

SENSITIZED PHOTOOXIDATION OF 2,5-FURANYLDIMETHYL DIBENZOATE¹

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Abstract — Sensitized photooxidation of 2,5-furanyldimethyl dibenzoate was carried out in acetonitrile and methanol respectively. Two products, 3 and 6, were obtained via O,O-diradical intermediate 15 which was discovered from ozonide for the first time.

Sensitized photooxidation of 2,5-dialkylfurans, 2,5-dimethylfuran², dicyclohexanofuran^{2a}, bisfuran 1³, bisfuranophane^{4a}, furanonaphthalenophane^{4b}, furanocyclophane^{4b}, and 2,5-furo-18-crown-6⁵, and 5-methylfurfural⁶ has been documented. We are interested in comparisons for the photooxidation and product distribution and studied the sensitized photooxidation for 2,5-furanyldimethyl dibenzoate 2. Compound 2, mp 72-73°C, which was prepared from furandimethanol with benzoyl chloride in pyridine. From the sensitized photooxidation of 2, two products 3 and 6 were isolated. These confirmed their formation via O,O-diradical 15 intermediate which would be formed from ozonide 10 by homolytic O-O cleavage. In the experiments described here, a solution of 2,5-furanyldimethyl dibenzoate 2 and methylene blue (100 mg) in acetonitrile (100 ml) was irradiated by 500 watt incandescent lamp at 10-15°C for 4 days by cooling with water while oxygen was slowly passed through the solution. Five products, 3 (1.3 %), 4 (8.0 %), 5 (4.1 %), 6 (0.4 %) and 7a (68.4 %), listed in the elution order from chromatography, were isolated from the reaction mixture. Similarly, photooxidation of 2 (1.6 g) in methanol solution (100 ml) gave 8a (6.1 %), 5 (23.2 %), 9a (46.1 %) and 8b (5.5 %) after irradiation for 2 days.

The structure of 3⁷ was confirmed by its physical data. The reaction of ethylene glycol with benzoyl chloride in pyridine afforded 3. Compound 4 is a butenolide derivative, its structure can be deduced from its physical data. When 4 was reacted with TsOH in MeOH, it gave methyl benzoate, benzoic acid, and 9b. Compounds 5 (mp 122-123°C) and 6 (mp 53-55°C) were identical with benzoic acid and maleic anhydride, respectively, by comparison of their physical data with authentic samples. Compound 7a was obtained in good yield. It afforded diacetate 7b by acetylation. Compound 8b was identical with glycolic acid benzoate which can be prepared from glycolic acid with benzoyl chloride in pyridine. When 8b was treated with CH₂N₂ in methanol, 8a was obtained which was also one of photooxidation products. By photooxidation

in methanol solution, 9a is a major product which afforded 9b and 5 by reaction with NaOH in aqueous methanol solution.

The formation of the products by photosensitized oxidation of 2,5-furanyldimethyl dibenzoate may be rationalized by the proposed mechanism which is depicted in Scheme 1. In methanol the addition of $^1\text{O}_2$ to 2 gave the ozonide 10 (major) and bisdioxetan 11 (minor). Homolytic cleavage of the O-O band of the latter 11 and afforded anhydride 12 which then underwent methanolysis to give 8a and 8b. Bisdioxetane cleavage was found only in photooxidation of 3,4-diethyl-2,5-dimethylpyrrole⁸ and yielded a diimide. Bisdioxetane intermediate was found for the first time in the photooxidation of furan derivative. The ozonide 10 underwent cleavage to form a zwitterion 13. The addition of methanol to 13 yielded an unstable hydroperoxide 14a which produced 9a, 5 and formaldehyde. In the acetonitrile solution, the addition of $^1\text{O}_2$ to 2 gave an ozonide 10 intermediate only, which cleaved into two species, zwitterion 13 and O,O-diradical 15. The addition of water to 13 yielded an unstable 14b which produced 4, 5 and formaldehyde. O,O-diradical intermediate was found only in photooxidation of alkylpyrrole and yielded the maleimide and its derivatives.⁹ In the photooxidation of furan derivative, O,O-diradical intermediate has not been discovered. Diradical 15 proceeded into two routes. The minor route is the formation of maleic anhydride 6 and 3. Bisepoxide 16 was formed from the major route, followed by hydrolysis to 7a via tetraol 17. According to the mechanism, 7a can be assigned as an erythro form.

