

NOTE**Phototransformation of a Six Membered Ring Formyl Ketone (2-Formyl-1-tetralone)**

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With a view to examine the structural dependence of photochemical change in β -dicarbonyl compounds irradiation of six membered ring formyl ketone *i.e.* 2-formyl-1-tetralone (I) was done in dry ethanol and benzene separately. This diketone was converted into 1-hydroxy-2-naphthaldehyde (II) in each case.

In the broad area of photochemistry a great deal of interest has been centred on the systems containing carbonyl chromophore, since the nature of initial electronic transitions in this group became better understood and also due to the fact that this function is encountered so frequently in the synthetic sequence. With a view to studying the structural dependence of photochemical change in β -dicarbonyl compounds irradiation of a six-membered ring formyl ketone was done.

Preparation of 2-Formyl-1-tetralone: 2-Formyl-1-tetralone was made from γ -keto- γ -phenyl-butyric acid in a three stage sequence in accordance with the procedure described in the literature.¹

Irradiation of 2-Formyl-1-tetralone (I) in ethanol

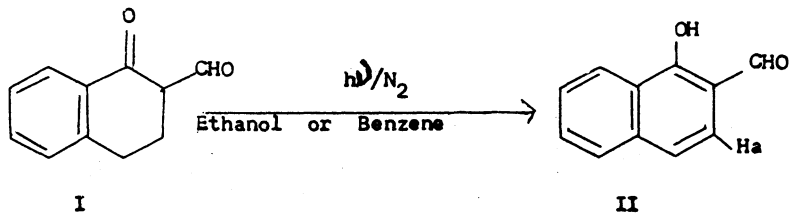
An oxygen free solution of 2-formyl-1-tetralone (1 g) in dry ethanol (150 mL) was irradiated for a total period of 25 h, using light from a 125 watts medium pressure mercury arc, in a pyrex reactor. Nitrogen gas was continuously bubbled through the solution during the entire course of reaction. Thereafter, ethanol was distilled off and residual material was chromatographed over silica gel (30 g, slurry made in pet. ether). Elution with benzene-pet.-ether mixture (1 : 3) yielded 60 mg of a thick oil which solidified on keeping. It was crystallized from pet.-ether. (m.p., 54°C). This formed a 2,4-dinitrophenyl hydrazone, m.p. 160°C and gave a positive test with ferric chloride.

Irradiation of 2-Formyl-1-tetralone (I) in benzene

When oxygen free solution of 1 g of 2-formyl-1-tetralone (I) was irradiated for 60 h under the conditions as described in the above experiment and the photolysate was worked up in the same manner. Chromatography of the residue (using silica gel and benzene-pet.-ether (1 : 3) eluent) furnished, in a reduced yield, aldehyde (II). Its identity was established through their superimposable IR spectra and undepressed mixture, m.p. 52°C, with authentic sample.²

In furtherance of the photochemical studies being carried out on β -dicarbonyl compounds³ and with a view to examining the structural dependence of the

manner of photochemical change in such compounds, the irradiations of a six membered ring formyl ketone *i.e.*, 2-formyl-1-tetralone(I) in ethanol and benzene have presently been examined separately. In each case it leads to produce a dehydrogenated derivative (II) of the substrate.



The low melting compound (II, 54°C) revealed the highest peak in its mass spectrum at m/e 172 (80%) suggesting it a dehydrogenated product of (I). Peaks at m/e 143 (showing loss of 29 mass units *i.e.* formyl radical) and m/e 126 (showing loss of both CHO and OH radicals from molecular ion) are suggestive of the presence of formyl and hydroxyl groups in the compound (II). Presence of CHO group in (II) was also revealed from a signal (a singlet) at δ 9.90⁴ in its 80 MC NMR spectrum (CDCl_3) though the C—H stretching vibrations due to —CHO in its IR spectrum (recorded in Nujol) could not be discerned. A look at the hydroxyl group region of IR spectrum showed only a weak band around 3100 cm^{-1} . The compound (II), however, gave a positive FeCl_3 test. However, a strong band around 1630 cm^{-1} suggested the presence of a chelated carbonyl group (which also accounts for the observed very weak hydroxyl band). In the UV, this compound (II) absorbed at 261 $m\mu$ (ϵ 27520) and 281 $m\mu$ (ϵ 7052).

