

SHORT
COMMUNICATIONS

Synthesis of Hexafluorophosphates of 9-Oxo-10-(4-heptoxyphenyl)thioxanthenium

V.A. Loskutov and V.B. Shelkovnikov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences,
Novosibirsk, 630090 Russia
e-mail: vsh@nioch.nsc.ru

Received April 26, 2005

DOI: 10.1134/S107042800212028X

Aryl-substituted and fused heterocyclic sulfonium salts prepared from the corresponding sulfoxides and derivatives of aromatic hydrocarbons in the presence of dehydrating agents are efficient initiators of cationic polymerization and find a number of other commercially important applications [1, 2]. In patents [3–7] as photo-initiators are recommended sulfonium salts based on derivatives of 9*H*-thioxanthen-9-one, thianthrene, dibenzothiophene, and other heterocyclic compounds. Aiming at preparation of photoinitiators applicable to initiation not only of cationic but also radical polymerization and therewith possessing good solubility and compatibility with the other components of photosensible composition we synthesized proceeding from mono- and disubstituted derivatives of 9*H*-thioxanthen-9-one **Ia–Id** previously unknown salts of thioxanthenium.

In the first stage it was necessary to convert thioxanthenones **Ia–Id** into the corresponding S-oxides. Although the literature treating sulfides oxidation is numerous (see, e.g., [8]), the choice of a method for preparation of sulfoxides avoiding further oxidation into sulfones is not a simple problem. In patents [3–7] the oxidation of thioxanthenones into S-oxides is recommended to perform with hydrogen peroxide, organic peracids, cerium ammonium nitrate, and other oxidants.

We carried out the oxidation of thioxanthenones **Ia–Id** with hydrogen peroxide and established that in acetic acid at boiling formed exclusively sulfones **IIa–IIId**. Under milder conditions (20–25°C) were formed sulfoxides **IIIa–IIIId**, but in the reaction mixtures were present also sulfones and (or) initial thioxanthenones, and only in the case of 1-chloro-4-propoxy-substituted compound **Id** we succeeded to isolate by recrystallization sulfoxide **IIIId** in a 55% yield. In the other cases the yield of monoxides

was considerably lower, and the individual compounds were isolated only by chromatography of the mixtures.

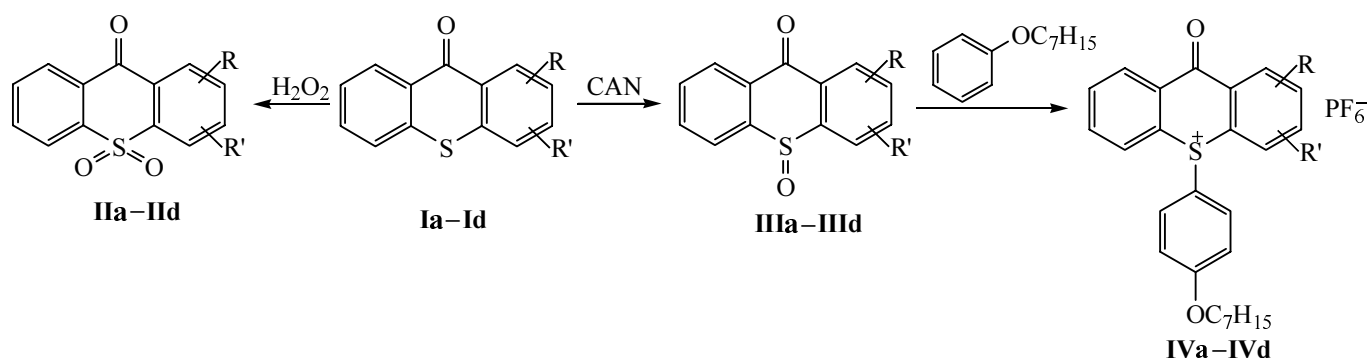
It was formerly reported [9] that the cerium ammonium nitrate was an efficient reagent for converting diaryl sulfides into sulfoxides. The use of the cerium ammonium nitrate really made it possible to oxidize thioxanthenones **Ia–Id** in acetonitrile at 20–25°C avoiding their excessive oxidation into sulfones, and S-oxides **IIIa–IIIId** were obtained in 75–95% yield.

