Journal of Organometallic Chemistry, 86 (1975) 109—118

THE FORMATION OF ETHYNYLFERROCENES IN REACTIONS OF STERICALLY CROWDED ACETYLFERROCENES WITH A GRIGNARD REAGENT

T.S. ABRAM and W.E. WATTS

School of Physical Sciences, New University of Ulster, Coleraine (Northern Ireland)

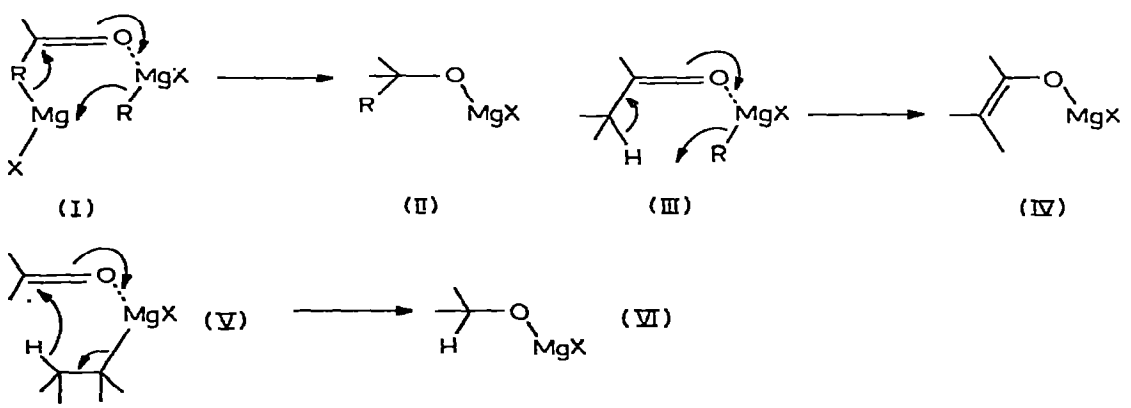
(Received August 21st, 1974)

Summary

Acetylferrocenes bearing a bulky 2-alkyl substituent react with isopropylmagnesium bromide to give enolate salts which are converted into ethynylferrocenes by a thermally induced elimination reaction.

Introduction

It is well known that a variety of products may be formed in reactions of ketones with Grignard reagents [1]. Ketones in which the carbonyl function is sterically encumbered, for example, have been found [2] to react with alkylmagnesium halides to give not only the conventional products (II) of 1,2-addition but also enolate salts (IV) and products (VI) of hydride reduction. Furthermore, as steric crowding at the reaction locus becomes more pronounced, the relative proportion of 1,2-addition product decreases with corresponding increase in the proportions of products of enolisation and/or hydride reduction [1, 2].

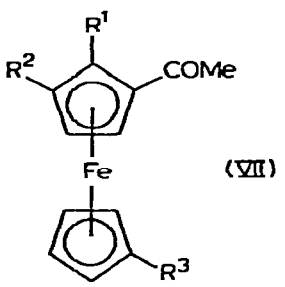


In reactions of this type in which transfer of an alkyl group from magnesium to carbonyl carbon in the Grignard—ketone complex I is sterically disfavoured, formation of enolates can be envisaged to occur via a six-centre transition state III with liberation of an alkane molecule [3]. From deuterium-labelling experiments [4] and other studies [2, 5], it has also been established that the products of hydride reduction arise by transfer of a β-hydrogen atom from the alkyl group of the Grignard reagent, again via a cyclic transition state V, with liberation of an alkene molecule.

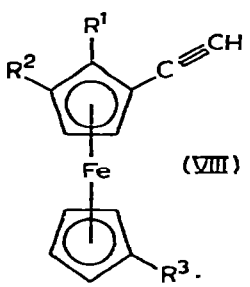
In this paper, we describe unusual transformations of sterically crowded acetylferrocenes which, on treatment with isopropylmagnesium bromide, undergo dehydration to give the corresponding ethynylferrocenes.

