

Gary A. Epling*, Kuei-Ying Lin, and Anil Kumar

Department of Chemistry, University of Connecticut,

Storrs, CT 06268

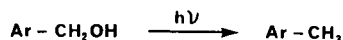
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The photoreduction of a family of quinolinemethanols has been examined both in the presence and absence of exciplex-forming additives. Photoreduction of the alcohol group and cleavage of the side chain occurs on direct photolysis. However, irradiation with triethylamine led to predominant cleavage of the side chain while irradiation with 1,3-dicyanobenzene predominantly led to photoreduction of the alcohol functionality. A variety of other experiments supported the involvement of exciplexes in these transformations.

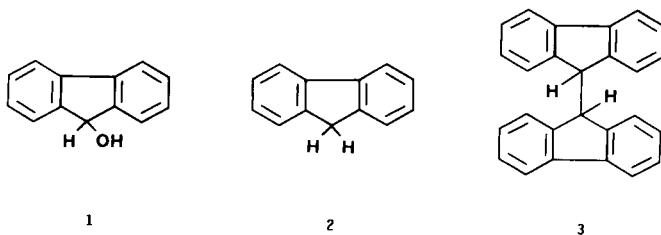
J. Heterocyclic Chem., **25**, 425 (1988).

Introduction.

The irradiation of simple alcohols in liquid or gas phase gives predominant homolytic O-H bond cleavage [1], but there have been a number of reports of photoreduction of pyridine- or quinolinemethanol compounds to produce "deoxy" materials [2-7].



We were intrigued by the different mode of cleavage (C-C bond cleavage) which occurs when a nitrogen is present in the side chain [8]. Though quinoline excimers have been reported [9] photoreaction of quinoline exciplexes has not been suggested in the aforementioned studies. Ohashi's study [10] of the photoreduction of fluoren-9-ol (**1**) established the importance of an exciplex in the formation of **2** and **3**. His mechanism, like that described by



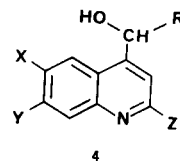
Bartrop [11] in the photoreduction of carbocyclic aromatics, involved reaction initiated by an electron transfer to the aromatic. Though a mechanism for photoreduction of the previously described heterocyclics involving homolysis has been proposed [3] an attractive alternative is a mechanism similar to Ohashi's involving an exciplex with considerable charge transfer character.

We have studied in detail the photoreduction of six quinolinemethanols under a variety of conditions to establish whether reaction might proceed through an exciplex. Our results indicate the involvement of exciplexes as reactive intermediates. However, the product of photoreduction, efficiency of photoreaction from the exciplex, and the extent of exciplex involvement varies from case to case.

Results and Discussion.

Photoreaction of Quinolinemethanols.

We studied the photoreaction of six quinolinemethanol compounds, **4a-4f**, which contain variously both electron-withdrawing and supplying substituents.



4a R = H, X = H, Y = H, Z = phenyl

4b R = H, X = CH₃O, Y = H, Z = *p*-tolyl

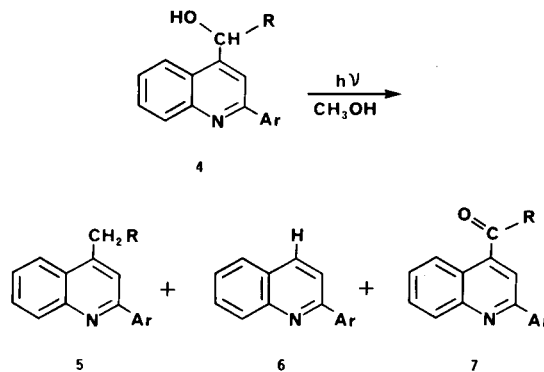
4c R = H, X = CH₃O, Y = H, Z = 3,4-dichlorophenyl

4d R = H, X = CH₃O, Y = Cl, Z = *p*-methoxyphenyl

4e R = CH₃, X = CH₃O, Y = H, Z = 3,4-dichlorophenyl

4f R = CH₃, X = CH₃O, Y = Cl, Z = *p*-methoxyphenyl

Irradiation of these compounds in neutral, alcohol solutions gave the expected photoreduction, though varying amounts of carbon-carbon bond cleavage (**6**) and aldehyde **7** were observed (see Table 1).



