

# Excited state carbon acids: irreversible photodeprotonation of the benzylic protons of 10-methyl- and 10-phenyl-thioxanthenium salts

Darryl Brousmiche, Deepak Shukla and Peter Wan\*

Department of Chemistry, Box 3065, University of Victoria, Victoria, British Columbia, Canada V8W 3V6

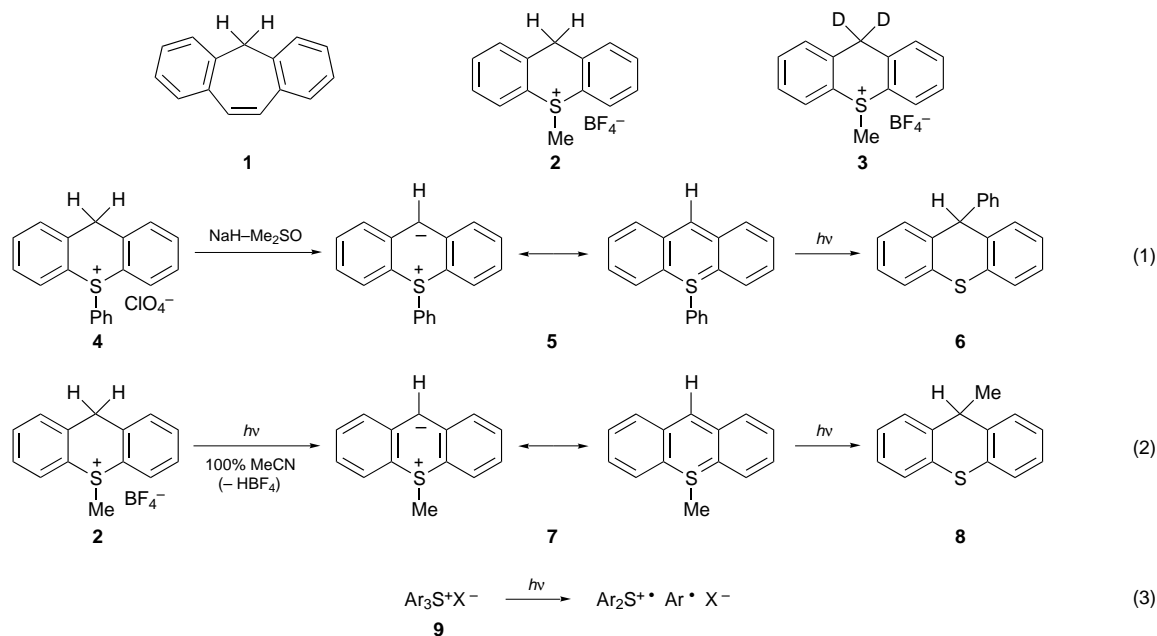
**The first examples of irreversible photodeprotonation of a C–H bond to generate a formal carbanion, via photolysis of thioxanthenium salts, is reported, which gives the corresponding sulfonium ylide (thiaanthracene) and acid (HBF<sub>4</sub> or HClO<sub>4</sub>).**

Carbanions and their associated carbon acids are of fundamental importance in chemistry. Carbanions are most commonly generated *via* deprotonation of the corresponding carbon acid although this process is generally slow.<sup>1</sup> We have reported<sup>2</sup> that the benzylic protons of dibenzosuberene **1** and related compounds are vastly more acidic in the excited singlet state than in the ground state, and hence can be deprotonated efficiently by water (in MeCN;  $k_d$  ca.  $2 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) on excitation, to give a formally antiaromatic ( $8\pi$ ) carbanion. Photodeprotonation rates approaching the diffusion controlled limit have been measured using primary amines such as ethamine as deprotonating base.<sup>3</sup> However, in all cases reported so far the deprotonation is entirely reversible; direct evidence for carbanion formation was obtained by observation of deuterium exchange of the methylene protons with deuteriated solvent in recovered substrate. Attempts to detect the intermediate carbanion by nanosecond laser flash photolysis have so far been unsuccessful, presumably due to the very short lifetimes (in the ground state) of these photogenerated, formally anti-aromatic, ( $8\pi$ ) carbanions. One approach in making the photodeprotonation step irreversible is to make the incipient carbanion longer lived or designing a carbanion that once formed rearranges to a stable product. To this end, we have chosen to study the potential excited state carbon acid behaviour (of the benzylic protons) of 10-methylthioxanthenium tetrafluoroborate, **2** and **3**, and 10-phenylthioxanthenium perchlorate **4**, systems that

