

BULLETIN

OF THE

KOREAN CHEMICAL SOCIETY

VOLUME 16, NUMBER 11
NOVEMBER 20, 1995

BKCS 16(11) 1007-1134
ISSN 0253-2964

Communications

An Effective Method for the Synthesis of New Photo- and Thermo-chromic Dyes, Unsymmetrical Bis-indolinospirobenzopyrans

Sam-Rok Keum*, Soon-Sung Lim, and Byung-Hun Min

Department of Chemistry,
College of Science and Technology,
Korea University, Jochiwon,
Choong-Nam 339-700, Korea

Received June 12, 1995

Thermo- and photochromic dyes,¹ indolinospirobenzopyrans (SPs) are of significant practical interest. Structurally, spiroopyran dyes consist of two pi systems linked by a tetrahedral spiro carbon. They form coloured merocyanine species on heating or irradiation with UV light, while the reverse process to the colorless form is induced by visible light, heat or can occur spontaneously.

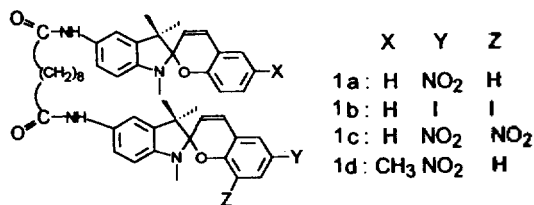


Spiropyran were found to be very useful for various practical applications,²⁻³ such as in recording, copying, and display materials. Since the stability of the spiropyran structure as well as the ultimate absorption associated with the merocyanine chromophore is strongly dependent on the substituents,⁴ it is of interest to investigate the influence of structural changes of the parent spiropyran. Structural modification of SPs has thus been an active area of research.

Spiropyran are also known⁵⁻⁶ for the formation of an aggregate (MC-MC) on UV irradiation in nonpolar solvents (cf. "quasicrystals" reported by Krongauz *et al.*⁶), including spiropyran-merocyanine (SP-MC) complexes. We have previously reported⁷ a synthetic work of the symmetric bis-indolinospirobenzopyrans (BSPs), in order to control the aggregate (MC-MC) growth.

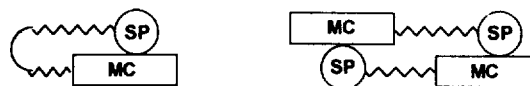
Continuing our studies of these thermo- and photochromic

bis-indolinospirobenzopyrans, in this paper we describe a synthetic work of unsymmetrical bis-indolinospirobenzopyran dyes (U-BSP, **1a-1d**), which have two different spiropyran units connected through a sebacamide linkage.



U-BSP

A major goal of this research was to demonstrate that these dyes are capable of intra- and intermolecular SP-MC aggregation in nonpolar solvents, as Krongauz⁶ suggested earlier. Non-activated spiropyran unit (SP^x; x=H or CH₃) is expected to stay as a closed SP-form and activated spiropyran unit (SP^y; y=NO₂ or I) as an opened MC-form on UV irradiation.

