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PHOTON INDUCED REACTIONS - II
NOVEL PHOTODIMER OF A 3-METHOXY CHROMONE

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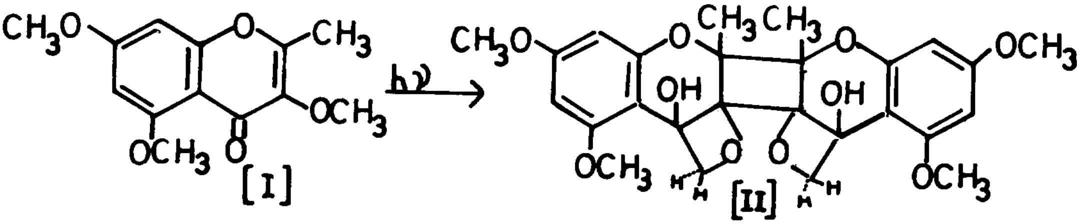
Amongst the reactions of photochemically excited carbonyl group, hydrogen abstraction[1] from the γ-position is well known and mechanistically well investigated. Photolysis of ω-methoxy ketones[2], their sulphur analogues[3] and other straight chain compounds[4] containing this feature, gives along with other products, oxetanols by cyclisation of biradical intermediates. In 3-methoxy flavones[5], the rigid planar-structure does not allow the radical produced from the methoxyl group to form an oxetanol, instead cyclisation with the side phenyl ring, through a six membered transition-state, becomes a highly favoured reaction. We wish to report here the photolysis of a 3-methoxy chromone where the absence of side phenyl ring results in an unusual simultaneous, dimerisation and oxetanol formation.



Irradiation (254 nm) of 2-methyl-3,5,7-trimethoxy chromone (I) in THF for 60 hr and subsequent work up, gave a yellow oil. Chromatography of this oil on silica gel and elution with EtOAc-benzene, gave (II), colourless plates from $CHCl_3$-CH_3OH, m.p. 258-60°, (tlc, EtOAc: C_6H_6-2:8, R_f 0.35). The molecular ion peak (M^+ 500) and elemental analysis, (Found: C, 62.6; H, 5.8. $C_{26}H_{28}O_{10}$ requires C, 62.4; H, 5.6%) showed that the product is a dimer. IR spectrum [ν_{max}^{Nujol} 3620 cm^{-1} (non-bonded OH), 950 and 850 cm^{-1} (cyclobutane ring[6])] did not show any carbonyl absorption indicating that the pyrone ring is involved in this dimerisation. The OH group is alcoholic as is shown by the absence of any alkali induced bathochromic shift in the UV maximum (λ_{max}^{MeOH} 258 nm). Presence of oxetanol ring[1,3] in the molecule is clearly indicated from its NMR spectrum $\left[CDCl_3\ \delta \right.$, 1.60 (s, 3H, CH_3); 3.85 (s, 3H, OCH_3); 3.90 (s, 3H, OCH_3); 4.80 (d, 1H, $C{<}^{H}_{H}$ of oxetanol ring, $J_{C{<}^{H}_{H}}$ 6.5 Hz); 5.38 (d, 1H, $C{<}^{H}_{H}$ of oxetanol ring, $J_{C{<}^{H}_{H}}$ 6.5 Hz); 5.80 (s, 1H,-O-H, D_2O induced collapse); 6.16 (s, 2H, aromatic)$\left. \right]$ which also showed the symmetrical nature of this dimer. The presence of oxetanol ring in this dimer is further confirmed by the presence of m/e 482 ($M^+ - H_2O$), m/e 464 ($M^+ - 2H_2O$) in its mass spectrum.

Of the several stereochemical possibilities for a dimeric oxetanol structure, accommodating the above data, the head to head structure (II) is preferred on the analogy of formation of similar dimers from thymine[7] and dihydro-γ-pyrone[8]. Existing data, however, does not allow us to distinguish between the cis-syn-cis and cis-anti-cis isomers of (II). An X-ray investigation of (II) is under progress.

As far as we know, this is the first case in literature of the simultaneous formation of an intramolecular oxetanol and an intermolecular dimerisation.

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