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A Green Synthesis of some Novel Spirocyclics: A Norrish Type II Process in 3-Cyclohexenyloxy-2-(furans-3-yl)-4*H*-chromen-4-ones

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Abstract

A green and clean route for the synthesis of diverse array of novel spirocyclics, the pyronospiropyrans, through the photoirradiation of 3-cyclohexenyloxychromones has been described. The synthesis of photoproducts from the substrates has been envisioned to occur through the intermediacy of 1,4-biradical produced via γ-hydrogen abstraction (A Norrish Type II process) from 3-cyclohexenyloxy moiety by the C=O group. The influence of the different substituents on the chromenone ring on formation and distribution of the spirocyclics has also been determined. The structures of the photoproducts formed were elucidated by IR, ^{1}H NMR, ^{13}C NMR and Mass spectral data. This study is an effort of devising the green route for the generation of new materials.

Keywords: Spirocyclics; 1,4-biradical; γ-hydrogen abstraction.

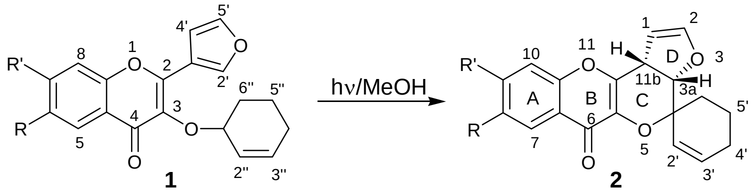
1. Introduction

Spirocyclic compounds in particular provide an intriguing subject for investigation, because these are known to exhibit wide ranging biological activity such as fungicidal (Pedras et al, 2006; Behera, 2006) herbicidal (Kobayashi et al, 1991), bactericidal (Padmavathi et al, 2005), and antimicrobial (Thadhaney et al, 2010). Spiropyrans have a great potential for application in optical devices, for example, as data storage films, 3-D memory and waveguides (Ramos García et al, 2003) mainly, because of their physical and chemical properties could be controlled by illumination. These find a very wide use in the information technologies like in the manufacture of heat sensitive copying papers (Miller and Cheng, 1963), holographic information recordings

(Lescinsky, 1970), and also find applications (Berkovic et al, 2000) in light filters, in display, in eye-protective laser goggles, and in self developing photography. A careful examination of their various synthetic methods indicates that most of these suffer from one or more limitations such as multistep synthesis, costly or rare availability of catalysts and starting materials, prolonged reaction times, use of toxic organic reagents and moreover lack of generality. These limitations necessitate the development of a more convenient and environment benign methodology and our laboratory has adopted an overall programme to synthesize spirocyclics (Gupta et al, 2007) by photochemical method, the greener route which is environmental friendly and non hazardous. In continuation of this, to further examine and explore the potential of this method for obtaining spiropyrans, in the present study, we have synthesized some new spirocyclics, the pyronospiropyrans, bearing fused dihydrofuryls.

2. Results and Discussions

The substrates chosen are some 2-(3'-furyl)-3-(cyclohexenyloxy)chromones **1(a-d)** which were synthesized by the condensation of 2-hydroxyl acetophenones with furan-3-carbaldehyde in the presence of NaOH/EtOH, followed by reacting the resulting chalcones with 50% H_2O_2/OH^- under Algar-Flynn-Oyamada conditions (Oyamada, 1934; Algar and Flynn, 1934) and subsequent alkylation of the 3-hydroxychromenones with cyclohexenyl bromide in the presence of dry acetone, freshly dried K_2CO_3 and tetra-*n*-butyl ammonium iodide. The deoxygenated methanolic solution (1.0 mM) of these substrates was purged with nitrogen for 30 min and irradiated under nitrogen with light from a 125W Hg vapor lamp for 30 min (Scheme 1). The removal of solvent under reduced pressure yielded a gummy mass that was chromatographed over a column of silica gel. The columns were eluted with increasing proportion of ethyl acetate in ethyl acetate-petroleum ether mixture to obtain the spirocyclic compounds **2(a-d)**.



