

A Different Behaviour of the Phthalimide Ion in $S_{RN}1$ Reactions

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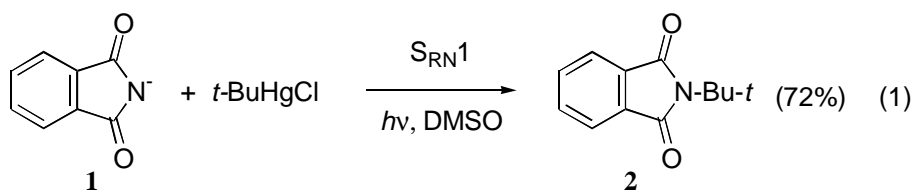
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Abstract: The phthalimide anion reacts by the $S_{RN}1$ mechanism under photostimulation with different substrates. Whilst with 1-iodonaphthalene only reduction of the naphthyl radical is observed, with 1-iodoadamantane coupling at the carbon instead of at the nitrogen takes place.

Introduction

The mechanism of Radical Nucleophilic Substitution ($S_{RN}1$) is a chain process with radicals and radical anions as intermediates [1]. Different substrates and nucleophiles participate in these reactions. It is known that within the nitrogen-centered nucleophiles, aromatic amines react with aryl halides to yield the substitution product on the carbon atom and none on the nitrogen atom. For example, the photoinduced reaction of 2-naphthylamine with aryl halides renders mainly 1-aryl-2-naphthylamines [2]. However, the phthalimide ion (**1**) reacts with *ter*-butyl radicals yielding *N-ter*-butylphthalimide (**2**) (eq.1) [3].

Taking into account these results we began to study the photoinduced reactions of phthalimide ion with different substrates.

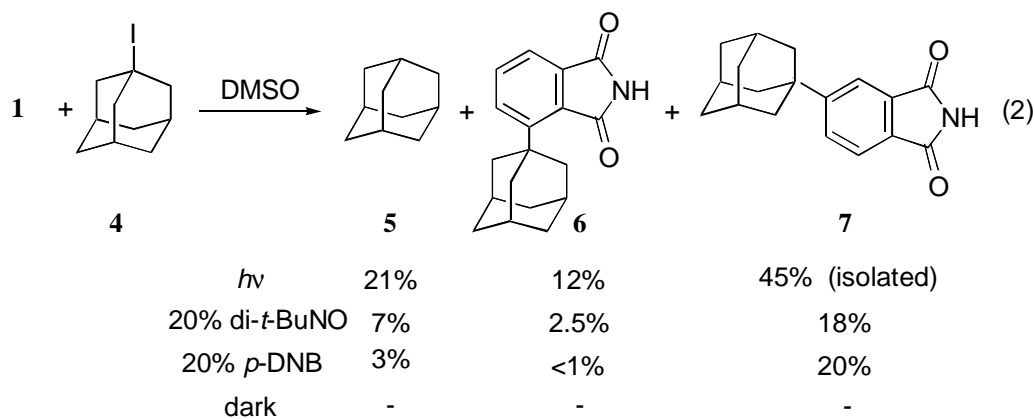


Results and Discussion

The photoinduced reaction of anion **1** with 1-iodonaphthalene (**3**) in dimethylsulfoxide (DMSO) and in the presence of 18-crown-ether renders 72% of iodide ions after three hours and naphthalene is the only product observed. This reaction does not occur in the dark.

The reaction of anion **1** with 1-iodoadamantane (**4**) under the same conditions, yields a 78% of io-

dide ions, adamantane (**5**) and the substitution products **6** and **7** which arise from the coupling reaction of the adamantyl radical at the carbon 4 and 5 of anion **1** respectively. When this reaction was performed in the presence of a radical trap as di-*ter*-butylnitroxide (di-*t*-BuNO) or a better electron acceptor than **4** as *p*-dinitrobenzene (*p*-DNB), results in strong inhibition. (eq.2). In the dark, no reaction was observed between **1** and **4**.



These results showed that a photoinduced electron transfer from anion **1** to substrates **3** and **4** renders the naphthyl or the adamantyl radical intermediates respectively. While only hydrogen abstraction is observed for the naphthyl radical yielding naphthalene as reduction product, the adamantyl radical adds surprisingly to the carbon atoms instead of the nitrogen atom giving distonic radical anions. This behavior is different from the previously described reaction of this anion with *ter*-butyl radicals [3]. In the present communication we will discuss the reactivity of this anion with different substrates.

References and Notes

- Rossi, R. A.; Pierini, A. B.; Peñeñory, A. B. Recent Advances in the $S_{RN}1$ Reaction of Organic Halides. In *The Chemistry of Functional Groups*; Patai, S.; Rappoport, Z., Eds.; John Wiley & Sons: 1995; Chapter 24, p. 1395-1485.
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