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THE ELECTROPHILIC ACETYLATION OF TRICARBONYL(CYCLOHEXA-1,3-DIENE)IRON

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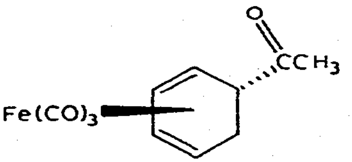
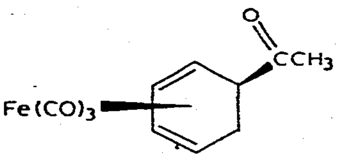
Summary

Friedel—Crafts acetylation of the title compound yielded as the major reaction product a 4/1 mixture of the 5-*exo*- and 5-*endo*-acetyl complexes. The major component of the mixture was shown to be the *exo* isomer by comparison with an authentic sample, synthesised stereospecifically.

In the course of other work we were interested in preparing tricarbonyl (5-acetylcyclohexa-1,3-diene)iron (II). Since conjugated dienes coordinated to the iron tricarbonyl moiety are known to undergo electrophilic substitution reactions [1—4], an obvious route to II would be Friedel—Crafts acetylation of tricarbonyl(cyclohexa-1,3-diene)iron (I). It has been shown by Lillya [3], however, that I is far less reactive towards acylation than the simple tricarbonyl(buta-1,3-diene)iron. More recently Gubin and co-workers found that acetylation of I could be achieved in refluxing dichloromethane [4]. They obtained reasonable yields of II together with the isomeric 1- and 2-acetyl substituted derivatives and the cyclohexadienyliron tricarbonyl cation V. The three isomeric acetyl derivatives were not separated, and represented a 28% yield in the ratio: 5-acetyl, 86% (II); 2-acetyl, 9%; 1-acetyl, 5%. We found, however, that higher yields of



(III)



(IV)

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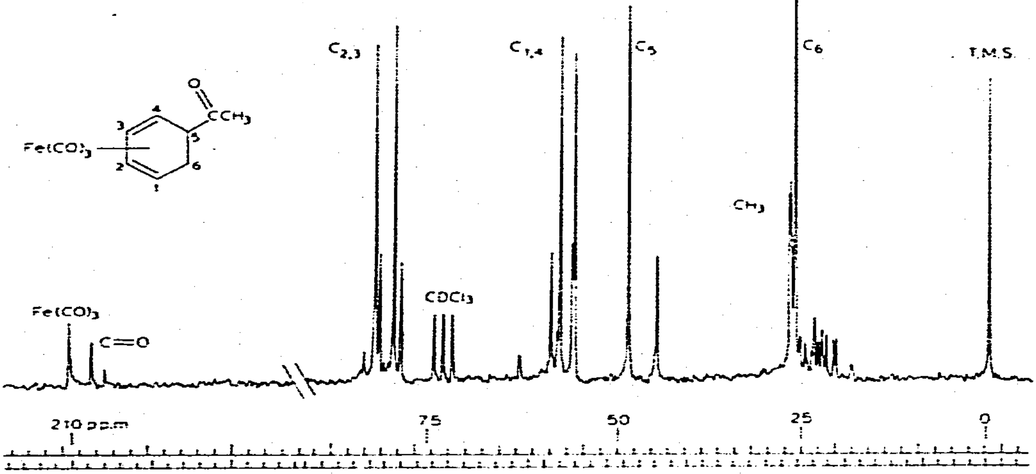
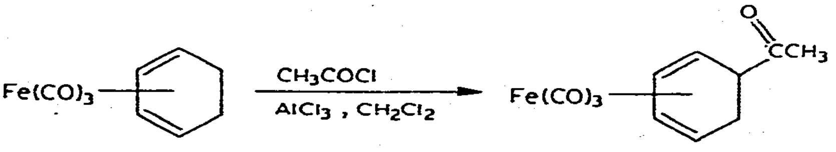


Fig. 1.

the ketones (ca. 40%) could be obtained by treating I with aluminium chloride/ acetyl chloride in dichloromethane at room temperature. V was also obtained to the extent of 10%.

