

SENSITIZED PHOTOOXIDATION OF 2-FURFURYL BENZOATE IN METHANOL

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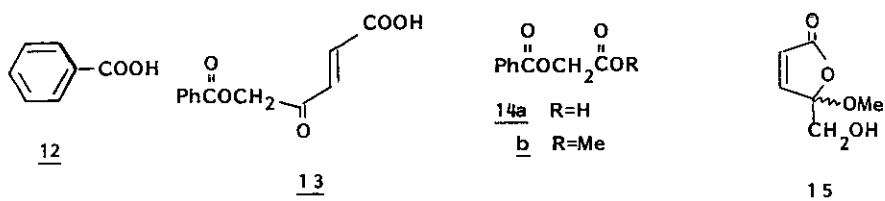
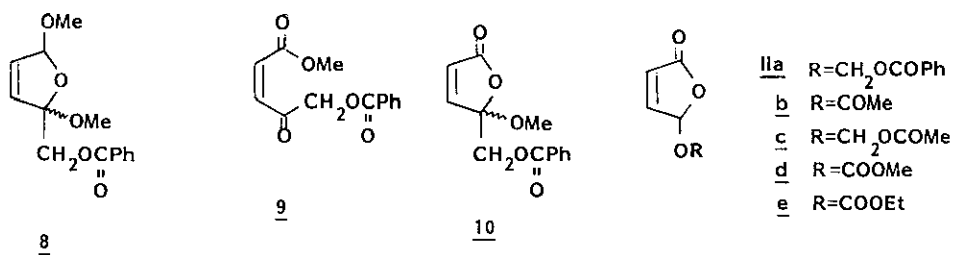
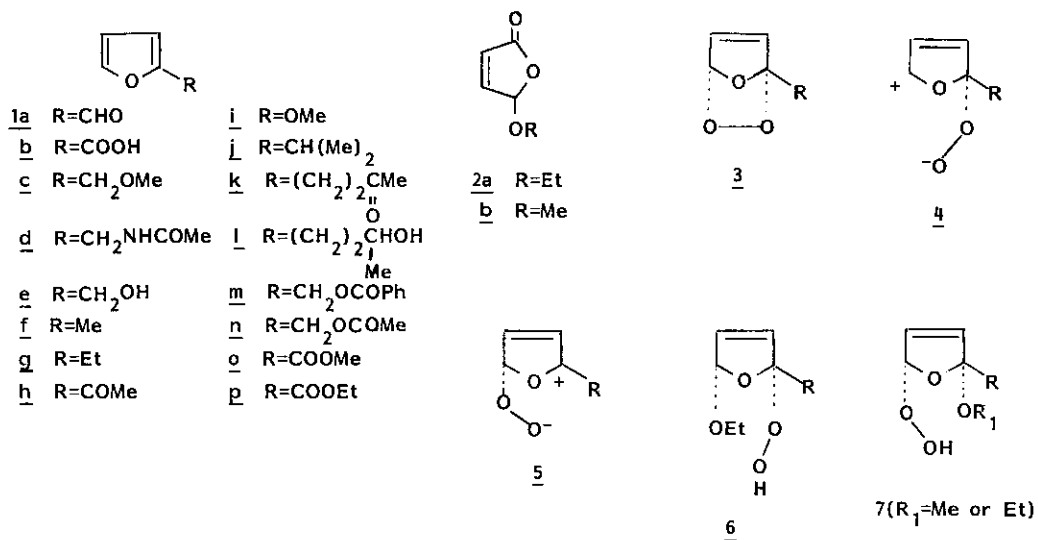
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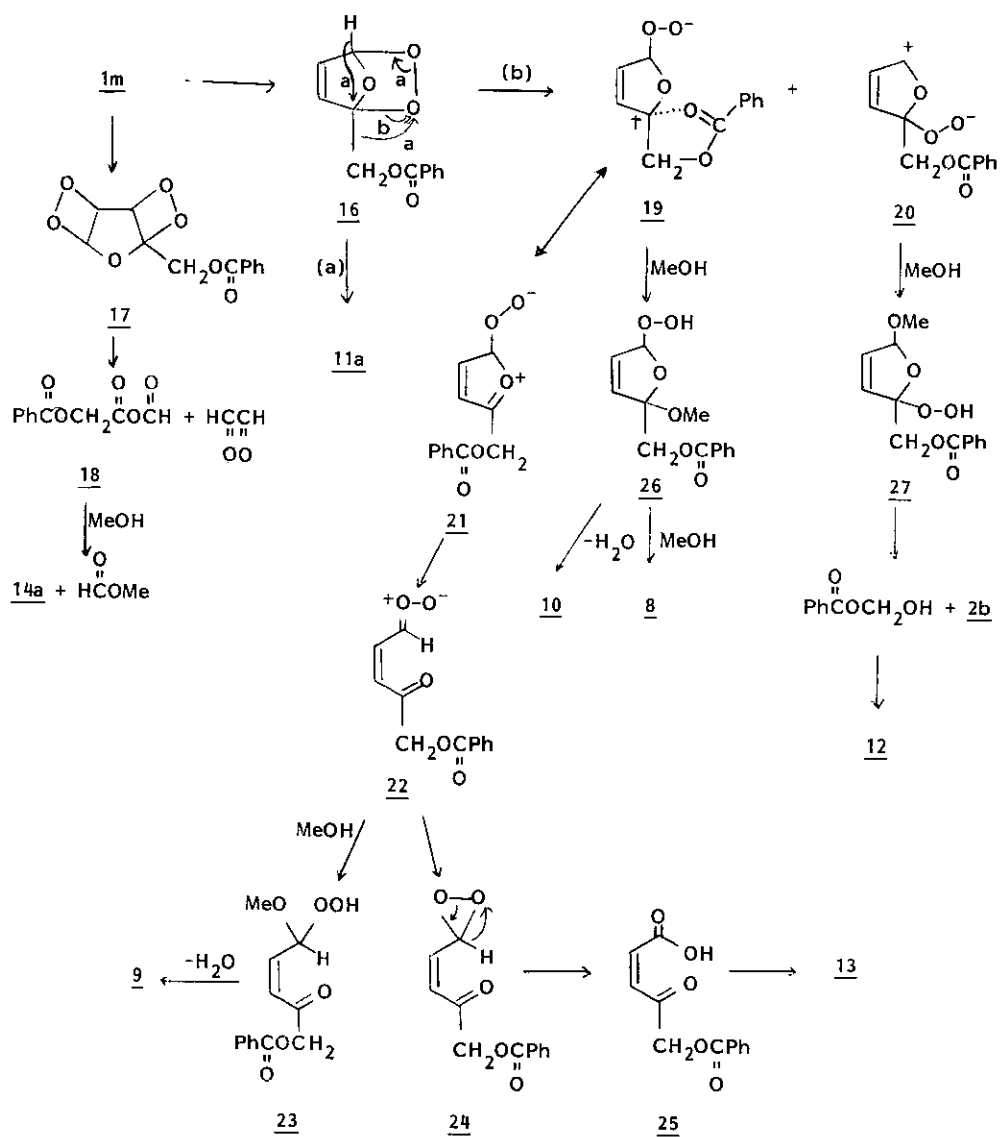
Abstract — Sensitized photooxidation of 2-furfuryl benzoate in methanol gave eight products. The mechanism for their formations are discussed.

