A Condensation Product from the Reaction of Ferrocene Carboxaldehyde with Excess Cyclohexanone. The Crystal Structure of 8-Ferrocenyl-2-hydroxytricyclo[7,3,1,$0^{2,7}$]tridecan-13-one

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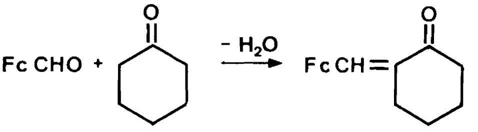
The title product was prepared by condensing ferrocenecarboxaldehyde with a large excess of cyclohexanone under otherwise customary Claisen-Schmidt conditions. Its crystal structure has been determined from X-ray diffraction data at −135 °C. The crystals are monoclinic, space group $P2_1/n$ with cell dimensions a = 7.436(5), b = 8.320(3), c = 30.718(10) Å, β = 95.64(4)° and Z = 4. Full-matrix least-squares refinement gave a conventional R of 0.057 for 2495 observed reflections. The result of the structure analysis shows that the condensation product can be formulated as 8-ferrocenyl-2-hydroxytricyclo[7,3,1,$0^{2,7}$]tridecan-13-one, $C_{23}H_{28}O_2Fe$. The unsubstituted cyclopentadienyl ring in the ferrocenyl group is disordered with a ca. 1:1 distribution of more or less eclipsed and staggered conformations of the ferrocene moiety. The cyclopentadienyl rings have an average C−C bond length of 1.418 Å. The average Fe−C distance in the ferrocenyl group is 2.044 Å. The organic substituent can be viewed as three fused cyclohexane rings, all with chair conformations, with the central 3-hydroxycyclohexanone ring bonded to one of the cyclopentadienyl rings.

Dedicated to Professor Otto Bastiansen on his 70th birthday

During a Claisen-Schmidt condensation of ferrocenecarboxaldehyde with a large excess of cyclohexanone, an unexpected product (**1**) resulted. The expected reaction would be:



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where Fc = ferrocenyl. However, the mass spectrum indicated that the product obtained had a molecular weight higher than expected. In addition, the presence of a hydroxy group was indicated from IR spectra.

In order to characterize the product and thereby clarify the reaction mechanism, it was decided to investigate its structure by means of X-ray crystallographic methods.

Experimental

Synthesis. To a solution of 20.7 ml (0.2 mol) of cyclohexanone in 5 ml of 95 % aq. ethanol was added a warm solution of 0.86 g (0.004 mol) of ferrocenecarboxaldehyde in 25 ml of 95 % aq. ethanol. To the resultant solution was then added dropwise, with stirring, 2.5 ml of 6 M aq. sodium hydroxide. The mixture was then allowed to stand for 22 days. After filtration the brownish precipitate was washed with cold 90 % ethanol.

Yield 0.55 g (35 %) of yellow crystals, m.p. 214 °C (decomp.). The IR spectrum displayed a strong band at 1710 cm^{-1} (carbonyl stretch) and a broad band centered at 3300 cm^{-1} (hydroxy stretch). The parent and base peaks in the mass spectrum were found at 392 amu. Another prominent peak was found at 295 amu, consistent with a cyclohexanonyl free radical fragmentation. An NMR spectrum of the product in $CDCl_3$ displayed a singlet at 3.8 δ, area corresponding to 5H, consistent with the unsubstituted ring in a ferrocenyl group at a saturated carbon.

X-ray data. The crystal used was obtained by recrystallization from 95 % ethanol. Unit cell dimensions and diffracted intensities were measured with an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. The measurements were made at ca. −135 °C and Mo*K*a radiation (λ = 0.71069 Å) was used. The crystal size was less than 0.25 mm in any direction. Cell parameters were determined from a least-squares fit to the diffractometer settings of 25 general reflections. The crystals are monoclinic, space group $P2_1/n$, with a = 7.436(5), b = 8.320(3), c = 30.718(10) Å, β = 95.64(4)°, Z = 4, d_x = 1.383 g cm^{-3} and μ(Mo*K*a) = 8.12 cm^{-1}. Reflection intensities were recorded using the ω-scan technique with a constant scan rate of 5° min^{-1} and a minimum scan width of 1.20° including background scans of 0.20° at the beginning and at the end of each scan. Crystal orient-

Table 1. Positional parameters and their estimated standard deviations.

