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Microwave-Assisted Lewis Acid Catalysis: Application to the Synthesis of Alkyl- or Arylhalogermanes

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Summary: Under microwave irradiation, alkyl- or arylhalogermanes R_nGeX_{4-n} (R = Et, Bu, Ph; X = Cl, Br) are obtained by redistribution reactions of R_4Ge with GeX_4. These experimental conditions permit the synthesis of such compounds in good yield in a few minutes at atmospheric pressure. The direct Friedel–Crafts germylation of benzene and toluene by germanium tetrachloride also has been performed, but yields were low.

Introduction

Investigations concerning the use of microwaves in organic and organometallic chemistry can be carried out in two different ways: there is the problem of specific activation of reactions by microwaves under controlled temperature conditions and there also is the possibility of using microwave heating to effect normally difficult reactions.

With regard to specific activation at a controlled temperature, in a homogeneous medium, debatable results appeared in the literature, and it seems now that such specific activation on a molecular scale does not occur.[1–8]

On the other hand, microwave heating of organic reagents by dielectric or conducting losses[9] permits a very rapid rise in temperature or attainment of much higher temperatures than is possible with conventional heating (marked increases in rates have often been observed). This subject was recently reviewed[9–13] and includes the synthesis of small organic molecules and polymers, biomass conversion, and biomedical applications. Many reactions have also been very efficiently performed on solid supports.[13]

In the area of group 14 organometallic synthesis, two papers have dealt with microwave-assisted hydrosilylation[14a] and ligand redistribution between Ph_4Sn and $BiCl_3$.[14b] Silyl Reformatsky reactions have been performed under dry-media conditions,[15a] and silylketene acetals also react with aldimines in the presence of Lewis acids.[15b] These reactions have been carried out in commercial multimode microwave ovens.

Our previous work on the organometallic chemistry of germanium led us to examine the possibility of obtaining, under microwave irradiation, the useful organogermanium halides R_nGeX_{4-n} using a monomode microwave cavity.

Results and Discussion

Redistribution Reactions. The redistribution reaction between alkyl (or aryl) and halide substituents of R_4Ge and GeX_4 compounds occurs in the presence of a large amount of the corresponding aluminum trihalide. With $GeCl_4$, this reaction was studied extensively in the 1960s by Van der Kerk[16] and by Neumann[17] using conventional heating. Although the effects of microwave irradiation on the temperature of solids have been reported for various compounds,[9] the behavior under such conditions of aluminum halides has not yet been described.

We have found that a suspension of powdered aluminum trichloride, in a solvent inert toward microwaves, was heated efficiently at 2450 MHz. (The temperature of a suspension of 1 g of aluminum trichloride in 10 mL of dry benzene reaches 73 °C after a 3-min irradiation period using the Prolabo Maxidigest reactor with 300-W power.) Thus microwave activation of the AlX_3 catalyst in a reaction between nonpolar reagents should result in useful increases in rate, and we decided to investigate the redistribution reactions shown in eqs 1–3 in the presence of $AlCl_3$ and $AlBr_3$.

$$3R_4Ge + GeX_4 \xrightarrow{AlX_3} 4R_3GeX \qquad (1)$$

$$R_4Ge + GeX_4 \xrightarrow{AlX_3} 2R_2GeX_2 \qquad (2)$$

$$R_4Ge + 3GeX_4 \xrightarrow{AlX_3} 4RGeX_3 \qquad (3)$$

$$R = Et, Bu, Ph; X = Cl, Br$$

(a) $AlCl_3$-Catalyzed Redistributions (Table 1). In the butyl series, the stoichiometry of eq 1 gives Bu_3GeCl

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(1) Laurent, R.; Laporterie, A.; Dubac, J.; Berlan, J.; Lefeuvre, S.; Audhuy, M. *J. Org. Chem.* **1992,** *57,* 7099.

(2) Bose, A. K.; Manhas, M. S.; Ghosh, M.; Shah, M.; Raju, V. S.; Bari, S. S.; Newaz, S. N.; Banik, B. K.; Chaudhary, A. G.; Barakat, K. J. *J. Org. Chem.* **1991,** *56,* 6968.

(3) Baghurst, D. R.; Mingos, M. P. *J. Chem. Soc., Chem. Commun.* **1992,** 674.

(4) Raner, K. D.; Strauss, C. R. *J. Org. Chem.* **1992,** *57,* 6231.

(5) Berlan, J.; Giboreau, P.; Lefeuvre, S.; Marchand, C. *Tetrahedron Lett.* **1991,** *32,* 2363.

