

Intramolecular Photorearrangement of a 2-Alkenyl-4-Chromanone to an Oxapentacyclotetradecanedione

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Abstract: A novel transformation of 7-hydroxy-2-methyl-2-(4-methyl-3-pentenyl)-4-chromanone (**1**) to intramolecular 1,3-arene-alkene photocycloadduct, (*1S,2R,5S,7S,10S,13R*)6,6,10-trimethyl-14-oxapentacyclo[8.3.1.0^{1,7}.0^{2,13}0^{5,13}]tetradecane-3,12-dione (**3**) via secondary photorearrangement of 1,2-arene-alkene photocycloadduct (**2**) has been described. © 1997 Published by Elsevier Science Ltd.

Intramolecular arene-alkene photocycloadditions have provided elegant strategies for the synthesis of difficultly accessible multicyclic organic compounds.¹ 2-Alkenyl-4-chromanones are attractive substrates for such photoaddition reactions as the alkenyl side chain of the heterocyclic ring provides an additional functionalised carbocyclic ring with several stereogenic centers. These features impart stereo- and regioselectivities and offer interesting possibilities for the synthesis of variety of fused multicyclic ring compounds. Earlier, we have shown that in 7-hydroxy-2-methyl-2-(4-methyl-3-pentenyl)-4-chromanone (**1**) and its alkyl ethers, the 4-methyl-3-pentenyl side chain undergoes intramolecular photocycloaddition with arene counterpart through triplet ketone furnishing 1,2-arene-alkene photocycloadduct **2**.² The product was characterized by extensive 2D NMR spectroscopy and X-ray crystallography.³ In the present communication we report yet another novel phototransformation of **1** to intramolecular 1,3-arene-alkenephotocycloadduct (**3**)⁴.

Photolysis of **1** in benzene gave the 1,2-arene-alkene photocycloadduct (**2**) in 30% yield². However, when **1** was photolysed in methanol as a solvent, a different product **3** (m.p. 94 °C) was formed as the major product (38% yield) while **2** was obtained as a minor component (>5%). The GC-MS analysis showed that **3** had a same molecular formula C₁₆H₂₀O₃ (M⁺, 260) as that of **2** but the mass spectral fragmentation was different. The IR, UV, 1D ¹H and ¹³C NMR spectra suggested the absence of enone system in **3**. The structure was derived by extensive use of multidimensional NMR spectroscopy (Table - I)⁵. The scalar coupling network was established by ¹H-¹H COSY. The multiplicity and resonances of the protonated carbons were assigned by ¹H - ¹³C HETCOR and DEPT experiments. Based on the data, **3** or the lumiketone type A photorearranged product **3a** could be proposed to the new photoproduct. The information on long range couplings derived from COLOC spectra was very useful in distinguishing structures **3** from **3a**. The three bond interactions between C-1 and H-8 as well as C-13 and H-4 observed in the COLOC spectrum could be explained only by **3** (Fig. 1). The absence of the interaction between C-13 and H-8 (as expected for **3a**) further supported the structure **3** for the photoproduct. The structure of the product was further confirmed as (*1S,2R,5S,7S,10S,13R*)6,6,10-trimethyl-14-oxapentacyclo[8.3.1.0^{1,7}.0^{2,13}0^{5,13}]tetradecane-3,12-dione⁶ (**3**) by X-ray crystallography.⁷ The perspective view of the molecular plot of **3** shows that the pyranone ring adopts a distorted chair conformation (Fig. 2).