Atom	x	y	z	B/Å^2
Fe	0.52545(9)	0.01281(8)	0.30754(2)	3.17(1)
O1	0.3572(5)	0.5595(4)	0.4320(1)	4.36(8)
O2	0.6206(5)	0.2815(4)	0.4849(1)	4.63(8)
C1	0.787(1)	−0.043(1)	0.2998(3)	4.2[a]
C2	0.758(1)	−0.056(1)	0.3430(3)	4.2[a]
C3	0.630(1)	−0.174(1)	0.3463(3)	4.2[a]
C4	0.577(1)	−0.234(1)	0.3055(3)	4.2[a]
C5	0.675(1)	−0.150(1)	0.2765(3)	4.2[a]
C′1	0.800(1)	−0.007(1)	0.3188(3)	4.2[a]
C′2	0.712(2)	−0.093(1)	0.3527(3)	4.2[a]
C′3	0.592(1)	−0.209(1)	0.3324(3)	4.2[a]
C′4	0.599(1)	−0.203(1)	0.2845(3)	4.2[a]
C′5	0.734(2)	−0.077(1)	0.2775(3)	4.2[a]
C6	0.2685(6)	0.0683(6)	0.3193(1)	3.1(1)
C7	0.2809(7)	0.0529(6)	0.2737(1)	3.8(1)
C8	0.4098(7)	0.1673(6)	0.2621(1)	4.1(1)
C9	0.4724(7)	0.2527(6)	0.3000(1)	3.5(1)
C10	0.3866(6)	0.1918(5)	0.3363(1)	2.54(9)
C11	0.3990(6)	0.2718(5)	0.3808(1)	2.68(9)
C12	0.2168(6)	0.3489(5)	0.3881(1)	2.89(9)
C13	0.1478(7)	0.4660(5)	0.3523(1)	3.7(1)
C14	−0.0388(7)	0.5292(6)	0.3600(2)	5.1(1)
C15	−0.0321(9)	0.6123(7)	0.4044(2)	5.9(1)
C16	0.0417(7)	0.5018(7)	0.4408(1)	4.9(1)
C17	0.2274(7)	0.4329(6)	0.4332(1)	3.4(1)
C18	0.4748(7)	0.1653(5)	0.4193(1)	3.2(1)
C19	0.4844(7)	0.2613(6)	0.4611(1)	3.6(1)
C20	0.2997(7)	0.3185(6)	0.4709(1)	3.6(1)
C21	0.1875(8)	0.1695(6)	0.4803(2)	5.0(1)
C22	0.1869(8)	0.0367(6)	0.4456(2)	4.8(1)
C23	0.3717(8)	0.0113(6)	0.4288(1)	4.5(1)

[a] Indicates the common isotropic thermal parameter. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

ation was checked at intervals of 400 recordings, and 3 standard reflections were re-measured every 2 h. These standard reflections showed no significant intensity change during the course of the measurements. Of the 4865 reflections with $2\theta \leq 56°$ measured, only 2495 had $I > 3\sigma(I)$ and were regarded as observed. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. Computer programs used in this investigation were supplied by Enraf-Nonius (SDP-plus 1983 and CAD 4-OS11).

Structure determination

The structure was solved by use of Patterson maps, and refined as described in Ref. 1 with $w = [\sigma(F)^2 + (0.03F)^2]^{-1}$. During refinement it soon became apparent that the unsubstituted cyclopentadienyl ring was disordered. A model in which the atoms of two statistically distributed "half"-rings C1–C5 and C′1–C′5 (Fig. 2) were given occupancies of 0.52 and 0.48, respectively, seemed to give the best result. Hydrogen atoms bonded to carbon were placed in fixed model positions with C–H bond lengths of 0.95 Å. The hydroxy hydrogen atom was not located in the difference maps and was therefore not included. All hydrogen atoms and the disordered carbon atoms were given constant isotropic *B* values of 4.2 during the last cycles of refinement. These values were the averages of the *B*'s found for the respective atoms during earlier refinement. The

Table 2. Interatomic distances (Å) and angles (°) with standard deviations.

