

## PHOTOCHEMICAL REACTIONS OF PSEUDOSACCHARIN 3-ALLYL ETHER (PROBENAZOLE) AND ITS ALKYL ETHER

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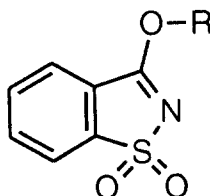
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**Abstract** — Photoreactions of pseudosaccharin ethers have been investigated. Pseudosaccharin 3-allyl ether undergoes a facile photoreaction via reaction pathways involving homolysis of bond between pseudosaccharyl oxygen and 3-allyl carbon, and excited nucleophilic substitution of allyloxy group by solvent which are not quenched by oxygen present in the reaction. Product yield demonstrates that the homolysis pathway predominates over the nucleophilic substitution in ca. 7:1 ratio. In contrast, pseudosaccharin alkyl ethers follow different reaction routes to produce two products, solvent-substituted pseudosaccharin alkyl ethers and reduction products, 3-alkoxy-1,2-benzisothiazoles. The formations of reduction products, 3-alkoxy-1,2-benzisothiazoles are completely quenched by oxygen.

### INTRODUCTION

Probenazole (**1a**, pseudosaccharin 3-allyl ether, 3-allyloxy-1,2-benzisothiazole-1,1-dioxide) is a non-fungicidal systemic controlling agent<sup>1-4</sup> against rice blast and bacterial leaf blight in practical use in Asia. Its action mechanism on both rice blast and bacterial leaf blight is suggested to be indirect and to be largely based on host-mediated defense action.<sup>5-11</sup> In contrast to many studies on its metabolic pathway in rice plant<sup>3,4,12</sup> and its degradation route after application on paddy soil,<sup>13</sup> report on its photochemical degradation is lack in spite that it is constituted with good chromophoric components and is doomed to be exposed to strong sun light. Thus in order to uncover its photoreactivity and photodegradation route we have investigated the photoreaction of probenazole (**1**) and further investigated those of its alkyl derivatives, pseudosaccharin alkyl ethers (**2-4**) for comparisons. Belows are described the results of these studies which uncover that probenazole (**1**) undergoes a facile and characteristic photoreaction through a homolytic cleavage of bond between allyl carbon and pseudosaccharin oxygen, and a nucleophilic substitution of allyloxy group by solvent molecule while its alkyl derivatives **2-4** undergo

nucleophilic substitution reactions followed by photochemical reductions of sulfone group.



- 1 : R = CH<sub>2</sub>CH=CH<sub>2</sub>
- 2 : R = CH<sub>3</sub>
- 3 : R = CH<sub>2</sub>CH<sub>3</sub>
- 4 : R = CH(CH<sub>3</sub>)<sub>2</sub>

### MATERIALS AND METHODS

*General.* Melting points were taken on Fisher-Johns Melting Point Apparatus. Preparative TLC was performed on glass plate with silica gel (silica gel G 60 F<sub>254</sub>) and compounds were visualized using on UV-lamp. Column chromatography was performed by Kiesel Gel 60 (70-230 mesh, Merck). <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Varian EM-360A, a Varian XL-100 and a Bruker WP-200 spectrophotometer with tetramethylsilane as internal standard. Ultraviolet spectrum was taken on a Hitachi-124 spectrometer. IR spectra were taken on a Perkin-Elmer 710B spectrometer. Low resolution mass spectral analyses were performed at 70 eV on a Hitachi RMU-6 mass spectrometer and high resolution mass spectral analyses were performed at 70 eV on a Hitachi-VG 7070 mass spectrometer. Preparative photolyses were conducted with an apparatus consisting of 450W Hanovia medium pressure mercury vapor lamp surrounded by Vycor filter in a quartz immersion well under inert atmospheres, and solvent used for photolyses was removed

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under reduced pressure. Drying of organic layers obtained by work-up of reaction mixtures was performed by standing over anhydrous sodium sulfate.

