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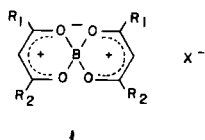
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Bis boron diketonates are prepared from  $\beta$ -diketones or *o*-acylphenols or naphthols with boron trichloride or boron tribromide. The bis boron diketonates that contain methyl groups reacted with some aromatic aldehydes, giving styryl dyes, most of which showed high extinction coefficients.

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Certain boron diketonates [1] and dyes derived from them [2] are compounds of practical interest in industry. Little chemistry has been done on a related class of compounds, the bis(1,3-diketonato)boronium salts **1** [3,4].



Since only a few examples of **1** have been reported, we have investigated the scope of one of the synthetic methods for preparing these compounds. A property of **1** of interest to us was the large extinction coefficient reported for these compounds [4]; for example, **1** ( $R_1 = R_2 = C_6H_5$ ) absorbs at 382 nm ( $\epsilon 1.12 \times 10^5$ ) and 400 nm ( $\epsilon 1.35 \times 10^5$ ) in dichloroethane. We investigated some reactions of derivatives of **1** ( $R_1 = \text{methyl}$ ) with several aldehydes and obtained styryl dyes with large  $\epsilon$  values.

Compound **1** has been prepared by five methods [4]. In the method we used, cold solutions of a  $\beta$ -diketone or an *o*-hydroxyarylketone in methylene chloride were mixed with a cold solution of 0.5 equivalent of boron trichloride in methylene chloride. In most cases the chloride anion of the resulting product was converted to the perchlorate

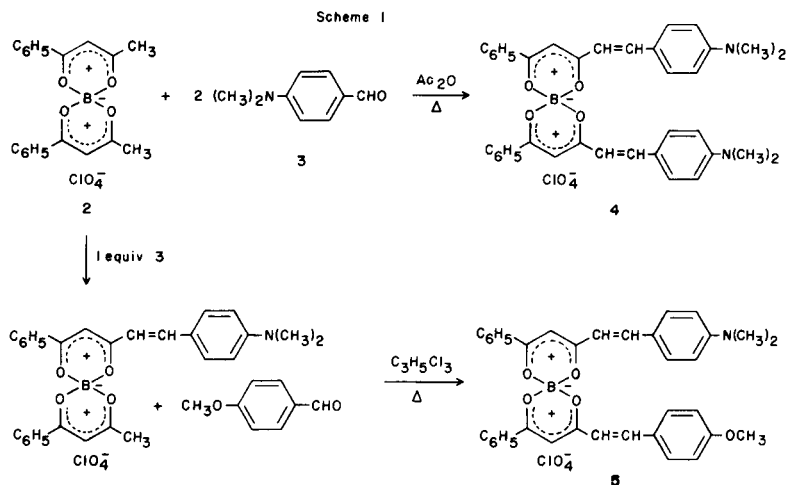
salt. The compounds prepared by this method are listed in Table I. Boron tribromide also gave **1**, and since boron tribromide is a convenient liquid, we now use this reagent. In one case (2-hydroxy-1-acetylnaphthalene), boron tribromide evidently caused nuclear bromination, since the bis boronium salt contained two molecules of bromine.

Boron diketonates containing a methyl group react with certain aldehydes to give dyes [5]. The derivatives of **1** that we used to prepare styryl dyes contained two methyl groups; thus a mixture of products could be obtained. We found that both of the methyl groups reacted with the aldehyde, and in addition, mixed styryl dyes could be prepared as shown in Scheme I.

Compound **4** was a blue dye ( $\lambda_{\text{max}}$  610 nm;  $\epsilon$  90,500 in methylene chloride) with limited solubility. Our reason for preparing the mixed styryl dye **5** was to take advantage of the two chromophores to obtain a black dye, and indeed **5** shows absorption from 400 to 650 nm. We were unable to prepare styryl dyes from the bis boron diketonate derived from 1-acetyl-2-naphthol, presumably because of the instability of the boron diketonate.

## EXPERIMENTAL

Melting points were obtained with a Mel-Temp apparatus and are uncorrected. The absorption spectra were recorded on a Cary-17 spectrometer. Elemental analyses were done by the Analytical Sciences Division,





I, R <sub>1</sub> = <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub> ; R <sub>2</sub> = R <sub>3</sub> = <i>p</i> -Me <sub>2</sub> NC <sub>6</sub> H <sub>5</sub> ,	263-264	93	63.7	5.3	3.7 (N)	589 (140.5)	338 (15.5)
			63.3	5.6	3.5	395 (36.2)	257 (13.5)
II, R = <i>p</i> -Me <sub>2</sub> NC <sub>6</sub> H <sub>5</sub> ,	362-363	56	67.8	4.8	3.8 (N)	629 (110.5)	
			67.5	4.9	4.1	572 (121.0)	

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The procedures are described for a specific compound. The other examples were prepared in the same way from appropriate starting materials.

#### Method A for Preparation of Bis Boron Diketonates.

A cold solution of 1.65 g (14 mmoles) of boron trichloride in 70 ml of methylene chloride was added with stirring to a cold (0-10°) solution of 5.2 g (28 mmoles) of 1-acetyl-2-naphthol in 20 ml of methylene chloride. The reaction was exothermic, and a solid separated. The mixture was stirred at room temperature for 15 minutes, and the solid was collected. The solid was dissolved in warm acetic acid, and 2 ml of 70% perchloric acid was added. The solid that separated was collected and washed with acetonitrile and then with ether.

#### Method B for Preparation of Bis Boron Diketonates.

A cold solution of 2.7 g (10 mmoles) of boron tribromide in 10 ml of methylene chloride was added with stirring to a solution of 3.8 g (20 mmoles) of 1-(4-methoxyphenyl)-butan-1,3-dione in 10 ml of methylene chloride at 0-10°. The reaction mixture was worked up as described for Method A.

#### Preparation of Styryl Dyes.

A mixture of 1.74 g (4 mmoles) of **1** (R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>, X = ClO<sub>4</sub>) and 1.2 g (8 mmoles) of *p*-dimethylaminobenzaldehyde in 5 ml of acetic

anhydride was refluxed for 30 minutes and then cooled to room temperature. The solid was collected and purified by extracting it into 100 ml of acetonitrile in a Soxhlet extractor (3 days). The crystalline material that separated from the hot extract was collected.

#### Preparation of Mixed Styryl Dyes.

A mixture of 1.74 g (4 mmoles) of **1** (R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>, X = ClO<sub>4</sub>) and 0.6 g (2 mmoles) of *p*-dimethylaminobenzaldehyde in 10 ml of acetic anhydride was refluxed for 30 minutes. The reaction mixture was evaporated to dryness, and 2 ml of *p*-anisaldehyde and 10 ml of 1,2,3-trichloropropane were added to the residue. The mixture was refluxed for 1 hour and chilled, and the solid was collected. The material was purified by extraction in a Soxhlet extractor as described above.

#### REFERENCES AND NOTES

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