GERMYLATION REACTION OF PHENOXYACETYLENE

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In reactions of nucleophiles, for example, R_3GeM (where M is an alkali metal) with acetylene derivatives the possibility of formation of adducts is determined mainly by the nucleophilicity of the R_3Ge anion and the electrophilicity of the π-electron system [1]. In the case of $RC\equiv CH$ compounds the metallation process [2, 3] normally competes with the addition reaction. We have shown that metallation predominates in the reaction of phenoxyacetylene with triethylgermyllithium in THF at a reagent ratio of 1 : 1. The reaction products (after hydrolysis) are phenoxyacetylene, isolated in a yield of 49.3%, triethylgermane (23.4%), and hexaethyldigermane (I) (19.3%), while the yields of 1-triethylgermyl-1-phenoxyethylene (II) and cis-1-triethylgermyl-2-phenoxyethylene (III) is not high (~3%).

$$(C_2H_5)_3GeLi + C_6H_5OC{\equiv}CH \rightarrow C_6H_5OC{\equiv}CLi + (C_2H_5)_3GeH + \\ + (C_2H_5)_3Ge(C_6H_5O)C{=}CHLi + \text{цис-}(C_2H_5)_3GeCH{=}C(Li)OC_6H_5 \qquad (1)$$

Compounds (I)-(III) were isolated as fractions having bp 89,5-90°C (1 mm) and were separated by the method of GLC. Formation of digermane (I) was observed earlier during metallation of di- and triphenylmethane with triethylgermylpotassium [4] and according to [5], is explained by the side reaction

$$(C_2H_5)_3GeH + (C_2H_5)_3GeLi \rightarrow LiH + (C_2H_5)_6Ge_2\,(I) \qquad (2)$$

Judging from formation of compounds (II) and (III), addition of triethylgermyllithium at the $C\equiv C$ bond occurs nonregiospecifically. The absence in the mixture of trans-isomer (III) indicates that formation of the β-adduct occurs stereospecifically by the mechanism of trans-nucleophilic addition. Trimethylsilyl(phenoxy)acetylene (IV) is formed in a yield of 52.6% upon carrying out the reaction (1) with subsequent addition of $(CH_3)_3SiCl$, which confirms the presence in the reaction mixture of $C_6H_5OC\equiv CLi$. A counter synthesis of (IV) was carried out by the equation

$$C_6H_5OC{\equiv}CMgBr + (CH_3)_3SiCl \rightarrow (CH_3)_3SiC{\equiv}COC_6H_5 + MgBrCl \qquad (3)$$

We note that upon carrying out reaction (1) in hexane only insignificant suppression of metallation due to an increase in yields of addition products (II) and (III) is observed. An analogous, but more expressed, solvent effect was observed in the reaction of $(C_2H_5)_3GeLi$ with phenylacetylene [3]. It was shown on the example of tetramethylethylenediamine that $(C_2H_5)_3GeLi$ gives stable complexes with Lewis bases, which increases the nucleophilicity of the $(C_2H_5)_3Ge$ anion and the metallating ability of the germyllithium compounds [6]. Phenoxyacetylene like other ethers, can form complex compounds with triethylgermyllithium, as a result of which substitution of THF by hexane does not decrease strongly its metalling effect.

To confirm the structure of adducts (II) and (III) we carried out addition of triethylgermanium to phenoxyacetylene in the presence of Spaier catalyst. This reaction does not have regio- and sterospecificity, which can be judged from formation of adducts (II), cis-(III), and trans-(III), separated by preparative GLC. Thie relative content in the reaction mixture is equal to 10, 45, and 45%, respectively. Isomers were identified by the PMR method from spin—spin coupling constants of the olefinic protons [7].

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EXPERIMENTAL METHOD

Reactions with triethylgermyllithium were carried out in evacuated ampoules by the method of [8]. Preparative separation of mixtures was carried out on a Chrom-3 chromatograph. The detector was a katharometer; column (280 × 1 mm) of steel; the adsorbent was Carbowax 20M on Chromaton, the column temperature was 170°, and the carrier gas was helium.

