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FACILE PHOTOLYTIC DEMETHOXYLATION OF 3-METHOXYCHROMONES

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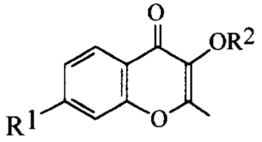
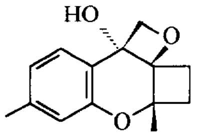
Abstract : Photolysis of 3-methoxychromones in methanol furnishes chromones through extrusion of the methoxy function. A conjugate addition of methanol followed by a double methoxy elimination has been proposed to account for the cleavage product. Copyright © 1996 Elsevier Science Ltd

The Norrish type II photoprocess involving an intramolecular hydrogen abstraction by a carbonyl group leading to cyclization and/or fragmentation has been extensively studied.[1] In the cases of alkyl and aryl alkyl ketones this procedure provides an efficient route to cyclobutanols. The α-alkoxy substituted carbonyl compounds furnish oxetanols as well as products from cleavage of the alkoxy function.[2] Photolysis of α-alkoxy α,β-unsaturated cyclenones has been reported to provide alkylidene oxetanols and oxo oxetanes and occasionally fragmentation to lead to the parent α,β-unsaturated carbonyl compound.[3] The extension of this to the photo behaviour of α-alkoxy α,β-enones that possess an endocyclic oxygen atom has not been well explored. The only report[4] involving photolysis of a 3-methoxychromone has been stated to yield a dimeric oxetanol. In this paper we present the first instance of a facile extrusion of the methoxy group in the photolysis of 3-methoxychromones in methanol and the probable mode of this extrusion.

In connection with our ongoing programme of synthesis of marine sesquiterpenes, we have reported[5] the photolytic ethylene addition to 3-methoxychromones to furnish oxetanols through a tandem cycloaddition and γ-hydrogen abstraction sequence (e.g. **1a** $\longrightarrow$ **2**). In view of the continued interest in the Norrish type II behaviour of various carbonyl substrates, we have initiated further studies to explore the photochemical reactions displayed by 3-methoxychromones in a variety of solvents. Irradiation of **1a** in methanol for 2h using a Hanovia 450W mercury lamp through a pyrex filter while a continuous flow of ethylene was maintained through the solution furnished the oxetanol **2**[5] as the major product alongwith the chromone **3a**[6] (15-20%). Arising out of our previous work[5], this reaction was done with a view to obtaining the primary photoadduct. However only the oxetanol **2** resulted even under short time photolysis. The chromone **3a** was obtained as the sole product when **1a** was irradiated for 2h in methanol in the absence of ethylene. The identity of **3a** was



1a: $R^1=R^2=Me$
1b: $R^1=R^2=H$
1c: $R^1=H$, $R^2=Me$
1d: $R^1=H$, $R^2=Et$



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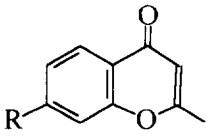
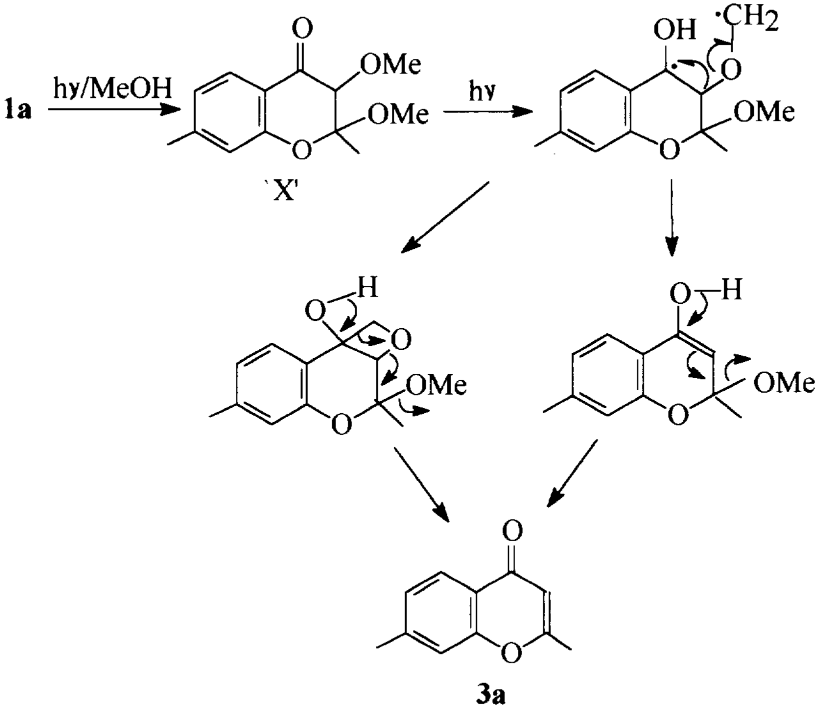
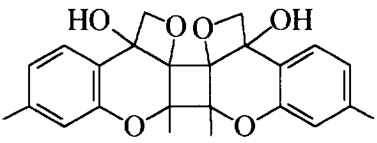


