Pergamon

Tetrahedron Letters 43 (2002) 6875–6877

TETRAHEDRON
LETTERS

# Photoisomerization of allyl ethers: syntheses of vinyl ethers

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Received 29 April 2002; revised 21 June 2002; accepted 28 June 2002

**Abstract**—A synthesis of vinyl ethers through the photoisomerization of allyl ethers is described. © 2002 Published by Elsevier Science Ltd.

Intramolecular hydrogen-abstractions initiated by the photoexcited C=O group have found several synthetic applications.[1] Ring systems containing 3–*n* atoms, spiropyrans, spirobenzofurans, lactams and some other systems have been synthesized using this method. These abstractions have also been investigated using steroidal moieties[2] and a series of *O*-alkylesters of 4-benzoylbenzoic acids[3] to determine the relationship between the chain length and the site of abstraction. In this communication, we report a facile synthesis of vinyl ethers through the application of hydrogen abstractions.

The allyl ethers **2a**–**g**,[4] synthesized by the alkylation of 3-hydroxychromones **1a**–**g** with methyl-γ-bromocrotonate were irradiated with pyrex filtered light from a 125 W Hg lamp in MeOH. A chromatographic work up of the photolysate produced vinyl ethers **5** and **6**[5] in 15–20% and 3–5% yields, respectively. Mechanistically the phototransformations may be envisaged to be initiated through hydrogen abstraction from the $OCH_2$ by the photoexcited C=O of the pyrone moiety to lead to the formation of 1,4-biradical **3**. Subsequent proton capture from the solvent (MeOH) forms the products; the involvement of the solvent was evident from the fact that no photoisomerization could be observed when the reaction was carried out in an aprotic solvent like $C_6H_6$. It is important to mention here that the photolysis of allyl ethers[6] **7** and **8** did not give any photoisomerized products but instead the tetracyclic products **9** and **10** were obtained, compounds similar to those formed during the photolysis of **11** and **12**.[7] Even **8** where the initially produced biradical is delocalized to produce a very stable tertiary radical **13**, did not experience any isomerization.

Thus it can be inferred that it is the presence of an electron captive group like $COOCH_3$ that is essential for such photoisomerization, a fact further corroborated by the unreactivity of the cinnamyloxy derivative **14** as reported by Sumathi et al.[1h] The importance of this photoconversion is that an allyl ether has been transformed into a vinyl ether. The rearrangement of α,β-unsaturated enones[8] to their β,γ-unsaturated isomers through a process of hydrogen abstraction is known. A few routes for the synthesis of vinyl ethers are available[9] but as far as we know this is the first photochemical route for the syntheses of vinyl ethers.

## Acknowledgements

Generous financial support by DST and CSIR, New Delhi is gratefully acknowledged.

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*Keywords*: allyl ethers; 1,4-biradical; vinyl ethers.

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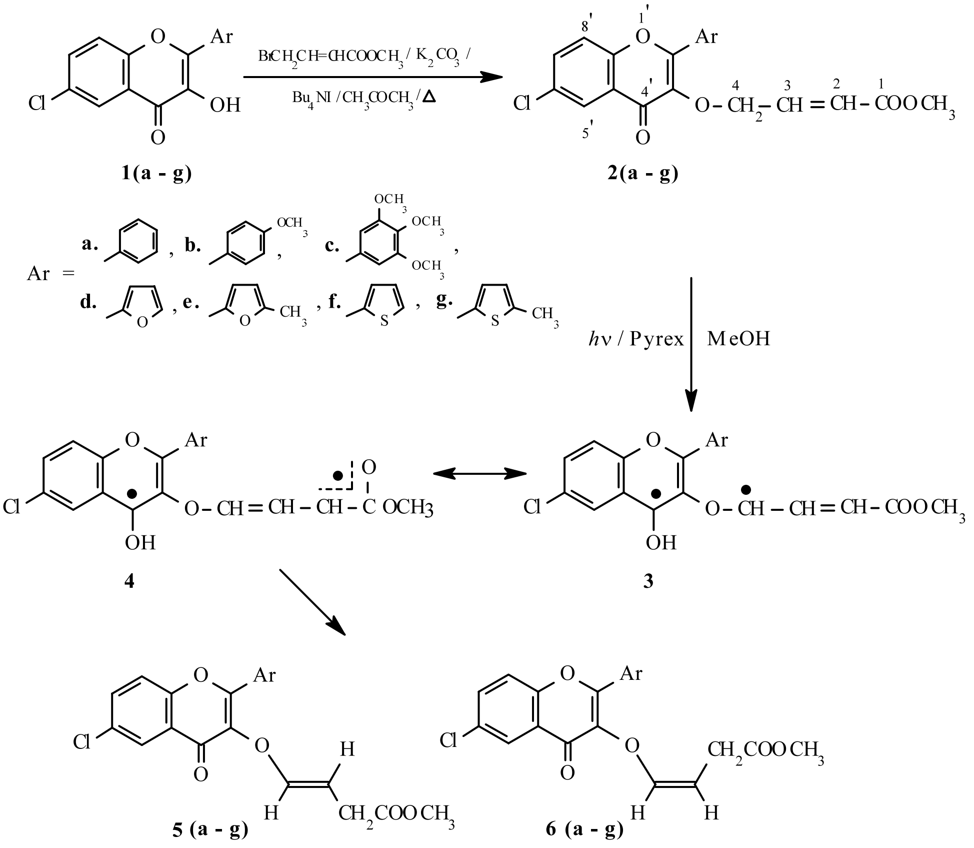
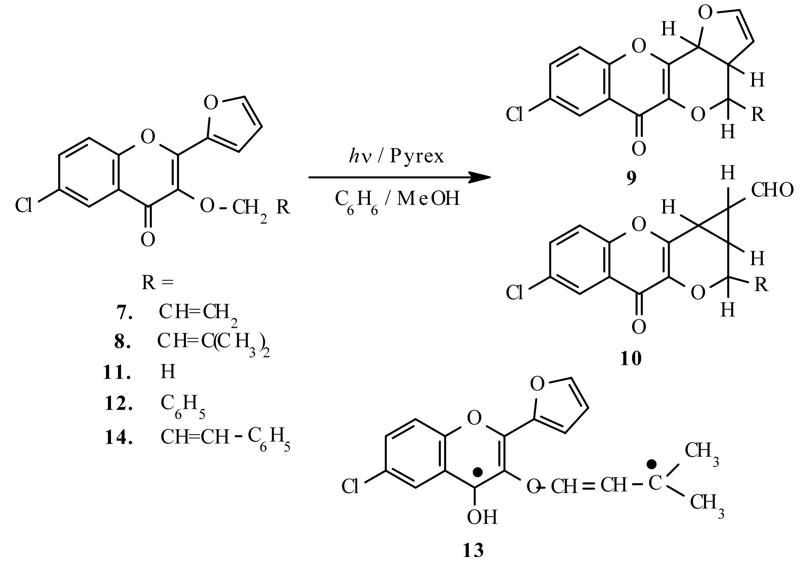
PII: S0040-4039(02)01366-7