**Materials.** Probenazole (**1**) and its alkyl derivatives **2-4** were prepared by reported method<sup>15</sup> from pseudosaccharin chloride<sup>16</sup> and allyl alcohol, methanol, ethanol or 2-propanol respectively. Probenazole (**1**); m.p. = 138-139°; <sup>1</sup>H-NMR (acetone-d<sub>6</sub>, 60 MHz) 5.11 (d, 2H, J = 6 Hz, -OCH<sub>2</sub>-), 5.27-5.75 (m, 2H, CH<sub>2</sub>=), 5.88-6.57 (m, 1H, -CH=), 7.75-8.20 (m, 4H, aromatic).

**Photolysis of probenazole in methanol.** A solution of probenazole (**1**, 300 mg, 1.35 mmol) in methanol (180 mL) was irradiated under N<sub>2</sub> and the reaction was followed by TLC (CHCl<sub>3</sub>). After irradiation for 2 h (100% conversion of **1**), the resulting photolyzate was concentrated under reduced pressure. From the residue, 99 mg (33%) of N-3-allylsaccharin (**5**), 93 mg (40%) of saccharin (**6**) and 27 mg (11%) of pseudosaccharin methyl ether (**2**) were isolated by column chromatography (ethyl acetate/hexane, 5:3). N-3-Allylsaccharin (**5**); m.p. = 175-176°; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 100 MHz) 4.36 (d, 2H, J = 7 Hz, allylic CH<sub>2</sub>), 5.20-5.60 (m, 2H, vinylic CH<sub>2</sub>=), 5.77-6.25 (m, 1H, vinylic -CH=), 7.75-8.15 (m, 4H, aromatic); IR (KBr) 1732 (C=O stretching), 1150 and 1305 cm<sup>-1</sup> (asymmetric and symmetric O=S=O stretching); MS (rel. intensity) 224 (M<sup>+</sup>+1, 2), 223 (M<sup>+</sup>, 7), 196 (M<sup>+</sup>-CH=CH<sub>2</sub>, 9), 184 (10), 159 (M<sup>+</sup>-SO<sub>2</sub>, 100), 158 (26), 130 (99), 117 (33), 104 (C<sub>8</sub>H<sub>8</sub>C≡O<sup>+</sup>, 44), 90 (10). Physical properties of isolated saccharin (**6**) and pseudosaccharin methyl ether (**2**) were identical to those of authentic sample of **6** and synthetic sample of **2**.

**Photolysis of probenazole in 2-propanol.** Irradiation of probenazole (**1**, 300 mg, 1.35 mmol) in 2-propanol (180 mL) under the condition as described above and similar work-up gave 129 mg (56%) of saccharin (**6**) as the sole product. N-3-allyl saccharin (**5**) and pseudosaccharin methyl ether (**2**) were not observed in TLC analysis of the photolyzate of **1**.

**Photolyses of pseudosaccharin alkyl ethers in methanol.** A solution of pseudosaccharin methyl ether (**2**, 300 mg, 1.52 mmol) in methanol (180 mL) was irradiated under N<sub>2</sub> for 10 h (50% conversion of **2**). After removal of solvent and purification by preparative TLC (CHCl<sub>3</sub>/hexane, 3:1), 3-methoxy-1,2-benzisothiazole (**7**, 109 mg, 87%) was obtained as the sole product. 3-Methoxy-1,2-benzisothiazole (**7**); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) 4.20 (s, 3H, CH<sub>3</sub>), 7.32-7.80 (m, 4H, aromatic); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 55.8 (OCH<sub>3</sub>), 120.2, 122.9, 124.4 and 128.6 (aromatic CH), 125.2 and 151.7 (aromatic C), 163.6 (O-C=N); MS (rel. intensity) 116 (M<sup>+</sup>+1, 11), 165 (M<sup>+</sup>, 100), 164 (M<sup>+</sup>-1, 27), 137 (18), 136 (78), 135 (29), 134 (5), 122 (15), 109 (16), 108 (18), 106 (17); high resolution MS, m/z 165.0239 (C<sub>8</sub>H<sub>7</sub>NOS requires 165.0249). Similar irradiations of pseudosaccharin alkyl ethers **3** and **4** in methanol and similar work-up gave pseudosaccharin methyl ether (**2**, ca. 40%) and 3-methoxy-1,2-benzisothiazole (**7**, ca. 45%).