3a: R=Me
3b:R=H



Scheme - 1



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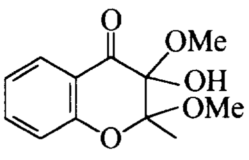

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established from spectral data and additionally from comparison with an authentic sample.[6] The formation of **3a** may be envisaged to proceed as follows. An initial photolytic addition of methanol to the double bond of **1a** produces the dimethoxychromanone 'X' which undergoes a γ-hydrogen abstraction to lead to a diradical. Collapse of this diradical with release of formaldehyde and concomitant elimination of methoxy group leads to **1a**. Alternatively the diradical may combine to an intermediate oxetanol which cleaves to finally afford **1a** (Scheme-I). The conjugate addition of methanol to cyclenones under photolytic conditions is precedented[7] and lends support to the premise of initial addition of methanol to **1a**. The thermal addition of methanol to **1a**, which also appeared possible, was excluded by control experiments. Thus, prolonged stirring of **1a** in methanol at ambient temperature or refluxing for 5h or addition of a catalytic amount of sodium methoxide[7] resulted only in recovery of **1a**. Attempted acid catalysed addition of methanol to **1a** was also unfruitful. The intermediacy of an oxo-oxetane[3] in the formation of **3a** could also be ruled out since photolysis of **1a** in benzene or acetonitrile yielded only the dimeric oxetanol **4**, in good yield. The structure of the dimer was deduced from the ^1H NMR spectrum which showed two singlets at δ 1.29 and 2.33 for the quaternary and aromatic methyl groups respectively and an AB quartet between δ 4.55 and 5.11 for the oxetanol methylene protons besides the aromatic protons. This revealed the symmetric structure of the dimer. Furthermore, the mass spectrum showed a molecular weight of 408. The formation of dimer **4** in non-nucleophilic solvents is in conformity with an earlier observation.[4] The head to head addition assignment to **4** is based on analogy with previous reports.[4,8] However no attempt has been made to establish the stereochemistry around the cyclobutane ring. Attempts to secure direct evidence for the intermediacy of 'X' were stymied due to difficulty in its isolation or preparation by other means. Whilst searching for alternatives, it was found that interaction of 3-hydroxychromone **1b** with iodobenzene diacetate[9] in methanol furnished the 2,3-dimethoxychromanone **5**. Analytical and spectral data attested to the assigned structure, although the stereochemistry of the hemiacetal has not been assigned. Photolysis of **5** in benzene or methanol afforded the 3-hydroxychromone **1b** in very good yield which supported the proposed mode of methoxy extrusion following an initial addition of methanol. The chromones **1c** and **1d** also on photolysis in methanol underwent facile extrusion of the alkoxy function to lead to the chromone **3b** as the sole product in near quantitative yield. The photolysis of **1a** was also investigated in isopropyl alcohol and t-butyl alcohol. In both cases it furnished only the dimeric oxetanol **4** suggesting that steric factors exclude the conjugate addition of these alcohols and that the operation of an alternate pathway in the photolysis of **1a**.

Experimental Section

Melting points are uncorrected. Solvents were reagent grade materials and were further purified by conventional methods. Petroleum ether refers to the fraction of b.p. 60-80°C. Preparative TLC was performed with silica gel $^{60}HF_{254}$ plates of 1mm thickness.

