

SHORT
COMMUNICATIONS

Synthesis of 10-(4-Heptyloxyphenyl)-2-[2-methyl-2-(4-methylphenylsulfonyl)-1-oxopropyl]-9-oxothioxanthenium Hexafluorophosphate(V)

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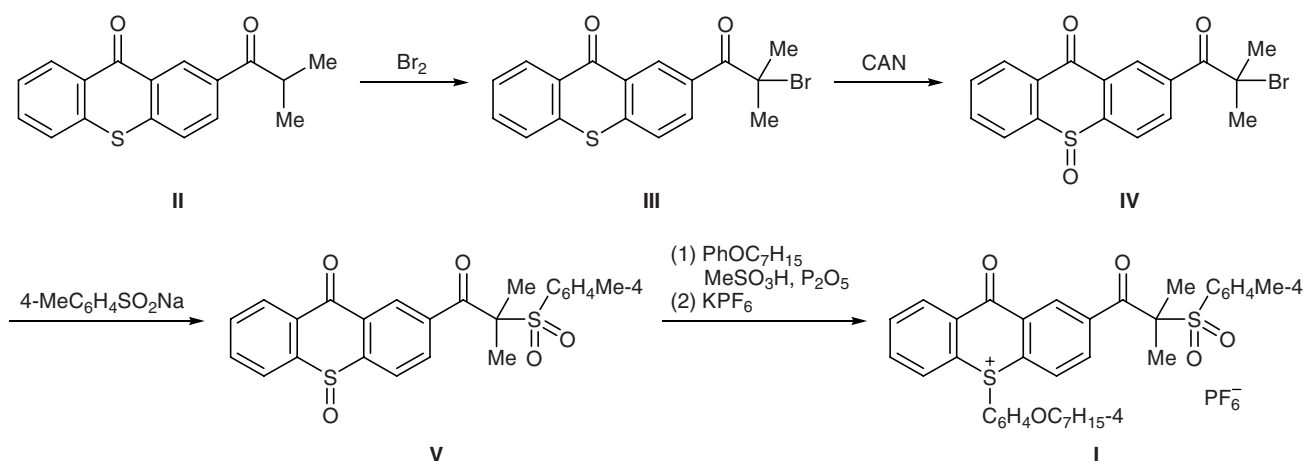
The efficiency of the initiation stage in photochemical polymerization of unsaturated compounds depends on the reactivity of initiator and radicals formed as a result of its decomposition by the action of light. We previously [1] synthesized new thioxanthen-9-one-based initiators of photopolymerization which, unlike known initiators, contained two photochemically active cationic centers, sulfonium and ammonium (or phosphonium). In the present communication we report on the synthesis of thioxanthenium hexafluorophosphate(V) containing a tosylisobutyryl residue. According to the data of [2], derivatives of α -sulfonyl ketones constitute a known class of highly effective photoinitiators. The target compound **I** was synthesized according to the scheme shown below.

Bromination of 2-isobutyrylthioxanthen-9-one (**II**) gave α -bromo ketone **III** which was oxidized to sulf-oxide **IV** with cerium(IV) ammonium nitrate (CAN) in acetonitrile. Compound **IV** reacted with sodium *p*-tol-

uenesulfinate to afford tosylisobutyryl derivative **V**, and condensation of the latter with heptyl phenyl ether in a mixture of methanesulfonic acid with phosphoric anhydride, followed by treatment with potassium hexafluorophosphate(V), resulted in the formation of 10-(4-heptyloxyphenyl)-2-[2-methyl-2-(4-methylphenylsulfonyl)-1-oxopropyl]thioxanthen-10-ium hexafluorophosphate(V) (**I**). The structure of the newly synthesized compounds was confirmed by spectral and analytical data.

Hexafluorophosphate **I** was used to initiate photochemical polymerization of acrylic monomers under laser flash excitation (both single- and two-photon). The results will be reported elsewhere.

2-(2-Methyl-1-oxopropyl)-9H-thioxanthen-9-one (**II**) was synthesized according to the procedure reported in [3], mp 140–144°C; published data [3]: mp 144–145°C.



2-(2-Bromo-2-methyl-1-oxopropyl)-9H-thioxanthen-9-one (III). A mixture of 2.4 g (8.5 mmol) of oxothioxanthene **II**, 0.9 ml (18 mmol) of bromine, and 15 ml of methylene chloride was kept for 20 h at 20–25°C. The precipitate was filtered off, washed with diethyl ether, and recrystallized from chloroform–ethanol. Yield 2.4 g (78%), mp 122–124°C. IR spectrum, ν , cm^{-1} : 1672, 1642 (C=O); 1592 (C=C). ^1H NMR spectrum, δ , ppm: 2.08 s (6H, CH_3), 7.59 m (3H, 5-H, 6-H, 7-H), 7.64 d (1H, 4-H, $J = 8.7$ Hz), 8.31 d.d (1H, 3-H, $J = 8.7, 1.9$ Hz), 8.61 d (1H, 8-H, $J = 8.0$ Hz), 9.47 d (1H, 1-H, $J = 1.9$ Hz). Found: m/z 359.98017 [M] $^+$. $\text{C}_{17}\text{H}_{13}\text{BrO}_2\text{S}$. Calculated: M 359.98201.