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4. **2a**–**g** were synthesized through condensation of 5-chloro-2-hydroxyacetophenone and the appropriate aromatic carboxaldehyde followed by cyclization ($H_2O_2$/NaOH) and *O*-alkylation of the resulting 3-hydroxychromone **1a**–**g** with methyl-γ-bromocrotonate ($K_2CO_3/CH_3COCH_3$); **2a**. Yield (60%), mp 120–21°C; $\lambda_{max}$ THF 319 nm (8000), 230 nm (28800) $\nu_{max}$ cm$^{-1}$ 1727 (C=O), 1645 (C=O), 1609 (C=C); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.21 (1H, d, $J_m$ 2.4 Hz, H-5′), 8.02 (2H, m, H-2″,6″), 7.64 (1H, dd, $J_{m,o}$ 2.4 Hz, 9.0 Hz, H-7′), 7.52 (4H, m, H-8′,3″,4″,5″), 6.95 (1H, t {d}, $J_{3,4}$ 4.8 Hz, $J_{3,2}$ 15.6 Hz, H-3), 6.12 (1H, t {d}, $J_{2,3}$ 15.6 Hz, $J_{2,4}$ 1.4 Hz, H-2), 4.80 (2H, dd, $J_{4,3}$ 4.8 Hz, $J_{4,2}$ 1.4 Hz, H-4), 3.73 (3H, s,-COO$\mathbf{CH_3}$); **2b**–**g** were identified similarly; **2b**. Yield (62%), mp 138–140°C; **2c**. Yield (55%), mp 135–137°C; **2d**. Yield (60%), mp 103–105°C; **2e**. Yield (60%), mp 124–26°C; **2f**. Yield (65%), mp 150–152°C; **2g**. Yield (60%), mp 126–28°C.
5. (a) Only **5** could be isolated in a pure state; **6** always remained contaminated with **5**; (b) **5a**. mp 110–112°C; $\lambda_{max}$ THF 303 nm (14 800), 250 nm (22 700); $\nu_{max}$ cm$^{-1}$ 1750 (C=O), 1646 (C=O); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.23 (1H, d, $J_m$ 2.4 Hz, H-5′), 7.98 (2H, m, H-2″,6″), 7.65 (1H, dd, $J_{m,o}$ 2.4 Hz, 9.0 Hz, H-7′), 7.54 (1H, d, $J_o$ 9.0 Hz, H-8′), 7.49 (3H, m, H-3″,4″,5″), 6.57 (1H, t {d}, $J_{4,2}$ 1.3 Hz, $J_{4,3}$ 12.5 Hz, H-4), 5.24 (1H, t {d}, $J_{3,2}$ 7.4 Hz, $J_{3,4}$ 12.5 Hz, H-3), 3.65 (3H, s, COO$\mathbf{CH_3}$), 3.00 (2H, dd, $J_{2,4}$ 1.2 Hz, $J_{2,3}$ 7.4 Hz, H-2); $M^+$ 370/372; (c) **5b**. mp 115–117°C $M^+$ 400/402; **5c**. mp 112–114°C $M^+$ 460/462; **5d**. mp 103–104°C $M^+$ 360/362; **5e**. mp 115–116°C $M^+$ 374/376; **5f**. mp 114–116°C $M^+$ 376/378; **5g**. mp 107–109°C $M^+$ 390/392; (d) The $^1$H NMR (300 MHz, $CDCl_3$) spectrum of **6** from the mixture of **5** and **6**; **6a** the aromatic protons were found similarly placed as in **5a**, $\delta$ 6.42 (1H, t {d}, $J_{4,2}$ 1.4 Hz, $J_{4,3}$ 6.0 Hz, H-4), 4.92 (1H, dd, $J_{3,2}$ 7.0 Hz, $J_{3,4}$ 6.0 Hz, H-3), 3.75 (3H, s, COO$\mathbf{CH_3}$), 3.32 (2H, dd, $J_{2,4}$ 1.4 Hz, $J_{2,3}$ 7.0 Hz, H-2).
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