(6) Marchelli, R.; Dossena, A.; Palla, G.; Audhuy, M.; Lefeuvre, S.; Carnevali, P.; Freddi, M. *J. Sci. Food. Agric.* **1992,** *59,* 217.

(7) Raner, K. D.; Strauss, C. R.; Vysok, F.; Mockbel, L. *J. Org. Chem.* **1993,** *58,* 950.

(8) Stuerga, D.; Gonon, K.; Lallemant, M. *Tetrahedron.* **1993,** *49,* 6229.

(9) Mingos, M. P.; Baghurst, D. R. *Chem. Soc. Rev.* **1991,** *20,* 1.

(10) Giguere, R. J. *Org. Synth. Theory Appl.* **1989,** *1,* 103.

(11) Abramovitch, R. A. *Org. Prep. Proced. Int.* **1991,** *23,* 683.

(12) (a) Bose, A. K.; Manhas, M. S.; Banik, B. K.; Robb, E. W. *Res. Chem. Intermed.* **1994,** *20,* 1. (b) Majetich, G.; Hicks, R. **1994,** *20,* 61. (c) Mingos, D. M. P. *Ibid.* **1994,** *20,* 85.

(13) Bram, G.; Loupy, A.; Villemin, D. In *Solid Supports and Catalysts in Organic Synthesis*; Smith, K., Ed.; Ellis Horwood PTR Prentice Hall: New York, 1992; Chapter 12, p 303.

(14) (a) Abramovitch, R. A.; Abramovitch, D. A.; Linar, K.; Tamareselvy, K. *Tetrahedron Lett.* **1991,** *32,* 5251. (b) Ali, M.; Bond, P. S.; Mbogo, S. A.; Mc Mhinnie, R. W.; Watts, P. M. *J. Organomet. Chem.* **1989,** *371,* 11.

(15) (a) Latouche, R.; Texier-Boullet, F.; Hamelin, J. *Tetrahedron Lett.* **1991,** *32,* 1179. (b) Texier-Boullet, F.; Latouche, R.; Hamelin, J. *Tetrahedron Lett.* **1993,** *34,* 2123.

(16) (a) Van der Kerk, G. J. M.; Rijkens, F.; Janssen, M. J. *Recl. Trav. Chim. Pays-Bas* **1962,** *81,* 764. (b) Rijkens, F.; Van der Kerk, G. J. M. *Recl. Trav. Chim. Pays-Bas* **1964,** *83,* 723. (c) Rijkens, F.; Bulten, E. J.; Drenth, W.; Van der Kerk, G. J. M. *Recl. Trav. Chim. Pays-Bas* **1966,** *85,* 1223.

(17) Kühlein, K.; Neumann, W. P. *Liebigs Ann. Chem.* **1967,** *702,* 17.

Table 1. $AlCl_3$-Catalyzed Redistributions between Tetraalkyl- or Tetraphenylgermanes and Germanium Tetrachloride under Microwave Irradiation (300 W)

		initial mixture ($\times10^{-2}$ mol)			exptl conditions		% products[a]			
R	run	$GeCl_4$	R_4Ge	$AlCl_3$	time (min)	reactor	R_4Ge	R_3GeCl	R_2GeCl_2	yield (%)[b]
n-Bu	1	0.70	2.20	0.40	3	open	15	85		95
	2	2.08	2.46	0.40	30	open		10	90	92
	3	1.04	1.23	0.20	15	closed		4	96	90
	4	1.04	1.23	0.20	15	open		84	16	89
Ph	5	0.52	0.57	0.10	20	open[c]	9	79	12	82
	6	1.72	0.57	0.10	13	open	5	16	78	80

[a] The products were analyzed by gas chromatography and by ^1H NMR after methylation. [b] Recovered Ge product. [c] The reaction was performed in 3 mL of cyclohexane.

