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BRIDGED FERROCENES

XIII *. FRIEDEL—CRAFTS REACTIONS OF FERROCENE AND ALKYLFERROCENES WITH α,β-UNSATURATED ACID CHLORIDES

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Summary

The reactions of ferrocene, butylferrocenes, and [3] ferrocenophane with α,β-unsaturated acid chlorides give mixtures of ketonic products resulting from introduction of either a propanoyl or a propenoyl substituent or a homo- or a hetero-annular three-carbon bridge.

Introduction

In Part XII [1], we reported that [3] ferrocenophan-1-one (Ia) can be prepared from ferrocene in one step by treatment with acryloyl chloride (IIa) under low-temperature Friedel—Crafts conditions (—78°C) **. At higher reaction temperatures, propanoylferrocene (Va) and ferricenium cation are also formed and a mechanism was suggested to account for the course of the reaction. Since this reaction, in principle, affords a convenient method of introduction of a three-carbon bridging group into the ferrocene system, we have explored the scope and synthetic potential of the procedure. In particular, we have investigated similar reactions of ferrocene with substituted acryloyl chlorides and of alkylferrocenes, ruthenocene, and cymantrene with acryloyl chloride.

Results and discussion

A series of Friedel—Crafts reactions of ferrocene with substituted acryloyl chlorides (IIb—IIf) was carried out using conditions previously found successful

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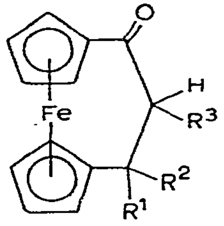
* For Part XII, see ref. 1.

** This annelation reaction was first discovered by Eisenstadt and Cais and reported at a Conference in 1967. The Abstracts [2] however, provide no experimental details or mechanistic comment.

for the preparation of Ia. It was found that the presence of a substituent on the β-vinyl carbon of the acid chloride prevented formation of a cyclised product. Thus, reactions with but-2-enoyl chloride (IIb) and with 3-methylbut-2-enoyl chloride (IIc) gave only the corresponding α,β-unsaturated ketones (IIIb,c) and the products of addition of HCl to these compounds (IVb,c). With cinnamoyl chloride (IId), the ketone (IIId) was the sole product. No trace of the bridged (Ib—Id) or unbridged (Vb—Vd) acylferrocenes was found in the products of these reactions in agreement with the findings of previous studies [3].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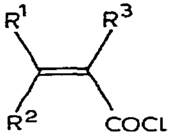
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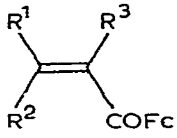
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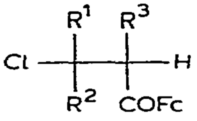
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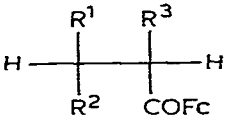
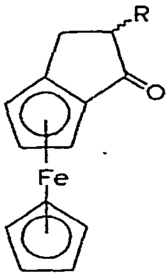

V

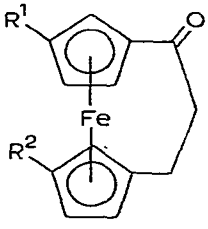
a : $R^1 = R^2 = R^3 = H$
b : $R^1 = Me$, $R^2 = R^3 = H$
c : $R^1 = R^2 = Me$, $R^3 = H$
d : $R^1 = Ph$, $R^2 = R^3 = H$
e : $R^1 = R^2 = H$, $R^3 = Me$
f : $R^1 = R^2 = H$, $R^3 = CH_2COCl$


VI

a : $R = CH_2CO_2Me$
b : $R = CH_2CO_2Et$
c : $R = CH_2COFc$
d : $R = CH_2COCl$
e : $R = CH_2CO_2H$

