

SYNTHESIS AND STRUCTURE OF [3][4]- AND [3][5]-FERROCENOPHANE-6-ONES

Yu.T. STRUCHKOV *, G.G. ALEKSANDROV, A.Z. KREINDLIN, and M.I. RYBINSKAYA
*Institute of Organo-Element Compounds of the U.S.S.R. Academy of Sciences, Vavilov
 St. 28, Moscow (U.S.S.R.)*

(Received November 18th, 1980)

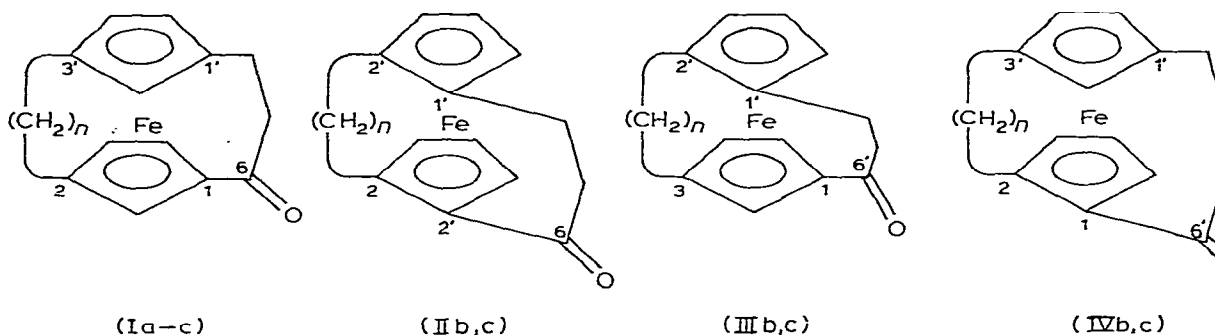
Summary

The interaction between $[n]$ -ferrocenophanes ($n = 4, 5$) and acryloyl chloride yields $[3](1,1')[n](3,3')$ - and $[3](1,1')[n](3,2')$ -ferrocenophane-6-ones. The structure of $[3](1,1')[4](3,2')$ -ferrocenophane-6-one has been determined by an X-ray analysis.

The synthesis of two-bridged $[3][4]$ - and $[3][5]$ -ferrocenophane-6-ones was carried out using the Turbitt and Watts reaction [1,2] in which a three-membered bridge was introduced in a single step by interaction between ferrocene or its derivatives and acryloyl chloride in the presence of $AlCl_3$ in CH_2Cl_2 at $-78^\circ C$. Turbitt and Watts also suggested the use of their method to introduce a second bridge into $[3]$ -ferrocenophane, and by conducting the reaction at $0^\circ C$ they isolated $[3](1,1')[3](3,3')$ -ferrocenophane-6-one (Ia, $n = 3$) with a 12% yield [2]. We have repeated this reaction at $-78^\circ C$ and isolated Ia with a 34% yield.

Using this reaction for the synthesis of $[3][4]$ -ferrocenophane-6-one from $[4]$ -ferrocenophane, we obtained two bridged products, one with melting point of $84-86^\circ C$ and the other with a melting point of $125-126^\circ C$, their yields being 12 and 11%, respectively. Theoretically, the formation of four two-bridged products should occur: $[3](1,1')[4](3,3')$ -ferrocenophane-6-one (Ib, $n = 4$), $[3](1,1')[4](2,2')$ -ferrocenophane-6-one (IIb, $n = 4$), $[3](1,1')[4](3,2')$ -ferrocenophane-6-one (IIIb, $n = 4$), and $[3](1,1')[4](2,3')$ -ferrocenophane-6-one (IVb, $n = 4$). Taking into consideration the result obtained by Turbitt and Watts, who obtained the $[3](1,1')[3](3,3')$ -isomer, it could be assumed that one of the products also had the $[3](1,1')[4](3,3')$ structure. Indeed, we identified the product with a melting point of $84-86^\circ C$ as Ib, as all its spectral characteristics (see Table 1) were found to be identical with those of the ketone described previously by two groups of investigators [3-5].