Separation of the neutral components of the reaction mixture proved difficult. Silica TLC plates caused extensive decomposition, and the compounds "smeared" on Alumina plates. Column chromatography on neutral silica proved the best method for separation and by this means we isolated in reasonable yield (30—35%) a yellow oil which we assumed to be the desired 5-acetyl derivative II. Spectroscopic analysis, however, showed this material to be a mixture of two components, in the ratio 4/1. This is clearly illustrated by the ^{13}C NMR spectrum (Fig. 1) which shows pairs of lines for every carbon, except for the iron carbonyls, and the methyl group.

For 5-substituted complexes such as II, there are two possible isomers, namely the 5-*exo*,III and 5-*endo*,IV species, and we therefore needed to determine which was the major and which the minor in the reaction mixture. Separation

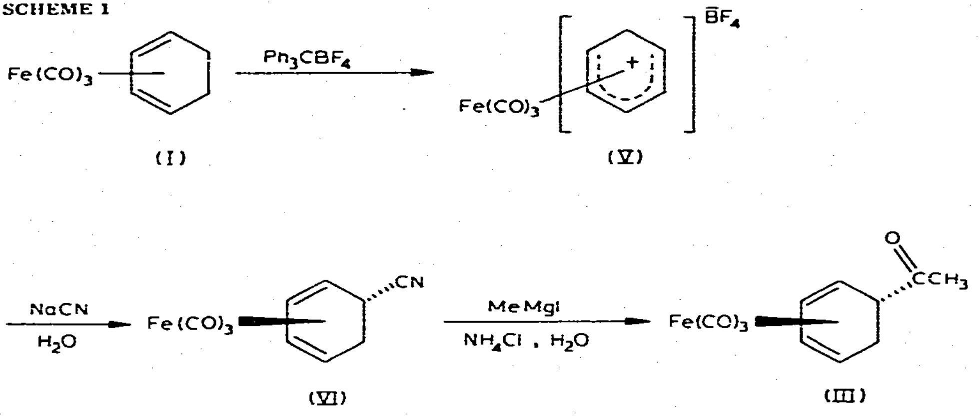


(I) (II)

of the two isomers was not possible, but we were able to show that the major isomer was the 5-*exo*-acetyl (III) by synthesising this molecule stereospecifically as outlined in Scheme 1.

This involves treating the cyclohexadienyl cation V (which is readily obtained from I) with aqueous sodium cyanide to give tricarbonyl(5-*exo*-cyanocyclo-

SCHEME 1



hexa-1,3-diene)iron (VI) [5]. (The stereochemistry of VI has always been assumed to be *exo* and we have recently confirmed this with a single crystal X-ray structure determination [6]. Treatment of V with methylmagnesium iodide followed by aqueous ammonium chloride gave III as the sole product. Since Grignards react with the cyanide group as outlined in Scheme 2 [7], in which the R—CN bond in not involved the acetyl product in this manner must have the same stereochemistry as VI.

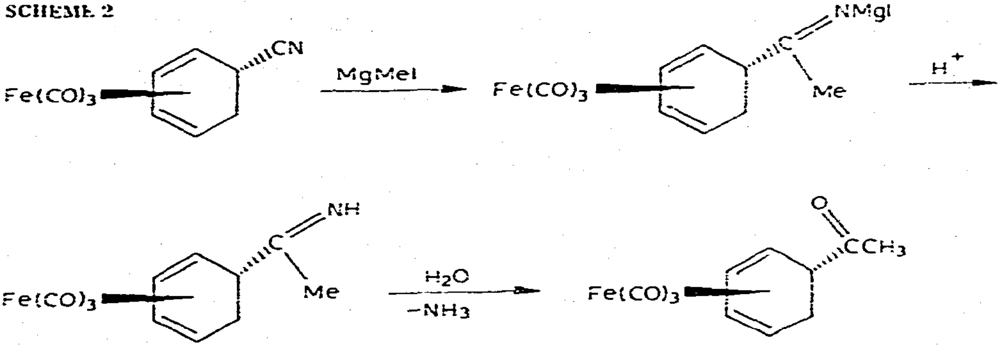
The spectroscopic data for the isomeric mixture obtained via Fridel—Crafts acetylation and those for compound III is presented in Table 1. These data clearly illustrate that the major component of the isomeric mixture is the 5-*exo*-acetyl derivative III.