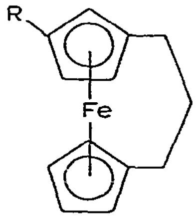
Annelation of ferrocene does occur, however, using α-substituted acryloyl chlorides and we previously reported [1] that the low-temperature reaction with 2-methylpropenoyl chloride (IIe) gives the ferrocenophanone (Ie) together with smaller amounts of 2-methylpropanoylferrocene (Ve) and ferricenium cation. A mixture of acidic and neutral products was obtained from a similar reaction of ferrocene with itaconoyl chloride (IIf). The acidic material was isolated, esterified with diazomethane, and the resulting mixture was separated by TLC. The spectroscopic properties (vide infra) of the main product thereby obtained were in accord with the keto-ester VIa. Several minor products were formed in insufficient amounts to permit characterisation. Separation of the neutral products by TLC gave three bands, one of which afforded the keto-ester VIa, identical with the product obtained previously. The other bands contained the ethyl ester VIb and the diketone VIc. The esters VIa and VIb, which could be interconverted by treatment with acidified ethanol and methanol respectively, must arise in the original reaction from the presence of alcohol stabilisers in the methylene chloride solvent since they were not formed when purified solvent was used.

These results suggest that the acid chloride VId is the initial product of the Friedel—Crafts reaction of ferrocene with itaconoyl chloride. In the presence of aluminium chloride, this product may then acylate ferrocene present (giving VIc), react with alcohols in the solvent (giving VIa and VIb), or undergo hydrolysis during work-up (giving VIe). The IR spectra of each of the products (VIa,b,c) contained strong bands characteristic [4] of an unsubstituted cyclopentadienyl ring. The ^{1}H NMR spectra of the esters VIa, b contained two cyclopentadienyl singlet resonances * of unequal intensities, suggesting that each consisted of an inseparable mixture of *exo*- and *endo*-epimers, and were clearly incompatible with a heteroannularly bridged structure (I; $R^1 = R^2 = H$, $R^3 = CH_2CO_2Me$ or CH_2CO_2Et).



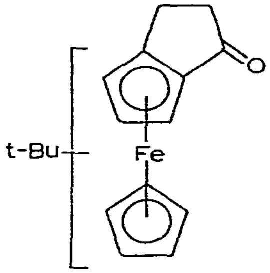
VII

a: R^1 = t-Bu, R^2 = H
b: R^1 = H, R^2 = t-Bu
c: R^1 = R^2 = t-Bu

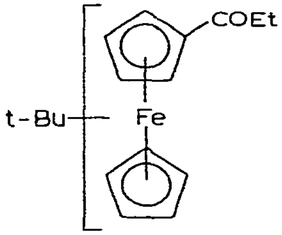


VIII

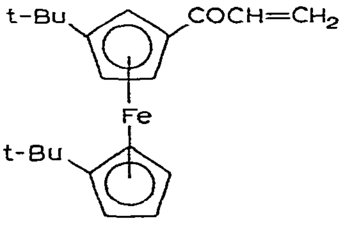
a: R = t-Bu
b: R = CMe_2OH



IX



X



XI

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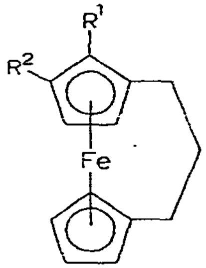
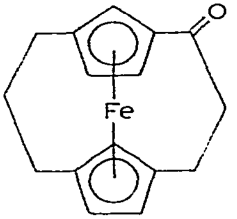
* These cyclopentadienyl singlets were further separated in the presence of added $Eu(fod)_3$ shift-reagent which also produced a resolution of the individual CO_2Me singlets of the VIa epimers.

