SYNTHESIS AND ACETYLATION OF METALLOCENE ANALOGUES OF CHALCONES. THE DOUBLE BOND ACETYLATION OF α,β-UNSATURATED KETONES

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Metallocene analogues of chalcones with a metallocene (ferrocene, ruthenocene, cymantrene) bound to the β-carbon atom of the multiple bond, or to the carbonyl group were prepared. The double bond of ferrocene and ruthenocene analogues of chalcones was acetylated when the metallocene was bound to the β-carbon atom of the double bond. No similar double bond acetylation was observed with cymantrene or N-methylpyrrole analogues of chalcones.

As reported in our previous papers[1,2] acetylation of α,β-unsaturated ketones having ferrocene bound to β-carbon atom afforded product of acetylation at ferrocene besides that at the double bond. We assume, therefore, that this reaction course was facilitated by a significant stability of α-ferrocenylcarbenium ions, which are intermediates in this reaction. On the other hand, no acetylation at the double bond was observed when acetylating chalcones having 2-furyl or 2-thienyl groups attached to β-carbon atom of the multiple bond.


$$I, R = H$$
$$II, R = COCH=CHC_6H_5$$
$$III$$
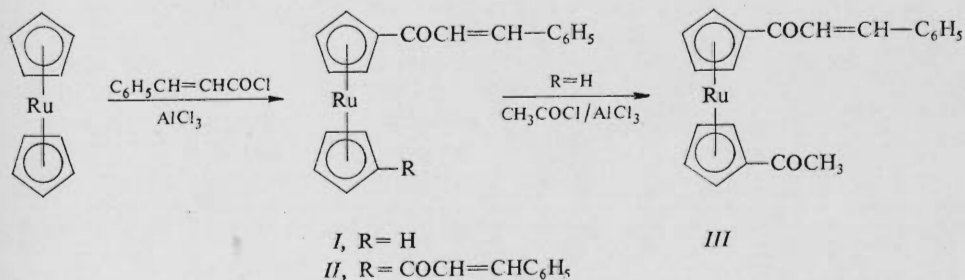
SCHEME 1

The aim of this paper was to prepare metallocene analogues of chalcones and to examine, whether acetylation at the double bond shall take place even then, when other metallocenes, e.g. ruthenocene or cymantrene are bound to β-carbon of the multiple bond; these are known to be able to stabilize α-carbenium ions[4,5]. Another goal

of this paper was to ascertain whether the direct interaction of a transition metal atom with the β-carbenium ion plays a substantial role in its stabilization.

Friedel–Crafts acylation of ruthenocene with cinnamoyl chloride furnished cinnamoylruthenocene (I) and 1,1'-bis(cinnamoyl)-ruthenocene in a 1 : 3 ratio. Acetylation of I with acetyl chloride gave the product of a heteroannular acetylation, *i.e.* 1-acetyl-1'-cinnamoylruthenocene (III) in a 77% yield (Scheme 1).

1-Phenyl-3-ruthenocenyl-2-propen-1-one (IV) was prepared by condensation of ru-thenocenecarbaldehyde with acetophenone in an alkaline medium; its acetylation afforded the product of electrophillic substitution at double bond, *i.e.* 1-phenyl--2-ruthenocenylmethylene-1,3-butanedione $(V$, Scheme 2$)$ in a 60% yield. ^{1}H-NMR spectrum of V lacked the AB quartet of ethylenic protons of the starting IV, and chemical shifts of α and β protons of the substituted ring appear as a broad four--proton singlet, analogous with that of the ferrocene analogue[1]. In addition to this product, traces of other acetylated products were detected by thin-layer chromato-graphy.
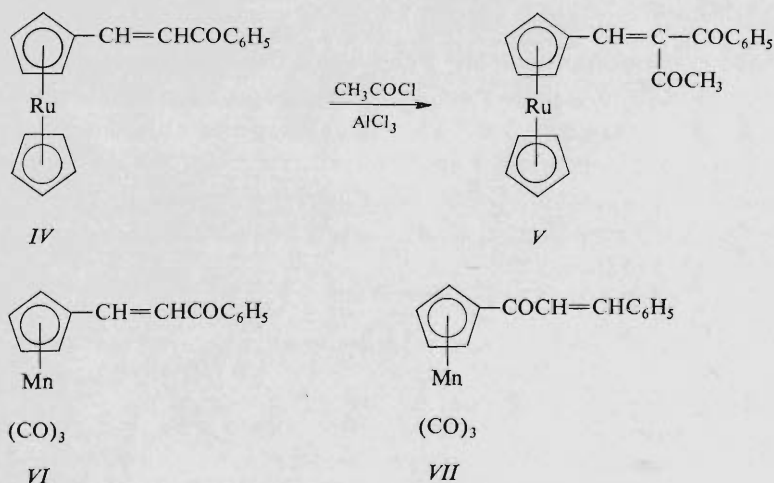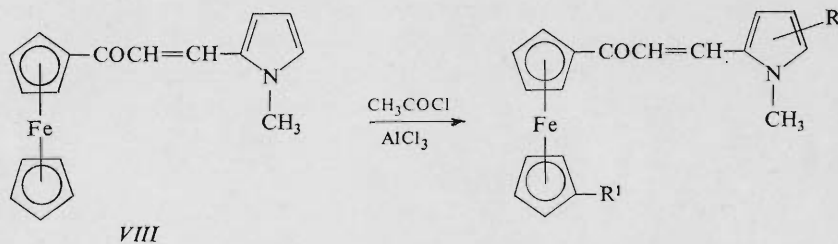

