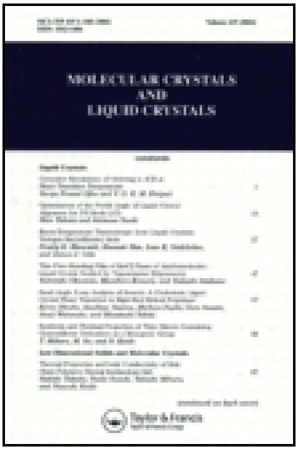

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Photochromic Spirotetrahydroazafluorenes: Part IV. First Trapping of Novel Type of cis-Fixed Photochromes Based on Pyridazinopyrrolo[1,2-b]isoquinoline

Saleh Abdel-Mgeed Ahmed [a]
[a] Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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Photochromic Spirotetrahydroazafluorenes: Part IV. First Trapping of Novel Type of *cis*-Fixed Photochromes Based on Pyridazinopyrrolo[1,2-b]isoquinoline

Saleh Abdel-Mgeed Ahmed
Chemistry Department, Faculty of Science, Assiut University,
Assiut, Egypt

Seven novel 2′,3′-diacetyl spirotertrahydroindolizines (THIs) ***3a–g*** *were synthesized in low yield via the nucleophilic addition of the substituted isoquinoline derivatives* ***2a–g*** *to diacetyl spirocyclopropene* ***1*** *in dry ether at −20°C under nitrogen atmosphere for 3 h, which undergo ring opening the corresponding betaines* ***3‴a–g*** *through betaine* ***3′a–g*** *and* ***3″a–g*** *as intermediates after irradiation with UV-light. The serious decomposition of these products during purification process was moderately prevented by using flash chromatography after many trials.* In situ *hydrazinolysis of THIs* ***3a–g*** *with hydrazine in ethanol at −40°C afforded a novel type of* cis-*fixed pyridazinopyrrolo[1,2-b]isoquinolines* ***4a–g*** *in moderate yield.*

Keywords: *cis*-fixed photochromes; flash photolysis; photochromism; spirotetrahydroazafluorenes

INTRODUCTION

Photochromic dihydroindolizines (DHIs) and tetrahydroindolizines (THI), which discovered and developed by ***Dürr*** in 1979 [1–3], they became a very interesting class of photochromic molecules and have been extensively studied and received particular attention owing to their remarkable photofatigue-resistance and wide broad photochromic properties [4–10].

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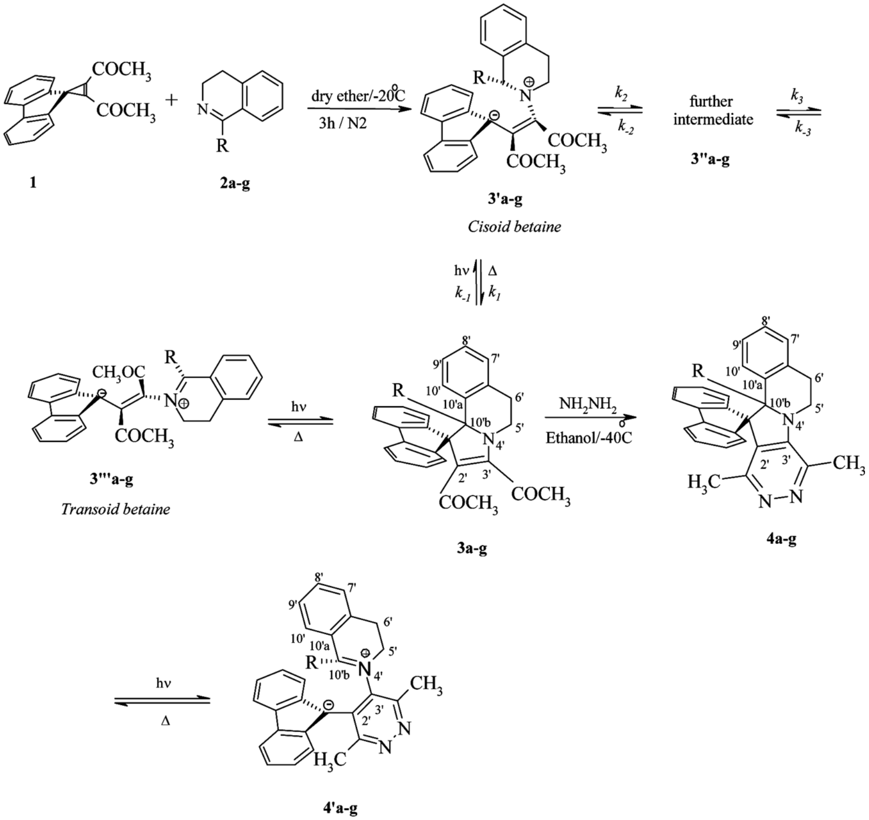
Address correspondence to Saleh Abdel-Mgeed Ahmed, Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt. E-mail: saleh_63@hotmail.com