To transform the sulfoxides obtained into sulfonium derivatives soluble in nonpolar organic solvents we carried out their condensation with an aromatic substrate containing a long aliphatic chain of seven carbon atoms (heptyl phenyl ether). To this end we applied the method described in [1] using as a dehydration agent a mixture of methanesulfonic acid with phosphorus pentoxide, 10:1. After keeping the reaction mixtures for 2–3 h at room temperature they were treated with water solution of KPF₆, and thioxanthenium hexafluorophosphates **IVa–IVd** were isolated as crystalline compounds soluble in organic solvents.

The composition and structure of compounds synthesized were proved by analysis and spectral data.

Thioxanthenone **Ia** was prepared from the thiosalicylic acid and p-bromotoluene by procedure [10], mp 123–125°C (120–123°C [10]); thioxanthenone **Ib** was obtained by bromination of thioxanthenone **Ia** with bromosuccinimide in the presence of benzoyl peroxide [11], mp 198–202°C (194–195°C [11]); thioxanthenone **Ic** and **Id** were purchased from Aldrich.

Oxidation of thioxanthenones Ia–Id with hydrogen peroxide. A mixture of 1 mmol of thioxanthenone **Ia–Id**, 8 ml of glacial AcOH, and 2 ml of 34% H₂O₂



R = 2-Me, R' = H (a); R = 2-CH₂Br, R' = H (b); R = R' = 2,4-Et (c); R = 1-Cl, R' = 4-OPr (d).

was boiled for 2 h, then was cooled and poured into water. The precipitate was separated and recrystallized from ethanol.

2-Methyl-9H-thioxanthen-9-one 10,10-dioxide (IIa). Yield 54%, mp 202–204°C (publ. mp 199°C [12]). IR spectrum, ν , cm⁻¹: 1673 (C=O), 1297, 1146 (SO₂). ¹H NMR spectrum, δ , ppm: 2.51 s (3H, CH₃), 7.64 d.d (1H, H³, *J* 8.5 and 1.5 Hz), 7.75 t.d, 7.85 t.d (2H, H^{6,7}, *J* 8.0 and 1.6 Hz), 8.04 d (1H, H⁴, *J* 8.5 Hz), 8.11 m (1H, H¹), 8.15 d.d (1H, H⁵, *J* 8.0 and 1.6 Hz), 8.31 d.d (1H, H⁸, *J* 8.0 and 1.6 Hz). Found [M]⁺ 258.0347. C₁₄H₁₀O₃S. Calculated *M* 258.0350.

2-Bromomethyl-9H-thioxanthen-9-one 10,10-dioxide (IIb). Yield 62%, mp 182–187°C. IR spectrum, ν , cm⁻¹: 1674 (C=O), 1302, 1146 (SO₂). ¹H NMR spectrum, δ , ppm: 4.54 s (2H, CH₂), 7.73–7.92 m (3H, H^{3,6,7}), 8.14 d (1H, H⁴, *J* 8.0 Hz), 8.16 d.d (1H, H⁵, *J* 8.0 and 1.5 Hz), 8.33 m (2H, H^{1,8}). Found, %: C 48.94; H 2.79; Br 24.18; S 9.69. [M]⁺ 335.9459. C₁₄H₉BrO₃S. Calculated, %: C 49.85; H 2.67; Br 23.74; S 9.49. *M* 335.9456.

2,4-Diethyl-9H-thioxanthen-9-one 10,10-dioxide (IIc). Yield 66%, mp 98–101°C. IR spectrum, ν , cm⁻¹: 2976, 2938, 2873 (C-H), 1664 (C=O), 1329, 1149 (SO₂). ¹H NMR spectrum, δ , ppm: 1.28 t, 1.39 t, 2.75 q, 3.29 q (10H, 2Et, *J* 7.6 Hz), 7.49 d (1H, H³, *J* 1.8 Hz), 7.73 td, 7.85 td (2H, H^{6,7}, *J* 7.6 and 1.4 Hz), 8.08 d (1H, H¹, *J* 1.8 Hz), 8.14 dd (1H, H⁵, *J* 7.6 and 1.4 Hz), 8.29 dd (1H, H⁸, *J* 7.6 and 1.4 Hz). Found [M]⁺ 300.0821. C₁₇H₁₆O₃S. Calculated *M* 300.0820.

