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# PHOTOCHEMICAL REACTIONS OF N-ALKYL- AND N-ALLYL-o-SULFOBENZIMIDES

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Photolysis of N-alkyl-o-sulfobenzimides 1 in isopropyl alcohol or in benzene was investigated. N-Alkylbenzamides 2 were the major product in isopropyl alcohol, while N-alkyl-o-phenylbenzamides 9 were formed in good yield in benzene. A reaction mechanism involving the homolysis of the N-S bond in 1 followed by the elimination of sulfur dioxide is proposed.

It is well known that N-alkylated phthalimides undergo photochemical hydrogen abstraction reactions, addition reactions, and cyclization reactions.[1] On the other hand, no example of photochemical reactions of o-sulfobenzimides, the sulfonyl analogous of phthalimides, has been reported. We wish herein to report the photolysis of N-alkyl- and N-allyl-o-sulfobenzimides 1 in isopropyl alcohol or in benzene.

In a typical example, a solution containing 200 mg (1.02 mmol) of N-methyl-o-sulfobenzimide 1b in 160 ml of isopropyl alcohol was irradiated under nitrogen with a 450-W medium pressure Hg-arc lamp (Hanovia) through a Corex sleeve for 3.5 h. Sulfur dioxide was evolved during the irradiation and the yield was determined (45%) by titration with 0.1 N sodium hydroxide solution after conversion to sulfuric acid with 3% hydrogen peroxide. Solvent was expelled from the reaction mixture to give the oily residue, which was diluted with benzene and washed with 5% aqueous sodium hydroxide solution. The organic layer was condensed again and subjected to the elution chromatography on silica gel. N-Methylbenzamide 2b (78 mg, 77%) and S-[o-(methylcarbamoyl)phenyl] o-(methylcarbamoyl)benzenethiosulfonate 3b in trace amount were obtained together with 50 mg (25%) of 1b unchanged. From the alkaline extract o-(methylcarbamoyl)benzenesulfonic acid 4b (16%) was isolated as benzylisothiouronium salt. Althogh the carbonyl group was known to be reduced to alcohol in the photochemical reaction of phthalimides, no reduced compound such as 5b was found in the reaction products. N-Alkyl-o-sulfobenzimides, R=H (1a), ethyl (1c), n-propyl (1d) and n-butyl (1e), and N-allyl-o-sulfobenzimide (1f) were irradiated in similar ways in isopropyl alcohol to give N-alkyl- and N-allylbenzamides 2 as the major products (52-76% yield) as summarized in Table 1.

On the basis of the reaction products thus obtained, the following mechanism is proposed. The o-sulfobenzimide 1 in the excited state breaks the N-S bond homolytically to give a radical intermediate 6. Abstraction of hydrogens by 6 from isopropyl alcohol affords a sulfinic acid 7, which subsequently disproportionates to 3 and 4. An 1,4-biradical 8, which is formed from 6 by elimination of sulfur dioxide, abstracts hydrogens from the solvent to give the benzamide 2.

