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FRIEDEL–CRAFTS ALKYLATIONS OF FERROCENE WITH UNSATURATED LACTONES. SOME UNUSUAL REACTIONS CAUSED BY THE β-FERROCENYLCARBENIUM ION

M. SALIŠOVÁ, Š. TOMA*
Department of Organic Chemistry, Comenius University, 842 15 Bratislava (Czechoslovakia)

and E. SOLČÁNIOVÁ
Institute of Chemistry, Comenius University, 842 15 Bratislava (Czechoslovakia)

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Summary

Friedel–Crafts alkylations of ferrocene with 5- and 6-membered unsaturated lactones have been studied. The expected alkylation products were isolated in the case of 5-membered lactones, while several products such as unsaturated ferrocenyllactones, ferrocenyldiketones as well as ferrocenylhydroxylactones were isolated in the case of 6-membered lactones. β-Ferrocenylcarbenium ion was suggested to be the key intermediate in this case.

Introduction

The utilization of ω-oxoacid chlorides in acylations of different metallocenes has been investigated previously [1]. We observed practically no reaction apart from the oxidation of ferrocene, when the acylation agent was prepared by treating $SOCl_2$ with $RCO(CH_2)_nCOOH$ ($n = 2$, 3 and R = Ph). Several ferrocene-containing products were isolated when PCl_3 was used in place of $SOCl_2$. Reaction of PCl_3 with the above-mentioned acids gives a mixture of unsaturated lactones (~ 80%) and acid chlorides (~ 20%). Therefore not only acylation but also alkylation of ferrocene took place.

In this work we used unsaturated lactones with more than 98% purity in order to compare the reaction of such alkylating agents with those studied previously and to give plausible explanation for the very different behaviour of the alkylating agents derived from the above-mentioned oxoacids with $n = 2$ and $n = 3$.

Results and discussion

Friedel–Craft alkylation of ferrocene with 4-phenyl-4-(3-butenolide) (lactone I) caused no problems and 4-ferrocenyl-4-phenyl-4-butanolide (Ia) was isolated as the main product of the reaction (Scheme 1).

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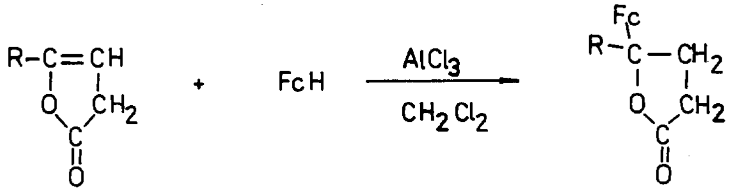


(I: R = Ph ; II: R = CH_3) Fc=ferrocenyl (Ia: R=Ph ; IIa: R=CH_3)

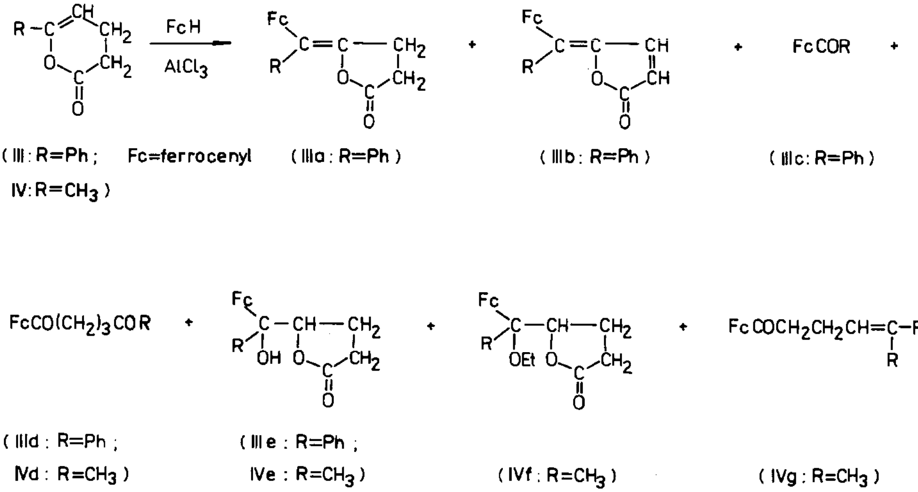
SCHEME 1

The structure of Ia was determined by ^1H, MS and IR spectroscopy (see Experimental). Compound Ia was in some cases accompanied by violet and orange compounds that turned green upon standing in air. Their structure could not be determined as attempts to purify them were unsuccessful.

