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SYNTHESIS OF TRIPHENYLBISMUTH BIS(2-METHYLPROPENOATE)

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Triphenylbismuth bis(2-methylpropenoate) $\text{Ph}_3\text{Bi}(\text{O}_2\text{CMe}=\text{CH}_2)_2$ has been obtained by the interaction of triphenylbismuth with methacrylic acid and hydrogen peroxide in tetrahydrofuran. Its structure has been determined by IR and ^1H NMR spectroscopy.

Keywords: triphenylbismuth bis(2-methylpropenoate), synthesis, structure, IR spectroscopy, NMR spectroscopy.

Introduction

Organometallic compounds of bismuth are the unique reagents in the arylation reactions of amines, alcohols, phenols, and glycols in the presence of catalytic amounts of copper, as well as unsaturated compounds under the catalytic action of palladium salts. Recently, chemistry of the metal-filled polymers, including bismuth-containing ones, develops intensively. Some known copolymers of various unsaturated bismuth compounds with organic monomers are already used for the synthesis of metal-containing polymers (including organic glasses) exhibiting the fungicidal and biocidal activity, X-ray protection properties [1]. For this reason the synthesis of new organic bismuth-containing compounds and their application as methylmethacrylate comonomers are important.

Methods for obtaining organobismuth compounds $\text{Ph}_3\text{Bi}(\text{O}_2\text{CR})_2$ by the reaction of triphenylbismuth dihalides with silver, sodium and ammonium salts of carboxylic acids [2–4], triphenylbismuth carbonate with carboxylic acids [5], triphenylbismuth with carboxylic acids in the presence of benzoyl peroxide, H_2O_2 , *t*-BuOOH [6], triphenylbismuth with anhydrides of carboxylic acids in the presence of *t*-BuOOH [7–11], triphenylbismuth with *tert*-butylperacetate and carboxylic acid [1], and triphenylbismuth with peracid [3] are known.

The aim of this work has been the synthesis of triphenylbismuth bis(2-methylpropenoate) by the reaction of triphenylbismuth with methacrylic acid and hydrogen peroxide. The presence of two methacrylate groups in the molecule can provide the use of the compound as a comonomer in the synthesis of a bismuth-containing polymer.

Experimental

Purification of solvents and reagents

Benzene, diethyl ether, tetrahydrofuran (THF) were dried over CaCl_2 , distilled and stored over sodium. Chloroform was distilled, petroleum ether and bromobenzene were used without primary purification. Methacrylic acid was purified by sublimation.

Synthesis of triphenylbismuth

Triphenylbismuth was prepared by a modernized technique [2]. Magnesium chips (12 g, 0.5 mol), 100 mL THF and 50 mL benzene were placed in a one-liter three-necked flask equipped with a stirrer, reflux condenser and dropping funnel. Bromobenzene (52.5 mL) was added, and then the mixture was heated for 1 h in an air bath. In the end the mixture was cooled, the flask was filled with argon and left overnight. Then the mixture was heated for dissolving of Grignard reagent, the residual magnesium was

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filtered through a wire filter. Solution of BiCl₃ (40 g, 0.13 mol) using benzene with THF (1:2) as solvent was added to the heated Grignard reagent. Then the reaction mixture was heated for 1 h in an air bath, then it was decomposed by 25 mL H₂O and 100 mL saturated NH₄Cl solution while cooling in a water bath. The top organic layer was dried by Na₂SO₄, the solvents were removed in a rotary evaporator at reduced pressure. The resultant triphenylbismuth had MP 76 °C after purification by recrystallization from hot isopropyl alcohol, the product yield was 77 %.

Synthesis of triphenylbismuth bis(2-methylpropenoate) (1)

Methacrylic acid (1.27 mL, 15 mmol) was added to Ph₃Bi solution (2.2 g, 5 mmol) in 20 mL ether, then 2.5 mL 2.03 M anhydrous H₂O₂ solution in diethyl ether was added dropwise at cooling with cold water. The mixture was left at 5 °C for 38 h. The solution attained weak yellowish color; large crystals of product **1** were formed at the bottom of the flask. The solution was decanted from the precipitate, and the crystals were washed with 4 mL of ether. The product yield was 79 %, MP: 149 °C (literature data for the product obtained by the reaction of triphenylbismuth, *tert*-butylperoxide and methacrylic acid were 165 °C [1]).

