Acetoacetyl pyrroles and their boron complexes

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Various boron complexes of acetoacetyl pyrrole have been synthesized and their nuclear magnetic resonance and infrared spectra showed that the complexes formed are six member chelate.

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Complexes of boron with acetylacetone are well known (1–3). In contrast no studies on boron complexes with acetoacetyl pyrroles have been recorded. This paper describes the preparation of the boron complexes of various 2- and 3-acetoacetyl pyrroles and an investigation of their structures utilizing nuclear magnetic resonance (n.m.r.) and infrared spectroscopy in addition to the chemical degradation. The 2-acetoacetyl pyrroles can form two types of complexes. In one case the complex is formed entirely with the acetoacetyl moiety resulting in the formation of a six member chelate (4–6), while in the other the pyrrole nitrogen participates with the complex formation resulting in a five member chelate (7).

The various acetoacetyl pyrroles used in this investigation were prepared by the reaction of the parent pyrroles with ketene dimer as described by Treibs and Michl (4). The particular pyrroles were chosen to provide three structurally distinct types having functional groups as follows (*i*) a 2-acetoacetyl group and an N—H, (*ii*) a 3-acetoacetyl group and an N—H but with methyl groups at 2 and 5, (*iii*) a 2-acetoacetyl group and an N—CH_3 group.

The infrared spectra of **1**–**4** showed a sharp band in the 3300 cm^{-1} region and a broad strong band in the 1600–1640 cm^{-1} region characteristic of the N—H and β-diketone function respectively. The spectrum of **5** lacked the N—H absorption but showed an absorption at 1600 cm^{-1} attributed to the free carbonyl.

The n.m.r. spectrum of **1** in $CDCl_3$ showed it to be a mixture of enol **1***ii* or **1***iii* (62%) and keto-1 (38%) tautomers. Similarly **2**–**5** were observed to be mixtures of enol and keto in the following ratios; 68:22, 62:38, 53:47 and 60:40.

On treatment with boron trifluoride etherate in benzene or ether the acetoacetyl pyrroles **1**–**5** all gave boron complexes in 80–90% yield. The infrared spectrum of **1***a* has bands at 3378 cm^{-1} (N—H) and 1565 cm^{-1} (chelated carbonyl (8, 9)). It is of special importance to point out that the N—H band showed an increase in frequency and the β-diketone band showed a decrease in frequency relative to those of **1**. This increase in frequency is attributed to the absence of hydrogen bonding to the N—H group in the complex. The N—H is hydrogen bonded in the original compound. The decrease in frequency of the β-diketone is attributed to the coordination of the acetoacetyl group to boron. The decrease in frequency is a measure of the degree of coordination (9) and quite strong coordination is indicated in this case. The infrared evidence points towards a complex involving only the acetoacetyl moiety.

The infrared spectra of **2***a*–**5***a* all resemble that of **1***a* and show the same shift relative to the starting material. That of **5***a* is similar except that it of course lacks the absorption of the N—H at 3200 cm^{-1}. This indicates that they too have structures analogous to **1***a*.

The n.m.r. spectra of **1** (Fig. 1) in $CDCl_3$ exhibit signals at (δ values) 2.05, 2.3, 3.85, 5.9, 6.3, 7.0, and 9.83 p.p.m. with relative intensities of 3:3:2:1:2:1. A comparison of the spectrum with that of the pyrrole leads to the assignment of the signals at 7.0 and 6.3 to the α- and β-hydrogen of the pyrrole ring respectively. The signals at 2.05 and 2.3 are assigned to the protons of the enolic and keto methyl groups, while those at 3.85 and 5.9 are attributed to the —CH= and —CH_2 groups in the keto and enol form.

