

## Synthesis, reactions and characterisation of some new $\beta$ -ketoester boroacetates

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**Abstract.** The reactions of methyl esters of aroyl pyruvic acids (aroyl = benzoyl, *p*-chlorobenzoyl, *p*-bromobenzoyl and *p*-methylbenzoyl) with boric acid in acetic anhydride solution yield derivatives of the general formula  $(\text{OAc})_2\text{B}[\text{OC}(\text{R})\text{CHCOCOOMe}]$  ( $\text{R} = \text{C}_6\text{H}_5$ , *p*- $\text{ClC}_6\text{H}_4$ , *p*- $\text{BrC}_6\text{H}_4$  and *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ). The reactions of these derivatives with protic ligands such as glycols, *o*-aminophenol and *o*-aminothiophenol have also been carried out. These derivatives have been characterised by elemental analysis and molecular weight measurements. The tetra-coordination around central boron atom has been established by IR,  $^1\text{H}$  NMR and  $^{11}\text{B}$  NMR spectral evidence.

**Keywords.**  $\beta$ -ketoester boroacetates; spectral data; tetra-coordinate boron.

### 1. Introduction

$\beta$ -Diketone derivatives of boron have been studied (Barabas *et al* 1968; Simpson and Porter 1972; Dey *et al* 1975; Cotton and Ilsey 1982; Shapel'KO *et al* 1970; Kopteva *et al* 1978) extensively but no attempt appears to have been made to study their  $\beta$ -ketoester analogues. Methyl ester of aroyl pyruvic acids which behave as  $\beta$ -ketoesters form corresponding metal and metalloid derivatives (Hugos and O'Conner 1974; Podolov *et al* 1974; Singh *et al* 1982). In the present paper the synthesis and characterisation of some  $\beta$ -ketoester boroacetate complexes are described and an attempt has been made to establish their probable structures on the basis of physico-chemical and spectral studies.

### 2. Experimental

Due to the hydrolysable nature of the  $\beta$ -ketoester boroacetate derivatives, care was taken to exclude moisture from the apparatus during the experiments. Toluene (BDH) was sodium-dried, acetic anhydride (BDH) was distilled before use (b.p. 153°C). Boric acid (BDH, AR) was used without further purification. Methyl esters of aroyl pyruvic acids were prepared by the method reported in literature (Lehninger and Witzemann 1942).

Boron was estimated as methyl borate (Thomas 1949). Acetoxy group/acetic acid was estimated by titrating against standard N/10 NaOH solution. Infrared spectra were recorded in nujol-mull using a Perkin-Elmer model 577 grating infrared spectrophotometer. The  $^1\text{H}$  NMR spectra were obtained from a Perkin-Elmer R-12B spectrometer. Molecular weights were determined ebullioscopically with Gallenkamp ebulliometer equipped with thermistor sensor.

Synthesis of *bis* (acetato)boron  $\beta$ -ketoester: Similar methods were followed in the

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Table 1. Synthetic, physical and analytical data of  $\beta$ -ketoester borooacetate