SCHEME 2

The finding that acetylation of the ferrocene analogue[1−3] proceeded at the double bond to only 8 − 15%, whereas product V was formed in a 60% yield let us conclude that ruthenocenyl stabilizes better the α-carbenium ion than does the ferrocenyl. A like effect was observed when studying the rotational barrier of analogous α-ferrocenyl and α-ruthenocenylcarbenium ions[4].

3-Cymantrenyl-1-phenyl-2-propen-1-one (VI) was prepared by a base catalyzed condensation of cymantrenecarbaldehyde with acetophenone in a 26% yield. The

attempted acetylation of *VI* with acetyl chloride under catalysis with $AlCl_3$ failed, probably for its low reactivity. As follows from experiments, the stabilizing effect of cymantrenyl, which is much smaller than that of ferrocenyl[5], does not activate enough the double bond towards an electrophillic attack with Perrier's complex. Since the chemical shifts in the ^{1}H-NMR spectrum of *VI* could not be unambiguously ascribed, a model substance, cinnamoylcymantrene (*VII*) was synthesized in a 70% yield by acylation of cymantrene with cinnamoyl chloride.

There is a persisting discussion concerning the possible, or necessary interaction of the iron atom with the electron-defficient centre of ferrocenyl carbeniumions[6−8]; therefore, we decided to prepare a chalcone analogue having an aromatic system bound to β-carbon with a similar σ_α^+ constant as that of ferrocenyl (-1.55), where the stabilization of positive charge by a transition metal is excluded and to study its acetylation. N-Methyl-2-pyrrolyl has been reported[9] to have $\sigma_\alpha^+ = -1.96$ and therefore, we prepared 1-ferrocenyl-3-(1-methylpyrrol-2-yl)-2-propenone (*VIII*) for this purpose (Scheme 3)). Three monoacetylated and one diacetylated products
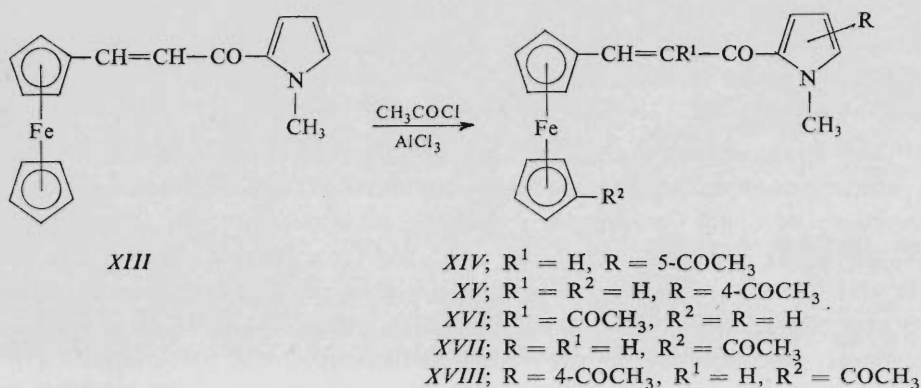

