isomerization and another leading to chemical and/or nonchemical radiationless decay. The remarkable effect of the dimethylamino group in **2** shows that this group surely must play a role in controlling the course of nonradiative decay of any state formed by interaction between the phenyl and unsaturated ester chromophores. We have no explanation for the apparent fact that the interaction should divert internal conversion so as to produce such a multitide of bond-breaking processes.

Light absorption by **3** must produce states with the excitation largely localized in arylamino group. That these states must have finite lifetimes is shown by the weak fluorescence. We suspect that the fluorescent state decays mainly by internal energy transfer to a delocalized state similar to that postulated for **1**. If so, decay of that state must be guided by the *N*-methylanilino group since the usual skeletal rearrangements disappear completely, or nearly so. Sixty-one per cent of the energy put into the molecules can be accounted for by geometric isomerization (triplet path?), so some 40% must be attributed to other nonradiative decay processes. These in turn may be related to quenching of fluorescent states of aromatic compounds by amines[33] although no long wave-emission similar to that seen with naphthalene derivatives having amino groups[20] attached to side chains has been observed.

We conclude that excitation decay in molecules containing several chromophoric units may involve complex interaction among all the groups in the system.

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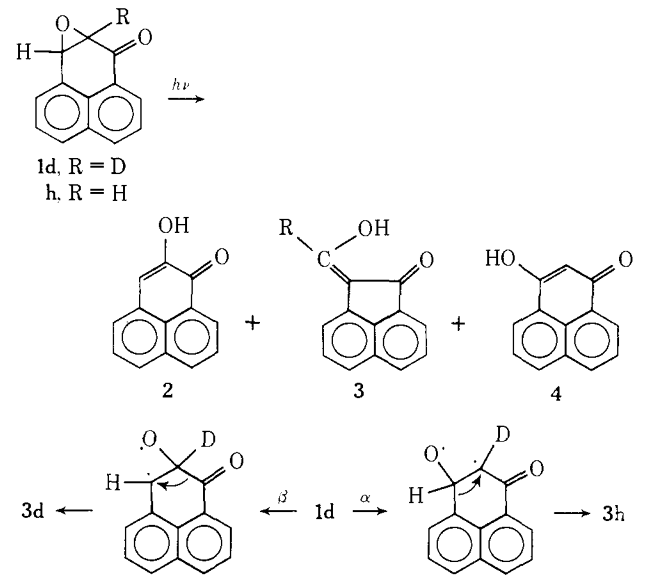
Photoisomerization of Phenalen-1-one Oxide. The Absence of α-Hydrogen Exchange in the Alkaline Peroxide Epoxidation of α,β-Unsaturated Ketones[1]

Sir:

Irradiation (>280 nm) of phenalen-1-one oxide (**1h**) in acetonitrile yields 2-hydroxyphenalen-1-one (**2**), acenaphthen-1-one-2-carboxaldehyde (**3h**), and 3-hydroxyphenalen-1-one (**4**) in approximately 30, 16, and 5% yields, respectively.[2] Whereas the formation of **2** and **4** are suggestive of initial C_β–O and C_α–O bond scission, respectively, followed by hydrogen migration, **3** may arise from either biradical intermediate. On the other hand, irradiation of **1d** is expected to provide **3h** by the α pathway and **3d** *via* β cleavage (Scheme I). Herein, we report on the synthesis and photorearrangement of **1d** which establish that (1) C_β–O bond cleavage precedes ring contraction to **3** and (2) α-H (D) exchange does not accompany alkaline peroxide epoxidation of α,β-unsaturated ketones.

Scheme I



We anticipated that alkaline peroxide epoxidation[3] of **5h** in deuteriated media would provide **1d** directly as a consequence of α-D exchange *via* the enolate adduct **6** which was expected to compete favorably with ring closure (Scheme II). Indeed, the pseudo-first-order rate constant for proton transfer from water to the α-C of an enolate (pK_a = 20) may be estimated to be on the order of 10^5 sec^{-1}.[4] However, epoxidation of **5h** with alkaline deuterium peroxide yielded **1h** (60% yield);[5] no deuterium incorporation was in evidence by nmr and mass spectrometry. Analogous results were obtained with benzalacetophenone. As expected, epoxidation of α-deuterio-phenalen-1-one (**5d**)[6] in protiated media[5] provided the desired epoxy ketone, **1d**. Apparently, α-H (D) exchange of the product does not occur under these conditions,[5] although exchange has been observed with sodium ethoxide catalysis.[7]

Previous studies have established that alkaline peroxide epoxidation is highly stereoselective in that, irrespective of the geometry of the α,β-unsaturated ketone, the product with the less hindered carbonyl group is kinetically favored.[8] These results implicate

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(4) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964). This reference provides the rate constant for the reverse process of proton transfer from the α-C of a ketone (acetone) to hydroxide ion (2.7×10^{-1} M^{-1} sec^{-1}), from which the desired rate constant may be obtained as discussed on p 10.

