

COMMUNICATION

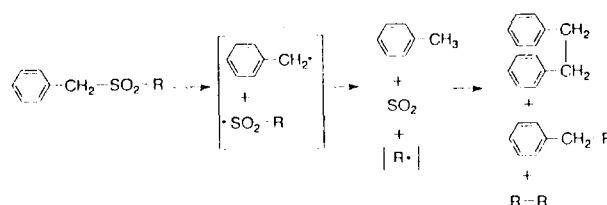
EXPLORATORY PHOTOCHEMICAL STUDY ON THE *o*-NITROBENZYL SULFONYL DERIVATIVES

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INTRODUCTION

The photochemistry of nitro chromophore has been the subject of intense study only in recent years.^{1,2} Unlike the carbonyl functional group, of which the photochemistry has been quite extensively studied and fairly well understood, as a result of excellent work done by numerous physical and organic photochemists alike, the nature of photochemistry of nitro group has only recently been systematically explored. The photochemistry of nitro group exhibits general features of the photochemistry of the carbonyl groups such as hydrogen abstraction by the diradical species generated from the $n-\pi^*$ excited state of the nitro group. Other photochemical pathways common to the carbonyl group such as the biradical intermediate formation, photocycloelimination, and cycloaddition reactions are also open for the nitro group. Of all the photochemical reactions of the nitro group mentioned above, hydrogen abstraction by the $n-\pi^*$ excited state of the nitro group has drawn much attention by synthetic

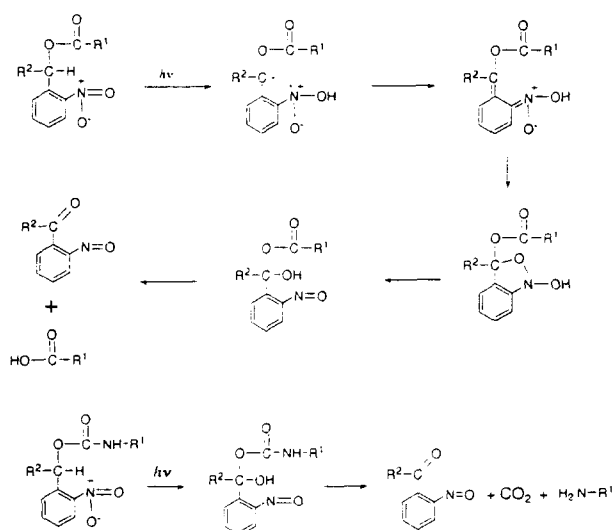


Scheme 2. Photochemistry of benzy sulfones

organic chemists and polymer chemists. In the field of organic synthesis, above mentioned photochemical reaction has been utilized in the photoprotection-deprotection chemistry. Thus the -OH and -NH₂ groups have been protected by *o*-nitrobenzyl group.³ Unlike any other protecting groups, *o*-nitrobenzyl group can be removed photochemically under very mild conditions (Scheme 1). The scope of this reaction has been further widened so the reaction could be utilized for generation of bases under photochemical condition. When *o*-nitrobenzyl ester of carbamic acid was irradiated, an amine and a nitroso compounds are liberated in high yields.⁴ The reaction is currently being actively studied for its use as a potential photo-base generator, which consists the key step in the photoresist chemistry.⁵

On the other hand, benzylic sulfonyl compounds with no nitro group on the *ortho*-position have attracted much attention.^{6,7} Those benzylic sulfonyl compounds, mainly benzylic sulfones, extrudes SO₂ to form radical recombination products upon UV irradiation, as shown in Scheme 2. This chemistry has been utilized in the synthesis of strained small ring compounds and cyclophanes.^{6,7}

However putting those two chemistries together, namely the photochemistry of *o*-nitrobenzylic and benzylic sulfonyl systems, has never been attempted, even though these two chromophores are photochemically quite active on their own rights. In other words, the photochemistry of *o*-nitrobenzyl esters or amides, and the photochemistry of benzylic sulfonyl derivatives were well studied separately, but little is known about the photochemistry of *o*-nitrobenzyl-sulfonyl derivatives. Thus we have initiated the study on the photochemistry of *o*-nitrobenzylsul-



Scheme 1. Photochemistry of *o*-nitrobenzyl esters and carbamates

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