have the required  $8\pi$  (anti-aromatic) electron count in the internal cyclic  $\pi$ -array for the incipient carbanion.<sup>†</sup> We show that photolysis of these compounds in MeCN results in efficient deprotonation of the benzylic proton, giving rise to a long-lived formal carbanion (an ylide), and formation of HBF<sub>4</sub> or HClO<sub>4</sub>. As such, these are the first examples of excited state carbon acids that undergo irreversible dissociation of the C–H proton, with detectable formation of acid.

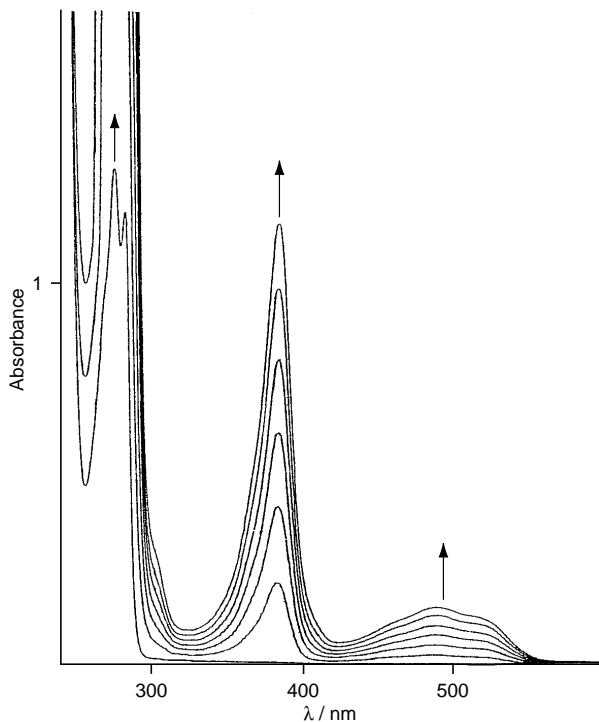
The thioxanthenium salts **2–4** were made according to procedures published by Mislow and co-workers.<sup>4</sup> Treatment of **2** and related thioxanthenium salts with available benzylic protons with a strong base (*e.g.* NaH–Me<sub>2</sub>SO or an organometallic reagent) is known to result in deprotonation of the benzylic proton, to give the unstable but highly coloured thiaanthracene **5** ( $\lambda_{\text{max}} = 388$  and 497 nm), which subsequently rearranges to the corresponding stable 9-substituted thioxanthene **6** [eqn. (1)].<sup>4,5</sup> The half-lives of some thiaanthracenes generated in basic Me<sub>2</sub>SO range from 1 min to several hours at 22 °C.<sup>4b</sup> These results indicate that the  $pK_{\text{a}}$ s of the benzylic protons of these compounds are significantly lower than those of thioxanthene or dibenzosuberene **1**, which have estimated  $pK_{\text{a}}$ s in the 30–35 range.<sup>2</sup>

Photolysis of initially colourless  $10^{-3}$  M solutions of **2–4** in dry MeCN (254 nm; argon-purged solutions) gave deep orange solutions, with visible absorption bands at ca. 380 and 485 nm (Fig. 1). No changes were observed without photolysis. These visible bands are identical to those observed for known thiaanthracenes (*e.g.* **5**).<sup>4</sup> However, whereas thermally generated thiaanthracenes in basic media are relatively short-lived, when photogenerated in 100% MeCN, they show no evidence of decay for several days. Additional evidence that thiaanthracenes are indeed photogenerated was obtained by taking the