In most cases photoreduction proceeded primarily to the deoxy compound in a manner analogous to the aforementioned cases. Photoreaction was particularly "clean" with the compounds containing halogens.

Table 1
Photoproducts from 4-Quinolinemethanols

Compound	Additive	Yield, %		
		4	5	6
4a	None	84.	0.2	11.
	triethylamine (0.05 <i>M</i>)	22.	24.	49.
	1,3-dicyanobenzene (0.002 <i>M</i>)	52.	0.0	47.
	HCl (0.2 <i>M</i>)	major		
4b	None	65.	9.	26.
	triethylamine (0.05 <i>M</i>)	22.	24.	49.
	1,3-dicyanobenzene (0.002 <i>M</i>)	53.		47.
	HCl (0.1 <i>M</i>)	16.	3.	81.
4c	None	90.	10.	0.0
	triethylamine (0.05 <i>M</i>)	1.	96.	0.0
	1,3-dicyanobenzene (0.002 <i>M</i>)	100.		
	HCl (0.1 <i>M</i>)	36.	2.	
4d	None	28.		65.
	triethylamine (0.05 <i>M</i>)	0.0	100.	0.0
	1,3-dicyanobenzene (0.002 <i>M</i>)	36.	2.	
4e	None	100.	0.0	0.0
	triethylamine (0.05 <i>M</i>)	85.	15.	0.0
	1,3-dicyanobenzene (0.002 <i>M</i>)	51.	11.	
4f	None	100.	0.1	0.0
	triethylamine (0.05 <i>M</i>)	0.0	99.	0.0
	1,3-dicyanobenzene (0.002 <i>M</i>)	24.		71.

Table 2
Quantum Efficiencies of
4-Quinolinemethanol Photoreactions

Compound	Concentration, mM	Additive	$\phi \times 10^4$
4a	0.85	None	8.7
	0.85	triethylamine (0.05 <i>M</i>)	4.3
	0.85	1,3-dicyanobenzene (0.002 <i>M</i>)	33.
	0.85	HCl (0.2 <i>M</i>)	54.
4b	0.71	None	59.
	0.71	triethylamine (0.05 <i>M</i>)	7.4
	0.71	1,3-dicyanobenzene (0.002 <i>M</i>)	225.
	0.71	HCl (0.1 <i>M</i>)	20.
4c	0.60	None	8.0
	0.60	triethylamine (0.05 <i>M</i>)	2.0
	0.60	1,3-dicyanobenzene (0.002 <i>M</i>)	7.0
	0.60	HCl (0.1 <i>M</i>)	3.0
	0.60	piperylene (0.10 <i>M</i>)	42.
4d	1.21	None	56.
	1.21	triethylamine (0.05 <i>M</i>)	32.
4e	1.15	None	27.
	1.15	triethylamine (0.05 <i>M</i>)	17.
	1.15	1,3-dicyanobenzene (0.002 <i>M</i>)	20.
4f	1.16	None	13.
	1.16	triethylamine (0.05 <i>M</i>)	34.
	1.16	1,3-dicyanobenzene (0.002 <i>M</i>)	60.

Quinolinemethanol Photoreaction in the Presence of Amines.

Trialkylamines are known to form exciplexes with many electronically excited aromatic compounds [12]. Our observation [13] that amines are efficient quenchers of the fluorescence of the 2-phenylquinoline chromophore suggested their photoreactivity might be subsequently altered. Irradiation of **4** with amines present affected both the rate and products of photoreaction. Table 1 shows the alteration in product distribution. In the presence of amines the minor product, **6**, encountered in direct photolysis generally became the major photoproduct. The rate of reaction (Table 2) was also affected, generally being retarded by the presence of amines. The reaction of **4c**, for example, was retarded 23% by the presence of 0.11 *M* triethylamine; more affected were the other compounds, with all showing a retardation of rate of reaction except **4f**, which reacted faster with amines present.