TABLE 1

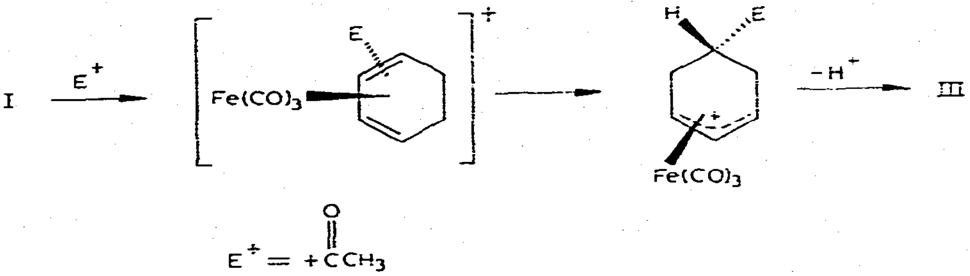
SPECTROSCOPIC DATA FOR THE ISOMERIC MIXTURE (A) OBTAINED VIA FRIEDEL—CRAFTS ACETYLATION OF I AND THESE FOR COMPOUND III

A	III
^{13}C NMR (δ, ppm)	
Major: C(1) 58.7; C(2) 84.1; C(3) 86.8; C(4) 60.7; C(5) 51.0; C(6) 27.5; C=O 207.9; CH_3 28.0; $Fe(CO)_3$ 211.1	C(1) 58.6; C(2) 84.1; C(3) 86.7; C(4) 60.6; C(5) 51.0; C(6) 27.5; C=O 208.0; CH_3 28.1; $Fe(CO)_3$ 211.0
Minor: C(1) 59.0; C(2) 83.1; C(3) 86.2; C(4) 62.0; C(5) 47.0; C(6) 28.2; C=O 206.0; CH_3 unresolved; $Fe(CO)_3$ 211.1.	
^{1}H NMR (δ, ppm)	
5.40 (2H, m, H(2,3)); 3.15 (3H, m, H(1,4,5)); 2.08, 2.12 (total 3H, 2 singlets, ratio 4(1); 1.93 (2H, m, CH(6,6′))	5.36 (2H, m, H(2,3)); 3.05 (3H, m, H(1,4,5)); 2.07 (3H, s, CH_3); 1.89 (2H, m, H(6,6′))
IR (cm^{-1})	
ν(C≡O) 2050(br), 1980(br); ν(C=O) 1718	ν(C≡O) 2048, 1795; ν(C=O) 1717
Mass spectrum	
M^+ 262	M^+ 262

SCHEME 2



SCHEME 3



It is probable that the reaction pathway for formation of the *exo* isomer of III is as depicted in Scheme 3, the acetyl chloride aluminium chloride complex attacking I on the opposite face to the iron tricarbonyl moiety. Formation of the *endo* complex IV may follow a similar pathway. However, for this case, involvement of the iron carbonyl group cannot be ruled out [1,8].

We have thus established that the electrophilic acetylation of I yields both the 5-*exo* and 5-*endo* isomers (III,IV), and have developed a more convenient preparative route for III [6].

