

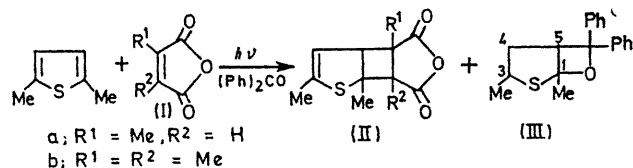
Synthesis of an Oxetan by Photoaddition of Benzophenone to a Thiophen Derivative

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Summary An oxetan has been synthesised by 1,2-photoaddition of benzophenone to 2,5-dimethylthiophen.

It is well known that benzophenone adds photochemically to furan and its methyl derivatives to form oxetans in good yield.¹⁻⁵ On the other hand, it has been reported,² and confirmed in this laboratory, that the photochemical cycloaddition of benzophenone to thiophen to form an oxetan does not occur under the same conditions used for the furan derivatives.



In the course of an investigation on the photoaddition of citraconic anhydride [Ia] and 2,3-dimethylmaleic anhydride (Ib) to several thiophen and benzo(b)thiophen derivatives sensitized by benzophenone, it was found that when 2,5-dimethylthiophen was used as the substrate, in addition to a small amount of the expected cycloaddition product (II), another crystalline compound was obtained in good yield.

The latter was identified by spectroscopic methods as the compound (III). The irradiation was repeated using

benzophenone (2g, 0.0109 mole) dissolved in 60 ml of 2,5-dimethylthiophenone in a nitrogen atmosphere; after 8 h exposure to u.v. light (Hanovia 450 W lamp with Pyrex filter at -10°) a crystalline solid (2g) was isolated in 61.9% yield, on the basis of benzophenone consumed. This solid partially precipitates out of the solution during the irradiation; after the illumination was stopped, the product was removed by filtration, the thiophen derivative used as the solvent distilled off, and the crystalline residue combined with the product already isolated. The crude compound was washed with carbon tetrachloride and crystallized from ethanol-acetone (1:1); m.p. $163-164^\circ$. The i.r. spectrum exhibited bands characteristic of a trimethylene oxide ring (970 cm^{-1}) and had ν_{max} 1660–2000w, 760s, 750s, 700s cm^{-1} ; n.m.r. [$(\text{CD}_3)_2\text{CO}$] δ 7.40 (aromatic, 10H, m); 4.9 (C-5, 1H, sextet, $J_{5,3-\text{Me}}$ 1.4, $J_{5,4}$ 2.8 Hz), 4.5 (C-4, 1H, sextet, $J_{4,3-\text{Me}}$ 1.4, $J_{4,5}$ 2.8 Hz), 1.8 p.p.m. (3-Me and 1-Me, 6H, t and s, respectively $J_{3-\text{Me},4}$ 1.4, $J_{3-\text{Me},5}$ 1.4 Hz). The n.m.r. assignments were made on the basis of data obtained previously;^{3,6} m/e^\dagger 294 (M), 182 (48%, Ph_2CO), 105 (100%, PhCO), 77 (100%, Ph); 113, 97, 59, 53, 51, 45, 39, 32, all of them correspond to the typical fractionation pattern of the thiophen moiety.⁷ The reaction was attempted with other thiophen derivatives such as 2-methyl- and 3-methyl-thiophen, but the corresponding compound could not be isolated.

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† The compound gave satisfactory elemental analysis.

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