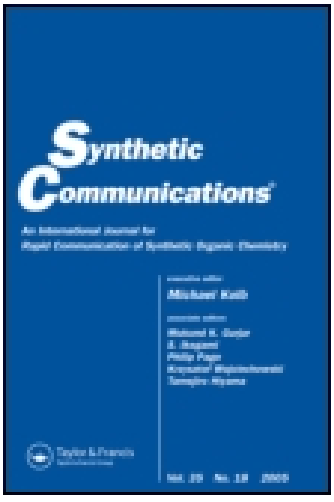

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Synthesis of Photochromic Monomers Derived from 1′-(2-Methacryloxyethyl)-3,3-Dimethyl-2-[2H]-Spirobenzopyran Indoline

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Abstract: The syntheses of five photochromic monomers derived from N- (2-methacryloxyethyl)-3′, 3′-dimethylspiro-[2H-1] benzopyrane-2, 2′-indoline are reported. The preparation of these compounds involves the heterogeneous reaction between the N-(hydroxyethyl)-2,3,3-trimethylindolenonium bromide and methacryloyl chloride in a polar solvent. The esterificated salt is easily purified by crystallization in chloroform-hexane. Further condensation with the proper 2-hydroxybenzaldehyde produces the photochromic monomer in high yield. This method can also be applied in the preparation of other spiropyrane derivatives.

Keywords: Photochromic monomers, spirobenzopyranes, photochromic polymers

INTRODUCTION

The preparation of functional optical materials based on compounds with photochromic properties has become one of the more promising topics in material sciences. These materials are used in the fabrication of several devices such as optical memories, switches, and holograms. These systems consist mainly of two components: the support media and the photoactive material.

The most-employed supporting materials for these devices are polymers. In some cases the polymers are doped with photochromic molecules.

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The process involves the dispersion of the photoactive molecule (i.e., spirobenzopyrane derivatives) in a polymer matrix as a solid solution. Unfortunately, after the dispersion takes place, the photochromic dye tends to agglomerate in J or H stacks, decreasing the photoactive capacity.[1]

In other cases, the photochromic molecule can be incorporated into a polymer chain through a covalent bond by a free radical copolymerization process, using photochromic monomers with a vinyl, acrylate, or methacrylate moieties.

There are several methods to incorporate the acryloyl moiety into spirobenzopyrane photochromic molecules. Those methods involves the substitution of the acryloyl fraction on the positions 4, 5, 7, or 8 of the benzopyrane ring[2–5] or in the 1′, 4′ or 5′ positions of the indoline ring (Fig. 1).[6–9] It is important that the substituted photoactive molecule preserves its photochromic properties. It is known that the substitution on the positions 4, 5, 7, or 8 decreases the reversibility and magnitude of the ring opening-closure process. This is because the resonance effect may be inhibited sterically in the open form (merocyanine).[10,11]

The reported synthetic process for the substitutions on the positions 4′, 5′ or 7′ uses phenylhydrazine derivatives as starting materials, by means of Fisher methodology,[12] which involves more than four steps, with the consequent purification of the reaction products on each step during the complete synthetic method.

Zaitseva[13] reported the preparation of N-(2-hydroxyethyl)-spirobenzopyrane indoline followed by esterification with methacryloyl chloride or methacrylic acid, according to Fig. 2. Unfortunately with this methodology low yields were obtained.[7]

In this paper, we report an alternative method for the synthesis of N-(2-hydroxyethyl)-spirobenzopyrane indoline derivatives that can be useful for the preparation of photochromic polymers.

EXPERIMENTAL

Materials

All organic materials and reagents were analytical grade and were used as purchased (Aldrich, Merck) unless otherwise noted. ^{1}H and ^{13}C NMR

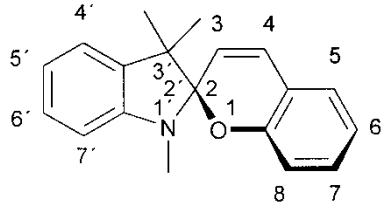

Figure 1. Spirobenzopyrane indoline photochromic molecule.

