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Photoalkylation of quinones with ethers

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Abstract

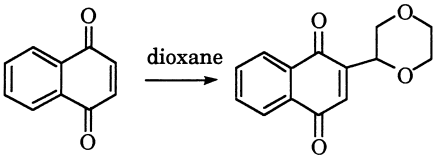
The photoalkylation reactions of benzoquinone with a number of ethers was studied. Some unusual regioselectivities were observed. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Photoalkylation; Benzoquinone; Photochemical alkylation

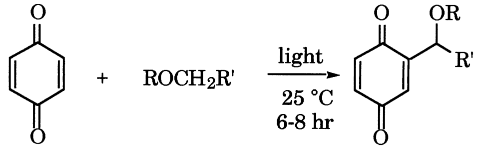
1. Introduction

The organic photochemistry of unsaturated carbonyl compounds has been extensively studied [1]. In contrast, our understanding of the photochemistry of quinones is less well defined. Reactions of quinones with alcohols, alkenes, and aldehydes have been reported. Although the reaction of quinones with alcohols leads to quantitative reduction to the hydroquinone, alkenes and aldehydes react to form new carbon–carbon bonds [2,3]. Maruyama has collated recent photochemical reactions of quinones in a timely review [4].

The photochemical alkylation of quinones with alkanes or ethers has been little studied. Isolated examples describing alkylation of quinones by solvents such as dioxane have been reported. An example is illustrated below [5]. A clever alkylation reaction of quinones with allylic silanes has been reported by Fujita [6].



As part of a program designed to develop photochemical reactions as benign alternatives to synthetic reactions which produce pollutants, we evaluated the photochemical alkylation of quinones as an alternative to certain Friedel-Crafts alkylation reactions [7]. This alkylation reaction may be significant, since simple hydroquinones such as tert-butylhydroquinone (TBHQ) are widely used as antioxidants. We report herein several photochemical reactions of quinones with ethers and acetals.



2. Experimental details

A typical experiment is conducted as follows: A round-bottom flask is charged with a teflon-coated stirring bar, ether and benzoquinone. Reactions were conducted using 10 mmol (1.08 g) of benzoquinone and 100 mmol (10 equivalents) of the ether. The flask is placed in a well-ventilated hood and irradiated with light from a medium pressure Hanovia lamp. The progress of the reaction is monitored by thin layer chromatographic analysis using commercially available thin layer chromatography plates coated with silica gel. When the limiting reagent (the starting quinone) has been consumed, the solvent is then removed in vacuo and all of the crude product is immediately purified by column chromatography using commercially available silica gel (flash chromatography) with a solvent mixture of ethyl acetate and hexanes.

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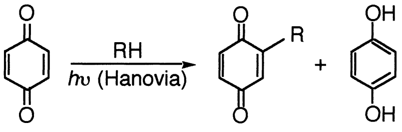
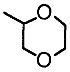
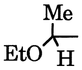
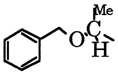
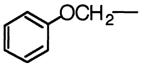
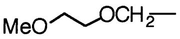
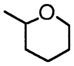
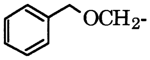
Table 1
Reactions of benzoquinone with ethers



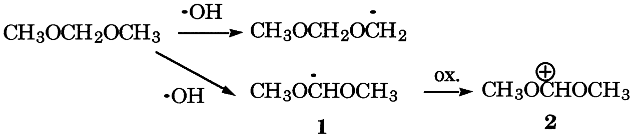
A

RH	Reaction time (h)	**A**	Yield (%)
Dioxane	18		10
Diethyl ether	18		26
Ethyl benzyl ether	22		30
Methyl tert-butyl ether	14	tBu–O–CH$_2$$^-$	40
Anisole	20		34
Dimethoxyethane	27		34
Tetrahydropyran	46		26
Dimethoxymethane	15	CH$_3$OCH$_2$OCH$_2$$^-$	14
Methyl benzyl ether	22		14

3. Results and discussion

We examined a variety of ethers including diethyl ether, methyl benzyl ether, methyl tert-butyl ether, dioxane, tetrahydrofuran and anisole. We also studied dimethoxymethane. The photochemical alkylation reaction produces an alkylated hydroquinone which reacts with benzoquinone to afford the alkylated quinone plus a molecule of hydroquinone. The results of the photochemical alkylation reaction are depicted in Table 1.

In the case of ethyl benzyl ether, we were surprised by the absence of products derived from hydrogen atom abstraction from the benzylic carbon atom. A similar result had been observed by Jacobsen and Torssell using dimethoxymethane for hydrogen atom abstraction using Fenton's reagent [8]. They rationalized their modest yields and the unexpected selectivity by postulating that the radical **1** was formed but was oxidized to cation **2** which afforded degradation products by fragmentation.



The same oxidation process is occurring in our system and is responsible for the modest yields and the unusual regioselectivity. An examination of the product mixture from the reaction of benzoquinone with methyl benzyl ether using gas chromatography showed that benzaldehyde, a product of the oxidation of the benzylic radical followed by fragmentation, was produced in 11–17% yield and that benzoic acid (presumably derived from oxidation of benzaldehyde) was also produced in 11–17% yield.

As the results of Table 1 show, the addition reactions show surprising regioselectivities with dialkyl ethers. Many of the isolated yields are modest; nevertheless, the starting materials are readily available. Additionally, the experimental conditions are operationally convenient.

Acknowledgements

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