IX; R = 3-$COCH_3$, .R· = H
X; R = 5-$COCH_3$, .R^1 = H
XI; R = 4-$COCH_3$, R^1 = H
XII; R = 4-$COCH_4$, R^1 = $COCH_3$

SCHEME 3

were obtained. The acetylation product *IX* was obtained in the highest yield (22%); it revealed very considerable changes in the ^{1}H-NMR spectrum. First of all, the AB quartet of ethylenic protons was shifted down field, the difference between their chemical shifts being minimal. Chemical shift of pyrrole protons forms a two--proton multiplet at $\delta = 6.71$ ppm. We assume this product to be acetylated at position 3. Virtually, no pure substitution at ferrocene was observed upon acetylation of *VII*, whilst 67% of products acetylated at pyrrole ring (*IX*, *X*, *XI*, *XII*) were formed. Therefore, we investigated the effect of carbonyl group on the reactivity of N-methylpyrrole; the acetylation of 3-ferrocenyl-1-(1-methylpyrrol-2-yl)-2-propenone was examined (*XIII*, Scheme 4). A mixture of products acetylated at the pyrrole ring was obtained in approximately the same yields as with ferrocene. Results of acetyla-

tion indicate that N-methyl pyrrole is more reactive towards electrophillic reagents than ferrocene.

XIV; $R^1 = H$, $R = 5\text{-}COCH_3$
XV; $R^1 = R^2 = H$, $R = 4\text{-}COCH_3$
XVI; $R^1 = COCH_3$, $R^2 = R = H$
$XVII$; $R = R^1 = H$, $R^2 = COCH_3$
$XVIII$; $R = 4\text{-}COCH_3$, $R^1 = H$, $R^2 = COCH_3$

SCHEME 4

Since double bond acetylation was not observed when a powerful heteroaryl group was attached to the β-carbon of the enone double bond we assume that interaction of the transition metal atom with the β-carbenium ion could play a substantial role in this reaction. This has recently been shown with benzoylation of 3-ferrocenyl--1-phenyl-2-propenone[11], nevertheles double bond nitration of thiophene analogues was recently described[10].

EXPERIMENTAL

The ^{1}H-NMR spectra were measured at 23°C with a Tesla BS 487 apparatus operating at 80 MHz in C^2HCl_3 (99·5% ^2H) with tetramethylsilane as an internal reference. Chemical shifts (ppm, δ scale) were read to $\pm 0\cdot01$ ppm. IR spectra of substances in nujol were recorded with a Specord 75 IR (Zeiss, Jena) spectrometer. For column chromatography on silica gel (Lachema, Brno) following eluents were used: benzene–ethyl acetate 9·5 : 0·5 and 9 : 1. Melting points were taken with a Kofler micro hot-stage. All experiments were carried out under purified nitrogen.

N-Methylpyrrole was prepared. according to[12], N-methylpyrrolcarbaldehyde according to a procedure of pyrrole formylation[13] in a 64% yield (physical constant in accord with[14]), and 2-acetyl-N-methylpyrrole was obtained in a 33% yield analogously, as reported[15]. Ruthenocene was prepared according to[16] in a 70% yield, ruthenocenecarbaldehyde according to the procedure[17] in a 58% yield with the exception that it was purified chromatographically over SiO_2 instead via an $NaHSO_3$ adduct. Cymantrenecarbaldehyde was obtained in a 13% yield by formylation of cymantrene with dichloromethyl methyl ether according to[18]. Attempt to formylate with dichloromethyl butyl ether failed for the intermediate does not hydrolyze to the aldehyde.

Acetylation of Ruthenocene with Cinnamoyl Chloride

Aluminium chloride (1·73 g, 13 mmol) was successively added to a stirred solution of ruthenocene (1·5 g, 6·5 mmol) and cinnamoyl chloride (1·62 g, 9·7 mmol) in dichloromethane (70 ml) at room