Table 2. $AlBr_3$-Catalyzed Redistributions between Tetraalkyl- or Tetraphenylgermanes and Germanium Tetrabromide under Microwave Irradiation[a]

		initial mixture ($\times10^{-2}$ mol)			exptl conditions		% products[b]					
R	run	$GeBr_4$	R_4Ge	$AlBr_3$	power (W)	time (min)	R_4Ge	R_3GeBr	R_2GeBr_2	$RGeBr_3$	$GeBr_4$	yield (%)[c]
Et	1	0.35	1.10	0.20	300	12		83	17			95
	2	0.78	0.92	0.15	300	30		3	78	6	13	81
	3	2.11	0.71	0.20	300	30			13	73	14	82
n-Bu	4	0.35	1.10	0.20	300	5		85	12	1		92
	5	0.52	0.61	0.10	300	8		8	84	8		87
	6	2.11	0.71	0.20	300	17		2	13	80	5	83
Ph	7	0.24	0.83	0.10	210	6	7	83	9	1		91
	8	0.52	0.57	0.10	210	7	3	9	82	6		96
	9	0.90	0.30	0.05	210	20	10		13	77		80

[a] All the reactions were performed in open reactors. [b] The products were analyzed by gas chromatography and by ^1H NMR after alkylation. [c] Recovered Ge product.

as the main product (the tri- and dichloride intermediates react with Bu_4Ge). Pure Bu_3GeCl has been obtained by Van der Kerk in 5 h at 200 °C in a sealed tube (85% yield). The reaction has also been carried out at the same temperature and under atmospheric pressure by adding the tetrahalide to the hot reactants.[16a,b] Under microwave irradiation, with the same reactant proportions, we obtained Bu_3GeCl in 85% yield, in only 3 min in an open reactor (Table 1, run 1). Upon addition of more $GeCl_4$, the initially formed Bu_3GeCl reacts to give Bu_2GeCl_2 under conventional heating in 5 h at 200 °C.[16] With microwave heating, this reaction can be carried out in 30 min under atmospheric pressure (run 2) but not in 15 min (run 4; Bu_3GeCl is the major product). However Bu_2GeCl_2 is obtained in 15 min in a closed Teflon vessel (run 3). Using the stoichiometry of eq 3, our attempts to obtain $BuGeCl_3$ were not successful when microwave irradiation was used in an open reactor. When this reaction was attempted in a closed Teflon vessel, the reactor burst open after a few minutes.

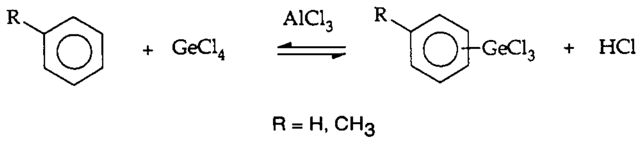
In the phenyl series, due to the heterogeneity of the mixture, suitable experimental conditions were difficult to adjust. However, using $GeCl_4$ in excess over the stoichiometries of eqs 1 and 2, we were able to prepare Ph_2GeCl_2 and Ph_3GeCl in open reactors (Table 1, runs 5 and 6). The latter is even better prepared in a few milliliters of cyclohexane.

(b) $AlBr_3$-Catalyzed Redistributions (Table 2). In order to avoid the difficulties arising in open vessels, from the low boiling point of $GeCl_4$, or from leaks and explosions in closed reactors, we carried out redistributions using $GeBr_4$ under atmospheric pressure. The only example of this reaction using conventional heating was reported by Mazerolles,[18] who has prepared Et_2GeBr_2 and Bu_2GeBr_2 by that procedure.

Using microwave heating, we prepared in open vessels the mono-, di-, and tribromogermanes of the ethyl, butyl, and phenyl series (Table 2). Each product was obtained in good purity, in yields greater than 80%, and in short (5–20 min) reaction times.

Under conventional conditions, the redistribution reactions occur slowly (5 h) at elevated temperatures and most often in sealed tubes, but these reactions are more easily carried out under microwave irradiation. We never observed a strong reflux of the reagents during the irradiations, even for the reactions conducted in a solvent. Therefore, we suppose that hot spots on the catalyst associated with superheating effects[19] are responsible for the microwave activation. In the case of $AlBr_3$-catalyzed reactions, the catalyst becomes soluble in the hot solution, and the temperature of the bulk solution (using a fiber optic thermometer) reaches 270 °C at the end of run 5 in Table 2.

Friedel–Crafts Germylation of Aromatic Compounds. Another method of preparation of $ArGeCl_3$ compounds could be the direct germylation of aromatic compounds with $GeCl_4$ using aluminum trichloride as catalyst.



In the case of benzene, we found that under reflux conditions this reaction is very slow (100 h), and the yield is low (20%).[20] For this reaction, microwave heating is efficient; after 2 h in refluxing benzene, under microwave irradiation, $PhGeCl_3$ was obtained in 25% yield. Longer irradiation times did not result in increased yields. The reaction is faster with toluene (1 h), but the $ArGeCl_3$ yield remains low (25%). The para/ortho ratio is 90/10, and no

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(18) Mazerolles, P. *Bull. Soc. Chim. Fr.* **1961**, 1911.