4-Propoxy-1-chloro-9H-thioxanthen-9-one 10,10-dioxide (IIId). Yield 56%, mp 136–138°C. IR spectrum, ν , cm⁻¹: 2970, 2946, 2882 (C-H), 1672 (C=O), 1303, 1156 (SO₂). ¹H NMR spectrum, δ , ppm: 1.13 t (3H, CH₃, *J* 7.4 Hz), 1.94 m (2H, CH₂), 4.14 t (2H, OCH₂, *J* 6.2 Hz), 7.19 d (1H, H², *J* 9.2 Hz), 7.62 d (1H, H³, *J* 9.2 Hz), 7.72 t.d, 7.81 t.d (2H, H^{6,7}, *J* 7.6 and 1.6 Hz),

8.09 d.d, 8.13 d.d (2H, H^{5,8}, *J* 7.6 and 1.6 Hz). Found [M]⁺ 336.0220. C₁₆H₁₃ClO₄S. Calculated *M* 336.0223.

4-Propoxy-1-chloro-9H-thioxanthen-9-one 10-oxide (IIIId).* A mixture of 1.5 g of thioxanthene **Id**, 250 ml of glacial ACOH, and 15 ml of 34% H₂O₂ was stirred at 20–25°C for 4 h, then poured into water, the precipitate was separated and recrystallized from ethanol. Yield 0.87 g (55%), mp 168–172°C. IR spectrum, ν , cm⁻¹: 2963, 2937, 2876 (C-H), 1673 (C=O), 1033 (S=O). ¹H NMR spectrum, δ , ppm: 1.11 t (3H, CH₃, *J* 7.5 Hz), 1.94 m (2H, CH₂), 4.12 m (2H, OCH₂), 7.14 d, 7.59 d (2H, H^{2,3}, *J* 9.0 Hz), 7.71 m (2H, H^{6,7}), 7.91 m (1H, H⁵), 8.15 m (1H, H⁸). Found, %: C 59.38; H 3.79; Cl 10.65; S 10.30. [M]⁺ 320.0272. C₁₆H₁₃ClO₃S. Calculated, %: C 60.00; H 4.06; Cl 10.92; S 9.98. *M* 320.0274.

Oxidation of thioxanthenones Ia-Id with the cerium ammonium nitrate. To a solution of 2 mmol of thioxanthene **Ia-Id** in 20–30 ml of acetonitrile was added a solution of 8 mmol of the cerium ammonium nitrate in 7 ml of water; the mixture was stirred at 20–25°C for 2 h and then poured into water. The resulting mixture was maintained at 5°C for 20 h, the precipitate was separated and recrystallized.

2-Methyl-9H-thioxanthen-9-one 10-oxide (IIIa). Yield 75%, mp 139–140°C (from ethanol). IR spectrum, ν , cm⁻¹: 1661 (C=O), 1023 (S=O). ¹H NMR spectrum, δ , ppm: 2.50 s (3H, CH₃), 7.61 m (1H, H³), 7.69 t.d, 7.82 t.d (2H, H^{6,7}, *J* 7.6 and 1.6 Hz), 8.02 d (1H, H⁴, *J* 7.8 Hz), 8.13 m (2H, H^{1,5}), 8.34 d.d (1H, H⁸, *J* 7.6 and 1.6 Hz). Found, %: C 69.19; H 3.94; S 13.47. [M]⁺ 242.0398. C₁₄H₁₀O₂S. Calculated, %: C 69.42; H 4.13; S 13.22. *M* 242.0401.

2-Bromomethyl-9H-thioxanthen-9-one 10-oxide (IIIb). Yield 75%, mp 171–176°C (from a mixture

* In patent [3] the synthetic procedure for compounds **IIIc** and **IIIId** is given without description of their characteristics.

chloroform–ethanol). IR spectrum, ν , cm^{-1} : 1657 (C=O), 1026 (S=O). ^1H NMR spectrum, δ , ppm: 4.57 s (2H, CH_2), 7.44 d.d (1H, H^3 , J 8.0 and 1.5 Hz), 7.85 m (2H, $\text{H}^{6,7}$), 8.14 m (2H, $\text{H}^{4,5}$), 8.35 m (2H, $\text{H}^{1,8}$). Found, %: C 52.23; H 3.23; Br 24.95; S 10.15. $[M]^+$ 319.9509. $\text{C}_{14}\text{H}_9\text{BrO}_2\text{S}$. Calculated, %: C 52.34; H 2.80; Br 24.92; S 9.97. M 319.9507.