The product was dissolved in 10 mL of warm freshly distilled chloroform for purification by recrystallization. Hexane (40 mL) was added in portions of 5 mL to the transparent solution. Fine-crystalline white precipitate was formed. For complete precipitation the solution was left in a refrigerator for 1.5 h. The product was filtered off by means of Shott filter, washed 2 times with 4 mL hexane, and then dried in the air. The product yield of compound **1** was 60 % (1.83 g), MP: 164 °C.

After recrystallization the product did not contain impurities of methacrylic acid and triphenylbismuth, which was determined by thin-layer chromatography method (hexane:ethylacetate eluent, 4:1 by volume).

IR spectrum

The IR absorption spectra were recorded on the IR-spectrometer «IR Prestige-21» of the company Shimadzu (Japan) in a potassium bromide pellet containing 1 % of the investigated compound.

NMR spectrum

The ¹H, ¹³C-NMR spectra were recorded on the NMR-spectrometer «Ajilent DD2 400» in deuteriochloroform. Decoding and modeling of spectra were performed using the program MestReNova (demo version).

Elemental analysis

Elemental analysis was carried out using the manual express gravimetric method based on pyrolytic burning of a substance in a quartz tube in oxygen flow. This method allows determination of carbon and hydrogen contents, as well as bismuth by the remainder of bismuth (III) oxide. An automatic CH-analyzer was used in parallel. We developed a titrimetric method of analysis of product **1** given in the results and discussion section.

Results and Discussion

Compound **1** has been obtained by the method of oxidative addition from triphenylbismuth, hydrogen peroxide, and excess of methacrylic acid, mixed in the 1:1:3 ratio, respectively:



Diethyl ether was used as solvent. The reaction was carried out at room temperature. Yield of target product with m. p. 164 °C equaled 60 % after recrystallization from the mixture of chloroform and hexane.

Compound **1** is white crystalline substance, air- and moisture-stable, well soluble in chloroform, THF, methyl methacrylate, styrene, benzene, sparingly soluble in hexane and isopropyl alcohol. Good solubility in styrene and methyl methacrylate makes the product promising in order to obtain bismuth-containing polymers.

For investigation of composition and structure of compound **1**, elemental analysis, ¹H, ¹³C NMR, and IR spectroscopy were used.

The elemental analysis data are in good agreement with the calculated values. Found, %: C 51.00; H 4.12; Bi 35.00 (manual apparatus for combustion); C 51.25; H 4.18 (automatic analyzer); Bi 34.23 (titrimetric bismuth determination). Calculated for C₂₆H₂₅O₄Bi, %: C 51.13; H 4.13; Bi 34.25.

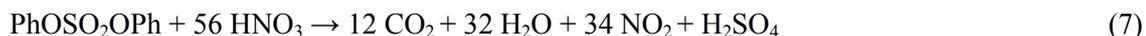
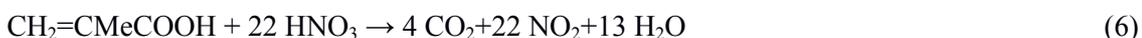
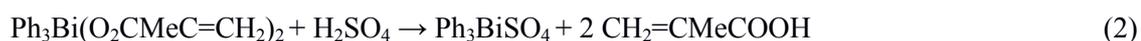
For titrimetric bismuth determination, which we had worked out for the first time, a sample of the analyzed compound (0.05–0.15 g) and 5 mL of concentrated H₂SO₄ were heated in 100 mL conical flask to appearance of white vapours. Then the solution was cooled, 5 mL of concentrated HNO₃ was added and the mixture was heated to its discoloration. After cooling of the mixture, 20 mL of water was added, followed by the concentrated solution of ammonia, until slightly acidic pH was reached. Xylenol orange indicator was added into the hot solution and it was titrated by 0.1 N solution of disodium EDTA, until the colour of the solution changed from pink to lemon yellow. Content of bismuth in the sample was determined according to the formula:

$$\omega(\text{Bi}) = 1.045V \cdot m^{-1},$$

V is the equivalent volume of 0.1 N solution of disodium EDTA, mL; m is the mass of the analyzed sample, g.