Schenck had postulated that furanendoperoxides (=ozonides) was primary products when furans were subjected to sensitized photooxidation.¹ Later he had studied the sensitized photooxidation of five 2-alkylfurans, 1a,² 1b,³ 1c,⁴ 1d,^{3,4} and 1e⁵ in ethanol and all gave only product pseudo-ester 2a in high yield (86%-98%). Recently, the further studies of photooxidation of 2-alkylfuran (1a, 1e, 1f, 1g, 1h, 1i, 1j, 1k and 1l) in protic and aprotic solvents were performed by Gollnick⁶ and Feringa.⁷ The addition of ¹O₂ to 2-alkylfurans gave ozonide 3 which was followed by cleavage to afford two zwitterions 4 or 5 in protic solvent.⁶ Those groups, -CHO, -COOH, -CH₂OMe, -CH₂NHCOMe, -CH₂OH, and -COCH₃ are all electron-withdrawing groups, therefore zwitterion 4 is a more favored species. The addition of ethanol to 4 yielded 6 (R=CHO etc) which was followed homolytic cleavage of O-O bond and then converted to pseudo-ester 2a. The electron-donating (R=CH₃, Et, OMe, and CH(CH₃)₂ etc) group favored to zwitterion 5 which was added with alcohol to yield 7. Now we present a photooxidation of furfuryl benzoate 1m in methanol solution showing opposed result with Schenck's one. Although -CH₂O^QCPh is an electron-withdrawing group, but product 2b is a minor product. Meanwhile, the product 11a was obtained via a new similar Baeyer-Villiger-like rearrangement which was found for the first time. And product 9 is the first example for trapping the intermediate carbonyl oxide by solvent. In the experiments described here a solution of 2-furfuryl benzoate 1m (3.65 g) and methylene blue (100 mg) in methanol was irradiated with 500 watt incandescent lamp for 2 days at 10-15°C, by cooling with water while oxygen passed through the solution. Eight products, 8, 2b, 9, 10, 11a, 12, 13, and 14a, listed in the elution order from chromatography on silica gel, were isolated from the reaction mixture. The structures of 8, 9, 10, 11a, 13, and 14 are confirmed by their physical data. Pseudo-ester 2b, a liquid, was identified with product of photooxidation of furfuryl alcohol 1e in methanol solution. It is a minor component by weight analysis of products. The presence of methyl carboxylate group in 9 (major product) proposed that the intermediate carbonyl oxide was trapped

