

Photoinitiated Reaction of β -Bromonaphthalene with Pinacolone Ion in DMSO

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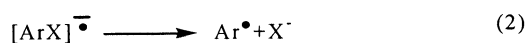
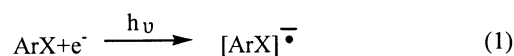
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Abstract: The photoinitiated reaction of β -bromonaphthalene with excess pinacolone enolate does not yield expected normal $S_{RN}1$ product 1- β -naphthyl-3,3-dimethyl-2-butanone, **3**, but a more complex molecule 2,2-dimethyl-5-(1',1'-dimethylethyl)-6- 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.

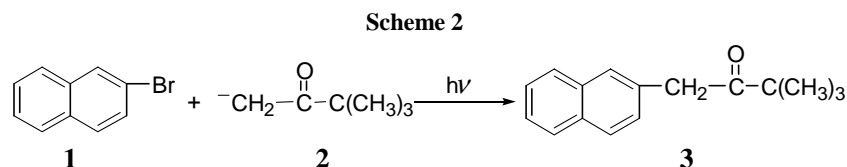
The radical nucleophilic substitution reaction ($S_{RN}1$) has been studied widely. The reaction has constituted an important synthetic possibility to achieve substitution of different substrates with different nucleophiles¹⁻³. The main steps of the reaction process are presented in **Scheme 1**.

Scheme 1.



Pinacolone enolate ions are widely used as nucleophiles within $S_{RN}1$ reaction⁴⁻⁶ 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 compound **3**, 1- β -naphthyl-3,3-dimethyl-2-butanone,

as normal $S_{RN}1$ 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

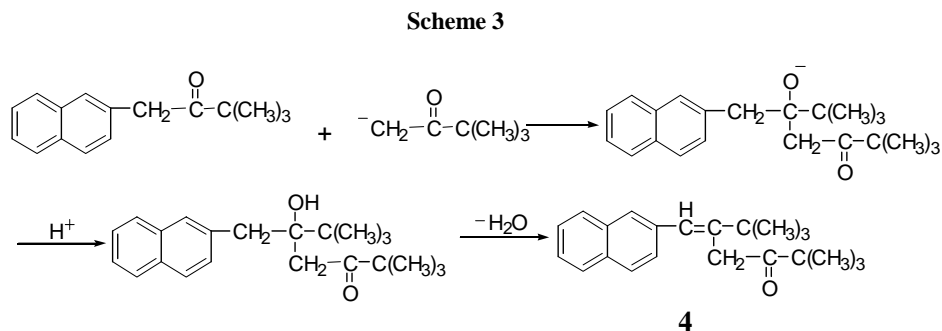
Expt.	Substrate 1 (mol)	<i>t</i> -Bu-OK (mol)	Pinacolone (mol)	DMSO (ml)	Conditions	Yield of Product 4 (%) ^b
1	0.01	0.05	0.05	20	<i>h v</i> , 1h	39
2	0.02	0.02	0.05	20	<i>h v</i> , 1h	34
3	0.01	0.05	0.05	20	Dark, 2h	0
4	0.01	0.05	0.05	20	<i>h v</i> , <i>m</i> -DNB	0

a. Irradiation is performed by a Rayonet Photochemical Chamber Reactor PPR-100 (The Southern New England Ultraviolet 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**



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10. Compound **4** was purified by two steps of silica-gel column chromatography, (for first step, eluent: petroleum 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) ν : 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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