1 L. RONCUCCI, G. FARAGLIA AND R. BARBIERI, *J. Organometal. Chem.*, 1 (1964) 427.
2 R. C. POLLER, *J. Organometal. Chem.*, 3 (1965) 321.
3 M. WADA, K. KAWAKAMI AND R. OKAWARA, *J. Organometal. Chem.*, 4 (1965) 159.
4 G. FARAGLIA, L. RONCUCCI AND R. BARBIERI, *Ric. Sci.*, 35 (II-A) (1965) 205.
5 C. BLACK, G. G. JORIS AND H. S. TAYLOR, *J. Chem. Phys.*, 16 (1948) 437.
6 M. J. JANSSEN, J. G. A. LUIJTEN AND G. J. M. VAN DER KERK, *J. Organometal. Chem.*, 1 (1964) 286.
7 E. G. ROCHOW, D. T. HURD AND R. N. LEWIS, *The Chemistry of Organometallic Compounds* Wiley, New York, 1957, pp. 184 and 192.
8 R. H. PRINCE, *J. Chem. Soc.*, (1959) 1783.
9 O. SCHMITZ-DUMONT, *Z. Anorg. Chem.*, 248 (1941) 289.

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Improved direct synthesis of methylgermanium halides

An improvement of the "Direct Synthesis"[1,*] of organogermanium halides involving the use of germanium and copper of smaller particle size and increased alkyl halide flow rate is reported. These modifications result in considerably larger amounts of crude reaction product produced per unit time than reported previously.

Experimental

Materials. Germanium powder (99.99 %) was obtained from A. D. Mackay, Inc., 198 Broadway, New York 38, N.Y., and exhibited an average particle diameter by microscopy of 0.02 to 0.05 mm, with high uniformity of size. Copper powder of electrolytic grade was purchased from Fisher Scientific and its particle size was the same as that of germanium. Methyl chloride and methyl bromide were supplied by the Matheson Company and methyl iodide was obtained from Fisher Scientific.

Apparatus and procedure. The methyl chloride or methyl bromide was passed (flow rate *ca.* 400–600 cc/min) through two wash bottles containing concentrated sodium hydroxide solution and concentrated sulfuric acid respectively and via a mercury safety valve into the reaction tube. The latter was a 25 mm I.D. Pyrex tube containing an intimate mixture of germanium powder and copper powder (weight ratio 10:4) distributed on glass wool. The 50 cm long tube was heated at 400 ± 10° in a 30 cm tube furnace. The methyl iodide was introduced at a rate of 100 drops per min directly into the reaction tube by means of a dropping funnel. The resulting liquid products were collected in a flask and the gaseous products separated in a dry-ice trap. The liquid materials were fractionated over a 100-cm heated column packed with glass helices.

The following boiling points were observed (at 750 mm): CH_3GeCl_3, 111°; $(CH_3)_2GeCl_2$, 122°; $(CH_3)_2GeBr_2$, 153°; CH_3GeBr_3, 170°; $(CH_3)_2GeI_2$, 62–64°/2 mm, CH_3GeI_3, 83–85°/12 mm, recrystallized from petroleum ether, m.p. 47°. The crude reaction products were assayed by proton nuclear-magnetic-resonance (NMR) spectroscopy of the neat liquids. The following chemical shifts were observed (in ppm relative to tetramethylsilane): CH_3Cl, —2.950; CH_3GeCl_3, —1.667; $(CH_3)_2GeCl_2$,

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[*] For a review of the "Direct Synthesis", see ref. 2.

—1.183; $(CH_3)_3GeCl$, —0.667; CH_3Br, —2.575; CH_3GeBr_3, —2.067; $(CH_3)_2GeBr_2$, —1.458; $(CH_3)_3GeBr$, —0.816; CH_3I, —2.117; CH_3GeI_3, —2.800; $(CH_3)_2GeI_2$, —1.900; $(CH_3)_3GeI$, —1.033.

Discussion

The "Direct Synthesis" of methylgermanium halides with methyl halides[1-5] has been studied to some extent earlier. Confirming Rochow's[6] postulate, all three methylgermanium halides, $(CH_3)_nGeX_{4-n}$, where $n = 1, 2,$ or 3, were found to be present in each case in the crude reaction mixture as evidenced by proton NMR, although the quantity of the trimethylgermanium halide was very small. A comparison of the amounts of crude reaction product produced per hour is shown in Table 1. The data indicate that in the runs reported in this paper, these yields were increased considerably, *e.g.* for the methyl chloride reaction by a factor of 20 to 35 as compared to previous data. No comparable data were available on the reaction with methyl bromide or iodide.

