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Synthesis of Pyrylium Salts Containing a β-Ketosulfonyl Fragment

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Abstract—Bis-acyl derivatives of diphenyl sulfide and diphenyl ether were synthesized by successive Friedel–Crafts acylations with 2-bromo-2-methylpropanoyl bromide and acetyl chloride. The subsequent reaction with sodium *p*-toluenesulfinate afforded the corresponding sulfones, and condensation of the latter with benzaldehyde in acetic acid in the presence of perchloric acid gave pyrylium salts with a β-ketosulfonyl fragment in the side chain.

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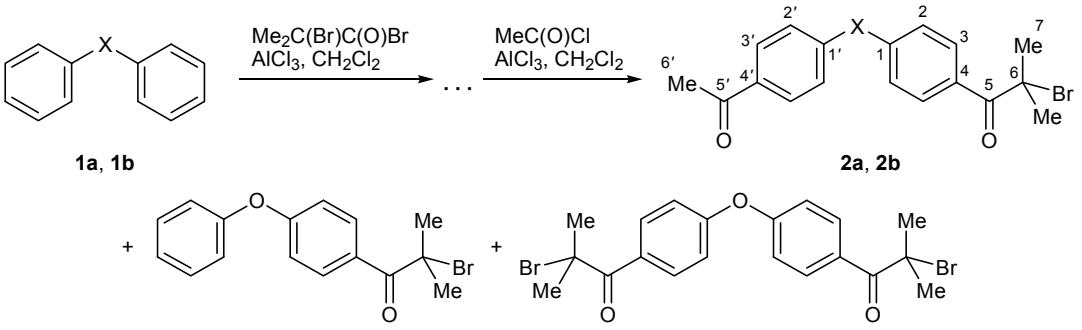
Photoinitiated polymerization is widely used in modern lithographic, UV and 3D printing, and holographic technologies. Photoinitiated radical polymerization requires light-sensitive compounds that decompose to generate free radicals. It is known that free radicals are formed by photoinitiated fragmentation of various β-keto sulfones via homolytic cleavage of the α-C–C bond with respect to the carbonyl group [1]. The action of other initiating systems is based on intermolecular transfer of an electron or hydrogen atom or decomposition of a cationic center in the initiator molecule (in cationic polymerization). Among such initiators, sulfonium, iodonium, and quinolinium salts have been reported [2]. A promising approach in the design of photoinitiators implies combination of two different photoinitiation centers in a single molecule. Examples are photoinitiators containing a benzophenone fragment and a ketosulfonyl group (Esacure 1001) [3] or a cationic sulfonium center and a ketosulfonyl group [4]. The activity of pyrylium salts in photoinitiated polymerization has recently been reported [5]. However, there are no published data on photoinitiators containing both pyrylium moiety and β-ketosulfonyl fragment.

The present work was aimed at developing a procedure for the synthesis of pyrylium salts with a side-chain β-ketosulfonyl group, i.e., compounds containing two different potentially photoactive centers.

A known method for the synthesis of pyrylium salts is based on the condensation of α,β-unsaturated ketones (chalcones) with carbonyl compounds [6]. β-Ketosulfonyl fragment may be assembled by Friedel–Crafts acylation of an aromatic substrate with 2-bromo-2-methylpropanoyl bromide, followed by replacement of bromine by a sulfonyl group. Insofar as aromatic carbonyl compounds cannot be acylated under Friedel–Crafts conditions, as aromatic substrates we selected diphenyl sulfide (**1a**) and diphenyl ether (**1b**) in which two benzene rings are separated by a sulfur or oxygen bridge.

Introduction of two different acyl groups into the *para* positions of diphenyl sulfide and diphenyl ether has been reported in [7, 8]. Following an analogous procedure, compounds **1a** and **1b** were subjected to successive Friedel–Crafts acylation with 2-bromo-2-methylpropanoyl bromide and acetyl chloride in methylene chloride in the presence of aluminum chloride (Scheme 1). The first acylation with 2-bromo-2-methylpropanoyl bromide was complete in one hour, while subsequent introduction of acetyl group required several days at room temperature. Bis-acyl diphenyl sulfide **2a** was thus obtained in almost quantitative yield. The reaction with diphenyl ether (**1b**) was not as selective as with **1a**, and the reaction mixture contained targeted unsymmetrical bis-acylated diphenyl ether **2b** together with small amounts of mono- and

Scheme 1.