IR Spectra are for $CHCl_3$ solutions. ^1H NMR spectra of CCl_4 or $CDCl_3$ solutions were recorded at 60 MHz and peak positions are indicated in ppm downfield from internal TMS in δ units.

The alkoxychromones **1a**, **1c-d** were prepared by alkylation with MeI (EtI for **1d**) in acetone in the presence of K_2CO_3 of the corresponding 3-hydroxychromones which in turn were prepared according to literature.[10] Full preparative and other details have been included in a submitted paper.[11]

Photolyses of 2,7-dimethyl-3-methoxychromone 1a. Formation of oxetanol 2 and chromone 3a

A solution of 2,7-dimethyl-3-methoxychromone **1a** (200 mg) in methanol (110 ml) was irradiated with a Hanovia 450W mercury lamp through a pyrex filter for 2h while a continuous flow of ethylene was maintained through the solution. At the end of this period the solvent was removed and the residue purified by preparative TLC using petroleum ether/ethyl acetate (19:1). This furnished the oxetanol 2 (135 mg, 60%) and 2,7-dimethylchromone **3a** (35 mg, 20%). The chromone **3a** showed m.p. 98-99°C (lit 98-99°C). IR 1640 cm^{-1}. ^1H NMR (CCl_4) δ 2.23 (s, 3H), 2.36 (s, 3H), 5.86 (s, 1H), 6.93-7.06 (m, 2H), 7.84 (d, J = 8 Hz, 1H). Additional confirmation was obtained from comparison with an authentic sample prepared as per literature.[6]

When the above photolysis was carried out without passage of ethylene, the chromone **3a** was obtained exclusively in 80% yield.

The dimeric oxetanol 4

A solution of the chromone **1a** (200 mg) in acetonitrile (100 ml) was irradiated as before for 2.5h. The solvent was removed and the residue purified by crystallisation from ether-petroleum ether to afford the dimer **4** as colourless crystals (160 mg, 80%). m.p. 212-213°C. IR 1620 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.29 (s, 6H), 2.33 (s, 6H), 4.55 (d, A of AB, J = 6 Hz, 2H), 5.11 (d, B of AB, J = 6 Hz, 2H), 5.33 (s, 2H, exchangeable with D_2O), 6.63-6.83 (m, 4H), 7.16 (d, J = 8 Hz, 2H). Anal. Calcd. for $C_{24}H_{24}O_6$: C, 70.57; H, 5.92. Found : C, 70.30; H, 5.75. Mass. 408(M^+).

The same dimeric oxetanol **4** was obtained in 70-80% yields when the chromone **1a** was photolysed in isopropyl alcohol or t-butyl alcohol.

Photolysis of chromones **1c** and **1d**

Photolysis of chromones **1c** and **1d** in methanol under conditions described for **1a** afforded the 2-methylchromone **3b** in 75-80% yield. The identity of **3b** was established from spectral and m.p. comparison with an authentic sample.[6]

2,3-Dimethoxy-2-methyl-3-hydroxychromanone 5

To a stirred solution of 2-methyl-2-hydroxychromone **1b** (540 mg) in methanol (35 ml), iodobenzenediacetate (1 gm) was added and stirred overnight. Next day it was diluted with water and extracted with ether. The ethereal layer was washed with water, dried (Na_2SO_4) and solvent distilled off. The colourless solid obtained was crystallised from chloroform-petroleum ether (620 mg, 85%); m.p. 92-94°C. IR 1690, 1610 cm^{-1}. ^1H NMR (CCl_4) δ 1.63 (s, 3H), 3.09 (s, 3H), 3.19 (s, 3H), 4.44 (br s, 1H, exchangeable with D_2O), 6.83-8 (m, 4H). Anal. Calcd. for $C_{12}H_{14}O_5$: C, 60.5; H, 5.9. Found : C, 60.07; H, 6.1%.

Photolysis of the chromanone 5

The chromanone 5 was subjected to photolysis in benzene or methanol for 2h under previously described conditions. Removal of solvent followed by crystallisation of the solid residue furnished 2-methyl-3-hydroxychromone **1b** in 80-85% yields. This was identified from comparative spectral and m.p. determination with an authentic sample.

Acknowledgement

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