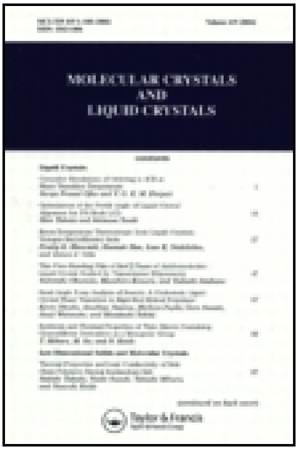

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Spectrokinetic Studies of a New Family of Dimethyl [2H]-Chromenes: Dimethyl 6-Aryl-2,2Dimethyl-[2H]-Chromene-7,8-Dicarboxylates

Alain Maggiani [a] , Arlette Tubul [a] , Pierre Brun [a] & André Samat [a]

[a] Faculté des Sciences de Luminy, GCOPL, ESA 6114, Université de la Méditerranée, 163 Avenue de Luminy, case 901, F-13288, Marseille, Cedex, 9, France

Version of record first published: 24 Sep 2006

To cite this article: Alain Maggiani, Arlette Tubul, Pierre Brun & André Samat (2000): Synthesis and Spectrokinetic Studies of a New Family of Dimethyl [2H]-Chromenes: Dimethyl 6-Aryl-2,2Dimethyl-[2H]-Chromene-7,8-Dicarboxylates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 344:1, 259-263

To link to this article: http://dx.doi.org/10.1080/10587250008023846

Mol. Cryst. Liq. Cryst., 2000, Vol. 344, pp. 259-263
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Synthesis and Spectrokinetic Studies of a New Family of Dimethyl [2*H*]-Chromenes: Dimethyl 6-Aryl-2,2Dimethyl-[2*H*]-Chromene-7,8-Dicarboxylates

ALAIN MAGGIANI, ARLETTE TUBUL, PIERRE BRUN and ANDRÉ SAMAT

Faculté des Sciences de Luminy, GCOPL, ESA 6114, Université de la Méditerranée, 163 Avenue de Luminy, case 901, F-13288, Marseille cedex 9, France

The synthesis of a series of dimethyl 6-aryl-2,2-dimethyl-[2*H*]-chromene-7,8-dicarboxylates is described. The photochromic properties of this new family of dimethyl-[2*H*]-chromenes have been studied in solution, under continuous irradiation. The presence of the methoxycarbonyl groups was shown to stabilise the coloured forms. The fading rates are generally low in comparison with the standard "naked" chromenes in the same experimental conditions. This stabilisation depends on the solvent used. We could observe the presence of one permanent opened form. Moreover, it seems that the synthesised molecules have a strong resistance toward photodegradation.

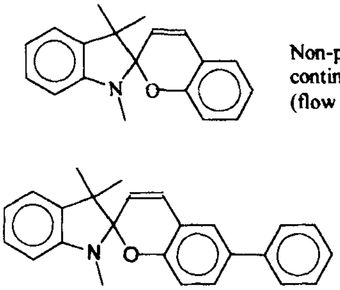
Keywords: propargylic ether; dimethyl 6-aryl-2; 2-dimethyl-[2*H*]-chromene-7; 8-dicarboxylates; photochromic compounds

INTRODUCTION :

Organic photochromic compounds have been extensively studied these last twenty years because of their potential applications for industrial purposes. [1-4]

Many works have been devoted to the influence of different substituents in order to establish structure-reactivity relationships [5,6] in the [2*H*]-chromene series, this class of compounds being used in lenses industry.[7] However the synthesis and the photochromic behaviour of phenyl substituted chromenes were not reported.

In a preliminary work on a another family of photochromic substrates, we have shown that the introduction of a phenyl group in a non-photochromic spiropyrane structure could allow the observation of the photochromic phenomenon (Scheme 1).[8] We present here our preliminary results with chromene derivatives.



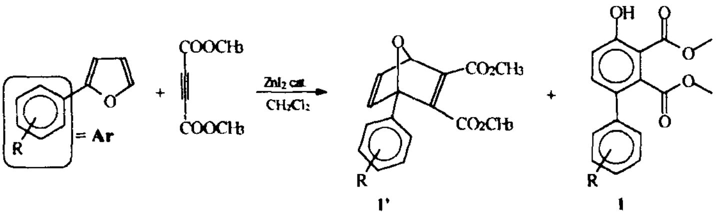
Non-photochromic compound in toluene under continuous irradiation with a Xenon lamp (flow of 200 W/m^2)

Photochromic in the same conditions
Open form, λ_{max} = 560 nm

SCHEME 1 : Comparison between "naked" and phenyl-spiropyrane

SYNTHESIS OF THE [2*H*]-CHROMENE DERIVATIVES :

The phenolic derivatives were synthesised by a Diels-Alder reaction between dimethyl acetylen dicarboxylates and the corresponding arylfurans (scheme 2).[9]