X = S (**a**), O (**b**).

symmetrical bis-acyl derivatives which were isolated by silica gel column chromatography and identified by ^{1}H NMR [8, 9].

Reactions of alkyl halides with alkali metal sulfinates are known to give the corresponding sulfones. The reactions of **2a** and **2b** with sodium *p*-toluenesulfinate were carried out in different solvents [10, 11], and the best results were obtained in DMF (Scheme 2). The structure of **2a**, **2b**, **3a**, and **3b** was confirmed by NMR, IR, and mass spectra and elemental analyses. All these compounds displayed in the IR spectra strong absorption bands due to stretching vibrations of the carbonyl groups and conjugated C=C bond, and characteristic SO_2 bands were observed in the spectra of **3a** and **3b**.

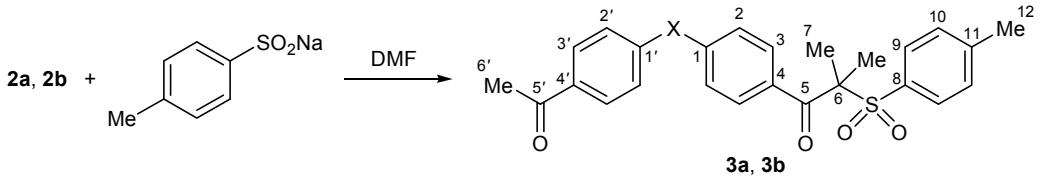
The ^{1}H NMR spectra of **2a** and **2b** contained two singlets from methyl groups with an intensity ratio of 2:1, and three methyl proton singlets with an intensity ratio of 2:1:1 were present in the spectra of **3a** and **3b**. The aromatic protons resonated as four (**2a**, **2b**) or six doublets (**3a**, **3b**) with equal intensities, indicating *para* substitution in each benzene ring of their molecules.

Compounds **2a** and **2b** showed in the ^{13}C NMR spectra two methyl carbon signals, and the signal from the carbon atom attached to bromine was displaced by ~30 ppm downfield relative to the former. Aromatic carbon signals appeared as four pairs of singlets, and the largest difference in the chemical shifts was observed for the C^4 and $C^{4'}$ atoms ($\Delta\delta_C \approx 3.0$ ppm), obviously due to *–I* effects of the acyl groups attached thereto. There were three methyl and six CH signals in the ^{13}C NMR spectra of **3a** and **3b**. Replacement of the bromine atom in **2** by toluenesulfonyl group led to downfield shifts of the C^6 (by 12–13 ppm) and C^5 and C^4 signals (by 2–3 ppm), whereas the C^7 signal shifted by ~10 ppm upfield.

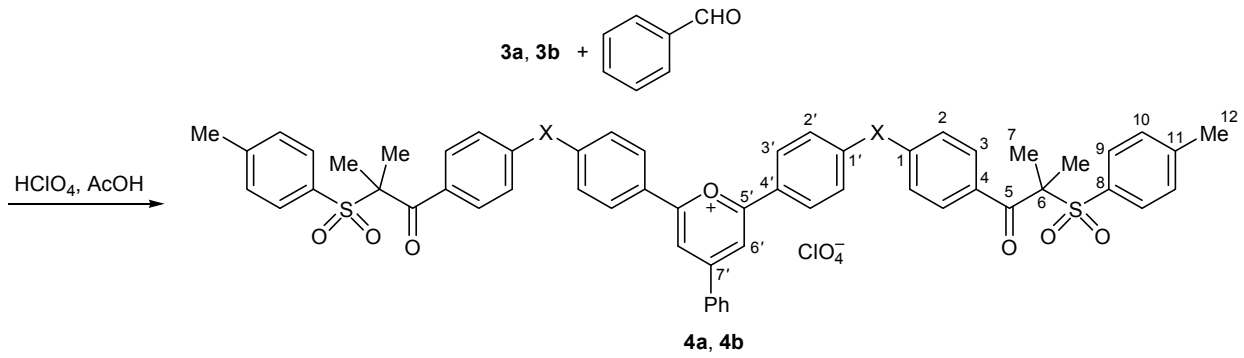
Our attempts to convert compounds **3a** and **3b** into the corresponding chalcones as pyrylium salt precursors by reaction with benzaldehyde in ethanol in the presence of alkali were unsuccessful. According to the ^{1}H NMR data, cleavage of the β-ketosulfonyl fragment occurred, but the products were neither isolated nor identified. Pyrylium salts **4a** and **4b** were synthesized in 27 and 35% yield, respectively, by condensation of **3a** and **3b** with benzaldehyde in acetic acid in the presence of 70% perchloric acid [11] (Scheme 3).