$H_3BO_3$ /borooacetate (g)	Ligand (g)	Product (% yield)	Physical state m.p. (°C)	% Analysis		Molecular weight
				%OAc or (g) Acetic acid	%B	
$H_3BO_3$ 0.68	PhCOCH <sub>2</sub> COCOOMe 2.27	(OAc) <sub>2</sub> B[OC(Ph)CHCOCOOMe] 80	Brown cry- stalline solid 176	35.02 (35.33)	3.21 (3.23)	358 (334)
$H_3BO_3$ 0.43	ClPhCOCH <sub>2</sub> COCOOMe 1.67	(OAc) <sub>2</sub> B[OC(ClPh)CHCOCOOMe] 79	Light brown crystalline solid 182	32.02 (31.82)	3.05 (2.92)	382 (369.5)
$H_3BO_3$ 0.37	BrPhCOCH <sub>2</sub> COCOOMe 1.71	(OAc) <sub>2</sub> B[OC(BrPh)CHCOCOOMe] 82	Light brown crystalline solid 134	28.31 (28.57)	2.75 (2.61)	— —
$H_3BO_3$ 1.19	CH <sub>3</sub> PhCOCH <sub>2</sub> COCOOMe 4.24	(OAc) <sub>2</sub> B[OC(CH <sub>3</sub> Ph)CHCOCOOMe] 79	Crimson cry- stalline solid 197	33.64 (33.91)	2.98 (3.10)	— —
OB <sub>2</sub> (OAc) <sub>4</sub> 0.66	ClPhCOCH <sub>2</sub> COCOOMe 1.15	(OAc) <sub>2</sub> B[OC(ClPh)CHCOCOOMe] 81	Light brown crystalline solid 182	31.98 (31.82)	3.09 (2.92)	— —
HSC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> 0.49	(OAc) <sub>2</sub> B[OC(CH <sub>3</sub> Ph)CHCOCOOMe] 1.36	$\overline{SC_6H_4NH_2}$ [OC(CH <sub>3</sub> Ph)CHCOCOOMe] 85	Red viscous solid	0.38 (0.38)	3.26 (3.20)	— —
HOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> 0.46	-do- 1.48	$\overline{OC_6H_4NH_2}$ [OC(CH <sub>3</sub> Ph)CHCOCOOMe] 80	Red powder 220	0.41 (0.43)	3.30 (3.35)	— —
HOCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OH 0.28	-do- 1.62	$\overline{GOB}$ [OC(CH <sub>3</sub> Ph)CHCOCOOMe] 76	-do- 238	0.54 (0.55)	3.22 (3.24)	— —

G = -CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>-

synthesis of all these derivatives. The methods of preparation of two representative compounds are described in detail and the results of the other experiments are summarised in table 1.

### 2.1 Synthesis of bis(acetato)boron (methyl 4-methyl $\alpha,\gamma$ -dioxabenzene butanoato $O^{\alpha} O^{\gamma}$ )

A calculated amount of methyl ester of *p*-methylbenzoyl pyruvic acid (4.24 g, 19.57 mM) was mixed with acetic anhydride solution of boric acid (1.19 g, 19.53 mM). The reaction mixture was refluxed till a distinct colour change (light yellow to dark brown) took place. The mixture was allowed to stand overnight and the pink coloured crystals separated out. The crystals were washed with ether and vacuum dried (yield 79%). Found B, 2.98; OAc, 32.64; Calcd. for  $C_{16}H_{17}O_8B$ , B, 3.10, OAc, 33.91%.

### 2.2 Reaction of bis(acetato)boron (methyl-4-methyl $\alpha,\gamma$ -dioxabenzene butanoato $O^{\alpha} O^{\gamma}$ ) with 2-aminothio phenol in 1:1 molar ratio

A toluene solution (~ 20 ml) of 2-aminothiophenol (0.49 g, 3.98 mM) was mixed with a toluene solution (~ 30 ml) of bis(acetato)boron pyruvate (1.33 g, 3.82 mM). The reaction mixture was heated under reflux using a fractionating column. The acetic acid liberated during the course of the reaction was fractionated out azeotropically with toluene and estimated periodically (Found 0.41 : Calcd, 0.43 g). After the completion of the reaction, the excess solvent was distilled off and the compound was dried under reduced pressure and the compound was recrystallised with benzene/*n*-hexane mixture (70:30) (yield, 85%). Found B, 3.26 Calcd. for  $C_{18}H_{16}NSB$ , B, 3.20%.

