$ and $Ar(ClCH_2)GeCl_2$ in each experiment were determined by GLPC. The relative rate constants were calculated using eqn. (9)[17], where I_{Ar} and I_{std} are the initial moles of the $ArGeCl_3$ whose relative reactivity is to be determined and of p-$MeOC_6H_4GeCl_3$, respectively, and P_{Ar} and P_{std} are the moles of methylenation product formed from each. The results of these experiments are listed in Table 1.

TABLE 1

RELATIVE RATE CONSTANTS FOR METHYLENATION OF SUBSTITUTED ARYLTRICHLOROGERMANES, p-$ZC_6H_4GeCl_3$

Z	k_{rel} (±5%)	σ^0
Cl	9.76	0.27
F	5.37	0.17
H	2.24	0
CH_3	1.29	−0.15
CH_3O	1.00	−0.16

$$k_{rel} = \frac{k(ArGeCl_3)}{k(p\text{-}MeOC_6H_4GeCl_3)} = \frac{P_{Ar}}{P_{std}} \times \frac{I_{std}}{I_{Ar}} \qquad (9)$$

It is immediately clear that electron-withdrawing substituents enhance the rate of the methylenation reaction, while those which supply electron density have a rate-retarding effect. A satisfactory linear correlation of k_{rel} with Taft's σ^0 substituent constants[18] was found*; this is shown in Fig. 1. The trend shown in Fig. 1 is consistent

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* It is apparent that k_{rel} for the p-tolyl compound is *ca.* 10% above the value expected. This deviation is, however, not significant in terms of Taft's[18] estimate of ±0.03 units as the error in determinations of σ^0 values.

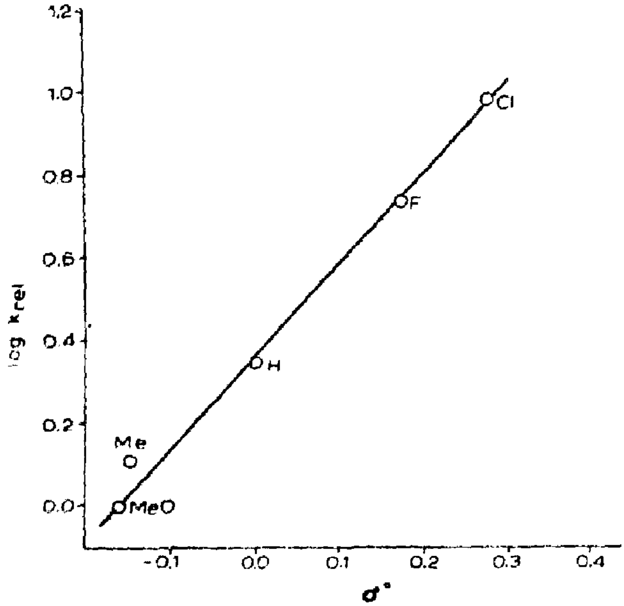
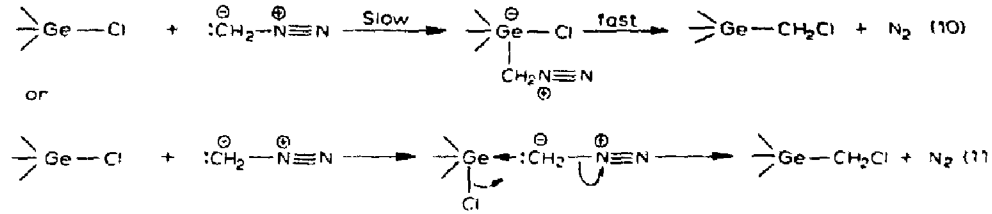


Fig. 1. Relative reactivities of p-$ZC_6H_4GeCl_3$ toward diazomethane (in ether at −78°) vs. σ^0.

with an S_N2 process with a transition state in which a higher electron density is localized on the reaction center than in the ground state, or in terms of a concerted process[19], a transition state in which bond-making is more developed than bond-breaking.

The findings summarized in Table 1 and Fig. 1 can be rationalized very nicely in terms of nucleophilic attack of diazomethane at the germanium atom, but they cannot be readily reconciled with the absence of nucleophilic character in free CH_2 generated by pyrolysis or photolysis of diazomethane (*cf.* refs. 20 and 21).