The structure of **4a** and **4b** was proved by NMR and IR spectra and elemental analyses. Their ^{1}H NMR spectra contained two singlets in the region δ 1.5–2.5 ppm with an intensity ratio of 2:1 (methyl groups) and six doublets in the aromatic region, the latter corresponding to three different *para*-substituted benzene rings. Aromatic protons of the tosyl group in **4a** and **4b** resonated in the same regions as those of **3a** and **3b**, and two protons in the pyrylium ring characteristically gave a singlet at δ 8.5 ppm. Protons of the benzene ring in the γ-position of the pyrylium ring appeared in the spectrum as a doublet (*o*-H) and two triplets (*p*-H, *m*-H) with an intensity ratio of 2:1:2.

Scheme 2.

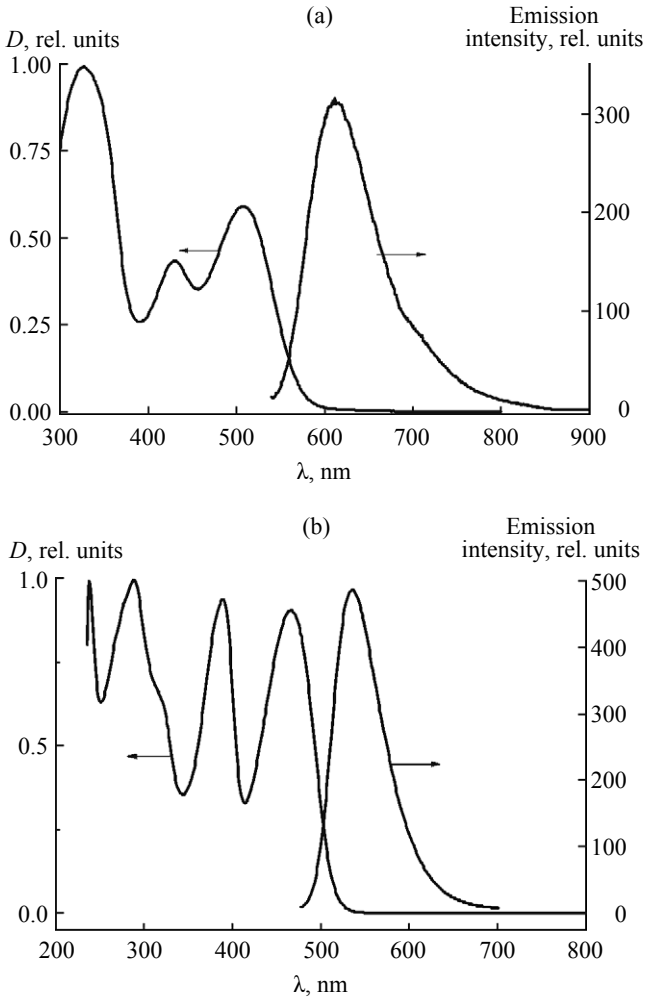


Scheme 3.



4a, **4b**

In going from the ^{13}C NMR spectra of **3a** and **3b** to those of **4a** and **4b**, the largest upfield shift was observed for the $C^{4'}$ signals ($\Delta\delta_C \approx 9.5$ ppm), while the signals from $C^{5'}$ and $C^{6'}$, which constitute now the pyrylium ring, displayed the largest downfield shifts (by 27 and 87 ppm, respectively). The benzene ring in the γ-position of the pyrylium ring gave rise to four signals in the region δ_C 129–135 ppm.