If addition of ammonia leads to precipitation of Bi(OH)₃, it is dissolved in concentrated HNO₃ and ammonia is again added, until slightly acidic pH is reached.

Triphenylbismuth dicarboxylate turns into triphenylbismuth sulfate Ph₃BiSO₄ at heating with concentrated H₂SO₄ according to equation (2); Ph₃BiSO₄ decomposes with decrease of Bi oxidation state according to equation (3). The phenyl derivative of Bi(III) is dephenylated to Bi₂(SO₄)₃ and benzene by sulfuric acid according to equation (4), benzene is sulfonated to benzenesulfonic acid according to equation (5):



Concentrated HNO₃ oxidizes all organic products to CO₂, H₂SO₄ and H₂O with formation of brown NO₂ in the presence of sulfuric acid according to equations (6–8).

During the titration, colour change is caused by the interaction of pink xylenol orange complex of triphenylbismuth sulfate with colourless disodium EDTA, that leads to formation of disodium xylenol orange complex with lemon yellow colour.

As the result of the chemical analysis, described above, reproducible results have been obtained. Percent of bismuth has been found to be 34.23 %; this is in good agreement with the combustion results, described above. The suggested volumetric method of bismuth content analysis of compound **1** is faster and more convenient than the known gravimetric method for bismuth determination in the BiOCl form [2].

In IR spectrum of the product, the medium absorption band, due to the stretching vibrations of Bi–C bonds, is at 679 cm⁻¹. The band at 449 cm⁻¹ belongs to the stretching vibration frequency of Bi–O bonds. The strong bands with maxima at 1362 cm⁻¹ and 1559 cm⁻¹ are related to the asymmetric and symmetric absorption vibration frequencies of COO groups, respectively. The band with maximum at 3045 cm⁻¹ belongs to the stretching vibration frequency of C–H bonds of phenyl groups. The wavenumbers of the noted vibrations are close to similar values for triphenylantimony dimethacrylate [12].

In ¹H NMR spectrum of compound **1** the multiplet of protons of Ph groups is observed in a weak field (δ 7.4–8.2 ppm); two singlets of CH₂ protons are observed in a stronger field (5.9 and 5.3 ppm); the singlet of CH₃ protons is observed in a strong field (1.8 ppm). The chemical shift values of these proton groups are close to similar values for triphenylantimony dimethacrylate [12]. In ¹³C NMR spectrum of

compound **1** the signals of carbon atoms of phenyl groups (130.5; 130.9; 133.8; 160.4 ppm) and methacrylate groups (19.0; 122.9; 139.1; 173.5 ppm) are present.

Conclusions

1. Triphenylbismuth *bis*(2-methylpropenoate) has been synthesized by the reaction of triphenylbismuth with hydrogen peroxide and methacrylic acid.
2. The compound is air- and moisture-stable, well soluble in chloroform, THF, methyl methacrylate, styrene, benzene, sparingly soluble in hexane and isopropyl alcohol.
3. Composition and structure of the product have been confirmed by means of IR, ^1H , ^{13}C NMR spectroscopy, and elemental analysis.
4. New technique for titrimetric bismuth content analysis of triphenylbismuth *bis*(2-methylpropenoate) has been suggested.