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7. All the new compounds in this paper gave the satisfactory elementary analyses. 3: mp 69-70°C; ν_{max} 1730, 1600, 1490, and 1260 cm^{-1} ; H nmr (CDCl_3) δ 4.68 (4H, s, $-\text{CH}_2\text{CH}_2-$), 7.35-7.65 (6H, m, $-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{H}$), and 8.03 (4H, dd, $J = 8, 2$ Hz, $-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{H}$). 4: mp 97-98°C; ν_{max} 3200, 1770, 1720, 1600, and 1490 cm^{-1} ; H nmr (CDCl_3) δ 4.47 and 4.73

(each 1H, d, $J = 12$ Hz, $-\text{CH}_2\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{Ph}$), 6.14 and 7.28 (each 1H, d, $J = 5.5$ Hz, $\text{H}-\text{C}=\text{C}-\text{H}$), 6.28 (1H, br s, -OH), 7.30-8.20 (5H, m, phenyl protons). **9b**: ν_{max} 3400, 3130 and 1760 cm^{-1} ; H nmr (CDCl_3) δ 3.12 (3H, s, $-\text{OCH}_3$), 3.60 and 3.80 (each 1H, d, $J = 14$ Hz, $-\text{CH}_2\text{OH}$), 5.90 (1H, br s, -OH), and 6.02 and 6.95 (each 1H, $J = 5$ Hz, $\text{H}-\text{C}=\text{C}-\text{H}$). **7a**: mp 147-148°C; ν_{max} 3400, 1720, 1705, and 1275 cm^{-1} ; H nmr (CD_3COCD_3) δ 4.70 (2H, br s, $-\text{CH}-\text{CH}-$), 5.17 and 5.47 (each 2H, d, $J = 18$ Hz, $-\text{OCH}_2\overset{\text{O}}{\overset{\parallel}{\text{C}}}-$), 5.43 (2H, br s, -OH), 7.30-8.21 (10H, m, phenyl protons). **7b**: mp 137-138°C; ν_{max} 1725, 1710, and 1270 cm^{-1} ; H nmr (CDCl_3) δ 2.18 (6H, s, $-\text{O}^{\text{O}}\text{CCH}_3$), 5.13 (4H, s, $-\text{OCH}_2\overset{\text{O}}{\overset{\parallel}{\text{C}}}-$), 5.80 (2H, s, $-\text{CH}-\text{CH}-$), 7.30-8.22 (10H, m, phenyl protons). **8b**: mp 104-106°C; ν_{max} 3200-2500, 1718, 1695 and 910 cm^{-1} ; H nmr (CDCl_3) δ 4.90 (2H, s, $-\text{OCH}_2\overset{\text{O}}{\overset{\parallel}{\text{C}}}-$), 7.30-8.25 (5H, m, phenyl protons), and 8.42 (1H, br s, -COOH). **8a**: ν_{max} 1710, 1590, 1520, and 1260 cm^{-1} ; H nmr (CDCl_3) δ 3.80 (3H, s, $-\text{COCH}_3$), 4.86 (2H, s, $-\text{OCH}_2\overset{\text{O}}{\overset{\parallel}{\text{C}}}-$), and 7.20-8.20 (5H, m, phenyl protons). **9a**: mp 61-62°C; ν_{max} 1780, 1715, 1620, and 1500 cm^{-1} ; H nmr (CDCl_3) δ 3.36 (3H, s, $-\text{OCH}_3$), 4.43 and 4.82 (each 1H, d, $J = 11.6$ Hz, $-\text{CH}_2\overset{\text{O}}{\overset{\parallel}{\text{C}}}-$), 6.28 and 7.22 (each 1H, d, $J = 5.6$ Hz, $\text{H}-\text{C}=\text{C}-\text{H}$), and 7.30-8.20 (5H, m, phenyl protons).

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