2,4-Diethyl-9H-thioxanthen-9-one 10-oxide (IIIc). Yield 96%, mp 94–99°C. IR spectrum, ν , cm^{-1} : 2966, 2935, 2872 (C–H), 1656 (C=O), 1021 (S=O). ^1H NMR spectrum, δ , ppm: 1.27 t, 1.41 t, 2.75 q, 3.24 m (10H, 2Et, J 7.4 Hz), 7.45 d (1H, H^3 , J 1.4 Hz), 7.71 t.d, 7.79 t.d (2H, $\text{H}^{6,7}$, J 7.4 and 1.8 Hz), 8.03 d.d (1H, H^5 , J 7.4 and 1.8 Hz), 8.10 d (1H, H^1 , J 1.4 Hz), 8.35 d.d (1H, H^8 , J 7.4 and 1.8 Hz). Found, %: S 11.56. $[M]^+$ 284.0870. $\text{C}_{17}\text{H}_{16}\text{O}_2\text{S}$. Calculated, %: S 11.27. M 284.0871.

4-Propoxy-1-chloro-9H-thioxanthen-9-one 10-oxide (IIIId). Yield 87%, mp 168–172°C (from ethanol).

Reaction of thioxanthenones IIIa–IIIId S-oxides with heptyl phenyl ether. At stirring 0.8 g of P_2O_5 was dissolved in 4 ml of freshly distilled methanesulfonic acid. To the mixture obtained was added 2 mmol of heptyl phenyl ether and 2 mmol of S-oxide III, the mixture was stirred for 2–3 h, a solution of 3 mmol of KPF_6 in 10 ml of water was added, and the mixture was stirred for 30 min. The tarry precipitate was separated, dissolved in dichloromethane, the organic layer was washed with water, dried over Na_2SO_4 , evaporated to a small volume, and ethyl ether was added thereto. The separated salt IV was isolated and once more reprecipitated with ether from dichloromethane.

Hexafluorophosphate of 2-methyl-9-oxo-10-(4-heptoxyphenyl)-9H-thioxanthenium (IVa). Yield 54%, mp 128.5–131°C. IR spectrum, ν , cm^{-1} : 2953, 2930, 2869 (C–H), 1672 (C=O), 843 (P–F). ^1H NMR spectrum, δ , ppm: 0.83 m (3H, CH_3), 1.24 m, 1.70 m (10H, 5CH_2), 2.56 s (3H, CH_3), 3.95 t (2H, OCH_2 , J 6.4 Hz), 6.99 d, 7.62 d (4H, C_6H_4 , J 9.2 Hz), 7.73 d.d (1H, H^3 , J 9.0 and 1.5 Hz), 7.87 d (1H, H^4 , J 9.0 Hz), 7.96 m (3H, H^{5-7}), 8.39 m (1H, H^1), 8.58 m (1H, H^8). ^{19}F NMR spectrum, δ , ppm: 89.75 d ($J_{\text{F-P}}$ 713.2 Hz). Found, %: C 58.40; H 4.78; F 20.08; S 5.80. $\text{C}_{27}\text{H}_{29}\text{O}_2\text{S}\cdot\text{PF}_6$. Calculated, %: C 57.65; H 5.16; F 20.28; S 5.69.

Hexafluorophosphate of 2-bromomethyl-9-oxo-10-(4-heptoxyphenyl)-9H-thioxanthenium (IVb). Yield 42%, mp 147–151°C. IR spectrum, ν , cm^{-1} : 2928, 2856 (C–H), 1670 (C=O), 843 (P–F). ^1H NMR spectrum, δ , ppm: 0.84 m (3H, CH_3), 1.24 m, 1.71 m (10H,

5CH_2), 3.97 t (2H, OCH_2 , J 6.4 Hz), 4.57 c (2H, BrCH_2), 7.02 d, 7.65 d (4H, C_6H_4 , J 9.0 Hz), 7.94 m (5H, H^{3-7}), 8.59 m (2H, $\text{H}^{1,8}$). ^{19}F NMR spectrum, δ , ppm: 89.9 d ($J_{\text{F-P}}$ 713.4 Hz). Found, %: C 51.30; H 4.26; Br 12.20; F 17.82; S 4.86. $\text{C}_{27}\text{H}_{28}\text{BrO}_2\text{S}\cdot\text{PF}_6$. Calculated, %: C 50.55; H 4.37; Br 12.48; F 17.78; S 4.99.

