Photoinitiated Reaction of β-Bromonaphthalene with Pinacolone Ion in DMSO

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Abstract: The photoinitiated reaction of β -bromonaphthalene with excess pinacolone enolate does not yield expected normal $S_{RN}1$ product $1-\beta$ -naphthyl-3,3-dimethyl-2-butanone, **3**, but a more complex molecule 2,2-dimethyl-5-(1',1'-dimethylethyl)-6- β -naphthyl-5-hexene-3-one, **4**, deriving from it. The reaction is inhibited by *m*-dinitrobenzene and do not occur in the absence of light. Structure analysis of the product, along with other evidence, indicates a mechanism for this reaction, where addition of a further pinacolone molecule to carbonyl group of **3** and subsequent elimination of a water molecule would afford product **4**, once the $S_{RN}1$ substitution product **3** has formed.

Keyword: S_{RN} 1 reaction, β -bromonaphthalene, pinacolone enolate, addition reaction.

The radical nucleophilic substitution reaction $(S_{RN}1)$ has been studied widely. The reaction has constituted an important synthetic possibility to achieve substitution of different substrates with different nucleophiles¹⁻³. The main steps of the reaction process are presented in **Scheme 1**.

Scheme 1. $ArX+e^{-} \xrightarrow{h_{\mathcal{V}}} [ArX]^{-}$ (1)

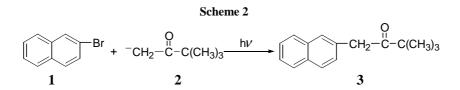
$$[ArX]^{\bullet} \longrightarrow Ar^{\bullet} + X^{\bullet}$$
(2)

$$Ar^{\bullet} + Nu^{-} \longrightarrow [ArNu]^{\bullet}$$
 (3)

 $[ArNu]^{\bullet}_{+ArX} \longrightarrow ArNu+[ArX]^{\bullet}$ (4)

Pinacolone enolate ions are widely used as nucleophiles within S_{RN} 1reaction⁴⁻⁶ because it can introduce six carbon atoms into substitution products. In the paper, the photoinitiated reaction of β -bromonaphthalene **1** with pinacolone enolate ion **2** (prepared by the acid base reaction of pinacolone with t-Bu-OK in DMSO) was investigated. It was expected that compourd **3**, 1- β -naphthyl-3,3-dimethyl-2-butanone,

as normal $S_{\text{RN}}1$ substitution product, would be formed (Scheme 2).



But, the experimental results showed that the reaction mainly afforded compound **4** 2,2-dimethyl-5-(1',1'-dimethylethyl)-6- β -naphthyl-5-hexene-3-one, with only a minor amount of **3**. Additionally, this reaction did not occur in the dark and in the presence of *m*-dinitrobenzene (*m*-DNB) (a quencher of radical) (**Table 1**).

Table 1 Photostimulated Reaction of β -Bromonaphthalene
with Excess Pinacolone Enolate in DMSO^a

Expt.	Substrate 1 (mol)	t-Bu-OK (mol)	Pinacolone (mol)	DMSO (ml)	Conditions	Yield of Product $4 (\%)^{b}$
1	0.01	0.05	0.05	20	h v, 1h	39
2	0.02	0.02	0.05	20	h ບ , 1h	34
3	0.01	0.05	0.05	20	Dark, 2h	0
4	0.01	0.05	0.05	20	h v ,m-DNB	0

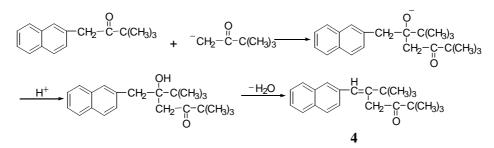
a. Irradiation is performed by a Rayonet Photochemical Chamber Reactor PPR-100 (The Southern New England Uitraviolet Company) under nitrogen.

b. Yields are determined by TLC-Densitometry.

Apparently, the presence of an excess of pinacolone appeared to be of crucial importance⁷. When the reaction was carried out with a larger excess (5 mol equiv. instead of 2) of 2, compound 4 became the main reaction product and no traces of 3 were detected.

It was thought that compound **3**, which is the product of the photoinitiated $S_{RN}1$ reaction of **1**, could behave as an intermediate in the formation of **4**. The addition of a further pinacolone molecule to the carbonyl group of compound **3** and subsequent elimination of a water molecule would afford product **4**. The addition may take place in two general ways: thermochemical process and photochemical process. The details of the thermochemical addition can be shown in **Scheme 3**

Scheme 3

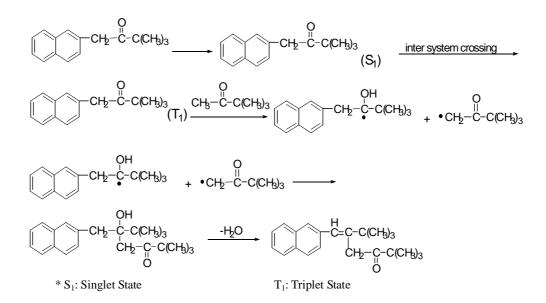


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In this process of addition the nucleophile uses its electron pair to form a bond to the carbonyl carbon. As this happens an electron pair of the carbon-oxygen π bond shifts out to the carbonyl oxygen. In the second step the oxygen associates a proton⁸.

The process of photoinduced addition can be shown in Scheme 4.

Scheme 4



This mechanism operates when **3** is irradiated in DMSO with pinacolone which plays a role of hydrogen donor⁹. The triplet $n \pi^*$ state of **3** (T₁) as the reactive state would carry out a hydrogen abstraction from pinacolone molecule resulting in formation of radical pair. The radical pair would couple leading eventually to product **4**¹⁰.

Acknowdgments

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- Compound **4** was purified by two steps of silica-gel column chromatography, (for first step, eluent: pertroleum ether; second step, eluent: 1, 2-dichloroethane). m. p. 152-154°C. The molecular structure was characterized by IR., ¹H NMR, MS. and elemental analysis. IR(KBr) ¥ : 3050, 2950, 1690, 1630, 1590, 855, 815, 800, 770, 755, 735cm⁻¹; ¹H NMR(CDCl₃) δ :1. 40 (S, 18H), 2. 25 (S, 2H), 5. 70 (S, 1H), 7. 40 (m, 7H)ppm; MS (*m*/*z*): 308(M⁺), 223, 181, 167, 141, 127, 85, 57. Anal. Calcd. For C₂₂H₂₈O (308. 46): C, 85. 66; H, 9. 15; O, 9. 15%. Found: C, 85. 94; H, 9. 22; O, 4. 84%.

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