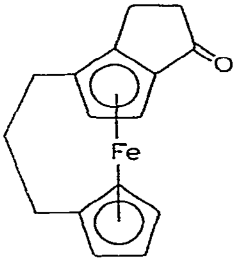
Mixtures of bridged and unbridged ketones were isolated from reactions of t-butyl- and 1,1′-di-t-butyl-ferrocene with acryloyl chloride (IIa). Alumina chromatography of the product from the former reaction gave three bands each of which gave a mixture of products (^{1}H NMR). The main band contained an approximately equimolar mixture of the heteroannularly bridged ketones VIIa and VIIb. Mixed-hydride reduction of this ketone mixture gave as expected a single product for which the structure VIIIa was confirmed by independent synthesis from the known alcohol VIIIb [5] by treatment with methylmagnesium iodide in refluxing toluene [cf. 6]. Mixtures of the homoannularly bridged ketones (IX; at least three isomers) and the unbridged ketones (X; mainly the 1,3- and 1,1′-isomers) were isolated from the other two chromatographic bands. The reaction of 1,1′-di-t-butylferrocene with acryloyl chloride gave mainly the unsaturated ketone XI and the ferrocenophanone VIIc. At least twelve other products were detected by TLC examination of the reaction mixture but these were formed in insufficient quantities for further investigation.



XII

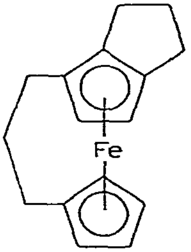


XIII



XIV

a : $R^1 = R^2 = H$
b : $R^1 = COEt$, $R^2 = H$
c : $R^1 = H$, $R^2 = COEt$
d : $R^1 = H$, $R^2 = COCH{=}CH_2$
e : $R^1 = H$, $R^2 = COCH_2CH_2Cl$
f : $R^1 = COCH_2CH_2Cl$, $R^2 = H$



XV

In an attempt to prepare doubly-bridged ferrocenes, the reaction of [3]-ferrocenophane (XIIa) with acryloyl chloride was carried out. The complex product mixture was separated by repeated TLC giving the propanoyl derivatives XIIb,c the unsaturated ketone XIId, and the ferrocenophanones XIII and XIV. These bridged ketones have been synthesised previously by Rinehart [7] and Tirouflet [8] by multi-step sequences. Mixed-hydride reduction of the homoannular ketone XIV, whose identity was confirmed by comparison with an authentic sample [8], gave the new [3][3]ferrocenophane (XV). The properties of the hetero-annular ketone XIII exactly matched those previously reported for this compound [7] and the structures of the other products (XIIb,c,d) were established by independent synthesis from [3]ferrocenophane (XIIa) (see Experimental).

Finally, we note that ruthenocene and cymantrene fail to undergo annelation on treatment with acryloyl chloride under conditions which successfully convert ferrocene to the bridged ketone Ia. In these reactions, the sole products obtained were the corresponding acryloyl derivatives which proved unstable and polymerised on standing.

Experimental

For general remarks, see Part XII [1]. Preparative TLC was carried out using plates coated with Merck Kieselgel G type 60. Aluminium chloride was sublimed before use. Light petroleum refers to the fraction of b.p. 40—60°C. ^1H NMR spectra were recorded for $CDCl_3$ solutions and IR spectra for films (liquids) or KBr pellets (solids). Yields of product are based on unrecovered starting material.

Reactions of ferrocene with acid chlorides (IIb,c,d)

Equimolar proportions of ferrocene, acid chloride, and $AlCi_3$ were allowed to react in CH_2Cl_2 solution at —78°C for 6 h. The reactions were worked up as described previously [1] and the products were separated by TLC. From IIb, there was obtained the ketone IIIb (88%), m.p. 108—109°C (lit. [3a] 110°C) and the ketone IVb (6%), m.p. 85—87°C (lit. [3a] 88°C). From IIc, there was obtained the ketone IIIc (82%), m.p. 102—104°C (lit. [3b] 103—104.5°C) and the ketone IVc (5%), an unstable orange solid which readily eliminated HCl to give IIIc. From IId, there was obtained the ketone IIId (79%), m.p. 139—140°C (lit. [3c] 139.5—139.7°C).

