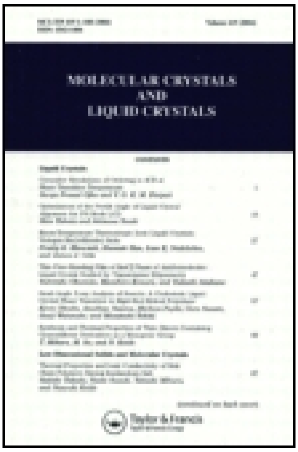

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COMPARATIVE STUDY OF CHROMENES CONTAINING DIFFERENT SPIRO-CARBOCYCLIC MOIETIES

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Abstract: Photochromic chromenes containing different spiro-carbocyclic moieties have been synthesized. A new pathway was developped to synthesize the required α,β-ethylenic aldehydes precursors. On the other hand, two complementary procedures of "chromenisation" were successfully used. A study of the photochromic behavior allowed us to evaluate the influence of structural modifications: strong parameters variations were actually observed.

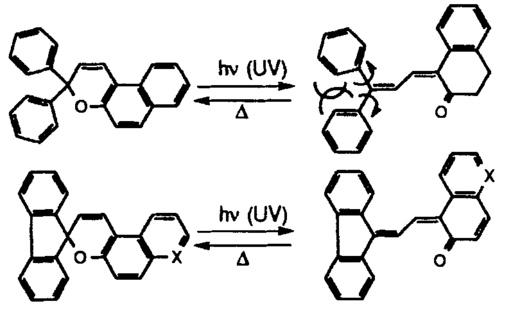
INTRODUCTION

Recently, we synthesized spiro[benzopyran-fluorenes] (**2**,**3**) and studied their photochromic behavior.[1] Compared to 2,2-diphenyl-2H-benzopyran series, the forced planarity of the phenyl groups in the fluorene moiety leads to photochromic characteristics changes. For instance, the extended Π system delocalization induces a bathochromic shift (25 nm in toluene) of the electronic absorption (λ_{max}) of the colored form (OF).

1

2: X = CH

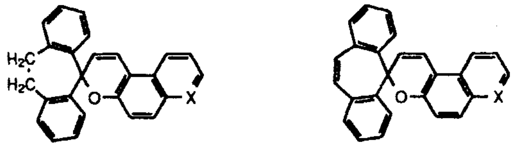
3: X = N



Colorless closed-forms (CF) Colored open-forms (OF)

Scheme 1

In the present work, we decided to study extensively the influence of the length and nature of the linkage between phenyl groups on photochromic parameters. Thus we extended our investigations to spiro[benzopyran-dihydrodibenzocycloheptene](**4**,**5**) and spiro[benzopyran-dibenzocycloheptene](**6**,**7**). Two benzopyran moieties were used : the 2H-naphtho[2,1-b]pyrane as reference and the 8H-pyrano [3,2-f]quinoline able to induce a weak bathochromic shift of the λ_{max} [2] and an increase of the fatigue resistance.[3]



4: X = CH
5: X = N

6: X = CH
7: X = N

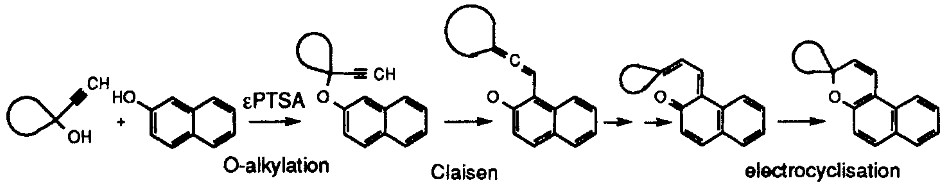
Scheme 2

SYNTHESIS

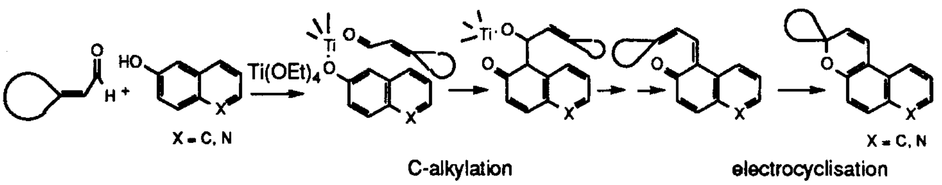
The synthesis of compounds **1** and **2** proceeds through the alkylation of a naphthol followed by a cyclisation reaction. Two complementary procedures, applied previously to the synthesis of 2,2-diarylbenzopyran and spiro[benzopyran-fluorenes] [3], were successfully used.

The first procedure requires intervention of an appropriate propargylic alcohol and 2-naphthol. The mechanism is based on pseudo-Claisen rearrangement of aryl propargylic ethers issued from naphthol "O-alkylation" under acidic catalysis (paratoluene sulfonic acid or others [4]).

The second procedure is useful in many cases and especially when the first method fails (for instance with nitrogenated heterocyclic naphthol) but also when propargylic alcohol is not easily obtained. This method is based on a "C-alkylation" reaction (the naphthol titanate reacting with α,β-ethylenic aldehyde).