$^1\text{H}$  (300 MHz) NMR spectrum of an exhaustively photolysed sample of **2** in  $\text{CD}_3\text{CN}$  (254 or 300 nm; 45–60 min), which showed formation of **8** with yields of up to 60% [eqn. (2)]. The thermal rearrangement of thiaanthracenes under basic conditions to the more stable 9-substituted thioxanthenes is well-known, as discussed above. It seems reasonable to propose that formation of **8** from **7** in an exhaustively photolysed sample of **2** is due to secondary photolysis of **7**. Indeed, the UV–VIS absorption bands of **7** (Fig. 1) was readily bleached when irradiated at 366 nm. A quantum yield of *ca.* 0.1 was measured (at low conversion) for the formation of **7** from **2** in MeCN using UV–VIS spectrophotometry to monitor the progress of the reaction ( $\lambda_{\text{excit}} = 280$  nm; potassium ferrioxalate actinometry).

Formation of **7** from photolysis of **2** in 100% MeCN $\ddagger$  implies loss of a proton from the benzylic position to form  $\text{HBF}_4$ . The increase in acidity of a photolysed solution in 100% MeCN was monitored by diluting aliquots at various photolysis times (at 254 nm) with an equal volume of  $\text{H}_2\text{O}$  and measuring the pH. An initial pH of 4.5 was observed which decreased to pH 3.4 after 5 min of photolysis, which represents about 50% conversion. No changes in pH were observed without photolysis. These results are consistent with excited state carbon acid deprotonation of the benzylic protons of **2**. That this deprotonation step is in fact the product forming step was the finding that the corresponding deuterated substrate **3** gave a reduced amount of **7**, as monitored by UV–VIS spectrophotometry. This can be quoted as an isotope effect on the quantum yield for forming **7**, *viz.*  $\Phi_{\text{H}}/\Phi_{\text{D}} = 1.39 \pm 0.05$ , which is a small primary isotope effect for C–H(D) bond cleavage. We have observed a similarly small primary isotope effect for benzylic C–H(D) bond cleavage for dibenzosuberene **1** using ethanolamine as deprotonating base in which the rate is close to the diffusion controlled limit.<sup>3</sup> The small isotope effect was interpreted as being due to an earlier transition state for proton removal by ethanolamine compared to water as base.<sup>3</sup> In the present case, we believe thioxanthenium salts **2–4** have early transition states for photodeprotonation of the C–H bond although additional studies are warranted to substantiate this claim.



**Fig. 1** UV–VIS traces showing formation of thiaanthracene **7** (visible bands at 383 and 485 nm) from photolysis of **2** in 100% MeCN ( $\lambda_{\text{excit}} = 254$  nm; each trace represents about 15 s photolysis)

Recent intense interest in the photochemistry of triaryl and trialkyl sulfonium salts is due to the fact that photolysis of many of these compounds results in efficient generation of a strong Brønsted acid which effectively initiates cationic polymerization and is therefore useful in photoimaging systems and related applications.<sup>6</sup> The commonly accepted mechanism<sup>6</sup> for Brønsted acid production in the photochemistry of triarylsulfonium salts **9** (and for some mixed alkylaryl systems) is the initial aryl–sulfur bond homolysis, to generate an aryl (or alkyl) radical and a diarylsulfinium radical cation [eqn. (3)].<sup>§</sup> Subsequent transformations of these species gives rise to the observed Brønsted acid. For example, intramolecular recombination of the radical pair *via* radical attack of  $\text{Ar}\cdot$  onto one of ring positions of  $\text{Ar}_2\text{S}^+$  results in overall loss of a proton from that ring position.<sup>6a,b</sup> Indeed, we are aware of two reports<sup>6e,f</sup> which show that photolysis of **2** and **4** results in generation of acid *via* the commonly accepted mechanism discussed above for triarylsulfonium salts. However, the results of our study demonstrate that photoacid production from these compounds arises from excited state carbon acid dissociation which may be regarded as a new mechanism for the production of Brønsted acid from photolysis of triarylsulfonium salts.