Other observations made during the course of this study speak against a free CH_2 mechanism for CH_2 insertion into the Ge–Cl bond. *If* such a process did indeed occur, in a two-step fashion (eqn. 5 and 6), then from a kinetic point of view, there would be three possibilities: (*1*) reaction (5) is fast, reaction (6) slow; (*2*) reaction (5) is slow, reaction (6) fast; (*3*) both reactions occur at comparable rates. For possibilities (*1*) (*2*) and (*3*), under comparable conditions of temperature and reagent concentrations, the rate of decomposition of diazomethane should be independent of the aryltrichlorogermane used. This, however, is not the case. When 0.1 mmole of ethereal diazomethane was added to 0.35 mmoles of (p-chlorophenyl)trichlorogermane at −78°, a *ca.* 30 min reaction time was required for discharge of the yellow diazomethane color, while a reaction time of about 240 min was necessary in an identical experiment carried out with p-$CH_3OC_6H_4GeCl_3$. Similar observations were made in the preparative experiments in which an excess of diazomethane was used (*cf.* Table 3). The times required for the discharge of the diazomethane color were *ca.* 1.5 h and in excess of 10 h for the p-chloro- and the p-methoxyphenyltrichlorogermanes, respectively. In contradiction to possibilities (*1*) and (*3*), an ethereal diazomethane solution of comparable concentration at the reaction temperature used decomposes only very slowly in the absence of added aryltrichlorogermane. Clearly, the rate of diazomethane consumption depends on the aryltrichlorogermane used, and we are thus led to the conclusion that a direct reaction between the diazomethane and aryltrichlorogermane is involved in the methylenation of the Ge–Cl bond of the latter, eqn. (10) or (11).



Two factors could serve to determine the observed substituent effects on the reactivity of substituted aryltrichlorogermanes toward diazomethane: (*a*) the inductive effects of the substituents, together with (*b*) the mesomeric effect, which could act at the reaction center via (C→Ge) p_π–d_π bonding. For example, in the case of *p*-$CH_3OC_6H_4GeCl_3$, contribution from (I) is a possibility. The fact that a satisfactory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linear correlation of log k_{rel} with σ^0 constants (Fig. 1) was observed is significant in this connection. The σ^0 constant was derived for and is expected to be valid for systems in which no conjugation between substituents and the reaction center by way of a connecting aromatic nucleus is possible, or in which the extent of such conjugation is essentially the same in the ground state and in the transition state[18]. At the present time there is no direct experimental evidence available concerning the possibility of contribution of (C→Ge) π-bonding to the stabilization of the ground state of aryltrichlorogermanes*. It may be mentioned that some experiments of Chatt and Williams[22] and Curtis and Allred[23] suggest that (C_{aryl}→Ge) π-bonding does occur to some extent, so that at present, the second possibility seems a likely one. Such a situation, correlation of log k_{rel} with σ^0, was encountered previously in the case of some solvolysis reactions of arylsilicon hydrides for which a bimolecular, nucleophilic process was proven[24].

We have also investigated briefly the copper catalysis of the aryltrichlorogermane + diazomethane reaction. In experiments in which 0.36 mmole of *p*-CH_3-$OC_6H_4GeCl_3$ and 0.1 mmole of diazomethane in 3.5 ml of ether at −78° were allowed to react, once in the absence of catalyst, once in the presence of 0.03 g of copper powder, the times required for discharge of the diazomethane color were 240 and 210 min, respectively. The effect of copper powder, if real, is not very significant. If a process such as shown in eqn. (10) obtains, it is difficult to understand a catalytic effect of copper powder. In a concerted process (eqn. 11), however, copper catalysis might be understood in terms of providing a surface for adsorption of the incipient nitrogen molecule. The values of $k(PhGeCl_3)/k(p\text{-}MeOC_6H_4GeCl_3)$ in the $ArGeCl_3$ + CH_2N_2 reaction in the absence of a catalyst and in the presence of catalytic amounts of copper powder were 2.26 and 2.13, respectively, *i.e.*, identical within experimental

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* Experiments are in progress which are directed to a consideration of this question.

TABLE 2

PREPARATION OF p-$ZC_6H_4GeCl_3$ BY THE $(p\text{-}ZC_6H_4)_2Hg + GeCl_4$ REACTION

Z	Reaction temp. (°C)	Reaction time (h)	$(p\text{-}ZC_6H_4)_2Hg$ (mmoles)	$GeCl_4$ (mmoles)	$GeCl_4$ recovery (%)	$p\text{-}ZC_6H_4GeCl_3$ yield (%)	B.p. [°C(mm)]	n_D^{25}	Analysis: found (calcd.) Carbon (%)	Analysis: found (calcd.) Hydrogen (%)
H	160–165	60	90	150	53	76	110–111 (20)	1.5532[a]	28.01 (28.11)	1.94 (1.97)
Cl	150–155	48	85	129	34	64	116–117 (10)	1.5678	24.72 (24.79)	1.45 (1.39)
F	160–165	72	82	178	47	34	106–107 (17)	1.5342	26.21 (26.29)	1.60 (1.47)
CH_3	180–190	120	74	168	56	45	129–131 (24)	1.5502	31.26 (31.11)	2.58 (2.61)
CH_3O	160–170	72	92	170	52	62	104–105 (5)	1.5610	29.21 (29.37)	2.62 (2.47)

[a] Mironov and Fedotov[27] report b.p. 118–119° (24 mm), n_D^{20} 1.5540.

