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REACTIONS OF ARYL HALIDES WITH TRIETHYLGERMYL ANIONS

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Summary

The reactions of aryl iodides, bromides, chlorides, and fluorides with triethylgermyl-lithium, -sodium, and -potassium in HMPA/ether have been investigated. The reactions of aryl halides with triethylgermyl anions proceed via two different processes whose relative rates depend on the nature of the halogen and the substrates. In the case of aryl iodides, bromides and fluorides, a radical process is usual. With aryl chlorides, a radical process and an aryne process are involved.

Introduction

The reactions of organic halides with alkali metal derivatives of organometal anions have been extensively utilized for the formation of carbon—metal σ bonds as illustrated below:

$$R_nM^-M'^+ + R'X \rightarrow R_nMR' + M'X \qquad (1)$$

This general area has been reviewed [1].

This approach to the formation of carbon—metal σ bonds has been particularly useful in Group 4B chemistry, and many tetraorganostannanes and -silicons have been synthesized. Because of its importance, considerable attention has been paid to the mechanism of these reactions. However, few examples of such reactions on germyl anions have been reported. Bulten and Noltes [2] investigated the reaction of $(C_2H_5)_3GeLi$ in HMPA with a variety of substrates, but no mechanistic conclusion could be drawn. Eaborn, Hill, and Simpson [3] investigated the reactions of optically active germyllithium (R_3Ge^*Li) with alkyl halides ($R'X$) to yield optically active compounds (R_3Ge^*R'). Processes proceeding with both predominant retention (e.g., CH_3Br, $PhCH_2Cl$, $CH_2{=}CHCH_2Cl$) and inversion (e.g., CH_3I, $PhCH_2I$, $CH_2{=}CHCH_2I$) at the germanium atom were identified. The retention process was suggested to involve direct coupling between R_3Ge^*Li and $R'X$ in a four-center process, whereas the inversion process resulted from halogen—lithium exchange to give R_3Ge^*X and $R'Li$ (four-center retention) followed by coupling between R_3Ge^*X and R′Li with inversion at the germanium atom. Kitching and co-workers [4] investigated stereochemical courses of $(CH_3)_3GeLi$ in HMPA with some 4-alkyl-cyclohexyl halides and suggested S_N2 displacement and halogen—lithium exchange for these reactions. Recently, Pereyre and coworkers [5] have reported briefly the reactions of germyllithiums with some aryl halides.

In this paper, we present the reactions of aryl iodides, bromides, chlorides, and fluorides with triethylgermyl-lithium, -sodium, and -potassium in HMPA/ether and discuss the mechanisms in detail.

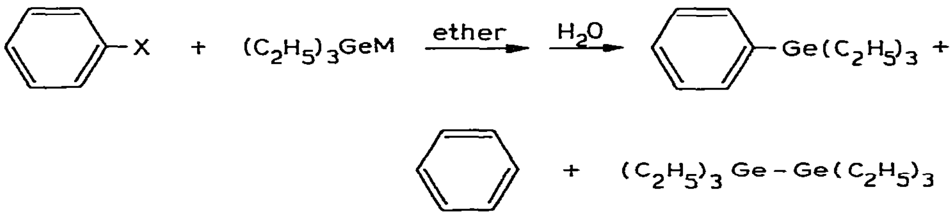
Results and discussion

Reactions of phenyl halides with triethylgermyl anions

The reactions of excess phenyl halides with triethylgermylalkali metals, prepared from triethylgermylchloride and alkali metals in HMPA/ether, were carried out at room temperatures for 2 h [6]. Hydrolyses of the reaction mixtures led to phenyltriethylgermane, benzene, and hexaethyldigermane.

$$(C_2H_5)_3GeCl + 2M \xrightarrow{HMPA} (C_2H_5)_3GeM + MCl \qquad (2)$$

M = Li, Na, and K



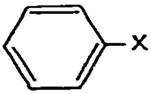
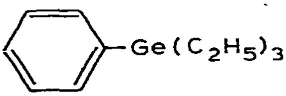
(3)

