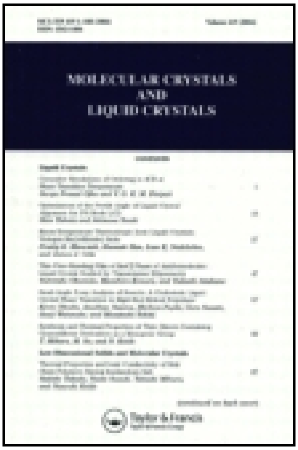

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New Photochromic 2,2-Diphenyl-[2H]-Chromenes Annellated With Nitrogenated Sex-Membered Ring

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NEW PHOTOCHROMIC 2,2-DIPHENYL-[2H]-CHROMENES ANNELLATED WITH NITROGENATED SIX-MEMBERED RING.

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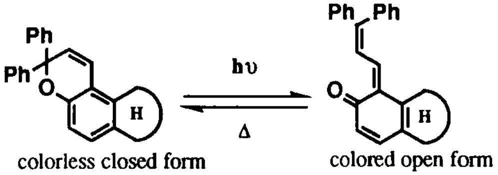
Abstract: New photochromic 2,2-diphenyl-[2H]-chromenes **1-6** annellated with nitrogenated six-membered ring have been synthetized by optimized reaction of suitable metal phenolates and β-phenyl cinnamaldehyde. All compounds exhibit photochromic behavior at room temperature. Chemical yields and photochromic characteristics depend significantly on the relative position of annellation on the chromenic moiety.

BACKGROUND

A photochromic compound is characterized by its ability to undergo a reversible color change between two forms, which is induced in at least one direction by the absorption of light. Although organic photochromes have long been attracting significant attention because of their potential practical applications such as in data storage or retrieval displays, etc... ,variable transmission materials remain the only major commercial exploitation [1]. In this latter field, while the spiropyrans and the related compounds, *e.g.* the spiroxazines, have been extensively studied, comparatively little work has been carried out on 2,2-diaryl-[2H]-chromenes [2,3] for which photochromic properties were first reported by Becker [4]. Absorption in the range of 330-370 nm for those compounds leads, by cleavage of the carbon-oxygen bond, to the formation of colored isomers named open form (O.F.) as opposed to the closed form (C.F.) which is colorless.

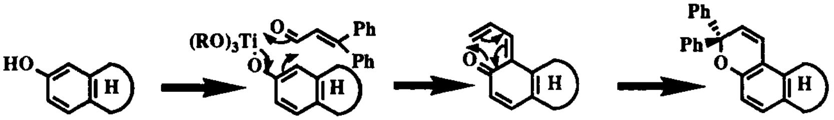
Scheme 1



Among structural modifications which could be carried out on chromenes, the heteroannellation represents interesting direction. Thus the purpose of the present work was to introduce different nitrogenated nuclei in different positions on the benzopyan moiety in order to cause changes for the photochromic properties.

The synthesis of 2,2-disubstitued-[2H]-chromenes may be approached either by the preparation of related ring system with subsequent variation of functionality, or by alkylation of a free phenol followed by cyclisation onto the aromatic ring. In 1979, Sartori et al. [5] reacted metal phenolates with α,β unsaturated carbonyl compounds and obtained good yields of 2,2-dialkyl-[2H]-chromenes and few flavenes. We adapted their procedure to heterocyclic phenol and extended the scope of their work to 2,2-diphenyl-[2H]-chromenes starting with β-phenyl cinnamaldehyde and the susmentionned heterocyclic compounds [6]. This method is the most convenient since the reaction based on the Claisen rearrangement of aryl propargyl ethers [7] fails with such compounds.

