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1963

SovietRxiv

Abstract

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Chemistry

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HOMOLYTIC REACTIONS OF TETRAETHYLGERMANE

In homolytic reactions, organometallic compounds of Group IV may be either sources of primary radicals or objects of radical attack. In the first case they decompose at the least strong metal-carbon bond ([1], [2]). In the second, the nature of the cleavage depends on the nature of the attacking radical and of the molecule attacked. As a result, it is not necessarily the weakest bond that undergoes homolysis.

Thus, for example, tetraethylgermane, when reacting with benzoyl and tert-butyl peroxides, acts as a hydrogen donor. We studied these reactions in the absence of solvents in a nitrogen atmosphere. Tetraethylgermane was used in a twentyfold molar excess. The results of the experiments are summarized in Table 1.

For the reactions one may propose a free-radical scheme, since they proceed under conditions in which the peroxides dissociate with formation of radicals $R\cdot$ ($R = C_6H_5$, C_6H_5COO, or tert.-C_4H_9O and CH_3)

$$R\cdot + (C_2H_5)_2Ge \rightarrow RH + (C_2H_5)_3Ge\dot{C}_2H_4. \quad (1)$$

(A)

The secondary germanium-containing radicals (A) mainly recombine. In this process a dehydrodimer is formed, with b.p. 150–155° at 5 mm; n_D^{20} 1.4887. Molecular weight: found 360.0, calculated 375.6.

Found, %:	C 51.55; H 10.25; Ge 38.34
$C_{16}H_{38}Ge_2$. Calculated, %:	C 51.15; H 10.20; Ge 38.65

The dehydrodimer, in turn, may be the object of free-radical attack. Ultimately this leads to the formation of a dihydrotrimer, which was isolated in the reaction with tert-butyl peroxide. B.p. 150–200° at 2 mm; n_D^{20} 1.4904.

Found, %: C 15.38; H 10.35; Ge 38.74

$C_{24}H_{56}Ge_3$. Calculated, %: C 51.24; H 10.04; Ge 38.72

The radicals (A), along with recombination, partially decompose according to equation (2), giving rise to ethylene

$$(C_2H_5)_3Ge\dot{C}_2H_4 \rightarrow C_2H_4 + (C_2H_5)_3Ge\cdot . \qquad (2)$$

The fate of the $(C_2H_5)_3Ge\cdot$ radicals could be followed only in the reaction with tert-butyl peroxide. In this case tert-butoxytriethylgermane was isolated, b.p. 95–100° at 5 mm; n_D^{22} 1.4760.

Found, %: C 51.76; H 9.99

$C_{10}H_{24}GeO$. Calculated, %: C 51.57; H 10.39

On treatment with hydrogen chloride in ether, this substance is converted into triethylchlorogermane, b.p. 60–61° at 15 mm; n_D^{20} 1.4595. The formation of tert-butoxytriethylgermane can be explained either by recombination of $(C_2H_5)_3Ge\cdot$ radicals with tert-butoxy radicals, or, more probably, by induced decomposition of the peroxide

$$(C_2H_5)_3Ge\cdot + (CH_3)_3COOC(CH_3)_3 \rightarrow (C_2H_5)_3GeOC(CH_3)_3 + (CH_3)_3CO\cdot . \qquad (3)$$

In the same way, in the reaction with benzoyl peroxide, part of the radicals (A) is converted into benzoyloxyethyltriethylgermane. B.p. 100–102° at 1 mm; n_D^{20} 1.5035. The substance is probably a mixture of the α- and β-isomers, since analysis for the hydrolyzable benzoate group (alkalimetry) gives low results.

$C_{15}H_{24}GeO_2$. Found, %: C 58.28; H 8.34; C_6H_5COO 33.50
Calculated, %: C 58.31; H 7.83; C_6H_5COO 39.20

A product analogous to benzoyloxyethyltriethylgermane could not be isolated in the reaction with tert-butyl peroxide. This, however, may be explained by the difficulty of isolating it from the rather complex reaction mixture.

On the basis of this and of previously published work (3), the following conclusions may be drawn regarding the influence of the nature of the central atom on the character of the decomposition of $(C_2H_5)_4M$ ($M = Si, Ge, Sn$, and Pb) in reaction with benzoyl peroxide.

As is known, the average heteroelement-carbon bond energy in these compounds decreases regularly (Si-C 64.1 ± 0.5; Ge-C 58.9 ± 1.5; Sn-C 46.9 ± 1.0 kcal (4,5)). In accordance with this, tetraethyllead is characterized by homolysis of the Pb-C bond: in the course of the reaction, the benzoate radical replaces ethyl in the molecule under attack. Conversely, in tetraethylsilane cleavage of the Si-C bond does not occur. The benzoate radical attacks the C-H bond and abstracts hydrogen, while the resulting $(C_2H_5)_3Si\dot{C}_2H_4$ radical recombines.