Quinolinemethanol Photoreaction in the Presence of 1,3-Dicyanobenzene.

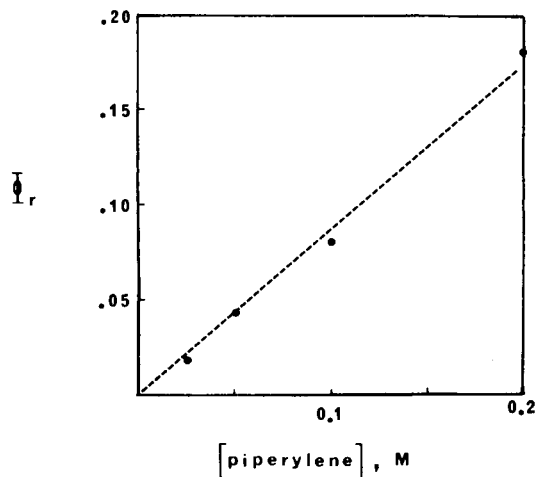
Since exciplexes from trialkylamines are most appropriately considered as having transferred an electron from the trialkylamine to the aromatic ring, an exciplex from an aromatic compound and 1,3-dicyanobenzene ("DCNB") would have the opposite type of charge separation (involving electron transfer *to* the DCNB). Irradiation of the quinolinemethanols in the presence of DCNB, like the amines, led to alteration of both reaction rate and products of reaction. Table 1 shows the alteration in product distribution, reflecting primarily a change to a greater amount of **7** and even less of **6** than direct photolysis. The reaction rate was slower in the presence of DCNB with some compounds, with other (*e.g.* **4b**) the reaction was faster (Table 2).

Effect of Acidity on Photoreaction.

Whereas previous studies of pyridine- or quinolinemethanol photoreduction have been performed in strongly acidic media, the photolyses discussed above involved neutral solutions. In a few instances photoreaction in strong acid was also studied, but these reactions were generally less efficient (Table 2). A shift in product distribution was also noted, with a greater tendency to form **7** being encountered in acid.

Photoreaction in the Presence of Piperylene.

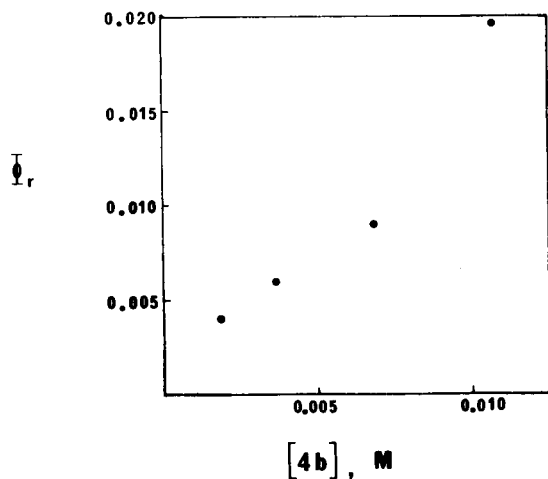
A few experiments examined the effect of piperylene, a typical excited state "quencher". In this case the effect was to increase the overall reactivity (Figure 1). However, as with DCNB and the presence of acid, the piperylene caused the formation of less **5** and a greater yield of **7**.

Figure 1. Piperylene Effect on Photoreaction of **4c**.

In this case it appears that deactivation of the excited triplet of **4** by energy transfer does not occur; exciplex formation with the piperylene appears to happen.

Concentration Effect on Efficiency of Photoreduction.

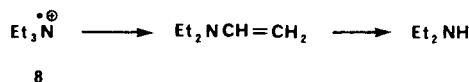
The observed alteration in quantum efficiency and products of photoreaction by the presence of exciplex-forming additives led us to examine the effect of concentration of the heterocyclic alcohol itself upon photoreduction. With **4c** there was no apparent effect of concentration on the rate of photoreaction. However with **4b** the photoreaction was more efficient at higher concentrations (Figure 2). This concentration dependence suggested the intermediacy of an excimer of **4b** as a precursor to photoreaction.