2-(2-Bromo-2-methyl-1-oxopropyl)-9H-thioxanthen-9-one 10-oxide (IV). A solution of 0.18 g (0.5 mmol) of compound **III** in 10 ml of acetonitrile was heated to 35–40°C, a solution of 1.1 g (2 mmol) of cerium(IV) ammonium nitrate in 3 ml of water was added, and the mixture was stirred for 0.5 h at that temperature (until it became homogeneous) and then for 2.5 h at 20–25°C. The mixture was poured into ice water, and the precipitate was filtered off. Yield 0.16 g (85%), mp 142.5–145°C (from ethanol). IR spectrum, ν , cm^{-1} : 1687, 1666 (C=O); 1589 (C=C); 1037 (S=O). ^1H NMR spectrum, δ , ppm: 2.03 s and 2.04 s (3H each, CH_3), 7.73 t.d and 7.87 t.d (1H each, 6-H, 7-H, $J = 8.0, 2.0$ Hz), 8.16 d.d (1H, 5-H, $J = 8.0, 2.0$ Hz), 8.24 d (1H, 4-H, $J = 8.0$ Hz), 8.36 d.d (1H, 8-H, $J = 8.0, 2.0$ Hz), 8.50 d.d (1H, 3-H, $J = 8.0, 1.6$ Hz), 9.03 d (1H, 1-H, $J = 1.6$ Hz). Found: m/z 375.97518 [M] $^+$. $\text{C}_{17}\text{H}_{13}\text{BrO}_3\text{S}$. Calculated: M 375.97692.

2-[2-Methyl-2-(4-methylphenylsulfonyl)-1-oxopropyl]-9H-thioxanthen-9-one 10-oxide (V). A mixture of 0.38 g (1 mmol) of thioxanthene oxide **IV**, 0.36 g (2 mmol) of sodium *p*-toluenesulfonate, and 6 ml of DMSO was stirred for 0.5 h at 20–25°C and was then left to stand for 40 h. The mixture was diluted with ice water, and the precipitate was filtered off. Yield 0.42 g (93%), mp 139–143°C. IR spectrum, ν , cm^{-1} : 1668 (C=O); 1587 (C=C); 1291, 1130 (SO_2); 1041 (S=O). ^1H NMR spectrum, δ , ppm: 1.68 s, 1.69 s, and 2.43 s (3H each, CH_3); 7.32 d and 7.66 d (4H, C_6H_4 , $J = 8.0$ Hz), 7.73 t.d and 7.86 t.d (1H each, 6-H, 7-H, $J = 8.0, 1.2$ Hz), 8.17 d.d (1H, 5-H, $J = 8.0, 1.2$ Hz), 8.25 d (1H, 4-H, $J = 8.2$ Hz), 8.36 d.d (1H, 8-H, $J = 8.0, 1.2$ Hz), 8.44 d.d (1H, 3-H, $J = 8.2, 1.8$ Hz), 8.72 d (1H, 1-H, $J = 1.8$ Hz). Found: m/z 452.07474 [M] $^+$. $\text{C}_{24}\text{H}_{20}\text{O}_5\text{S}_2$. Calculated: M 452.07521.

10-(4-Heptyloxyphenyl)-2-[2-methyl-2-(4-methylphenylsulfonyl)-1-oxopropyl]thioxanthen-10-ium hexafluorophosphate(V) (I). Compound **V**, 0.2 g

(0.44 mmol), and heptyl phenyl ether, 0.16 g (0.83 mmol), were added to a 10:1 mixture of methanesulfonic acid with phosphoric anhydride, 3 ml, and the resulting mixture was stirred for 3.5 h at 20–25°C. Ice was added to cool the mixture to 5°C, a solution of 0.26 g (1.4 mmol) of KPF_6 in 3 ml of water was added, and the mixture was stirred for 0.5 h and treated with methylene chloride. The organic phase was separated, washed with water, dried over anhydrous sulfate, and evaporated to dryness. The residue was reprecipitated from methylene chloride with diethyl ether and additionally recrystallized from ethanol. Yield 0.16 g (47%), mp 93–98°C. IR spectrum, ν , cm^{-1} : 2929, 2857 (C–H); 1680 (C=O); 1587 (C=C), 843 (P–F). ^1H NMR spectrum, δ , ppm: 0.87 t (3H, CH_3CH_2 , $J = 6.8$ Hz); 1.28 m and 1.74 m (10H, CH_2); 1.62 s and 2.44 s (9H, CH_3); 3.99 t (2H, OCH_2 , $J = 6.8$ Hz); 7.05 d, 7.33 d, 7.62 d, and 7.71 d (8H, C_6H_4 , $J = 8.0$ Hz); 7.93 m (3H, 5-H, 6-H, 7-H), 8.03 m (1H, 4-H), 8.37 m (1H, 8-H), 8.59 m (1H, 3-H), 9.05 m (1H, 1-H). ^{19}F NMR spectrum: δ_{F} 89.85 ppm, d ($J_{\text{FP}} = 713.6$ Hz). Found, %: C 57.53; H 5.04; F 15.14; S 8.35. $\text{C}_{37}\text{H}_{39}\text{O}_5\text{S}_2\cdot\text{PF}_6$. Calculated, %: C 57.51; H 5.05; F 14.76; S 8.29.

The IR spectra were recorded in KBr on a Vector 22 instrument. The ^1H and ^{19}F NMR spectra were obtained on a Bruker AC-200 spectrometer from solutions in CDCl_3 ; the chemical shifts were measured relative to the residual solvent signal (^1H) or C_6F_6 (^{19}F , internal reference). The molecular weights and elemental compositions were determined from the high-resolution mass spectra which were recorded on a Finnigan MAT-8200 mass spectrometer. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using benzene or chloroform as eluent.

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