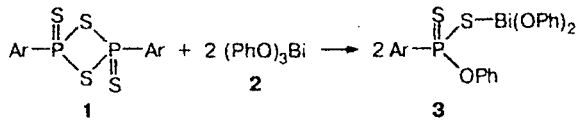
Letters to the Editor

Diphenoxybismuth(III) *O*-phenyl 4-methoxyphenylphosphonodithioate

I. S. Nizamov, A. V. Matseevskii, and E. S. Batyeva*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Research Center of the Russian Academy of Sciences, 8 ul. Arbuzova, 420088 Kazan', Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: nizamov@glass.ksu.ru

Among phosphorus- and sulfur-containing organic derivatives of Group VA elements, incorporating the P(S)SE fragment (E = As, Sb, Bi), bismuth compounds are the least studied. Their structural variations are limited to dithiophosphate and dithiophosphinate ligands.[1–8] These compounds are synthesized by reactions of the corresponding dithiophosphoric and dithiophosphinic acids or their salts with bismuth(III) oxide or chloride, phenylbismuth diethoxide, or triorganylbismuth.[1,5–7] However, to solve some fundamental problems (complex formation, the effect of heteroatoms in the P(S)SBi fragment, inter- and intramolecular P=S...Bi interactions, conjugation, stereochemistry, reactivity, *etc.*), it is necessary to synthesize new types and classes of compounds containing the P(S)SBi fragment and a wider range of substituents at the P and Bi atoms. We propose a new approach to the preparation of these compounds from 1,3,2,4-dithiadiphosphetane 2,4-disulfides. We found that 2,4-bis(4-methoxyphenyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane (the Lawesson reagent, **1**) reacts with bismuth(III) phenoxide in anhydrous benzene (**2**) over a period of 8 h at 25 °C to give diphenoxybismuth(III) *O*-phenyl 4-methoxyphenylphosphonodithioate (**3**).



1 **2** **3**

Ar = 4-$MeOC_6H_4$

Under mild conditions, this reaction involves only one Bi—O bond. Product **3** is thermally unstable and decomposes on attempted purification by molecular film distillation even in a high vacuum. Compound **3** is the first representative of a new type of phosphorus- and sulfur-containing bismuth(III) derivatives, incorporating the CP(S)(OC)SBi structural fragment.

Diphenoxybismuth(III) *O*-phenyl 4-methoxyphenylphosphonodithioate (3). Dithiadiphosphetane **1** (1.0 g, 2.5 mmol) was added in portions in a flow of dry argon at 20 °C to compound **2** (2.4 g, 4.9 mmol) in 5 mL of benzene. The mixture was stirred for 8 h at 20 °C and centrifuged. The liquid layer was decanted and kept *in vacuo* (0.05 Torr) for 2 h at 50 °C. This gave 1.0 g (30%) of compound **3**, n_D^{20} 1.5499. Found (%): P, 4.84. $C_{25}H_{22}BiO_4PS_2$. Calculated (%): P, 4.49. IR, ν/cm^{-1}: 3095, 3050, 3030 (=C—H, Ar); 1595, 1500 (C=C, Ar); 1235 (BiO—Ph); 1230 (P—OC); 930, 760 (Bi—OC); 690 (P=S); 612, 533, 507 (P—S); 466, 375, 276 (Bi—S). ^1H NMR (C_6D_6), δ: 3.13 (s, 3 H, $\underline{CH_3}OC_6H_4$); 6.38—7.00 (m, 4 H, $CH_3OC_6\underline{H_4}$; 15 H, $C_6\underline{H_5}$). ^{31}P NMR (162 MHz, in relation to 85% H_3PO_4, C_6H_6), δ: 79.1. MS (EI, 70 eV), m/z (I_{rel} (%)): 488 $[M-Ph-PhO]^+$ (15), 279 $[M-Ph-PhO-Bi]^+$ (44), 202 $[M-PhO-Bi(OPh)_2]^+$ (10).

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First observation of IR chemiluminescence of Nd^{III} and Yb^{III} perchlorates in the reaction with dispiro(adamantane-1,2-dioxetane) in a melt

*A. I. Voloshin, E. V. Zharinova, and V. P. Kazakov**

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066. E-mail: chemlum@ufanet.ru

Previously,[1] it has been established that electronic excitation and chemiluminescence of lanthanide (Ln^{III}) perchlorates upon catalysis of decomposition of dispiro(adamantane-1,2-dioxetane) ($(—Ad—O)_2$) in acetonitrile solutions were observed in the visible region of the spectra only in the case of Eu^{III} and Tb^{III}. These phenomena are determined both by the efficiency of the intramolecular energy transfer from the triplet adamantanone molecule ($Ad{=}O_T^*$) to excited levels of Ln^{3+} and by the quantum yield of luminescence of Ln^{3+}, which strongly depends on the composition of the coordination sphere of the ion.[1] This raises the question of whether electronic excitation of other lanthanides in the dioxetane—Ln^{III} system is possible. According to the theory of the inductive-resonance energy transfer, the strongest interactions that cause radiationless transitions are realized in solutions with the participation of molecular groups immediately adjacent to the Ln^{3+} ion.[2] In this connection, the Nd^{3+} and Yb^{3+} ions in H-containing media exhibit virtually no luminescence upon excitation due to the transfer of the energy of electronic excitation to the vibrational modes of the O—H and C—H oscillators. Therefore, the rate constant of nonradiative deactivation of Nd^{3+} and Yb^{3+} ions is much larger than the radiative rate constant: $k_{nr} >> k_r$. We expected that elimination of water molecules, which are generally present in acetonitrile solutions, by concentrating an aqueous—acetonitrile azeotrope would enable us to observe chemiluminescence of Nd^{3+} and Yb^{3+} in the reaction with $(—Ad—O)_2$. Actually, we observed chemiluminescence in the near IR region of the spectrum upon thermolysis (90 °C) of a melt containing $Ln(ClO_4)_3$ (0.15 mmol) and $(—Ad—O)_2$ (0.03 mmol), which was prepared by evaporating MeCN (3 mL). The luminescence spectra, which were obtained on a wide-aperture spectrometer equipped with a cooled FEU-83 instru-

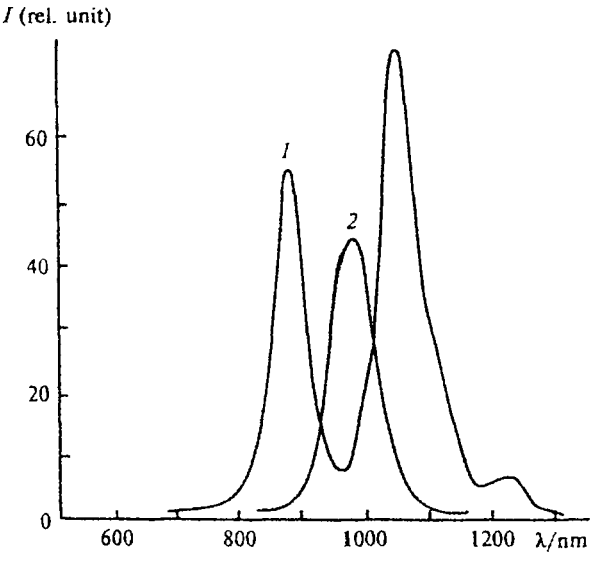

Fig. 1. Chemiluminescence spectra of Nd^{III} (*1*) and Yb^{III} (*2*) upon thermolysis of a melt containing their perchlorates (0.15 mmol) and $(—Ad—O)_2$ (0.03 mmol); 90 °C; the spectral resolution was 15 nm.

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