**Photolyses of pseudosaccharin alkyl ether (**2-3**) in 2-propanol.** Solutions of pseudosaccharin alkyl ethers (**2**, 300 mg, 1.52 mmol; **3**, 300 mg, 1.42 mmol) in 2-propanol (180

mL) were irradiated under N<sub>2</sub> for 10 h and 14 h. Removal of solvent and preparative TLC (CHCl<sub>3</sub>/hexane, 3:1) gave 66 mg (56%) of 3-isopropoxy-1,2-benzisothiazole (**9**) and 18 mg (18%) of 3-methoxy-1,2-benzisothiazole (**7**) from the photolyzate of **2**, and gave 55 mg (50%) of 2-isopropoxy-1,2-benzisothiazole (**9**) and 19 mg (19%) of 3-ethoxy-1,2-benzisothiazole (**8**) from the photolyzate of **3**. 3-Ethoxy-1,2-benzisothiazole (**8**); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) 1.50 (t, 3H, J = 7.1 Hz, CH<sub>3</sub>CH<sub>2</sub>-), 4.59 (q, 2H, J = 7.1 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 7.31-7.93 (m, 4H, aromatic); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 14.6 (CH<sub>3</sub>), 64.5 (CH<sub>2</sub>), 120.0, 123.0, 124.2 and 128.5 (aromatic CH), 125.5 and 151.5 (aromatic C), 163.1 (O-C=N); MS (rel. intensity) 180 (M<sup>+</sup>+1, 7), 179 (M<sup>+</sup>, 58), 164 (M<sup>+</sup>-CH<sub>3</sub>, 10), 152 (13), 151 (100), 150 (6), 136 (10), 122 (10), 96 (30); high resolution MS, m/z 179.0407 (C<sub>10</sub>H<sub>9</sub>NOS requires 179.0405). 3-Isopropoxy-1,2-benzisothiazole (**9**); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) 1.45 (d, 6H, J = 6.2 Hz, (CH<sub>3</sub>)<sub>2</sub>CH-), 5.38 (sept, 1H, J = 6.2 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 7.30-7.90 (m, 4H, aromatic); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 22.1 (CH<sub>3</sub>), 71.7 (CH), 120.0, 123.2, 124.2 and 128.5 (aromatic CH), 126.0 and 151.3 (aromatic C), 162.6 (O-C=N); MS (rel. intensity) 194 (M<sup>+</sup>+1, 1), 193 (M<sup>+</sup>, 7), 179 (15), 151 (100), 136 (3), 108 (5), 96 (20); high resolution MS, m/z 193.0562 (C<sub>10</sub>H<sub>11</sub>NOS requires 193.0553).

**Photolysis of probenazole (**1**) in the presence of oxygen.** A solution of probenazole (**1**, 300 mg, 1.35 mmol) in methanol (180 mL) was irradiated under purging with a stream of O<sub>2</sub> for 2 h (ca 100% conversion of **1**). Similar work-up to that of photolyzate of **1** under N<sub>2</sub> gave 78 mg (26%) of **5**, 84 mg (36%) of **6** and 19 mg (7%) of **2**.

**Oxygen quenching of photoreaction of pseudosaccharin methyl ether (**2**) in methanol.** A solution of pseudosaccharin methyl ether (**2**, 300 mg, 1.52 mmol) in methanol (180 mL) was irradiated under purging with a stream of O<sub>2</sub> for 10 h and the reaction was examined by TLC. The TLC analysis showed no noticeable change in the reaction.

