Perkin Communications

Bromine-induced Photochemical Protodesilylation of Benzyltrimethylsilanes by Hydrogen Bromide

Enrico Baciocchi,[*,a] **Manuela Crescenzi**[a] **and Tiziana Del Giacco**[b]
[a] Dipartimento di Chimica, Università 'La Sapienza,' Piazzale A. Moro, 5 00185 Roma, Italy
[b] Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 8 06100 Perugia, Italy

Benzyltrimethylsilanes are efficiently converted into toluenes by a Br_2-induced photochemical chain process in the presence of HBr.

Recently, it was discovered that, depending on the substrate structure and solvent, the photochemical bromination of benzyltrimethylsilanes can follow an electron transfer pathway.[1] Bromine atoms oxidize the substrates to radical cations which are converted into benzyl radicals by fast desilylation. Reaction of the benzyl radicals with molecular bromine propagates the chain leading to the products (benzyl bromides) and to bromine atoms.

Here we report that, under conditions where the electron transfer mechanism is operating, small amounts of bromine in the presence of HBr, promote a novel photochemical protodesilylation converting benzyltrimethylsilanes into the corresponding toluenes. Thus, we have observed that, whereas no reaction takes place when a 5×10^{-3} mol dm^{-3} solution of 4-methoxybenzyltrimethylsilane **1** and 0.1 mol dm^{-3} HBr in AcOH is irradiated (at λ/nm 366) by an OSRAM Super Pressure Mercury Lamp (HBO 500W/2 L1), the addition of a very small amount of Br_2 (2.5×10^{-4} mol dm^{-3}) induces a very fast and efficient protodesilylation leading to the almost quantitative conversion (91% in 2 h) of **1** into 4-methoxytoluene **2**.† Under the same conditions, but changing the solvent to a 1:1 mixture of acetic and trifluoroacetic acid, benzyltrimethylsilane forms toluene (50% yield after 3 h). In both cases we have checked that no protodesilylation takes place in the absence of light.
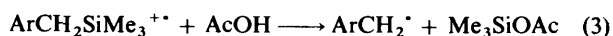
To obtain information on the actual nature of this process we have carried out quantum yield (Φ) measurements for the formation of **2** in acetic acid at λ/nm 366 ($W_{\frac{1}{2}} = 5$ nm) under a variety of conditions and the results are reported in Table 1. With 2.5×10^{-4} mol dm^{-3} Br_2 and 0.1 mol dm^{-3} HBr (entry 1) Φ is 8 ± 1, which clearly suggests a chain process. The HBr concentration appears to play an important role since Φ drops to 0.2 when the concentration of the acid is 0.01 mol dm^{-3}. A decrease in the quantum yield is also observed when the Br_2 concentration is increased (compare entry 1 with entries 4 and 5, Table 1). Under the latter conditions, compound **2** is formed together with 4-methoxybenzyl bromide and products of nuclear bromination. The latter products certainly derive from the dark reaction of compound **1** with Br_2 which takes place before the solution is subject to irradiation.‡ Finally, no protodesilylation occurs ($\Phi = 0$) when Br_2 is used in the presence of H_2SO_4 or LiBr (entries 7 and 8, Table 1), nor when Br_2 is used alone (entry 6). In these experiments only ring brominated products are formed. On the basis of the above results we propose that the protodesilylation of **1** occurs by the mechanism described in eqns. 1–5, where the key step is the oxidation of the benzylsilane by $Br^{\cdot}$. The radical cation formed undergoes fast desilylation (presumably by assistance of the solvent)[2] to give a benzyl radical which, by reaction with HBr, forms the methylaromatic derivative. Of course, reaction with

Table 1 Quantum yields (Φ) for the formation of 4-methoxytoluene by photolysis of 4-methoxybenzyltrimethylsilane in AcOH at different concentrations of Br_2 and HBr[a]

Entry	$[Br_2]$/mol dm^{-3}	[HBr]/mol dm^{-3}	Quantum yield[b]
1	2.5×10^{-4}	0.1	8[c]
2	—	0.1	0[d]
3	2.5×10^{-4}	0.01	0.2[e]
4	1×10^{-3}	0.1	5[f]
5	5×10^{-3}	0.1	0.02[g]
6	5×10^{-3}	—	0[h]
7	5×10^{-3}	H_2SO_4, 0.1 mol dm^{-3}	0[h]
8	5×10^{-3}	LiBr, 0.1 mol dm^{-3}	0[h]