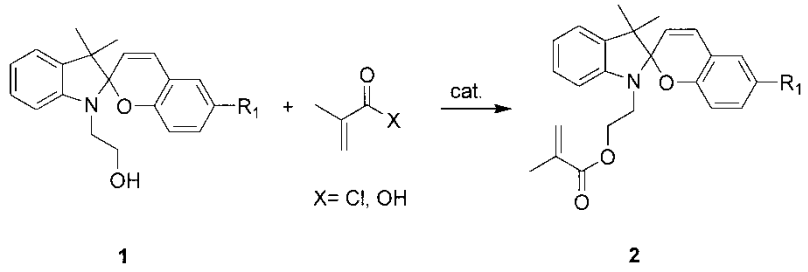

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Figure 2. Reported methodology for the preparation of the N-(2-methacryloxyethyl)-spirobenzopyrane indoline.

spectra were obtained using a 300 MHz Jeol-JNM-ECP300 spectrometer, using $CDCl_3$ as solvent and tetramethyl silane as standard, at room temperature. Routine infrared spectra were performed on a Magna Nicolet 550 Infrared Spectrometer. Elemental analyses were determined on a Perkin Elmer 2400 Series Analyzer and UV-Vis spectra on a HP 8452 spectrometer. The chromatograms were run on a G.C.-M.S. Hewlett packard HP-5971.

Synthesis of N-(2-hydroxyethyl)-2,3,3-trimethylindoleine Bromide (3)

A mixture of 5.59 mL (34.8 mmol) of 2,3,3-trimethylindoline, 2.47 mL (34.9 mmol) of 2-bromo ethanol and 4.36 mL of 2-butanone were placed in a Schlenk tube under inert atmosphere. The reaction mixture was evacuated and frozen in liquid nitrogen temperature. Then, after reaching the room temperature, the mixture was heated at 140°C for 10 h. The solid obtained was purified by soxhlet extraction with benzene for 24 h, and then dried for 48 h in vacuum. ^{1}H NMR (300 MHz, DMSO d6) δ: 7.81 (m, 2H), 7.73 (m, 2H), 4.71 (t, 2H, J = 8 Hz), 4.23 (t, 2H, J = 8 Hz), 2.21 (s, 3H), 1.7 (s, 6H). ^{13}C (50 MHz, DMSO d6) δ: 200.75, 144.4, 143.46, 132.5, 131.56, 126.07,117.8, 60.85, 57.41, 52.85, 24.69, 12.65. FT-IR (KBr) ν max 3200, 1100 cm^{-1}.

Synthesis of N-2-methacryloxy ethyl-2,3,3-trimethylindolenine Bromide (4)

In a 100 mL three-neck round-bottom flask equipped with magnetic stirring and condenser were placed 5.2 g (18.9 mmol) of N-(2-hydroxyethyl)-2,3,3-trimethylindoline bromide and 20 mL of dry acetone. Then, 1.8 mL (19.1 mmol) of methyl methacryloyl chloride were added, and the reaction mixture was kept at reflux for 24 h. Then, the acetone was distilled, and the solid obtained was dissolved in chloroform followed by precipitation in hexane.

The product was recovered after filtration yielding 88%, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.87 (m, 2H), 7.65 (m, 2H), 5.86 (s, 1H), 5.72 (s, 1H), 5.23 (t, 2H, J = 6 Hz), 4.86 (t, 2H, 6Hz), 3.12 (s, 3H), 1.82 (s, 3H), 1.80 (s, 3H). ^{13}C (50MHz, $CDCl_3$) δ: 197.91, 178.70, 141.60, 141.18, 130.11, 129.93, 129.55, 127.45, 123.16, 115.86, 58.60, 51.84, 42.25, 23.41, 18.28, 16.97. FT-IR (KBr Film) ν max 1719, 1160 cm^{-1}.

General Procedure for Preparation of Derivatives of N-(2-Methacryloxyethyl)-3′, 3′-dimethylspiro-[2H-1] Benzopyrane-2,2′-indoline 2 (a–e)

A mixture of 1.56 g (9.36 mmol) of 2-hydroxy-5-nitrobenzaldehyde, 3.14 g (9.36 mmol) of N-(2-methacryloxyethyl)-2,3,3-trimethylindolenine bromide, 2 mL (14.7 mmol) of triethylamine and 25 mL of distilled ethanol was placed in a three-neck round-bottom flask and heated under reflux for 12 h. Then, the reaction mixture was rotoevaporated and the residue redissolved in 50 mL of chloroform and extracted with 20 mL of aqueous solution of 10% sodium hydroxide. The precipitate was recovered and washed with cold ethanol and then recrystallized in ethanol.