## RESULTS AND DISCUSSION

Absorption spectrum of probenazole, pseudosaccharin 3-allyl ether (**1**) exhibits a strong absorption in the region of 200-310 nm with absorption maxima at 268 nm (ε 4500) and 227 nm (ε 9400) and those of pseudosaccharin alkyl ethers (**2-4**) show essentially the same absorption properties as that of **1**. Photoreactions of probenazole (**1**) and its alkyl derivatives **2-4** were explored. Photoreactions were performed by irradiation of methanol or 2-propanol solutions of pseudosaccharin ethers (7.4-8.4 mM) by using Vycor filtered-light and products were separated by silica gel chromatography. Products distributions and yields along with reaction conditions employed are given in Table 1.

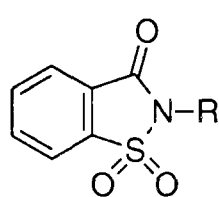
Irradiation of probenazole (**1**) in methanol leads to rapid productions of N-3-allylsaccharin (**5**, 33%),

saccharin (**6**, 40 %), and pseudosaccharin methyl ether (**2**, 11 %). However, photoreaction of **1** in 2-propanol lead to exclusive production of saccharin **6** (56 %). Irradiation of **1** in methanol in the presence of oxygen leads to rapid productions of products **5** (26 %), **6** (36 %) and **2** (7 %) in similar yields to those under N<sub>2</sub> purging. In contrast, photoreactions of pseudo saccharin alkyl ethers (**2-4**) in methanol occur more slowly and produce the reduced product 3-methoxy-1,2-benzisothiazole **7** as a major product along with solvent-substituted product, pseudosaccharin methyl ether (**2**). Irradiations of **2** and **3** in 2-propanol lead to two different reduction products **7** (18 %), and 3-isopropoxy-1,2-benzisothiazole (**9**, 56 %), and 2-ethoxy-1,2-benzisothiazole (**8**, 19 %) and **9** (50 %) respectively.

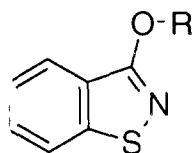
Table 1. Photoreactions of pseudosaccharin 3-allyl ether and its alkyl ethers

Pseudosaccharin ether	Concentration (mM)	Solvent	Condition	Reaction time(h)	Products (yield)
<b>1</b>	7.5	methanol	N <sub>2</sub>	2	<b>5</b> (33%), <b>6</b> (40%), <b>2</b> (11%)
<b>1</b>	7.5	methanol	O <sub>2</sub>	2	<b>5</b> (26%), <b>6</b> (36%), <b>2</b> (7%)
<b>1</b>	7.5	2-propanol	N <sub>2</sub>	2	<b>6</b> (56%)
<b>2</b>	8.4	methanol	N <sub>2</sub>	10	<b>7</b> (87%) <sup>a</sup>
<b>2</b>	8.4	methanol	O <sub>2</sub>	10	no reaction
<b>2</b>	8.4	2-propanol	N <sub>2</sub>	10	<b>7</b> (18%), <b>9</b> (56%)
<b>3</b>	7.9	methanol	N <sub>2</sub>	10	<b>2</b> (40%), <b>7</b> (45%)
<b>3</b>	7.9	2-propanol	N <sub>2</sub>	10	<b>8</b> (19%), <b>9</b> (50%)
<b>4</b>	7.4	methanol	N <sub>2</sub>	10	<b>2</b> (40%), <b>7</b> (45%)

<sup>a</sup> Yield is based on consumed **2** (ca. 50 %)