X= F, Cl, Br, and I

No biphenyl was detected. The results are summarized in Table 1. Unreacted triethylgermylalkali metals were converted to triethylgermane by hydrolysis. All products were isolated by preparative GLC (SE30 20% 2 m or 30% Apiezon L 2 m) and identified by comparing their IR, NMR, and retention times on GLC with those of authentic samples. The yields of the relative amounts of phenyltriethylgermane and benzene varied with the phenyl halides and the alkali metals as shown in Table 1. The yields of the products increased in the order $(C_2H_5)_3Ge$-Na $\ll$ -Li, -K for triethylgermylalkali metals and in the order PhF $<$ PhCl, PhBr, PhI for the phenyl halides within experimental errors. These orders are consistent with the recognized reactivities of alkali metal derivatives of organometal anions and the bond strength between the carbon and the halogen in the reactions that known to proceed by way of an initial electron-transfer step [7]. The relative ratio of benzene to phenyltriethylgermane increased in the order PhF $<$ PhCl, PhBr $<$ PhI in the case of $(C_2H_5)_3GeLi$. With $(C_2H_5)_3Ge$-Na and -K, the ratio increased in the order PhCl, PhBr $<$ PhF, PhI.

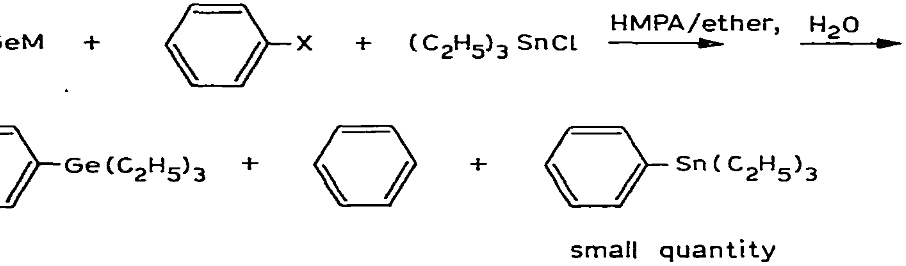
The reactions of triethylgermylalkali metals with phenyl halides in the presence of excess triethyltin chloride were investigated under the same conditions.

TIONS OF PHENYL HALIDES WITH TRIETHYLGERMYLALKALI METALS

	Products (relative ratio)		Yields (%) [a]
			
F	86	14	38.5
Cl	80	20	100
Br	80	20	100
I	69	31	96.7
F	49	51	11.0
Cl	77	23	28.0
Br	76	24	65.2
I	63	37	60.6
F	60	40	41.4
Cl	91	9	91.3
Br	69	31	86.1
I	60	40	79.6

of at least 2 determinations. Yields of $PhGe(C_2H_5)_3$ and benzene are based on the concen-
iethylgermylalkali metals.

es of the reaction mixtures led to phenyltriethylgermane, benzene, tri-
nyltriethyltin, and a small quantity of phenyltriethyltin. Phenyl-



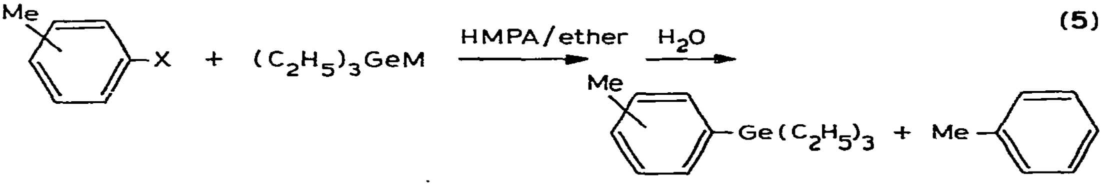
(4)

eacted with a mixture of triethylchlorogermane and triethyltin chlo-
ve a large quantity of phenyltriethyltin and a small quantity of phenyl-
ermane. Therefore, the formation of phenyltriethylgermane cannot be
l adequately as the result of halogen—alkali metal exchange to give
kalies and triethylgermylhalides followed by coupling between phenyl-
nd triethylgermylhalides.

