The generation of hydroxide and methoxide ions by photo-irradiation: use of aromatization to stabilize ionic photo-products from acridine derivatives

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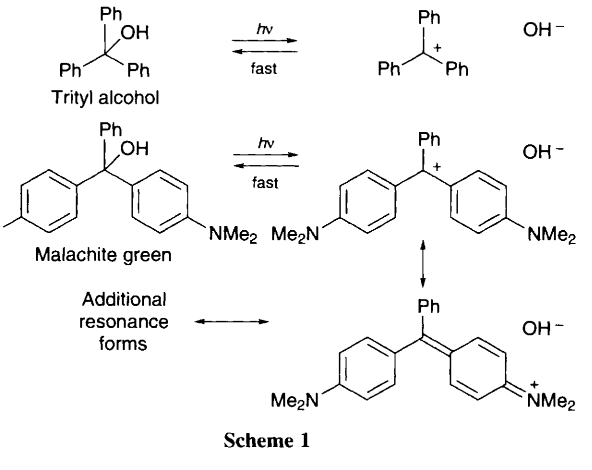
The photolysis of 9-hydroxy-10-methyl-9-phenyl-9,10-dihydroacridine 1 or its 9-methoxy derivative 2 occurs with heterolytic cleavage of a C–O bond and formation of the desired strong base together with a cation that stabilizes itself through aromatization.

The development of photolabile sources of radicals has ushered significant growth in polymer science, in particular in the area of photocuring.[1] More recently, the development of practical sources of photogenerated acids,[2] has led indirectly to the development of an entire generation of state-of-the-art resist materials[3] that are in commercial use in the microelectronics industry today.

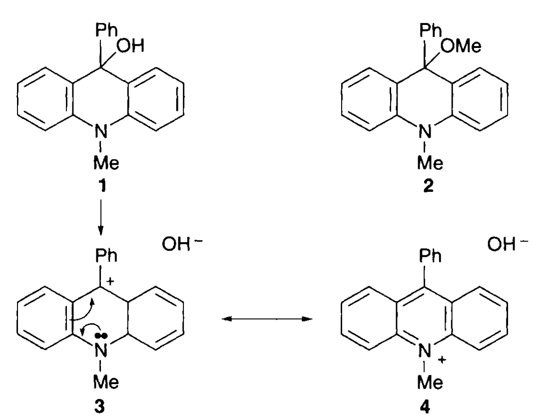
Despite the importance of general base catalysis in chemical processes, the development of both materials and applications for photogenerated bases has been slow. We have reported[4] that two mechanistically separate families of photolabile carbamates liberate amines upon irradiation. These amine photo-precursors are already finding uses in imaging processes. Here we report the preparation of photo-active compounds that liberate stronger bases, hydroxide or alkoxide, upon irradiation.

Our design for these new photoprecursors of bases is based on the early work of Irie[5] who demonstrated that photochemical heterolytic cleavage of the C–O bond in trityl alcohols could be used to produce hydroxide ions. While the strength of the base produced photochemically is related to the nature of the anionic species itself, the organic counterion largely determines its lifetime once irradiation is ended. In particular, the intrinsic stability of the cation is a key component in controlling the rate of recombination. For example, heterolytic cleavage of the C–O bond of Malachite green generates a cation that is more stabilized than that obtained from trityl alcohol itself because the aminomethyl groups contribute to charge delocalization (Scheme 1).

The selection of 9-hydroxy-10-methyl-9-phenyl-9,10-dihydroacridine **1** and its 9-methoxy derivative **2** as photoprecursors of strong base rests on the following arguments. Compound **1** is a trityl alcohol that is expected to undergo heterolytic cleavage of its C–O bond upon irradiation. The resulting trityl cation **3**, with its empty p orbital on C-9, should then stabilize itself *via* aromatization involving participation of the lone pair of electron on the ring nitrogen. This process is expected to afford the very stable 9-phenyl-10-methyl acridinium cation **4** (Scheme 2). Once the central ring has aromatized, it would have to give up all the energy gained by aromatization before recombination with the anion would be possible. In contrast, the trityl cation obtained from Malachite green is only stabilized through electron donation from its rings and ring substituents. This effect is likely to be much weaker because participation of the phenyl rings requires a certain extent of de-aromatization for electron donation from the satellite nitrogen atoms as shown in the resonance form depicted in Scheme 1. In practice, it has been demonstrated that the lifetime of the hydroxide ions generated by photoirradiation of trityl alcohol is too short to be of practical value, while impoved results are obtained with Malachite green despite the pronounced recombination decay of its anion.[5]