## 3. Results and discussion

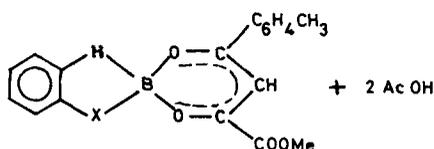
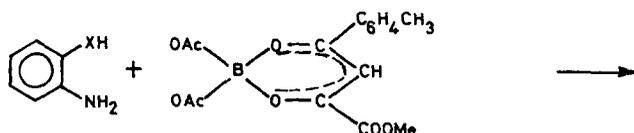
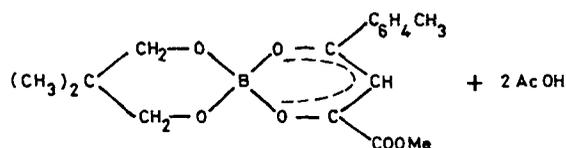
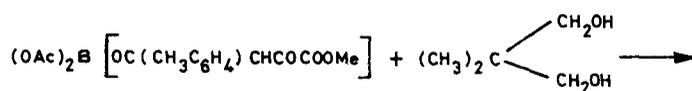
Boric acid reacts with methyl esters of aroyl pyruvic acids (aroyl = benzoyl, *p*-chlorobenzoyl, *p*-bromobenzoyl and *p*-methylbenzoyl) in 1:1 molar ratios in acetic anhydride solution to give bis(acetato)boron pyruvates, which crystallises out from the reaction mixtures on allowing them to stand overnight at room temperature.

These reactions appear to take place through the formation of oxy-bis(diacetato borane) which further interact in the presence of acetic anhydride with ligands to give bis(acetato)boron pyruvates. The second step of the above reaction was confirmed by studying the reaction of one of the ligands with oxy-bis(diacetato borane) in acetic anhydride solution. The resulting product was found to have the similar composition and physico-chemical characteristics.

These derivatives are non-volatile coloured crystalline solids having sharp melting points. They are soluble in common organic solvents, hydrolytically unstable and monomeric in refluxing benzene. Their important physical properties have been summarised in table 1.

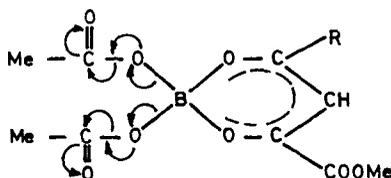
The acetoxy groups in bis(acetato)boron pyruvate derivatives are quite reactive and can easily be replaced by protic organic ligands like glycols, *o*-aminophenol and *o*-aminothiophenol. The reactivity of these derivatives is in contrast to the earlier observations of Singh and Tandon (1979, 1980) who reported the inert nature of the acetoxy groups in bis(acetato)boron Schiff's base derivatives.

The reactivity of the acetate groups in bis(acetato)boron-pyruvates is enhanced due to the presence of free carbonyl group (acetate) which attracts the bonding electrons of



(X = S or O)

the B–O bond (acetoxo group); as a result the bond is weakened and ruptured under the influence of the protic reagents.



### 3.1 IR spectra

On the basis of their comparative study with corresponding ligands, an attempt has been made to draw some conclusions regarding the mode of bonding in these derivatives. The IR spectra of *bis*(acetato)boron pyruvates exhibit a broad band at 1720–1740  $\text{cm}^{-1}$  and is assigned to C=O stretching frequency (Niedenzu and Fritz 1965; Alcock *et al* 1976). In the spectra of the ligand a sharp band is observed at  $\sim 1720 \text{ cm}^{-1}$  and the broadening of this band indicates that the two carbonyl frequencies (one of the acetate group and another of the ester group of the ligand) overlap in this region. The presence of  $\nu_{\text{C=O}}$  absorption band (due to acetate) in this

region indicates the unidentate nature of acetate group (Singh and Tandon 1980; Niedenzu and Fritz 1965). Moreover the absence of any appreciable shift in the position of C=O bond (due to ligand) indicates that the ester group of the ligand does not take part in the complex formation.