Results and discussion

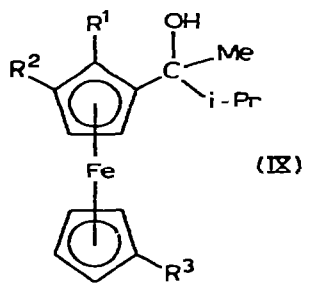
In connection with other research [6], we wished to prepare the alcohol IXa and the reaction between 2-acetyl-t-butylferrocene [7] (VIIa) and isopropylmagnesium bromide was chosen as an obvious method. When the ketone was added to a solution of a large excess of the Grignard reagent in benzene/ether at 70°, the red colour characteristic of acylferrocenes was discharged after ca. 15 min. However, hydrolysis of the reaction mixture gave back mainly starting ketone with only very small amounts of the desired alcohol (ca. 3% yield). When the reaction was allowed to proceed for ca. 60 h at 70°, the alkyne VIIIa was surprisingly isolated as the major product (ca. 68% yield). In later experiments using refluxing benzene as solvent, small amounts of the alcohol Xa resulting from hydride reduction were also obtained.



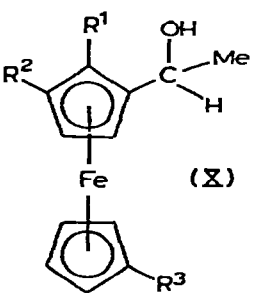
(VII)



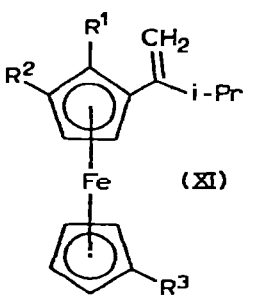
(VIII)



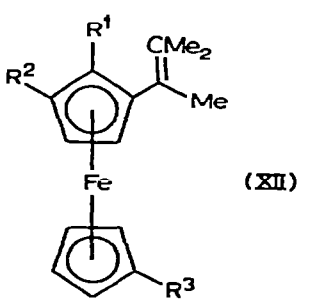
(IX)



(X)

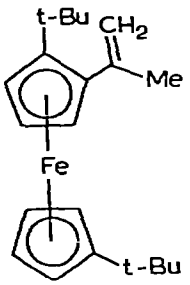


(XI)



(XII)

(a), R^1 = t-Bu; R^2 = R^3 = H
(b), R^1 = R^3 = t-Bu; = R^2 = H
(c), R^1 = H; R^2 = R^3 = t-Bu
(d), R^1 = R^3 = i-Pr; R^2 = H



(XIII)

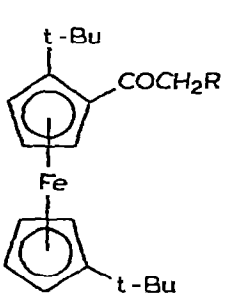
The structure of the alkyne VIIIa was indicated by elemental analysis, infrared (ν_{max} 2110 cm^{-1}; C≡C stretch) and ^1H NMR (τ 7.26, 1H singlet; C≡CH) spectroscopy [8], and was confirmed by chemical means. The compound underwent smooth catalytic hydrogenation, with uptake of two moles H_2 per mole, to give 2-ethyl-t-butylferrocene while treatment with trifluoroacetic acid followed by hydrolysis regenerated [9] the ketone VIIa.

Similar results were found for the reaction of 2-acetyl-1,1′-di-t-butylferrocene [10] (VIIb) with isopropylmagnesium bromide in benzene/ether at 70°. After a reaction time of 120 h, the alkyne VIIIb was obtained as the main product (ca. 82% yield). Small amounts of the 1,2-addition alcohol IXb and related alkene* XIb were also isolated.

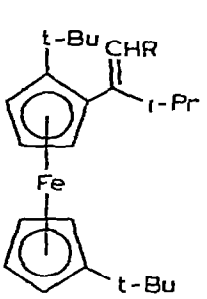
The dehydration of a methyl ketone to an alkyne on treatment with a Grignard reagent is unprecedented. The success of the transformations VIIa → VIIIa and VIIb → VIIIb can be attributed to a unique combination of steric and electronic factors which operate in this case. Steric shielding of the carbonyl group in the precursors is clearly important. The 3-acetyl compound [10] VIIc, in which such constraint is absent, reacts normally with isopropylmagnesium bromide by 1,2-addition to give after hydrolysis a mixture consisting solely of the alcohol IXc and related alkenes* XIc and XIIc. The steric bulk of the alkyl group in the Grignard reagent is also important. The ketone VIIb was found to undergo normal 1,2-addition of methylmagnesium iodide, giving the alkene XIII, and no trace of the alkyne VIIIb was found in the product mixture from this reaction. The importance of steric factors is further illustrated by the reaction of 2-acetyl-1,1′-diisopropylferrocene [11] (VIId) with isopropylmagnesium bromide. Although the alkyne VIIId was isolated (ca. 16% yield) from this reaction, the products IXd, XId and XIId resulting from 1,2-addition predominated (ca. 44% yield in total) [cf. corresponding reaction of the ketone VIIb described previously].