temperature. After 4 h the temperature was risen to 35°C and kept for another 2 h. The mixture was then poured into ice-cold water, the organic material extracted with dichloromethane, washed with water, dried over Na_2SO_4, filtered, the solvent evaporated and the residue chromatographed. The first chromatographic band afforded ruthenocene (0·05 g, 3·3%), the next one 0·7 g (28% cinnamoylruthenocene (*I*), m.p. 147—150°C (benzene–light petroleum). For $C_{19}H_{16}ORu$ (361·4) calculated: 63·14% C, 4·46% H; found 63·63% C, 4·40% H. IR spectrum, cm^{-1}: $\nu(C{=}O)$ 1 640, $\nu(C{=}C)$ 1 590. ^1H-NMR spectrum: 7·34 (m, 5 H, C_6H_5); 7·70 (d, 1 H, —CH=); 7·06 (d, 1 H, $J_{AB} = 15\cdot50$ Hz, CO=CH); 5·21 (t, 2 H, H_α); 4·83 (t, 2 H, H_β); 4·59 (s, 5 H, C_5H_5). The last band contained 1,1'-bis(cinnamoylruthenocene (*II*, 0·29 g, 9%), m.p. 203—205°C (benzene–light petroleum). For $C_{28}H_{22}O_2Ru$ (492·5) calculated: 68·40% C, 4·50% H; found 69·0% C, 4·55% H. IR spectrum, cm^{-1}: $\nu(C{=}O)$ 1 660, $\nu(C{=}C)$ 1 600. ^1H-NMR spectrum: 7·23 (m, 10 H, C_6H_5); 7·63 (d, 2 H, —CH=); 6·85 (d, 2 H, $J_{AB} = 15\cdot5$ Hz, CO=CH); 5·25 (t, 4 H, H_α); 4·86 (t, 4 H, H_β).

1-Acetyl-1'-cinnamoylruthenocene (*III*)

Acetyl chloride (0·12 g, 1·5 mmol) and $AlCl_3$ (0·4 h, 3 mmol) in dichloromethane (10 ml) were added to a stirred solution of cinnamoylruthenocene (0·35 g, 1 mmol) in dichloromethane (25 ml) at room temperature. Further acetyl chloride (0·12 g) and $AlCl_3$ (0·4 g) were added after 2 h, the mixture was then stirred at room temperature for 3 h, at 35°C for 2 g, and worked up in an usual manner. Yield 0·05 g (14%) of the starting compound and 0·3 g (77%) of *III*; m.p. 160 to 162°C (benzene–light petroleum). For $C_{21}H_{18}O_2Ru$ (403·5) calculated: 62·52% C, 4·50% H; found 62·30% C, 4·35% H. IR spectrum, cm^{-1}: $\nu(C{=}O)$ 1 660 and 1 640, $\nu(C{=}C)$ 1 590. ^1H-NMR spectrum: 7·29 (m, 5 H, C_6H_5); 7·70 (d, 1 H, —CH=); 6·97 (d, 1 H, $J_{AB} = 15\cdot7$ Hz, CO=CH); 5·23 (t, 2 H, $H_{\alpha'}$); 5·10 (t, 2 H, H_α); 4·85 (t, 2 H, $H_{\beta'}$); 4·79 (t, 2 H, H_β); 2·18 (s, 3 H, $COCH_3$).

1-Phenyl-3-ruthenocenyl-2-propenone (*IV*)

Aceptophenone (0·23 g, 2 mmol) and ruthenocenecarbaldehyde (0·5 g, 2 mmol) were added to a stirred solution of NaOH (0·08 g, 2 mmol) in ethanol (95%, 25 ml) at room temperature. The mixture was stirred for 4 h and left to stand overnight; the separated precipitate was filtered off, washed with water to neutral reaction, and the residue dissolved in water extracted with ether. The organic layer was dried with Na_2SO_4, ether removed and the combined product was chromatograpned. Yield 0·54 g (82%), m.p. 159—161°C (benzene–light petroleum). For $C_{19}H_{16}$. .ORu (361·4) calculated: 63·14% C, 4·46% H; found: 63·00% C, 4·37% H. IR spectrum, cm^{-1}: $\nu(C{=}O)$ 1 660, $\nu(C{=}C)$ 1 600. ^1H-NMR spectrum: 7·70 (m, 5 H, C_6H_5); 7·60 (d, 1 H, —CH=); 7·06 (d, 1 H, $J_{AB} = 15\cdot4$ Hz, CO=CH); 4·96 (t, 2 H, H_α); 4·75 (t, 2 H, H_β); 4·58 (s, 5 H, C_5H_5).