TABLE 1

REACTION DATA OF THE "DIRECT SYNTHESIS" OF METHYLGERMANIUM HALIDES

	Rochow[1]	*Schmidt and Ruidisch*[3]	*This paper*	*Ponomarenko and Vzenkova*[4]	*This paper*	*This paper*
X in CH_3X and $(CH)_nGeX_{4-n}$	Cl	Cl[a]	Cl	Br	Br	I
Quantity of Ge (g)	85	30	100	400	100	50[b]
Quantity of Cu (g)	21	12	40	100	40	20
Reaction temp. (°C)	320–360	360	400	450	400	400
Reaction time (h)	196	144	15		6	4
Yield of crude reaction prod.						
in g	132	56	216	614[c]	371	256
in g/g Ge	1.6	1.9	2.2	1.5[c]	3.7	5.3
in g/h	0.7	0.4	14.4		62.0	66.4
Composition of crude reaction prod. (mol %)[d], yield based on amount of germanium used in parentheses						
CH_3X			16.5		20.3	62.0
CH_3GeX_3			20.0 (20.2)	48.3 (18.4)[c]	40.4 (42.8)	10.8 (33.4)
$(CH_3)_2GeX_2$	71[e] (46.9)	70[e] (54.6)	60.8 (60.7)	51.7 (19.7)[c]	37.8 (39.9)	15.9 (26.2)
$(CH_3)_3GeX$			2.7 (2.7)		1.2 (1.5)	1.3 (2.9)

[a] Experiment 7 of ref. 3. [b] Reacted with 300 g of CH_3I. [c] Based on the amount of the two pure fractions reported in ref. 4. [d] Assayed by proton NMR, assuming negligible amounts of GeX_4. [e] Weight % of crude reaction product.

Since none of the previous investigators of the "Direct Synthesis" report any quantitative data on the particle size* of the germanium powder and copper powder

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* According to ref. 1, "germanium powder and copper were pressed into a disc and broken into lumps.". The authors in ref. 3 use "finely powdered germanium having a bluish-gray appearance".

used, the observed high yields of crude reaction products reported in this paper are attributed to an increased reactivity of the mixture of germanium and copper powder due to a smaller average particle size. Also, the flow rate of methyl chloride is significant. In these studies the average flow rate was of the order of 400 to 600 cc/min as compared to *ca.* 2–3 bubbles per sec (approximately 50 cc/min) reported by others[3]. At such high flow rates, a considerable amount of methyl chloride passes through the reaction zone without having reacted and condenses in the cold trap. However, the condensed methyl chloride can be recycled directly by connecting the trap to the reaction tube and letting the contents warm up to room temperature. The flow rate is then just about of the same order of magnitude as required.

For methyl bromide, the yield per hour in terms of crude reaction product in this case could be increased to about 60 g per hour and only about 20 % of the methyl bromide had passed through the reaction tube unreacted and had collected in the cold trap. In total, three moles of methyl bromide had been used per gram-atom of germanium. Similar results were obtained for the methyl iodide reaction. From these data, it appears that the reaction with methyl bromide is the method of choice when larger amounts of methylgermanium halides are to be prepared conveniently within a short period of time.

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1 E. G. ROCHOW, *J. Am. Chem. Soc.*, 69 (1947) 1729.
2 J. J. ZUCKERMAN, *Advan. Inorg. Chem. Radiochem.*, 6 (1964) 383.
3 M. SCHMIDT AND I. RUIDISCH, *Z. Anorg. Allgem. Chem.*, 311 (1961) 331.
4 V. A. PONOMARENKO AND G. YA. VZENKOVA, *Bull. Acad. Sci. USSR (Engl. Transl.)*, (1957) 1020.
5 R. ZABLOTNA, K. AKERMAN AND A. SZUCHNIK, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, 12 (1964) 695; *Chem. Abstr.*, 62 (1965) 13167*b*.
6 E. G. ROCHOW, *J. Am. Chem. Soc.*, 70 (1948) 436.

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Proton magnetic resonance spectra of tetravinyltin and tetraallyltin: d_π–p_π bonding

Considerable evidence for d_π–p_π interaction between Si and sp^2 carbon orbitals has been reported by a variety of spectroscopic studies[1–6]. In particular, the anomalous low-field shifts in the proton resonance spectra of a number of vinylsilanes[7–9] have been interpreted in terms of back-donation of electron density from the vinyl group to the vacant *d* orbitals of the Si atom. It is reasonable to expect that the deshielding due to d_π–p_π interaction should be enhanced in vinyl derivatives of higher Group IVB

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