Absorption and luminescence spectra of substituted pyrylium salts (a) **4a** and (b) **4b**.

The differences in the chemical shifts of 2-H, 2′-H, 3-H, and 3′-H in diphenyl sulfide derivative **4a** and its oxygen analog **4b** are the same as for compounds **2** and **3**. Replacement of sulfur in **3a** and **4a** by oxygen (**3b**, **4b**) is accompanied by downfield shift of the C^1 and $C^{1'}$ signals by 19–25 ppm, which may be due to stronger negative inductive effect of the oxygen atom. On the other hand, stronger +*M* effect of oxygen leads to upfield shift of the C^2, $C^{2'}$ (by 10–12 ppm) and C^4, $C^{4'}$ signals (by ~3 ppm). Molecules **3a** and **4a** are characterized by higher degree of electron density delocalization over the benzene rings linked through the sulfur atom as opposed to **3b** and **4b**. The chemical shifts of C^8–C^{12} (tosyl group) are similar for all compounds.

Pyrylium salts **4a** and **4b** showed luminescence. Figure shows their absorption and luminescence spectra in chloroform. Compounds **4a** and **4b** are characterized by strong absorbance in the visible region and are luminescent dyes. The absorption and luminescence maxima of diphenyl sulfide derivative **4a** (λ_{abs} 507, λ_{lum} 611 nm) are located at longer wavelengths that those of its oxygen analog **4b** (λ_{abs} 465, λ_{lum} 535 nm). Triphenylpyrylium ion absorbs and emits at shorter wavelengths (λ_{abs} 410 nm, λ_{lum} 460 nm) [12]. The appreciable shift of the absorption and luminescence maxima depending on the presence of a heteroatom and is nature (O, S) in the substituents indicates that they are conjugated with the aromatic system of the pyrylium ring and are electron-donating toward the latter.

In summary, we have synthesized pyrylium salts containing β-ketosulfonyl fragments in the substituents, which exhibit luminescence properties and are potential photopolymerization initiators possessing reaction centers of two different types.

EXPERIMENTAL

The IR spectra were recorded on a Bruker Vector 22 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on Bruker AV-300 SY (300.13 MHz for ^{1}H) and AM-400 instruments (400.13 MHz for ^{1}H) relative to the residual proton and carbon signals of the solvent. The high-resolution mass spectra (electron impact, 70 eV) were obtained on DFS and Finnigan Mat 8200 mass spectrometers with direct sample admission into the ion source (ion source temperature 314°C). The electronic absorption and luminescence spectra were recorded at room temperature from solutions in chloroform on a Varian Cary Eclipse spectrofluorometer equipped with a xenon flash lamp (luminescence measuring at an angle of 90°) using 10-mm quartz cells.

1-[4-(4-Acetylphenylsulfanyl)phenyl]-2-bromo-2-methylpropan-1-one (2a). 2-Bromo-2-methylpropanoyl bromide, 3.8 mL (7.13 g, 31 mmol), was added under stirring at room temperature to a solution of 5.0 mL (5.57 g, 30 mmol) of diphenyl sulfide (**1a**) in 20 mL of methylene chloride. The mixture was cooled to 5°C, and 4.14 g (31 mmol) of powdered anhydrous aluminum chloride was added in portions over a period of 20 min (each next portion was added after dissolution of the preceding one). The cooling bath was removed, and the mixture was stirred for 20 min to allow it to warm up to room temperature and was then stirred for 1 h at room temperature. The mixture was cooled to 5°C, 2.4 mL (2.60 g, 33 mmol) of acetyl chloride was added, and 4.40 g (33 mmol) of aluminum chloride was then added. The cooling bath was removed, and the mixture was stirred for 3 h and then kept for 4 days at room temperature. The dark brown viscous solution was poured into a mixture of 150 g of ice with 5 mL of concentrated aqueous HCl and 20 mL of methylene chloride under vigorous stirring. The organic layer was separated, and aqueous layer was extracted with methylene chloride. The extract was combined with the organic phase, washed with water, and dried over $CaCl_2$, and the solvent was distilled off. Yield 10.9 g (96%), oily material; the product was used without additional purification. IR spectrum (film), ν, cm^{-1}: 3060, 3005, 2974, 2928, 1680, 1585, 1555, 1458, 1398, 1358, 1167, 1105, 1084, 1011, 980, 957, 885, 824, 621, 592. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.99 s (6H, CH_3), 2.56 s (3H, CH_3), 7.33 d (2H, 2-H, J = 8.6 Hz), 7.40 d (2H, 2′-H, J = 8.5 Hz), 7.87 d (2H, 3′-H, J = 8.5 Hz), 8.08 d (2H, 3-H, J = 8.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.5 ($C^{6'}$), 31.5 (C^7), 60.2 (C^6), 129.2 ($C^{2'}$), 129.8 (C^2), 130.7 ($C^{3'}$), 131.0 (C^3), 133.2 ($C^{4'}$), 135.8 (C^4), 140.3 ($C^{1'}$), 140.6 (C^1), 195.5 ($C^{5'}$), 197.1 (C^5). Found: m/z 376.0127 $[M]^+$. $C_{18}H_{17}BrO_2S$. Calculated: M 376.0128.

