

Excited State Carbon Acids: Base Catalysed Photoketonization of Dibenzosuberanol to Dibenzosuberone *via* Initial C–H Bond Heterolysis from S_1

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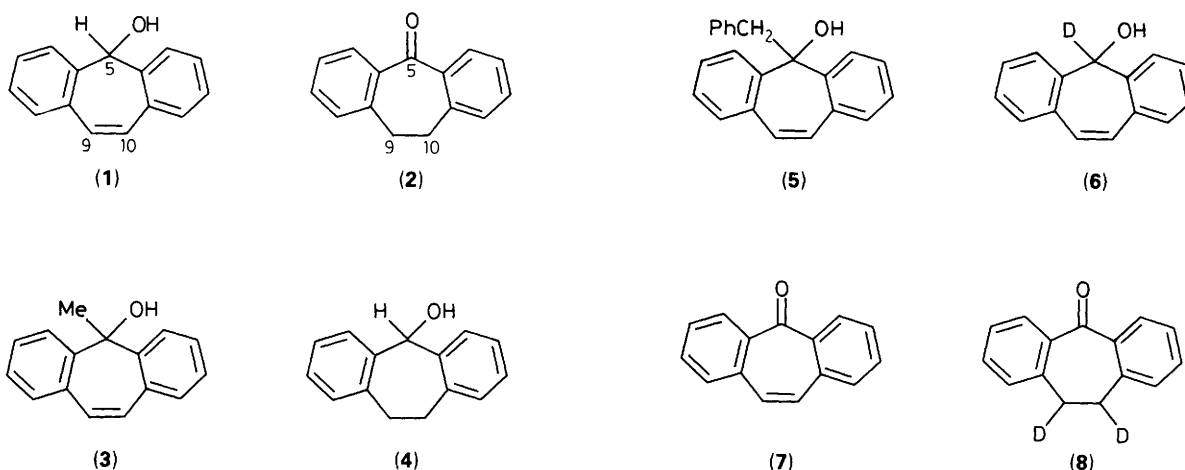
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A new photoreaction, the photoketonization of dibenzosuberanol (**1**) to dibenzosuberone (**2**) in aqueous solution, is reported, the mechanism of which is believed to involve initial ionization of the C–H proton at the 5-position (in S_1), to generate a 5-hydroxy-5-dibenzosuberanyl (**9**) carbanion intermediate.

The study of the formation and chemistry of carbanions in the ground state is an area of fundamental interest.^{1–5} The most commonly used method for carbanion generation in the ground state is *via* ionization of a C–H bond with an appropriate base. Because of the wide scope of this process, all compounds with at least one C–H bond are potential carbon acids in the ground state. Much less understanding is available for excited state carbon acids. Although a number of Förster cycle calculations^{6–9} have shown that many hydrocarbons with benzylic hydrogens become much more acidic in S_1 , the first report of an ionizing carbon acid in the excited state was not available until recently.⁹ It appears that attainment of an 8π ($4n$) electron arrangement in the internal cyclic array (ICA)^{9,10} of these compounds is a necessary condition for efficient carbanion generation.^{9,10} What is not known at this

time is whether photogenerated carbanions *via* this process can undergo chemistry besides simple reprotonation, *i.e.*, whether the photogenerated carbanion can be sufficiently long lived for processes other than reprotonation to compete. We report here a new photochemical reaction which converts dibenzosuberanol (**1**) to dibenzosuberone (**2**) in aqueous solution. The reaction is base catalysed and evidence is presented which supports a mechanism involving initial C–H bond heterolysis from S_1 , to give a 5-hydroxy-5-dibenzosuberanyl carbanion intermediate (**9**), which on reprotonation at the 9-position, gives an enol, which subsequently ketonizes to (**2**).

Photolysis of dibenzosuberanol (**1**) in aqueous solution at pH 7 (typically 30–40% MeCN used as cosolvent, 10^{-3} M substrate, Rayonet RPR 100 photochemical reactor, 254 nm



