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A NOVEL SYNTHESIS OF BENZO-1,4-DITHIENE

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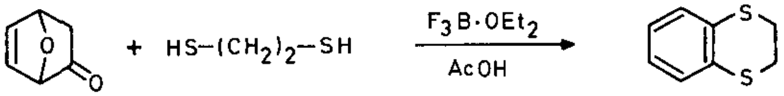
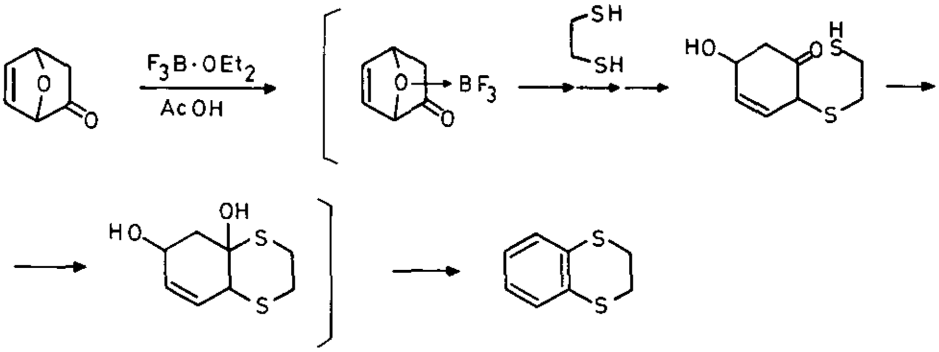
Abstract- A novel synthesis of benzo-1,4-dithiene from 1-oxanorbornen-2-one is described.

Benzo-1,4-dithiene derivatives display a promising fungicide activity[1]. To our knowledge, there is only one method in the literature for the preparation of the parent compound [2]; this three step route utilizes aromatic precursors and proceeds in approximately 60% overall yield. In this report we describe an alternative procedure starting from the readily available 1-oxanorbornen-2-one[3] by reaction with ethanedithiol in acetic acid in the presence of $BF_3 \cdot OEt_2$ (Scheme 1).



Scheme 1

A tentative rationalization of this result is shown in Scheme 2. Coordination of the bridge oxygen with the Lewis acid renders the bridgehead carbon particulary susceptible to nucleophilic attack.



Scheme 2

This position is also activated by the vicinal carbonyl group. Subsequent intramolecular hemithioketal formation and aromatization afford the observed product. It should be mentioned that the reaction with ethylene glycol, under the same conditions, does not yield the corresponding benzo-1,4-dioxane; instead, the starting ketone is recovered together with 1,2-diacethoxyethane. The scope of this method is currently being researched in our laboratories.

EXPERIMENTAL

1-Oxanorbornen-2-one was prepared by a literature procedure[3].

1,4-Benzodithiene

To a solution of 1.00 g (9.10 mmol) of oxanorbornen-2-one and 5.14 g (54.6 mmol, 4.28 ml) of ethanedithiol in 25 ml of acetic acid was added a catalytic amount of $BF_3 \cdot OEt_2$ and the reaction mixture was stirred at room temperature overnight. The solvent was then removed *in vacuo* and the residue was taken up into dichloromethane (3x25 ml). The combinated organic extracts were washed with 10% sodium hydroxide solution (2x25 ml) and water (2x25 ml) and then dried over anhydrous magnesium sulfate.

Removal of the drying agent and concentration *in vacuo* afforded 1.89 g of pale yellow oil wich was purified by column chromatography on silica gel (benzene) to give 0.89 g (69% yield) of pure 1,4-benzodithiene as a colorless viscous oil.

Ir ν cm^{-1} (KBr) 2920, 1455, 1420, 1290, 1250, 745, 680; ^{1}H-nmr (80 MHz, $CDCl_3$) δ ppm 3.17 (s, 4H; - S-$(CH_2)_2$-S-); 6.80-7.30 (m, 4H; aromatic); ^{13}C-nmr (80 MHz, $CDCl_3$) δ ppm 28.95 (S-C-C-S); 124.94 (C1 and C8); 128.57 (C6 and C9); 131.10 (C5 and C10); Mass spectrum, m/e (relative intensity): 168(94), 153(100), 140(43), 96(26); Anal. Calcd for $C_8H_8S_2$: C,57.14; H,4.76; S,38.09; Found: C,57.21 S,38.11.

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