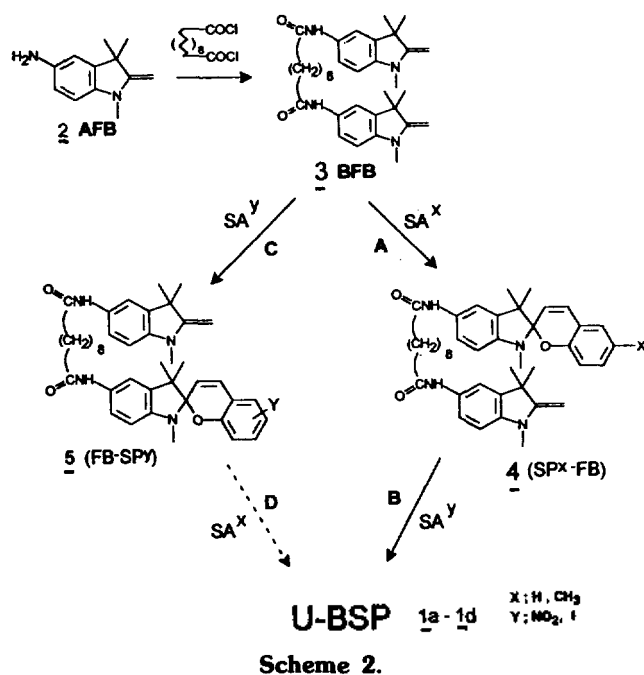
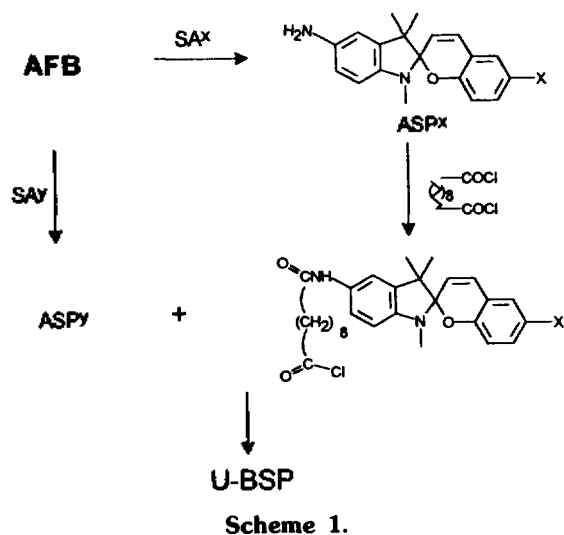


INTER & INTRAMOLECULAR PI STACKING

One might expect that diacid halides (sebacoyl chloride) would react with one mole of 5-amino-1,3,3-trimethylspiro(indolino-2,2'-benzopyran) derivatives (ASP) to form an indolinobenzospiroopyran monosebacamide, followed by a further consecutive reaction with the second 5-amino-ASP molecule to form an unsymmetrical bis-indolinospirobenzopyran sebacamide, as shown in Scheme 1.

As we have discussed in our previous paper,⁷ ASP requires a multistep synthesis from 5-amino Fischer base, **2c**. Several tedious steps for blocking of the amino group and deblocking were needed in the reaction with salicylaldehydes since **2c** has an extra nucleophilic center in the amino group, in addition to the methylene group of Fischer base.

We undertook a synthetic study making use of sebacoyl acid halides both as blocking group of the amino function



and as carbon chains to make the connection between two spiropyranyl groups, as shown in Scheme 2. From BFB, steps A & B was recommended, whereas steps C & D was not, with no clear reason. We have found a great deal of difficulties in separation of a precursor, (FB-SP^y) from the reaction mixture in step C, with no clear reason.

Commercially available Fluka grade Fischer base (FB, 1,3,3-trimethyl-2-methyleneindoline) was nitrated with H₂SO₄/HNO₃ to form 5-nitro Fischer base (NFB), which was then reduced with stannous chloride dihydrate and concentrated hydrochloric acid to form 5-amino Fischer base (AFB), 2, according to a previously described procedure.

The bis-Fischer base (BFB), [bis{5-(2-methylene-1,3,3-trimethylindoline)}- α,ω -sebacamide], 3, was obtained from the reaction of sebacoyl chloride with excess molar ratio of AFB, adapting Gales' method.⁸ A portion (10.6 mmol) of sebacoyl acid in 30 mL methylene chloride and triethylamine (20 mL)

Table 1. Characterization of the synthesized unsymmetrical BSPs (1a-1d) and their precursors (3-4)

Compound/	X	Y	Z	M.p. (°C)	Colour	Yield (%)	T/P ^a
3				143-145	White	91	
4a	H			151-155	camel	39	
4b	CH ₃			144-145	mauve	36	
1a	H	NO ₂	H	140-143	blue-green	71	T/P
1b	H	I	I	145-150	jade-green	64	T/P
1c	H	NO ₂	NO ₂	214-220	violet	61	T/P
1d	CH ₃	NO ₂	H	187-192	blue-gray	82	T/P

^aT and p denote thermo- and photochromic, respectively

was added dropwise to a solution of 2c (4 g, 21.1 mmol) in 50 mL methylene chloride, which was stirred for 3 h at room temperature. The white solid which was formed then recrystallized from methylene chloride/hexane to give product 3, in 91% yield, mp 143-145 °C.