Table 1

Reaction of benzoyl peroxide (BP) and tert-butyl peroxide (TBP) with tetraethylgermane in the absence of oxygen[1]

Reaction products[2]	Yield in moles per 1 mole of peroxide: reaction with BP	Yield in moles per 1 mole of peroxide: reaction with TBP
CO_2	0.76	–
C_6H_5COOH	0.60[3]	–
CH_4	–	0.08
C_2H_6	0.02	–
C_2H_4	0.39	0.25
$(CH_3)_3COH$	–	1.25[3]
CH_3COCH_3	–	0.06
C_6H_6	0.32	–
$[(C_2H_5)_3GeC_2H_4]_2$	0.29	0.23
$C_{24}O_{56}Ge_3$	–	0.11
$(C_2H_5)_3GeOC(CH_3)_3$	–	0.07
$(C_2H_5)_3GeC_2H_4OCOC_6H_5$	0.18	–

[1] For the experimental procedure see ([3]). In the reaction, 0.026 mole of peroxide and 0.53 mole of tetraethylgermane were used. In the case of BP, the reaction mixture was heated for 12 h to 100°; in the case of TBP, for 16 h to 130°.

[2] Analysis of gas mixtures, and identification of acetone and tert-butyl alcohol, were carried out by the chromatographic method.

[3] The yield was determined by the Chugaev–Tserevitinov method.

Tetraethyltin and tetraethylgermane occupy an intermediate position. In the former case, the substitution reaction of $C_2H_5\cdot$ radicals predominates, but the reaction of hydrogen abstraction by benzoate radicals also takes place. The radicals $(C_2H_5)_3Sn\dot{C}_2H_4$ formed immediately decompose according to an equation analogous to (2). Conversely, in the case of tetraethylgermane the substitution reaction is practically suppressed, as may be judged from the absence of ethane —the disproportionation product of $C_2H_5\cdot$ radicals. The $(C_2H_5)_3Ge\dot{C}_2H_4$ radicals formed by hydrogen abstraction only partially dissociate at the Ge–C bond (equation 2).

To elucidate the structure of the dehydrodimer formed upon recombination of radicals (A), we attempted to synthesize one of its possible isomers by gradually adding the calculated amount of triethylbromogermane to a solution of

1,4-dilithiobutane in ether cooled to −5°, followed by stirring (2 h) at room temperature. The unexpected product of this reaction is hexaethyldigermane. Yield 55.6%; b.p. 86-90° at 2 mm; n_D^{20} 1.4920. Literature data (^{6}): b.p. 61-62° at 0.007 mm; n_D^{20} 1.4960.

The residue with b.p. 130-150° at 5 mm; n_D^{20} 1.4785, judging by analysis, is contaminated $(C_2H_5)_3Ge(CH_2)_4Ge(C_2H_5)_3$. Yield 12.3%. Mol. wt. found—

found 348, calculated 375.6.

$C_{16}H_{38}Ge_2$.	Found, %:	C 50.47;	H 10.11;	Ge 39.42
	Calculated, %:	C 51.15;	H 10.20;	Ge 38.65

As far as we know, reductive condensation of organogermanium compounds of the type described is more characteristic of Grignard syntheses (^{7}).

Finally, we carried out homolytic chlorination of tetraethylgermane with sulfuryl chloride in the presence of benzoyl peroxide. Conditions were used under which tetraethylsilane is converted into α-chloroethyltriethylsilane and triethylchlorosilane in yields of 50 and ∼ 7%, respectively (^{8}).

In our case analogous products are formed. However, the yield of α-chloroethyltriethylgermane, calculated on the tetraethylgermane that entered into the reaction, is only 25.8%. B.p. 81—82° at 15 mm; n_D^{20} 1.4655.

$C_8H_{19}GeCl$.	Found, %:	Cl 16.27
	Calculated, %:	Cl 15.88

The yield of triethylchlorogermane is 16.8%; b.p. 176—178°; n_D^{20} 1.4565.

$C_6H_{15}GeCl$.	Found, %:	Cl 18.00
	Calculated, %:	Cl 18.16

In addition, as in the case (^{8}), the reaction mixture contains a high-boiling residue, which was not investigated further.

Thus, as in the reaction with peroxides, homolysis of C—H bonds occurs in the homolytic chlorination of tetraethylgermane. Triethylchlorogermane may have arisen as a result of β-decomposition of β-chloroethyltriethylgermane or as a consequence of homolytic cleavage of radicals (A) according to equation (2) and subsequent interaction of $(C_2H_5)_3Ge\cdot$ radicals with sulfuryl chloride.

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Received
4 VII 1963

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