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THE BORON TRIFLUORIDE/ACETIC ANHYDRIDE SYSTEM AND ITS REACTION WITH FERROCENE

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SUMMARY

The BF_3-catalysed acetylation of ferrocene with acetic anhydride in chlorinated solvents has been reinvestigated. Using a 2/1 molar ratio of anhydride to ferrocene and excess BF_3, both diacetylferrocenes and monoacetylferrocene were obtained; low concentrations of HF inhibit the formation of the diacetylated products and this may explain the results of earlier workers. Monoacetylferrocene appears to be the intermediate for both diacetyl derivatives. Yields of the 1,2-isomer of up to 5% of the total diacetylated products were obtained. The product of the reaction between BF_3 and acetic anhydride has been shown to be 3,3,9,9-tetrafluoro-5,7-dimethyl-2,4,8,10-tetraoxa-3,9-diborabicyclo[4.4.0]deca-1,5,7-triene, the bis(boron difluoride)derivative of α-acetylacetoacetic acid (I). Acetoacetylferrocene reacts with BF_3 to give the expected (1-ferrocenyl-1,3-diketonato)boron difluoride (II).

INTRODUCTION

Earlier studies[1,2] of the acetylation of ferrocene with acetic anhydride, using excess boron trifluoride as the catalyst, showed that monoacetylferrocene, MAF, was formed in high yield (80–90%) and that no further acetylation of MAF occurred, even in the presence of excess acetic anhydride. We have also used this reaction and have obtained very satisfactory yields of MAF. However, when the reaction was repeated using BF_3 from a different cylinder (Imperial Smelting Corporation) appreciable amounts of 1,1'- and 1,2-diacetylferrocenes, DAF, were also obtained. A number of substituted ferrocenes also undergo diacetylation under the same conditions[3]. Since it is easier to work up the products of a BF_3/acetic anhydride reaction than those of an $AlCl_3/CH_3COCl$ reaction and since the highest yield of 1,2-DAF reported[4] for the latter reaction is so low (1.2%), we proceeded to investigate the BF_3-catalysed reaction and, in particular, the influence of impurities in the reagents on the course of the reaction.

RESULTS AND DISCUSSION

Typical reaction conditions are described in the experimental section. It was

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convenient to follow the progress of the acetylation by thin layer chromatography on alumina; samples from the reaction system were spotted on the Al_2O_3-coated microscope slides. Diethyl ether eluted the ferrocene derivatives in the following sequence: ferrocene (yellow), MAF (pale orange), 1,2-DAF (pale orange) and 1,1'-DAF (red-orange). The colours of the three acetylated products adsorbed on Al_2O_3 were found to be reasonably distinct, however, it was noticed that intensely and characteristically coloured spots were produced when the plates were exposed to BF_3 gas. MAF and 1,1'-DAF give rise to indigo coloured BF_3 adducts, whereas 1,2-DAF forms a red-brown adduct; the ferrocene spot is unaffected.

Although column chromatography of the mixture of acetylferrocenes provides a satisfactory way of separating them, a preliminary separation was found to be desirable because of the preponderance of 1,1'-DAF in the product mixture. It was noted that 1,2-DAF is more soluble than the 1,1' isomer in aliphatic hydrocarbon solvents and, therefore, a Soxhlet extraction of the crude solid products was performed with 40–60 petroleum. This removes nearly all the unreacted ferrocene, MAF, and 1,2-DAF with only a little 1,1'-DAF. Subsequent chromatography of this extract on an alumina column enabled a fair separation of the 1,2-DAF to be achieved. The residue in the Soxhlet thimble, after an extended extraction, was found to be almost entirely 1,1'-DAF contaminated with some polymeric material.

The yields of purified products from three ferrocene/acetic anhydride/BF_3 reactions are listed in Table 1. Also included are the products obtained from a ferrocene/acetyl chloride/$AlCl_3$ reaction under similar conditions. It is noticeable that the ratio of the yields of 1,2-DAF/1,1'-DAF is constant at about 1/20 in the BF_3-catalysed reactions. Rather less 1,2-DAF (ratio 1/28, *cf.* Richards and Curphey's[4] result 1/30) was obtained from the $AlCl_3$-catalysed reaction but an even less favourable ratio (1/63) was reported by Rosenblum and Woodward[5]: in our view these lower yields of the 1,2-isomer are a result of its decomposition during the acetylation reaction and subsequent work up. It seems likely that the 1,2-isomer is less stable than 1,1'-DAF. Thus we have found that only the homoannular isomer is decomposed in the He–Ne (6328 Å) laser beam, although both DAFs have similar UV/visible absorption spectra.