Experimental

^{13}C nuclear magnetic resonance spectra were recorded on a Varian Associates XL 100 spectrometer operating in the Fourier Transfer mode at 25.2 MHz. All ^{13}C NMR spectra were ^{1}H decoupled. Chemical shifts are related to TMS. ^{1}H NMR spectra were recorded on a Varian Associates CFT 20 spectrometer operating in the Fourier Transform mode at 80 MHz, or on a Varian R24 60 MHz. Mass spectral data were recorded on an AEI MS 12 spectrometer, and infrared data on a Perkin—Elmer 257 spectrophotometer.

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* The preparative usefulness of this reaction has been further explored and will be reported in due course [9].

Tricarbonyl(cyclohexa-1,3-diene)iron (I), the cyclohexadienyl cation V and tricarbonyl(5-*exo*-cyanocyclohexa-1,3-diene)iron (VI) were prepared according to literature procedure [1]. Aluminium chloride was sublimed prior to use.

Friedel Crafts acetylation of I

I (5 g, 23 mmol) in dichloromethane (10 ml) was slowly added (ca. 10 min) to a well stirred solution of aluminium chloride (8 g, 60 mmol) and acetyl chloride (6 g, 76 mmol) in dichloromethane (20 ml) under nitrogen at room temperature. After a further 15 min, the reaction mixture was poured onto ice, the organic layer removed, and the aqueous layer extracted with ether. The combined extracts were washed with water, dried ($MgSO_4$), and evaporated to give a yellow oil (4.5 g). The cyclohexadienyl cation V as its hexafluorophosphate salt (1 g, 12%) was isolated from the aqueous layer by addition of excess ammonium hexafluorophosphate.

The neutral material showed several spots (TLC silica petroleum ether/ether 4/1) two of which appeared to be in greater yield R_f 0.9, 0.5. This mixture on subjection to column chromatography (Kieselgel 60, 70—230 mesh) gave; elution with 40/60 petroleum ether recovered starting material I (1.5 g, R_f 0.9) elution with 40/60 petroleum ether/ether 5/1 gave a yellow oil (1.7 g, R_f 0.6) which was shown to be a mixture of III and IV in the ratio 4/1. Spectroscopic data are given in the text. Elution with greater relative amounts of ether yielded a mixture of compounds in low yield which were not characterised further.

Reaction of VI with methylmagnesium iodide

Methyl iodide (1.45 g, 10.2 mmol) in ether (10 ml) was added to magnesium turnings (0.25 g, 0.01 g-atom) under nitrogen. Reaction proceeded smoothly, and to the resultant solution was added VI (0.5 g, 2.0 mmol) in ether (20 ml). Reaction was complete within 5 min (TLC) and treatment of the reaction solution with aqueous ammonium chloride followed by work-up with ether gave tricarbonyl(5-*exo*-acetylcyclohexa-1,3-diene)iron (III, 0.4 g, 1.5 mmol, 75%). The spectroscopic data for this material are given in the text.

References

1 E.D. Greaves, C.R. Knox and P.L. Pauson, J. Chem. Soc. Chem. Commun., (1969) 1124.
2 A.N. Nesmeyanov, K.N. Anismov and G.K. Magom, Izv. Akad. Nauk SSSR, Ser. Khim., (1970) 715, 959.
3 R.E. Graf and C.P. Lillya, J. Amer. Chem. Soc., 94 (1972) 8282.
4 N.S. Nametkin, A.I. Nekhaev, U.D. Tyarin and S.P. Gubin, Izv. Akad. SSSR, Ser Khim., (1975), 676.
5 A.J. Birch, P.E. Cross, J. Lewis, D.A. White and S.B. Wild, J. Chem. Soc. A, (1968) 332.
6 B.F.G. Johnson, J. Lewis, D.G. Parker and P.R. Raithby, to be published.
7 R.O.C. Norman, Principles of Organic Synthesis, Methuen, London, 1970, p. 210.
8 E.O. Greaves, G.R. Knox, P.L. Pauson, S. Tima, G.A. Sim and D.I. Woodhouse, J. Chem. Soc. Chem. Commun., (1974) 257.