Unsuccessful attempts to extend the scope of this alkyne synthesis to disubstituted ethynes were also carried out. The 2-phenylacetyl and 2-propanoyl derivatives, XIVa and XIVb respectively, of 1,1′-di-t-butylferrocene were prepared in the usual way by Friedel—Crafts acylation reactions. Treat-

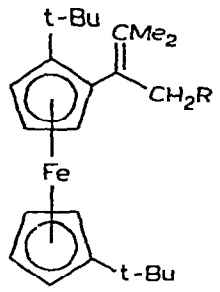
* The isolation of alkenylferrocenes from addition reactions of acylferrocenes with Grignard reagents has previously been noted [15].



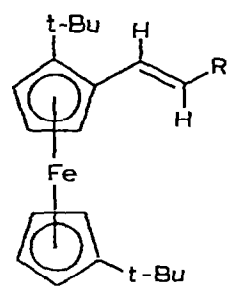
(XIV)



(XV)



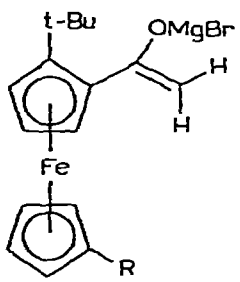
(XVI)



(XVII)

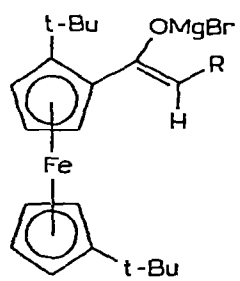
(a), R = Ph
(b), R = Me

ment of the former with isopropylmagnesium bromide in benzene/ether at 70° led to the disappearance of the ketone (colour change). However, even after prolonged reaction periods, hydrolysis of the mixture gave back mainly starting ketone. Relatively minor amounts of the alkene XVIIa resulting from hydride reduction, whose identity was confirmed by independent synthesis (see Experimental), and traces of the alkenes XVa and XVIa resulting from 1,2-addition were the only products detected. Similar results were obtained with the ketone XIVb. Although this compound reacted smoothly with the Grignard reagent (colour change), hydrolysis of the reaction mixture gave mainly starting material and only low yields of the alkenes XVb, XVIb, and XVIIb, even when a reaction temperature of 95° (toluene/benzene solvent) was employed.



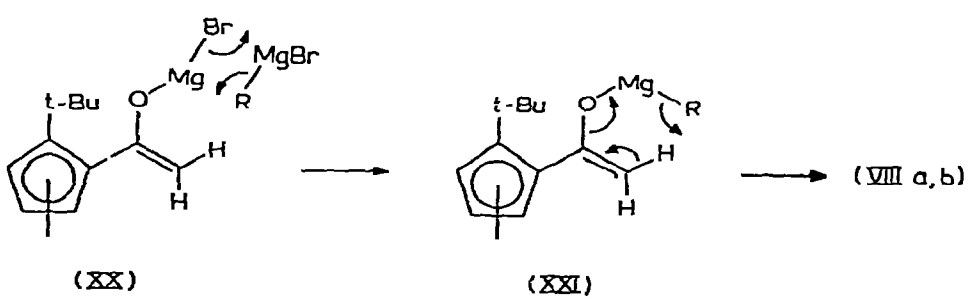
(XVIII)

(a), R = H
(b), R = t-Bu



(XIX)

(a), R = Ph
(b), R = Me



(XX) (XXI)

These results can be rationalised as follows. In the situation where steric compression in the transition state (cf. I) for 1,2-addition of the Grignard reagent to the carbonyl group of the ketones VIIa, b and XIVa, b is brought about by the presence of the proximate tert-butyl group, enolisation then becomes the predominant reaction pathway (cf. III → IV). Hydride reduction (cf. V → VI) occurs only to a very minor extent. We have noted that elimination from the enolates XVIIIa, b to generate the corresponding alkynes* VIIIa, b proceeds sluggishly, even at 70°, while the substituted enolates XIXa, b fail to undergo this process. It seems probable that the latter enolates would be generated from the ketone precursors XIVa, b with the stereochemistry shown XIX in which the R group is located *trans* to the bulky butylferrocenyl group.