Spectroscopic Properties of N-(2-Methacryloxyethyl)-3′,3′-dimethylspiro-[2H-1] Benzopyrane-2,2′-indoline 2a

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.09 (m, 2H), 7.07 (m, 2H), 7.01 (m, 2H), 6.83 (d, 1H, J = 12 Hz), 6.81 (m, 1H), 6.68 (d, 1H, J = 8 Hz), 6.09 (d, 1H, J = 1.5 Hz), 5.69 (d, 1H, J = 12 Hz), 5.56 (d, 1H, J = 1.5 Hz), 4.28 (t, 2H, J = 6.5 Hz), 3.53 (m, 2H), 1.93 (s, 3H), 1.309 (s, 3H), 1.15 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 167.40, 154.26, 147.36, 136.52, 129.97, 129.62, 126.94, 125.88, 121.91, 119.71, 118.38, 115.26, 106.65, 104.64, 63.27, 52.50, 42.72, 30.85, 20.41, 18.73. E.I.-M.S. D.I.P. m/z, (intensity, %) 159 (100), 375 (4). FT-IR (KBr Film) ν max 1718, 1160 cm^{-1}. Anal Calcd for $C_{24}H_{25}NO_3$: C, 76.8%; H, 6.7 %; N, 3.7% Found C, 75.85%; H, 7.01%; N, 3.40%.

Spectroscopic Properties of N-(2-Methacryloxyethyl)-3′,3′-dimethylspiro-[2H-1] Benzopyrane-6-methyl-2,2′-indoline 2b

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.25 (m, 2H), 7.05 (m, 2H), 7.95 (d, 1H, J = 7 Hz), 6.83 (d, 1H, J = 10.5 Hz), 6.75 (d, 1H, J = 7 Hz), 6.54 (d, 1H, J = 8 Hz), 6.09 (d, 1H, 1.5 Hz), 5.77 (d, 1H, 10.5 Hz), 5.48 (d, 1H, J = 1.5 Hz), 4.28 (t, 2H J = 6.5 Hz), 3.53 (m, 2H), 2.25 (s, 3H),

1.96 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 167.40, 152.11, 147.42, 136.59, 130.51, 129.68, 127.73, 127.33, 121.92, 119.38, 118.38, 115.07, 106.67, 104.71, 63.39, 52.51, 42.82, 26.30, 20.89, 20.53, 18.85. E.I.-M.S. D.I.P. m/z, (intensity, %) 159 (100), 389 (12), FT-IR (KBr Film) ν max 1718, 1160, 815, 743 cm^{-1}. Anal Calcd for $C_{25}H_{27}NO_3$: C, 77.1%; H, 7.0%; N, 3.6% Found C, 76.10%; H, 7.34%; N, 3.15%.

Spectroscopic Properties of N-(2-Methacryloxyethyl)-3′,3′-dimethylspiro-[2H-1] Benzopyrane-6-nitro-2,2′-indoline 2c

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.05 (m, 2H), 7.45 (m, 2H), 7.15 (d, 1H, J = 7 Hz), 6.92 (d, 1H, J = 12 Hz), 6.87 (d, 1H, J = 7 Hz), 6.79 (d, 1H, J = 8 Hz), 6.16 (1H, J = 1.5 Hz), 5.81 (d, 1H, 12 Hz), 5.51 (d, 1H, J = 1.5 Hz), 4.54 (t, 2H, J = 6.45 Hz), 3.53 (m, 2H), 1.96 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 167.3, 159.53, 146.81, 141.25, 136.22, 135.85, 128.47, 128.03, 126.13, 122.95, 121.98, 120.12, 118.61, 115.75, 106.96, 62.90, 53.10, 42.73, 26.18, 20.17, 18.70. E.I.-M.S D.I.P. m/z, (intensity, %) 159 (100), 420 (28). FT-IR (KBr Film) ν max 1718, 1518, 1163, 953, 746 cm^{-1}. Anal Calcd for $C_{24}H_{24}N_2O_5$: C, 68.6%; H 5.8%; N, 6.7%, Found C, 68.58%; H, 5.93%; N, 6.41%. M.P. 84°C