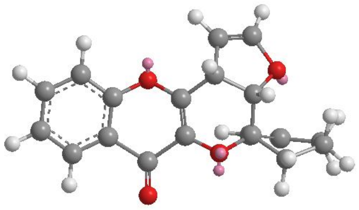
1a, 2a: R = H, R' = H; **1b, 2b**: R = Cl, R' = CH_3
1c, 2c: R = CH_3, R' = H;**1d, 2d**: R = Cl, R' = H

Scheme 1

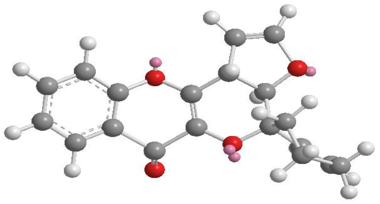
The spirocyclics obtained as photoproducts **2(a-d)** were afforded only by the clipping at C-2′ with no photoproducts by clipping at C-4′ (Fig. 1) showing the regioselective photocyclization in these molecules. Further, no spirocyclic fused with cyclopropane aldehyde, the ring contracted product (Gupta et al, 2007) was obtained as were realized in our earlier studies on 2-(2'-furyl)-3-(cycloalkenyloxy)chromones.

The structures of these spirocyclics **2(a-d)** were arrived at from the analysis of their spectral parameters. For example, the IR spectrum of spiropyran **2a** exhibited a strong absorption at 1641 cm^{-1}(C=O) and 1611 cm^{-1} (C=C). The ^{1}H NMR spectrum (300MHz, $CDCl_3$) of it proved quite useful in arriving at structure **2a**. The protons, H-7 and H-10 were present as doublets at δ 8.17 and 7.40, respectively. The other two benzenoid protons H-8 and H-9 were present as multiplet at δ 7.57. The protons belonging to dihydrofuran ring, H-2 and H-1 showed resonances at 6.45 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2) and 5.34 (1H, dd, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 2.7 Hz, H-1). The ring junction protons H-11b and H-3a exhibited signals at δ 4.81 (1H, dd, $J_{11b,3a}$ = 9.0 Hz, $J_{11b,1}$ = 2.7 Hz) and 3.99 (1H, d, $J_{3a,11b}$ = 9.0 Hz) respectively. The two ethylenic protons H-2' and H-3' of the cyclohexene ring appeared as multiplet at δ 5.76-5.73 and 6.14-6.09. Rest of the protons belonging to cyclohexene ring produced unresolved clusters between δ 2.32-2.10.

For making a decision regarding the stereochemical disposition of ring C/D in **2a**, the co-relations between J/Φ (Karplus equation) were invoked (Gupta et al, 1995). The vicinal coupling constant $J_{11b,3a}$ = 9.0 Hz indicates that the planes carring protons H-11b and H-3a should be tending to possess a Φ (dihedral angle) 0^{o}, thus pointing to the *cis*-axial relationship between H-11b and H-3a and in turn making the C/D ring fusion *cis* (Structure I) which expectantly is energetically more stable (MM2 Programme) than *trans* configuration(Structure II).

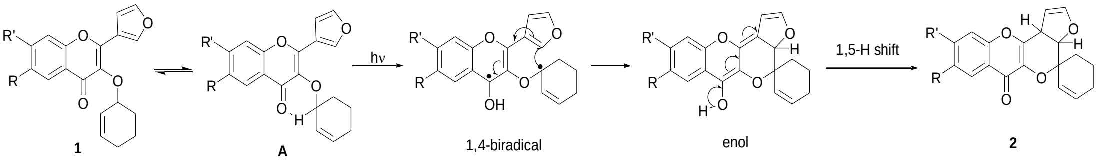


Structure I (E = 15.6586 kcal/mole)



Structure II (E = 22.1906 kcal/mole)

These photoconversions of the cyclohexenyloxy chromones **1(a-d)** to pyronospiropyrans **2(a-d)** can be visualized as having occurred through an initial abstraction of the O-methine proton of cyclohexenyl group by the excited carbonyl of the pyrone moiety to produce 1,4-biradical *via* Norrish type-II process. The easy abstraction may be the result of a possible six-membered transition state, **A** (Scheme 2). The spirocyclic **2**, is then formed through bond formation between the O-methine carbon radical and the C-2′ of the furan ring which is followed by 1,5-H migration *via* ketonisation in the enol.