The apparent inability of the enolates XIX to form alkynes, even under forcing conditions, suggests that alkyne formation occurs by stereospecific elimination of a vinyl hydrogen atom *cis* to the (OMgBr) group in the enolate precursor. The stereochemistry suggested for the enolates XIX would preclude such a process. In the case of those enolates XVIII in which *cis*-elimination is possible, this reaction may occur by concerted four-centre elimination of Mg(OH)Br or, more probably, by a six-centre cyclic process as indicated involving the alkylmagnesium complex XXI. The formation of the latter by an exchange reaction XX between the enolate XVIII and the Grignard reagent represents a process well known in organomagnesium chemistry [12]. Irrespective of the details of mechanism, the success of these alkyne syntheses is no doubt directly related to the powerful electron-releasing capacity of the ferrocenyl group [13] which facilitates heterolysis of the C—O bond. Related nucleophilic displacements of the (OMgX) group from alcoholates of the type $FcCR_2OMgX$ have previously been encountered [14].

Experimental

All reactions were carried out under an atmosphere of pure, dry N_2. PMR spectra were recorded for $CDCl_3$ solutions on a Perkin—Elmer R12A spectrometer at 60 MHz using TMS as internal reference. IR spectra were recorded for CCl_4 solutions on a Perkin—Elmer 457 spectrometer. Melting points were taken in sealed, evacuated capillaries and are uncorrected. Ligroin refers to petrol b.p. 40-60°. Chromatographic separations of reaction product mixtures were carried out using columns (Al_2O_3; Spence Grade H, deactivated) or preparative thin-layer plates (Merck Kieselgel Type 60). Yields of product are based on unrecovered starting material. Microanalyses were performed by the Alfred Bernhardt Laboratory, Mulheim, West Germany.

2-Ethynyl-t-butylferrocene (VIIIa)

A solution of 2-acetyl-t-butylferrocene [7] (0.8 g, 2.8 mmol) in benzene (20 ml) was added to a solution of isopropylmagnesium bromide [from Me_2

* Under the reaction conditions in the presence of an excess of the Grignard reagent, these products would be converted to their bromomagnesium salts (RC≡CMgBr), the alkynes being regenerated by hydrolysis during work-up.

CHBr (12.3 g, 0.1 mol)] in refluxing (70°) benzene/ether (50 ml). The resulting solution was refluxed for 60 h, then cooled, and poured cautiously into water. The organic layer was separated and combined with several ether extracts of the aqueous layer. The total extract was washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was separated by TLC using ligroin as solvent. The *alkyne* VIIIa (0.49 g; 68%) was thereby obtained as an orange-yellow liquid. (Found: C, 72.3; H, 6.7. $C_{16}H_{18}Fe$ calcd.: C, 72.2; H, 6.8%.) $\nu_{max.}$ 2110 cm^{-1} (C≡C stretch); PMR: τ 5.66 (1H; t), 6.00 (2H; d)(C_5H_3), 5.87 (5H; s; C_5H_5), 7.26 (1H; s; C≡CH), and 8.65 (9H; s; CMe_3). The *alcohol* IXa (29 mg; 3%) was obtained as orange-yellow needles (pentane), m.p. 68-69°. (Found: C, 69.5; H, 8.5. $C_{19}H_{28}FeO$ calcd.: C, 69.5; H, 8.6%.) PMR: τ 5.77 (5H; s; C_5H_5), 5.8-6.0 (3H; m; C_5H_3), 7.5-8.1 (1H; m; CH), 7.70 (1H; s; OH), 8.64 (12H; s; *Me*COH and CMe_3), and 8.97, 9.44 (3H and 3H; 2d; $CHMe_2$).

When this reaction was repeated using refluxing benzene as solvent, there was obtained the alkyne VIIIa (57%), the alcohol IXa (9%), and the *alcohol* Xa (2%) which was obtained as a yellow liquid. (Found: C, 67.8; H, 7.9. $C_{16}H_{22}FeO$ calcd.: C, 67.2; H, 7.8%.) PMR: τ 5.07 (1H; q; CH), 5.6-5.95 (3H; m; C_5H_3), 5.77 (5H; s; C_5H_5), 7.90(br) (1H; s; OH), 8.65 (3H; d; Me), and 8.70 (9H; s; CMe_3). This product was identical with the alcohol obtained by $LiAlH_4$ reduction of the ketone VIIa.