Scheme 1



Scheme 2

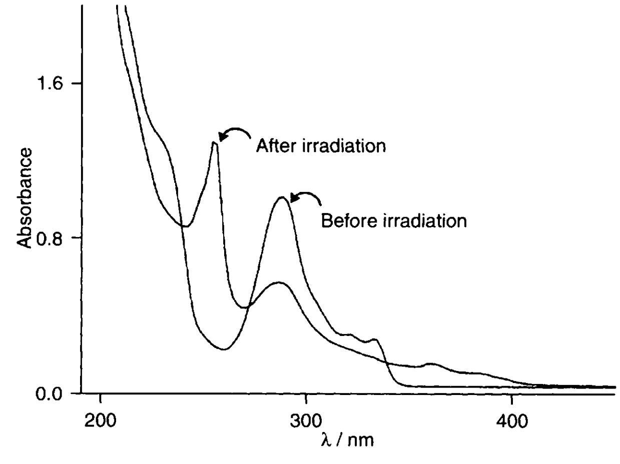


Fig. 1 UV spectrum of a solution of 9-hydroxy-10-methyl-9-phenyl-9,10-dihydroacridine, **1**, before and after exposure to UV radiation at 280 nm

Both **1** and **2** are easily obtained from acridone[6] by reaction with phenyl magnesium bromide followed, in the case of **2**, by methoxylation of the alcohol **1**.

The aromatization of **1** upon irradiation at 280 nm can be followed by UV and NMR spectrometry. Because of increased conjugation of its π system to a 14 atom acridinium system, the UV spectrum of **4** shows increased absorbance between 340 and 400 nm (Fig. 1). The ^{1}H NMR spectrum of **1** also changes significantly upon irradiation to reflect the occurrence of both ionization and the concurrent aromatization. Signals for the protons of the original aromatic rings are shifted downfield from δ 6.5–7.5 to 7–8.5 reflecting the presence of a positive charge in the new ring system. In addition, the signal for the methyl proton attached to nitrogen shifts from δ 3.46 to 5.46 while, as a result of shielding, the hydroxy peak moves upfield from δ 2.5 to about 0.1. Similar observations are made for the irradiation of the methoxy analogue **2** with changes in both UV and NMR spectra qualitatively similar to those observed for **1**.

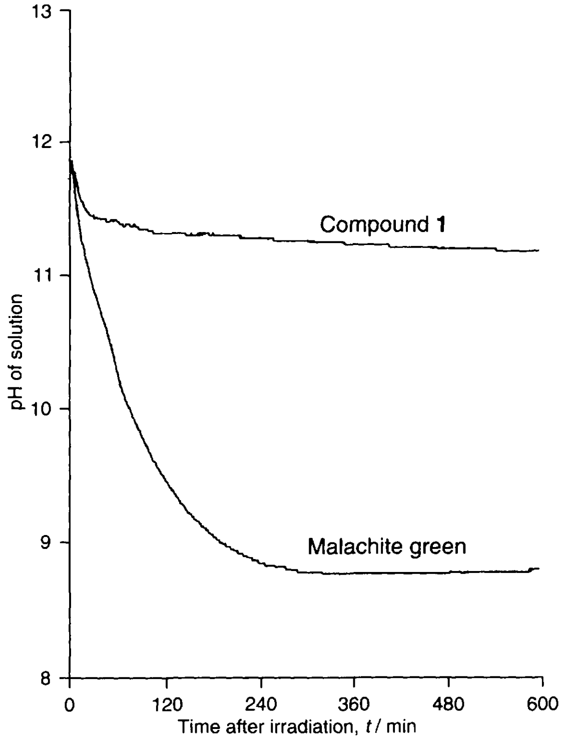


Fig. 2 Plot of pH *vs.* time for a solution of compound **1** or of malachite green in 3 : 1 acetonitrile–water after 2.5 min irradiation at 280 nm using a Rayonnet photochemical reactor. The initial pH after irradiation is *ca.* 12.5 for both solutions.

For example, the methoxy group of **2** shifts from δ 2.90 to about -1.3 as would be expected for an alkoxide. The quantum yield for the ionization process can be determined by quantitative ultraviolet spectroscopy as described earlier[7] for photoactive carbamates. For example, typical experiments for compound **2** using irradiation at 280 nm afford quantum yield values of 0.13 or 0.11 depending on whether the measurements are made at 286 or at 254 nm, the absorbtion wavelengths for the product and the reactant, respectively. In order to negate the inner filter effect[8] the quantum yield measurements were performed for an extent of reaction of 15–20%.

The pH of a 5.38×10^{-2} mol dm^{-3} solution of **1** in acetonitrile–water (3 : 1) increases rapidly upon irradiation at 280 nm to reach a value well in excess of pH 12. However, unlike trityl alcohol and even Malachite green, the ions that are formed upon irradiation do not recombine rapidly when irradiation is stopped. Therefore, the pH of an irradiated solution of **1** remains over 11 after an elapsed time of 10 h confirming the great stability of the resonance stabilized cation **4**. In contrast, the pH of a solution of Malachite green fall rapidly to below a value of 11, and below 9 in 3 h under analogous conditions (Fig. 2). The enhanced lifetime of the photogenerated hydroxide or methoxide ions, obtained from **1** or **2** respectively, allows ample time for their use as catalysts in photo-triggered reactions.

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