A more complicated mixture of products was obtained when the reaction was carried out with 5-phenyl-5-(4-pentenolide) (lactone III). Usually 8–10 ferrocene derivatives were detected on TLC plates of which five could be identified (Scheme 2). In each case (reactions were repeated several times) the mixture contained about 50% of unchanged ferrocene. The number of products and their mutual ratio were very dependent on the purity of reactants and solvent.

The structure of compounds IIIa–IIIe was determined by ^1H NMR and IR spectroscopy, together with the UV spectra for IIIa and IIIb and with ^{13}C NMR (Fig. 1) and MS spectroscopy for IIIa and IIIe (see Experimental). However, only after RTG analysis (to be published separately [2]) was the structure of IIIe unambigously confirmed.

Attempts to hydrolyse lactone IIIe in both acidic and basic media were unsuccessful and the only product we were able to isolate was benzoylferrocene (IIIc).



(III: R=Ph ; IV: R=CH_3) Fc=ferrocenyl (IIIa: R=Ph) (IIIb: R=Ph) (IIIc: R=Ph) (IIId: R=Ph ; IVd: R=CH_3) (IIIe: R=Ph ; IVe: R=CH_3) (IVf: R=CH_3) (IVg: R=CH_3)

SCHEME 2

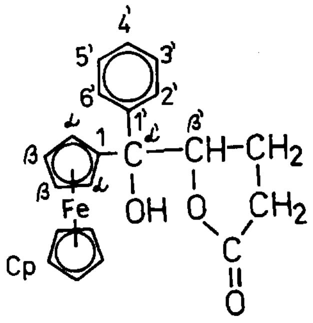
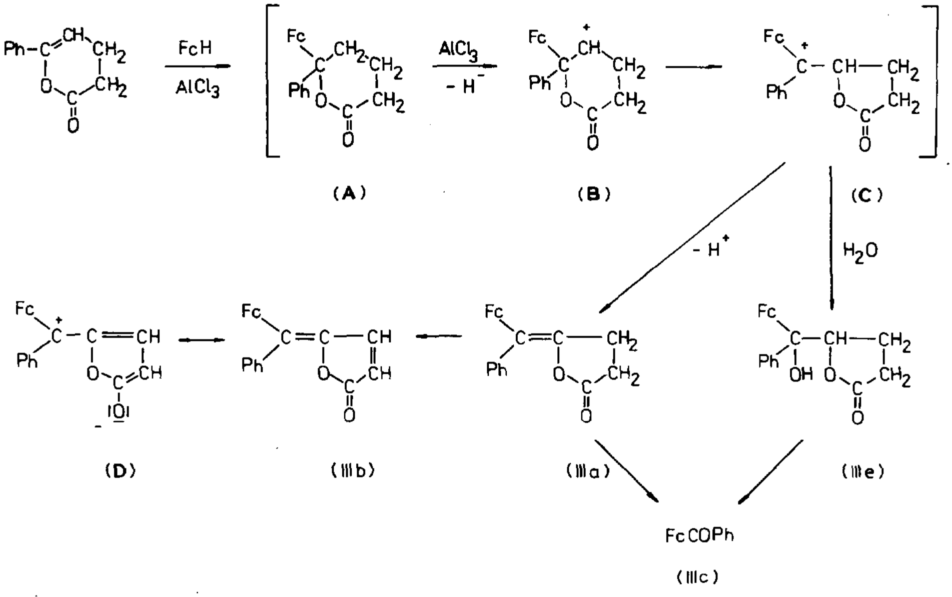


Fig. 1. The structure of compound IIIe.