However, as far as the other two-bridged product is concerned, ascribing a



particular structure to it was difficult due to the fact that different authors attributed different structures to the isomer with a melting point of 125–126° C. Hisatome et al. [4] attributed to this compound the [3](1,1')[4](3,2')-structure, while Brown et al. [5] assumed it to be the [3](1,1')[4](2,2')-isomer. Because of this discrepancy and the impossibility of unambiguously determining its structure from spectral data we have subjected the isomer mentioned to an X-ray analysis.

By this study we have established that IIIb is [3]-(1,1')[4](3,2')-ferrocenophane-6-one. The structure of IIIb with bond lengths is shown in Fig. 1 and bond angles are listed in Table 1.

An interesting feature of IIIb is the presence of three- and four-membered bridges, and as expected, the three-membered bridge exerts a stronger pulling-together effect on the Cp rings linked by it than does the four-membered bridge (the geometry of ferrocenophane with short bridges ($n = 2-4$) has been treated in detail earlier [6]. This effect disturbs the parallelism of the Cp ligands (dihedral angle of 12.2°) and the equality of the Fe–C(Cp) bond lengths: the distances of 1.955(3) and 2.008(3) Å from Fe to C(1) and C(1'), i.e. to the atoms linked by a three-membered $-\text{CH}_2\text{CH}_2\text{C}(\text{O})-$ bridge, are substantially shorter than those to the unbridged β -atoms C(4) and C(4') (2.061(3) and 2.066(3) Å). The difference in the pulling-together effect of the three- and

TABLE I
BOND ANGLES (DEGREES)

Angle	Angle	Angle			
C(2)C(1)C(5)	106.8(3)	C(2')C(1')C(5')	106.7(3)	OC(6)C(1)	121.7(3)
C(2)C(1)C(6)	124.5(3)	C(2')C(1')C(8)	129.6(3)	OC(6)C(7)	121.2(3)
C(5)C(1)C(6)	124.8(3)	C(5')C(1')C(8)	123.6(3)	C(1)C(6)C(7)	117.1(3)
C(1)C(2)C(3)	109.3(3)	C(1')C(2')C(3')	107.5(3)	C(6)C(7)C(8)	115.4(3)
C(2)C(3)C(4)	106.7(3)	C(1')C(2')C(12)	126.9(3)	C(1')C(8)C(7)	116.8(3)
C(2)C(3)C(9)	125.4(3)	C(3')C(2')C(12)	125.6(3)	C(3)C(9)C(10)	115.9(3)
C(4)C(3)C(9)	127.9(3)	C(2')C(3')C(4')	109.0(3)	C(9)C(10)C(11)	119.3(3)
C(3)C(4)C(5)	109.0(3)	C(3')C(4')C(5')	107.5(3)	C(10)C(11)C(12)	118.6(3)
C(1)C(5)C(4)	108.1(3)	C(1')C(5')C(4')	109.2(3)	C(2')C(12)C(11)	116.8(3)

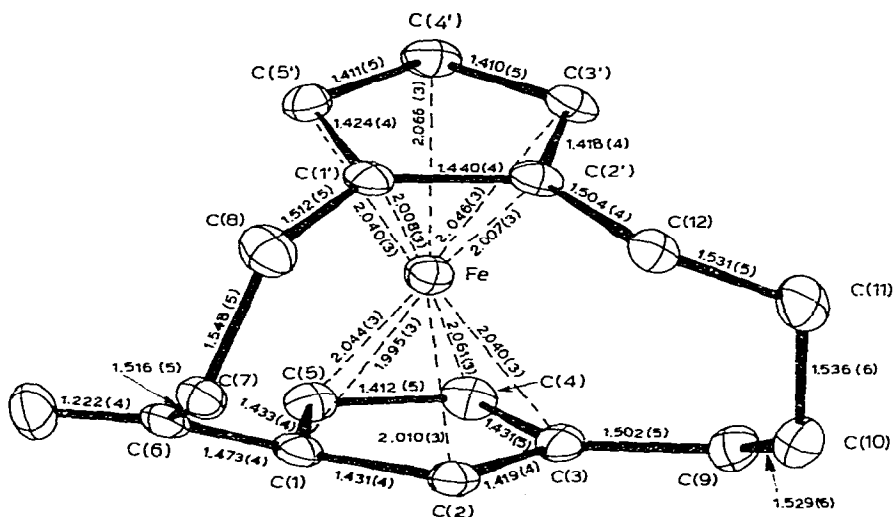


Fig. 1. The structure of compound IIIb.