sults in Table 1 suggest strongly that the reactions of phenyl halides
hylgermylalkali metals in HMPA/ether may involve a free radical pro-
er than a simple bimolecular nucleophilic reaction and halogen—metal

s of tolyl halides with triethylgermyl anions

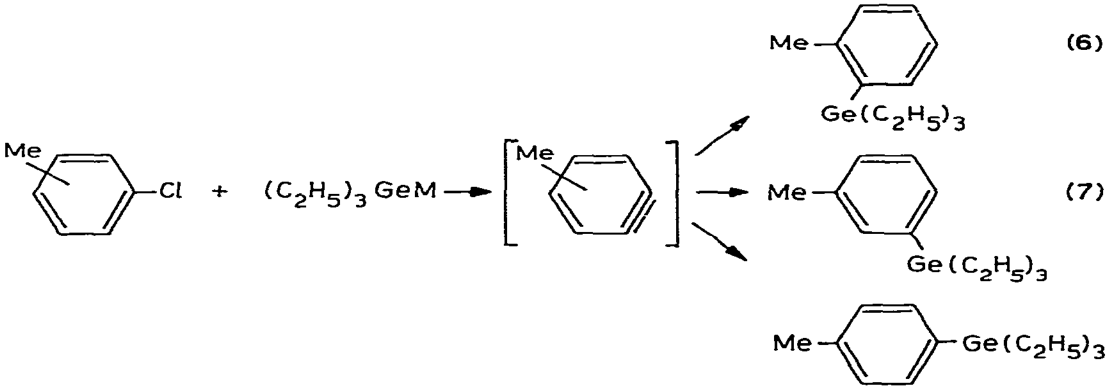
er to get further information on the mechanism of the reactions of mixtures led to tolyltriethylgermanes and toluene. Hexaethyldigermane was



(5)

X = F, Cl, Br, and I M = Li, Na, and K

detected. The results are summarized in Table 2. The reactions of iodo- and bromo-toluenes with triethylgermylalkali metals occurred in a complete regiospecific way to give substitution products and fluorotoluenes gave almost regiospecific substitution products. On the other hand, the reactions of chlorotoluenes with triethylgermylalkali metals gave cine substitution products. The regiospecific substitution products probably result from a free radical process, whereas cine substitution products are results of an aryne process. The reactions of *ortho*-tolyl chlorides with triethylgermylalkali metals gave rise to *ortho*- and *meta*-tolyltriethylgermanes. The reactions of *meta*-tolyl chlorides gave rise to *ortho*-, *meta*-, and *para*-tolyltriethylgermanes. The reactions of *para*-tolyl chlorides gave rise to *meta*- and *para*-tolyltriethylgermanes. The isomer distribution of tolyltriethylgermanes varied with the triethylgermylalkali metals. However, the isomer distribution in the reactions of tolyl chlorides with triethylgermylalkali metals in Table 2 may not accurately represent the percentage of isomers formed in the aryne reactions. It is reasonable that the observed isomer distribution in the reactions of tolyl chlorides may represent the total percentage of isomers formed in the aryne and a free radical processes.



(6)

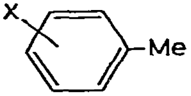
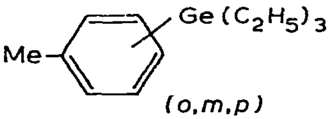
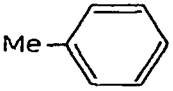
(7)

(8)

Cine substitution products are the results of *ortho*-proton—alkali metal exchange and elimination of alkali metal chlorides followed by metallation of the aryne by triethylgermane [8]. Therefore, the formation of cine substitution products depends on the availability of the *ortho*-position, the acidity of the protons on the benzene ring, and the nucleophilicity of triethylgermylalkali metals [8]. There are no *ortho*-protons to the chloride in the mesityl chloride. Therefore, the formation of arynes in the reactions of mesityl chloride with triethylgermylalkali metals cannot occur. In fact, the products from these