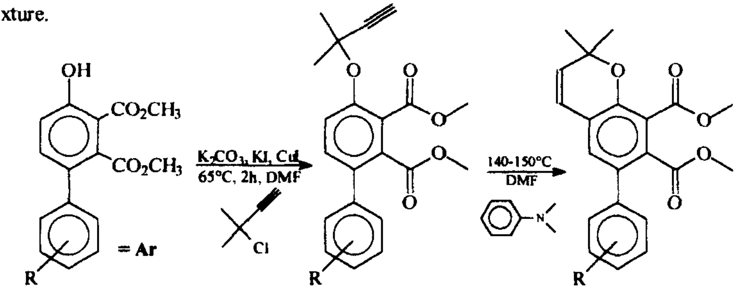


SCHEME 2 : Synthesis of the phenolic derivatives

The oxabicyclic derivatives are easily opened by using H_2SO_4 or HCl in ethyl ether or by using specific Lewis acid such as $ZnBr_2$ in methylene chloride.[10]

The chromenes were synthesised in two steps using the procedure described by BELL and MAN [11] (Scheme 3 and Table 1) :

- formation of the propargylic ether
- thermal cyclization of the propargylic ether in a DMF-dimethylaniline mixture.



1 2 3

SCHEME 3 : Synthesis of the dimethyl 6-aryl-2,2-dimethyl-[2*H*]-chromene-7,8-dicarboxylates

RESULTS AND DISCUSSION :

Ar	Yields (%)		Ar	Yields (%)	
	2	**3**		**2**	**3**
C_6H_5	31	49	4-PhO C_6H_4	86	51
α-Naphtyl	91	59	4-MeO C_6H_4	58	50
2-Ph C_6H_4	53	61	4-Br C_6H_4	88	47
4-Ph C_6H_4	38	70	4-MeCO C_6H_4	82	35
2-PhO C_6H_4	73	63			

As can be seen from Table 1 the yields in propargylic ethers are modest to good.

The spectrokinetic studies were realised using a Beckman Spectrophotometer modified as previously described.[12] A 5.10^{-4} M solution of the photochromic compound is irradiated under U.V. (Xenon lamp) at 23°C using a flux of 400 W/m^2, during about 1.5 hour. The irradiation is then stopped and the thermal bleaching is monitored by observation of the decrease of the absorbance of the opened forms. Our results are reported in Table 2 in which λ_{max} (nm) is the absorption of the coloured form in the visible range, k_Δ (s^{-1}) is the fading rate constant and A_{eq} the absorption measured at the λ_{max}, at the end of the irradiation period.

TABLE 2 : Photochromic properties of the synthesised dimethyl-{2*H*}-chromenes

	Acetonitrile			**Toluene**		
Ar	λ_{max}(2) (nm)	k_Δ (s^{-1})	A_{eq}	λ_{max}(2) (nm)	k_Δ (s^{-1})	A_{eq}
C_6H_5	411	5.10^{-4} 2.10^{-4}	0.11	420	8.10^{-4} 10^{-4}	0.09
α-Naphtyl	405	4.10^{-4} 3.10^{-4}	0.05	418	3.10^{-4} 10^{-4}	0.16
4-Ph C_6H_4	406	4.10^{-4} 2.10^{-4}	0.09	416	3.10^{-4} 2.10^{-4}	0.2
4-Br C_6H_4	455	2.10^{-4}	0.03	432	5.10^{-4} 2.10^{-4}	0.03
4-CH_3O C_6H_4	409	0	0.11	420	4.10^{-4} 10^{-3} 4.10^{-4}	0.17
4-CH_3CO C_6H_4	437 562	9.10^{-4} 10^{-4}	0.08	437	2.10^{-4}	0.04

In the two solvents used, the highest value for the λ_{max} of the opened form are obtained when an electron-withdrawing group is located in the 4- position of the biphenyl framework. In this case, it must be also noted that, in acetonitrile two absorption bands are observed.

The presence of the methyl carboxylate groups was shown to stabilise the opened forms. This stabilisation depends on the solvent and in one case, with an electron-donating group (Ar=$CH_3OC_6H_4$ in CH_3CN) we observed the formation of stable opened forms. Using a mercury lamp, we have also shown that this family of [2*H*]-chromenes presents a strong resistance to photodegradation.

CONCLUSION :

The synthesis of a new family of photochromic [2*H*]-chromenes, substituted by aromatic groups, is described. Moderate to good yields are obtained depending on the nature of the substituents located on the biphenyl framework.

The spectrokinetic studies of these compounds show that their bleaching kinetic constants are slower than the ones of the unsubstituted corresponding [2*H*]-chromenes. This effect can be related with the stabilising effect introduced by the presence of the two carbomethoxy groups. Such an effect is reinforced by the presence of an electron-donating group and by solvation effects and can be strong enough to lead to the formation of stable opened forms.

Furthermore, that new family of [2*H*]-chromenes seems to present a much more better resistance to photodegradation, compared to the parent molecules, when irradiated by a mercury lamp.

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