Synthesis of Photochromic Monomers with Silyloxy Substituents

Bhaskar D. Hosangadi,* Sharmila K. Thakur

Department Of Chemistry, University Of Bombay, Vidyanagari, Santacruz (E), Bombay 400 098, India
Fax +91(22)6145772

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The preparation of photochromic spirobenzopyrans with silyloxy groups is described.

Photochromic systems can be incorporated in polymers via polymerizable organic functional groups and are of scientific and technological interest. Although a considerable amount of the work on photochromic spiropyrans and spirooxazines is reported, much of it is shrouded in the patent literature.

We have been interested in the synthesis of photochromic monomers with polymerizable silyloxy groups in spirobenzopyrans as these molecules are commercially important.[1] We have employed *O*-alkylation as a means of synthesizing silyloxy-substituted photochromic monomers. The recent report by Dürr and co-workers[2] prompted us to publish our own results. These workers have introduced a silyloxy side chain via *O*-linkage in a spirooxazine photochromic system using anhydrous K_2CO_3 and MeCN for *O*-alkylation.

We have exploited the versatility of the method of phase transfer catalysis (PTC) which enables the reaction to take place in a facile manner under mild conditions at room temperature. The PTC methodology was chosen mainly because of the acid labile nature[3] as well as thermochromic properties of spirobenzopyrans. The synthetic approach is discussed in the present paper.

Before introducing the silyloxy side chain the experimental conditions were standardized for *O*-alkylation/*O*-arylation of 1′,3′-dihydro-6-hydroxy-1′-3′-3′-trimethylspiro-[2*H*-1-benzopyran-2,2′-(1*H*)indole] (6-hydroxy BIPS, **3**). Benzyltriethylammonium chloride (TEBA) catalyzed two phase alkylation of phenols[4] is reported to give exclusively the *O*-alkylation product.

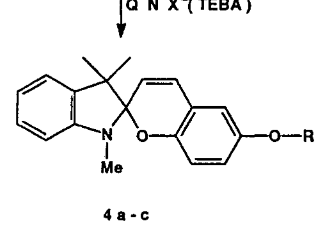
We carried out the *O*-alkylation of 6-hydroxy BIPS **3** in ethanol using TEBA and different alkyl or aryl halides (Scheme 1). In this way 6-methoxy BIPS **4a**, 6-benzyloxy BIPS **4b** and 6-(2-nitrophenyloxy) BIPS **4c** were prepared (Table). All these compounds were obtained as pale yellow coloured crystals except the nitro compound **4c** which had a more intense yellow colour. All of them show violet colour when adsorbed on silica gel and show a change of colour when their solutions in organic solvents are exposed to UV light. The latter observation is in agreement with typical examples of photochromically active indolinospirobenzopyrans.[5]

Since the colour changing properties on irradiation with UV light and parent BIPS skeleton are similar to classic examples of BIPS derivatives given in literature,[6] we believe that the photochromic reaction takes place similarly.

