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UNUSUAL PATTERNS OF REACTIVITY IN THE PHOTOLYSIS OF A SUBSTITUTED 4-ACETYLQUINOLINE

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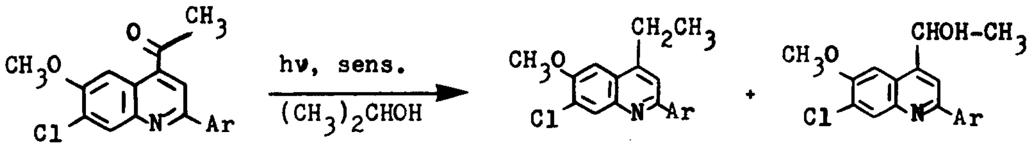
The reported phototoxicity of many 2-arylquinoline derivatives[2] has prompted us to study patterns of photochemistry of similarly substituted quinolines. In contrast to the well-studied benzene and naphthalene compounds, little is known about the photochemistry of substituted quinolines. We wish to report some intriguing differences between the photochemistry of a quinoline ketone and similar carbocyclic aromatics.

The 2-(p-methoxyphenyl)-4-acetyl-6-methoxy-7-chloroquinoline (1) was synthesized from the known[3] 2-(p-methoxyphenyl)-6-methoxy-7-chloroquinoline-4-carboxylic acid and methyllithium. Sensitized photolysis of 1 (using xanthone, benzophenone, or acetophenone) under nitrogen in isopropyl alcohol gave a single product. This product was identified as the 4-ethylquinoline 2, mp 158-160°, by independent synthesis[4] (Wolff-Kishner reduction of 1). When the photolysis was interrupted at 60% conversion, about 5% of a second product was present. The new product, which was separated from the mixture by silica gel chromatography, proved to be alcohol 3, mp 176-78°, which could be synthesized by reduction of ketone 1 with lithium aluminum hydride.



1 Ar = p-CH_3O-C_6H_4 2 3

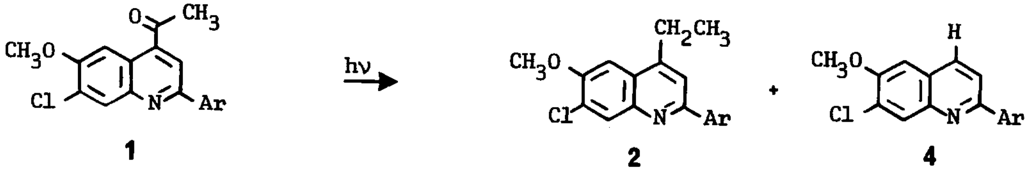
Additionally, it was determined that photolysis of 3 under the same conditions as described for 1 gave 2 as the sole product. Consequently, 2 is likely produced in a multi-step mechanism involving two photons.

$$1 \xrightarrow{h\nu} 3 \xrightarrow{h\nu} 2$$

The conditions were such that the sensitizer absorbed >95% of the light (pyrex filter, large molar excess of the sensitizer). Since no change in behavior was noted with xanthone, a sensitizer generally[5] unreactive as a "chemical sensitizer", a triplet state is probably involved both in the formation of 2 and 3. This assignment is consistent with the quenching results presented later.

The rapidity of formation of product (complete conversion of 200 mg of 1 by a 30 min photolysis with a 450W Hanovia medium-pressure mercury lamp) suggested that the quantum yield would be high. Using benzophenone/benzpinacol actinometry,[6] and irradiating with a Rayonet Preparative Reactor equipped with RUL 3500 lamps (3500 Å) the overall quantum yield for formation of 2 was determined to be 0.05. If 2 is formed by two sequential photochemical steps, this overall quantum yield equals ½ the product of the Φ for each step. The quantum yield for conversion of 3 to 2 was determined to be 0.1. This indicates that the Φ for the first step (conversion of 1 to 3) would be near unity.

The direct photolysis of 1 in isopropyl alcohol led to a second surprising result. Irradiation with a Hanovia lamp and vycor filter under nitrogen led to formation of two products in about equal amounts.



The involvement of a singlet state in the formation of **4** was suggested by quenching experiments. Photolysis of **1** in the presence of cyclohexadiene (or alternatively in an oxygen-saturated solution) did not suppress the formation of **4**, but decreased the incidence of **2** so that it was a minor product. The results can be summarized:

	2	**4**
direct photolysis	major product	major product
added quencher	minor product	major product
sensitized photolysis	major product	not detected

The efficient photoreaction of **1** contrasts with the low quantum yields of photoreduction of carbocyclic analogs. 1-Naphthaldehyde ("not reactive" in isopropyl alcohol),[7] 2-acetonaphthone ("not reactive" in isopropyl alcohol),[7,8] and β-naphthyl n-butyl ketone ($\Phi = 0.002$)[9] react much less efficiently. The characteristically low reactivity of $^3\pi,\pi^*$ states towards photoreduction[10,11] is responsible for the low reactivity in such systems. The enhanced reactivity of this quinoline ketone suggests that the complication of the heteroatom may have a profound affect on the reactivity of similar quinoline compounds.

Although the formation of **4** can be rationalized by a Type I cleavage, such a cleavage of the sp^2-sp^2 bond is unprecedented and has been suggested to be unlikely on energetic grounds.[12] A more complex mechanism involving initial reduction of the quinoline ring must be considered. We intend further studies to elucidate the mechanism of formation of **2**, **3**, and **4**, and to clarify the enhanced efficiency of reaction of this quinoline system.

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