We acknowledge support of this research by the Natural Sciences and Engineering Research Council (NSERC) of Canada. D. B. thanks the University of Victoria for a graduate fellowship.

### Footnotes

$\dagger$  All dissociating excited state carbon acids reported by us<sup>2,3</sup> so far require an incipient carbanion that is cyclically delocalized with  $8\pi$  electrons. One of the lone pairs of the sulfur atom of **2–4** is used for bonding with the methyl or phenyl group while the second lone pair of electrons can come into  $\pi$  conjugation on deprotonation of the benzylic proton giving rise to an  $8\pi$  system, which is formally an ylide or a thiaanthracene.

$\ddagger$  We have avoided photolysis in aqueous MeCN and other protic solvents owing to the possibility of thermal solvolytic decomposition of the substrates.

$\S$  However, Crivello and Lam<sup>6d,g-i</sup> and Crivello and Lee<sup>6d,j</sup> have shown that the mechanisms for photoacid generation from dialkylphenacylsulfonium and dialkyl-4-hydroxyphenylsulfonium salts involve formal loss of a C–H and O–H proton, respectively, rather than *via* the standard mechanism shown in eqn. (3). The mechanism for the deprotonation from the C–H bond in the former does not appear to involve an excited state carbon acid.<sup>6d,j</sup>

### References

- 1 A. J. Kresge, *Acc. Chem. Res.*, 1978, **8**, 354.
- 2 (a) P. Wan, E. Krogh and B. Chak, *J. Am. Chem. Soc.*, 1988, **110**, 4073; (b) P. Wan, D. Budac, M. Earle and D. Shukla, *J. Am. Chem. Soc.*, 1990, **112**, 8048; (c) P. Wan and D. Budac, *J. Org. Chem.*, 1992, **57**, 887; (d) P. Wan and D. Shukla, *Chem. Rev.*, 1993, **93**, 571; (e) D. Budac and P. Wan, *Can. J. Chem.*, 1996, **74**, 1447.
- 3 D. Budac and P. Wan, *J. Photochem. Photobiol. A*, 1996, **98**, 27.
- 4 (a) B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr. and K. Mislow, *J. Am. Chem. Soc.*, 1975, **97**, 2718; (b) F. Ogura, W. D. Hounsell, C. A. Maryanoff, W. J. Ritcher and K. Mislow, *J. Am. Chem. Soc.*, 1976, **98**, 3615.
- 5 (a) M. Hori, T. Kataoka, H. Shimizu, H. Hori and S. Sugai, *Chem. Pharm. Bull.*, 1974, **22**, 2754; (b) M. Hori, T. Kataoka, H. Shimizu, M. Ikemori and Y. Aoyama, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1209.
- 6 (a) F. D. Saeva, *Top. Curr. Chem.*, 1990, **156**, 59; (b) J. L. Dektar and N. P. Hacker, *J. Chem. Soc., Chem. Commun.*, 1987, 1591; (c) J. D. Coyle, *The Chemistry of the Sulphonium Group*, Part 1, ed. C. J. M. Stirling, Wiley, Chichester, 1981, ch. 5; (d) J. V. Crivello, *Adv. Polym. Sci.*, 1984, **62**, 1; (e) J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 977; (f) R. S. Davidson and J. W. Goodin, *Eur. Polym. J.*, 1982, **18**, 589; (g) J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 2877; (h) *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**, 1021; (i) *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**, 2697; (j) J. V. Crivello and L. J. Lee, *Macromolecules*, 1983, **16**, 864.

Received, 16th December 1996; Com. 6/08434F