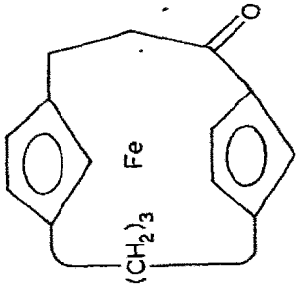
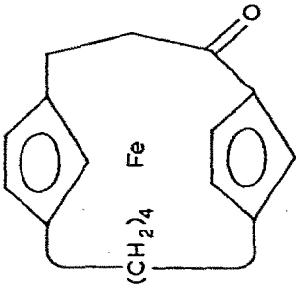
four-membered bridges in IIIb is illustrated by deviations of the C atoms linked with the Cp-ring from the mean planes of the latter: C(6) and C(8) deviate 0.495 and 0.085 Å, respectively, and C(9) and C(12) by 0.101 and 0.044 Å towards the Fe atom. The mutual orientation of the Cp rings is intermediate between eclipsed and staggered and one ring is rotated relative to the other by the angle $\varphi = 27^\circ$. The geometry of the ferrocene moiety is characterized by average Fe—C and C—C bond lengths of 2.032(3) and 1.431(5) Å, respectively, which are close to those found in other ferrocenophanes [6,7] and ferrocene [8]. The bond lengths in the bridging groups, C(bridge)—C(Cp) 1.506(4) Å, C(bridge)—C(bridge) 1.536(4) Å, C(6)—C(Cp) 1.473(4) Å, and C(6)=O 1.222(4) Å are close to the standard values [9] for C(sp^3)—C(sp^2) 1.504, C(sp^3)—C(sp^3) 1.534, C(sp^2)—C(sp^2) 1.474, and C(sp^2)=O 1.215 Å.

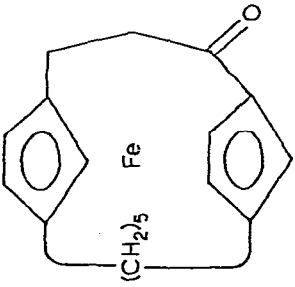
The presence of two bridges in IIIb leads to the formation of a 12-membered cycle with the C(1), C(6), C(8), C(3), C(9), C(11), and C(12) atoms lying in the same plane (the maximum deviation from the mean plane of these seven atoms are -0.15 and 0.15 Å for C(6) and C(8), respectively) and with C(2), C(7) and C(10) at distances of -0.59 , -0.78 , and -0.85 Å on one side of this plane and with C(1) and C(2) at distances of 1.16 and 1.20 Å on the other side. The torsion angles characterizing the conformation of the 12-membered macrocycle are as follows: C(1)C(2)C(3)C(9), 175; C(7)C(6)C(1)C(2), 10; C(2)C(3)C(9)-C(10), -21 ; C(6)C(1)C(2)C(3), -156 ; C(3)C(7)C(10)C(11), -76 ; C(10)C(11)-C(12)C(2'), -82 ; C(9)C(10)C(11)C(12), 81; C(1')C(12)C(2')C(1'), 150; C(1')-C(8)C(7)C(6), -32 ; C(12)C(2')C(1')C(8), -2 ; C(9)C(7)C(6)C(1), 77; C(2')-C(1')C(8)C(7), -94° .

Having established the structure of the products of the reaction between [4]-ferrocenophane and acryloyl chloride, we used the above method to introduce a second bridge into [5]-ferrocenophane.

