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Short Communications

Formation of 2-Benzoyl-3, 5-diphenylthiophene and 2-Benzoyl-3,5-diphenylfuran from 2,4,6-Triphenylpyrylium Ion

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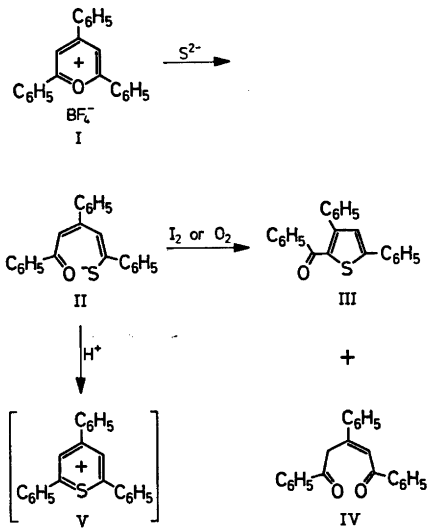
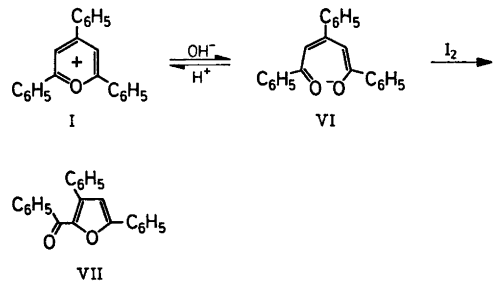
The reaction between 2,4,6-triarylpyrylium salts and sodium sulfide is a well known method for the preparation of the analogous thiopyrylium salts.[1–4] Addition of an aqueous solution of sodium sulfide to the triphenylpyrylium salt I dissolved in acetone gives an intensely coloured solution, possibly due to formation of the anion II.[1] Upon addition of acid, II cyclizes to the thiopyrylium ion V (Scheme 1).



We found that the anion II was readily converted to 2-benzoyl-3,5-diphenylthiophene (III) when treated with mild oxidizing agents, *e.g.* air or iodine. The latter is more conveniently used owing to better yield and considerably shorter reaction time. Besides compound III small amounts of the so-called pseudobase IV was formed.* The structure of compound III was established by comparison (IR, mixed melting point) with a sample prepared independently.[5]**

On the basis of this result, it seemed interesting to examine whether this type of reaction could be extended to include preparation of other heterocyclic systems. While treatment of the 2,4,6-triphenylpyrylium ion with weak oxygen bases (*e.g.* acetate or hydrogen carbonate) gave the pseudobase IV [6,7] treatment with hydroxide ion or carbonate ion gave a red-coloured solution due to formation of the anion of the pseudobase VI[1,6,8]. This anion was similarly, although more slowly, converted to the furan VII (Scheme 2) when oxidized with



iodine. The structure of the product was established by comparison (IR, mixed melting point) with a sample prepared by benzoylation of 2,4-diphenylfuran [9] (see experimental). Furthermore, its spectroscopic features (see experimental section) support the proposed structure. In spite of these findings, attempts to prepare the selenophene and the pyrrole (the latter by oxidation of the monoimine [10] of the pseudobase IV) by an analogous procedure, failed.

The conversion of pyrylium salts to furans has been described previously. Thus, 2,4,6-trialkylpyrylium salts were oxidized with hydrogen peroxide to 2-acyl-3,5-dialkylfurans [11,12] and

* Compound IV was identical with a sample prepared from pyrylium salt I and sodium hydrogen carbonate.[6]

** All compounds showed satisfactory elemental analysis.

hydrolysis of 2,3,4,6-tetraphenylpyrylium perbromide gave 2-benzoyl-3,4,5-triphenylfuran.[13] Similar ring contractions were observed by oxidation of other heteroaromatic cations with manganese dioxide,[14,15] *e.g.* the oxidation of the parent thiopyrylium ion to 2-thiophenecarboxaldehyde. However, the thoroughly investigated 2,4,6-triphenylpyrylium ion, from which many heterocyclic systems are available,[4,16,17] has not previously been converted to a furan and a thiophene.