Acetylation of *IV*

Acetyl chloride (0·14 g, 1·7 mmol) and $AlCl_3$ (0·46 g, 3·5 mmol) were successively added to a stirred and cooled solution of *IV* (0·4 g, 1·2 mmol) in dichloromethane (50 ml). The mixture was stirred 3 h at an ambient temperature and 2 h at 34°C, then poured into water and worked up as above. Dichloromethane was removed and the residue chromatographed. The first band gave the starting compound (0·24 g, 60%), the second one 1-phenyl-2-ruthenocenylmethylene- -1,3-butanedione (*V*, 0·24 g, 60%, yellow crystals), m.p. 171—174°C (benzene–light petroleum). For $C_{21}H_{18}O_2Ru$ (403·5) calculated: 62·52% C, 4·50% H; found: 62·40% C, 4·63% H. IR

spectrum, cm^{-1}: ν(C=O) 1 660, ν(C=C) 1 600. ^{1}H-NMR spectrum: 7·70 (m, 5 H, C$_6$H$_5$); 7·50 (s, 1 H, —CH=); 4·60 (s, 4 H, C$_5$H$_4$); 4·50 (s, 5 H, C$_5$H$_5$); 2·25 (s, 3 H, COCH$_3$). A trace amount of another acetylated product was isolated, which could not be, however, identified.

1-Phenyl-3-cymantrenyl-2-propenone (*VI*)

Cymantrenecarbaldehyde (0·5 g, 2 mmol) and acetophenone (0·26 g, 2 mmol) were added to a stirred solution of NaOH (0·08 g, 2 mmol) in ethanol (95%, 25 ml) at room temperature. During a 4 h-stirring the product precipitated; it was filtered off, washed with water to a neutral reaction, the remaining amount was extracted from the aqueous layer with ether, the solvent washed with water, dried over Na$_2$SO$_4$, distilled off, and the residue chromatographed. Yield of the title product 0·18 g (26%, yellowbrown crystals), m.p. 124—126°C (ethanol–water). For C$_{17}$H$_{11}$MnO$_4$ (334·2) calculated: 61·1% C, 3·32% H; found: 61·97% C, 3·54% H. IR spectrum, cm^{-1}: ν(C=O) 2 030, 1 950, ν(C=O) 1 660, ν(C=C) 1 580. ^{1}H-NMR spectrum: 7·94 (m, 2 H, 7·55 m, 3 H, 7·28 m, 2 H, C$_6$H$_5$ + CH=CH); 5·2 (t, 2 H, H$_\alpha$); 4·85 (t, 2 H, H$_\beta$).

Attempted acetylation: Acetyl chloride (0·12 g, 1·5 mmol) and AlCl$_3$ (0·4 g, 3 mmol) were added to solution of *VI* (0·35 g, 1 mmol) in dichloromethane (25 ml) under stirring. The mixture was stirred 4 h at room temperature and 2 h at 35°C. No formation of the desired product was observed (thin-layer chromatography) and therefore, the activity of the reagent was verified by adding some crystals of ferrocene; after 30 min the formation of acetyl- and diacetylferrocene was monitored by TLC. The usual work-up of the mixture afforded the starting material (0·3 g, 85%).

Cinnamoylcymantrene (*VII*)

Aluminium chloride (1·33 g, 10 mmol) was gradually added to a cooled (0°C) and stirred solution of cymantrene (1 g, 5 mmol). Stirring was continued at room temperature for 4 h, the mixture poured into water, extracted with dichloromethane, the organic layer washed with water, dried over Na$_2$SO$_4$, and the residue after evaporation of the solvent was crystallized from ethanol-–water 2 : 1. Yield 1·16 g (70%) of *VIII*, m.p. 103—105°C. For C$_{17}$H$_{11}$MnO$_4$ (334·2) calculated: 61·10% C, 3·31% H; found: 61·38% C, 3·22% H. IR spectrum, cm^{-1}: ν(C≡O) 2 020 and 1 940, ν(C=O) 1 650, ν(C=C) 1 590. ^{1}H-NMR spectrum: 7·36 (m, 5 H, C$_6$H$_5$); 7·69 (d, 1 H, —CH=); 7·06 (d, 1 H, J_{AB} = 16 Hz, CO=CH); 5·55 (t, 2 H, H$_\alpha$); 4·88 (t, 2 H, H$_\beta$).