**5** : R=CH<sub>2</sub>-CH=CH<sub>2</sub>  
**6** : R=H



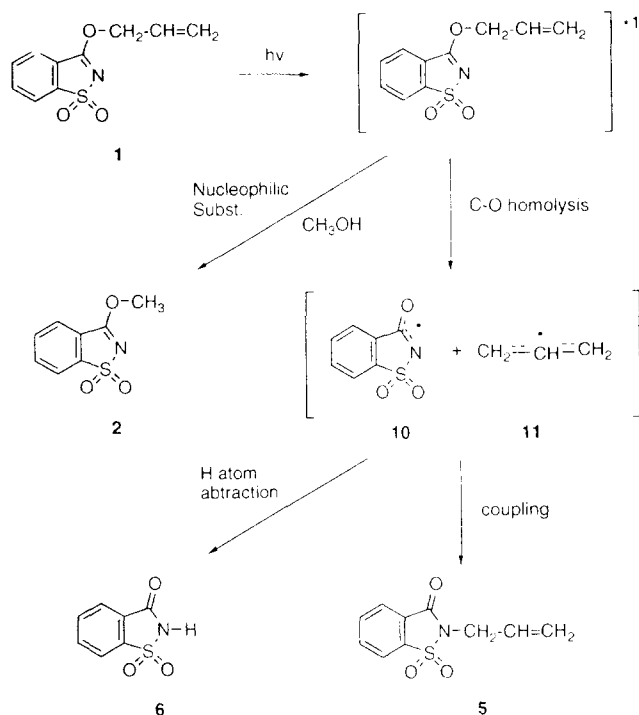
**7** : R=CH<sub>3</sub>  
**8** : R=CH<sub>2</sub>CH<sub>3</sub>  
**9** : R=CH(CH<sub>3</sub>)<sub>2</sub>

Oxygen purging in the photoreaction of pseudosaccharin methyl ether (**2**) in methanol leads to complete quenching of reaction. Structural assignments of photoproducts **5**, **7-9** were made on the basis of spectroscopic data. Mass spectrum of photoproduct **5** show molecular ion peak at m/z 223 which indicates

that photoproduct **5** has the same molecular formula as the starting compound probenazole (**1**). Its <sup>1</sup>H-NMR spectrum clearly shows resonances which correspond to the presence of allylic and aromatic hydrogens. In addition its IR spectrum show strong absorption peaks at 1732 cm<sup>-1</sup> for carbonyl stretching and at 1150 and 1305 cm<sup>-1</sup> for asymmetric and symmetric sulfone vibrations. These spectral features are consistent with the rearrangement of allyl group from 3-allyloxy oxygen to sulfonimide nitrogen of probenazole (**1**). <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the reduced photoproducts **7-9** shows resonances for the corresponding alkoxy groups, methoxy, ethoxy, and isopropoxy respectively and aromatic hydrogens. Disappearance of peaks for sulfone stretching vibrations near 1150 and 1300 cm<sup>-1</sup> in their IR spectra clearly support for reduction of sulfone group. Along with all these spectral features, their mass spectral data are in complete with the structures assigned.

The observation presented above show that probenazole (**1**) undergoes characteristic photoreaction in methanol to generate N-3-allyl saccharin (**5**) and saccharin (**6**) as major products and pseudosaccharin methyl ether (**7**) as a minor product. The photoreaction in a better hydrogen donating solvent, 2-propanol leads to a marked change in product distributions. The rearranged product **5** is almost completely quenched and that of saccharin (**6**) is significantly increased (Table 1). Further oxygen present in the photoreaction of probenazole (**1**) in methanol does not significantly affect the product distributions and the reaction rate which indicates that the reactive state for the photoreaction of probenazole is a singlet. Results obtained in this study suggest that the photoreaction of probenazole (**1**) follows the excited singlet state mechanism involving pathways of homolysis of bond between pseudosaccharyl oxygen and 3-allyl carbon, and a nucleophilic substitution of allyloxy group by solvent molecule, methanol (shown in Scheme 1).

Accordingly the homolysis in singlet excited pseudosaccharin results in generation of stable radical intermediates **10** and **11** which might undergo radical coupling in radical cage leading to N-3-allylsaccharin (**5**) or escape out of the cage and abstract hydrogen atom from solvent to produce saccharin (**6**). The reaction pathways from the generated radical intermediates **10** and **11**, the radical coupling and hydrogen abstraction could compete and the latter becomes predominant in a better hydrogen atom donating 2-propanol leading to the exclusive production of saccharin (**6**). The excited state nucleophilic substitution of 3-allyloxy group by methanol leads to generation of pseudosaccharin