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References

1. Gushchin A.V. *Poluchenie organicheskikh proizvodnykh sur'my(V), vismuta(V) i primeneniye ikh v organicheskoy sinteze: dis. ...d-ra khim. nauk* [Obtaining organic derivative compounds of antimony(V), bismuth(V) and their use in organic synthesis: thesis... D.Sc (Chemistry)]. Nizhny Novgorod, State University of Nizhny Novgorod Publ., 1998. 283 p.
2. Kocheshkov K.A., Skoldinov A.P., Zemlyanskii N.N. *Metody elementoorganicheskoi khimii. Sur'ma, vismut* [Methods of Organometallic Chemistry. Antimony, Bismuth]. Moscow, Nauka Publ., 1976. 483 p.
3. Suzuki H. *Organobismuth Chemistry*. Amsterdam-London-New York-Oxford-Paris-Shannon-Tokyo, Elsevier, 2001. 619 p.
4. Finet J.-P. *Ligand Coupling Reactions with Heteroatomic Compounds*. New York, Pergamon, 1998, pp. 159–204.
5. Challenger F., Goddard A. E. L XXXII. Organo-derivatives of Bismuth. Part III. The Preparation of Derivatives of Quinquevalent Bismuth. *J. Chem. Soc.*, 1920, vol. 117, no. 692, pp. 762–773.
6. Dodonov V.A., Gushchin A.V., Brilkina T.G. [Synthesis and Some Reactions of Triphenylbismuth Diacylates]. *Zhurn. Obshch. Khimii* [Journal of General Chemistry], 1985, vol. 55, no. 1, pp. 73–80. (in Russ.)
7. Dodonov V.A., Gushchin A.V., Ezhova M.B. [Synthesis of Triphenylbismuth Diacylates]. *Zhurn. Obshch. Khimii* [Journal of General Chemistry], 1988, vol. 58, no. 9, pp. 2170–2171. (in Russ.)
8. Sharutin V.V., Sharutina O.K. Synthesis and Structure of Triphenylbismuth *Bis*(pentachlorobenzoate). *Russian Journal of Inorganic Chemistry*, 2014, vol. 59, no. 6, pp. 558–560. DOI: 10.1134/S0036023614060199.
9. Sharutin V.V., Senchurin V.S., Sharutina O.K. Synthesis and Structure of Triphenylbismuth *Bis*(1-adamantanecarboxylate). *Russian Journal of Inorganic Chemistry*, 2011, vol. 56, no. 10, pp. 1565–1567. DOI:10.1134/S0036023611100202
10. Sharutin V.V., Senchurin V.S., Sharutina O.K., Bregadze V.I., Zhigareva G.G. Synthesis and Structure of Triphenylbismuth *Bis*(phenylcarboranylcarboxylate). *Russian Journal of General Chemistry*, 2010, vol. 80, no. 10, pp. 1941–1944. DOI: 10.1134/S1070363210100117
11. Sharutin V.V., Egorova I.V., Kazakov M.A., Sharutina O.K. Synthesis and Structure of Triphenylbismuth *Bis*(2-Phenylaminobenzoate). *Russian Journal of Inorganic Chemistry*, 2009, vol. 54, no. 7, pp. 1095–1098. DOI: 10.1134/S0036023609070171
12. Gushchin A.V., Shashkin D.V., Prytkova L.K., Somov N.V., Baranov E.V., Shavyrin A.S., Rykalin V.I. Synthesis and Structure of Triphenylantimony Dimethacrylate. *Russian Journal of General Chemistry*, 2011, vol. 81, no. 3, pp. 493–496. DOI: 10.1134/S107036321103008X

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СИНТЕЗ БИС(2-МЕТИЛПРОПЕНОАТА) ТРИФЕНИЛВИСМУТА

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Взаимодействием трифенилвисмута с метакриловой кислотой и пероксидом водорода в тетрагидрофуране получен бис(2-метилпропеноат) трифенилвисмута $\text{Ph}_3\text{Bi}(\text{O}_2\text{CMe}=\text{CH}_2)_2$, строение которого подтверждено данными ИК- и ^1H ЯМР-спектроскопии.

Ключевые слова: бис(2-метилпропеноат) трифенилвисмута, синтез, строение, ИК-спектроскопия, ЯМР-спектроскопия.

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