COMMUNICATION

EXPLORATORY PHOTOCHEMICAL STUDY ON THE o-NITROBENZYLSULFONYL 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 intermidiate 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- π^* excited state of the nitro group has drawn much attention by synthetic

Scheme 1. Photochemistry of o-nitrobenzyl esters and carbamates

Scheme 2. Photochemistry of benzylsulfones

organic chemists and polymer chemists. In the field of organic synthesis, above mintioned 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 benzylsulfonyl compounds, mainly benzylsulfones, 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 benzylsulfonyl systems, has never been attempted, even though these two chromphores are photochemically quite active on their own rights. In other words, the photochemistry of o-nitrobenzyl esters or amides and the photochemistry of benzylsulfonyl derivatives were well studied separately, but little is known about the photochemistry of o-nitrobenzylsulfonyl derivatives. Thus we have initiated the study on the photochemistry of o-nitrobenzylsul-

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Scheme 3. Synthesis and photolysis of o-nitrobenzyl-sulfonate esters and amides

fonyl chromophore. The synthesis and photolysis of the target compounds, o-nitrobenzylsulfonyl esters and amides, are described in Scheme 3. o-Nitrobenzylsulfonyl chloride has been reacted with corresponding alcohols and amines to provide the esters and amides 1-4 in 71-79% yields. The results from the photolysis. Thus the photolysis of the cyclohexyl ester described below might well serve as a representative model for the photochemistry of o-nitrobenzylsulfonate esters and amides.

Photolysis was done in MeOH and Et₂O with no appreciable difference in results. When the methanolic solutions of sulfonate esters 1 and 2 had been irradiated with 254 nm UV, isolated was cyclohexanol 5, as evidenced by GC/MS.* When progress of the photolysis was monitored by GC, the amount of the sulfonyl ester 1 was stayed unchanged after 16 h of irradiation in the Rayonet Reactor using 16 RPR-2537 lamps.* Pseudo-photo stationary state has been eatablished consisting of 55 mol% of the ester 1 and 45 mol% of photolysis product, cyclohexanol.* The pseudo-photo

stationary state was caused by the internal filter effect of the other photolysis product, o-nitrosobenzaldehyde. When the solvent from the reaction mixture was removed and the photolysate was extracted by H₂O, the pH of the aqueous fraction was 1.5. Addition of BaCl₂ to this solution resulted in the formation of white precipitate of which the structure was confirmed by IR as BaSO₄. An attempt to quantitatively measure the amount of SO₂ liberated during the photolysis has failed. Mechanistic work on this system is under way.

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- 8. The structures of the photolysis products were determined by spectroscopic methods including NMR (Bruker AC 100) and IR (JASCO Report-100) and UV (Milton Roy 1201).
- 9. Photolysis was performed using either Rayonet Photochemical Reactor or 450W Hanovia medium pressure mercury lamp.
- 10. Analytical GC work was done by HP 5890 Gas Chromatograph (FID) using 30m Supelco SE-30 wide-bore capillary column. Decaline was the internal standard employed to calculate relative response factor.