The yields of MAF recorded in Table 1 are more variable. Moreover, our results show that the quality of the BF_3 used in the $(CH_3CO)_2O/BF_3$ reactions has a marked effect on the extent of diacetylation. In order to investigate this further we

TABLE 1

COMPOSITION OF THE MIXTURE OF ACETYLFERROCENES OBTAINED FROM THE ACETYLATION OF FERROCENE IN CH_2Cl_2

Acetylating agent	Product yields (wt.%)[a]		
	MAF	1,2-DAF	1,1'-DAF
$(CH_3CO)_2O[2.0]/BF_3[\text{excess}]$[b,c]	1.2	4.9	93.9
	22.5	3.7	73.8
	3.8	4.4	91.8
$CH_3COCl\ [2.8]/AlCl_3[2.3]$[b,d]	1.3	3.4	95.3

[a] Reaction time 1 h. [b] [ ] indicates the molar proportion of reagent per mole ferrocene. [c] At 0°. [d] At 20°.

carried out acetylations of MAF with pure BF_3, generated from the benzonitrile–BF_3 complex[6]: excess BF_3 effectively catalysed the formation of diacetylated products, although smaller amounts, *e.g.* 5 moles per mole ferrocene, caused partial acetylation only. Mixture of silicon tetrafluoride, a likely contaminant in commercial BF_3, and pure BF_3 were also effective in catalysing further acetylation of MAF. On the other hand, the addition of hydrogen fluoride to ferrocene/acetic anhydride/BF_3 reactions in CH_2Cl_2 in a closed system was found to modify the composition of the reaction products (see Table 2). Clearly in an open system, in which excess BF_3 is passed through the reaction mixture, traces of HF impurity in the BF_3 may accumulate in the mixture. We suggest that this is the explanation of the failure of earlier workers to obtain diacetylation in this system.

TABLE 2

INFLUENCE OF THE HF CONTENT OF CATALYST ON THE COMPOSITION OF THE PRODUCTS IN FERROCENE–$(CH_3CO)_2O$–BF_3 REACTIONS[a]

Catalyst composition (mmoles)		Molar product composition [MAF/DAF (both isomers)]
BF_3[b]	HF	
4.5	0	0.30
4.5	0.3	1.17
4.5	1.5	4.92

[a] Solvent CH_2Cl_2 (10 ml), ferrocene (1.05 mmoles), $(CH_3CO)_2O$ (2.21 mmoles) temperature 0°, reaction time 1 h. [b] Commercial grade, low in HF.

The acetylation of ferrocene with acetic anhydride in liquid HF, as described by Weinmayr[7], yields predominantly MAF. We have also used this reaction, at about 20°, to prepare MAF and can confirm that only traces of DAFs are produced. Thus it appears that the MAF–BF_3 adduct, a purple compound described by Hauser and Lindsay[1], is susceptible to further acetylation, whereas protonated MAF, as formed in liquid HF[8] or by $H^+BF_4^-$ in mixtures of HF and BF_3, is relatively inert. On the other hand, MAF–$H^+AlCl_4^-$ adducts, which are probably present in the $CH_3COCl/AlCl_3$ acetylation of ferrocene, are not inert to further substitution.

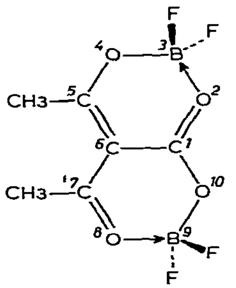
Our attempts to prepare triacetylferrocenes by the direct acetylation of either 1,1'- or 1,2-DAF have been unsuccessful. (No confirmation of Sweeney's claim[9] to have prepared tetraacetylferrocene has been found in the open literature.) Presumably the various DAF–Lewis acid complexes are all inert to further acetylation. The lack of reactivity of the unsubstituted ring in 1,2-DAF towards acetylation is particularly surprising. The implication is that this is due to interannular effects, although the possibility should be considered that triacetyl derivatives are formed but decompose before they can be isolated.