A portion of BFB (1 g, 1.84 mmol) in 50 mL ethanol was then added to a stirred solution containing 2.27 mmol salicylaldehyde (SA) in 50 mL ethanol. The solution was stirred at 60 °C for 30 min. After the reaction finished, 50 mL of water was added to the solution, followed by basification with 0.5 g NaOH. The crude material was extracted with 50 mL of methylene chloride twice and the resultant solution was dried with anhydrous magnesium sulfate. Column chromatography has been used for separation of the mixture of BSP and precursor (SP^x-FB), 4, which were formed simultaneously, using silica gel (100-200 mesh) with CHCl₃/EtOAc (9:1) as an eluent. The key intermediate (SP^x-FB), 4a (X = H) & 4b (X = Me), in the unsymmetric bis-indolinospirobenzopyrans synthesis was obtained after column separation. The yields and mp's are in Table 1.

Unsymmetrical BSP's, 1a-1d were then obtained from the reaction of the key intermediate, 4, and correspondingly substituted salicylaldehydes. Thus A solution of 4 (0.07 mmol) in 5 mL ethanol was poured into a ethanolic solution (3 mL) of salicylaldehyde derivatives (0.07 mmol) slowly and stirred for 30 min. at 60 °C. After the reaction finished, 10 mL of water was added to the solution, followed by basification with 0.01 g of NaOH. The crude material was extracted with 10 mL of methylene chloride twice, after the resultant solution being dried with anhydrous magnesium sulfate. The crude material was recrystallized from methylene chloride/hexane. The yields and mp's of the synthesized unsymmetrical BSPs (1a-1d), including their precursors (3-4) are shown in Table 1.

The structures of the precursors, 3-4, and unsymmetrical BSPs, 1a-1d were identified by ¹H NMR. The N-Me and 2-methylene peaks of Fischer base units of the compounds, 3-4, are very characteristic and resonated at *ca.* 3.80 and 3.00 ppm, respectively. As SP units were formed from the reaction of FBs and SA derivatives, vinyl peaks (H-3') and N-Me peaks of SP units were newly appeared at *ca.* 5.56-5.85 ppm and 2.61-2.70 ppm, respectively. The N-Me and vinyl (H-3') protons of spiropyran of U-BSPs give 1:1 integrational ratios between α and ω rings in their ¹H NMR spectra, as given in Table 2.

Table 2. Characteristic ¹H NMR data of U-BSPs, 1a-1d and their precursors, 2, 3 & 4 in the region of 2.5-6.5 ppm (in CDCl₃)

Compound	methylene (=CH ₂)	N-Me (FB)	N-Me (SP) ^a		vinyl (H-3') ^a		ratio ^b
			α / ω	α / ω	α / ω	α / ω	
2 (AFB)	3.73	2.96					
3 (BFB)	3.80	2.99					
4a (SP ^β -FB)	3.83	3.01	2.69		5.65		
4b (SP ^{MC} -FB)	3.82	2.98	2.67		5.62		
1a			2.69	2.70	5.67	5.85	1:1
1b			2.63	2.69	5.66	5.71	1:1
1c			2.70	4.05 ^c	5.82	6.54 ^c	1:1
1d			2.61	2.64	5.56	5.76	1:1

^aThe α & ω denote the corresponding peak of α- & ω-ring of U-BSPs. ^bIntegration ratios of the corresponding peak of α- & ω-ring. ^cThe values are of the opened MC form of 1c.

Table 3. Electron-Spray (ES) mass spectral data^a of U-BSPs, 1a-1d

Compound	Mw	Molecular Ion	
		(m/z)	rel. int. (%)
1a	795.96	796.24	25
1b	1002.76	1003.40	43
1c	840.96	841.21	32
1d	809.96	810.10	12

^aES mass spectra was recorded on a VG Quattro mass spectrometer at Queen's University.

Electron Spray (ES) mass spectral data of the synthesized U-BSPs are summarized in Table 3. Unlikely to the symmetrical bis-spiropyran,⁷ relative intensities of U-BSPs were quiet low.

Investigations on the intra- and intermolecular SP-MC aggregation behaviors are currently underway.

Acknowledgment. This work was supported partly by research fund from the Korea Science and Engineering Foundation (941-0300-006-2) and partly from the Korean Ministry of Education of the Republic of Korea under the Basic Research Program (BSRI-94-3406).

