Pergamon

Tetrahedron Letters, Vol. 35, No. 44, pp. 8161-8162, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01772-7

Formation Of Radicals By Irradiation Of Alkyl Halides In The Presence Of Triethylamine

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Abstract: The irradiation of alkyl halides in the presence of triethylamine leads to the formation of the corresponding reduction products or to the cyclized products when an unsaturation is present.

Studies on the photochemistry of alkyl iodides have shown that the irradiation of alkyl halides in solution affords mixtures of radical and ionic products, with the latter usually greatly predominant [1]. As the ionic products are usually obtained in high yield the reaction is of synthetic value [2]. On the contrary, the alkyl bromides led to radical-derived products in low yield [3]. If photochemically generated ketyl radicals can be used as one electron reductants of halide derivatives [4], radical generators such as trialkyltin halide or trialkyldistannane are most commonly used for the chemical radical cleavage of C-Br bonds or C-I bonds [5]. However this reaction is troublesome as the purification of the products from trialkyltin halide is difficult, although a partial solution to this problem has been found by using polymer-supported organotin compounds [6].

Here, we would like to report a very fast, convenient and chemoselective photochemical reaction that allows the formation of radicals either from alkyl bromides or from alkyl iodides.

$$\text{R-X} \xrightarrow[\text{NEt}_3]{\substack{h\nu \\ 254\text{ nm}}} \text{R}^{\bullet} \qquad \text{X = Br, I}$$

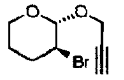
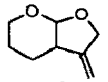
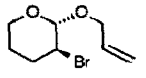
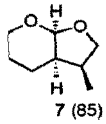
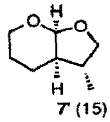
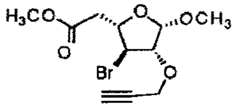
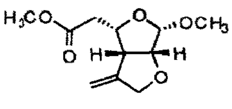
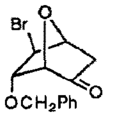
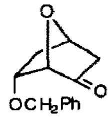
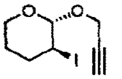
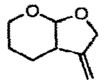
Irradiation of compound **1** at 254 nm [7], in an acetonitrile solution (10^{-2} M), in the presence of 10 equivalents of triethylamine for 30 mn leads to the formation of the cyclized product **6** with a quantitative yield (94%). In this reaction the work-up is very simple as no secondary products are formed. After removal of the solvent *in vacuo*, the cyclized product was purified by flash chromatography. The reaction was generalized to compounds **2** and **3**. In the case of compound **2**, two products **7** and **7'** [8] were formed in a ratio 85/15 with a yield of 80%. The irradiation of compound **3** in the presence of 10 equivalents of triethylamine allows the isolation of compound **8** with a yield of 60%. We have to point out that the reaction is chemoselective as the ester function was not reduced. Furthermore, when the bromoketone **4** was irradiated, the only product that could be isolated after 30 mn was the ketone **9** (60%). No trace of the corresponding alcohol was detected [9].The irradiation of the alkyl iodide **5**, in the presence of triethylamine led exclusively to the formation of **6** (90 %).

Under these conditions, there is probably the formation of an amine-halide exciplex that involves the formation of a radical R° and of an halide anion. The radical can be trapped very efficently by an internal π-bond system, or it can abstract a hydrogen atom to the resulting amino radical cation when no unsaturation is present.

$$(R\text{-}X\ \ NEt_3)^{\bullet} \longrightarrow R\text{-}X^{\bar{\bullet}}\ \ {}^{+\bullet}NEt_3 \longrightarrow R^{\bullet} + X^{-}$$

This strategy is very promising for the construction of carbo- and heterocyclic natural products.

Table: Irradiation at 254 nm of alkyl halides in the presence of triethylamine

Starting material	Product	Yield (%)
 1	 6	94
 2	 7 (85)  7' (15)	80
 3	 8	60
 4	 9	60
 5	 6	90

Acknowledgements: One of us (J.L.R.) thanks the Ministère de la Recherche et de la Technologie for a grant.

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(*Received in France* 2 *August* 1994; *accepted* 7 *September* 1994)