(19) Baghurst, D. R.; Mingos, M. P. *J. Chem. Soc., Chem. Commun.* **1992**, 674.

(20) Mazerolles, P.; Cousse, H. *Bull. Soc. Chim. Fr.* **1972**, *4*, 1361.

meta isomer is formed. Here, as in the case of aromatic silylation under Friedel–Crafts conditions,[21,22] the low yields may be due to the facile reverse reaction.

In the $AlCl_3$-catalyzed reaction of Me_3SiCl with benzene, Olah tried to trap the HCl with a Hünig base.[23] Under drastic conditions, he detected the formation of phenyltrimethylsilane but only in 0.3% yield.

Using diisopropylethylamine as HCl scavenger, we were not able, under microwave heating, to increase the yield of the Friedel–Crafts silylation or germylation of benzene by Me_3SiCl or $GeCl_4$.

Another possibility of scavenging the HCl was to use metallic aluminum as hydrogen chloride acceptor as described by Ponomarev.[24] However, under microwave heating, the reaction between benzene and germanium tetrachloride in the presence of aluminum trichloride and aluminum powder did not give higher yields of $PhGeCl_3$.

Conclusion

Taking advantage of the specificities of microwave heating (generation of hot spots on the heterogeneous catalyst and superheating effects), we were able to accelerate $AlCl_3$- and $AlBr_3$-catalyzed reactions in organogermanium chemistry. Thus, the ligand redistribution occurs rapidly in high yield and at atmospheric pressure.

Experimental Section

All the reactions were carried out under an argon atmosphere. Germanium tetrachloride was distilled before use; tetraalkyl- or tetraarylgermanes were prepared from $GeCl_4$ and the corresponding Grignard reagents and purified by distillation or crystallization. Germanium tetrabromide was obtained by refluxing for 12 h a vigorously stirred mixture of $GeCl_4$ with an excess of 62% HBr followed by distillation of the lower phase (bp 176 °C).

^1H NMR spectra ($CDCl_3$) were recorded on a Bruker AC 80 spectrometer; chemical shifts are referenced with respect to tetramethylsilane. Gas chromatographic identifications were carried out on a Delsi Series 30 instrument equipped with a 2-m OV 17 10% column. Temperature measurements were carried out with a Luxtron optical fiber thermometer (755 multichannel Fluoroptic thermometer).

Redistribution reactions were performed on a 0.01 M scale of reagents with a 20% amount of catalyst (AlX_3) (see Tables 1 and 2). The reactants were placed in a Pyrex tube adapted to the cavity of a Prolabo Maxidigest microwave generator. A condensor, swept by a light stream of argon, was fitted to the Pyrex tube. The microwave power is, for each run, indicated in the tables. Each reaction was conducted as follows: The microwave power was applied during 3-min periods separated by 1-min interruptions. During the irradiation periods, the reactor was slowly rotated by hand. When the generator was switched off, the mixture, which progressively turned brown, was vigorously shaken. The alkylation reactions of the crude mixtures were performed with an excess of the corresponding Grignard reagent. Phenyl- and butylhalogermanes were methylated, while ethylhalogermanes were butylated.

Friedel–Crafts germylations were carried out with the same equipment. Benzene (4.70 g, 60 mmol), $GeCl_4$ (4.30 g, 20 mmol), and powdered $AlCl_3$ (1.60 g, 15 mmol) were placed in the Pyrex tube, with N_2 bubbling. A 300-W microwave power was applied during four periods of 15 min each separated by 1 min for thorough shaking. Then, an additional amount (1.60 g) of $AlCl_3$ was added, and microwave irradiation was continued, as before, for another hour. The mixture was then treated with $POCl_3$ and filtered in order to remove aluminum salts. Methylation was performed with CH_3MgI in excess. The reaction with toluene was conducted in the same way during a 1-h period.

The products of each reaction were identified by comparison of NMR, GCMS, or gas chromatographic data, after alkylation, with those of authentic samples.

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[21] O'Brien, D. H.; Hairston, T. J. *Organomet. Chem. Rev. A* **1971**, *7*, 139.

[22] Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

[23] Olah, G. A.; Bach, T.; Prakash, G. K. S. *J. Org. Chem.* **1989**, *54*, 3770.

[24] Ponomarev, V. V.; Golubtsov, S. A.; Andrianov, K. A.; Penskii, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 508.