References

- (a) Brown, G. H., editor, *Photochromism*, in *Techniques of Chemistry*, Wiley, New York, 1971; Vol. 3. (b) Durr, H.; Bouas-Laurent, H. editors in *Photochromism, Molecules and Systems*; Elsevier, 1992.
- (a) Levy, D.; Avnir, D. *J. Phys. Chem.* **1988**, *92*, 4734; (b) Tamaki, T.; Chimura, K. *J. Chem. Soc. Chem. Commun.* **1989**, 1477. (c) Durr, H. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 413. (d) Inouye, M.; Kim, K.; Kitao, T. *J. Am. Chem. Soc.* **1992**, *114*, 778. (e) Miyata, A.; Unuma, Y.; Higashigaki, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 993.
- Williams, D. J. in *Nonlinear Optical Properties of Organic and Polymeric Materials*; ACS Symposium Series, **1983**, *233*, pp. 135-151.

- (a) Keum, S. R.; Hur, M. S.; Kazmair, P. M.; Buncel, E. *Can. J. Chem.* **1991**, *69*, 1940. (b) Keum, S. R.; Lee, K. B.; Kazmair, P. M.; Buncel, E. *Magn. Res. Chem.* **1992**, *30*, 1128. (c) Keum, S. R.; Yun, J. H.; Lee, K. W. *Bull. Kor. Chem. Soc.* **1992**, *13*, 351. (d) Keum, S. R.; Lee, K. W. *Bull. Kor. Chem. Soc.* **1993**, *14*. (e) Keum, S. R.; Lee, K. B.; Kazmair, P. M.; Buncel, E. *Tet. Lett.* **1994**, *35*, 1015. (f) Keum, S. R.; Lee, M. J.; Yun I. K. *J. Sci. Tech.* **1995**, in press.
- (a) Wyn-Jones, E.; Gormally, J. in *Aggregation Processes in Solution*; editor Elsevier, 1983, Chapter 10-12. (b) Miyata, A.; Unuma, Y.; Higashigaki, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 993.
- Krongauz, V. A.; Shartsman, F. P. *J. Phys. Chem.* **1984**, *88*, 6448.
- (a) Keum, S. R.; Lee, J. H.; Seok, M. K.; Yoon, C. M. *Bull. Kor. Chem. Soc.* **1994**, *15*, 275. (b) Keum, S. R.; Lee, J. H.; Seok, M. K. *Dyes and Pigments*, **1994**, *25*, 21. (c) Keum, S. R.; Lim, S. S.; Min, B. H.; Kazmaier, P. M.; Buncel E. *Dyes and Pigments*, **1995**, in press.
- Gale, D. J.; Whilshire, J. F. *J. Soc. Dyers Colour.* **1974**, *90*, 97.

Selective Reduction of α,β-Unsaturated Aldehydes and Ketones to Allylic Alcohols with Diisobutylchloroalane

Jin Soon Cha*, Oh Oun Kwon, and Sang Yong Kwon

Department of Chemistry, Yeungnam University,
Kyongsan 712-749, Korea

Received July 21, 1995

Diisobutylaluminum hydride (DIBAL-H) and triisobutylaluminum (TIBAL) have secured their place as reducing agents in organic synthesis.^{1,2} As may be expected, aldehydes and ketones are easily reduced to the corresponding alcohols on treatment with either of the reducing agents.¹⁻³ Although the reaction of carbonyl compounds with the reagents affords the same reduction products, the modes of reduction are different. Thus, the reduction with DIBAL-H involves hydride shift from the aluminum⁴; the reduction with TIBAL involves hydride shift from the β-carbon atom and thus proves to be very similar to a Meerwein-Ponndorf-Verley reduction process.^{4,5} In general, TIBAL is a mild reducing agent, and hence most organic functional groups, except aldehydes and ketones, are compatible with the reagent^{1,2}; on the other hand, DIBAL-H is a strong one, and hence most organic functional groups are reactive with the reagent even at low temperature.³ These differences led us to extend the use of diisobutylchloroalane (DIBAL-Cl) as a reducing agent, up to now the systematic study on the reagent has been scarcely appeared.⁶ Based on these considerations, we have therefore undertaken an investigation of the reactivity of DIBAL-Cl towards general organic functionalities. In the course of this