The n.m.r. spectra of **1***a* (Fig. 2) in $CDCl_3$ exhibit signals at 2.25, 6.2, 6.7, 7.25, and 9.76 p.p.m. with relative intensities of 3:1:1:2:1. A comparison of this with the spectrum of **1** leads to the assignment of the signals at 7.25 and 6.7 to the α- and β-hydrogen of the pyrrole and the signals at 6.2 and 2.25 to the —CH= and methyl protons of the acetoacetyl moiety respectively. The disappearance of the peaks

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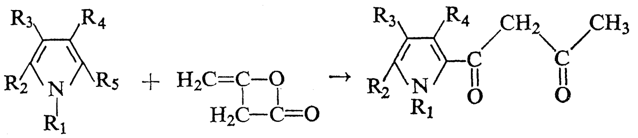
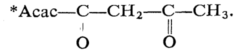
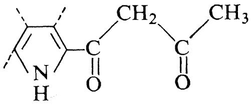


1-5

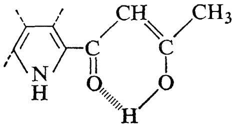
	R_1	R_2	R_3	R_4	R_5
1	H	H	H	H	Acac*
2	H	CH_3	H	CH_3	Acac
3	H	CH_3	C_2H_5	CH_3	Acac
4	H	CH_3	H	Acac	CH_3
5	CH_3	CH_3	H	CH_3	Acac



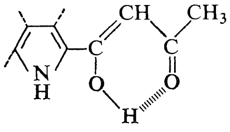
$*Acac—\underset{\|\atop O}{C}—CH_2—\underset{\|\atop O}{C}—CH_3.$



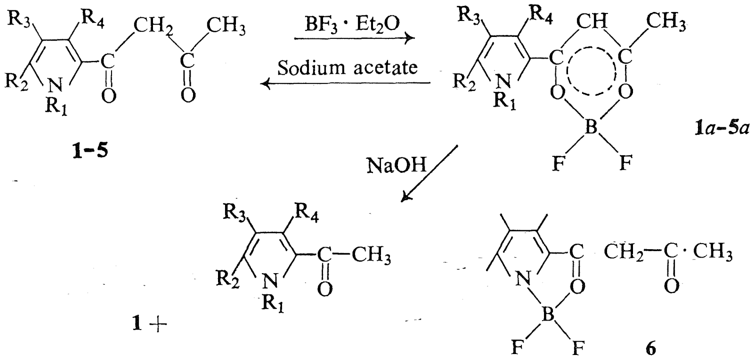
1*i*



1*ii*



1*iii*



at 2.3 and 3.85 and a broadening of the signal for N—H at 9.76 p.p.m. in conjunction with the frequency shift observed in the infrared spectra clearly show that the complex has formed on the acetoacetyl moiety in the formation of a six member chelate and does not involve reaction with the nitrogen.

The n.m.r. spectra of the complexes derived from **2**–**5** similarly show only the signals attributed to the enol form of the acetoacetyl groups. This shows they all have the same type of structure as postulated for **1***a*.

Refluxing the boron complexes with aqueous sodium acetate regenerated the starting acetoacetyl pyrroles (10, 11). Similar treatment with aqueous sodium hydroxide gave both the starting acetoacetyl pyrrole and the corresponding acetyl compound, presumably due to ketonic cleavage of the regenerated starting material.

Experimental

All melting points are uncorrected. Nuclear magnetic resonance (n.m.r.) measurements were carried out in $CDCl_3$ containing tetramethylsilane as internal standard using Varian A-60 machine. Infrared spectra were obtained in Nujol on Perkin–Elmer Infracord model 137E.

1,3-Butanedione-1(2-pyrryl) (1)

This compound was prepared according to the method of Treibs and Michl (4) m.p. 85–87°. Infrared spectrum (Nujol): N—H 3268 cm^{-1}, C═O 1639 cm^{-1}.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.50; H, 6.00; N, 9.27. Found: C, 63.58; H, 5.98; N, 9.23.