1-[4-(4-Acetylphenoxy)phenyl]-2-bromo-2-methylpropan-1-one (2b). 2-Bromo-2-methylpropanoyl bromide, 2.2 mL (4.1 g, 17.8 mmol), was added under stirring at room temperature to a solution of 2.8 mL (3.0 g, 17.6 mmol) of diphenyl ether (**1b**) in 10 mL of methylene chloride. The solution was cooled to 5°C, and 2.4 g (18 mmol) of powdered anhydrous aluminum chloride was added in portions over a period of 20 min (each next portion was added after dissolution of the preceding one). The cooling bath was removed, and the mixture was stirred for 20 min (the temperature rose to ambient) and then for 1 h at room temperature. The mixture was cooled to 5°C, 1.3 mL (1.42 g, 18 mmol) of acetyl chloride was added, and 2.4 g (18 mmol) of aluminum chloride was then added. The cooling bath was removed, and the mixture was stirred for 3 h and kept for 3 days at room temperature. The dark brown viscous solution was poured into a mixture of 100 g of ice with 5 mL of concentrated aqueous HCl and 15 mL of methylene chloride under vigorous stirring. The organic phase was separated, the aqueous phase was extracted with methylene chloride, the extract was combined with the organic phase, washed with water, and dried over $CaCl_2$, and the solvent was distilled off. The residue, 6.6 g, was a dark thick oily material. It was dissolved in 5 mL of methylene chloride and subjected to column chromatography on silica gel (50–160 μm) using methylene chloride–petroleum ether (bp 70–100°C; 1:1) as eluent. Yield 4.40 g (69%). IR spectrum (KBr), ν, cm^{-1}: 3065, 2976, 2930, 2876, 1672, 1647, 1593, 1504, 1360, 1304, 1263, 1223, 1200, 1165, 1111, 980, 961, 862, 837, 590, 582. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.02 s (6H, CH_3), 2.57 s (3H, CH_3), 7.03 d (2H, 2-H, J = 9.0 Hz), 7.08 d (2H, 2′-H, J = 8.9 Hz), 7.96 t (2H, 3′-H, J = 8.9 Hz), 8.21 d (2H, 3-H, J = 9.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.1 ($C^{6'}$), 31.1 (C^7), 59.9 (C^6), 117.7 ($C^{2'}$), 118.4 (C^2), 129.5 ($C^{4'}$), 130.3 ($C^{3'}$), 132.3 (C^3), 132.6 (C^4), 159.2 ($C^{1'}$), 159.5 (C^1), 194.4 ($C^{5'}$), 196.0 (C^5). Found: m/z 360.0349 $[M]^+$. $C_{18}H_{17}BrO_3$. Calculated: M 360.0356.

According to the ^{1}H NMR data [8, 9], the product contained 2-bromo-2-methyl-1-(4-phenoxyphenyl)-propan-1-one (0.63 g, 11%) and 2-bromo-1-{4-[4-(2-

bromo-2-methyl-1-oxopropyl)phenoxy]phenyl}-2-methylpropan-1-one (0.34 g, 4%).