Although there are theoretical[4,10] as well as experimental[11] reasons for expecting that 1,2-DAF is formed rather than the 1,3 isomer, we considered the possibility that the 1,2 isomer is formed from MAF by a different mechanism, namely via the methylcarbon-acetylated intermediate. This compound, acetoacetylferrocene, is well known and has been described by several workers[12]. The reaction of acetoacetylferrocene with BF_3 was investigated and the BF_2 derivative of the enol form was isolated. This new compound (II) is remarkably inert towards hydrolysis and showed no tendency to rearrange to give 1,2-DAF.

It is noteworthy that acetoacetylferrocene is most conveniently formed by a base-catalysed condensation (Claisen) from MAF, whereas acetoacetylcymantrene cannot be made by the analogous reaction. On the other hand, Fischer and Plesske[13] have reported that the latter compound can be prepared by the acetylation of monoacetylcymantrene with acetic anhydride and BF_3: under these conditions MAF would undergo nuclear acetylation. This difference in reactivity between MAF and monoacetylcymantrene reflects not only the presence of an unsubstituted ring in MAF but also the reluctance of MAF to form an enol in the presence of Lewis acid catalysts, such as BF_3. For this reason we think it unlikely that an *O*-acetyl intermediate is responsible for the formation of 1,2-DAF. Moreover, such an intermediate could not be postulated in the formation of 1,2-dibenzoylruthenocene[14] from the monobenzoyl compound. Nevertheless we did try to prepare *O*-acetylated MAF, an enol acetate, by refluxing isopropenyl acetate and MAF in the presence of trifluoroacetic acid or *p*-toluenesulphonic acid (*cf.* ref. 15). We did not attempt to isolate the readily hydrolysable intermediate from the reaction mixture; however, treatment with BF_3 yielded only MAF.

The reaction between acetic anhydride and BF_3 was also re-investigated because the nature of the crystalline reaction product was not known; earlier workers have described it as $(CH_3CO)_2O \cdot nBF_3$, with $n=1$ or $n=2$(?)[17], or a $3BF_3$ adduct of diacetoacetic anhydride[18]. Our product was slowly precipitated from a solution of acetic anhydride in CH_2Cl_2 treated with an excess of BF_3. (The compound is not an acetylating agent towards ferrocene.) It could be recrystallised from trifluoroacetic acid and melted at 195–197° in reasonable agreement with the literature values, 190° or 192–193° [16] and 194° [18]. Thus, it seems that our product is the same as that obtained previously. Our analytical data, for C and H only, differ somewhat from those in the literature. The mass spectrum of the compound indicates a molecular weight of 240: from the relative intensities of the parent ion (P) and the P–1 and P–2 ions, it is clear that the compound contains 2 boron atoms. Proton and ^{19}F NMR spectra of the compound in liquid SO_2 each showed a single solute resonance. Hydrolysis of our product gave acetylacetone, carbon dioxide and fluoroborate anions: similar results were reported by Meerwein[18] for his compound.

Only structure (I), 3,3,9,9-tetrafluoro-5,7-dimethyl-2,4,8,10-tetraoxa-3,9-dibo-



I

rabicyclo[4.4.0]deca-1,5,7-triene, is fully consistent with these results and with the IR data. Thus (I) absorbs strongly at 1585, 1460, 1380 cm^{-1} and in the range 1200 to 1040

cm^{-1} and the spectrum resembles closely that of the (1,3-diketonato)boron difluorides[19]. The so-called BF_3 adducts [18] of the anhydrides of propionic and butyric acids clearly deserve to be reinvestigated: they cannot be derivatives of (I) and, indeed, it was reported that they decompose mainly into monoketones.

EXPERIMENTAL

Acetylation of ferrocene with acetic anhydride and BF_3

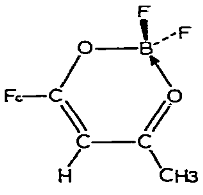
A stirred solution of ferrocene (0.1 mole) and redistilled acetic anhydride (0.2 mole) in dry, oxygen-free dichloromethane (150 ml) was saturated with boron trifluoride at 0°. The orange coloured solution rapidly turned purple. After stirring for $\frac{1}{2}$ h the excess boron trifluoride was expelled with nitrogen and saturated sodium acetate solution added. The aqueous layer was reduced with titanium(III) chloride and the dichloromethane layer was separated, washed with sodium bicarbonate and with water. The organic layer was dried briefly with calcium sulphate and then evaporated to dryness.