Benzoylferrocene was also formed when lactone IIIe was left to stand or when chromatographed on Al_2O_3 or even on SiO_2. These results explain why in some cases we isolated benzoylferrocene as the main product of the reaction shown in Scheme 2. Moreover, benzoylferrocene was formed in low yield after a solution of IIIa in benzene was left to stand in air.

The formation of compounds IIIa, IIIb and IIIe can be presumed to follow a route via an intermediate β-ferrocenylcarbenium ion which subsequently rearranges to give more stable α-ferrocenylcarbenium ion (Scheme 3).

In view of similarities between the alkylation of ferrocene with lactone I and with lactone III the presence of a saturated lactone A was assumed which, however, could not be isolated, but was "probably" detected by TLC. The ability of $AlCl_3$ to abstract the hydride ion was observed in cases where a stabilized carbonium ion such as tropylium could be formed [3,4]. The likelihood that ferrocene stabilizes



SCHEME 3

carbonium ion in the β-position was confirmed in the case of [4]ferrocenophane derivatives [5–8]. Carbonium ion generated from the [4]ferrocenophane-2-ol is almost as stable as that generated from [4]ferrocenophane-1-ol [5]. Neshwad et al. claimed that β-ferrocenylcarbenium ion is stabilized by the interaction of Fe *d*-orbitals with favourably oriented vacant *p*-orbitals of the carbocation [8]. The same stabilization occurs also in α-ferrocenylcarbonium ions [9,10].

Scheme 3 shows possible pathways for the formation of compounds IIIa–IIIe with the rearrangement of β-carbocation **B** to the more stable α-carbocation **C** as a key step.

In the IR spectra of IIIb ν_{CO} vibration bands are too low. We suggest that the real structure of IIIb is given by the canonical formulae shown in the Scheme 3.

Taking into account Ortaggi's findings [11] that cycle conformation has a strong influence on the stability of α-ferrocenylcarbenium ions, the question why such a great difference was observed at the alkylation with 5- and 6-membered unsaturated lactones, can be answered by inspection of the Dreiding models of Ia and A. The β-carbon atom in A is ~ 5 ppm closer to the Fe atom than it is in Ia.

To answer the question whether the phenyl group has some special effect on the course of the reaction we alkylated ferrocene with lactones II and IV – i.e. the methyl analogues of I and III.

The alkylation of ferrocene with unsaturated lactone II gave results very similar to those of the alkylation with I. 4-Ferrocenyl-4-methyl-4-butanolide was isolated as the main product in even higher yields.

Alkylation with unsaturated lactone IV gave a greater variety of products than with III. Ferrocenyldiketone IVd and ferrocenylhydroxylactone IVe were isolated as main products. Several other ferrocene derivatives were detected by TLC but could not be isolated and identified.

In one experiment technical grade CH_2Cl_2 (containing about 0.5% of ethanol) was used as the solvent. In that case the main product was ferrocenylethoxylactone IVf. In other experiments we isolated as major product 1,5-diferrrocenyl-4-hexene-1-one (IVg). (In both cases a mixture of unsaturated lactone and acid chloride was used as reagent.) In a previous report [1] we described methods for obtaining similar products.

This work gives some indirect evidence for the existence of the ferrocene-stabilized cations in α- and β-positions as intermediates.

The Friedel–Crafts alkylation of ferrocene with pure unsaturated lactones gave comparable results with a mixture of unsaturated lactones and corresponding acid chlorides as alkylating agents. Several attempts to alkylate cymantrene with unsaturated lactones or with the above mixture were unsuccessful.