1-{4-[(4-Acetylphenyl)sulfanyl]phenyl}-2-methyl-2-(4-methylbenzenesulfonyl)propan-1-one (3a). Sodium *p*-toluenesulfinate, 1.0 g (5.6 mmol), was added in portions over a period of 1 h under stirring to a solution of 1.9 g (5.0 mmol) of compound **2a** in 7 mL of DMF, and the mixture was stirred for 2 h at room temperature. The mixture was poured into 100 mL of water and extracted with methylene chloride, the extract was dried over $CaCl_2$, the solvent was distilled off, and the residue was subjected to column chromatography on silica gel (50–120 μm) using petroleum ether (bp 70–100°C) as eluent. Removal of the solvent from the main fraction gave 1.48 g (75%) of **3a** as a thick oily material which was used without additional purification. IR spectrum (film), ν, cm^{-1}: 3062, 2978, 2937, 2871, 1682, 1585, 1557, 1456, 1398, 1358, 1313, 1302, 1261, 1151, 1130, 1080, 968, 957, 820, 712, 671, 600. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.66 s (6H, CH_3), 2.42 s (3H, CH_3), 2.57 s (3H, CH_3), 7.30 d (2H, 10-H, J = 8.2 Hz), 7.36 d (2H, 2-H, J = 5.7 Hz), 7.40 d (2H, 2′-H, J = 5.7 Hz), 7.63 d (2H, 9-H, J = 7.2 Hz), 7.88 d (2H, 3′-H, J = 8.1 Hz), 7.93 d (2H, 3-H, J = 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.3 (C^7), 22.3 (C^{12}), 26.1 ($C^{6'}$), 73.0 (C^6), 128.9 (C^9), 129.1 (C^{10}), 129.7 ($C^{2'}$), 129.8 (C^2), 130.0 ($C^{3'}$), 130.3 (C^3), 131.8 (C^8), 135.6 ($C^{4'}$), 136.0 (C^4), 139.6 ($C^{1'}$), 140.4 (C^1), 145.0 (C^{11}), 196.7 ($C^{5'}$), 197.5 (C^5). Found: m/z 452.1102 $[M]^+$. $C_{25}H_{24}O_4S_2$. Calculated: M 452.1111.

1-[4-(4-Acetylphenoxy)phenyl]-2-methyl-2-(4-methylbenzenesulfonyl)propan-1-one (3b). Sodium *p*-toluenesulfinate, 1.2 g (6.7 mmol), was added in portions over a period of 1 h under stirring to a solution of 2.13 g (6.0 mmol) of compound **2b** in 15 mL of DMF, and the mixture was stirred for 3 h at room temperature. The mixture was poured into 100 mL of water and extracted with methylene chloride, the extract was dried over $CaCl_2$, the solvent was distilled off, and the residue was washed with hexane to obtain 2.4 g (73%) of **3b** as an oily crystalline material which was used without additional purification. mp 98–99°C [from petroleum ether (70–100°C)–EtOH, ~1:1]. IR spectrum (KBr), ν, cm^{-1}: 3067, 3001, 2980, 2926, 1695, 1660, 1587, 1497, 1302, 1265, 1234, 1170, 1151, 1128, 1180, 980, 959, 871, 862, 840, 819, 667, 586. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.68 s (6H, CH_3), 2.43 s (3H, CH_3), 2.59 s (3H, CH_3), 7.05 d (2H, 2′-H, J = 8.8 Hz), 7.08 d (2H, 2-H, J = 8.8 Hz), 7.30 d (2H, 10-H, J = 8.0 Hz), 7.63 d (2H, 9-H, J = 8.0 Hz), 7.98 d (2H, 3′-H, J = 8.8 Hz), 8.07 d (2H, 3-H, J = 8.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.5 (C^7), 22.5 (C^{12}), 26.3 ($C^{6'}$), 73.2 (C^6), 118.1 ($C^{2'}$), 118.6 (C^2), 129.2 (C^9), 130.0 ($C^{3'}$), 130.5 (C^{10}), 131.7 (C^3), 132.0 (C^8), 132.8 ($C^{4'}$), 132.9 (C^4), 141.1 (C^{11}), 159.2 ($C^{1'}$), 159.8 (C^1), 196.4 ($C^{5'}$), 196.9 (C^5). Found, %: C 69.30; H 5.52; S 7.23. $C_{25}H_{24}O_5S$. Calculated, %: C 68.78; H 5.54; S 7.35.

