by analysis. The total deviation from the value calculated by gas analysis was −2.1, 1.5 and 0.1 mole per cent., respectively, for the three independent samples.

Annealed Mixtures.—Mixtures of the iron(II) halides were prepared by grinding together weighed samples of the pure components in a dry carbon dioxide atmosphere. The powder was transferred to Pyrex tubes of 10-ml. volume which were evacuated and baked out at 400° prior to sealing. The tubes were heated at 510° for two to fourteen days, cooled slowly over a two-hour period to 400°, then removed from the furnace. The composition of the resulting solid solutions was then checked by analysis.

Powder Patterns.—Pyrex capillaries 0.4 mm. i.d. were prepared, filled with the ground sample in the dry-box and subsequently sealed with a flame. X-Ray diffraction patterns were obtained using Cu Kα radiation (nickel-filtered; North American Phillips unit; 30 kv., 20 ma.) in a cylindrical camera of 11.49 cm. radius (calibrated with sodium chloride). Exposures varied from 15 to 48 hours.

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NOTES

The Addition Reaction between Trichlorogermane and an Olefin

BY ALBERT K. FISCHER, ROBERT C. WEST AND E. G. ROCHOW

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Sommer, Pietrusza and Whitmore have described the addition reaction between an olefin and trichlorosilane,[1] for which an applicable free-radical mechanism has been discussed by Kharasch, Jensen and Urry.[2] It was desired to determine whether the analogous reaction

$$\text{RCH}{=}\text{CH}_2 + \text{GeHCl}_3 \xrightarrow[\text{catalyst}]{\text{peroxide}} \text{RCH}_2\text{CH}_2\text{GeCl}_3$$

would proceed.

Experimental.—A mixture of 80% GeHCl_3 and 20% GeCl_4 was prepared according to the procedure described by Delwaulle and Francois.[3] The components are difficult to separate because an azeotrope of 70% GeHCl_3 and 30% GeCl_4 distils, but since SiCl_4 does not add to olefins it was expected that GeCl_4 would not interfere. Therefore the direct product was used in these experiments. Benzoyl peroxide was chosen as catalyst, and the olefin which was used was 1-hexene (Phillips Research Grade). Amounts of materials taken were: GeHCl_3, 18.9 g. (actual), 0.10 mole; 1-hexene, 18.5 g., 0.22 mole; benzoyl peroxide, 0.7 g., 0.003 mole.

The reactants were refluxed under a pressure about 5 cm. above one atmosphere at 62–64° for 35 hours in a flask fitted with two water-cooled condensers in series connected to a mercury seal to keep out air.

The product was distilled at a pressure of 40–50 mm. A fraction boiling at 122–125° and weighing 5.5 g. was obtained. This product was redistilled at 14 mm. with a constant boiling point of 97°, and yielded a clear and colorless liquid with a refractive index of $n^{25}\text{D}$ 1.4719.

Anal. Calcd. for $\text{C}_6\text{H}_{13}\text{GeCl}_3$: Cl, 40.27; H, 4.96; C, 27.28; Ge, 27.49. Found: Cl, 39.65; H, 4.81; C, 27.34; Ge, 28.20 (by difference).

The 5.5 g. of product represents a 22% yield of hexyltrichlorogermane, calculated on the basis of GeHCl_3.

Discussion.—The results show that the Ge–H bond of GeHCl_3 acts like the Si–H bond of SiHCl_3 in adding to the double bond of an olefin to produce an organogermanium compound. The position of addition of the GeHCl_3 to the olefin is not certain, but it seems reasonable that the Ge adds to the 1-position in accordance with experience with Si–H compounds, and because the radical which is formed in this manner ($\text{R}\dot{\text{C}}\text{H}{-}\text{CH}_2\text{GeCl}_3$) is more stable and longer-lived than the radical which would be formed if the Ge were to bond to the 2-position ($\text{RCH(GeCl}_3\text{)CH}_2\cdot$).

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An Improved Method for Obtaining High-Purity Zirconium and Hafnium Oxides

BY A. W. HENDERSON AND K. B. HIGBIE

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The need for high-purity zirconium and hafnium compounds for use as spectrographic standards is becoming more important as the knowledge of the uses for these metals increases. Because of the complex nature of the chemistry of these elements, the present purifying procedures mainly involve formation of oxychloride or sulfate compounds. Herzfield,[1] in 1914, patented the process of crystallizing zirconium oxychloride octahydrate from a concentrated solution of hydrochloric acid to remove large amounts of silica. A second recrystallization step was possible by dissolving the readily soluble crystals in water, adding concentrated hydrochloric acid, and boiling. The oxychloride octahydrate again crystallized out upon cooling. Venable,[2] Brauer,[3] and Spink and Wilhelm[4] have published variations of this basic method. The application of the method in large-scale production of zirconium metal has been summarized by Kalish.[5] The prepa-

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