In continuation of our pervious work dealing with the synthesis and photochromic properties of dihydroindolizines (DHIs) and tetrahydroindloizines THIs [4,10–13], this manuscript will describe: (1) different attempts for the trapping of diacetylspirodihydroindolizines **3**, (2) their conversion into a novel type of *cis*-fixed pyridazinopyrrolo [1,2-b]isoquinolines **4**, and (3) photochromic behavior of the colored betaines.

RESULT AND DISCUSSIONS

When diacetylspirocyclopropene **1** [14] was allowed to react with *p*-substituted 1-phenyl-3,4-dihydroisoquinolines **2a–g** which, were prepared by modification of the Bischler-Napieraski reaction [15] in dry ether solution at room temperature for 24 h, the desired products



SCHEME 1

were not isolated and a black decomposed product was detected. The photochromic THIs **3a–g** were successfully isolated when the reaction temperature was cooled down to -20°C and the reaction time decreased to only three hours (TLC Controlled). A serious decomposition of these products was observed during the purification process by SiO_2 column chromatography. A very poor yield (8–22%) of diacetyl THIs **3a–g** was obtained when the flash chromatography was applied for purification of these products (Scheme 1).

Due to the low yield of photochromic THIs **3a–g**, we decided to synthesize the new photochromic spirotetrahydroazafluorenes **4a–g** via treatment of the *in situ* prepared THIs **3a–g** with hydrazine hydrate in ethanol under cold condition (-40°C) for 20 h. The pure products were obtained after twice column chromatography using CH_2Cl_2 as eluent in 27–46% yield based on the starting diacetylspirocyclopropene **1**. The chemical structures of the new pyridazinopyrrolo [1,2-b]pyradazines **4a–g** were clearly assigned by both analytical and spectroscopic tools. The pyradazine ring only slightly modifies the NMR spectra of its precursor **3a–g** show the acetyl signals at $\delta = 1.08$ and 2.69 ppm, whereas in **4** these signals occur at $\delta = 1.42$ and 2.83 ppm. Both prodcuts **3a–g** and **4a–g** are formed regioselectivity [1]. Details will be published elsewhere.

Photophysical Properties

The UV-spectra of the pale yellow THI **3a–g** show a maximum between 363 and 401 nm, whereas the structurally related THF **4a–g** show a hypsochromic shift up to 62 nm (Table 1). As established previously, these absorption bands can be assigned to the locally excited $\pi-\pi^*$-transition (LE) located in the butadienyl-vinyl-amine

TABLE 1 Yield [%] and m.p [°C] of the New THIs **3a–g** and Pyridazinopyrrolo[1,2-b]isoquinolines **4a–g**

		3		**4**	
Compound	R^1	Yield [%]	m.p [°C]	Yield [%]	m.p [°C]
a	phenyl	18	189	46	232
b	p-CH_3-phenyl	22	146	32	215
c	p-OCH_3-phenyl	13	132	40	207
d	p-Cl-phenyl	10	166	36	241
e	p-Br-phenyl	13	172	34	243
f	p-I-phenyl	15	174	42	246
g	p-NO_2-phenyl	8	202	27	276