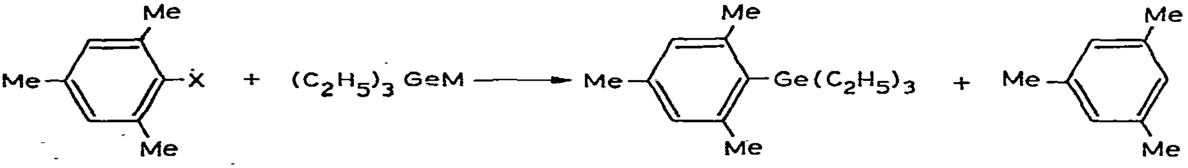
TABLE 2

THE REACTIONS OF TOLYL HALIDES WITH TRIETHYLGERMYLALKALI METALS

Reactants		Products, yields (%), (relative ratio) [a]	
$(C_2H_5)_3GeM$			
Li	*o*-F	57.2 (100, trace, 0)	2.2
	m-F	17.4 (0, 100, 0)	3.9
	p-F	3.6 (0, trace, 100)	3.1
	o-Cl	53.7 (85, 15, 0)	22.4
	m-Cl	40.3 (8, 88, 4)	14.0
	p-Cl	35.0 (0, 13, 87)	22.8
	o-Br	30.8 (100, 0, 0)	23.5
	m-Br	22.9 (0, 100, 0)	16.8
	p-Br	21.5 (0, 0, 100)	14.8
	o-I	33.2 (100, 0, 0)	50.6
	m-I	38.6 (0, 100, 0)	47.4
	p-I	38.1 (0, 0, 100)	61.8
Na	*o*-F	3.0 (100, trace, 0)	1.4
	m-F	3.3 (0, 100, 0)	5.6
	p-F	2.7 (0, trace, 100)	2.3
	o-Cl	26.5 (76, 24, 0)	12.9
	m-Cl	18.5 (15, 80, 5)	10.2
	p-Cl	13.1 (0, 36, 64)	6.8
	o-Br	63.1 (100, 0, 0)	22.5
	m-Br	73.0 (0, 100, 0)	21.3
	p-Br	32.0 (0, 0, 100)	8.2
	o-I	25.2 (100, 0, 0)	20.9
	m-I	35.0 (0, 100, 0)	16.0
	p-I	28.3 (0, 0, 100)	15.7
K	*o*-F	28.7 (100, 0, 0)	17.2
	m-F	37.9 (0, 100, 0)	26.6
	p-F	22.9 (0, 0, 100)	23.2
	o-Cl	69.7 (62, 38, 0)	19.6
	m-Cl	79.7 (20, 67, 13)	17.0
	p-Cl	68.1 (0, 50, 50)	10.9
	o-Br	64.2 (100, 0, 0)	33.1
	m-Br	52.0 (0, 100, 0)	28.9
	p-Br	49.6 (0, 0, 100)	37.3
	o-I	41.2 (100, 0, 0)	49.6
	m-I	40.3 (0, 100, 0)	44.7
	p-I	30.4 (0, 0, 100)	46.3

[a] An average of at least 2 determinations. Yields are based on the concentrations of triethylgermylalkali metals.

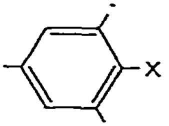
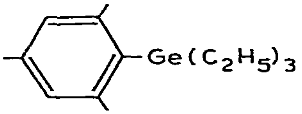
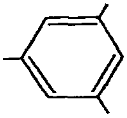
reactions were mesityltriethylgermane and mesitylene. The results are sum-



X = Cl, Br   M = Li, Na, and K   (9)

TABLE 3

THE REACTIONS OF MESITYL HALIDES WITH TRIETHYLGERMYLALKALI METALS

Reactants		Products [a]	
$(C_2H_5)_3GeM$			
Li	Cl	15.6	11.8
	Br	37.8	23.2
Na	Cl	4.4	8.3
	Br	33.8	23.6
K	Cl	22.8	25.9
	Br	46.6	29.5

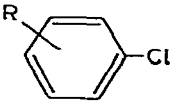
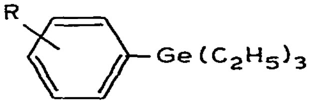
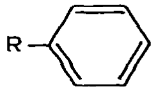
[a] An average of at least 2 determinations. Yields are based on the concentrations of triethylgermylalkali metals.

marized in Table 3 together with those of mesityl bromide.

The acidity of protons *ortho* to the chloride is profoundly influenced by the substituents on the aryl chlorides [8]. The effects of the substituents on some aryl chlorides on the formation of cine substitution products were investigated. The results are summarized in Table 4. From tolyl and anisyl chlorides with triethylgermyllithium, cine substitution products were formed. However, electron-withdrawing groups such as CF_3-substituted aryl chlorides gave rise to regiospecific substitution products in low yields.