2,6-Bis[4-({4-[2-methyl-2-(4-methylbenzenesulfonyl)-1-oxopropyl]phenyl}sulfanyl)phenyl]-4-phenylpyrylium perchlorate (4a). Compound **3a**, 0.50 g (1.1 mmol), was dissolved in 0.70 mL of glacial acetic acid under stirring for 0.5 h at room temperature, 0.07 mL (0.073 g, 0.7 mmol) of benzaldehyde was added, and 0.18 mL of 70% $HClO_4$ was then added dropwise. The mixture was heated for 1 h at 60°C and kept for 60 h at room temperature. The mixture was then poured into 100 mL of diethyl ether under stirring, and a dark red oily material separated. The ether solution was separated by decanting, the oily residue was dissolved in methylene chloride, the solution was passed through a layer of silica gel (50–160 μm, h = 35 mm, d = 40 mm), and the sorbent was washed with methylene chloride until complete elution of a yellow fraction. The red substance that remained adsorbed on silica gel was eluted with acetonitrile. Removal of the solvent gave 0.16 g (27%) of a dark red crystalline substance which was purified by reprecipitation from methylene chloride with diethyl ether. IR spectrum (KBr), ν, cm^{-1}: 3061, 2924, 1674, 1622, 1587, 1491, 1460, 1300, 1290, 1248, 1150, 1126, 1080, 1010, 968, 833, 818, 768, 710, 623, 600. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 1.63 s (12H, CH_3), 2.45 s (6H, CH_3), 7.42 d (4H, 10-H, J = 8.2 Hz), 7.55 d (4H, 2-H, J = 8.4 Hz), 7.64 d (4H, 2′-H, J = 8.4 Hz), 7.68 d (4H, 9-H, J = 8.2 Hz), 7.73 t (2H, *m*-H, J = 7.5 Hz), 7.82 t (1H, *p*-H, J = 7.5 Hz), 7.94 d (4H, 3-H, J = 8.4 Hz), 8.25 d (2H, *o*-H, J = 7.5 Hz), 8.29 d (4H, 3′-H, J = 8.4 Hz), 8.60 s (2H, 6′-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.4 (C^7), 22.3 (C^{12}), 73.0 (C^6), 113.6 ($C^{6'}$), 125.6 ($C^{4'}$), 128.8–130.0 (C^2, $C^{2'}$, $C^{3'}$, C^9, C^{10}, C^o, C^m, C^p), 131.5 (C^4), 131.6 ($C^{1'}$), 132.1 (C^3), 135.9 (C^8), 137.3 (C^i), 145.2 (C^{11}), 146.9 (C^1), 164.5 ($C^{7'}$), 168.7 ($C^{5'}$), 197.9 (C^5). Found, %: C 64.32; H 4.5; Cl 3.14; S 11.20. $C_{57}H_{49}ClO_{11}S_4$. Calculated, %: C 63.76; H 4.60; Cl 3.30; S 11.95.

2,6-Bis(4-{4-[2-methyl-2-(4-methylbenzenesulfonyl)-1-oxopropyl]phenoxy}phenyl)-4-phenylpyrylium perchlorate (4b). Compound **3b**, 0.44 g