This time too, two doubly bridged products with melting points of 149—

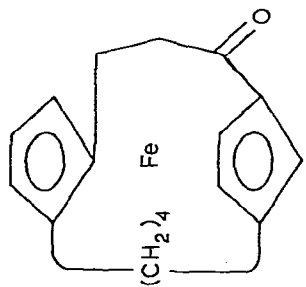
TABLE 2
PROPERTIES OF THE COMPOUNDS SYNTHESIZED

Compound	Melting point (°C)	IR spectrum, $\nu(\text{CO})$ (cm^{-1})	Mass spectrum (m/e)	PMR spectrum (ppm)		Elemental analysis		
				C_5H_3	CH_2	Found	(calcd.) (%)	
 <p>(Ia) $\text{C}_{16}\text{H}_{16}\text{FeO}$</p>	105-107 (heptane)	1670 ^a	280 M^+ 252 ($M - \text{CO}$) ⁺	4.83(1) 4.61(1) 4.52(1) 4.44(1) 4.23(1) 3.79(1)	3.01(2) 2.13(8)	68.68 (68.59)	5.74 (5.76)	20.10 (19.94)
 <p>(Ib) $\text{C}_{17}\text{H}_{16}\text{FeO}$</p>	84-86 (heptane)	1670	294 M^+ 266 ($M - \text{CO}$) ⁺ 251 ($M - \text{COCH}_3$) ⁺ 238 ($M - \text{COC}_2\text{H}_4$) ⁺	4.88(1) 4.63(2) 4.39(1) 4.27(1) 3.92(1)	2.81(4) 2.23(4) 1.81(4)	69.25 (69.34)	6.21 (6.26)	—



(Ic)
 $C_{18}H_{20}FeO$

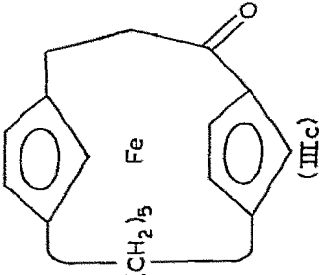
104-106 (heptane)	1665 ^c	308 M^+ 280 ($M - CO$) ⁺	4.76(1) 4.54(2) 4.27(1) 3.92(1)	2.09(4) 1.78(6)	70.61 (70.15)	6.65 (6.54)
----------------------	-------------------	--	--	--------------------	------------------	----------------



(IIIb)
 $C_{17}H_{18}FeO$

125-126 (heptane)	1650 ^d	294 M^+ 266 ($M - CO$) ⁺ 251 ($M - COCH_3$) ⁺ 238 ($M - COC_2H_4$) ⁺	4.90(1) 4.43(2) 4.26(2) 3.90(1)	3.14(4) 2.87(4) 2.23(4)	69.07 (69.34)	6.07 (6.26)
----------------------	-------------------	--	--	-------------------------------	------------------	----------------

TABLE 2 (continued)
 PROPERTIES OF THE COMPOUNDS SYNTHESIZED

Compound	Melting point (°C)	IR spec-trum, $\nu(\text{CO})$ (cm^{-1})	Mass spectrum (m/e)	PMR spectrum (ppm)		Elemental analysis		
				C_5H_5	CH_2	Found (calcd.) (%)	C H Fe	
 <p>(IIIc) $\text{C}_{10}\text{H}_{20}\text{FeO}$</p>	149-151 (hexane)	1680	308 M^+ 280 ($M - \text{CO}$) ^a 265 ($M - \text{COCH}_3$) ^a 251 ($M - \text{COC}_2\text{H}_5$) ^a	4.79(1) 4.52(1) 4.39(1) 4.23(1) 4.05(1) 3.72(1)	2.92 2.78 2.44 1.93	69.73 (70.15)	6.54 (6.27)	18.12 (18.12)

^a $\nu(\text{CO}) = 1665 \text{ cm}^{-1}$ [15]; ^b $\nu(\text{CO}) = 1662 \text{ cm}^{-1}$ [3], 1680 cm^{-1} [5]; ^c $\nu(\text{CO}) = 1660 \text{ cm}^{-1}$ [5]; ^d $\nu(\text{CO}) = 1663 \text{ cm}^{-1}$ [4]. For the (1,1') [3] (2,2') [4]-isomer $\nu(\text{CO}) = 1650 \text{ cm}^{-1}$ [5], 1648 cm^{-1} [4]; for the (1,1') [3] (2,2') [5] isomer $\nu(\text{CO}) = 1680 \text{ cm}^{-1}$ [5].