Reaction of Triethylgermyllithium with Phenoxyacetylene. A solution of $(C_2H_5)_3GeLi$, obtained from 15.14 g of bis(triethylgermyl)mercury, 4 g of lithium, and 20 ml of THF by the method of [5], was added to 6.71 g of phenoxyacetylene. The mixture was heated at 60° for 6 h, then at ~20°, and hydrolyzed with degassed water (5 ml). The organic layer was extracted with ether and the extract was dried over Na_2SO_4. Fractionation yielded 2.19 g (23.4%) of triethylgermane, 3.34 g (49.3%) of phenoxyacetylene with bp 64° (40 mm); n_D^{20} 1.5164, and 2.35 g of a fraction with bp 89.5-90° (1 mm). Preparative GLC of the fraction yielded: hexaethyldigermane (relative content 76.8%), n_D^{20} 1.4970. Found: C 45.51; H 9.45; Ge 43.16%. $C_{12}H_{30}Ge_2$. Calculated: C 45.10; H 9.45; Ge 45.43%; adduct (II), n_D^{20} 1.5060. Found: C 60.38; H 7.94; Ge 26.36%. $C_{14}H_{22}GeO$. Calculated: C 60.29; H 7.94; Ge 26.03%. PMR spectrum (δ, ppm): 6.77 m (C_6H_5); 4.70 d; 4.39 d (CH_2, ${}^2J = 1.6$ Hz); 1.07 m [$(C_2H_5)_3Ge$]; cis-adduct (III); n_D^{20} 1.5170. Found: C 59.92; H 7.86; Ge 26.03%. $C_{14}H_{22}GeO$. Calculated: C 60.29; H 7.94; Ge 26.03%. IR spectrum (ν, cm^{-1}): 1620 (C=C). PMR spectrum (δ, ppm): 6.77 m (C_6H_5); 7.15 d (=CH—O); 4.76 d (=CHGe, ${}^3J = 7.0$ Hz); 1.07 m[$(C_2H_5)_3Ge$].

In a parallel experiment excess trimethylchlorosilane was added to the reaction mixture instead of water. The mixture was left overnight. Fractional distillation separated a fraction with bp 80-83° (3 mm). Yield was 52.6%). According to data of preparative GLC the fraction contained 96% compound (IV), n_D^{20} 1.4978, d_4^{20} 0.9360. IR spectrum (ν, cm^{-1}): 2190 (C≡C). PMR spectrum (δ, ppm): 7.35 m (C_6H_5), 0.12 s (Me_3Si).

Trimethylsilyl(phenoxy)acetylene (IV). To a solution of $C_6H_5OC \equiv CMgBr$ obtained by treatment of 5.9 g of phenoxyacetylene with an equimolar amount of C_2H_5MgBr in 50 ml of ether was added 5.5 g of trimethylchlorosilane. The mixture was heated for 30 min at 40°. The ether solution was filtered from the precipitate. Distillation of the filtrate separated 5.8 g (50.8%) of compound (IV), bp 63° (0.5 mm), n_D^{20} 1.4980, d_4^{20} 0.9333. Found: C 69.01; H 7.63; Si 14.63%. $C_{11}H_{14}OSi$. Calculated: C 69.14; H 7.41; Si 14.75%. IR spectrum (ν, cm^{-1}): 2190 (C≡C). PMR spectrum (δ, ppm): 7.35 m (C_6H_5), 0.12 s (Me_3Si).

Hydrogermylation of Phenoxyacetylene. A mixture of 3.54 g of phenoxyacetylene, 4.83 g of triethylgermane, and 0.01 ml of an isopropanol solution of H_2PtCl_6 was heated for 2 h at 80°. Distillation yielded 6.3 g of a fraction with bp 108-148° (3 mm), separation of which by GLC yielded adduct (II) with n_D^{20} 1.5060 and cis-adduct (III) with n_D^{20} 1.5171. Their structure was confirmed by IR and PMR spectral data, agreeing with those presented above. In addition, trans-adduct (III) was isolated with n_D^{20} 1.5170. Found: C 59.90; H 7.93; Ge 26.28%. $C_{14}H_{22}GeO$. Calculated: C 60.29; H 7.94; Ge 26.03%. IR spectrum (ν, cm^{-1}): 1630 (C=C). PMR spectrum (δ, ppm): 7.04 (C_6H_5); 6.35 d (=CH—O), 5.05 d (=CHGe, ${}^3J = 14.0$ Hz); 1.07 m [$(C_2H_5)_3Ge$].

CONCLUSIONS

1. The metallation process dominates in reaction of $(C_2H_5)_3GeLi$ with phenoxyacetylene, leading to $C_6H_5OC \equiv CLi$. Addition at the acetylene bond proceeds nonregiospecifically with formation of α- and cis-β-adducts.

2. Addition of $(C_2H_5)_3GeH$ to phenoxyacetylene under the effect of Spaier catalyst leads to a mixture of α-, cis-β-, and trans-β-adducts.

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