Spectroscopic Properties of N-(2-Methacryloxyethyl)-3′,3′-dimethylspiro-[2H-1] Benzopyrane-6-chloro-2,2′-indoline 2d

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45 (m, 2H), 7.35 (m, 2H), 7.05 (d, 1H, J = 7 Hz), 6.93 (d, 1H, J = 10.5 Hz), 6.85 (d, 1H, J = 7 Hz), 6.64 (d, 1H, J = 8 Hz), 6.09 (d, 1H, 1.5 Hz), 5.77 (d, 1H, 10.5 Hz), 5.48 (d, 1H, J = 1.5 Hz), 4.28 (t, 2H J = 6.5 Hz), 3.53 (m, 2H), 1.96 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 167.3, 152.76, 147.14, 136.27, 135.25, 131.47, 129.67, 128.68, 127.81, 122.95, 121.98, 120.12, 116.57, 106.71, 104.98, 89.75, 63.13, 52.66, 42.69, 26.19, 20.31, 18.69. E.I.-M.S. D.I.P. m/z, (intensity, %) 159 (100), 409 (14), 411 (4), FT-IR (KBr Film) ν max 1718, 1162, 965, 744 cm^{-1}. Anal Calcd for $C_{24}H_{24}ClNO_3$: C, 70.3%; H 5.9%; Cl, 8.6%; N, 3.4% Found C, 69.12%; H, 5.90%; N, 3.10%. M.P. 76°C

Spectroscopic Properties of N-(2-Methacryloxyethyl)-3′,3′-dimethylspiro-[2H-1] Benzopyrane-6-bromo-2,2′-indoline 2e

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41 (m, 2H), 7.35 (m, 2H), 7.05 (d, 1H, J = 7 Hz), 6.90 (d, 1H, J = 10.5 Hz), 6.65 (d, 1H, J = 7 Hz), 6.45 (d, 1H, J = 8 Hz), 6.09 (d, 1H, 1.5 Hz), 5.80 (d, 1H, 10.5 Hz), 5.48 (d, 1H,

J = 1.5 Hz), 4.32 (t, 2H J = 6.5 Hz), 3.53 (m, 2H), 1.96 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H). ^{13}C (50 MHz, $CDCl_3$) δ: 167.23, 157.33, 148.81, 141.25, 136.32, 132.55, 128.61, 127.83, 125.94, 121.92, 121.06, 120.48, 119.64, 117.07, 106.71, 63.05, 52.61, 42.61, 26.10, 20.19, 18.57. E.I.-M.S. D.I.P. m/z, (intensity, %) 159 (100), 453 (20), 445 (20). FT-IR (KBr Film) ν max 1718, 1163, 814, 744 cm^{-1}. Anal Calcd for $C_{24}H_{24}BrNO_3$: C, 63.4%; H 5.3%; Br, 17.6%; N, 3.1% Found C, 62.42%; H, 5.41%, Br, 17.90%; N, 2.96%. M.P. 83°C

RESULTS AND DISCUSSION

In our experimental work, we observed that substitution over the N atom in the indoline fraction resulted in monomers with better photochromic properties. These monomers are also named T monomers. Our synthetic approach is showed on Fig. 3. In this scheme, the synthesis begins with the alkylation of the 2,3,3-trimethylindolenine with a proper alpha-omega halohydroxyalkyl derivative, followed by the heterogeneous esterification with methacryloyl chloride.