[a] In all experiments the concentration for the substrate was 5×10^{-3} mol dm^{-3}. [b] Determined as described in the Experimental section. [c] The error is ±1. In addition to **2** only traces of ring brominated products were observed. [d] No reaction product was detected. [e] Only 0.2% of 4-methoxytoluene was formed in 5 min. No other product was detected. [f] The error is ±1. In addition to **2** (9.6% in 3 min), 4-methoxybenzyl bromide (1%) and ring brominated products (12%) were observed. [g] Yield of **2** is only 0.2% after 4.5 min. The yield of 4-methoxybenzyl bromide is 5% and that of ring brominated products 45%. [h] Ring brominated compounds (ca. 40%) are formed.

bromine to give a benzyl bromide is also possible (eqn. 5). In both reactions (4) and (5) $Br^{\cdot}$ is produced and the chain is established.

$$Br_2 \xrightarrow{h\nu} 2Br^{\cdot} \tag{1}$$

$$Br^{\cdot} + ArCH_2SiMe_3 \longrightarrow ArCH_2SiMe_3^{+\cdot} + Br^{-} \tag{2}$$

$$ArCH_2SiMe_3^{+\cdot} + AcOH \longrightarrow ArCH_2^{\cdot} + Me_3SiOAc \tag{3}$$

† Interestingly, the protodesilylation can also be performed by using a commercial solution of HBr in AcOH since it always contains traces of Br_2!

‡ Under the conditions used for quantum yield measurement it is impossible to avoid the non-photochemical process occurring when the Br_2 concentration is sufficiently large. In preparative experiments however, Br_2 is slowly added to the solution under irradiation. Under these conditions the formation of ring brominated products can be minimized and, moreover, efficient protodesilylation can also be accomplished in the absence of added HBr. Thus, at 60 °C, 4-methoxybenzyltrimethylsilane is converted into 4-methoxytoluene, in a 77% yield when Br_2 is slowly added to a solution of the substrate in AcOH with irradiation by a high pressure mercury lamp (Pyrex filter), if no care is taken to neutralize the HBr formed.

$$ArCH_2{}^{\bullet} + HBr \longrightarrow ArCH_3 + Br^{\bullet} \qquad (4)$$

$$ArCH_2{}^{\bullet} + Br_2 \longrightarrow ArCH_2Br + Br^{\bullet} \qquad (5)$$

The reaction rate of a benzyl radical with HBr is not much slower than that with Br_2[3] and it is, therefore, plausible that, under our reaction conditions (high HBr/Br_2 molar ratio) the former is the largely preferred reaction of the benzyl radical. In line with this interpretation we have found that the quantum yield for the formation of **2** decreases as we decrease the HBr/Br_2 molar ratio either by increasing the concentration of Br_2 or by decreasing the concentration of HBr.* Interestingly, as we increased the Br_2 concentration, the reaction of the benzyl radical with the halogen molecule becomes competitive and 4-methoxybenzylbromide is preferentially formed with respect to 4-methoxytoluene (entry 5).

This mechanism also accounts for the observation that the photochemical protodesilylation of benzyltrimethylsilane does not occur in AcOH whereas it does take place in an AcOH–TFA mixture. Accordingly, we have previously observed that $Br^{\bullet}$ in AcOH reacts with benzyltrimethylsilane by a hydrogen atom transfer mechanism; with this substrate (less easily oxidizable than 1) an electron transfer mechanism becomes operational in the AcOH–TFA mixture where we also observe protodesilylation.[1]

---

* This behaviour is predicted by the quantum yield expression based on the proposed mechanism,

$$\Phi = \frac{k_2 k_4 [HBr][ArCH_2SiMe_3]}{k_4[HBr] + k_5[Br_2]}\left(\frac{I_a}{k_{-1}}\right)^{\frac{1}{2}}$$

where I_a is the absorbed light, k_{-1} is the rate constant for the recombination of $Br^{\bullet}$ and k_2, k_4 and k_5 refer to the reactions described in eqns. 2, 4 and 5, respectively.

Experimental

Acknowledgements

References

1 E. Baciocchi and M. Crescenzi, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 658.
2 J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P. Todd and S. L. Maltes, *J. Am. Chem. Soc.*, 1989, **111**, 8973.
3 A. Zavitas, G. Fogel, K. E. Halwagy and P. A. Donnazuma Lagotte, *J. Am. Chem. Soc.*, 1983, **105**, 6960.