Reaction of ferrocene with itaconoyl chloride (IIf)

A solution of freshly distilled itaconoyl chloride [9] (16.6 g; 0.1 mol) in CH_2Cl_2 (50 ml) was added over 0.5 h to a stirred solution of ferrocene (18.6 g; 0.1 mol) in CH_2Cl_2 (150 ml) containing $AlCl_3$ (20 g; 0.15 mol) at —78°C. The mixture was stirred for two days at —78°C and then poured into ice-water. The organic layer was separated, washed thoroughly with dilute NaOH aq. to remove acidic material, dried ($MgSO_4$), and evaporated. The residue was separated by column chromatography (Al_2O_3) and TLC giving the following products (in order of increasing polarity): unchanged ferrocene (8.2 g; 44% recovery): the ester VIb (epimeric mixture) (0.52 g; 3%), an orange oil; τ 5.1—5.3 (1H) and 5.4—5.65 (2H) (2m, C_5H_3), 5.83 and 5.92 (5H, 2s, C_5H_5), 5.80 (2H, q, OCH_2), 6.8—7.7 (5H, m, CH_2CHCH_2), and 8.72 (3H, t, Me): ν_{max} 1730 and 1670 (CO) and 1105 and 1005 cm^{-1} (C_5H_5): the ester VIa (epimeric mixture) (0.51 g; 3%), an orange oil; τ 5.0—5.2 (1H), 5.3—5.6 (2H) (2m, C_5H_3), 5.77 and 5.85 (5H, 2s, C_5H_5), 6.30 (3H, s, OMe), and 6.8—7.7 (5H, m, CH_2CHCH_2); ν_{max} 1730 and 1665 (CO) and 1106 and 1000 cm^{-1} (C_5H_5); (Found: C, 61.4; H, 5.4. $C_{16}H_{16}FeO_3$ calcd.: C, 61.6; H, 5.2%): the diketone VIc (0.21 g; 2%), an orange solid, m.p. 164—165°C; τ 5.05—5.2 (3H) and 5.3—5.5 (4H) (2m, C_5H_3 + C_5H_4), 5.72 and 5.74 (10H, 2s, C_5H_5) and 7.1—7.5 (5H, m, CH_2CHCH_2); ν_{max} 1668 and 1645 (CO) and 1105 and 1000 cm^{-1} (C_5H_5); (Found: C; 64.6; H, 4.9. $C_{25}H_{22}Fe_2O_2$ calcd.: C, 64.4; H, 4.8%).

The aforementioned NaOH extract was acidified with HCl aq. and extracted with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated and the residual acidic material (containing VIe) was dissolved in ether and esterified with CH_2N_2. TLC separation of the resulting mixture gave the ester VIa (2.26 g; 16%), identical with the product described above. Other products present in much smaller amounts were not characterised.

The ester VIa was converted to the ester VIb in refluxing EtOH containing a few drops of conc. H_2SO_4 and the reverse reaction occurred on treatment of VIb with acidified MeOH. These esters were not formed in the original reaction when purified CH_2Cl_2 (alcohol-free) solvent was used.

Reaction of t-butylferrocene with acryloyl chloride

A solution of freshly distilled acryloyl chloride [1] (0.91 g; 0.01 mol) in CH_2Cl_2 (20 ml) was added dropwise to a stirred suspension of finely ground $AlCl_3$ (1.34 g; 0.01 mol) in CH_2Cl_2 (100 ml) containing t-butylferrocene [6] (2.42 g; 0.01 mol) at −78°C. The mixture was stirred overnight at this temperature and then poured directly into water (100 ml). Sufficient $TiCl_3$ aq. was added to reduce ferricenium ions present, and the organic layer was separated and combined with several CH_2Cl_2 extracts of the aqueous layer. The total extract was washed (H_2O), dried ($MgSO_4$), evaporated to low bulk and chromatographed on Al_2O_3. Light petroleum eluted unchanged t-butylferrocene (1.9 g; 80% recovery). Light petroleum/ether (3/1) eluted three clearly separated bands. The first afforded a mixture of the homoannular ketones IX (90 mg; 12%), a viscous oil which could not be separated further either by column or TLC; τ 5.2—5.4 (m), 5.45—5.65 (m), 5.92br (s), 5.95—6.1 (m) (7H, ferrocenyl), 7.1—7.3 (4H, m, CH_2CH_2), and 8.77, 8.82 and 8.84 (9H, 3s, t-Bu); (Found: C, 69.3; H, 6.8. $C_{17}H_{20}FeO$ calcd.: C, 68.9; H, 6.8%). The second band contained a mixture of the ketones X (120 mg; 16%), a viscous oil which was not further examined; τ 5.1—5.3 (m), 5.4—5.6 (m), 5.80 (s), and 5.8—6.0 (m) (8H, ferrocenyl), 7.25br (2H, q, $COCH_2$) and 8.65—8.95 (12H, m, Me + t-Bu). The third band afforded a mixture of the heteroannular ketones VIIa + VIIb (340 mg; 61%), an orange solid, m.p. 64—66°C; τ 5.1—6.15 (7H, m, ferrocenyl), 7.0—7.2 (4H, m, CH_2CH_2), and 8.82 and 8.87 (9H, 2s, t-Bu); (Found: C, 69.2; H, 6.8. $C_{17}H_{20}FeO$ calcd.: C, 68.9; H, 6.8%).