2-Ethyl-t-butylferrocene

The alkyne VIIIa (0.10 g; 0.3 mmol) was dissolved in benzene (40 ml) and the solution was stirred under H_2 with PtO_2 (20 mg). When uptake of H_2 had ceased, the solution was filtered. Evaporation of the filtrate gave the title compound (100%) as an orange-yellow liquid. (Found: C, 71.0; H, 8.1. $C_{16}H_{22}Fe$ calcd.: C, 71.1; H, 8.2%.) PMR: τ 5.8-6.1 (3H; m; C_5H_3), 5.92 (5H; s; C_5H_5), 7.3-7.7 (2H; m; CH_2), 8.69 (9H; s; CMe_3), and 8.85 (3H; t; Me).

Hydration of VIIIa

The alkyne VIIIa (30 mg, 0.1 mmol) was dissolved in CF_3CO_2H (1 ml) and the solution was immediately quenched by pouring into an excess of saturated $NaHCO_3$ aqueous solution. The product was extracted with ether and found to consist solely of the ketone VIIa, identical with an authentic sample [7].

2-Ethynyl-1,1'-di-t-butylferrocene (VIIIb)

The reaction of the ketone VIIb [10] (0.16 g, 0.5 mmol) with a large excess of isopropylmagnesium bromide was carried out exactly as described in the first experiment (reaction time 120 h) and the product was separated by TLC. The *alkyne* VIIIb (0.12 g, 82%) was obtained as an orange-yellow liquid. (Found: C, 74.5; H, 8.0. $C_{20}H_{26}Fe$ calcd.: C, 74.5; H, 8.1%.) $\nu_{max.}$ 2115 cm^{-1} (C≡C stretch). PMR: τ 5.6-6.0 (7H; m; ferrocenyl protons), 7.20 (1H; s; C≡CH), and 8.63, 8.79 (9H and 9H; 2s; CMe_3). The *alcohol* IXb (8 mg; 4%) was obtained as yellow needles (pentane), m.p. 95-96°. (Found: C, 72.2; H, 9.4. $C_{23}H_{36}FeO$ calcd.: C, 71.9; H, 9.4%.) PMR: τ 5.75-6.0 (7H; m; ferrocenyl protons), 7.6-8.05 (2H; m; CH and OH), 8.65 (12H; s; *Me*COH

and CMe_3), 8.79 (9H; s; CMe_3), and 8.97, 9.44 (3H and 3H; 2d; $CHMe_2$). The *alkene* XIb (13 mg, 8%) was obtained as an orange-yellow liquid. (Found: C, 75.8; H, 9.5. $C_{23}H_{34}Fe$ calcd.: C, 75.4; H, 9.4%.) PMR: τ 4.85-5.05 (2H; m; vinyl protons), 5.65-6.2 (7H; m; ferrocenyl protons), 7.35-7.8 (1H; m; CH), 8.78, 8.98 (3H and 3H; 2d; Me), and 8.79, 8.81 (9H and 9H; 2s; CMe_3). A small amount of the ketone VIIb (4%) was recovered.

Reaction of ketone VIIc with isopropylmagnesium bromide

The reaction of the ketone VIIc [10] (0.34 g, 1.0 mmol) with a large excess of isopropylmagnesium bromide was carried out exactly as described in the first experiment (reaction time 16 h) and the product was separated by TLC. Both alkenes XIc and XIIc (total yield 0.2 g; 54%) were present. The *alkene* XIc was obtained as an orange-yellow liquid. (Found: C, 75.6; H, 9.5. $C_{23}H_{34}Fe$ calcd.: C, 75.4; H, 9.4%.) PMR: τ 4.84, 5.13 (1H and 1H; 2m; vinyl protons), 5.7-6.25 (7H; m; ferrocenyl protons), 7.15-7.65 (1H; m; CH), 8.79 (18H, s; CMe_3), and 8.84 (6H; d; Me). The *alkene* XIIc was obtained as an orange-yellow liquid. (Found: C, 75.6; H, 9.5. $C_{23}H_{34}Fe$ calcd.: C, 75.4; H, 9.4%.) PMR: τ 5.7-6.25 (7H; m; ferrocenyl protons), 8.00(br), 8.22(br), 8.30(br) (each 3H; 3s; Me), and 8.79 (18H; s; CMe_3). The *alcohol* IXc was obtained in its diastereoisomeric forms. The ψ-*endo* isomer (16 mg, 4%) was obtained as yellow-orange needles (pentane), m.p. 54-55°. (Found: C, 72.2; H, 9.6. $C_{23}H_{36}FeO$ calcd.: C, 71.9; H, 9.4%.) PMR: τ 5.8-6.2 (7H; m; ferrocenyl protons), 7.74 (br) (1H; s; OH), 8.15-8.6 (1H; m; CH), 8.57 (3H; s; *Me*COH), 8.81 (18H; s; CMe_3), and 9.12, 9.35 (3H and 3H; 2d; $CHMe_2$). The ψ-*exo* isomer (41 mg, 11%) was obtained as an organge-yellow liquid. (Found: C, 72.5; H, 9.5. $C_{23}H_{36}FeO$ calcd.: C, 71.9; H, 9.4%.) PMR: τ 5.85-6.1 (7H; m; ferrocenyl protons), 7.88(br) (1H; s; OH), 8.15-8.65 (1H; m; CH), 8.53 (3H; s; *Me*COH), 8.79, 8.82 (9H and 9H; 2s; CMe_3), and 9.15, 9.34 (3H and 3H; 2d; $CHMe_2$).