1-Ferrocenyl-3-(1-methylpyrrol-2-yl)-2-propenone (*VIII*)

Acetylferrocene (2·28 g (10 mmol) and N-methylpyrrole-2-carbaldehyde (1·1 g, 10 mmol) were added to a stirred solution of NaOH (0·44 g, 11 mmol) in ethanol (95%, 30 ml) at room temperature; after 14 h the separated precipitate was filtered off and washed with water to neutral reaction. The residue of the product was extracted from water with ether, the organic layer was washed with water ad dried with Na$_2$SO$_4$. Ether was distilled off and the combined product was chromatographed. Yield 0·2 (18%) of acetylferrocene and 1·21 g (40%) of *VIII*; m.p. 128 to 130° C (benzene–light petroleum). For C$_{18}$H$_{17}$FeNO (319·2) calculated: 67·74% C, 5·37% H; 4·38% N, 17·50% Fe; found: 67·38% C, 5·30% H, 4·10% N, 17·30% Fe. IR spectrum, cm^{-1}: ν(C=O) 1 630, ν(C=O) 1 580. ^{1}H-NMR spectrum: 7·71 (d, 1 H, —CH=); 6·82 (d, 1 H, J_{AB} = = 15 Hz, CO—CH=); 6·77 (m, 2 H, H$_{3,5}$); 6·20 (dd, 1 H, H$_4$); 4·86 (t, 2 H, H$_\alpha$); 4·51 (t, 2 H, H$_\beta$); 4·19 (s, 5 H, C$_5$H$_5$); 3·73 (s, 3 H, N—CH$_3$).

Acetylation of *VIII*

Acetyl chloride (0·39 g, 4·5 mmol) in dichloromethane (25 ml) and AlCl$_3$ (1·2 g 9 mmol) were stepwise added to a stirred solution of *VIII* (1 g, 3 mmol) in dichloromethane (40 ml). The mixture was afterwards stirred at ambient temperature for 4 h and at 35°C for additional 2 h, poured into water, extracted with dichloromethane and worked up. Chromatographic separation gave the starting material (0·11 g, 11%) from the first, and 1-ferrocenyl-2-(1-methyl-3-acetylpyrrol--2-yl)-2-propenone (*IX*) (0·25 g, 22%, darkviolet crystals), m.p. 163—164°C (benzene–light petroleum) from the second band. For C$_{20}$H$_{19}$FeNO$_2$ (361·2) calculated: 66·6% C, 5·30% H, 3·87% N; found: 66·41% C, 5·25% H, 3·76% N: IR spectrum, cm^{-1}: ν(C=O) 1 640, ν(C=C) 1 580. ^{1}H-NMR spectrum: 8·05 (d, 1 H, CH=); 7·85 (d, 1 H, J_{AB} = 15·7 Hz, CO=CH); 6·71 (dd, 2 H, H$_4$ $_5$); 4·99 (t, 2 H, H$_\alpha$); 4·58 (t, 2 H, H$_\beta$); 4·27 (s, 5 H, C$_5$H$_5$); 3·80 (s, 3 H, N—CH$_3$); 2·55 (s, 3 H, COCH$_3$). The next band afforded 1-ferrocenyl-3-(1-methyl-5-acetylpyrrol-2-yl)--2-propenone (*X*, 0·22 g, 20%), m.p. 147—149°C (benzene–light petroleum). For C$_{20}$H$_{19}$FeNO$_2$ (361·2) calculated: 66·5% C, 5·30% H, 3·87% N; found: 66·83% C, 5·47% H, 3·92% N. IR spectrum, cm^{-1}: ν(C=O) 1 642, ν(C=C) 1 580. ^{1}H-NMR spectrum: 7·87 (d, 1 H, =CH—); 7·04 (d, 1 H, J_{AB} = 15·3 Hz, —CO—CH=); 6·97 (d, 1 H, H$_3$); 6·71 (d, 1 H, $J_{3,4}$ = 4·4 Hz, H$_4$); 4·89 (t, 2 H, H$_\alpha$); 4·59 (t, 2 H, H$_\beta$); 4·20 (s, 5 H, C$_5$H$_5$); 4·06 (s, 3 H, N—CH$_3$); 2·45 (s, 3 H, COCH$_3$). Another isolated product was found to be 1-ferrocenyl-3-(1-methyl-4-acetylpyrrol--2-yl)-2-propenone (*XI*, 0·2 g, 17%, red crystals), m.p. 178—181°C (benzene–light petroleum). For C$_{20}$H$_{19}$FeNO$_2$ (361·2) calculated: 66·5% C, 5·30% H, 3·87% N; found: 67·25% C, 5·60% H, 3·70% N. IR spectrum, cm^{-1}: ν(C=O) 1 640, 1 647 ν(C=C) 1 580. ^{1}H-NMR spectrum: 7·63 (d, 1 H, —CH=); 6·98 (d, 1 H, J_{AB} = 15 Hz, CO=CH); 7·34 (d, 1 H, H$_5$); 7·19 (d, 1 H, H$_3$);, 4·88 (t, 2 H, H$_\alpha$); 4·57 (t, 2 H, H$_\beta$); 4·21 (s, 5 H, C$_5$H$_5$); 3·77 (s, 3 H, N—CH$_3$); 2·42 (s, 3 H, COCH$_3$). The last band furnished 1-(1′-acetylferrocenyl)-3-(1-methyl-4-acetylpyrrol-2-yl) --2-propenone (*XII*, 0·1 g, 8%, violet crystals), m.p. 79—81°C (benzene–light petroleum). For C$_{22}$H$_{21}$FeNO$_3$ (408·2) calculated: 65·53% C, 5·25% H, 3·47% N; found: 64·81% C, 5·27% H, 3·26% N. IR spectrum, cm^{-1}: ν(C=O) 1 660, 1 640, 1 642 (sh), ν(C=C) 1 580. ^{1}H-NMR spectrum: 7·64 (d, 1 H, —CH=); 6·89 (d, 1 H, J_{AB} = 14·9 Hz, COCH=); 7·34 (d, 1 H, H$_5$); 7·23, (d, 1 H, H$_3$); 4·86 (t, 2 H, H$_\alpha$); 4·75 (t, 2 H, H$_{\alpha'}$); 4·56 (t, 2 H, H$_\beta$); 4·49 (t, 2 H, H$_{\beta'}$); 3·79 (s, 3 H N—CH$_3$); 2·43 (s, 3 H, COCH$_3$); 2·33 (s, 3 H, COCH$_3$).