Difluoro[1(2-pyrryl)-1,3-butanediono]borane (1a)

A solution of **1** (75 mg) in benzene (5 ml) was treated with $BF_3 \cdot Et_2O$ (90 mg) and stirred, the complex separated

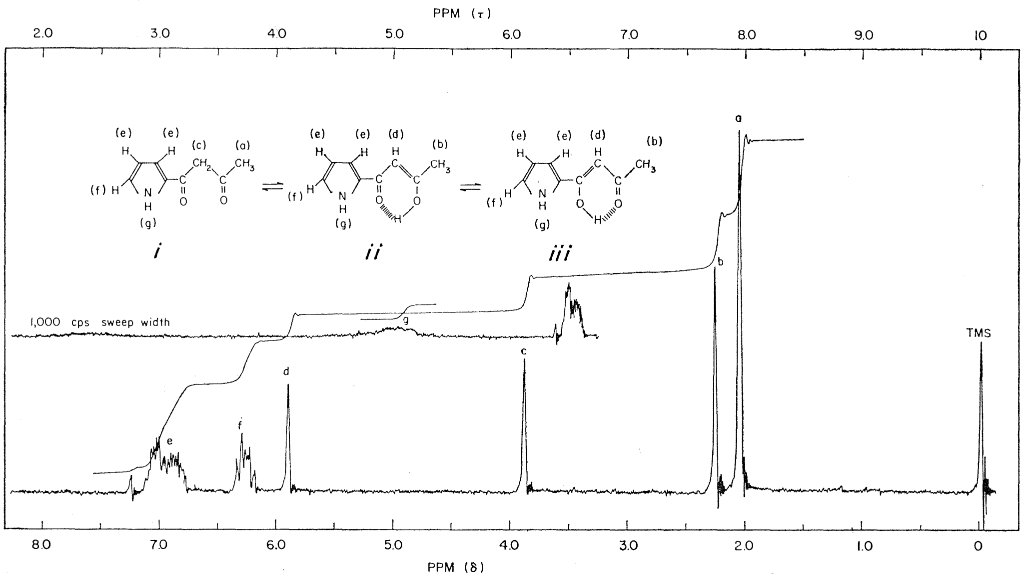


FIG. 1. The nuclear magnetic resonance spectrum of **1** (**1***i*, **1***ii*, and **1***iii*) in $CDCl_3$.

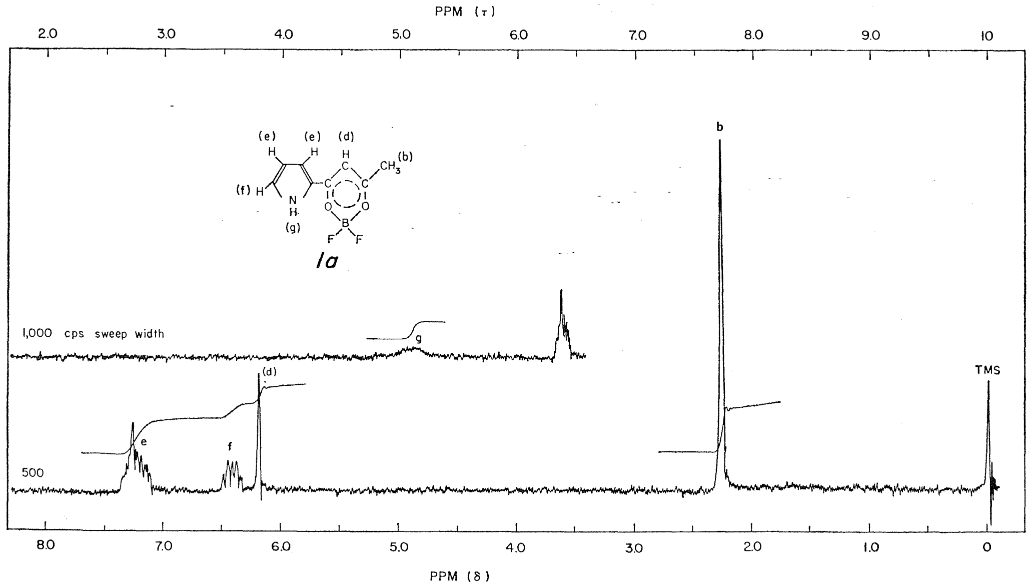


FIG. 2. The nuclear magnetic resonance spectrum of **1***a* in $CDCl_3$.

out, was filtered, washed, dried, and crystallized from benzene gave (75 mg) of the boron complex m.p. 144–146°; infrared spectrum (Nujol): N—H 3378 cm^{-1}, C═O 1565 cm^{-1}.