Experimental

^{1}H NMR spectra were recorded at 25 °C on a Tesla Brno BS 487 instrument at 80 MHz, or on a Bruker 300 instrument, ^{13}C NMR spectra were recorded on a JEOL FX 100 instrument, in $CDCl_3$ (99.5% of deuterium) solutions with tetramethylsilane as internal standard. Chemical shifts are given in δ values. IR spectra were recorded on Perkin–Elmer 567 or Zeiss Specord 75 IR instruments in $CHCl_3$. UV spectra were recorded on a Perkin–Elmer 450 instrument in methanol. Melting points were determined on a Köfler apparatus and are uncorrected. Chromatography was carried out on SiO_2 (Kavalier Votice or Lachema Brno) or on Al_2O_3 (Reanal Budapest).

The unsaturated lactones I, III and IV were prepared by the standard procedure for III [12] from the corresponding ω-oxoacids and acetanhydride.

4-Phenyl-4-(3-butenolide) (I) – white crystals (m.p. 92–94 °C [13]) were obtained in 10% yield. ^1H NMR: 3.35 (d, 2H, CH_2); 5.73 (t, 1H, CH); 7.2–7.75 (m, 5H, C_6H_5) ppm.

5-Phenyl-5-(4-pentenolide) (III), b.p. 137–140 °C/0.66 kPa was obtained in 90% yield [12]. ^1H NMR: 2.25–2.80 (m, 4H, CH_2); 5.80 (t, 1H, CH); 7.15–7.75 (m, 5H, C_6H_5) ppm.

5-Methyl-5-(4-pentenolide) (IV), b.p. 74–78 °C/1.99 kPa [14] was obtained in 39% yield. ^1H NMR: 1.95 (s, 3H, CH_3); 2.10–2.70 (m, 4H, CH_2); 5.05 (t, 1H, CH).

4-Methyl-4-(3-butenolide) (II) b.p. 65–70 °C/1.99 kPa was prepared from 4-oxopentanoic acid and syrupy H_3PO_4 by Helberg's procedure [15], in 55% yield.

General procedure for alkylation of ferrocene with unsaturated lactones I–IV

To a stirred solution of 0.16 mol of ferrocene in 50 ml of anhydrous CH_2Cl_2 at 0–5 °C under N_2 was added at once 0.17 mol of the corresponding unsaturated lactone (I–IV) in 50 ml of anhydrous CH_2Cl_2, and then 0.3 mol of anhydrous $AlCl_3$ was added during 30 min. The reaction mixture was allowed to warm to room temperature, stirred for 3 h, then poured into 500 ml of cold water. The organic material was extracted with dichloromethane. (When necessary $Na_2S_2O_4$ was added for reduction of ferricinium salts.) The combined extracts were washed with water and dried over anhydrous Na_2SO_4. After the Na_2SO_4 had been filtered off, the dichloromethane was evaporated off, and the residue was chromatographed on SiO_2 with benzene or with a 3–30% mixture of ethyl acetate in benzene, as eluent.

Alkylation of ferrocene with lactone I

About 45% of unchanged ferrocene was isolated from the first band. 4-Ferrocenyl-4-phenyl-4-butanolide (Ia) (32%) was isolated from the third band as orange-yellow crystals, m.p. 151–152 °C (benzene/petroleum ether). Found: C, 69.68; H, 5.23; Fe, 16.32; For $C_{20}H_{18}FeO_2$ mol. wt. 346.2 calc.: C, 69.38; H, 5.24; Fe, 16.13%. ^1H NMR: 2.5–2.9 (m, 4H, CH_2); 3.95–4.25 (m, 9H, Fe); 7.2–7.5 (m, 5H, C_6H_5) ppm. IR: ν_{CO} 1768 cm^{-1}. MS *m/e*: $(C_{20}H_{18}FeO_2)^{\dot{+}}$ 346 → $(C_{19}H_{18}Fe)^{\dot{+}}$ 302 → $(C_{18}H_{16}Fe)^{\dot{+}}$ 288 → $(C_{11}H_9Fe)^{+}$ 197 → $(C_{10}H_9Fe)^{+}$ 185 → $(C_5H_5Fe)^{+}$ 121 → $(C_5H_5)^{+}$ 65.