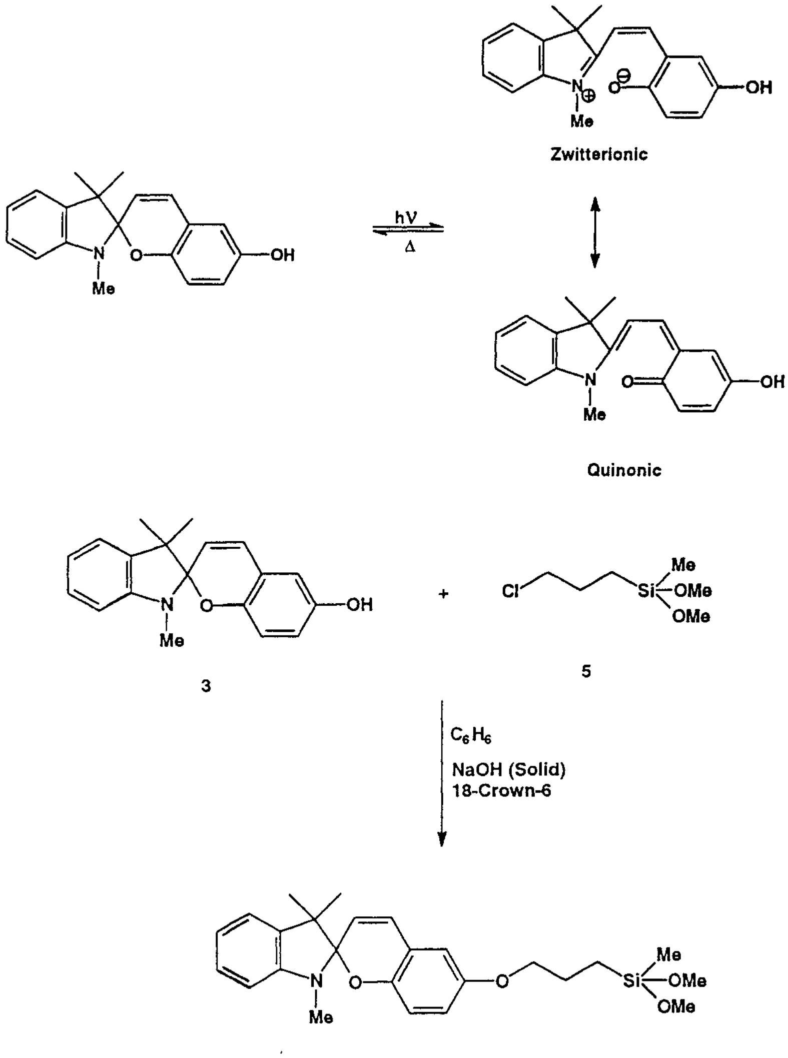
However, the *O*-alkylation procedure did not work for 6-hydroxy BIPS **3** when 3-chloropropyldimethoxymethylsilane **5** was used. There was a quantitative recovery of 6-hydroxy BIPS **3**. At the same time, the reaction mixture showed the absence of chlorosilane **5**. This may be attributed to the easily hydrolyzable nature of silyloxy compounds under basic conditions (Scheme 2).

Since crown ethers are known to effectively catalyze *O*-alkylation under two phase conditions, namely solid-liquid phase,[7] this mode was adopted successfully. Thus *O*-alkylation of **3** was carried out using **5** in the presence of solid NaOH and 18-crown-6. The reaction mixture showed a violet colouration on the TLC plate (silica gel). An oil was isolated using silica gel column chromatography and was confirmed to be 6-[3-dimethoxymethylsilylpropoxy] BIPS **6**, based on spectral data and gel permeation chromatography (GPC).

^{1}H NMR were obtained on FT Bruker (80 MHz) and Bruker AM 500 MHz, FT-NMR. IR spectra were measured using Shimadzu



Scheme 1



Scheme 2

Table. Compounds **4a–c** Prepared

Product[a]	R	X	Yield (%)	mp (°C)	IR (KBr) ν (cm^{-1})	UV (EtOH) λ_{max} (nm)	^{1}H NMR (CDCl$_3$/TMS) δ, J (Hz)
4a	Me	I	39	67[b]	1250, 970	320	1.2 (s, 3H, CH_3), 1.3 (s, 3H, CH_3), 2.7 (s, 3H, CH_3), 3.6 (s, 3H, OCH_3), 5.6 (d, 1 H_{arom}, J = 9.6), 6.3–7.6 (m, 8 H_{arom})
4b	$PhCH_2$	Cl	41	90	1250, 970	332	1.14 (s, 3H, CH_3), 1.3 (s, 3H, CH_3), 2.7 (s, 3H, NCH_3), 4.9 (s, 2H, OCH_2), 5.7 (d, 1 H_{arom}, J = 10.2), 6.4–7.4 (m, 13 H_{arom})
4c	2-$NO_2C_6H_4$	Cl	38	106–108	1520, 1250, 970	297	1.2 (s, 3H, CH_3), 1.3 (s, 3H, CH_3), 2.7 (s, 3H, NCH_3), 5.7 (d, 1 H_{arom}, J = 10.2), 6.4–7.4 (m, 12 H_{arom})

[a] Satisfactory microanalyses obtained: C, H, N ± 0.4%.
[b] Lit.[5] mp 68 °C.