by methanol. The ozonization of olefin in methanol solution always gives methyl carboxylate.⁸ Carbonyl oxide served as oxidant for oxidation of carbonyl, olefin, dimethyl sulfide, and phenol etc. are documented,⁹ but trapping of it by solvent has not been reported. It is the first time for the trapping of carbonyl oxide intermediate by solvent in the studies of photooxidation of furans. Compound 10 (second major product) afforded 15 and benzoic acid 12 by basic hydrolysis. An other butenolide 11a is a new similar Baeyer-Villiger-like rearrangement product. In acidic methanol solution, 11a afforded pseudo-ester 2b and methyl benzoate. Compound 12 was identical with benzoic acid by comparison with authentic sample. An acidic product 13 was obtained via an intermediate dioxirane 24. The successive fraction is 14a which was isolated with the methyl ester form 14b.

The formation of the products by photosensitized oxidation of 2-furfuryl benzoate 1m may be rationalized by the proposed mechanism which is depicted in Scheme I. The addition of $^1\text{O}_2$ to 1m gave two species, ozonide 16 (major) and bisdioxetane 17 (minor). The latter was homolytically cleaved at the O-O bond to afford biformyl and anhydride 18. Methanolysis of anhydride 18 gave the acid 14a. Bisdioxetane was found only in photooxidation of pyrrole derivative¹⁰ which yielded the diimide. Unstable ozonide 16 subsequently cleaved into three species. The formation of 11a from 16 is via a new Baeyer-Villiger-like rearrangement (path a) which was shown in Scheme I. This new type rearrangement has not been discovered. On our series of furans' studying, we have isolated the same type products such as that photooxidation of 1h, 1n, 1o and 1p yielded 11b, 11c, 11d, and 11e, respectively, in low yield.¹¹ The main path (path b) of cleavage of 16 is via zwitterions 19 and 20. By the product analysis, zwitterions 19 is more favored than zwitterion 20. Although the group $-\text{CH}_2\overset{\text{O}}{\text{C}}\text{Ph}$ is an electron-withdrawing group, but carbonyl group can chelate with carbocation and stabilized it, therefore zwitterion 19 shows more stable than zwitterion 20. Compound 21, a resonance form of 19, rearranged to carbonyl oxide 22 which was trapped by methanol to yield hydroperoxide 23 and then decomposed to 9. Dioxirane is an unusual intermediate which presented in photooxidation of α -silyldiazoalkane¹² and 2-methyl-5-trimethylsilylfuran.¹³ Compound 22 gave the dioxirane 24 which underwent intramolecular Baeyer-Villiger rearrangements to afford 25 and then isomerized to 13. The addition of methanol to 19 yielded hydroperoxide 26 and then followed decomposition to 10 or methanolysis to 8. Methanol was added to 20 and obtained 27 which degraded to 2b and 12.





Scheme 1

EXPERIMENTAL

Melting point were uncorrected. NMR spectra were determined on a Zoel JNM-FX-100 or Varian EM-390 in the indicated solvents. Chemical shifts and coupling constants were measured in ppm (δ) and J(Hz) with respect to TMS. IR spectra were run as KBr disc or neat on a Perkin Elmer 700 spectrometer.