6-t-Butyl[3]ferrocenophane (VIIIa)

(a). A solution of VIIa,b (from previous experiment) (170 mg; 0.6 mmol) in ether (5 ml) was added to a stirred suspension of $LiAlH_4$ (70 mg) and finely ground $AlCl_3$ (290 mg) in ether (50 ml). The mixture was stirred for 2 h, then MeOH was added to discharge unreacted hydride, and the mixture was poured into water. The residue gave a single band on TLC which afforded the product VIIIa (160 mg; 90%), a yellow oil; τ 6.00br and 6.08br (7H, 2s, ferrocenyl), 8.07 (6H, s, methylene), and 8.83 (9H, s, t-Bu); (Found: C, 72.2; H, 7.8. $C_{17}H_{22}Fe$ calcd.: C, 72.4; H, 7.9%).

(b). Treatment of the alcohol VIIIb [5] with a sixfold excess of methylmagnesium iodide in refluxing toluene [6] gave an almost quantitative yield of the compound VIIIa, identical in all respects with that described above.

Reaction of 1,1'-di-t-butylferrocene with acryloyl chloride

The reaction between 1,1'-di-t-butylferrocene [10] (2.82 g; 9.5 mmol), acryloyl chloride (3.20 g; 35 mmol), and $AlCl_3$ (4.40 g; 30 mmol) in CH_2Cl_2 (150 ml) at 0°C was carried out as described above for the acylation of t-butylferrocene. The product was separated by column chromatography and TLC, affording the following compounds (in order of increasing polarity): unchanged dibutylferrocene (1.71 g; 60% recovery): the unsaturated ketone XI (260 mg; 20%), a red oil; τ 3.0—4.5 (3H, *ABX* pattern, vinyl), 5.1—6.2 (7H, m, ferrocenyl), and 8.76 and 8.83 (18H, 2s, t-Bu); (Found: C, 71.5; H, 8.15. $C_{21}H_{28}FeO$ calcd.: C, 71.6; H, 8.0%): the heteroannular ketone VIIc (184 mg; 14%), an orange solid, m.p. 104—105°C; τ 5.05—5.15 (1H), 5.3—5.45 (2H), 5.55—5.65 (1H), 5.7—5.8 (1H), and 6.05—6.15 (1H) (5m; ferrocenyl), 6.3—7.8 (4H, m, methylene), and 8.77 and 8.86 (18H, 2s, t-Bu); (Found: C, 71.55; H, 8.1. $C_{21}H_{28}FeO$ calcd.: C, 71.6; H, 8.0%). At least twelve other minor bands were observed by TLC.

