ORGANIC LETTERS

2002
Vol. 4, No. 18
3143−3145

Multinuclear NMR Structural Characterization of an Unprecedented Photochromic Allene Intermediate

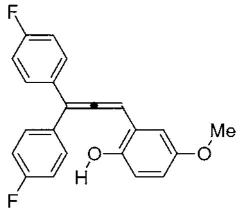
Stephanie Delbaere, Jean-Claude Micheau,[†] and Gaston Vermeersch*

Laboratoire de Physique et LARMN, UMR CNRS 8009, Faculté de Pharmacie,
Université de Lille 2, F-59006 Lille, France

gvermeer@phare.univ-lille2.fr

Received July 9, 2002

ABSTRACT



An *o*-allenyl-*p*-methoxyphenol intermediate (Int) was for the first time proved to be involved in the photochromic reaction of 2,2-di(4-fluorophenyl)-6-methoxy-2*H*-1-chromene (FC). Transoid-cis (TC) and transoid-trans (TT) photomerocyanines and the intermediate Int are generated by UV irradiation of FC. Visible light converts TC and TT into Int. The monitoring of the reactions was carried out on the basis of ^{1}H, ^{13}C, ^{19}F, and ^{2}H NMR spectroscopy.

Photochromism is the photoinduced transformation of a molecular structure, photochemically or thermally reversible, that produces a spectral change, typically of color.[1]

Spiropyrans[2] and spirooxazines[3] are the most well-known class of organic photochroms. Low temperature[4] and time-resolved[5] studies have shown that after breaking of the carbon−oxygen spirobond, the photochromic molecule is in an unstable form (the so-called X intermediate). This unstable isomer is still under investigation with the most recent ultrafast techniques and quantum calculation methods.[6] It undergoes a series of rearrangements and at the photo-steady state forms a mixture of the more stable photomerocyanines. The 2*H*-chromenes[7,8] (2*H*-1-benzopyrans) display photochromic behavior closely related to that of spiropyrans. For this reason, and because they exhibit a broad visible light spectral range and fatigue resistance, they are attracting a good deal of interest.

Here, we report the original results obtained by high-resolution NMR spectroscopy after irradiation of the spiro 2,2-di(4-fluorophenyl)-6-methoxy-2*H*-1-chromene (**FC**) (see Scheme 1). The fluorine atoms on a para position of both phenyl groups are used as ^{19}F NMR molecular probes to follow the behavior of the photochromic system.[9] 6-Substitution by a methoxy group was chosen to reduce spin−spin coupling in the aromatic part and to cause electrodonor substitution at this position.

[†] Present address: Laboratoire IMRCP, UMR CNRS 5623, Université Paul Sabatier, F-31062 Toulouse, France.

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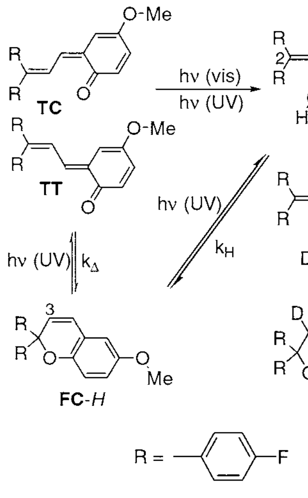
10.1021/ol0264859 CCC: $22.00

Scheme 1



When low-temperature solutions of **FC** (Figure 1a) were exposed to UV irradiation, two photomerocyanines **TC** (transoid-cis) and **TT** (transoid-trans) were formed, together with a new structure hereby called **Int** as it plays the role of intermediate in fluoro-chromene photochromism. The course of the reaction was monitored by ^{19}F NMR spectroscopy, showing the formation of both photomerocyanines,[10] each characterized by two resonances, resulting from the inequivalence of the two fluorine atoms. On the contrary, in **FC** and also in **Int** the two fluorine atoms are magnetically equivalent (Figure 1b). When the UV irradiated solution was exposed to visible light, a significant conversion of the red merocyanines (**TC** and **TT**) to the colorless structure **Int** was observed (Figure 1 c). When kept in the dark at ambient temperature, compound **Int** reverted slowly to the initial fluorochromene (**FC**).

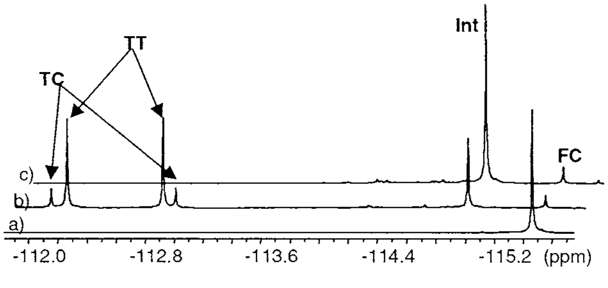


Figure 1. ^{19}F NMR spectra at 228 K of a 10^{-2} M solution of **FC** in acetone-d_6: (a) before, (b) after 30 min of UV irradiation, and (c) after 30 min of UV + 15 min of visible irradiation.

At 228 K, **Int** was obtained almost exclusively and no significant thermal decay was observed. An *o*-allenyl-*p*-methoxyphenol structure was unambiguously determined by the combination of ^{1}H, ^{13}C 1D and 2D NMR experiments (Cosy, Roesy, HSQC, and HMBC). The allenic system was deduced from the ^{13}C NMR resonances at 111.2, 210.2, and 92.4 ppm of C-2, C-3, and C-4, respectively. Interesting is the downfield shift of the sp-hybridized[11] central carbon nucleus C-3.