Anal. Calcd. for $C_8H_8NO_2BF_2$: C, 48.31; H, 4.05; N, 7.03; B, 5.44; F, 19.10. Found: C, 48.24; H, 4.12; N, 7.21; B, 5.24; F, 18.65.

*1,3-Butanedione-1(2,4-dimethyl 5-pyrryl) (**2**)*

2 was prepared by reacting 2,4-dimethyl pyrrole with diketene dimer (4) m.p. 106–108°. Infrared spectrum (Nujol): N—H 3279 cm^{-1}, C═O 1639 cm^{-1}. Nuclear magnetic resonance spectrum in $CDCl_3$ showed signals at 2.1, 2.26, 2.3, and 2.35 (singlets, 3H each, enol CH_3, keto CH_3 α- and β-CH_3) 3.9 (singlet, 2H, keto CH_2)

5.86 (broad triplet, enol H and β-H) and 9.83 p.p.m. (singlet, 1H, NH).

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.00; H, 7.31; N, 7.82. Found: C, 66.91; H, 7.23; N, 8.12.

Difluoro[1(2,4-dimethyl 5-pyrryl)-1,3-butanediono]-borane (2a)

A solution of **2** (1.5 g) in benzene (10 ml) was treated with $BF_3{\cdot}Et_2O$ (1.8 g) the yellow complex separated, was filtered, washed, and crystallized from alcohol (1.9 g) as yellow needles m.p. 216–218°. Infrared spectrum (Nujol): N—H 3367 cm^{-1}, C=O 1575 cm^{-1}. Nuclear magnetic resonance spectrum in pyridine ($CDCl_3$ insoluble) 2.16, 2.26, and 2.33 (singlets, 3H each, enol CH_3, α- and β-CH_3) 5.96 (doublets, β-H), and 6.16 p.p.m. (singlet, enol H).

Anal. Calcd. for $C_{10}H_{12}NO_2BF_2$: C, 52.90; H, 5.29; N, 6.17; B, 4.76; F, 16.76. Found: C, 52.81; H, 5.54; N, 6.23; B, 4.36; F, 15.75.

1,3-Butanedione-1(2,4-dimethyl 3-ethyl 5-pyrryl) (3)

2,4-Dimethyl 3-ethyl pyrrole was treated with diketene (4) to give **3** m.p. 86–88°. Infrared spectrum (Nujol): N—H 3279 cm^{-1}, C=O 1629 cm^{-1}. Nuclear magnetic resonance spectrum in $CDCl_3$ 6.2 (triplet, 3H, $\mathit{CH_3}$—CH_2) 2.8, 2.16, 2.26 (singlets, 3H each) 2.5 (quartet, 2H, CH_3—$\mathit{CH_2}$) 3.86 (singlet, 2H, keto CH_2) 5.83 (singlet, 1H, enol H) and 9.65 p.p.m. (singlet, NH).

Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 69.55; H, 8.26; N, 6.79. Found: C, 69 43; H, 8.18; N, 6.59.

Difluoro[1(2,4-dimethyl 3-ethyl 5-pyrryl)-1,3-butanediono] borane (3a)

This was prepared from **3** (56 mg) in benzene (5 ml) and $BF_3{\cdot}Et_2O$ (45 mg), the complex separated, was filtered, washed, and crystallized from benzene (54 mg) as yellow needles m.p. 150–152°. Infrared spectrum (Nujol): N—H 3356 cm^{-1}, C=O 1577 cm^{-1}. Nuclear magnetic resonance spectrum in $CDCl_3$ 6.2 (triplet, 3H, $\mathit{CH_3}CH_2$) 2.21, 2.33 (singlet, 3H, 6H) 2.5 (quartet, 2H, $CH_3\mathit{CH_2}$) 6.05 (singlet, 1H, enol H) and 9.43 p.p.m. (singlet, N—H).