Experimental. Preparative layer chromatography (PLC) was performed on 20 × 100 cm plates with a 2.5 mm thick layer of silica gel (Merck $PF_{254}{}_{+366}$). The plates were developed 1 – 2 times with benzene.

Pyrylium salt. This was prepared according to the method of Lombard and Stephan.[7]

Preparation of 2-benzoyl-3,5-diphenylthiophene (III) by oxidation with iodine. A mixture of 2,4,6-triphenylpyrylium tetrafluoroborate (1.00 g, 2.52 mmol) in acetone (50 ml) and sodium sulfide nonahydrate (1.21 g, 5.04 mmol) in water (10 ml) was stirred for ½ h. Iodine (2.00 g, 7.88 mmol) was then added, and stirring was continued for 2 min. After addition of chloroform, excess iodine was removed by extraction with dilute sodium thiosulfate. The organic phase was separated and dried over sodium sulfate. After partial evaporation of the chloroform, the solution was separated by PLC into (1) 2-benzoyl-3,5-diphenylthiophene (III) (0.48 g ~56 %, m.p. 103 – 104 °C (methanol), Ref. 5 96.5 – 98 °C), IR (in KBr) 1625 cm^{-1} (C=O), ^1H NMR (60 MHz, $CDCl_3$) only aromatic protons at δ 7.8 – 7.0, UV (96 % ethanol) λ_{max} at 248 and 342 nm with log ε 4.26 and 4.14, respectively, and (2) 1,3,5-triphenyl-1,5-pentenedione (IV) (0.08 g ~9 %).

Preparation of 2-benzoyl-3,5-diphenylthiophene (III) by oxidation with air. 2,4,6-Triphenylpyrylium tetrafluoroborate (1.00 g, 2.52 mmol) dissolved in acetone (50 ml) was mixed with sodium sulfide nonahydrate (1.21 g, 5.04 mmol) in water (10 ml). After stirring for ½ h acetone (50 ml) was added, and air was sucked through the mixture for 22 h. The reaction mixture was then worked up as described above into (1) 2-benzoyl-3,5-diphenylthiophene (III) (0.38 g ~44 %) and (2) 1,3,5-triphenyl-1,5-pentenedione (IV) (0.08 g ~9 %).

Preparation of 2-benzoyl-3,5-diphenylfuran (VII). A mixture of 2,4,6-triphenylpyrylium tetrafluoroborate (1.00 g, 2.52 mmol) in acetone (50 ml) and aqueous potassium carbonate (5.0 ml, 1 M) was stirred for 2 h. Iodine (2.00 g, 7.88 mmol) was added and stirring was continued for 16 h. The reaction mixture was then worked up as described above yielding 2-benzoyl-3,5-diphenylfuran (0.43 g ~53 %, m.p. 117 – 118 °C (methanol)), IR (in KBr) 1640 cm^{-1} (C=O), ^1H NMR (60 MHz, $CDCl_3$) δ 8.0 – 7.1 (m, 15 H), 6.90 (sharp s, 1 H), UV (96 % ethanol) λ_{max} at 267 and 346 nm with log ε 4.59 and 4.43, respectively.

Preparation of 2-benzoyl-3,5-diphenylfuran (VII) from 2,4-diphenylfuran. 2,4-Diphenylfuran (0.80 g, 3.6 mmol) was dissolved in carbon disulfide (8.0 ml). Benzoyl chloride (0.60 g, 4.3 mmol) and aluminium chloride (0.60 g, 4.5 mmol) were added and the reaction mixture was stirred for 48 h. It was then poured into water and the organic material was extracted with chloroform. After drying the chloroform solution over sodium sulfate and partial evaporation, the resulting solution was separated by PLC into (1) starting material (0.29 g) and (2) 2-benzoyl-3,5-diphenylfuran (0.67 g ~90 % from reacted starting material).

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