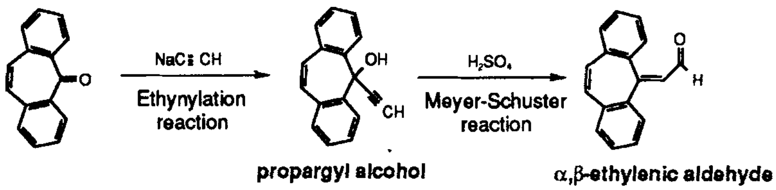


Scheme3: First method



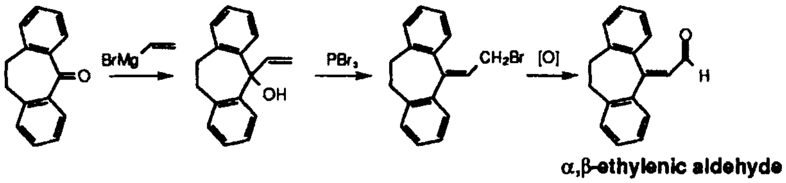
Scheme3: Second method

Convenient precursors (propargylic alcohol or α,β-ethylenic aldehyde) were easily obtained in the case of the dihydrodibenzocycloheptene series. Propargylic alcohol is obtained by nucleophilic addition of sodium acetylure on 5-suberenone.[5] This precursor gives rise to the α,β-ethylenic aldehyde by Meyer-Schuster rearrangement (1,3-migration) [6] under acidic catalysis (H_2SO_4).



Scheme 4

Unfortunatly this classic procedure could not be applied to the 5-suberone. Indeed, in this case the propargylic alcohol is totally consummed to give an identified biproduct. A new pathway has been developped to obtain aldehyde from ketone.[7] Thus, the allylic alcohol issued from the addition of vinyl magnesium bromide on ketone, leads to the wished compound through halogenation and then oxydation.



Scheme 5

PHOTOCHROMIC BEHAVIOR

A toluenic solution of the photochromic compound is irradiated by U.V. light untill the photochemical and thermal equilibrium state is reached. Spectroscopic analysis at the λ_{max} of the colored form (on a specifically equipped U.V. spectrometer [8]) gives the absorbance under steady state conditions (A_{eq}). A_{eq} value depends on several parameters ($\Phi_{col.}$, ε_{OF}, operative conditions, light power fluctuation, ...), but thermal fading rate is the main factor. In fact, our systems involving a slow kinetic, the curve giving the variation of absorbance in terms of time, exhibits a high slope part followed, not by a plateau as expected for the steady state, but by a low slope moiety. In first approximation we point out as A_{eq}, the absorbance measured when the slope of the curve becomes less than 0.02. On the other hand, when irradiation is stopped, the decrease of absorbance allows to measure the thermal fading rate (k_Δ).

RESULTS AND DISCUSSION

Table 1

Compounds	λ_{max} (nm)	A_{eq}	k_1 (s^{-1})	$k_2 . 10^4$ (s^{-1})
Reference				
1	432	0.11	0.10	3
2	457	0.23	0.10	3
3	465	0.09	0.11	3
4	425	>5 0.17[a]	/	0.9
5	431	>5 0.14[a]	/	1
6	430	>5 0.16[a]	/	3
7	440	>5 0.12[a]	/	4

Experimental conditions: $C = 5.10^{-4}$ mol.l^{-1} (toluene), T = 25°C, light power = 115 W.m^{-2}
a) $C = 10^{-5}$ mol.l^{-1}.

Influence on λ_{max}

In contrast to the fluorene series, dihydrodibenzocycloheptene (**4**,**5**) and dibenzocycloheptene (**6**,**7**) moieties do not induce a bathochromic shift of the λ_{max}. Whatever the nature of the junction (dimethylenic or ethylenic) between the phenyl groups, it seems that the Π system is not extended enough, certainly due to a non-planarity of this part of the molecule.

On the other hand, 8H-pyrano[3,2-f]quinoline moiety induces in any case a weak bathochromic shift (6-10 nm).

Influence on thermal fading rates

In the spiro-fluorene series (**2**,**3**) as in the 2,2-diphenyl one (**1**), a biexponential kinetic is observed. The fast kinetic (k_1) and the slow kinetic (k_2) are quasi the same in both series and could be attributed to two different isomers of the colored form.

In the case of dihydrodibenzocycloheptene (**4**,**5**) and dibenzocycloheptene (**6**,**7**) series, kinetics become monoexponential and fading rates are significantly slowed. It seems that, in these cases, only the most stable stereoisomer is involved. But, at this state of the work, we cannot identify really this one.

Influence on absorbance at apparent photostationnary state

High values of A_{eq} are obtained for compounds **4-7**. In these cases, the lack of a fast fading kinetic allows to accumulate open form during irradiation and consequently absorbance increases.

CONCLUSION

The main synthetic difficulty resided in preparation of precursors. Thus, suitable propargyl alcohols and α,β-ethylenic aldehyde have been synthesized using known methods and developping new pathway. In a next step, two complementary procedures were successfully used to synthesize desired spiro-carbocyclic-chromenes.

Photochromic behavior has been studied under continuous irradiation. It appears that the length of the linkage between phenyl groups has a strong influence on photochromic parameters, in contrast to the nature of the linkage (conjugated or not conjugated).

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