TABLE 4

REACTIONS OF ARYL CHLORIDES WITH TRIETHYLGERMYLLITHIUM

Reactants	Products, yields (%), (relative ratio) [a]	
	 (o,m,p)	
o-Me	53.7 (85, 15, 0)	22.4
o-OMe	35.1 (83, 17, 0)	13.8
o-CF_3	16.6 (100, 0, 0)	36.9
m-Me	40.3 (8, 88, 4)	14.0
m-OMe	51.4 (10, 90, 0)	5.2
m-CF_3	0	27.4
p-Me	35.0 (0, 13, 87)	22.8
p-OMe	35.4 (0, 35, 65)	17.8
p-CF_3	11.9 (0, 0, 100)	32.7

[a] Based on the concentrations of triethylgermyllithium.

The yields of cine substitution products for $(C_2H_5)_3GeM$ increased in the order M = K > Li > Na as shown in Table 2. This order is consistent with the nucleophilicity of triethylgermyl anions.

Substitution mechanism for the reactions of aryl halides with triethylgermyl anions

The data presented here demonstrated that the mechanism of the reactions of aryl halides with triethylgermyl anions is sensitive to changes in the nature of the halogen and substrates. Taken together with related studies, they establish the following reaction profile.

First, the formation of the reduction products observed in the reactions of aryl halides with triethylgermyl anions implies strongly that substitution with aryl halides proceeds by a free radical process. The yields and the relative amount of reduction products to substitution products in Tables 1, 2, 3, and 4 depend on the halides and gegen ions. Such results cannot be explained by nucleophilic aromatic substitution of aryl halides with germyl anions followed by halodephenylation to give reduction products. The reactivity of aryl halides in nucleophilic aromatic substitution is in the order ArF ≪ ArBr. The reactivity order in Tables 1 and 2 is reversed. Halogen—metal exchange between aryl halides and triethylgermylalkali metals is not important. In the reactions of phenylhalides with triethylgermyl anions in the presence of triethyltin chloride, little phenyltriethyltin was detected.

Second, cine substitution products in the reactions of tolyl chlorides with triethylgermyl anions as in Tables 2 and 4 imply that substitution with aryl chlorides proceeds in part by a pathway involving an aryne process.

A reasonable mechanistic interpretation of these data is that a free radical process is competing with an aryne process depending on the halides and gegen ions. From the ability of germyl anions to act as one-electron reducing agents [9], the first step in the free radical process is an electron-transfer from germyl anions to aryl halides that leads to aryl halide anion radicals and germyl radicals as illustrated in Scheme 1.

SCHEME I

PROPOSED MECHANISM FOR THE FREE RADICAL PROCESS

$$ArX + R_3Ge^- \rightarrow [ArX^{\overset{\bullet}{-}} R_3Ge^\bullet] \rightarrow [Ar^\bullet X^- \, {}^\bullet GeR_3]$$

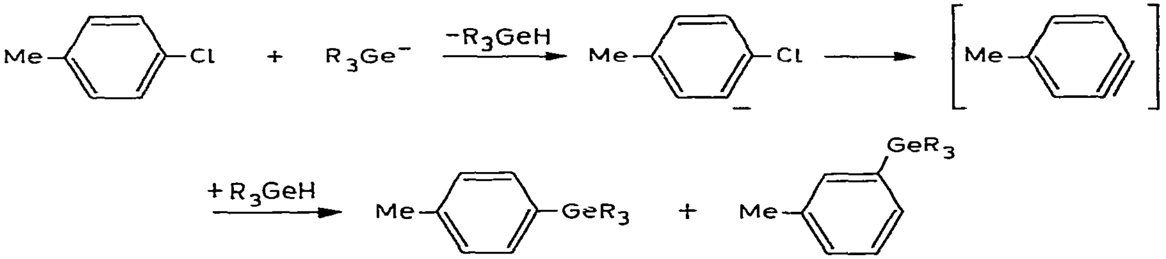
$$[Ar^\bullet X^- \, {}^\bullet GeR_3] - \begin{array}{l} \rightarrow Ar{-}GeR_3 \\ \rightarrow Ar^\bullet + {}^\bullet GeR_3 \end{array}$$

$$Ar^\bullet \xrightarrow{SH} ArH$$

Subsequent dissociation of aryl radicals from unstable aryl halide anion radicals followed by combination with germyl radicals and by proton abstraction from solvents would provide arylgermanes and reduction products, respectively. The free radical process is a major path in the reactions of aryl halides with triethylgermyl anions. However, an aryne process must be considered to be involved as a minor path in the reactions of aryl chlorides with germyl anions. Cine substitution products are formed by metallation of the aryne with triethylgermane as illustrated in Scheme 2 in the case of *para*-tolyl chlorides.