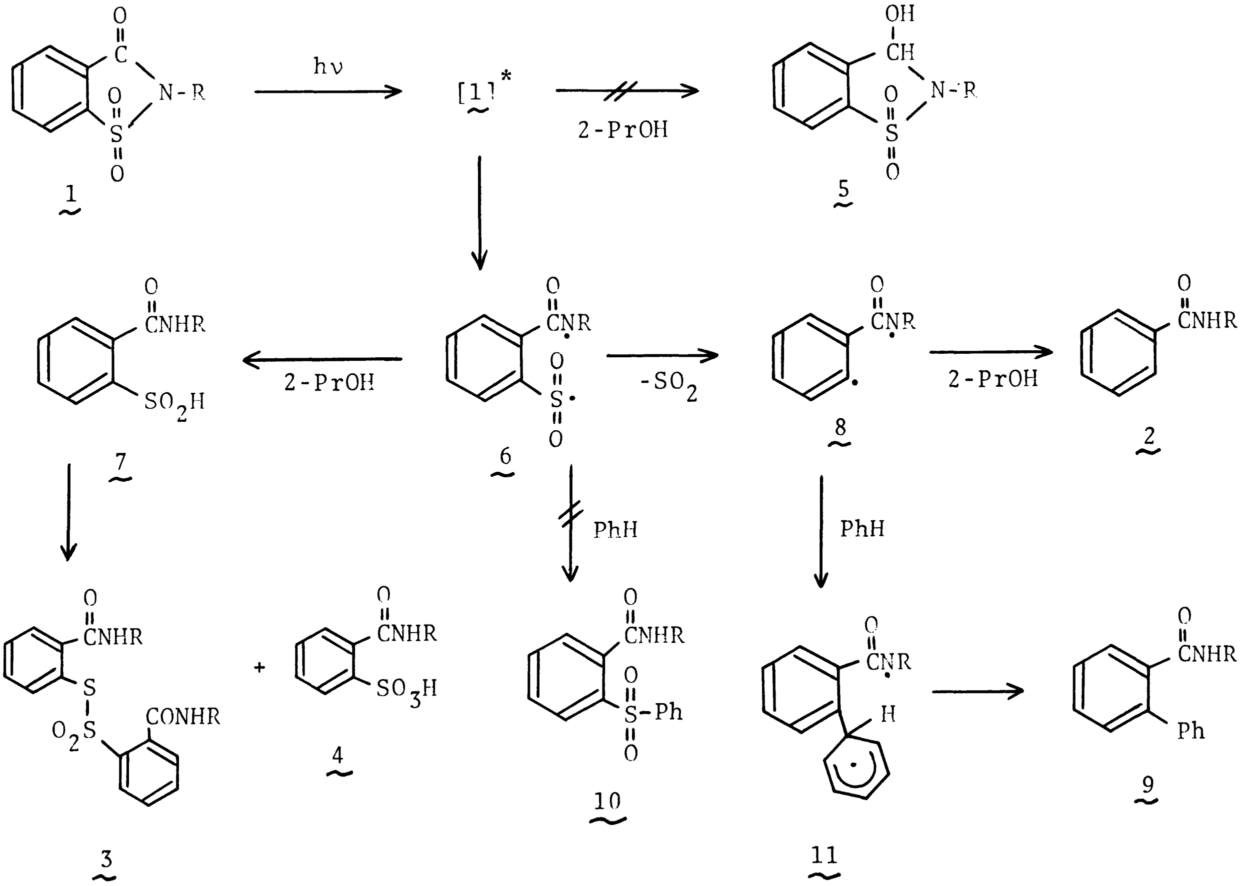

Table 1. Photolysis of o-Sulfobenzimides **1** Isopropyl Alcohol

| **1** | | | Irrad. Time(h) | Products, % | | | | |
|---|---|---|---|---|---|---|---|---|
| R in **1** | | mmol | | **2** | (mp, °C) | $SO_2$ | **3** | **4** |
| a | H | 1.09 | 5.0 | 52 | 129 | | | |
| b | Me | 1.02 | 3.5 | 77 | 80 | 45 | trace | 16 |
| c | Et | 1.02 | 3.5 | 76 | 69 | | | |
| d | n-Pr | 2.22 | 6.0 | 57 | 85 | | | |
| e | n-Bu | 2.09 | 6.0 | 59 | oil | | | |
| f | $CH_2CH=CH_2$ | 0.92 | 4.0 | 55 | oil | | | |

When **1** was irradiated in benzene, o-phenyl-N-alkylbenzamides **9** and sulfur dioxide were formed in good yields, and no sulfone **10** was detected. The results are summarized in Table 2.

Table 2. Photolysis of o-Sulfobenzimides **1** in Benzene

| **1** | | | Irrad. Time(h) | Products, % | | |
|---|---|---|---|---|---|---|
| R in **1** | | mmol | | **9** | (mp, °C) | $SO_2$ |
| a | H | 1.09 | 3.0 | 41 | 172 | |
| b | Me | 1.01 | 3.5 | 77 | 172 | 74 |
| c | Et | 1.02 | 5.0 | 52 | 79 | |
| d | n-Pr | 0.89 | 3.0 | 55 | 91 | |
| e | n-Bu | 2.09 | 9.0 | 58 | 73 | |
| f | $CH_2CH=CH_2$ | 2.24 | 6.0 | 60 | 85 | |

The photolysis of **1** in benzene solution would proceed in a similar mechanism to that in isopropyl alcohol. The o-sulfobenzimide **1** forms an intermediate **6** from its excited state, which then loose sulfur dioxide to yield **8**. The biradical **8** attacks the solvent benzene to give a cyclohexadienyl radical **11**, which is converted into **9** probably by intramolecular hydrogen abstraction by an internal acylaminyl radical.

The detailed mechanism including additional evidence of the formation of the 1,4-biradical **8** in the photochemistry of **1** is under investigation.

## References and Note

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2) All products gave satisfactory spectral properties. The yield was based on the consumed imide.

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