Reaction of ketone VIIb with methylmagnesium iodide

The reaction of the ketone VIIb [10] (80 mg; 0.24 mmol) with methylmagnesium iodide [from MeI (14.2 g, 0.1 mol)] in refluxing benzene/ether (70°) was carried out exactly as described in the first experiment (reaction time 100 h) and the product was separated by TLC. A small amount of the ketone VIIb (9 mg; 11%) was recovered. The *alkene* XIII (50 mg; 70%), an orange-yellow liquid, was obtained as the sole product. This alkene was rather unstable and satisfactory analytical data were not obtained; PMR, τ 4.65-4.85 (2H; m; vinyl protons), 5.75-6.1 (7H; m; ferrocenyl protons), 7.94(br) (3H; s; Me), and 8.71, 8.79 (9H and 9H; 2s; CMe_3).

2-Ethynyl-1,1'-diisopropylferrocene (VIIId)

The reaction of the ketone VIId [11] (156 mg, 0.5 mmol) with a large excess of isopropylmagnesium bromide was carried out exactly as described in the first experiment (reaction time 68 h) and the product was separated by TLC. The *alkyne* VIIId (24 mg, 16%) was obtained as an orange-yellow liquid. (Found: C, 73.6; H, 7.6. $C_{18}H_{22}Fe$ calcd.: C, 73.5; H, 7.5%) $\nu_{max.}$ 2118 cm^{-1} (C≡C stretch); PMR: τ 5.71 (1H; t), 5.9-6.05 (6H; m)(ferrocenyl

protons), 6.9-7.6 (2H; m; CH), 7.21 (1H; s; C≡CH), and 8.66, 8.83, 8.90 (3H, 6H, and 3H respectively; 3d; Me). The *alcohol* IXd (10 mg; 6%) was obtained as a yellow liquid. (Found: C, 71.0; H, 9.0. $C_{21}H_{32}FeO$ calcd.: C, 70.8; H, 9.1%.) PMR: τ 5.85-6.15 (7H; m; ferrocenyl protons), 6.2-8.3 (3H; m; CH), 7.53(br) (1H; s; OH), 8.64 (3H; s; *Me*COH), and 8.72 (3H; d), 8.83 (6H; d), 8.85 (3H; d), 8.94 (3H; d), 9.41 (3H; d)($CHMe_2$). The *alkene* XId (46 mg; 29%) was obtained as an orange-yellow liquid. (Found: C, 74.8; H, 8.9. $C_{21}H_{30}Fe$ calcd.: C, 74.6; H, 8.9%.) PMR: τ 4.61 (1H; d), 4.80 (1H; m) (vinyl protons), 5.9-6.2 (7H; m; ferrocenyl protons), 7.0-7.7 (3H; m; CH), 8.85 (6H; d; $CHMe_2$), and 8.66, 8.91, 9.04, 9.07 (each 3H; 4d; $CHMe_2$). The *alkene* XIId (16 mg; 9%) was obtained as an orange-yellow liquid. (Found: C, 74.7; H, 8.9. $C_{21}H_{30}Fe$ calcd.: C, 74.6; H, 8.9%.) PMR: τ 5.9-6.2 (7H; m; ferrocenyl protons), 7.0-7.7 (2H; m; CH), 7.81(br), 8.32(br), 8.5(br) (each 3H; 3s; Me), 8.63, 9.24 (3H and 3H; 2d; $CHMe_2$), and 8.855 (6H; d; $CHMe_2$).