TABLE 3

PREPARATION OF $(p\text{-}ZC_6H_4)(ClCH_2)GeCl_2$ COMPOUNDS

Z	$p\text{-}ZC_6H_4GeCl_3$ (mmoles)	CH_2N_2 (mmoles)	Et_2O (ml)	$p\text{-}ZC_6H_4(ClCH_2)$-$GeCl_2$ yield (%)	n_D^{25}	$\delta(CH_2Cl)$ (ppm)	$\delta(H_{arom.})$ (ppm)	Analysis: found (calcd.) Carbon (%)	Analysis: found (calcd.) Hydrogen (%)
H	12.1	16	65	95	1.5640	3.60	7.39–7.82 (m)[c]	31.26 (31.11)	2.45 (2.61)
Cl	5.25	6.3	40	98	1.5777	3.58	7.36–7.68 (m)	27.75 (27.59)	2.16 (1.99)
F	8.8	11	50	~100	1.5473	3.59	7.02–7.93 (m)	29.01 (29.16)	2.14 (2.10)
CH_3	12.6	16.3	90	98	1.5599	3.58[a]	7.21–7.61 (m)	34.02 (33.74)	3.19 (3.19)
CH_3O	5.4	6.7	43	99	1.5707	3.57[b]	6.87–7.67 (m)	32.01 (32.00)	3.31 (3.03)

[a] $\delta(CH_3)$ 2.42 ppm. [b] $\delta(OCH_3)$ 3.80 ppm. [c] (m) = multiplet.

error. This suggests to us that the reaction mechanism does not change in the presence of added copper powder.

Qualitative evidence has suggested that organogermanium halides are much more reactive toward diazomethane than are organosilicon halides[2]. In an attempted competition between phenyltrichlorogermane and phenyltrichlorosilane only a trace of a product with the GLPC retention time of $Ph(ClCH_2)SiCl_2$[15] was formed. The small yield prevented its conclusive identification, but if this peak did indeed correspond to this compound, then $k(PhGeCl_3)/k(PhSiCl_3)$ can be estimated as 109 ± 7, and this value serves to emphasize the difference between chlorogermanes and chlorosilanes in their reactivity toward diazomethane.

An extrapolation of the results of this study with aryltrichlorogermanes to halides of other elements is not strictly warranted, but we venture to suggest that for those halides of metal(loids) which are quite susceptible to nucleophilic attack at the central metal(loid) atom (*e.g.*, Hg, Al, Si, Sn, Pb), the methylenation reaction with diazomethane occurs via a mechanism represented by eqn. (2), (3) or (4).

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen. Elemental anlyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded using a Perkin-Elmer Infracord 337 spectrophotometer, NMR spectra in CCl_4 solution using a Varian Associates A60 NMR spectrometer. Chemical shifts are given in ppm downfield from internal tetramethylsilane.

Preparation of starting materials

The required diarylmercury compounds were prepared by reaction of the appropriate Grignard reagent with mercuric chloride in THF solution. The yields of pure product were in the range of 70–75 %, and the melting points of recrystallized material agreed well with those recorded previously in the literature.

Solutions of diazomethane in diethyl ether were prepared from bis(N-methyl-N-nitroso)terephthalamide (du Pont EXR-101) following the published procedure[25], were dried over KOH pellets and anhydrous $CaSO_4$ and were standardized according to published directions[26].

Preparation of aryltrichlorogermanes[16]

A solution of the diarylmercurial (36–46 mmoles) and germanium tetrachloride (65–90 mmoles) in dry *o*-xylene (35 ml) was sealed off under nitrogen in an 80 ml, heavy-walled Pyrex tube and heated (with efficient shaking) at 150–190° for 2–5 days. The cooled reaction tube then was opened. The contents were filtered (to remove ArHgCl) at −5° to 0°. Distillation of the filtrate (with added residue xylene washings) at atmospheric pressure gave unconverted germanium tetrachloride (b.p. 84–87°). When the head temperature reached the boiling point of solvent, the fractional distillation was continued at 10–20 mm. The fraction containing the desired product usually was contaminated with a small amount of dispersed Ar_2Hg (which had sublimed into the distillation head). To remove the latter, anhydrous hydrogen chloride was passed through the distillate for 10 min. The resulting solution was allowed to stand overnight, filtered to remove precipitated ArHgCl and redistilled using a 20 theoretical plate, platinum spinning band column to give pure $ArGeCl_3$. Purity was assessed by GLPC. Experimental details are summarized in Table 2.