Distance			
Fe–C6	2.032(3)	C14–C15	1.525(5)
Fe–C7	2.031(4)	C15–C16	1.509(5)
Fe–C8	2.026(4)	C16–C17	1.534(5)
Fe–C9	2.044(4)	C17–C12	1.546(4)
Fe–C10	2.060(3)	C17–O1	1.432(4)
C6–C7	1.417(5)	C17–C20	1.553(5)
C7–C8	1.422(5)	C11–C18	1.540(4)
C8–C9	1.404(5)	C18–C19	1.509(5)
C9–C10	1.432(4)	C19–O2	1.201(4)
C10–C6	1.417(5)	C19–C20	1.512(5)
C10–C11	1.514(4)	C20–C21	1.537(5)
C11–C12	1.536(5)	C21–C22	1.538(6)
C12–C13	1.521(4)	C22–C23	1.528(6)
C13–C14	1.524(5)	C23–C18	1.536(5)
Angle			
C6–C7–C8	107.4(3)	C16–C17–O1	110.4(3)
C7–C8–C9	107.8(3)	C16–C17–C12	109.8(3)
C8–C9–C10	109.3(3)	C16–C17–C20	111.5(3)
C9–C10–C6	106.1(3)	O1–C17–C12	106.5(3)
C10–C6–C7	109.4(3)	O1–C17–C20	106.6(3)
C6–C10–C11	129.2(3)	C17–C20–C19	107.4(3)
C9–C10–C11	123.7(3)	C17–C20–C21	118.7(3)
C10–C11–C12	109.9(3)	C19–C20–C21	107.7(3)
C10–C11–C18	115.1(3)	C20–C19–O2	124.3(3)
C12–C11–C18	112.9(3)	C20–C19–C18	111.6(3)
C11–C12–C13	113.6(3)	C18–C19–O2	124.0(4)
C11–C12–C17	110.6(3)	C20–C21–C22	114.4(3)
C13–C12–C17	110.1(3)	C21–C22–C23	113.0(4)
C12–C13–C14	110.9(3)	C22–C23–C18	115.5(3)
C13–C14–C15	110.2(4)	C23–C18–C11	118.4(3)
C14–C15–C16	111.4(3)	C23–C18–C19	105.2(3)
C15–C16–C17	112.4(3)		

Table 3. Molecular planes.

No. of plane	Atoms in plane	Δ^a	Dist. to other atoms/Å	Interplanar angles/°
1	C1–C5	0.007	C6–C10:3.255–3.408	1–2 2.5
2	C′1–C′5	0.009	C6–C10:3.132–3.375	1–3 4.0
3	C6–C10	0.005		2–3 5.9

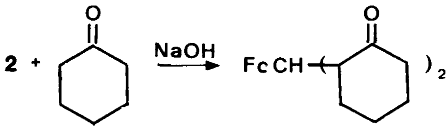
[a]Represents the maximum deviation from planarity.

other atoms were refined with anisotropic temperature factors. The refinement resulted in a final conventional R = 0.057; R_ω = 0.059, S = 1.77. A final difference map had no spurious peaks higher than 0.57 e Å^{-3}.

Results and discussion

Atomic parameters are listed in Table 1, interatomic distances and angles in Table 2, and molecular planes in Table 3. Listings of observed and calculated structure factors, anisotropic temperature factors and hydrogen atom parameters are available from one of the authors (K.M.-M.) on request. Fig. 1 shows the structure of the substituted cyclopentadienyl ring and its substituent. Fig. 2 shows the structure of the ferrocenyl group with the disorder indicated.

Structure and probable reaction mechanism. The structural results show that the reaction between ferrocenecarboxaldehyde and cyclohexanone has resulted in the formation of 8-ferrocenyl-2-hydroxytricyclo[7,3,1,0^{2,7}]tridecan-13-one (**1**). This product is also consistent with the molecular weight found from the mass spectrum. It is quite different from the Claisen-Schmidt reaction product expected, viz. **2**. However, **2** may react with excess cyclohexanone (Michael addition) according to:



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An internal aldol condensation then takes place in **3**, resulting in the observed product **1** (Fig. 1).

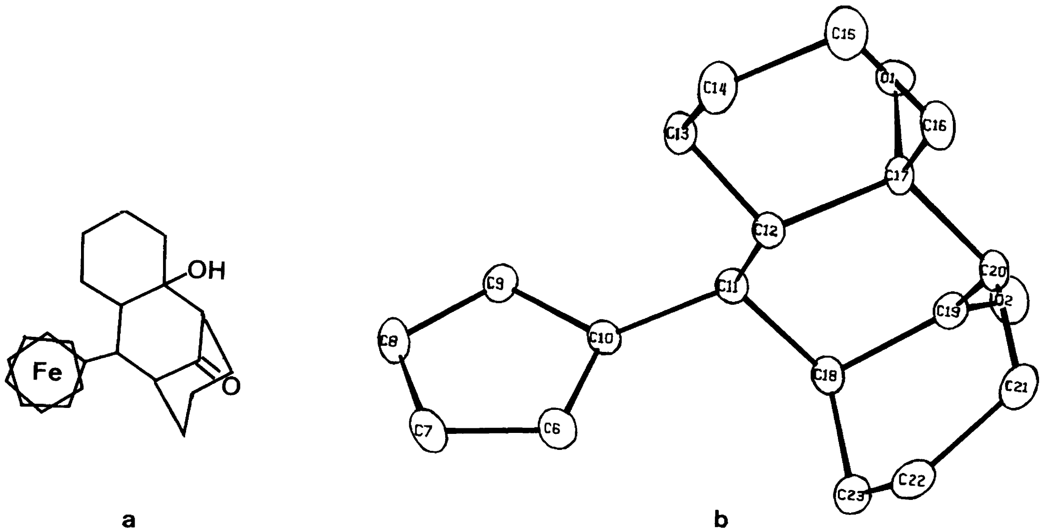

Fig. 1. (a) The schematic structure of the molecule **1**. (b) The structure of the substituted cyclopentadienyl ring and its substituent.