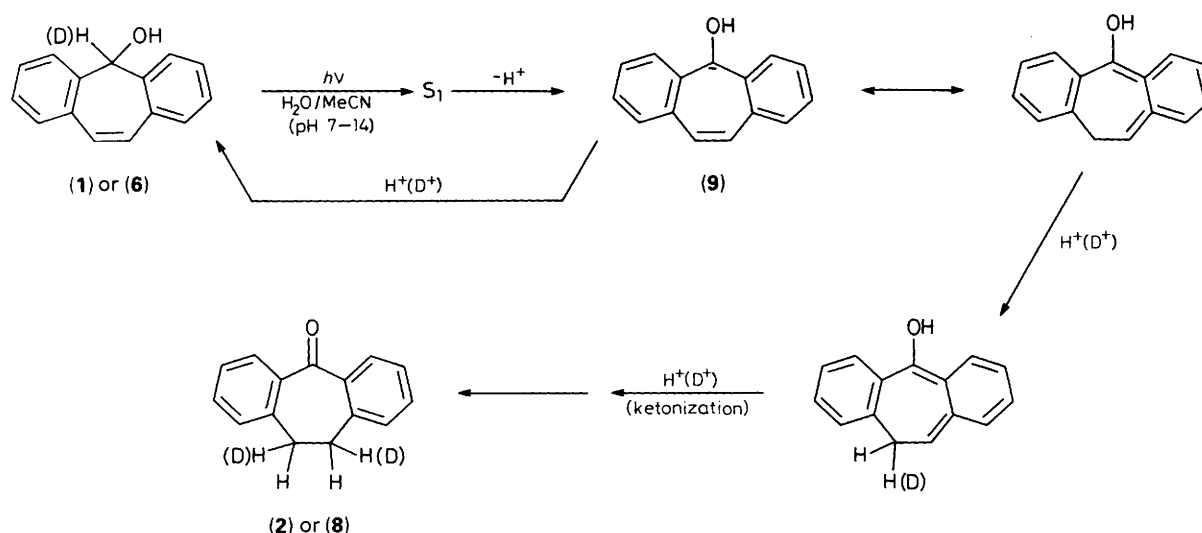
lamps, argon purged solutions, 10–60 min) gave a low yield (~10%) ($\phi \sim 0.003$) of dibenzosuberone (**2**). When 0.25 M aqueous NaOH was used, the yield of (**2**) increased to ~20% ($\phi 0.011 \pm 0.003$). Photolysis of (**3**) and (**4**) under the above conditions gave no reaction whereas (**5**) gave bibenzyl and dibenzosuberone (**7**) (conversion $\leq 20\%$). The latter reaction clearly involves homolysis of the benzylic C–C bond of (**5**) on photolysis, to give benzyl and 5-hydroxy-5-dibenzosuberonyl radicals, which subsequently lead to bibenzyl and (**7**), respectively. With this observation, it is clear that the photochemical transformation of (**1**) to (**2**) does not involve the 5-hydroxy-5-dibenzosuberonyl radical. Additional insights into the mechanism of reaction came from solvent deuterium isotope effects and photolysis of the 5-deuteriated derivative (**6**). Thus, photolysis of (**1**) in neutral or basic D_2O -MeCN gave (**6**) and (**8**)[†] (yields ~10%) and photolysis of (**6**) in 0.20 M aqueous NaOH-MeCN gave (**1**) (8%) and (**2**) (12%). The observations of deuterium incorporation at the 5-position of (**1**) on photolysis in D_2O and the loss of deuterium from the 5-position of (**6**) on photolysis in H_2O indicate that the proton (or deuterium) at the 5-position of dibenzosuberone (**1**) is very acidic in the excited state since neutral water (or hydroxide solutions of modest concentration) can deprotonate this position. Since photolysis of (**1**) in D_2O also gave dibenzosuberone deuteriated once at each of the 9- and 10-positions [*i.e.*, (**8**)], the mechanism of transformation of (**1**) to (**8**) probably involves the same intermediate as the exchange process. That the singlet states of (**1**) and (**6**) are involved in these reactions is supported by fluorescence quenching studies which showed that water is an excellent quencher (in MeCN) of S_1 , resulting in linear Stern–Volmer plots with the quenching rate constants displaying a substantial kinetic isotope effect: $k_q = 1.2 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for (**1**) and $k_q =$

$0.42 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for (**6**) ($k_q^H/k_q^D = 2.9$). The fluorescence lifetime of (**1**) was also very sensitive to the presence of water in the solvent, ranging from $\tau 2.3 \pm 0.2 \text{ ns}$ in pure MeCN to $\tau 0.92 \pm 0.5 \text{ ns}$ in 80% H_2O -MeCN (all first order decays). On the other hand, none of (**3**)–(**5**) [which do not react in the manner described for (**1**)] displayed this behaviour. These results suggest that water (in neutral solution) is the deprotonating base at the 5-position, as demonstrated in the excited state carbon acid behaviour of dibenzosuberone.⁹ Hydroxide ion competes as the deprotonating base at high pH, as suggested by the enhancement in ϕ on going to aqueous hydroxide solutions.

The proposed mechanism of reaction consistent with the results is presented in Scheme 1, where the primary photochemical event after excitation to S_1 is C–H bond heterolysis from the 5-position (assisted by water as the base), to generate the 5-hydroxy-5-dibenzosuberonyl carbanion intermediate (**9**). Reprotonation of (**9**) gives back (**1**) or (**6**) (in D_2O). However, reprotonation at the 9-position gives an enol intermediate which on ketonization gives (**2**) or (**8**) (in D_2O). The partition ratio between reprotonation at the 5- and 9-positions is about 40:60, respectively, as suggested by the distribution of the products (**1**) and (**2**) on photolysis of (**6**) in H_2O -MeCN, although this calculation takes no account of the percentage of reprotonation *via* internal return of the departing deuterium. The results indicate that a novel type of photoketonization mechanism is operative in these systems which takes advantage of the fact that dibenzosuberonyl systems can display excited state carbon acid behaviour. In addition, the reaction has shown that the photochemically generated carbanion (at the 5-position) has substantial delocalization of the negative charge to the 9- (or 10-) position. Additionally, since carbanions of the type (**9**) cannot, in general, be made *via* ground state methods since the hydroxy proton is much more acidic than the C–H proton, the photochemical method provides a unique way for generating and studying the chemistry of these species.

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[†] Control experiments showed that (**2**) is not converted to (**8**) in D_2O -MeCN in the absence or presence of irradiation. All assigned structures were consistent with spectroscopic data. The structure of (**8**) was assigned with the help of ^{13}C NMR, by noting that the methylene carbons (9- and 10-positions) of (**8**) come as a 1:1:1 triplet ($J 20 \text{ Hz}$; due to coupling to one deuterium atom) at $\delta 34.5$. The possibility that there is a residual amount of methylene carbons with no deuterium atom attached was ruled out by carrying out distortionless enhancement by polarisation transfer (DEPT) experiments which showed the ^{13}C signals in this region are not of the $-CH_2-$ kind.



Scheme 1

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