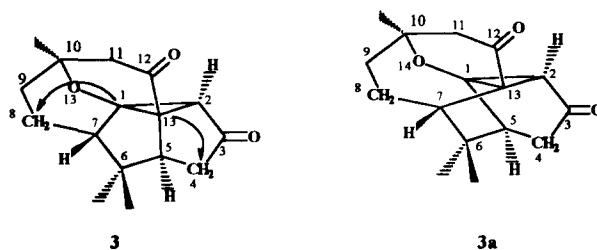
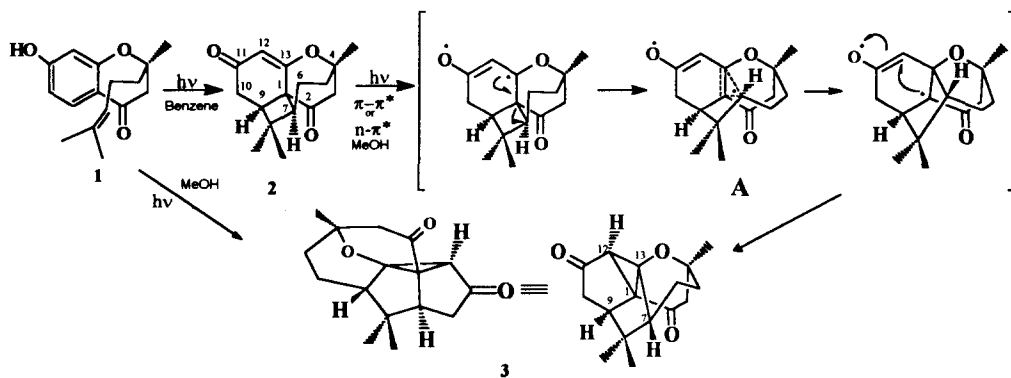


Fig. 1 Important COLOC interactions in 3

Apparently, the structure 3 corresponds to an intramolecular 1,3-arene-alkene photocycloadduct of 1. A careful monitoring of the progress of the photoreaction (TLC and GLC) revealed that 2 was formed in the initial stages. On continued photolysis, the concentration of 2 showed a progressive decrease while that of 3 increased. After photolysis for 5 hr, 3 was found to be the major product. This suggested that the 1,2-arene-alkene photocycloadduct (2) could be the primary transformation product of 1 while 3 could be a secondary phototransformation product. In order to investigate this hypothesis, photolysis of 2 was carried out. The phototransformation of 2 proceeded smoothly in *t*-butanol as well as methanol and 3 was obtained as a crystalline solid (63% yield).



Scheme-1

The pathway for the formation of 2 was established in our earlier communication². The mechanism for the stereospecific internal rearrangement of 2 to 3 is proposed in Scheme 1. The photoproduct 2 has a highly strained tetracyclic system with enedione chromophore (α,β -enone with respect to the carbonyl at C-11 and β,γ -enone with respect to C-2 carbonyl). The formation of 3 can be explained by bond rearrangement of fused cyclobutane and cyclohexenone ring systems via 1,2-shift involving α,β -enone. Zimmerman's propositions of 1,2-shift in α,β -enone rearrangements⁸ may be applicable to this phototransformation. Thus, the excitation of α,β -enone ($n-\pi^*$ or $\pi-\pi^*$) chromophore of 2 followed by the scission of the C-1 -C-7 bond gives the diradical intermediate A with delocalised electrons between C-1, C-7 and C-13. The formation of a new bond between C-7 and C-13 takes place from the *front* side while that between C-1 and C-12 from the *rear* face in a concerted manner. The steric constraints in the structure leads to a highly stereospecific bond formations. In this rearrangement relative stereochemistry at C-1, C-4, and C-9 remained unaffected while there is inversion at C-7.

Thus, above evidences suggest that though **3** apparently corresponds to an intramolecular 1,3-arene-alkene photocycloadduct, in fact, it is formed *via* internal photorearrangement of the 1,2- arene-alkene photocycloadduct **2** and therefore is not a true case of *meta* photocycloaddition of **1**. This presents a novel example of secondary transformation of *ortho* to *meta* photocycloadduct. This photoreaction allows easier access to highly functionalised oxapentacyclic fused ring system in one pot.