(1.0 mmol), was dissolved in 1.5 mL of glacial acetic acid under stirring for 0.5 h at room temperature, 0.06 mL (0.06 g, 0.6 mmol) of benzaldehyde was added, and 0.12 mL of 70% $HClO_4$ was then added dropwise. The mixture was heated for 3 h under reflux, cooled to room temperature, and poured into 100 mL of diethyl ether under stirring. A dark red oily material separated, the diethyl ether solution was separated by decanting, the oily residue was dissolved in methylene chloride, and the solution was passed through a layer of silica gel (50–160 μm, h = 35 mm, d = 30 mm). The sorbent was washed with methylene chloride until complete elution of a light yellow fraction, and the yellow material that remained adsorbed on silica gel was eluted with acetonitrile. Removal of the solvent left 0.18 g (35%) of a yellow crystalline substance which was purified by reprecipitation from methylene chloride with diethyl ether, mp 147–148°C. IR spectrum (KBr), ν, cm^{-1}: 3067, 2927, 1672, 1624, 1591, 1494, 1462, 1300, 1290, 1246, 1173, 1150, 1123, 1107, 1080, 968, 843, 770, 714, 673, 623, 590. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 1.65 s (12H, CH_3), 2.45 s (6H, CH_3), 7.24 d (4H, 2-H, J = 8.8 Hz), 7.35 d (4H, 2′-H, J = 8.8 Hz), 7.42 d (4H, 10-H, J = 8.2 Hz), 7.67 d (4H, 9-H, J = 8.2 Hz), 7.74 t (2H, m-H, J = 7.4 Hz), 7.82 t (1H, p-H, J = 7.4 Hz), 8.05 d (4H, 3-H, J = 8.8 Hz), 8.26 d (2H, o-H, J = 7.4 Hz), 8.43 d (4H, 3′-H, J = 8.8 Hz), 8.57 s (2H, 6′-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.6 (C^7), 22.7 (C^{12}), 73.3 (C^6), 113.4 ($C^{6'}$), 119.2 ($C^{2'}$), 119.6 (C^2), 123.3 ($C^{4'}$), 129.3 (C^p), 129.4 (C^9), 129.7 (C^m), 130.0 (C^o), 130.2 (C^3), 131.2 (C^{10}), 131.8 (C^8), 132.1 ($C^{3'}$), 134.9 (C^i), 145.3 (C^{11}), 157.8 ($C^{1'}$), 162.6 (C^1), 164.8 ($C^{7'}$), 169.0 ($C^{5'}$), 197.1 (C^5). Found, %: C 65.94; H 4.54; Cl 3.10; S 5.97. $C_{57}H_{49}ClO_{13}S_2$. Calculated, %: C 65.73; H 4.74; Cl 3.40; S 6.16.

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REFERENCES

1. Allonas, X., Lalevée, J., and Fouassier, J.-P., *J. Photopolym. Sci. Technol*., 2004, vol. 17, no. 1, p. 29.
2. Yagci, Y., Jockusch, S., and Turro, N.J., *Macromolecules*, 2010, vol. 43, p. 6245.
3. Allonas, X., Lalevée, J., Morlet-Savary, F., and Fouassier, J.P., *Polymer*, 2006, vol. 51, nos. 7–8, p. 497.
4. Loskutov, V.A. and Shelkovnikov, V.V., RU Patent no. 2330033, 2008; *Chem. Abstr*., 2008, vol. 149, no. 187332v.
5. El-Roz, M., Lalevée, J., Morlet-Savary, F., Allonas, X., and Fouassier, J.P., *J. Polym. Sci., Part A: Polym. Chem*. 2008, 46, 7369.
6. Dorofeenko, G.N., Sadekova, E.I., and Kuznetsov, E.V., *Preparativnaya khimiya pirilievykh solei* (Preparative Chemistry of Pyrylium Salts), Rostov-on-Don: Rostov. Univ., 1972, p. 35.
7. Norcini, G., Romagnano, S., Visconti, M., and Li Bassi, G., WO Patent Appl. no. 2005/14515; *Chem. Abstr*., 2005, vol. 142, no. 221238m.
8. Norcini, G., Romagnano, S., Visconti, M., and Li Bassi, G., WO Patent Appl. no. 2005/40083; *Chem. Abstr*., 2005, vol. 142, no. 430709e.
9. Eastwood, A., Parri, O.L., and Slaney, K., EP Patent Appl. no. 1388538, 2004.
10. Giaroni, P., Di Battista, P., and Li Bassi, G., US Patent no. 6162841, 2000.
11. Loskutov, V.A. and Shelkovnikov, V.V., *Russ. J. Org. Chem*., 2009, vol. 45, p. 158.
12. Anbazhagan, V., Kathiravan, A., Asha Jhonsi, M., and Renganathan, R., *Z. Phys. Chem*., 2007, vol. 221, p. 929.