The crude reaction mixture was extracted with 40–60 petroleum until no more 1,2-DAF could be detected in the extracts. The residue was recrystallised from benzene to give pure 1,1'-DAF (m.p. 128°). The extracts were evaporated to dryness and chromatographed on alumina (Spence type H). Unreacted ferrocene (a trace only) was eluted with 40–60 petroleum and MAF was eluted with an equivolume mixture of diethyl ether and 40–60 petroleum. The crude MAF was recrystallised from 40–60 petroleum to give analytically pure material (m.p. 85–86°). Continued elution with a 3/1 ether/petroleum mixture caused an orange coloured band (1,2-DAF) to separate from the red 1,1'-DAF band. The bulk of the 1,2 isomer was eluted before the heteroannular isomer and was recrystallised (m.p. 94–95°) from 40–60 petroleum. The 1,1' isomer was eluted with acetone and recrystallised. The yields are shown in Table 1.

Preparation of the boron difluoride derivative of acetoacetylferrocene

Acetoacetylferrocene (0.34 g) was dissolved in dry dichloromethane (20 ml) at 0° and the solution was saturated with boron trifluoride. The colour of the solution changed from red to purple as soon as the boron trifluoride was added. The excess boron trifluoride was expelled with nitrogen and the reaction mixture was hydrolysed with water without affecting the colour of the organic phase. The dichloromethane layer was neutralised, washed and dried. Removal of the solvent left a maroon coloured solid, insoluble in petroleum, slightly soluble in ether. Recrystallisation from toluene gave ruby red plates (m.p. 184–185°) of (ferrocenoylacetonato)boron difluoride (II) 0.25 g (53% yield). (Found: C, 53.2; H, 4.3. $C_{14}H_{13}BF_2FeO_2$ calcd.: C, 52.9; H, 4.1%.)

The molecular weight 318 (calcd.: 317.9) was found from the mass spectrum



II

Fc= C5H4FeC5H5

which consisted of the following principal peaks: P, P–F, P–C_5H_5, C_5H_5FeF. The ^1H NMR spectrum in deuteriochloroform was consistent with the formulation (II); the vinyl proton resonated at τ 3.95 and the protons on the substituted cyclopentadienyl ring were at τ 4.97 and 5.10, to low field of those in parent enol (τ 5.24 and 5.52, respectively). The IR spectrum was similar to those of other (1,3-diketonato)boron difluorides[19].

The boron difluoride derivative is air-stable and is unaffected by dilute acids and even cold concentrated sodium hydroxide. In warm sodium acetate solution the β-diketone is regenerated in 70% yield.

Preparation of the bis(boron difluoride) derivative of α-acetylacetoacetic acid (I)

A solution of acetic anhydride (5 g) in dichloromethane (100 ml) was saturated with boron trifluoride at 0°. The white crystalline precipitate, which formed slowly, was filtered off under dry nitrogen, was washed with 40–60 petroleum and pumped *in vacuo*. The substance is slowly affected by moisture and was therefore transferred to an inert atmosphere box. Recrystallisation from trifluoroacetic acid gave white crystals of (I) melting at 195–197°. (Found: C, 29.8; H, 2.7. $C_6H_6B_2F_4O_4$ calcd.: C, 30.1; H, 2.5%.)

The compound is freely soluble in liquid sulphur dioxide. The ^1H NMR spectrum in this solvent showed a single resonance at τ 7.02 due to the methyl groups: the ^{19}F spectrum consisted of a singlet upfield from trifluoroacetic acid. The mass spectrum contained the following peaks: P($m/e=240$), P–CH_3, P–F, P–F–BF_2 and CH_3CO. The IR spectrum was very complex: the principal absorptions (in Nujol) are as follows: 1585 vs (br), 1460 vs, 1380 s, 1365 m, 1200 s, 1150 m, 1100 m, 1040 vs (br), 932 s, 850 s, 795 s, 740 m, 670 s, 605 s, 605 ms, 525 m, 499 m cm^{-1}.

Degradation of the complex occurred very slowly in water to give carbon dioxide, fluoroborate anions and acetylacetone, identified as the copper(II) complex. No reaction of (I) with ferrocene in dichloromethane at room temperature could be detected after several hours.

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