SCHEME 2

PROPOSED MECHANISM FOR THE ARYNE PROCESS



The aryne process would become important in the reactions of germyl anions with aryl halides whose *ortho*-proton relative to the halogen is acidic. *ortho*-Protons in fluorotoluenes and trifluoromethyltolyl chlorides are more acidic than those in chlorotoluenes. However, no cine substitution product was detected. In fluorotoluenes and trifluoromethyltolyl chlorides, one-electron transfer from germyl anions to these chlorides also occurs very easily [7]. Therefore, the reactions of fluorotoluenes and trifluoromethyltolyl chlorides with germyl anions proceed by a free radical process rather than an aryne process on a delicate balance.

Experimental section

Materials

Fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, *o*-, *m*-, *p*-fluorotoluenes, and *o*-, *m*-, *p*-trifluoromethyltolyl chlorides were obtained commercially and were distilled prior to use. *o*-Chlorotoluene, b.p. 68—69°C/22 mmHg, *m*-chlorotoluene, b.p. 58—60°C/18 mmHg, *p*-chlorotoluene, b.p. 58—62°C/18 mmHg, *o*-bromotoluene, b.p. 69°C/22 mmHg, *m*-bromotoluene, b.p. 83—85°C/25 mmHg, *p*-bromotoluene, b.p. 85°C/30 mmHg, *o*-iodotoluene, b.p. 95—98°C/30 mmHg, *m*-iodotoluene, b.p. 92—98°C/23 mmHg, *p*-iodotoluene, b.p. 90—98°C/20 mmHg, *o*-chloroanisole, b.p. 87—88°C/17 mmHg, *m*-chloroanisole, b.p. 84.5°C/17 mmHg, *p*-chloroanisole, b.p. 88°C/16 mmHg, mesitylchloride, b.p. 84°C/14 mmHg, mesitylbromide, b.p. 98—103°C/15 mmHg were prepared according to the literature [10]. Triethylchlorogermane, b.p. 178°C [11], phenyltriethylgermane, b.p. 116—117°C/13 mmHg [12], triethyltin chloride, b.p. 100—101°C/16 mmHg [13], phenyltriethyltin, b.p. 113—114°C/6 mmHg [14], *o*-triethylgermyl toluene, b.p. 99°C/4 mmHg [15], *m*-triethylgermyltoluene, b.p. 90°C/2 mmHg [15], *p*-triethylgermyltoluene, b.p. 136°C/16 mmHg [15], *o*-triethylgermylanisole, b.p. 128—129°C/7 mmHg [15], *m*-triethylgermylanisole, b.p. 128°C/2 mmHg [15], *p*-triethylgermylanisole, b.p. 103—104°C/3 mmHg [15], and mesityltriethylgermane, b.p. 152°C/9 mmHg [15] were prepared according to the cited literature.

Preparation of o-, m-, and p-triethylgermyltrifluoromethyltoluenes

As a representative example, the preparation of *p*-triethylgermyltrifluoromethyltoluene is described.

A Grignard reagent was prepared from *p*-trifluoromethyltolyl chloride (4.2 g, 23 mmol) and magnesium (0.6 g, 24 mmol) in 20 ml of THF. To the Grignard reagent was added triethylgermyl chloride (2.9 g, 15 mmol) in 5 ml of THF. The reaction mixture was stirred with reflux for 10 h. After hydrolysis with water, the organic layer was dried over sodium sulfate. Fractional distillation gave *p*-triethylgermyltrifluoromethyltoluene, b.p. 60—65°C/0.8 mmHg; NMR * (δ in $CDCl_3$) 0.79—1.29 (m, 15 H), 7.36—7.74 ppm (m, 4 H); n_D^{20}: 1.4782. Anal. Found: C, 51.48; H, 6.12. Calcd. for $C_{13}H_{19}F_3Ge$: C, 51.22; H, 6.28%.