Scheme 2

3. Conclusion

In conclusion, we report here a green and clean route for the synthesis of some novel spirocyclics, dihydrofuryl pyronospiropyrans through the photoirradiation of 3-cyclohexenyloxychromones which may find some biological/industrial applications.

4. Experimental

4.1 General

The nuclear magnetic resonance ^{1}H NMR (300 MHz) and proton-decoupled ^{13}C NMR (75.4MHz) spectra were recorded on Bruker spectrometer using TMS as internal standard. The infrared (IR) spectra were scanned in KBr pellets on a MB3000 FT-IR with HORIZON MB^{TM} FTIR software from ABB Bomen. The mass spectral data were obtained on WATERS, Q-TOF MICROMASS (LC-MS) spectrometer. Melting points were determined in open capillaries and are uncorrected. The photoirradiation of the deaerated solution of substrates was carried out using a pyrex filter under nitrogen atmosphere from 125W Hg lamp. The columns for chromatographic separation were packed in pet. ether with silica gel and were eluted with pet. ether and ethyl acetate mixture (99:1).

4.1.1 Synthesis of 3-Cyclohexenyloxy-2-(furans-3-yl)-4H-chromen-4-ones, 1

In a mixture of 0.002mol of 2-(furan-3-yl)-3-hydroxychromenone (Kamboj et al, 2009) and dry K_2CO_3 in dry acetone was added 0.0022mol of 3-bromocyclohexene and phase transfer catalyst, $Bu_4N^+I^-$ (0.050g). The reaction mixture was refluxed for 5h with constant stirring (color changed from red to dark brown). The reaction mixture was then filtered, distilled and then poured in ice cold water. The gummy material thus obtained was percolated through a column of silica-gel (100-200 mesh) using petroleum ether-ethyl acetate (1%) as eluent to get white solid, **1**.

4.1.2 3-(Cyclohex-2-enyloxy)-2-(furan-3-yl)-4H-chromen-4-one 1a

Yield 72%, white solid, mp 85-86 ^{o}C; ν_{max} (cm^{-1}): 1637 (C=O), 1605 (C=C); δ_{H} ($CDCl_3$): 8.35 (1H, s, H-2'), 8.24 (1H, dd, J_o = 7.8 Hz, J_m = 2.4 Hz, H-5), 7.57-7.34 (4H, m, H-6, 7, 8, 5'), 7.04 (1H, dd, $J_{4',2'}$ = 0.9 Hz, $J_{4',5'}$ = 1.8 Hz, H-4'), 5.93-5.85 (2H, m, H-2", 3"), 5.34 (1H, m, H-1"), 2.11-1.62 (6H, m, H-4", 5", 6"); δ_{13C} ($CDCl_3$): 172.89, 154.40, 152.78, 144.36, 142.33, 130.57, 130.23, 129.96, 127.70, 127.12, 124.78, 121.67, 119.36, 112.75, 75.55, 55.87, 28.43, 24.38, 18.67.

4.1.3 6-Chloro-3-(cyclohex-2-enyloxy)-7-methyl-2-(furan-3-yl)-4H-chromen-4-one 1b

Yield 77%, white solid, mp 133-134 ^{o}C; ν_{max} (cm^{-1}): 1640 (C=O), 1619 (C=C); δ_{H} ($CDCl_3$): 8.34 (1H, s, H-2'), 8.18 (1H, d, J_m = 2.4 Hz, H-5), 7.54 (1H, dd, $J_{5',2'}$ = 0.9 Hz, $J_{5',4'}$ = 1.8 Hz, H-5'), 7.41 (1H, d, J_o = 9.0 Hz, H-8), 7.02 (1H, dd, $J_{4',2'}$ = 0.9 Hz, $J_{4',5'}$ = 1.8 Hz, H-4'), 5.90-5.87 (2H, m, H-2", 3"), 5.36 (1H, m, H-1"), 2.52 (3H, s, CH_3), 2.23-1.76 (6H, m, H-4", 5", 6"); δ_{13C} ($CDCl_3$): 171.23, 153.47, 149.48, 142.38, 141.70, 131.33, 130.72, 129.96, 127.70, 123.55, 121.78, 119.60, 111.79, 75.82, 53.75, 29.34, 24.37, 22.32, 17.96.