Note: Small amounts of a yellow compound from the second band and a violet compound from the fourth band that turned green upon standing in air could not be identified because attempts to purify them were unsuccessful.

Alkylation of ferrocene with lactone II

Unchanged ferrocene (about 30%) was isolated from the first band and orange-yellow 4-ferrocenyl-4-methyl-4-butanolide (50%) (IIa) was isolated from the third band (m.p. 81–84 °C) (benzene/hexane). Found: C, 63.30; H, 5.71; Fe, 19.67. For $C_{15}H_{16}FeO_2$ mol. wt. 284.14 calc: C, 63.41; H, 5.68; Fe, 19.66%. ^1H NMR: 1.7 (s, 3H, CH_3); 2.05–2.75 (m, 4H, CH_2); 4.17 (bs, 9H, Fc) ppm. IR: ν_{CO} 1745 cm^{-1}.

Alkylation of ferrocene with lactone III

Unchanged ferrocene (ca. 50%) was isolated from the first band, and (ca. 28%) orange 4-(ferrocenylphenylmethylene)-4-butanolide (IIIa) was isolated from the third band (m.p. 200–205 °C) (benzene/hexane). Found: C, 70.26; H, 5.04; Fe, 15.44. For $C_{21}H_{18}FeO_2$ mol. wt. 358.22 calc: C, 70.41; H. 5.06; Fe, 15.59%. ^{1}H NMR: 2.62 (s, 4H, CH_2); 4.12 (s, 5H, Cp); 4.18 (t, 2H, H_β); 4.42 (t, 2H, H_α); 7.37 (m, 5H, Ph). ^{13}C NMR: 25.6 (CH_2–C=); 27.1 (CH_2–CO); 68.5 (C_α); 68.8 (C_β); 69.0 (Cp); 82.3 (C(1)); 116.2 ($C_{\alpha'}$); 127.2 (C(4′)); 128.4 (C(2′), C(6′)); 129.9 (C(3′), C(5′)); 138.1 (C(1′)); 143.6 ($C_{\beta'}$); 175.0 (CO) ppm. IR: ν_{CO}1795 cm^{-1}. UV: λ_{max}278 nm. MS (*m/e*): $(C_{21}H_{18}FeO_2)^{+\cdot}$ 358 → $(C_{20}H_{18}Fe)^{+\cdot}$ 314 → $(C_{17}H_{14}Fe)^{+\cdot}$ 274 → $(C_{10}H_9Fe)^{+\cdot}$ 185.

Deep-violet crystals of 4-(ferrocenylphenylmethylene)4-(2-butanolide) (IIIb) (ca. 0.5%) were isolated from the fourth band (m.p. 205–208 °C) (benzene/hexane). Found: C, 70.48; H, 4.55. For $C_{21}H_{16}FeO_2$ mol. wt. 358.21 calc: C, 70.81; H, 4.53%. ^{1}H NMR: 4.14 (s, 5H, Cp); 4.45 (t, 2H, H_β); 4.70 (t, 2H, H_α); 6.03 (d, 1H, =CH, J_{AB}6 Hz); 7.05 (d, 1H, =CH, J_{AB} 6 Hz); 7.38 (m, 5H, Ph) ppm. IR: ν_{CO} 1580w; 1615s; 1645w cm^{-1}. UV: λ_{max} 355 nm.

Note: In many cases this compound was obtained along with the starting lactone, III.

Benzoylferrocene was isolated from the next band as red crystals (ca. 10%) (m.p. 106–108 °C) [16]. Found: C, 70.52; H, 4.92; Fe, 19.09. For $C_{17}H_{14}FeO$ mol. wt. 290.15 calc: C, 70.37; H, 4.86; Fe, 19.24%. ^{1}H NMR: 4.20 (s, 5H, Cp); 4.55 (t, 2H, H_β); 4.88 (t, 2H, H_α); 7.25–7.60 (m, 5H, Ph) ppm.