Reaction of [3] ferrocenophane with acryloyl chloride

The reaction between [3] ferrocenophane [11] (1.8 g; 8 mmol), acryloyl chloride (2.0 g; 22 mmol), and $AlCl_3$ (2.25 g; 17 mmol) in CH_2Cl_2 (150 ml) at 0°C was carried out as in preceding experiments. Separation of the products by column chromatography and TLC gave the following compounds (in order of increasing polarity): unchanged ferrocenophane (0.93 g; 52% recovery): the ketone XIIb (110 mg; 10%), an orange oil; τ 5.38 (1H, t), 5.70 (2H, d), and 5.7—6.4 (4H, 4m) (ferrocenyl), 7.1—7.6 (2H, m, $COCH_2$), 7.8—8.2 (6H, m, bridge), and 8.90 (3H, t, Me); (Found: C, 68.3; H, 6.5. $C_{16}H_{18}FeO$ calcd.: C, 68.1; H, 6.4%): the ketone XIId (11 mg; 1%), an orange oil; τ 3.0—4.5 (3H, *ABX* pattern, vinyl), 5.3—6.3 (7H, m, ferrocenyl), and 7.8—8.2 (6H, m, bridge); (Found: C, 68.4; H, 5.9. $C_{16}H_{16}FeO$ calcd.: C, 68.6; H, 5.7%): the ketone XIIc (142 mg; 13%), an orange oil; τ 5.36 (2H, d), 5.6—5.9 (3H, m), and 6.0—6.15 (2H, m) (ferrocenyl), 6.35 (2H, q, $COCH_2$), 8.03 (6H, s, bridge), and 8.84 (3H, t, Me); (Found: C, 68.4; H, 6.4. $C_{16}H_{18}FeO$ calcd.: C, 68.1; H, 6.4%): the heteroannular ketone XIII (130 mg; 12%), an orange-yellow solid, m.p. 106—108°C (lit. [7] 107—110°C); τ 5.1—6.4 (6H, m, ferrocenyl), 6.4—7.3 (4H, m, $COCH_2CH_2$), and 7.5—8.3 (6H, m, $CH_2CH_2CH_2$); (Found: C, 68.7; H, 5.9. $C_{16}H_{16}FeO$ calcd.: C, 68.6; H, 5.7%): the homoannular ketone XIV (32 mg; 3%), an orange solid, m.p. 133—135°C (lit. [7] 132—133°C; [8] 136°C); τ 5.37 and 5.55 (2H, 2d, C_5H_2), 5.5—6.5 (4H, 4m, C_5H_4), 7.05—7.3 (4H, m, $COCH_2CH_2$), and 7.7—8.1 (6H, m, $CH_2CH_2CH_2$); this compound was identical in all respects with an authentic sample [8].

Propanoylation of [3] ferrocenophane

The reaction of equimolar amounts of [3] ferrocenophane, propanoyl chloride, and $AlCl_3$ in CH_2Cl_2 under standard Friedel—Crafts conditions gave the isomeric ketones XIIb and XIIc, identical with the compounds described in the preceding experiment.

Preparation of ketone XIId

The reaction between equimolar amounts of [3] ferrocenophane, 3-chloropropanoyl chloride and $AlCl_3$ in CH_2Cl_2 gave a mixture of the ketones XIIe and XIIf which were not characterised. Chromatography of XIIe on Al_2O_3 caused dehydrochlorination giving the ketone XIId, identical with the compound described in a previous experiment.

Preparation of ferrocenophane (XV)

Reduction of the ketone XIV with $LiAlH_4/AlCl_3$ in ether as described in a previous experiment gave a quantitative yield of compound XV, a yellow solid, m.p. 76—77°C; τ 5.95—6.0 (1H), 6.0—6.25 (4H), and 6.45—6.6 (1H) (3m, ferrocenyl), and 7.73 and 8.05 (12H, 2s, methylene); (Found: C, 72.5; H, 7.2. $C_{16}H_{18}Fe$ calcd.: C, 72.2; H, 6.8%).

Reactions of ruthenocene and cymantrene with acryloyl chloride

Treatment of ruthenocene or cymantrene in CH_2Cl_2 at —78°C with equimolar quantities of acryloyl chloride and $AlCl_3$ as described previously for ferrocene [1] gave only the corresponding acryloyl derivatives which were unstable, particularly the cymantrene product, and polymerised on standing. These compounds were not characterised.

Acknowledgements

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