Preparation of aryl(chloromethyl)dichlorogermanes

Into a 100 ml, three-necked flask equipped with a nitrogen-inlet tube, a pressure-equalizing dropping funnel topped with a drying tube, a pentane thermometer and a magnetic stirring assembly was charged 5–13 mmoles of the aryltrichlorogermane and 40–90 ml of anhydrous ether. The flask contents were cooled to −60° and 6–16 mmoles of diazomethane in ether was added dropwise. (The exact quantities used are given in Table 3). The reaction mixture was stirred at −60° to −70° for 8 h after completion of the addition and then allowed to warm to room temperature. The solvent was removed by distillation and the product isolated by fractional distillation at reduced pressure or by preparative GLPC. GLPC analysis (F&M Model 700, 25% General Electric Co. SE-30 on Chromosorb P, 180–205°, 40 ml per min helium flow) established the yields listed in Table 3.

Competition reactions

These experiments were carried out in a 50 ml, three-necked flask equipped as described in the previous experiment. The flask was purged with dry nitrogen, charged with a mixture of $p\text{-}CH_3OC_6H_4GeCl_3$ and $ArGeCl_3$ (total 0.6–1.2 mmoles) in 5 ml of anhydrous ether and cooled to −78° under nitrogen. The required volume of ethereal diazomethane was added in one portion by pipet and the reaction mixture was stirred at −77° (±1°) for 12 h. The solution then was allowed to warm to room temperature, most of the ether was distilled off and the residual liquid was analyzed by GLPC (F&M Model 700, 6 ft. × $\frac{1}{8}$″ o.d. aluminum column packed with 10% SE-30 on Chromosorb P, 150° oven temperature, 50 ml per min helium flow rate, dual flame detector). Eqn. (9) was used to calculate the relative rate constants, where

TABLE 4

COMPETITION REACTIONS: $ArGeCl_3$ *vs.* $p\text{-}CH_3OC_6H_4GeCl_3$ (STANDARD)

Ar in *$ArGeCl_3$*	I_{Ar} (*mmoles*)	I_{std} (*mmoles*)	A_{Ar}	A_{std}	*RF*	k_{Ar}/k_{std}
$p\text{-}ClC_6H_4$	0.350	0.498	261	94	2.48	9.80
	0.235	0.386	176	73		9.72
$p\text{-}FC_6H_4$	0.516	0.661	115	68	2.42	5.22
	0.318	0.619	192	170		5.32
	0.373	0.600	96	69		5.35
	0.380	0.496	98	55		5.62
C_6H_5	0.923	0.795	212	234	2.85	2.21
	0.572	0.642	141	200		2.26
	0.417	0.513	142	226		2.22
	0.576	0.480	183	190		2.28
$p\text{-}CH_3C_6H_4$	0.463	0.502	182	125	0.808	1.27
	0.467	0.430	255	146		1.30
C_6H_5[a]	0.360	0.410	115	83	1.35	2.13

[a] 0.06 g copper powder added.

$P_{Ar}/P_{std} = A_{Ar}/A_{std} \times RF$. A_{Ar} and A_{std} are the GLPC peak areas for $Ar(ClCH_2)GeCl_2$ and p-$MeOC_6H_4(ClCH_2)GeCl_2$, respectively, in each experiment and RF is the response factor, (A_{std}/mmoles std) × (mmoles Ar/A_{Ar}), determined in separate experiments by analysis of known mixtures of $Ar(ClCH_2)GeCl_2$ and p-$MeOC_6H_4(ClCH_2)$-$GeCl_2$. The data obtained in these experiments are listed in Table 4.

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SUMMARY

Competition experiments have established the following relative rate constants for the reaction of diazomethane with substituted aryltrichlorogermanes, p-ZC_6H_4-$GeCl_3$, as determined by the yields of the p-$ZC_6H_4(ClCH_2)GeCl_2$ products formed: MeO, 1.0; Me, 1.29; H, 2.24; F, 5.37; Cl, 9.76. Furthermore, the rate of consumption of diazomethane appears to depend upon the nature of Z in the same way. These observations suggest that the mechanism of the methylenation of the Ge–Cl bond in these compounds involves nucleophilic attack by diazomethane at germanium, rather than a process in which free CH_2 is an intermediate. These reactions were carried out in ether at −78° and on a preparative scale gave product in high yield.

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