Another medium intensity band at  $\sim 1260 \text{ cm}^{-1}$  may be assigned to the  $\nu_{\text{C-O}}$  frequencies (acetate group) (Alcock *et al* 1976). A strong band observed in the range  $1580\text{--}1590 \text{ cm}^{-1}$  in the spectra of bis(acetato)boron pyruvates may be assigned to C=O ligand. This band occurs at  $1600\text{--}1535 \text{ cm}^{-1}$  in the free ligands. The shift  $\sim 50 \text{ cm}^{-1}$  in (C=O stretching frequency) towards lower wave number may be due to the coordination of the carbonyl oxygen to the central boron atom. A strong band at  $1510\text{--}1520 \text{ cm}^{-1}$  observed in the spectra of these derivatives may be assigned to C=C + C=O.

A medium intensity band observed in the region  $710\text{--}720 \text{ cm}^{-1}$  may be assigned to B  $\leftarrow$  O stretching (Gates and Mooney 1968).

### 3.2 $^1\text{H NMR}$ spectra

The  $^1\text{H NMR}$  spectra of these complexes have been recorded in  $\text{CDCl}_3$  using TMS as internal reference and are summarised in table 2. The absence of any signal for  $\text{--OH}$  proton in the spectra of the complexes ( $\delta 10.6$  ppm in the ligand) shows the deprotonation of the  $\text{--OH}$  proton during complex formation.

A singlet observed at  $\delta 3.98$  ppm which was earlier assigned to the methyl protons does not show any appreciable shift in its position ( $\delta 4$  ppm) on complexation. This shows that C=O group does not take part in bonding between ligand and the central boron atom.

A down-field shift has been observed in the signal due to  $\text{--CH}$  proton. This signal appeared at  $\delta 7.1$  ppm in the ligand and observed at  $\delta 7.3$  ppm in the corresponding boron complexes. This shift of  $0.2$  ppm may be attributed to the delocalization of electrons in the complex which induces additional stability to the complexes.

A singlet due to  $\text{CH}_3$  protons of the acetate group has been observed at  $\delta 2.10$  ppm in the spectra of these boron derivatives (Singh *et al* 1983).

### 3.3 $^{11}\text{B NMR}$ spectra

The  $^{11}\text{B NMR}$  spectrum of one of the representative compound  $(\text{OAc})_2\text{B}[\text{OC}(\text{ClC}_6\text{H}_4)\text{--CHCOCOOMe}]$  has been recorded in  $\text{CDCl}_3$ . The spectrum shows a sharp singlet at  $\delta 1.82$  ppm with reference to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ . The appearance of only one sharp signal

Table 2.  $^1\text{H NMR}$  spectra data for  $\beta$ -ketoester boroacetates

Compound	COOMe (s)	$\text{--CH}$ (s)	$\text{CH}_3$ (acetate) (s)	Phenyl (m)
$(\text{OAc})_2\text{B}[\text{OC}(\text{C}_6\text{H}_5)\text{CHCOCOOMe}]$	3.90	7.30	2.00	7.4–8.0
$(\text{OAc})_2\text{B}[\text{OC}(\text{ClC}_6\text{H}_4)\text{CHCOCOOMe}]$	4.00	7.30	2.10	7.4–7.6
$(\text{OAc})_2\text{B}[\text{OC}(\text{BrC}_6\text{H}_4)\text{CHCOCOOMe}]$	3.90	7.30	2.15	7.4–8.1
$(\text{OAc})_2\text{B}[\text{OC}(\text{CH}_3\text{C}_6\text{H}_4)\text{CHCOCOOMe}]$	3.90	7.30	2.05	7.4–7.5 8.0–8.15

s = singlet, m = multiplet

confirm the existence of boron atom in only one environment and also the purity of the compound. A comparison of  $^{11}\text{B}$  chemical shift with the values reported in the literature confirm that the boron atom in this complex has a coordination number of four (Onak *et al* 1959; Brown and Bladon 1969; Hohaus and Riepe 1973, 1976).

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