For other triethylgermyltrifluoromethyltoluenes, NMR data, physical properties, and analytical data are indicated. *o*-Triethylgermyltrifluoromethyltoluene, b.p. 65°C/0.5 mmHg; NMR (δ in $CDCl_3$) 0.76—1.26 (m, 15 H), 7.34—7.76 ppm (m, 4 H); n_D^{20}: 1.4786. Anal. Found: C, 51.46; H, 6.08. Calcd. for $C_{13}H_{19}F_3Ge$: C, 51.22; H, 6.28%. *m*-Triethylgermyltrifluoromethyltoluene, b.p. 65°C/0.5 mmHg; NMR (δ in $CDCl_3$) 0.81—1.34 (m, 15 H), 7.34—7.76 ppm (m, 4 H); n_D^{20}: 1.4747. Anal. Found: C, 51.32; H, 6.16. Calcd. for $C_{13}H_{19}F_3Ge$: C, 51.22; 6.28%.

Preparation of triethylgermyllithium

This reagent was prepared basically in the manner described by Bulten and Noltes [6]. Lithium metal (0.4 g, 0.05 g atom) was cut into small pieces and placed in the reaction vessel containing anhydrous HMPA (10 cc, 0.05 mol) under Ar gas. The vessel (100 ml three-necked flask) was fitted with a condenser, drying tube Ar inlet, and pressure equalizing dropping funnel. Triethylchlorogermane (3.9 g, 0.02 mol) was dissolved in dry ether (12 cc) and placed in the dropping funnel. The reaction vessel was blanketed with Ar and Li/HMPA was stirred vigorously. The color of the solution changed to blue. The triethylchlorogermane solution was added dropwise and the change from blue to orange-yellow usually appeared after about 30 min. Stirring was continued for 2 h. The yield of triethylgermyllithium was determined from the concentration of triethylgermane after hydrolysis (60—70% yield).

Preparation of triethylgermylsodium

Triethylgermylsodium was prepared as described above for triethylgermyllithium. The yield of triethylgermylsodium was 60—70%.

Preparation of triethylgermylpotassium

Triethylgermylpotassium was prepared as described for triethylgermyllithium. The yield of triethylgermylpotassium was 80—90%.

Reaction of triethylgermyllithium with bromobenzene

A typical example for the reactions of triethylgermylalkali metals with aryl halides was described. Triethylgermyllithium (5 mmol) was prepared from triethylchlorogermane and lithium metal in HMPA. To this triethylgermyllithium

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* NMR spectra were taken on a Varian FT-80A instrument.

solution, bromobenzene (3.1 g, 20 mmol) was added and stirred for 2 h. After hydrolysis, the reaction mixture was extracted with ether. The organic layer was dried over anhydrous sodium sulfate.

Reaction of triethylgermyllithium with bromobenzene in the presence of triethyltin chloride

Triethylgermyllithium (0.24 mmol) was prepared from triethylchlorogermane and lithium metal in HMPA. To this triethylgermyllithium solution, a mixture of bromobenzene (0.11 g, 0.71 mmol) and triethyltin chloride (0.18 g, 0.74 mmol) was added and stirred for 2 h. After hydrolysis, the reaction mixture was extracted with ether. The organic layer was dried over anhydrous sodium sulfate. Phenyltriethylgermane (0.05 mmol, 20.0% yield), benzene (0.045 mmol, 18.3% yield), phenyltriethyltin (0.01 mmol, 5.0% yield), and triethylgermyltriethyltin (0.02 mmol, 10.0% yield) were determined by GLC.

Reaction of phenyllithium with a mixture of triethylgermyl chloride and triethyltin chloride

Phenyllithium (1.28 mmol) was prepared from phenyl bromide and lithium metal in ether. To this phenyllithium solution, a mixture of triethylgermyl chloride (0.94 g, 4.81 mmol) and triethyltin chloride (1.16 g, 4.83 mmol) was added and stirred for 2 h. After hydrolysis, the reaction mixture was extracted with ether. The organic layer was dried over sodium sulfate. Phenyltriethylgermane (0.61 mmol, 36% yield) and phenyltriethyltin (1.09 mmol, 64% yield) were determined by GLC.

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