1-Ferrocenyl-5-phenyl-1,5-pentanedione (IIId) [1], was isolated from the next band as orange crystals (ca. 9%) (m.p. 94–95 °C) (benzene/petroleum ether). Found: C, 70.25; H, 5.66; Fe, 15.61. For $C_{21}H_{20}FeO_2$ mol. wt. 360.24 calc: C, 70.02; H, 5.59; Fe, 15.50%. ^{1}H NMR: 2.14 (q, 2H, CH_2); 2.83 (t, 2H, CH_2COCp); 3.09 (t, 2H, CH_2COPh); 4.16 (s, 5H, Cp); 4.46 (t, 2H, H_β); 4.78 (t, 2H, H_α); 7.3–8.1 (m, 5H, Ph) ppm. IR: ν_{CO} 1670 cm^{-1}.

4-(Ferrocenylhydroxyphenylmethyl)-4-butanolide (IIIe), was isolated from the next band as yellow crystals (ca. 12%) (m.p. 162–165 °C) (benzene/petroleum ether). Found: C, 67.23; H, 5.50; Fe, 14.54. For $C_{21}H_{20}FeO_3$ mol. wt. 376.24 calc: C, 67.04; H, 5.35; Fe, 14.84%. ^{1}H NMR: 1.5–2.4 (m, 4H, CH_2); 2.9 (s, 1H, OH); 3.98 (m, 1H, H_α); 4.1–4.4 (m, 7H, Cp + H_β); 4.7 (m, 1H, H_α); 4.94 (m, 1H, CH); 7.1–7.5 (m, 5H, Ph). ^{13}C NMR: 22.4 (CH_2–CH); 27.6 (CH_2CO); 66.9 (C_α); 67.8 (C_β); 68.5 (Cp); 74.3 (C(1)); 84.5 ($C_{\beta'}$); 97.3 ($C_{\alpha'}$); 126.7 (C(2′), C(6′)); 127.4 (C(4′)); 127.7 (C(3′), C(5′)); 140.7 (C(1′)); 177.3 (CO) ppm. IR: ν_{CO} 1763 cm^{-1}. MS (*m/e*): $(C_{21}H_{20}FeO_3)^{+\cdot}$ 376 → $(C_{21}H_{18}FeO_2)^{+\cdot}$ 358 → $(C_{17}H_{15}FeO)^{+\cdot}$ 291) → $(C_{20}H_{18}Fe)^{+\cdot}$ 314 → $(C_{17}H_{14}Fe)^{+\cdot}$ 274 → $(C_{10}H_9Fe)^{+\cdot}$ 185 → $(C_5H_5Fe)^{+\cdot}$ 121 → $(C_5H_5)^{+\cdot}$ 65.

A small amount of 5-oxo-5-phenylpentanoic acid was isolated from the last band.

Alkylation of ferrocene with 5-methyl-5-(4-pentenolide)

Unchanged ferrocene (ca. 65%) was isolated from the first band. Some compounds from bands 3–5 were not identified. 1-Ferrocenyl-1,5-hexanedione (IVd), was isolated from the next band as orange crystals (ca. 6%) (m.p. 75.5–77.5 °C) (benzene/hexane). Found: C, 63.84; H, 6.04. For $C_{16}H_{18}FeO_2$ mol. wt. 298.17 calc: C, 64.45; H, 6.08%. ^{1}H NMR: 2.03 (qv, 2H, CH_2); 2.13 (s, 3H, CH_3); 2.55 (t, 2H,

CH_2); 2.70 (t, 2H, CH_2); 4.19 (s, 5H, Cp); 4.47 (t, 2H, H_β); 4.78 (t, 2H, H_α) ppm. IR: ν_{CO} 1668, 1717 cm^{-1}.