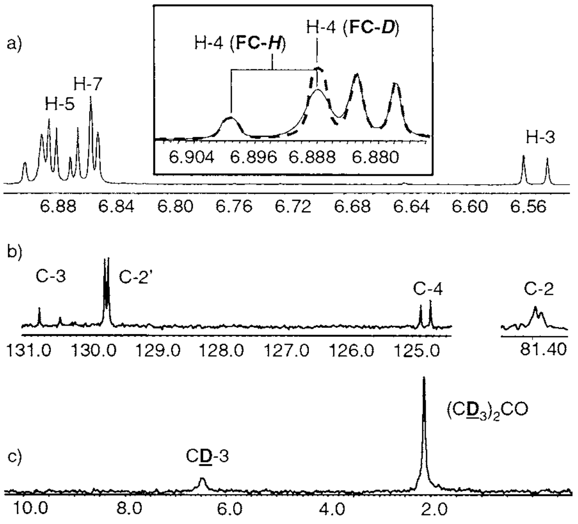


Figure 2. (a) ^{1}H NMR spectra (dotted line: ^{2}H-decoupled), (b) ^{13}C upfield resonance shifts, and (c) ^{2}H NMR spectrum, of isotopomers H−D mixture **FC** at 293 K.

The phenol function on carbon C-1a was demonstrated by deuteration. At 228 K, a drop of water-d_2 was added cautiously, taking care not to stir the sample. The drop crossed the solution and froze at the bottom of the tube. After the separation of the frozen water, the solution was restored to room temperature, in the dark, until complete conversion of **Int** into **FC**. The extent of conversion was followed by ^{19}F NMR spectroscopy. During this process, deuterium incorporation in **FC** is expected at the C-3 position.

Figure 2 exhibits several convergent results demonstrating the C-3 deuterium incorporation. On ^{1}H spectra (Figure 2a) each resonance was retrieved with the corresponding value of integration ($I = 1$), except on H-3 ($I = 0.22$). Moreover, H-4 was split into three signals: the expected doublet centered at 6.892 ppm ($I = 0.22$) and a new broad singlet at 6.886 ppm ($I = 0.78$). These variations are explained by the presence of a deuterium atom in position 3. Consequently, after this treatment, the fluorochromene (**FC**) is composed of a mixture of two isotopomers: 78% are the deuterated form (**FC-*D***) and 22% the protonated form (**FC-*H***). ^{2}H decoupling suppresses the broadening of the singlet signal at 6.886 ppm (H-4 in **FC-*D***). To gain more experimental evidence for the position of the deuterium atom, the ^{13}C spectrum with ^{1}H and ^{2}H decoupling and the ^{2}H spectrum were also recorded. In the ^{13}C spectrum of **FC-*D*** and **FC-*H*** (Figure 2b), the ^{13}C resonances of C-3, C-4, and C-2

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experiencing an isotopic shift are split into two separate lines. Their positive upfield resonance shifts upon deuteration are defined as a $\Delta^{n=1}$ of 322 ppb for C-3, a $\Delta^{n=2}$ of 147 ppb for C-4, and a $\Delta^{n=2}$ of 58 ppb for C-2, which are in agreement with the values reported by Hobley et al. for the spiropyran family.[12] In the ^{2}H NMR spectrum, except traces of residual acetone-d_6, the only other signal detected at 6.55 ppm can be attributed to a deuterium atom in position 3 (Figure 2c). This ^{2}H NMR spectroscopy is of great interest because the chemical shifts of isotopes (^{1}H and ^{2}H) are essentially identical.

Scheme 1 shows the mechanism of the **FC** photochromic process. Photomerocyanines **TC** and **TT** and the *o*-allenyl-*p*-methoxyphenol **Int** are generated by UV irradiation of **FC**. On the contrary, visible light induces conversion of **TC** and **TT** into **Int**. A [1,5] hydrogen (or deuterium) shift of *o*-allenyl-*p*-methoxyphenol followed by electrocyclization yields the closed 2*H*-chromene.

There are very few reports on allene intermediates in chromene chemistry. The only well-known exception is the paper of Gericke et al.[13] These authors showed that under the action of a strong base, deprotonation of a chromene derivative takes place in position 3, opens the ring, and generates a transient allenyl phenol able to recycle in solution. This shows that the chromene−allenyl−phenol isomerization is relatively easy to observe, although it was obtained in very different conditions. To get better insight into the chromene isomerization mechanism, another interesting question should be asked: Are the so-called X and **Int** related? This question is not trivial because, although postulated in 1962, the exact structure of intermediate X is still questionable. From transient kinetics measurements and quantum calculations[14] X is believed to be a high-energy isomer of the merocyanine in which the configuration of the spiropyran or the spirooxazine[15,16] is still partly retained, but with the C−O spirobond broken. From these considerations, it is clear that the X intermediate occurring in the early stages of the reaction is different from an *o*-allenylphenol structure derived from a still reoriented (i.e. delayed) structure. *o*-Allenylphenol structures have never been detected in spiropyran and spirooxazine series.[17] The experimental results presented here pave the way for further theoretical approaches, because such a tautomeric effect or atom migration has never been investigated for quantum calculations of chromene photochromism.

Acknowledgment. The 300-MHz NMR facilities were funded by the Région Nord-Pas de Calais (France), the Ministère de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche (MENESR), and the Fonds Européens de Développement Régional (FEDER).We thank Dr. M. Campredon (Laboratoire Photochimie Organique Appliquée, University Méditerranée, Marseille, France) for the gift of fluoro[2*H*]chromene.

Supporting Information Available: Irradiation techniques, deuteration mechanistic analysis, NMR technique details, and interpretation of multinuclear NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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