Anal. Calcd. for $C_{12}H_{16}NO_2BF_2$: C, 56.52; H, 6.31; N, 5.49. Found: C, 56.65; H, 6.14; N, 5.56.

1,3-Butanedione-1(2,5-dimethyl 3-pyrryl) (4)

2,5-Dimethyl pyrrole was reacted with diketene (4) to give **4**, m.p. 87–88°. Infrared spectrum (Nujol): N—H 3270 cm^{-1}, C=O 1630 cm^{-1}.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.00; H, 7.31; N, 7.82. Found: C, 67.18; H, 7.21; N, 7.76.

Difluoro[1(2,5-dimethyl 3-pyrryl)-1,3-butanediono]-borane (4a)

A solution of **4** (90 mg) in benzene (10 ml) was treated with $BF_3{\cdot}Et_2O$ (90 mg) and allowed to stand at room temperature. The complex separated, was filtered, washed, and crystallized from benzene (95 mg) as yellow needles m.p. 155–157°. Infrared spectrum (Nujol): N—H 3370 cm^{-1}, C=O 1570 cm^{-1}. Nuclear magnetic resonance spectrum in $CDCl_3$ 2.25 and 2.57 (singlets, 6H, 2 times CH_3, α- and α′-CH_3 and 3H, enol CH_3) 6.08 (singlet, 1H, enol H) 6.3 (multiplet, 1H, β-H) and 9.16 p.p.m. (singlet N—H).

Anal. Calcd. for $C_{10}H_{12}NO_2BF_2$: C, 52.90; H, 5.29; N, 6.17; B, 4.76; F, 16.76. Found: C, 52.78; H, 5.35; N, 6.25; B, 4.36; F, 15.98.

1,3-Butanedione-1(1,2,4-trimethyl 5-pyrryl) (5)

1,2,4-Trimethylpyrrole (12) was treated with diketene to give **5**, m.p. 58–60°. Infrared spectrum (Nujol): C=O 1600 cm^{-1}. Nuclear magnetic resonance spectrum in $CDCl_3$ 2.08, 2.2, 2.3 (singlets, 3H, 3H and 2 times 3H) 3.76 (singlet, 3H N—CH_3) 3.85 (singlet, 2H, keto CH_2) 5.72 (singlet, 1H, enol H) 5.8 p.p.m. (multiplet, 1H, β-H).

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.38; H, 7.82. Found: C, 68.20; H, 7.52.

Difluoro[1-(1,2,4-trimethyl 5-pyrryl)-1,3-butanediono]-borane (5a)

A solution of **5** (96 mg) in benzene (5 ml) was treated with $BF_3{\cdot}Et_2O$ (90 mg) and stirred, the complex separated, was filtered, washed, and crystallized from benzene (1.02) as yellow needles m.p. 135–137°. Infrared spectrum (Nujol): C=O 1580 cm^{-1}. Nuclear magnetic resonance spectrum in $CDCl_3$ 2.25, 2.28, 2.36 (singlets 3H each, enol CH_3, α- and β-CH_3) 3.83 (singlet, 3H, N—CH_3) 6.01 p.p.m. (multiplet, 2H, enol and β-H).

Anal. Calcd. for $C_{11}H_{14}NO_2BF_2$: C, 54.80; H, 5.85; N, 5.81. Found: C, 54.72; H, 5.96; N, 5.78.

Hydrolysis of **2a**

(i) By Sodium Acetate

2a (20 mg) was refluxed with 10% sodium acetate (10 ml) for 10 min, allowed to cool, the solid separated, was filtered, washed, dried, and identified as **2** m.p. and mixture m.p. 108°.

(ii) By Sodium Hydroxide

2a (20 mg) was heated with dilute sodium hydroxide (5 ml) for 10 min. It was cooled, the colorless crystalline precipitate separated, was filtered, washed, dried and identified as 2,4-dimethyl 5-acetyl pyrrole m.p. and mixture m.p. 120°. The mother liquor was acidified with dilute acetic acid, the precipitate separated, was filtered, washed, dried, and identified as **2** m.p. and mixture m.p. 108°.

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