4-(1-Ferrocenyl-1-hydroxyethyl)-4-butanolide (IVe), was isolated from the last band as yellow crystals (ca. 2.5%) (m.p. 180–185 °C) (benzene/hexane). Found: C, 59.96; H, 6.32. For $C_{16}H_{18}FeO_3$ mol. wt. 314.17 calc: C, 61.16; H, 5.77%. ^1H NMR: 1.61 (s, 3H, CH_3); 1.75–2.45 (m, 5H, CH_2 + OH); 4.0–4.4 (m, 9H, Fc) ppm. IR: ν_{CO} 1755 cm^{-1}.

Note: In experiments where technical grade CH_2Cl_2 containing 0.5% of ethanol was used 4-(1-ethoxy-1-ferrocenylethyl)-4-butanolide (IVf), as a deep red oil (ca. 17%), was isolated. Found: C, 65.83; H, 6.97; Fe, 16.83. For $C_{18}H_{23}FeO_3$ mol. wt. 342.21 calc: C, 63.18; H, 6.48; Fe, 16.32%. ^1H NMR: 1.21 (t, 3H, CH_3); 1.92 (bs, 3H, CH_3); 2.33 (bs, 4H, CH_2); 3.85–4.45 (m, 11H, Fc + OCH_2); 5.57 (t, 1H, CH) ppm. IR: ν_{CO} 1780 cm^{-1}.

In another experiment we isolated 1,5-diferrocenyl-4-hexene-1-one (IV g) as the main product (deep red crystals (ca. 20%)) (m.p. 110–114 °C) (benzene/hexane). Found: C, 66.03; H, 5.59; Fe, 23.72. For $C_{26}H_{26}Fe_2O$ mol. wt. 466.19 calc: C, 66.99; H, 5.62; Fe, 23.96%. ^1H NMR: 1.98 (s, 3H, CH_3); 2.35–2.90 (m, 4H, CH_2); 4.07 (s, 5H, Cp); 4.18 (s, 7H, Cp + H_β); 4.32 (t, 2H, H_α); 4.47 (t, 2H, H_β); 4.78 (t, 2H, H_α); 5.66 (t, 1H, CH). IR: ν_{CO} 1665 cm^{-1}. In the last two experiments a mixture of unsaturated lactone and corresponding acid chloride was used as reagent.

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References

1 M. Sališová and Š. Toma, Chem. Papers, 40 (1986) 619.
2 Y.T. Struchkov, A.S. Batsanov, Š. Toma and M. Sališová, J. Organomet. Chem., in preparation.
3 O.A. Reutov, Teoret. Osnovy Org. Khim., Universitet Moskva, 1964, 524,
4 M.E. Volpin, A.S. Achrem and D.N. Kursanov, Izv. Akad. Nauk SSSR, OCHI, 1957, 760.
5 G. Ortaggi, P. Ricio and I. Tritto, J. Org. Chem., 44 (1979) 2920.
6 M. Hisatome and K. Yamakawa, J. Organomet. Chem., 133 (1977) C9.
7 M. Hisatome and K. Yamakawa, Tetrahedron Lett., (1971) 3533.
8 G. Neshwad, R.M.G. Roberts and J. Silver, J. Organomet. Chem., 240 (1982) 265.
9 A.A. Koridze, N.M. Astakhova and P.V. Petrovskii, J. Organomet. Chem., 254 (1983) 345.
10 A.A. Koridze, Uspechi Chim., 55 (1986) 277.
11 G. Ortaggi, Congr. Naz. Chim. Inorg. (Atti) 13 (1980) 183; Chem. Abstr. 95 (1981) 42109.
12 M.Y. Lurje, I.S. Trubnikov, N.P. Schuscherina and R.Y. Levina, Zh. Obshch. Khim. 28 (1958) 1351.
13 M. Kugel, Ann. 299, 50.
14 Vorländer and Knötzsch, Ann. 294, 319.
15 J.A. Helberg, S. Ulubay and H. Cilvelekoln, Ann. 561 (1949) 215.
16 M. Rosenblum, Chemistry of the Iron Group Metallocenes, John Wiley & Sons, New York, 1965, p. 93.