REACTION OF BENZOYLTRIETHYLGERMANE WITH TRIETHYLGERMYLLITHIUM

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We have discovered that triethylgermyllithium (I) reacts with benzoyltriethylgermane (II) in hexamethylphosphorotriamide (HMPTA) at 20°C with the formation of hexaethyldigermane (III) and phenyllithium (IV). Spectra of the radical-anions of (II) and dibenzene were detected in this mixture. Only the radical-anion of benzoylgermane (II) ($a_p = 6.5$, $a_o = 5.0$, $a_o = 3.9$, $a_m = 1.3$, $a_m = 1.3$ Oe) was detected upon carrying out the reaction at −78°C in HMPTA—tetrahydrofuran. Apparently, this radical-anion decomposes at 20°C to the radical-anion of dibenzene according to the reported scheme [1]. Derivatives (II) and (IV) are also the products of the decomposition of the radical-anion of (II), which is accompanied by decarbonylation. Triethylgermyltrimethylsilane and (III) in 2:1 ratio were detected in the reaction of trimethylsilyllithium (V) with benzoylgermane (II) in HMPTA along with phenyllithium. Thus, the reaction of (II) with (I) and (V) in HMPTA proceeds by two competing pathways: 1) one-electron transfer and 2) nucleophilic cleavage of the carbonyl Ge—C bond. In the case of (I), both pathways lead to the same products. The reaction mixture from triethylgermyllithium with (II) in hexane is not paramagnetic. The major product of their reaction after hydrolysis is bis(triethylgermyl)phenylcarbinol (VI), which, in contrast to Et_3GeR_2COH (R = alkyl or aryl) [2], is readily oxidized in the air to give hexaethyldigermanoxane and benzoyloxytriethylgermane. The 50% conversion of carbinol (VI) at 20°C required 120 min.

Bis(triethylgermyl)phenylcarbinol (VI). A mixture of 6.00 g (0.02 mole) germane (II) and 3.77 g (0.02 mole) reagent (I) in 30 ml hexane was stirred at 20°C for 2 h. Hydrolysis, drying, and fractionation were carried out in an argon atmosphere to give 6.74 g (70%) carbinol (VI), bp 109-110°C (0.06 mm), n_D^{20} 1.5390. Found, %: C 52.20, H 8.31, Ge 34.12. $C_{19}H_{36}Ge_2O$. Calculated, %: C 53.62, H 8.47, Ge 34.15. IR spectrum (ν, cm^{-1}): 3660 (OH). The ESR spectra were taken on an RE-1307 spectrometer in special two-pronged 0.1-mm cells. All the reactions were carried out in evacuated sealed ampuls.

LITERATURE CITED

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