From its mass spectrometric molecular weight (172) and from NMR and mass spectral evidence structure(II) for this compound is suggested. Other features of its NMR spectrum were a one-proton doublet (tendency to split further) centred at δ 3.35 ($J = ca$ 80 ps) which is ascribable to Ha in (II) and unresolved multiplets spread in the region δ 7.50–7.20 (aromatic Hs).

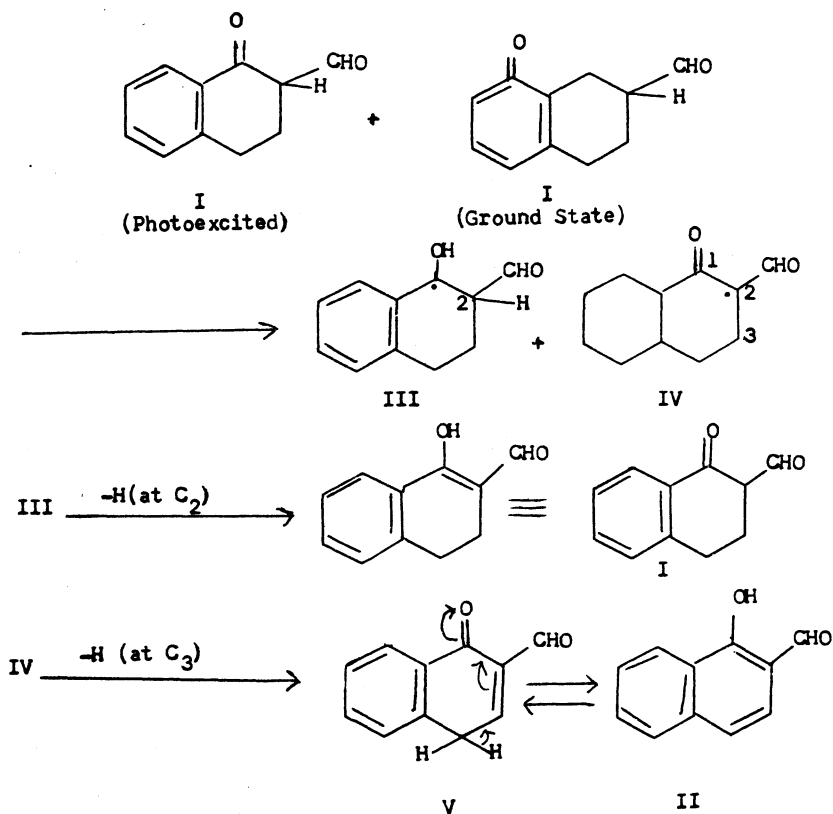
Lit.² records m.p. 55°C for 1-hydroxyl-2-naphthaldehyde (II).

A few comments might here be made on the mechanism of photodehydrogenation of (I) to lead to (II). A sequence that might be operative here should involve the intermolecular hydrogen abstraction by the photo-excited formyl-ketone (II) to lead to the twin radicals (III) and (IV).

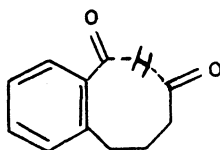
The mono radical (III) through further loss of an H radical (at C_2) should revert to the starting formyl-ketone (I), while the other mono radical (IV) perhaps suffers loss of an H radical (at C_3) to form 2,3-dehydro derivative (V) which reorganizes in the manner show to produce the hydroxy aldehyde (II).

A support to such a mechanism comes from the observation that this photo^{5,6} transformation (I to II) does not show strong solvent dependence.

It might here be recalled that the photolysis of 2-formyl-3-phenyl- and (3-methyl)-1-indanone have been observed to produce the corresponding aldehyde esters.^{5,6} The absence of such a course in the presently studied photo conversion of (I) appears to be due to the fact that this would have required the intervention of an eight-membered high energy cyclic transition state (VI) in an



intramolecular hydrogen abstraction. Also in the present case, no product of photoreduction (of I) could be detected in the photolysis mixture.



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