Hexafluorophosphate of 2,4-diethyl-9-oxo-10-(4-heptoxyphenyl)-9H-thioxanthenium (IVc). Yield 66%, mp 125–128°C. IR spectrum, ν , cm^{-1} : 2932, 2871 (C–H), 1675 (C=O), 845 (P–F). ^1H NMR spectrum, δ , ppm: 0.84 m (3H, CH_3), 1.28 m, 1.72 m (10H, 5CH_2), 1.35 t, 2.90 m, 3.18 m (10H, 2Et, J 7.6 Hz), 3.94 t (2H, OCH_2 , J 6.7 Hz), 6.98 d, 7.64 d (4H, C_6H_4 , J 9.0 Hz), 7.63 d (1H, H^3 , J 2.3 Hz), 7.90 m (2H, $\text{H}^{6,7}$), 8.32 m, 8.50 m (2H, $\text{H}^{5,8}$), 8.35 d (1H, H^1 , J 2.3 Hz). ^{19}F NMR spectrum, δ , ppm: 89.7 d (J 713.2 Hz). Found, %: C 60.05; H 5.79; F 18.94; S 5.35. $\text{C}_{30}\text{H}_{35}\text{O}_2\text{S}\cdot\text{PF}_6$. Calculated, %: C 59.60; H 5.79; F 18.87; S 5.30.

Hexafluorophosphate of 4-propoxy-1-chloro-9-oxo-10-(4-heptoxyphenyl)-9H-thioxanthenium (IVd). Yield 53%, mp 171–173°C. IR spectrum, ν , cm^{-1} : 2932, 2858 (C–H), 1681 (C=O), 845 (P–F). ^1H NMR spectrum, δ , ppm: 0.83 m (3H, CH_3), 0.99 t (3H, CH_3 , J 7.6 Hz), 1.26 m, 1.72 m, 1.90 m (12H, 6CH_2), 3.94 t, 4.20 t (4H, 2OCH_2 , J 6.4 and 7.0 Hz), 7.98 d, 7.58 d (4H, C_6H_4 , J 9.1 Hz), 7.45 d (1H, H^2 , J 9.0 Hz), 7.90 m (3H, $\text{H}^{3,6,7}$), 8.15 d.d, 8.39 d.d (2H, $\text{H}^{5,8}$, J 6.5 and 3.5 Hz). Found, %: C 54.27; H 5.32; Cl 5.50; F 18.42; S 5.20. $\text{C}_{29}\text{H}_{32}\text{ClO}_3\text{S}\cdot\text{PF}_6$. Calculated, %: C 54.37; H 4.99; Cl 5.54; F 17.80; S 4.99.

IR spectra were recorded on a Vector 22 instrument from KBr pellets; ^1H and ^{19}F NMR spectra were registered on a spectrometer Bruker AC-200 in CDCl_3 (internal references the residual proton signal in the solvent and C_6F_6 respectively), mass spectra were measured on a mass spectrometer Finnigan MAT-8200 (the molecular mass and composition of compounds was established from the precise mass of the molecular ion). The reaction progress was monitored and the purity of compounds was checked by TLC on Silufol UV-254 plates (eluent benzene or chloroform).

The study was carried out under the financial support of the Presidium of the Russian Academy of Sciences (projects 5–2, 8–3) and Siberian Division of the Russian Academy of Sciences (integration project 84).

REFERENCES

1. Akhtar, S.R., Crivello, J.V., Lee, J.L., and Smitt, M.L., *Chem. Mater.*, 1990, vol. 2, p. 732.

2. Gomurashvili, Z. and Crivello, J.V., *Macromolecules*, 2002, vol. 35, 2962.
3. Herlihy, S.L., WO Patent 03 072567; *Chem. Abstr.*, 2003, vol. 139, 231972y.
4. Herlihy, S.L., WO Patent 03, 072568; *Chem. Abstr.*, 2003, vol. 139, 231973z.
5. Norcini, G., Casiraghi, A., Visconti, M., and Li Bassi, G., WO Patent 03 008404; *Chem. Abstr.*, 2003, vol. 138, 137739k.
6. Davidson, R.S. and Pratt, J., WO Patent 03, 002557; *Chem. Abstr.*, 2003, vol. 138, 91475r.
7. Taniguchi, N. and Yokoshima, M., Japan Patent 102 12286, 1998; *Chem. Abstr.*, 1998, vol. 129, 190509a.
8. *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 8; Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1985, vol. 8, pp. 504–505.
9. Ho, T.L. and Wong, C.M., *Synthesis*, 1972, p. 561.
10. Filippatos, E., Papadaki-Valinari, A., Roussakis, Ch., and Verbist, J.-F., *Arch. Pharm. (Weinheim)*, 1993, vol. 326, p. 451.
11. Vasiliu, G., Rasanu, N., and Maior, O., *Rev. Chim.*, 1968, vol. 19, p. 561.
12. Mayer, F., *Ber.*, 1910, vol. 43, p. 584.