FORMATION OF LINEAR META-OLIGOPHENYLS IN THE DECOMPOSITION OF POLYMERIC MERCURY DERIVATIVES OF META-SUBSTITUTED BENZENE COMPOUNDS BY POWDERS OF METALS

V. N. Vinogradova and L. G. Makarova

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In the decomposition of insoluble polymer polymercury compounds, of variable composition, formed in the reactions of m-diiodo- or m-dibromobenzene with sodium amalgam, using silver powders, we obtained diphenyl- and a mixture of linear oligophenyls, of which we identified m-terphenyl, m-pentaphenyl, and m-nonaphenyl. This indicates a probable linear structure of the initial organomercury polymers as well. A comparison of the data obtained on the basis of the structure of the oligophenyls formed, experiments on decomposition (see Experimental), and elemental analysis do not permit an unambiguous judgement of the alternation of a number of phenyl rings and mercury atoms in the fragments of the polymer chain in the initial mercury polymers. A study of the products of thermal and catalytic destruction of m-nonaphenyl under the action of metals, as well as the behavior of individual m-oligophenyls with a lower number of phenyl rings under these conditions, might resolve this question.

EXPERIMENTAL

Reaction of m-Dihalobenzene with Sodium Amalgam. A mixture of 0.1-mole of the m-dihalobenzene (dibromo- or diiodo-) and sodium amalgam (from 4 g of Na and 200 g of Hg) in 50 ml of xylene, mesitylene, or dioxane in the presence of 2 ml of ethyl acetate was heated to boiling for 10-12 h in a stream of N_2. The solvent was distilled off, the residue washed with water and alcohol. Hg was removed by sublimation, and the residue extracted with benzene, toluene, or xylene. Diphenyl, diphenyl mercury, and in the case of m-diiodobenzene – phenylmercury iodide – were isolated from the combined alcohol and hydrocarbon extracts. The undissolved cream-colored precipitate represents a mercury polymer or a mixture of polymers containing 28-30% C, 1.7-1.8% H, 66-68% Hg, and always 1.50-1.80% Hal. These polymers are insoluble in the usual organic solvents, and their molecular weight could not be determined. When they were boiled with I_2 in xylene, we isolated m-diiodobenzene with mp 35-36° and IC_6H_4HgI with mp 199-200° (from xylene). Found: C 13.64; 13.60; H 0.73; 0.76; Hal 47.7; 47.6; Hg 37.53; 37.18%. $C_6H_4I_2Hg$. Calculated: C 13.58; H 0.76; Hal 47.84; Hg 37.81%. The IC_6H_4HgI obtained is the meta-isomer: when boiled with iodine in benzene it gives m-diiodobenzene.

Decomposition of Mercury Polymers by Metal Powders. A 1.3-g sample of the polymer and the metal powder, 1.4 g of Ag or 0.65 g of Pd, was heated in a sealed tube for 12 h at 260°. The reaction mixture was successively extracted with boiling benzene (extract *a*), with m-xylene (extract b), and with tetralin (extract c). The residue was noncombustible. The solvents were distilled off, and the residues from *a* (boiling range 65-80°), b (boiling range 80-100°), and c (boiling range 100-150°) were separately subjected to thin-layer chromatography on Al_2O_3 with reference standards: diphenyl and m-oligophenyls, synthesized according to [1]. Development with UV light after chromatography with hexane demonstrated the presence of diphenyl and m-terphenyl (primarily in the residues from *a* and b), and in the case of chromatography of the mixture with benzene : hexene, 1 : 1 (primarily in the residue from c) in the case of decomposition with Pd – the presence of m-pentaphenyl and m-nonaphenyl, and in the case of decomposition of Ag only m-nonaphenyl.

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CONCLUSIONS

Decomposition of polymer organomercury compounds, obtained from m-diiodo- and m-dibromobenzene and sodium amalgams with powders of palladium or silver, leads to diphenyl and noncyclic m-oligophenyls.

LITERATURE CITED

1. M. Busch and W. Weber, J. Prakt. Chem., 146, 1 (1936).