Sensitized Photooxidation of 2-Furfuryl Benzoate 1m

A solution of 1m (3.65 g) and methylene blue (100 mg) in methanol (100 ml) was irradiated with 500 W incandescent lamp. During the irradiation, oxygen was bubbled through the solution which was cooled at 10-15°C. The reaction was completed within two days. After removal of the methanol in vacuo, the residue was subjected to chromatography on silica gel. Eight products, 8 (31 mg), 2b (25 mg), 9 (894 mg), 10 (831 mg), 11a (43 mg), 12 (30 mg), 13 (463 mg), and 14a, listed in the elution order, were isolated from the residue. The fraction, eluted by 50% hexane in ethyl acetate solvent system, was purified by treatment with diazomethane and obtained the methyl ester 14b (10 mg). The original product must be an acid 14a. The structures of 2b and 12 are identified with authentic samples.

8; IR(film)(vcm^{-1}) 3060, 1710, 1580, 1500; ^1H NMR (CDCl_3) δ : 3.20 (3H, s), 3.42 (3H, s), 4.39 (1H, d, J 11), 4.57 (1H, d, J 11), 5.80 (1H, br s), 6.00 (1H, d, J 6), 6.15 (1H, d, J 6), 7.30-8.20 (5H, m); Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_5$: C, 63.62; H, 6.10. Found: C, 63.87; H, 6.01.

9, mp 91-92°C; IR(KBr)(vcm^{-1}) 1725, 1710, 1625, 1230; ^1H NMR (CDCl_3) δ : 3.77 (3H, s), 5.06 (2H, s), 6.13 (1H, d, J 11), 6.48 (1H, d, J 11), 7.30-8.20 (5H, m); Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_5$: C, 62.90; H, 4.87. Found C, 62.68; H, 4.78.

10, mp 61-62°C; IR(KBr)(vcm^{-1}) 3090, 1820, 1780, 1715; ^1H NMR (CDCl_3) δ : 3.36 (3H, s), 4.43 (1H, d, J 11.6), 4.82 (1H, d, J 11.6), 6.28 (1H, d, J 5.6), 7.22 (1H, d, J 5.6), 7.30-8.20 (5H, m); Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_5$: C, 62.90; H, 4.87. Found C, 62.98; H, 4.81.

11a; IR(film)(vcm^{-1}) 1780, 1750, 1715, 1600, 1580, 1480; ^1H NMR (CDCl_3) 5.64 (1H, d, J 6), 5.73 (1H, d, J 6), 14 6.25 (1H, d, J 6.5), 7.25 (1H, d, J 6.5), 6.30 (1H, s), 7.30-8.20 (5H, m). Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_5$: C, 61.54; H, 4.30. Found C, 61.40; H, 4.29.

13, mp 156-157°C; IR(KBr)(vcm^{-1}) 2500-3200, 1720, 1685, 1620, 1495; ^1H NMR (CD_3OD) δ : 5.22 (2H, s), 6.78 (1H, d, J 15), 7.18 (1H, d, J 15), 7.30-8.20 (5H, m). Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_5$: C, 61.54; H, 4.30. Found C, 61.74; H, 4.35.

14b; IR(film)(vcm^{-1}) 1710, 1595, 1520; ^1H NMR (CDCl_3) δ : 3.80 (3H, s), 4.86 (2H, s), 7.30-8.20 (5H, m). Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_4$: C, 61.85, H, 5.19. Found C, 61.97; H, 5.11.

Hydrolysis of Compound 10

Compound 10 (60 mg) and NaOH (55 mg) were added to 5 ml of 50% aqueous methanol solution, left overnight, and then dropped into water. The water solution was extracted with ethyl acetate. Aqueous layer yielded benzoic acid 12 (27 mg) after acidify. From organic layer, it got 15 (32 mg); IR(film)(vcm^{-1}) 3400, 3130, 1760; ^1H NMR (CDCl_3) δ : 3.12 (3H, s), 3.60 (1H, d, J 14), 3.80 (1H, d, J 14), 5.90 (1H, br s -OH), 6.02 (1H, d, J 5), 6.95 (1H, d, J 5).

Methanolysis of Compound 11a

Compound 11a (40 mg) and p-toluenesulfonic acid (20 mg) was added to 5 ml of methanol at room temperature. After two days, the reaction mixture was subjected to chromatography on silica gel. Methyl benzoate (21 mg) and pseudo-ester 2b (17 mg) were isolated.

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