Scheme 2



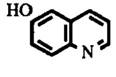
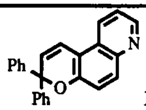
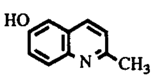
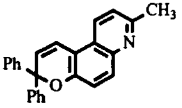
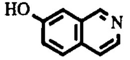
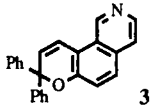
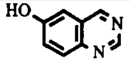
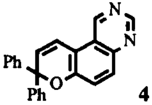
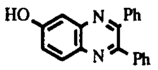
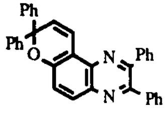
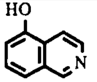
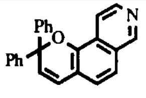
MATERIALS AND METHODS

Titanium ethoxide seems to be the most promising reagent among the organometallic compounds tested by Sartori. A typical procedure would be addition of equimolar toluenic solution of titanium ethoxide to convenient phenol followed by azeotropic distillation of formed ethanol. β-phenyl cinnamaldehyde is then added and the reactionnal mixture is refluxed for 3 hrs in toluene. After hydrolysis, the organic layer is dried and the solvent is removed under reduced pressure to afford the photochromic chromenes. Corresponding yields are listed in table 1. The structure of the chromenes was characterized by ^{1} H and ^{13} C NMR , microanalysis, UV and IR spectroscopies and for compound **1** by X-Ray analysis [8]. The characteristic signals of ^{1} H NMR spectra of 2,2-diphenyl-[2H]-chromenes are for the hydrogen atoms of the pyranic ring, *i.e.* 6.35 and 7.35 ppm (J= 10Hz) for compounds **1-5** and 6.30 and 6.75 ppm (J= 10Hz) for the isoquinoline derivative **6**. The quaternary carbon (*ca.* 83 ppm) bearing the two phenyl groups is also characteristic for a such moiety.

RESULTS AND DISCUSSION

Table 1 clearly shows that chemical yield is directly dependent on structures of starting phenols. It is estimated that efficiency for cyclisation is strictly reliable to electronic density of ortho attacked position. For all compounds bearing hydroxy group on a β position (I-V), the yield is quite good except for 6-hydroxy-2,3-diphenyl-quinoxaline which could be explained by its poor solubility in reactionnal mixture.

Table 1

Starting phenol	yield (%)	m.p. °C	[2H]-chromenes	λmax (nm) O. F. (Toluene)
 I	62	226	 1	435
 II	55	197	 2	436
 III	53	148	 3	443
 IV	42	163	 4	441
 V	17	159	 5	473
 VI	7	184	 6	485

With the other relative position of hydroxy group, the yields are much less good. The reaction totally failed for 8-hydroxyquinoline, for which specific complexation of organometallic compound desactived the phenol towards cyclisation.

All the described chromenes exhibit photochromic behavior at room temperature in toluene. Based on the spectral data given in table 1, introduction of one or two nitrogen atoms induces slight changes in comparison of corresponding 3,3-diphenyl-[3H]-naphtho[2,1-b]pyrans (432 nm) and 2,2-diphenyl-[2H]-naphtho[1,2-b]pyrans (480 nm) .

However, compound **5** manifests a bathochromic shift which could be explained by the extended conjugation by introduction of two other phenyl groups. On the other hand, preliminary studies of the photochromic equilibrium of those compounds show significative variations of the other parameters (thermal bleaching rate, efficiency of coloration).

CONCLUSION

A one step synthesis of new 2,2-diphenyl-[2H]-chromenes annellated with nitrogenated six-membered ring has been achieved, which has permitted us to develop a general method using easily available heterocyclic phenols and α,β unsaturated aldehydes. All the resultant chromenes show photochromic properties at room temperature. The chemical yields of preparation and the photochromic parameters are both strictly reliable on relative position of annellation.

ACKNOWLEDGEMENTS

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REFERENCES

1. C.B. Mc Ardle, in Applied Photochromic Polymer Systems, edited by C.B. Mc Ardle (Blackie, London, 1992), Chap. 1, pp. 1-27
2. B. Van Gemert and M.P. Bergomi, US Patent 5066818 (1991)
3. T. Tanaka, T. Imura, K. Tanaka and Y. Kida, Jap. Patent 3133988 (1991)
4. R.S. Becker and J. Michl, J.Amer. Chem. Soc, 88, 5931 (1966).
5. G. Sartori, G. Casiraghi, L. Bolzoni and G. Casnati, J.Org. Chem., 44, 803 (1979)
6. J.L Pozzo, A. Samat and R. Guglielmetti, Eur. Patent 93400688 (1993)
7. I. Iwai and J. Ide, Chem.Pharm. Bull., 11, 1042 (1963)
8. J.L. Pozzo, V.A. Lokshin, S.M. Aldoshin, A. Samat and R. Guglielmetti, Acta Cryst. (to be published)