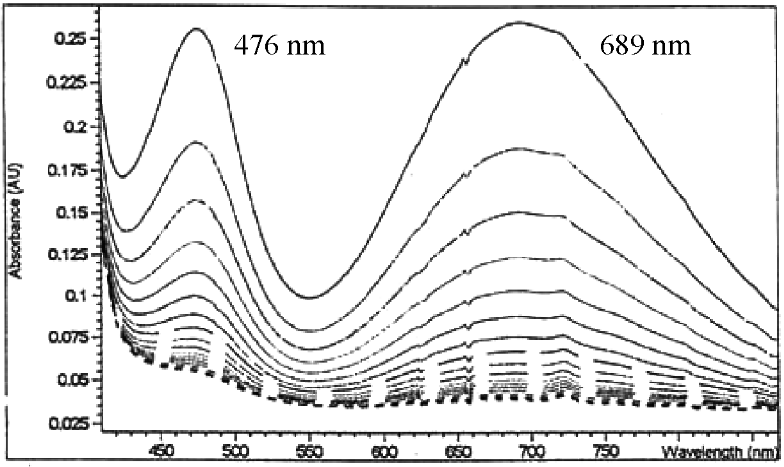


FIGURE 1 Kinetic UV-Vis spectrum of the thermal fading of betaine forms of THI **3f** (cycle time = 2 s, run time = 40 s) in CH_2Cl_2 ($c = 1 \times 10^{-4}$ mol l^{-1}) at 296 K.

chromophore [1,18–20] of the THIs system. Irradiation of THI **3a–g** with polychromatic light in dichloromethane solution ($c = 1 \times 10^{-4}$ M/l), afforded the colored betaines **3‴a–g** through the intermediate **3′a–g** and **3″a–g** with absorption maximum ranged between 462, 477 and 680, 700 nm depending on the substituents in the 10′ b-phenyl ring of the THI skeleton (Figs. 1, 2). The betaine forms of THIs **3a–g** loss their photochromic properties under continuous irradiation for several cycles and drastic decomposition of both THI **3a–g** and their corresponding betaines was recorded through their absorption spectra.

Due to the chemical unstability of these THIs and their corresponding betaines, the low yield formation and hard purification of these kind of photochromic materials can be proofed. The pyridazino-pyrrolo[1,2-b]pyradazines **4a–g** showed no visible change of color on irradiation of **4a–g** in solution neither at room temperature nor at 183 K (dry ice/methanol). Only in a glass matrix at 77 K on irradiation of **4a–g**, the color of **4′a–g** persisting some seconds up to a few minutes was observed.

In conclusion, novel type of photochromic THIs **3a–g** and THF **4a–g** was successfully prepared after many trails by changing the reaction condition. UV/VIS and millisecond flash photolysis were used for determination of both absorption maxima and half-lives of the

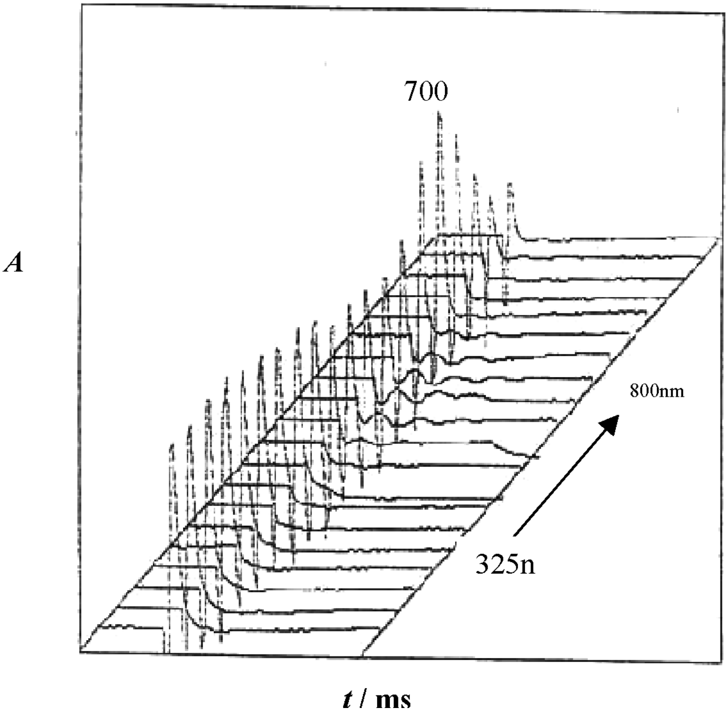


FIGURE 2 Millisecond flash photolysis spectrum of the betaine form of THI **3g** for determination of the absorption maxium of the betaine form at different wavelengths (325–800 nm every 25 nm) in CH_2Cl_2 at 296 K.

corresponding colored betaines. The new system is an interesting candidate for pattern recognition system and it will find its application.

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