(5) The alkaline peroxide solution was prepared by adding 7.0 g of sodium peroxide to 30 ml of deuterium oxide (or water) with cooling, allowing the mixture to stand for 3 hr at room temperature, and filtering. The resulting solution contained approximately 5% peroxide. A 10-ml aliquot was slowly added to 1.0 g of the α,β-unsaturated ketone in 30 ml of dioxane at 50°. After 1 hr, the solution was partitioned between chloroform and water; and, after drying, the chloroform solution was evaporated to dryness. The residue, which contained substantial amounts of starting ketone, was resubjected to the same conditions two or three additional times to afford pure epoxy ketone after recrystallization.

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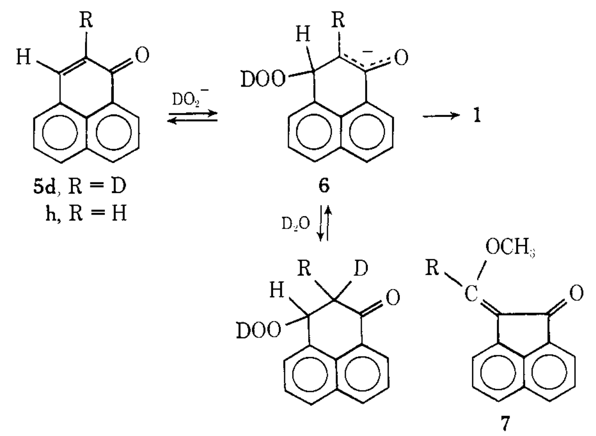
Scheme II



an intermediate, presumably the enolate adduct, which undergoes C_α–C_β rotational equilibration during its lifetime. The present results indicate that cyclization to epoxide is considerably faster than ketonization of the enolate which, we consider, constitutes a remarkably high, lower limit for nucleophilic attack on the peroxide linkage. The facility of this process, which appears to be unprecedented in peroxide reactivity toward nucleophiles,[9] probably reflects a favorable disposition of the enolate carbon orbital. The results further demonstrate that reversal of hydroperoxide addition, for which evidence has been presented,[7] occurs faster than ketonization.

Irradiation of **1d** yielded a product mixture from which the desired aldehyde was conveniently and cleanly separated by adsorption on basic alumina and elution with basic methanol. Unfortunately, neither nmr nor mass spectrometry was useful for determining the extent of deuterium retention: the former because of its complexity, the latter because of a major M-1 fragmentation. However, complete retention of deuterium was demonstrated by conversion into the corresponding methyl ether, **7d**,[10] as evidenced by mass spectrometry.

Thus, aldehyde **3** and, presumably, α-diketone **2**, which represent 90% of the isolated products, are generated by C_β–O scission. This mode of fragmentation is considered diagnostic of the low-lying π,π^* triplet of naphthyl ketones, in which excitation is "localized" in the aromatic chromophore: a model based on phosphorescence data[11,12] and supported by low photoreactivity of these systems in typical, n,π^* reactions.[13] The formation of β-diketone **4** may occur *via* C_α–O cleavage of the low-lying singlet, which has been postulated as the reactive state[14] in this mode of photoisomerization of epoxyketones.[15] These excited-state designations are also in accord with findings on intramolecular photocyclization of α- and β-naphthyl ketones which implicate competing T_1 and S_1 reactivity.[16]

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Simplified Preparation of π-Vinyl Alcohol Platinum(II) Complexes[1]

Sir:

The recent literature has evidenced a growing interest in π-vinyl alcohol complexes, stimulated in part by the postulated π-vinyl alcohol intermediate[2] in the Wacker process,[3] the palladium-catalyzed oxidation of ethylene to acetaldehyde. At present three π-vinyl alcohol transition metal complexes have been isolated,[4–6] and nmr evidence for the formation of a fourth has been reported.[7] In a study of oxoalkyl iron complexes, Ariyaratne and Green[4] found that cyclopentadienyldicarbonyl(β-oxoethyl)iron could be protonated to give a complex which they tentatively described as the π-vinyl alcohol. Wakatsuki, Noyakura, and Murahashi[5] synthesized 1,3-bis(π-ethenol)-2,4-dichloro-μ-dichloro-platinum(II); however, Thyret[7] recently reported that the synthesis was not reproducible and reported nmr evidence for the formation of tetracarbonyl(π-ethenol)iron at −80°.

Due to the stability and high solubility of the chloro(acetylacetonato)(π-ethenol)platinum(II) complex, prepared in this laboratory, it has been possible to well characterize this vinyl alcohol complex by nmr,[6] X-ray diffraction,[8] and exchange studies.[9] The reported preparation[6] involved the formation and hydrolysis of the intermediate vinyl trimethylsilyl ether complex, the same general procedure employed by Wakatsuki and Thyret. Since the preparation of the readily hydrolyzed vinyl trimethylsilyl ether[10] and the subsequent formation and hydrolysis of the metal–vinyl ether complex require carefully controlled reaction conditions[6,10] and considerable time, we report a novel, simplified preparation of this complex and the analogous π-propen-2-ol complex by the direct reaction of chloro(acetylacetonato)(π-ethylene)platinum(II) with acetaldehyde and acetone. This facile method of

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