CHEMISTRY

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1958

SovietRxiv

Abstract

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SYNTHESIS OF AROMATIC GERMANIUM COMPOUNDS BY MEANS OF ARYLDIAZONIUM BOROFLUORIDES

Aromatic compounds of tin and lead were obtained via diazo compounds by one of us and K. A. Kocheshkov with co-workers (^{1}). In the case of tin, diarylated derivatives are formed chiefly. In the decomposition of double salts of stannous chloride and aryldiazonium chlorides by metallic tin powder, the best, though still low, yields (23%) were obtained when Ar = C_6H_5. Higher yields of diaryldichlorostannanes (up to 40%) were obtained by us (^{2}) in the decomposition of aryldiazonium borofluorides in the presence of stannous chloride in acetone with zinc dust.

For organolead compounds as well, the best results are obtained by decomposition of aryldiazonium borofluorides with metallic lead powder (^{3}), and also with a lead-sodium alloy (^{4}) in acetone. Thus tetraphenyllead was obtained in a yield of 15% (decomposition with lead) and up to 30% (decomposition with the alloy), and tetraparatolyllead in a yield of 15% (decomposition with the alloy).

The present work reports on the possibility of applying the diazo method to the synthesis of aromatic germanium compounds. In contrast to $SnCl_4$ and $PbCl_4$, $GeCl_4$ does not form double salts with aryldiazonium chlorides. Aryldiazonium borofluorides were subjected to decomposition by metal powders in the presence of $GeCl_4$. The best of the reducing metals proved to be zinc (as dust), and the solvent absolute acetone.

As a result of the reaction, monoarylated germanium compounds are obtained. Germanium compounds of a higher degree of arylation are not formed under these conditions.

Aryltrichlorogermanes were isolated and analyzed in the form of anhydrides of arylgermanic acids. The latter are infusible colorless powders. Anhydrides of arylgermanic acids were obtained with Ar = C_6H_5, n-$CH_3OC_6H_4$—, n-$C_2H_5OC_6H_4$—, n-BrC_6H_4—, n-ClC_6H_4—. The anhydride of phenylgermanic acid was obtained in a yield of 28% of theory; for the other aryls the yields are lower.

Decomposition of phenyldiazonium borofluoride in the presence of

$GeCl_4$ **and Zn dust in acetone.** The reaction was carried out in a long narrow beaker equipped with a Witt stirrer and a thermometer. Into a suspension cooled to −8° of 17.4 g of zinc dust in a solution of 25.15 g of $GeCl_4$ in 80 ml of dry acetone, with vigorous stirring, 50 g of phenyldiazonium borofluoride was introduced in small portions over 20 min. The very first portions of diazonium compound caused the temperature of the reaction mass to rise to 5°. Thereafter the rate of addition was regulated so that the temperature did not rise above 5°. After completion of the addition of the diazonium compound, stirring was continued for 5 hr with cooling. On the following day 40 ml of dry acetone was added to the reaction mass, and stirring was continued until complete decomposition of the diazonium compound (negative reaction with β-naphthol). The reaction mixture was treated with a 20% NaOH solution. The precipitate that formed was filtered off after 3 h and washed with acetone (filtrate I). From the precipitate, by treatment with 20% NaOH solution on heating, followed by acidification of the alkaline filtrates with conc. HCl, the main quantity of phenylgermanic acid anhydride was isolated. After this, the residue, washed until rejection with acetone, alcohol, and ether, no longer burned, indicating the absence in it of $(C_6H_5)_2GeO$. Filtrate I was separated into two layers: an alkaline layer, from which on acidification an additional amount of $(C_6H_5GeO)_2O$ was isolated, and an acetone layer. The latter was combined with the acetone, alcohol, and ether filtrates from the washings; the solvents were evaporated in the cold, and the residue—a thick resinous mass—was treated several times with benzene. The benzene extracts were combined, washed with 10% NaOH solution (to extract possible impurities of GeO_2), the benzene was evaporated in the cold, and the residue was transferred to a quartz test tube and treated with a mixture of conc. H_2SO_4 and HNO_3 to destroy all organic compounds. After many hours of boiling, evaporation of the excess acids, and ignition of the residue, no GeO_2 was detected in it (the residue was

Ar	ArN_2BF_4, g	Zn, g	$GeCl_4$, g	Acetone, ml	Temperature, °C, initial	Temperature, °C, max.	Yield, $(ArGeO)_2O$, g	Found, %, C	Found, %, H	Calculated, %, C	Calculated, %, H
p-$CH_3OC_6H_4$	28.7	8.65	16.6	75	−7	+6	0.23	40.71; 40.78	3.43; 3.59	41.26	3.46
p-$C_2H_5OC_6H_4$	25.1	7.0	15.0	80	−4	+5	0.47	44.38; 44.52	4.38; 4.52	44.12	4.16
p-ClC_6H_4	30.0	8.66	14.4	70	−7.5	−0.5	0.3	34.33; 34.17	2.09; 2.20	34.62	1.94
p-BrC_6H_4	67.0	16.17	26.9	80	−11	−5	1.0	29.43; 29.38	1.86; 1.81	28.53	1.59

Table 1. Decomposition of ArN_2BF_4 in the presence of $GeCl_4$, Zn dust in acetone

extracted with alkali; after addition of a large excess of conc. HCl the solution was saturated with H_2S; GeS_2 did not precipitate), which indicates the absence of $[(C_6H_5)_3Ge]_2O$ and $(C_6H_5)_4Ge$ in the benzene extracts. Unreacted $GeCl_4$ was isolated from the reaction mixture in the form of GeS_2 by precipitation of the hydrochloric acid filtrates with H_2S.

Obtained $(C_6H_5GeO)_2O$, 5.58 g (27.3% of theory). It was purified by repeated reprecipitation with HCl from 10% NaOH solution on heating, followed by washing with pyridine (once), water, alcohol, and ether.

Found, %: C 41.21; 40.96; H 3.18; 3.08
$C_{12}H_{10}O_3Ge_2$. Calculated, %: C 41.5; H 2.90

Data on the preparation, under analogous conditions, of anhydrides of other arylgermanic acids are summarized in Table 1.

Received
11 VI 1958

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