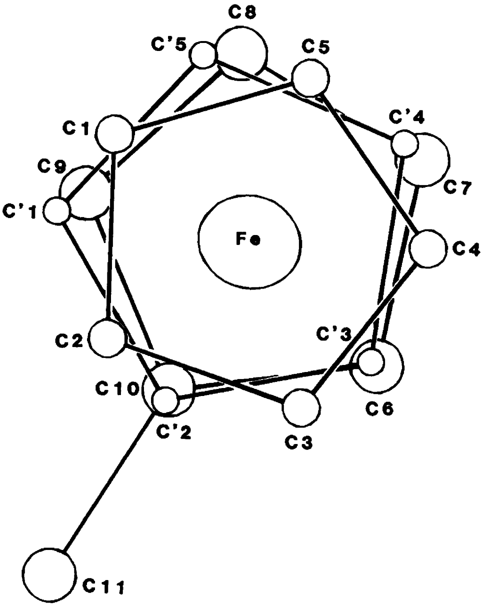

Fig. 2. The structure of the ferrocenyl group seen along the normal to the substituted cyclopentadienyl ring. The spherical atoms represent in order of decreasing size: Ring **A** (ordered), ring **B** (disordered, atoms C1–C5, occupancies = 0.52) and ring **C** (disordered, atoms C'1–C'5; occupancies = 0.48).

In the solid state, the molecules are knitted together in pairs across centers of symmetry by means of O1···O2 hydrogen bonds of length 2.867(4) Å. There are no other particularly short intermolecular contacts.

The ferrocenyl group. The substituted cyclopentadienyl group, (**A**), has normal bond lengths and angles. The C–C bond lengths are in the range 1.404–1.432 Å with an average of 1.418 Å. In the unsubstituted, disordered ring, made up of two approximately half-weight rings, C1–C5 (**B**) and C'1–C'5 (**C**), the corresponding averages are 1.377 and 1.456 Å. These values may be compared to average values of 1.400, 1.421 and 1.391 Å found in other mono-substituted ferrocenes,[2,3,4] or to 1.429 and 1.395 Å found in low-temperature studies of the monoclinic and orthorhombic forms of ferrocene itself.[5,6] The disordered part of the ferrocenyl group is not accurately determined. However, large differences between rings in ferrocenes where high values of the thermal parameters for one ring indicated the possibility of disorder have also been found earlier.[4] The average Fe–C distances are 2.039, 2.053 and 2.039 Å for rings **A**, **B** and **C**, respectively. These values are normal for ferrocenes.[2,4,7]

Fig. 2 shows the ferrocene moiety seen along the normal to the plane of the substituted cyclopentadienyl ring. Rings **A**, **B** and **C** are indicated by spherical atoms of decreasing size. With **A** as a reference, ring **B** is rotated ca. 25.5° (36° represents a staggered conformation) and ring **C** is rotated ca. −5.5° (0° represents an eclipsed conformation). Ferrocene itself seems to prefer an eclipsed or nearly eclipsed conformation.[5,6,8] However, in the disordered ferrocene structures, more than two conformations were also suggested.[6,9] In any case, the barrier to internal rotation was found to be only 3.8(13) kJ mol^{-1}.[10] The cyclopentadienyl rings are planar (Table 3) and the distances from the iron atom to the ring planes are 1.643(1), 1.685(1) and 1.619(1) Å for **A**, **B** and **C**, respectively. They may be compared to 1.654 and 1.652 Å found in ferrocenylmethylmethane *S*-methyltrithiocarbonate.[4] The large differences in the C–C bond lengths and in ring plane-to-metal distances for the disordered rings **B** and **C** are probably due to correlation effects. It is a bit surprising that the half-weight ring **B**, which represents the most staggered conformation, is further away from iron than ring **C**, which is nearly eclipsed with respect to ring **A**.

The substituent. The 2-hydroxytricyclo[7,3,1,0^{2,7}]-tridecan-13-one group is shown in Fig. 1. It consists of three fused cyclohexane rings with chair conformations. Bridgehead atoms (C1 and C9) correspond to C20 and C18 in the figure. The central ring may be considered as being a hydroxycyclohexanone. The two rings with three common atoms are somewhat irregular, especially the C18–C23 ring. This may in part be due to the effect of the *sp*^{2} hybridization of C19 (carbonyl) which belongs to both rings. The hydroxy group is connected to C17, and this group forms hydrogen bonds to the carbonyl oxygen in neighbour molecules as mentioned above. Bond lengths and angles within the substituent are normal.

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