4.1.4 3-(Cyclohex-2-enyloxy)-2-(furan-3-yl)-6-methyl-4H-chromen-4-one 1c

Yield 68%, white solid, mp 85-86 ^{o}C;ν_{max} (cm^{-1}): 1635 (C=O), 1612 (C=C); δ_H ($CDCl_3$): 8.36 (1H, s, H-2'), 8.04 (1H, d, J_m = 2.4 Hz, H-5), 7.53 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-7), 7.49 (1H, dd, $J_{5',2'}$ = 0.9 Hz, $J_{5',4'}$ = 1.8 Hz, H-5'), 7.42 (1H, d, J_o = 9.0 Hz, H-8), 7.06 (1H, dd, $J_{4',2'}$ = 0.9 Hz, $J_{4',5'}$ = 1.8 Hz, H-4'), 5.95-5.87 (2H, m, H-2", 3"), 5.37 (1H, m, H-1"), 2.48 (3H, s, CH_3), 2.14-1.76 (6H, m, H-4", 5", 6"); δ_{13C} ($CDCl_3$): 171.58, 152.62, 149.30, 142.43, 139.55, 131.26, 130.54, 129.13, 127.79, 123.68, 122.45, 119.66, 117.25, 109.57, 72.47, 51.34, 28.63, 22.56, 21.44, 18.76.

4.1.5 6-Chloro-3-(cyclohex-2-enyloxy)-2-(furan-3-yl)-4H-chromen-4-one 1d

Yield 74%, white solid, mp 116-118 ^{o}C; ν_{max} (cm^{-1}): 1640 (C=O), 1605 (C=C); δ_H ($CDCl_3$): 8.38 (1H, s, H-2'), 8.21 (1H, d, J_m = 2.4 Hz, H-5), 7.62 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-7), 7.55 (1H, dd, $J_{5',2'}$ = 0.9 Hz, $J_{5',4'}$ = 1.8 Hz, H-5'), 7.49 (1H, d, J_o = 9.0 Hz, H-8), 7.03 (1H, dd, $J_{4',2'}$ = 0.9 Hz, $J_{4',5'}$ = 1.8 Hz, H-4'), 5.90-5.87 (2H, m, H-2", 3"), 5.36 (1H, m, H-1"), 2.14-1.75 (6H, m, H-4", 5", 6"); δ_{13C} ($CDCl_3$): 173.43, 154.40, 151.45, 141.61, 140.02, 132.21, 131.69, 129.76, 128.98, 125.86, 123.78, 119.52, 118.15, 111.80, 73.47, 54.83, 27.53, 23.55, 17.82.

4.2 Photolysis of 3-cyclohexenyloxy-2-(furans-3-yl)-4H-chromen-4-ones, 1

A deoxygenated solution of **1** (1.0 mM) in dry methanol was irradiated in a pyrex glass vessel under nitrogen atm. for 30 min with a 125W Hg vapor lamp. Progress of the reaction was monitored by tlc. The removal of solvent under reduced pressure yielded a gummy mass that was chromatographed over a column of silica gel (100-200 mesh) to yield the photoproduct **2**.