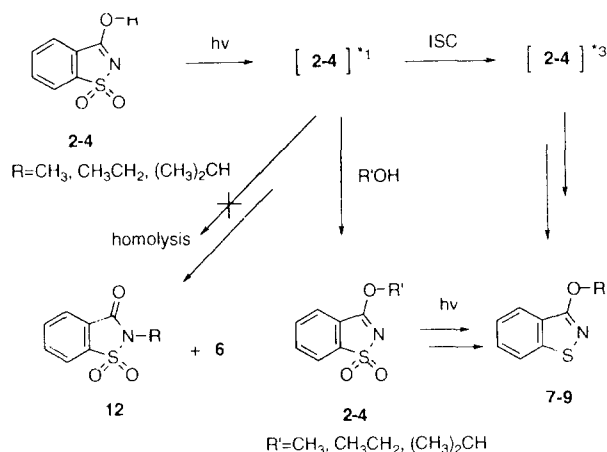


Scheme 1

methylether (**2**) and competes with homolysis leading to product **5** and **6**. As the product yields demonstrate, the homolysis process predominates over the excited nucleophilic substitution ( $5+6:2=73\%:11\%$ ). In contrast, photoreactions of pseudosaccharin alkyl ethers (**2-4**) neither leads to the generation of rearranged product like **12** nor saccharin (**6**) and instead to produce solvent-substituted product **2** and the reduced product **7-9**. Further photoreduction leading to the production of **7** was observed to be completely quenched by oxygen in the photoreaction of **2** in methanol which indicates that the reactive state for photoreduction of sulfonyl group of pseudosaccharin alkyl ether (**2-4**) is a triplet.

The results suggest that similar homolysis observed in the photoreaction of probenazole, pseudosaccharin 3-ally ether (**1**) is inefficient due to the generation of less stable alkyl radical than allyl radical (**11**) and instead slow singlet excited nucleophilic substitution and triplet photoreduction of sulfone group become predominant in photoreactions of pseudosaccharin alkyl ethers (**2-4**) (shown in Scheme 2). As shown in Table 1, 3-methoxy-1,2-benzisothiazole (**7**) and pseudosaccharin methyl ether (**2**) are generated as the sole reduction product and substitution product in photoreactions of pseudosaccharin alkyl ethers (**2-4**) in methanol regardless of the kind of alkoxy group

such as methoxy, ethoxy and isopropoxy present in **2-4**. However photoreactions of pseudosaccharin (**2-3**) in 2-propanol lead to the production of only two kind of reduction products **7** and **9**, and **8** and **9** respectively without solvent-substituted product **4**.



Scheme 2

The observation indicates that the singlet excited nucleophilic substitution by methanol is not significantly influenced by steric demand of alkoxy group present in **2-4** and is believed to be faster than the triplet photoreduction of sulfone group. However rate of the triplet photoreduction seems to be enhanced in 2-propanol and could compete with the singlet excited nucleophilic substitution by 2-propanol. It is noteworthy that the singlet excited nucleophilic substitution by 2-propanol. It is noteworthy that the singlet excited nucleophilic substitution of alkoxy group by methanol is fast and is sterically little affected by alkoxy group present in pseudosaccharin alkyl ethers.

Because the excited substitution reactions liberate alcohols from pseudosaccharin alkyl ethers which could be easily prepared by heating of pseudosaccharin chloride and various alcohols,<sup>15,16</sup> the reaction sequence involving preparation of pseudosaccharin alkyl ether and subsequent photochemical nucleophilic substitution might constitute a method for protection-deprotection of alcohol group.

We are continuing to explore the photoreactions of pseudosaccharin alkyl ethers in effort to probe mechanistic issues associated with sulfonimide reduction in triplet pseudosaccharin ether excited states and to develop new alcohol group protection method.

## CONCLUSION

This study demonstrates that pseudosaccharin 3-allyl ether undergoes a facile photoreaction mainly via a mechanistic pathway involving singlet homolysis of bond between pseudosaccharyl oxygen and 3-allyl carbon. However the singlet homolysis observed in photoreaction of pseudosaccharin 3-allyl ether does not occur in those of alkyl derivatives where less efficient singlet nucleophilic substitution by solvent and triplet sulfonimide photoreduction become predominant.

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