Figure 2. Concentration Dependence of Photoreaction of **4b**.

Dealkylation of Added Amines.

Photoreactions involving exciplexes with amines have been carefully studied by Cohen [14], who established that

electron transfer from the amine (to give **8**) leads to fragmentation of the amine. When triethylamine was the donor the subsequent fragmentation gave diethylamine.



We determined that such a reaction *was* occurring upon irradiation of **4** in the presence of amines, providing further evidence for exciplex formation. These secondary amines were conveniently quantitated with Sanger's reagent (fluoro-2,4-dinitrobenzene) which reacts with the dialkylamine to produce a product that absorbed strongly at 380 nm. In two typical irradiations in the presence of methyl-di-*n*-butylamine we observed a 43% yield (from **4c**) and 39% yield (from **4b**) of di-*n*-butylamine, based upon reacted starting material, at concentrations of amine sufficiently high to completely quench the fluorescence of **4**.



Deuterium Incorporation into Photoproducts.

To probe the mechanism of the photoreduction the photolysis of **4c** was examined in monodeuteriomethanol. Photoreaction proceeded as in ordinary methanol. The protio product **6c** was determined by both ms and nmr to have incorporated 20% of a deuterium; the methyl compound (**5c**) incorporated 91% of a deuterium. Similarly, the irradiation of **4b** led to the protio compound **6b** which had 8% deuterium incorporation. Thus, the major path that leads to the protio compound involves a hydrogen atom abstraction, whereas a proton becomes incorporated in the major route to the methyl compound.

Multiplicity of Reactive Excited State.

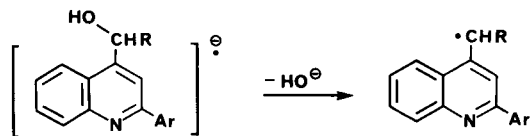
The possibility of photoreaction from triplet states of **4** led us to attempt sensitized irradiations. Since the triplet energy of **4** is approximately 60 Kcal/mole [15], benzophenone and xanthone were chosen as photosensitizers. Under conditions where the sensitizers absorbed greater than 90% of the incident light an enhancement of reaction rate of a factor of 30 to 50 was observed, with **5** observed as the major photoproduct. Lower energy photosensitizers (Michler's ketone and 2'-acetonaphthone) also led to enhanced photoreactivity, but the product mixture became complex (as with photoreaction in the presence of piperylene) and a variety of products were observed. It is likely that with those compounds an efficient transfer of triplet energy did not occur, but exciplex formation may have occurred.

The ability of triplet sensitizers to enhance photoreactivity implicates the triplet state as a precursor to photoreaction. Supporting this conclusion was the observed

quenching of photoreaction of **4a** and **4c** by oxygen. Complicating the assignment of the multiplicity of the reactive excited states involved is the apparent ability of exciplexes to undergo photoreaction. Consequently, the triplet "quencher" piperylene in fact led to enhanced photoreactivity by exciplex formation. This behavior has precedence-enhanced photoreactivity of aryl chlorides due to exciplex formation with dienes [16]. In spite of these complications, it is apparent that formation of the triplet state leads to enhanced photoreactivity. Increased photoreactivity may partially be a consequence of its longer lifetime, allowing exciplex formation (a bimolecular process) to be more efficient. Inefficient formation of the triplet from direct photolysis in alcohol is evidenced in part by the high efficiency of fluorescence [13,15] and inefficient phosphorescence, in contrast with efficient phosphorescence in hydrocarbons [15].

