Some Reactions of 2H-[1]Benzothieno[3,2-b]pyran-2-ones and Related Compounds

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The conversion of 2H-[1]benzothieno[3,2-b]pyran-2-ones into mono- and di-thio-derivatives and the preparation of some dibenzothiophenes, sulphines and pyridones are described.

(Keywords: [1] Benzothienopyranones; Thiopyrano[1]benzothiophenones)


Introduction

Previously [1] we reported thiation reactions of 4-phenyl-2H-[1]benzothieno[3,2-b]pyran-2-one 1a, the isomeric 1-phenyl-3H-[1]benzothieno[3,2-c]pyran-3-one 2 and the corresponding dioxides 3a and 4. In continuation of this work we now describe the preparation of thiono-, thiolo- and dithio-derivatives of the 4-methyl (1b and 3b) and 4-unsubstituted (1c and 3c) analogues and report on some Diels-Alder and oxidation reactions of members of these series.

Results

The pyrones 1b and c, obtained [2, 3] by the acid-catalysed reaction of o-mercaptobenzoic acid and the appropriate 2-pentenedioic acid were oxidised to the dioxides 3b and 3c. Compounds 1b, 1c and 3b were converted into the thiono-analogues 5b, 5c and 6b with phosphorus pentasulphide. Treatment of the sulphone 3b with sodium sulphide in methanol followed by acidification gave, as minor product, the thiolo-pyrone 7b and, as major product, an acidic compound which on heating...
1 \( X = Y = O \)
5 \( X = O; \ Y = S \)
10 \( X = Y = S \)
20 \( X = O; \ Y = \text{NNHPh} \)

3 \( X = Y = O \)
6 \( X = O; \ Y = S \)
7 \( X = S; \ Y = O \)
9 \( X = Y = S \)
18 \( X = S; \ Y = \text{SO} \)
19 \( X = \text{NMe}; \ Y = O \)

a \( R = \text{Ph} \);
\( b \ R = \text{CH}_3 \);
\( c \ R = \text{H} \)

8

a \( X = S \)
\( b \ X = O \)

11 \( Z = S \)
12 \( Z = \text{SO}_2 \)

a \( R = \text{Ph} \);
\( b \ R = \text{CH}_3 \)

13 \( Z = S \)
14 \( Z = \text{SO}_2 \)