Chemistry

==========

1962

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR M. M. Koton, F. S. Florinskii

Synthesis of Polymerizable Organothallium Compounds

In recent years, derivatives of acrylic and methacrylic acids containing atoms of mercury ([1]), lead ([1,2]), tin ([3,4]), germanium ([5]), and antimony ([6]) have been synthesized. Recently, organometallic derivatives of *p*-vinylbenzoic acid were obtained ([7]). Continuing these studies, we have for the first time synthesized organothallium derivatives of acrylic, methacrylic, and *p*-vinylbenzoic acids.

The following were synthesized: diphenylthallium acrylate $CH_2{=}CH{-}COOTl(C_6H_5)_2$, diphenylthallium methacrylate $CH_2{=}C(CH_3){-}COOTl(C_6H_5)_2$, and diphenylthallium *p*-vinylbenzoate $p{-}CH_2{=}CH{-}C_6H_4COOTl(C_6H_5)_2$.

The synthesis of unsaturated organothallium compounds was carried out by the reaction of diphenylthallium bromide with acrylic, methacrylic, and *p*-vinylbenzoic acids in the presence of silver oxide in methanol solution ([8]), according to the equations:

$$2(C_6H_5)_2TlBr + Ag_2O + 2CH_2{=}C(R){-}COOH \rightarrow \\ \rightarrow 2CH_2{=}C(R)COOTl(C_6H_5)_2 + H_2O + 2AgBr, \quad (1)$$

where $R = H;\ CH_3$.

$$2(C_6H_5)_2TlBr + Ag_2O + 2CH_2{=}CH{-}C_6H_4{-}COOH \rightarrow \\ \rightarrow 2nCH_2{=}CH{-}C_6H_4COOTl(C_6H_5)_2 + H_2O + 2AgBr. \quad (2)$$

The organothallium monomers are colorless crystalline substances with high melting points, soluble in organic solvents. These monomers polymerize with difficulty (in decalin solution) in the presence of radical-polymerization initiators (tert-butyl peroxide), forming high-melting, thermostable powders insoluble in organic solvents.

Experimental Part

(with the participation of S. V. Troitskii)

Diphenylthallium bromide was obtained by the reaction of bromobenzene with thallium trichloride, in the form of colorless crystals that do not melt up to 300° ([9]).

Preparation of diphenylthallium acrylate. A mixture of 4.4 g (0.01 mole) of diphenylthallium bromide, 1.2 g of silver oxide, 1.1 g (50% excess) of acrylic acid, and 50 ml of methanol was heated for two hours at the boiling point of methanol. The hot solution was filtered from silver bromide. Colorless crystals precipitated from the filtrate. Yield 3.6 g (83.7% of theory). After two recrystallizations from methanol, m.p. 247–249° with decomposition.

Found, %:	C 41.76; 41.75;	H 3.53; 3.25;	Tl 47.39; 47.34
$C_{15}H_{13}TlO_2$. Calculated, %:	C 41.91;	H 3.02;	Tl 47.60

Preparation of diphenylthallium methacrylate was carried out in an analogous manner. On reaction of 4.4 g (0.01 mole) of diphenylthallium bromide, 1.2 g of silver oxide, 1.3 g (50% excess) of methacrylic

acid in 50 ml of methanol, 3.8 g (85.4% of theory) of colorless crystals was obtained. After two recrystallizations from methanol, m.p. 230–231° with decomposition.

Found, %:	C 43.63; 43.40;	H 3.45; 3.57;	Tl 46.24; 45.86
$C_{16}H_{15}TlO_2$. Calculated, %:	C 43.30;	H 3.38;	Tl 46.09

Preparation of diphenylthallium *p*-vinylbenzoate was analogous to the preparation of diphenylthallium acrylate and methacrylate, with the difference that heating of the reaction mixture was continued for three hours. For 8.8 g (0.02 mole) of diphenylthallium bromide and 2.4 g of silver oxide, 4 g (35% excess) of *p*-vinylbenzoic acid and 200 ml of methanol were taken. 6.6 g (65.4% of theory) of colorless crystals was obtained. After two recrystallizations from ethanol, the crystals turn yellow at 207°, and at 220° melt with simultaneous polymerization and decomposition.

Found, %:	C 49.97; 50.02;	H 3.61; 3.57;	Tl 40.07; 40.53
$C_{21}H_{17}TlO_2$. Calculated, %:	C 49.86;	H 3.36;	Tl 40.44

Analysis for the Tl content in the monomers was carried out by the method of Nametkin and Melnikov [10], volumetrically, with an accuracy of 0.2–0.5%.

Diphenylthallium acrylate, methacrylate, and *p*-vinylbenzoate were also obtained by us in good yields through the reaction of diphenylthallium oxide with

acrylic, methacrylic, and *p*-vinylbenzoic acids according to the following equations:

$$[(C_6H_5)_2Tl]_2O+2CH_2=C(R)-COOH \rightarrow 2CH_2=C(R)-COOTl(C_6H_5)_2+H_2O,$$

where R = H; CH_3.

$$[(C_6H_5)_2Tl]_2O+2CH_2=CH-C_6H_4COOH \rightarrow 2CH_2=CH-C_6H_4COOTl(C_6H_5)_2+H_2O.$$

Diphenylthallium oxide was obtained by heating diphenylthallium bromide with an aqueous-alcoholic solution of caustic potash in the form of a colorless crystalline powder, infusible up to 300° [11].

Reaction of organothallium monomers with an alcoholic solution of HCl. Diphenylthallium methacrylate (acrylate) and diphenylthallium *p*-vinylbenzoate, at room temperature upon mixing with an alcoholic solution of HCl, decompose with formation of the free unsaturated acids and diphenylthallium chloride according to the equations:

$$CH_2=C(R)-COOTl(C_6H_5)_2+HCl \rightarrow CH_2=C(R)COOH+(C_6H_5)_2TlCl,$$

where R = H; CH_3.

$$n\text{-}CH_2=CH-C_6H_4-COOTl(C_6H_5)_2+HCl \rightarrow n\text{-}CH_2=CH+C_6H_4COOH+(C_6H_5)_2TlCl.$$

Institute of High-Molecular Compounds
Academy of Sciences of the USSR

Received
20 VI 1962

REFERENCES CITED

1. M. M. Koton, T. M. Kiseleva, F. S. Florinskii, *Vysokomolek. soed.*, **2**, 1639 (1960).

2. D. A. Kochkin, DAN, **135**, 857 (1960).

3. M. M. Koton, T. M. Kiseleva, V. A. Paribok, DAN, **125**, 1263 (1959).

4. D. A. Kochkin, V. N. Kotrelev et al., *Vysokomolek. soed.*, **1**, 482 (1959).

5. G. S. Kolesnikov, S. L. Davydova, N. V. Klimentova, *Vysokomolek. soed.*, **2**, 563 (1960).

6. M. M. Koton, F. S. Florinskii, DAN, **137**, 1368 (1961).

7. M. M. Koton, T. M. Kiseleva, *Izv. AN SSSR, OKhN*, 1961, 1783.

8. A. Goddard, *J. Chem. Soc.*, **123**, 1161 (1923).

9. A. Goddard, D. Goddard, *J. Chem. Soc.*, **121**, 257 (1922).

10. S. S. Nametkin, N. N. Melnikov, *Zs. anal. Chem.*, **98**, 414 (1934).

11. A. Goddard, *J. Chem. Soc.*, **121**, 482 (1922).

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