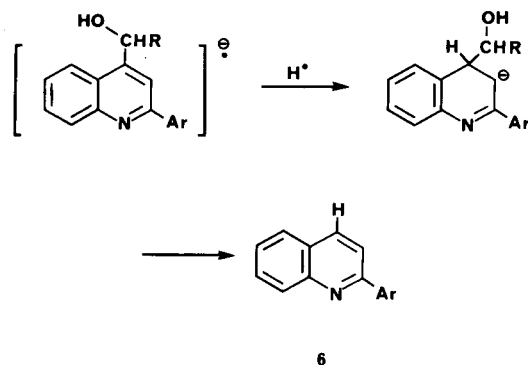
Mechanisms of Photoreaction.

The most surprising mechanistic conclusion is that the photoreduction of **4** to **5** is quite different from the amine-enhanced photoreduction of **1** to **2**. In the presence of amines the efficiency of reaction of **4** generally diminished, and the preferred reaction pathway was altered. Consequently, the formation of an exciplex that is electron-rich on **4** does *not* undergo efficient photoreaction by loss of the hydroxy group as observed by Ohashi [10]. However, the previously-proposed mechanisms involving protonation in strong acid also do not appear important, since



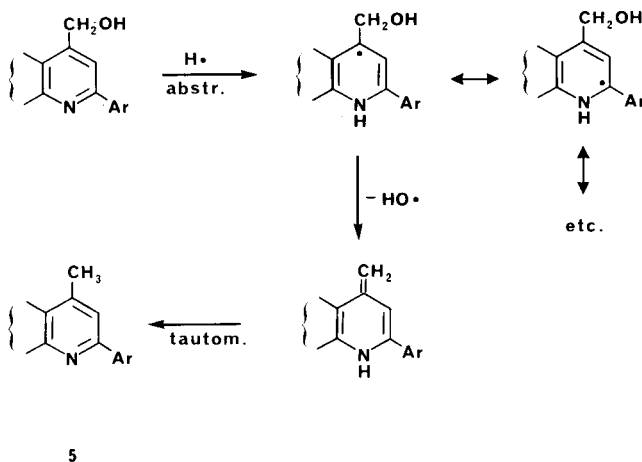
acid diminishes both the quantum efficiency of photoreaction and the tendency to give **5**. Nevertheless, the enhanced photoreactivity of **4c** at higher concentrations, apparently from excimer formation, suggests that the inherent photoreactivity of an exciplex of **4** depends not only on whether an exciplex is formed, but on the amount of charge transfer and stability of the exciplex. Thus, a charge transfer from amines leads to a less reactive exciplex than an exciplex involving piperylene. Similarly, in some cases an exciplex involving DCNB becomes more reactive, in some cases less reactive. Consequently, it is difficult to write "classical" mechanisms of photoreaction (involving a specific number of electrons), since photoreaction may well be triggered by partial charge transfer but quenched by transfer of a whole charge.

The photoreaction of **4** to **6** illustrates this point. A mechanism involving a negatively charged aromatic ring might proceed by a hydrogen atom abstraction, then fragmentation.

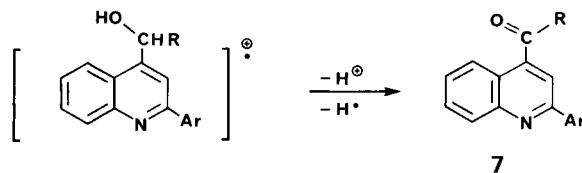


Abstraction of a hydrogen atom is consistent with the results of deuterium labeling experiments, though a *proton* abstraction *a priori* might seem more plausible due to the negative charge.

Photoreaction of **4** to **5**, which clearly involves incorporation of a proton on the α carbon from the deuterium labeling studies, might proceed by the abstraction of a hydrogen atom on the aromatic ring, loss of a hydroxyl radical, then tautomerization (which would predominantly lead to the observed deuterium incorporation in monodeuteriomethanol).



The formation of aldehyde (or ketone) **7** is an oxidative process that involves both the loss of a hydrogen atom and a proton from an excited state that is electron poor.



Conclusions.

The photoreactions of the quinolinemethanols are clearly altered under circumstances that are conducive to exciplex formation. Both the photoreactivity and the ulti-

mate products are changed, though the effect on reactivity varies with the structure of the heterocyclic compound and the direction of charge transfer. In some cases direct photoreaction of the unprotonated compound is more efficient than reaction of an exciplex, but with every compound evidence points to exciplex involvement in some paths of reaction.

