Chemistry

M. M. Koton and T. M. Kiseleva

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Abstract

Full Text

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Synthesis of Polymerizable Unsaturated Organomercury Compounds

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Recently, unsaturated organomercury compounds have begun to attract the attention of researchers. Allylic ([1]) and isopropenylic ([2]) mercury compounds, as well as mercury derivatives of stilbene ([3]), were synthesized first; comparatively recently, various vinyl derivatives of mercury ([4–6]) and perfluorodivinylmercury ([7]) have been obtained. At the same time, information was lacking on the ability of these unsaturated organomercury compounds to polymerize. From the few literature data ([8,9]), the existence is known of mercury-containing polymers stable up to 250–300°. We have for the first time synthesized a vinyl derivative of diphenylmercury capable of polymerization and copolymerization ([10]). Thus, in the interaction of para-vinylphenylmagnesium chloride and phenylmercuric bromide in tetrahydrofuran solution, crystalline phenyl-*p*-vinylphenylmercury (I) is obtained according to the equation:

$$CH_2{=}CH{-}C_6H_4MgCl + BrHgC_6H_5 \rightarrow CH_2{=}CH{-}C_6H_4Hg{-}C_6H_5 + MgClBr.$$

(I)

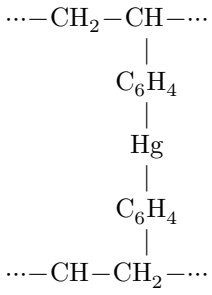
Compound (I) readily polymerizes and copolymerizes without initiators or in the presence of azodiisobutyric acid nitrile. The use of benzoyl peroxide, cationic-polymerization catalysts, and complex catalysts is excluded (even at low temperatures), since they enter into chemical reactions with monomer (I).

In the course of polymerization of (I), disproportionation of phenyl-*p*-vinylphenylmercury (I) occurs, with formation of diphenylmercury and a new unsaturated organomercury compound—bis-*p*-vinylphenylmercury (II), according to the equation:

$$2CH_2{=}CH{-}C_6H_4{-}Hg{-}C_6H_5 \rightarrow (C_6H_5)_2Hg + CH_2{=}CH{-}C_6H_4{-}Hg{-}C_6H_4{-}CH{=}CH_2.$$

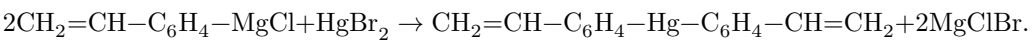
(I) (II)

Compound (II) very readily polymerizes with formation of an insoluble and infusible cross-linked polymer (III), which decomposes at temperatures above 250° with liberation of metallic mercury:



(III)

To prove the correctness of the proposed assumption, bis-*p*-vinylphenylmercury was synthesized by the interaction of chloro-*p*-vinylphenylmagnesium with mercuric bromide in a tetrahydrofuran solution, in the form of a crystalline substance:



Monomer (II) is readily polymerized, forming a polymer having the same structure (III) as the disproportionation product of phenyl-*p*-vinylphenylmercury.

Experimental Part*

The synthesis of phenyl-*p*-vinylphenylmercury (I) was carried out in a medium of dry, freshly distilled tetrahydrofuran under a stream of nitrogen. From 1.94 g of magnesium, 5.6 g of *p*-chlorostyrene in 30 ml of tetrahydrofuran, and 10.0 g of dry phenylmercuric bromide, a colorless viscous oil was obtained, which became solid upon cooling to −40°. After three recrystallizations from ethyl alcohol, colorless crystals were obtained, m.p. 84–86°, soluble in benzene and alcohol. Yield 2.7 g (25% of theory).

Found, %: C 43.99; H 3.46; Hg 52.35

$C_{14}H_{12}Hg$. Calculated, %: C 44.15; H 3.16; Hg 52.70

When an alcoholic solution of HCl acts on phenyl-*p*-vinylphenylmercury at a temperature from 0° to +20°, styrene, C_6H_5HgCl, and $HgCl_2$ are formed; when the temperature is lowered to −5°, styrene and C_6H_5HgCl are formed.

The synthesis of bis-*p*-vinylphenylmercury (II) was carried out under the same conditions as (I). From chloro-*p*-vinylphenylmagnesium and mercuric bromide, colorless crystals were obtained, m.p. 140–145°, soluble in alcohol and benzene. Yield 30% of theory.

Found, %: C 46.85; H 3.81; Hg 48.81; 49.42
$C_{16}H_{14}Hg$. Calculated, %: C 47.22; H 3.44; Hg 49.33

Upon polymerization of (I) in bulk in a nitrogen atmosphere in the absence of initiators, or in xylene solution in the presence of 0.3% azodiisobutyric acid nitrile as initiator, a brittle, pale-yellow, transparent polymer (III) is obtained, which is insoluble in all organic solvents. The yield of polymer is 50%. After treatment of the polymer with solvents, white crystals of diphenylmercury with m.p. 120–121° were isolated from the solution. The polymer (III), dried to constant weight, was analyzed.

Found, %: C 47.99; H 4.05; 3.99; Hg 48.38
$(C_{16}H_{14}Hg)_n$. Calculated, %: C 47.22; H 3.44; Hg 49.33

When heated to 250°, the polymer darkens, and upon further heating to 270–300° it decomposes with liberation of metallic mercury. Upon polymerization of (II) under the same conditions as (I), a transparent light-yellow brittle infusible polymer is formed, corresponding in composition and properties to polymer (III) obtained from (I).

(I) and (II) form copolymers with styrene in the form of transparent, colorless, insoluble masses.

Institute of Macromolecular Compounds
Academy of Sciences of the USSR

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References

1. E. Rothstein, R. Saville, J. Chem. Soc., 1952, 2987.
2. A. N. Nesmeyanov, A. E. Borisov, N. V. Novikova, DAN, 96, 289 (1954).
3. A. N. Nesmeyanov, A. E. Borisov, N. A. Vol' kenau, Izv. AN SSSR, OKhN, 1956, 162.
4. D. Seyferth, J. Org. chem., 22, 478 (1957).

5. G. Reynolds, R. Dessy, H. Jaffe, J. Org. chem., 23, 1217 (1958).

6. B. Bartocha, F. Stone, Zs. Naturforsch., 13b, 347 (1958).

7. R. N. Strelin, Li Wei-gan, I. L. Knunyants, Izv. AN SSSR, OKhN, 1959, 1506.

8. K. Broderson, L. Kunkel, Chem. Ber., 91, 2698 (1958).

9. T. Traylor, J. Polym. Sci., 32, 541 (1959).

10. M. M. Koton, T. M. Kiseleva, F. S. Florinskii, Izv. AN SSSR, OKhN, 1959, 948.

* With the participation of I. L. Arkhipova.

Note: Figure translations are in progress. See original paper for figures.