We prepared the 2,3,3-trimethylindolenine according to the Nakazaki procedure[14] by reacting phenylhydrazine and 3-methyl-2-butanone in

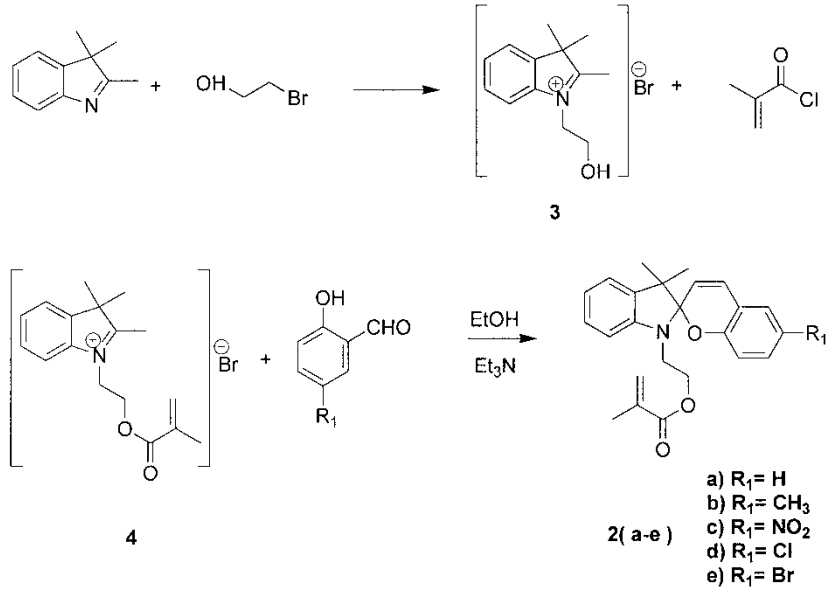

Figure 3. Preparation of the N-(2-methacryloxyethyl)-spirobenzopyrane indoline.

toluene as solvent, followed by cyclation with zinc chloride. Purification with liquid chromatography yielded 85% of 2,3,3-trimethylindolenine.

The alkylation reaction was carried out in a sealed Schlenk tube with 2-bromoethanol, and 2-butanone as solvent. The first attempts yielded only 25% of the alkylated product. This reaction was optimized by an experimental design using a 2^3 factorial strategy. It was found that the reaction of the 2,3,3-trimethylindolenine with 2-bromoethanol at 1:1 molar ratio in 8 M concentration in 2-butanone at 140°C for 10 h produce N-(2-hydroxyethyl)-2,3,3-trimehtylindolenine bromide in an almost quantitative yield (98%).

We obtained the N-(methacryloxyethyl)-2,3,3-trimethylindolenine bromide (4) by direct esterification of the bromide salt (3) with methacryloyl chloride in acetone using dimethyl amino pyridine as catalyst for 24 h at 60°C. The main feature of this reaction is its simplicity. The purification process can be performed by dissolving the solid residue of the reaction mixture in chloroform, where the starting materials (3) are not soluble, and further precipitation in hexane. The esterificated indolenine bromide salt was recovered in 88% yield. The NMR of the product in chloroform showed the characteristic singlet signals at 5.86 and 5.72 ppm for the vinyl protons of the methacryloxy moiety. Also a pair of triplets at 5.23 and 4.86 ppm confirms the ethyl substitution on the indolenine.

Preliminary work showed that the N-(methacryloxyethyl)-2,3,3-trimethylindolenine bromide can also be obtained from trans-esterification of the bromide salt (3) with methylmethacrylate in toluene using dibutyltin as catalyst.

The photochromic monomers were obtained by reaction of the N-(methacryloxyethyl)-2,3,3-trimethylindolenine bromide (4) with the proper substituted 2-hydroxy benzaldehyde and triethylamine in the molar ratio 1:1:3 respectively in ethanol. All molecules were obtained in good yields, purified by liquid chromatography and characterized by spectroscopic techniques. The yield obtained is shown on Table 1.

The NMR of the photochromic monomers showed for the N-(methacryloxyethyl) derivative, a triplet signal at 4.28 ppm for the methylene linked to

Table 1. Yields obtained for the photochromic monomers

Molecule	R	Yield (%)
2a	H	76
2b	CH3	80
2c	NO2	92
2d	Cl	86
2e	Br	90

the oxygen atom and a multiplet at 3.53 ppm for the diasterotopic methylene protons attached to the nitrogen in the indoline ring.

Due to the simplicity, good yields. and purity of the molecules obtained, we believe that this methodology can contribute in the development of the photoactive materials. Additionally, this methodology can be applicable to the preparation of the other spiroindoline photochromic molecules such as sipirooxazines.

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