REFERENCES AND NOTES

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2. Kalena, G. P.; Pradhan, P.; Banerji, A. *Tetrahedron Lett.* **1992**, *33*, 7775.
3. Kabaleswaran, V.; Rajan, S. S.; Kalena, G. P.; Pradhan P.; Banerji, A. *Acta Cryst.* **1995**, *C52*, 1981.
4. A part of this work was presented at the IUPAC - Post ICOS-10 Symposium, *New Horizons in Organic Synthesis*, Regional Research Laboratory, Trivandrum (India), 1994, p. 23.
5. **Table - I NMR data of compound 3[#]**

Carbon No	δ (¹³ C) in ppm	Carbon multiplicity DEPT	δ (¹ H) based on HETCOR ppm	Proton numbers		
				COSY	NOESY	COLOC
C-12	55.5	CH	2.81		H-10", H-10', Me-8'	
C-9	47.9	CH	2.70	H-10', H-10"	Me-4'	Me-8", Me-8'
C-3	51.9	CH ₂	1.86, 2.08			Me-4'
C-10	45.6	CH ₂	1.98, 2.13	H-9		
C-7	47.3	CH	2.04	H-6', 156	Me-8", H-6'	Me-8", Me-8', H-5'
C-6	21.9	CH ₂	1.46, 1.56	H-5', H-5", H-7	H-7, 1.14, H-5"	
C-5	31.0	CH ₂	1.31, 1.10	H-6', H-6"	H-6', Me-4'	H-7, H-3', H-6', Me-4'
C-4'	27.5	CH ₃	0.90		H-10', H-5'	H-5'
C-4	80.0	>C<				Me-4', H-6', H-3'
C-8'	28.0	CH ₃	0.71		H-9	H-7, Me-8"
C-8"	28.8	CH ₃	0.40		H-7	H-9, Me-8'
C-8	44.7	>C<				Me-8", Me-8', H-5", H-7
C-13	77.8	>C<				H-9, H-7, H-6'-H-6"
C-1	55.6	>C<				H-7, H-10', H-10"
C-2	202.2	CO				H-3', H-3"
C-11	206.1	CO				H-12, H-10"

[#]Spectra were recorded in C₆D₆ on Bruker AC-200 (200MHz) NMR spectrometer.

6. The IUPAC name of **3** was generated with the courtesy of ACD LabsTM through internet.

7. The crystal and molecular structures of the photoproduct **3**, $C_{16}H_{20}O_3$ has been determined from single crystal X-ray diffraction. The compound crystallizes in monoclinic centrosymmetric space group $P2_1/c$ from n -hexane. The cell parameters are $a = 7.237(2)\text{\AA}$, $b = 19.977(1)\text{\AA}$, $c = 9.850(2)\text{\AA}$, $\beta = 107.92(1)^\circ$, $V = 1354.9(5)\text{\AA}^3$, $Z = 4$, $D = 1.276\text{ Mg/m}^3$, $F(000) = 560$, $\mu = 0.811\text{ cm}^{-1}$, $T = 295\text{ K}$, $R = 6.55$ and $R_w = 7.38$. The detailed structure will be discussed elsewhere.

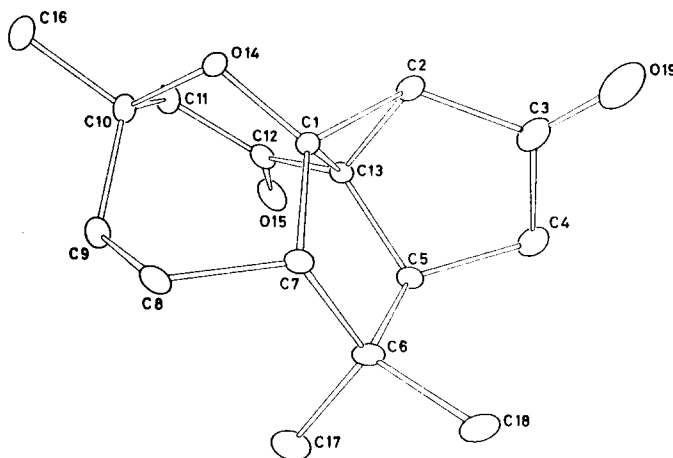


Fig. 2 X-ray crystal structure of **3**

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