2a: Yield 44%, white solid, mp 142-143 ^{o}C; ν_{max} (cm^{-1}): 1641 (C=O), 1611(C=C); δ_H ($CDCl_3$): 8.17 (1H, d, J_o = 9.0 Hz, J_m = 2.4 Hz, H-7), 7.57 (2H, m, H-8, 9), 7.40 (1H, d, J_o = 9.0 Hz, J_m = 2.4 Hz, H-10), 6.45 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 6.14-6.09 (1H, m, H-3'), 5.76-5.73 (1H, m, H-2'), 5.34 (1H, dd, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 2.7 Hz, H-1), 4.81 (1H, dd, $J_{11b,3a}$ = 9.0 Hz, $J_{11b,1}$ = 2.7 Hz, H-11b), 3.99 (1H, d, $J_{3a,11b}$ = 9.0 Hz, H-3a), 2.32-2.10 (6H, m, H-4', 5', 6'); δ_{13C} ($CDCl_3$): 172.36, 153.72, 147.68, 137.55, 134.63, 131.34, 129.5, 128.32, 125.24, 123.59, 117.89, 100.82, 80.56, 74.27, 53.35, 35.79, 24.65, 21.56, 20.83.

2b: Yield 49%, white solid, mp 110-112 ^{o}C; ν_{max} (cm^{-1}): 1641 (C=O), 1611(C=C); δ_H ($CDCl_3$): 8.12 (1H, s, H-7), 7.32 (1H, s, H-10), 6.58 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 6.23-6.15 (1H, m, H-3'), 5.97-5.79 (1H, m, H-2'), 5.86 (1H, dd, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 2.7 Hz, H-1), 4.76 (1H, dd, $J_{11b,3a}$ = 9.0 Hz, $J_{11b,1}$ = 2.7 Hz, H-11b), 3.98 (1H, d, $J_{3a,11b}$ = 9.0 Hz, H-3a), 2.43 (3H, s, CH_3), 2.45-2.17 (6H, m, H-4', 5', 6'); δ_{13C} ($CDCl_3$): 171.79, 154.81, 149.72, 139.55, 134.34, 135.31, 128.53, 128.16, 126.19, 125.89, 118.67, 103.46, 82.55, 75.29, 56.34, 35.09, 25.96, 25.31, 22.58, 20.35.

2c: Yield 41%, white solid, mp 156-157 ^{o}C; ν_{max} (cm^{-1}): 1640 (C=O), 1611(C=C); δ_H ($CDCl_3$): 8.02 (1H, d, J_m = 2.4 Hz, H-7), 7.51 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.37 (1H, d, J_o = 9.0 Hz, H-10), 6.41 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 6.12-6.10 (1H, m, H-3'), 5.83-5.77 (1H, m, H-2'), 5.32 (1H, dd, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 2.7 Hz, H-1), 4.80

(1H, dd, $J_{11b,3a}$ = 9.0 Hz, $J_{11b,1}$ = 2.7 Hz, H-11b), 3.97 (1H, d, $J_{3a,11b}$ = 9.0 Hz, H-3a), 2.42 (3H, s, CH_3), 2.31-2.08 (6H, m, H-4', 5', 6'); δ_{13C} ($CDCl_3$): 171.82, 155.33, 148.67, 139.45, 135.12, 133.98, 129.53, 128.57, 127.35, 124.86, 119.57, 102.68, 80.65, 74.29, 53.34, 34.73, 25.04, 24.45, 22.17, 20.19.

2d: Yield 57%, white solid, mp 206-208 °C; ν_{max} (cm^{-1}): 1642 (C=O), 1611(C=C); δ_H ($CDCl_3$): 8.22 (1H, d, J_m = 2.4 Hz, H-7), 7.57 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.40 (1H, d, J_o = 9.0 Hz, H-10), 6.45 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 6.14-6.09 (1H, m, H-3'), 5.76-5.73 (1H, m, H-2'), 5.34 (1H, dd, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 2.7 Hz, H-1), 4.81 (1H, dd, $J_{11b,3a}$ = 9.0 Hz, $J_{11b,1}$ = 2.7 Hz, H-11b), 3.99 (1H, d, $J_{3a,11b}$ = 9.0 Hz, H-3a), 2.32-2.10 (6H, m, H-4', 5', 6'); δ_{13C} ($CDCl_3$): 174.79, 156.57, 148.39, 138.67, 135.63, 132.98, 129.87, 129.78, 125.33, 124.59, 119.36, 102.16, 83.58, 76.46, 54.35, 36.15, 24.68, 22.77, 21.25.

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