FTIR-4200 and UV spectra on Shimadzu UV-160A. 2-Methylene-1,3,3-trimethylindoline (Fischer base **1**) and 2,5-dihydroxybenzaldehyde (**2**) are commercially available (Fluka). 3-Chloropropyldimethoxymethylsilane was a gift from industry. Petroleum ether used had bp 40–60 °C.

Melting points are uncorrected. GPC analysis was carried out on 6000 Å Waters instrument and using Ultrastyragel column (500, 100 Å) with THF as mobile phase.

6-Hydroxy BIPS **3** was prepared by the condensation of equimolar quantities of 2,5-dihydroxybenzaldehyde (**2**) and the Fischer base **1** in anhyd EtOH and crystallized from petroleum ether; mp 152–153 °C (Lit.[8] mp 152–153 °C).

***O*-Alkylation/*O*-Arylation of 6-Hydroxy BIPS 3; General Procedure:** 6-Hydroxy BIPS (**3**; 1.47 g, 5 mmol) was stirred in 50% aq NaOH for about 1 h. To this was added benzene (6 mL) followed by the corresponding alkyl halide (5 mmol) and benzyltriethylammonium chloride (TEBA) (0.1 equiv). The mixture was stirred at r.t. and the reaction was monitored by TLC (silica gel with 13% $CaSO_4$; eluent petroleum ether/EtOAc 99 : 1). After completion, the reaction mixture was worked up by dilution with H_2O (100 mL) and extraction with Et_2O (3×100 mL). The organic phases were combined, dried (Na_2SO_4) and concentrated. From the residual sticky mass, the product was isolated by silica gel column chromatography. Mixed solvent consisting petroleum ether with 2% EtOAc was used for elution. The compounds were further purified by crystallization from petroleum ether (Table).

1′,3′-Dihydro-6-[3-dimethoxymethylsilylpropyloxy]-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-(2*H*)indole] (6):
To a solution of 6-hydroxy BIPS (**3**; 1.47 g, 5 mmol) in benzene was added solid NaOH (0.2 g, 5 mmol) and the mixture was stirred at r.t. Then chlorosilane **5** (0.91 g, 5 mmol) was added followed by 18-crown-6 (about 20 mg). Stirring was continued and the reaction was monitored by TLC. After about 4 h of standing, the mixture was allowed to settle down. Then the organic layer was decanted and the residual oil was washed with benzene. The benzene extracts were combined and concentrated at r.t. under reduced pressure. The residual oil obtained after complete removal of benzene was passed over a silica gel column using petroleum ether containing 1% EtOAc for elution. Removal of solvent afforded **6** as an oil which showed violet colouration on silica gel; molecular weight: 450 (GPC, standard: soya oil).

^1H NMR ($CDCl_3$/TMS): $\delta = 0.7$ (m, 5 H, $SiCH_3$, $SiCH_2$), 1.2 (S, 3 H, CH_3), 1.3 (s, 3 H, CH_3), 1.8 (m, 2 H, CH_2), 2.8 (s, 3 H, NCH_3), 3.5 (s, 6 H, OCH_3), 3.9 (t, 2 H, $J = 12$ Hz, OCH_2), 5.8 (d, 1 H, $J = 10$ Hz, H-4), 6.4–7.3 (m, 8 H, 7 H_{arom}, H-3).

IR (Film): $\nu = 954$ (C_{spiro}—O), 1060–1120 (Si—O, Si—C), 1260 cm^{-1} (ArO—CH_2).

UV (EtOH): $\lambda_{max} = 333$ nm.

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