3-Ferrocenyl-1-(1-methylpyrrol-2-yl)-2-propenone (*XIII*)

Ferrocenecarbaldehyde (1·6 g, 7·5 mmol) and N-methyl-2-acetylpyrrole (0·93 g, 7·5 mmol) were successively added to a stirred solution of NaOH (0·3 g, 7·5 mmol) in ethanol (95%, 30 ml) at room temperature. The separated product was after 18 h filtered off, washed with water to neutral reaction, the water-soluble residue extracted with ether and worked up as usual. Column chromatography of the crude product afforded the title product (1·3 g, 48%), m.p. 143—144°C (benzene–light petroleum). For C$_{18}$H$_{17}$FeNO (319·2) calculated: 67·74% C, 5·37% H, 4·38% N; found: 68·28% C, 5·45% H, 4·46% N. IR spectrum, cm^{-1}: ν(C=O) 1 640, ν(C=C) 1 580. ^{1}H-NMR spectrum: 7·63 (d, 1 H, —CH=); 7·01 (d, 1 H, J_{AB} = 15·2 Hz, CO=CH); 7·02 (dd, 1 H, H$_5$); 6·70 (dd, 1 H, H$_3$); 6·15 (dd, 1 H, H$_4$); 4·53 (t, 2 H, H$_\alpha$); 4·39 (t, 2 H, H$_\beta$); 4·12 (s, 5 H, C$_5$H$_5$); 3·99 (s, 3·99 (s, 3 H, N—CH$_3$).

Acetylation of *XIII*

Acetyl chloride (0·35 g, 4·5 mmol) in dichloromethane (20 ml) was added to a stirred solution of *XIII* (1 g, 3 mmol) in the same solvent (50 ml) and finally, AlCl$_3$ was gradually added to the mixture, which was then stirred at 35°C for 2 g and at room temperature for 4 h. The usual work-up