EXPERIMENTAL

General.

Microanalyses were performed by Galbraith Laboratories (Knoxville, TN) or Baron Consulting Co. (Orange, CT). Melting points were determined on a Mel-Temp apparatus in capillary tubes. Ultraviolet spectra were recorded on a Cary 17D or Perkin-Elmer Lambda 4B spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Model 283 or 337 spectrophotometer. Proton nmr spectra were recorded on a Varian EM-360, Bruker HX270, Bruker WH90D, or IBM AF-270. Mass spectra were obtained on an AEI-MS-10 or a Hewlett Packard 5970B Mass Selective Detector attached to a 5980A Gas Chromatograph equipped with a cross-linked methyl silicone gum column, 12 m x 0.2 mm. Fluorescence spectra were obtained with a Spex Fluorolog spectrofluorometer.

Preparation of Authentic Compounds for Photolysis and Structure Confirmation.

Both the family of alcohols, **4**, and the photoproducts encountered, **5-7**, were prepared from the appropriately substituted 2-phenylquinoline-4-carboxylic acids. These acids were prepared by a Doebner condensation as previously reported [13,17]. Alcohols **4a-4d** were obtained directly from the acids by reduction with lithium aluminum hydride in THF [13]. Alcohols **4e** and **4f** were obtained from the methyl ketones as previously described [18]. The methyl compounds **5** were prepared by conversion of **4** to the corresponding benzylic chloride by treatment of the alcohol with thionyl chloride [19], followed by reduction of the chloride with sodium borohydride in DMSO at 50°. The protio compounds **6** were obtained by thermal decarboxylation of the 2-phenylquinoline-4-carboxylic acids [18]. The aldehydes (or ketones), **7**, were obtained by oxidation of the corresponding alcohol with manganese dioxide in chloroform [17].

Analytical and physical data for **4e** are: mp 177-178°.

Anal. Calcd. for C₁₈H₁₅Cl₂NO₂: C, 62.08; H, 4.34. Found: C, 62.18; H, 4.55.

Analytical and physical data for **5e** are: mp 107-109°.

Anal. Calcd. for C₁₈H₁₅Cl₂NO: C, 65.08; H, 4.55. Found: C, 65.15; H, 4.91.

Analytical and physical data for **6b** are: mp 138-141°.

Anal. Calcd. for C₁₇H₁₅NO: C, 81.90; H, 6.06. Found: C, 81.78; H, 5.97.

Analytical and physical data for **7e** are: mp 156.5-158°.

Anal. Calcd. for C₁₈H₁₃Cl₂NO₂: C, 62.45; H, 3.78; Found: C, 62.70; H, 3.86.

References to other compounds are: **4a**, [21]; **4b**, [19]; **4c**, [8]; **4d**, [18]; **4f**, [7a]; **5a**, [21]; **5b**, [19]; **5c**, [8]; **5d**, [18]; **5f**, [7a]; **6a**, [22]; **6c**, [8]; **6d**, [7a]; **7a**, [21]; **7b**, [17]; **7c**, [8]; **7d**, [18]; and **7f**, [7a].

Photolysis.

Typically 50 to 200 mg of compound was irradiated in 600 ml of alcohol. Most frequently the irradiations used a Rayonet Preparative Chamber Reactor equipped with a circular array of RUL-2537 (low pressure mercury, emitting at 254 nm) lamps inside a reflecting surface. A cylindrical vessel containing the solution to be photolyzed was placed in the center of the apparatus. Nitrogen was usually passed through the solution during photolysis. For quantum yield experiments benzophe-

none/benzpinacol actinometry was utilized.

Analysis of Mixtures.

The composition of photoproduct mixtures was principally determined by isolation of the components using silica gel column chromatography and comparison of the nmr spectra with those of authentic compounds. Quantitative data was obtained both from isolation and direct hplc analysis of the photoproduct mixture.

Acknowledgements.

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