Phenylacetylation of 1,1'-di-t-butylferrocene

A solution of $PhCH_2COCl$ (10.3 g, 67 mmol) in CH_2Cl_2 (20 ml) was added slowly to a stirred solution of 1,1'-di-t-butylferrocene [16] (14.9 g; 50 mmol) in CH_2Cl_2 (100 ml) at 0° containing finely ground Al_2Cl_6 (8.9 g, 34 mmol). The mixture was stirred for 6 h and then poured into water. The organic layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was separated by column chromatography. Some starting material (1.7 g, 11%) was recovered. The *ketone* XIVa (0.52 g, 3%) was obtained as a red oil. (Found: C, 74.9; H, 7.8. $C_{26}H_{32}FeO$ calcd.: C, 75.0; H, 7.8%.) PMR: τ 2.72 (5H; s; Ph), 5.24 (1H; t), 5.5-5.7 (2H; m; C_5H_3), 5.75-5.95 (6H; m; C_5H_4 + CH_2), and 8.65, 8.79 (9H and 9H; 2s; CMe_3). The *3-phenylacetyl isomer* (9.4 g, 51%) was obtained as a red oil. (Found: C, 75.0; H, 7.9. $C_{26}H_{32}$-FeO calcd.: C, 75.0; H, 7.8%.) PMR: τ 2.69 (5H; s; Ph), 5.2-5.35 (2H; m), 5.62 (1H; t; C_5H_3), 5.7-6.2 (4H; m; C_5H_4), 6.05 (2H; s; CH_2), and 8.78, 8.83 (9H and 9H; 2s; CMe_3).

Propanoylation of 1,1'-di-t-butylferrocene

This reaction was carried out exactly as described in the previous experiment using EtCOCl (6.2 g, 67 mmol), 1,1'-di-t-butylferrocene [16] (19.7 g, 66 mmol), and Al_2Cl_6 (8.9 g, 34 mmol), and the product was separated by column chromatography. Starting material (2.7 g, 18%) was recovered. The *ketone* XIVb (0.6 g, 4%) was obtained as a red oil. (Found: C, 71.3; H, 8.4. $C_{21}H_{30}FeO$ calcd.: C, 71.2; H, 8.5%) PMR: τ 5.39 (1H; t), 5.55-5.75 (2H; m) (C_5H_3), 5.9-6.0 (4H; m; C_5H_4), 7.05-7.5 (2H; dq; CH_2), 8.65, 8.83 (9H and 9H; 2s; CMe_3), and 8.82 (3H; t; Me). The *3-propanoyl isomer* (8.8 g, 62%) was obtained as a red oil. (Found: C, 71.2; H, 8.3. $C_{21}H_{30}FeO$ calcd.: C, 71.2; H, 8.5%.) PMR: τ 5.3-5.4 (2H; m), 5.65 (1H; t; C_5H_3), 5.75-6.15 (4H; m; C_5H_4), 7.32 (2H; q; CH_2), 8.77, 8.80 (9H and 9H; 2s; CMe_3), and 8.84 (3H; t; Me).

1-(2,1'-Di-t-butylferrocenyl)-2-phenylethanol

The ketone XIVa (70 mg, 0.17 mmol) was reduced with $LiAlH_4$ in ether and the product was separated by TLC. The *ψ-endo* isomer (15 mg,

21%) of the title *alcohol* was obtained as a yellow liquid. (Found: C, 74.8; H, 8.3. $C_{26}H_{34}FeO$ calcd.: C, 74.6; H, 8.2%.) PMR: τ 2.75 (5H; s; Ph), 5.65-6.0 (8H; m; ferrocenyl protons + CH), 7.0-7.3 (2H; m; CH_2), 7.75(br) (1H; s; OH), and 8.72, 8.78 (9H and 9H; 2s; CMe_3). The *ψ-exo* isomer (38 mg, 54%) was obtained as yellow plates (pentane), m.p. 143-145°. (Found; C, 74.7; H, 8.2. $C_{26}H_{34}FeO$ calcd.: C, 74.6; H, 8.2%.) PMR: τ 2.68 (5H; s; Ph), 5.65-6.05 (8H; m; ferrocenyl protons + CH), 6.35-7.35 (2H; m; CH_2), 8.47(br) (1H; s; OH), and 8.65, 8.78 (9H and 9H; 2s; CMe_3).