with dichloromethane and chromatography gave the starting material (0·15 g, 15%) from the first, and 3-ferrocenyl-1-(N-methyl-5-acetyl-pyrrol-2-yl)-2-propenone (*XIV*, 0·1 g, 11%), m.p. 158—160°C (benzene–light petroleum) from the second band. For $C_{20}H_{19}FeNO_2$ (361·2) calculated: 66·5% C, 5·30% H, 3·87% N; found: 66·9% C, 5·33% H, 3·85% N. IR spectrum, cm^{-1}: $v(C=O)$ 1 660, 1 640, $v(C=C)$ 1 590. ^{1}H-NMR spectrum: 7·68 (d, 1 H, —CH=); 6·96 (d, 1 H, J_{AB} = 15·1 Hz, CO=CH); 6·90 (s, 2 H, $H_{3,4}$); 4·57 (t, 2 H, H_α); 4·47 (t, 2 H, H_β); 4·29 (s, 5 H, C_5H_5); 4·15 (s, 3 H, N—CH$_3$); 2·50 (s, 3 H, COCH$_3$). Further isolated substances were: 2-ferrocenylmethylene-1-(1-methylpyrrol-2-yl)-1,3-butanedione (*XV*, 0·15 g, 15%), m.p. 94—96°C (benzene–light petroleum). For $C_{20}H_{19}FeNO_2$ (361·2) calculated 66·5% C, 5·30% H, 3·87% N; found: 66·07% C, 5·53% H, 3·80% N. IR spectrum, cm^{-1}: $v(C=O)$ 1 730, 1 650, $v(C=C)$ 1 590. ^{1}H-NMR spectrum: 7·50 (s, 1 H, —CH=); 7·4—6·4 (m, 3 H, CH-pyrrol); 4·49 (m, 4 H, C_5H_4); 4·20 (s, 5 H, C_5H_5); 3·70 (s, 3 H, N—CH$_3$); 2·45 (s, 3 H, COCH$_3$). 3-Ferrocenyl-1-(1-methyl--4-acetylpyrrol-2-yl)-2-propenone (*XVI*), m.p. 86—90°C (benzene–light petroleum). For $C_{20}H_{19}$.FeNO$_2$ (361·2) calculated: 66·5% C, 5·30% H, 3·87% N; found: 65·92% C, 5·41% H, 3·85% N. IR spectrum, cm^{-1}: $v(C=O)$ 1 660, 1 640, $v(C=C)$ 1 590. ^{1}H-NMR spectrum: 7·68 (d, 1 H, —CH=); 7·01 (d, 1 H, J_{AB} = 15·3 Hz, CO=CH); 7·37 (m, 2 H, $H_{3,5}$); 4·57 (t, 2 H, H_α); 4·46 (t, 2 H, H_β); 4·15 (s, 5 H, C_5H_5); 4·03, (s, 3 H, N—CH$_3$); 2·42 (s, 3 H, COCH$_3$). 3-(1'-Acetylferrocenyl)-1-(1-methylpyrrol-2-yl)-2-propenone (*XVII*), m.p. 133—135°C (benzene–light petroleum). For $C_{20}H_{19}FeNO_2$ (361·2) calculated: 66·5% C, 5·30% H, 3·87% N; found: 66·28% C, 5·28% H, 3·87% N. IR spectrum, cm^{-1}: $v(C=O)$ 1 660, 1 640, $v(C=C)$ 1 580. ^{1}H-NMR spectrum: 7·50 (d, 1 H, —CH=); 7·01 (d, 1 H, J_{AB} = 15·4 Hz CO=CH); 7·05 (dd, 1 H, H_5); 6·85 (dd, 1 H, H_3); 6·17 (dd, 1 H, H_4); 4·72 (t, 2 H, $H_{\alpha'}$); 4·53 (t, 2 H, H_α); 4·42 (m, 4 H, $H_{\beta\beta}$); 3·99 (s, 3 H, N—CH$_3$); 2·27 (s, 3 H, COCH$_3$). The last band afforded 3-(1'-acetylferrocenyl)-1-(N-methyl--4-acetylpyrrol-2-yl)-2-propenone (*XVIII*), m.p. 147—151°C (benzene–light petroleum). For $C_{22}H_{21}FeNO_3$ (403·2) calculated: 65·53% C, 5·25% H, 3·47% N; found: 65·29% C, 5·36% H, 3·74% N. IR spectrum, cm^{-1}: $v(C=O)$ 1 730, 1 660, $v(C=C)$ 1 590. ^{1}H-NMR spectrum: 7·53 (d, 1 H, —CH=); 7·00 (d, 1 H, J_{AB} = 15·1 Hz, CO=CH); 7·45 (m, 2 H, $H_{3,5}$); 4·75 (t, 2 H, $H_{\alpha'}$); 4·57 (t, 2 H, H_α); 4·47 (m, 4 H, $H_{\beta\beta'}$); 4·02 (s, 3 H, N—CH$_3$); 2·43 (s, 3 H, COCH$_3$); 2·30 (s, 3 H, COCH$_3$);

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Translated by Z. Votický.