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Jiro Tatsugi^a; Naoki Shimazaki^a

^a Department of Applied Chemistry, Faculty of Engineering, Aichi Institute of Technology, Japan

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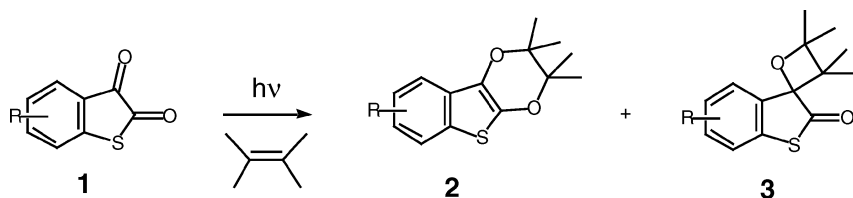
Department of Applied Chemistry, Faculty of Engineering,
Aichi Institute of Technology, Japan

*Photochemical reactions of benzo[*b*]thiophene-2,3-diones with 2,3-dimethylbut-2-ene gave dioxene derivatives in excellent yields.*

Keywords 2,3-Dimethylbut-2-ene; [4+2] cycloaddition; cyclic vicinal dicarbonyls; dioxene derivatives

In the course of our studies on photochemical behavior of cyclic vicinal polycarbonyls,¹ we have investigated the photochemical reactions of benzo[*b*]thiophene-2,3-diones (**1a–i**) with alkenes. We describe the photochemical reactions of **1a–i** with 2,3-dimethylbut-2-ene in degassed benzene solution, which underwent [4 + 2] cycloaddition to give dioxene derivatives **2a–i** in excellent yields.

Before irradiation, the vicinal dicarbonyl compounds **1a–i** in benzene in Pyrex[®] tubes were degassed by an ultrasonic generator under purging argon and cooled with ice water for 20 min. Irradiation of **1a–i** in degassed solutions at 15 with a 300 W high-pressure mercury lamp



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Address correspondence to Jiro Tatsugi, Department of Applied Chemistry, Faculty of Engineering, Aichi Institute of Technology, Yachigusa, Yakusa-cho, Toyota 470-0392, Japan. E-mail: jtatsugi@aitech.ac.jp

TABLE I Photochemical Reactions of 1a-i with 2,3-dimethylbut-2-ene in Benzene

| 1 | R | Irr. time (min) | Conv. (%) | 2:3 ratio |
|----------|----------|------------------------|------------------|------------------|
| a | H | 3 | 90 | 97:3 |
| b | 4-Me | 1 | 91 | 100:0 |
| c | 5-Me | 3 | 70 | 100:0 |
| d | 6-Me | 1 | 90 | 100:0 |
| e | 7-Me | 1.5 | 71 | 100:0 |
| f | 4,6-diMe | 3 | 95 | 100:0 |
| g | 4,7-diMe | 1 | 71 | 100:0 |
| h | 5,6-diMe | 10 | 84 | 100:0 |
| i | 5,7-diMe | 8 | 89 | 100:0 |

gave product that were analyzed by GC-MS. The photoproducts were also separated by column chromatography and characterized by IR, ^1H -, and ^{13}C -NMR, and MS spectroscopies. The results of the photochemical reactions of **1 a-i** with 2,3-dimethylbut-2-ene are summarized in Table 1.

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