trans-1-(2,1'-Di-t-butylferrocenyl)-2-phenylethene (XVIIa)

A mixture of the diastereoisomers of the alcohol from the preceding experiment (30 mg, 0.07 mmol) was dissolved in CF_3CO_2H (1 ml) and the solution was quenched by pouring into an excess of saturated $NaHCO_3$ aqueous solution. The product was extracted with ether and purified by TLC. The *alkene* XVIIa (18 mg; 60%), m.p. 112-114° (pentane) was obtained as the sole product. (Found: C, 77.9; H, 7.9. $C_{26}H_{32}Fe$ calcd.: C, 78.0; H, 8.1%.) PMR: τ 2.45-2.8 (5H; m; Ph), 2.66, 3.33 (2H; ABq; J 16 Hz; vinyl protons), 5.48 (1H; t), 5.80 (2H; d)(C_5H_3), 5.85-6.0 (4H; m; C_5H_4), and 8.62, 8.79 (9H and 9H; 2s; CMe_3).

Reaction of the ketone XIVa with isopropylmagnesium bromide

The ketone XIVa (0.34 g, 0.95 mmol) was treated with a large excess of isopropylmagnesium bromide exactly as described in the first experiment (reaction time 125 h). The product was separated by TLC. Some starting ketone (0.12 g, 32% recovery) was isolated. A very small amount (3 mg) of a mixture of alkenes, probably XVa and XVIa from PMR spectroscopic evidence, was obtained in insufficient quantity for proper characterisation. The alkene XVIIa (27 mg, 12%) was also isolated and shown to be identical with the compound described in the preceding experiment.

Reaction of the ketone XIVb with isopropylmagnesium bromide

The ketone XIVb (0.34 g, 0.95 mmol) was treated with a large excess of isopropylmagnesium bromide as described in the first experiment using refluxing toluene/benzene (95°) as solvent (reaction time 120 h). The product was separated by TLC. Mainly unchanged starting ketone was recovered. PMR spectral analysis showed the presence of the alkenes XVb, XVIb and XVIIb, which were rather unstable and were obtained in insufficient quantities for proper characterisation.

Acknowledgement

The authors thank the Northern Ireland Department of Education for a maintenance grant (to T.S.A.).

References

1 T. Eicher, in S. Patai (Ed.), The Chemistry of the Carbonyl Group, Ch 13, Interscience, New York, 1966.
2 F.C. Whitmore and R.S. George, J. Amer. Chem. Soc., 64 (1942) 1239.
3 R.E. Lutz and C.J. Kibler, J. Amer. Chem. Soc., 62 (1940) 360.

4 G.E. Dunn and J. Warkentin, Can. J. Chem., 34 (1956) 75.
5 H.S. Mosher and E.M. LaCombe, J. Amer. Chem. Soc., 72 (1950) 3994.
6 T.S. Abram and W.E. Watts, J. Chem. Soc., Perkin Trans. I, in press.
7 R.A. Benkeser, Y. Nagai and J. Hooz, J. Amer. Chem. Soc., 86 (1964) 3742.
8 Cf. M. Rosenblum, N. Brawn, J. Papenmeier and M. Applehaum, J. Organometal. Chem., 6 (1966) 173.
9 Cf. D. Kaufman and R. Kupper, J. Org. Chem., 39 (1974) 1438.
10 T.D. Turbitt and W.E. Watts, J. Chem. Soc., Perkin Trans. II, (1974) 189.
11 K.L. Rinehart, K.L. Motz and S. Moon, J. Amer. Chem. Soc., 79 (1957) 2749.
12 See E.C. Ashby, Quart. Rev., 21 (1967) 259.
13 M. Rosenblum, Chemistry of the Iron Group Metallocenes, Part 1, Interscience, New York, 1965; M. Cais, Organometal. Chem. Rev., 1 (1966) 435.
14 W.M. Horspool, P. Stanley, R.G. Sutherland and B.J. Thomson, J. Chem. Soc. C, (1971) 1365.
15 W.M. Horspool, R.G. Sutherland and J.R. Sutton, Can. J. Chem., 47 (1969) 3085.
16 G.R. Knox and P.L. Pauson, J. Chem. Soc., (1961) 4610.