151°C and 104–105°C were isolated in a 1 : 6 ratio. The isomer with the melting point of 104–105°C is described in the literature and its structure was determined as being [3](1,1')[5](3,3') [5]. Bearing this fact in mind, and taking into account the results of introducing a second bridge into [3]- and [4]-ferrocenophanes, we believe that the product with the melting point of 104–105°C has a [3](1,1')[5](3,3') structure (Ic, $n = 5$), while the product with the melting point of 149–151°C seems to be a [3](1,1')[5](3,2') isomer (IIIc, $n = 5$).

The properties of all the compounds synthesized are summarized in Table 2 which also lists the values of $\nu(\text{C}=\text{O})$ taken from the literature. As can be seen from Table 2, the IR spectra have a $\nu(\text{C}=\text{O})$ band at 1648–1680 cm^{-1} and the tabulated data also show that there is no clearly defined correlation between a $\nu(\text{C}=\text{O})$ value and the structure, although attempts to establish such a correlation have been made earlier [4]. Other spectral characteristics do not provide any unambiguous data as to the structure of these compounds.

The mass spectra of all compounds have peaks corresponding to the M^+ and $(M - \text{CO})^+$ ions, and others. In the PMR spectra one can see two groups of complex multiplets in the 1.70 to 3.20 and 3.70 to 4.90 ppm regions typical of protons of the $-\text{CH}_2-$ groups in bridges and C_5H_3 rings, respectively.

In conclusion we should also like to note the changes in the ratios between products of the reaction of [4]- and [5]-ferrocenophanes with acryloyl chloride. For example, the ratio of [3](1,1')[4](3,2') to [3](1,1')[4](3,3') is 1 : 1.15, while that of [3](1,1')[5](3,2') to [3](1,1')[5](3,3') is 1 : 6. As in the case of acetylation this change seems to be due to the greater steric hindrance caused by the five-membered bridge compared to that caused by the four-membered bridge [10].

Experimental

The PMR spectra were measured in CDCl_3 solution using a Perkin-Elmer R 12 spectrometer (60 MHz), chemical shifts being given with respect to TMS. The IR spectra were measured with a UR-20 spectrometer and the mass spectra with an AEI MS-30 instrument.

The X-ray analysis was carried out using a Syntex P2₁ 4-circle automatic diffractometer (room temperature) λ_{Mo} ; graphite monochromator; $2 \leq 2\theta \leq 50^\circ$, $\theta/2\theta$ scan; 1727 reflections with $F^2 \geq 2\sigma$; heavy-atom method; full-matrix least squares refinement (anisotropic for non-hydrogen and isotropic for hydrogen atoms); $R = 0.0328$, $R_G = 0.0321$. Crystals of IIIb are monoclinic, at 20°C $a = 7.455(5)$, $b = 19.976(9)$, $c = 9.154(6)$ Å, $\beta = 107.87(4)^\circ$, $V = 1297(1)$ Å³, $M = 294.2$, $d_{\text{calc}} = 1.51$ g cm^{-3} , $Z = 4$, space group $P2_1/n$. Atomic coordinates and temperature factors are given in Table 3.

The [3]-ferrocenophane-6-one (IV) [1], [4]-ferrocenophane-7-one (V) [5], [5]-ferrocenophane-6-,10-dione (VI) [11], and acryloyl chloride [14] used in this work prepared by known methods. The reduction of IV, V and VI with $\text{NaBH}_4/\text{AlCl}_3$ mixture in THF [12], $\text{LiAlH}_4/\text{AlCl}_3$ in benzene/ether [13], and $\text{NaBH}_4/\text{AlCl}_3$ in THF [12] has been described earlier. The resulting [3]-, [4]- and [5]-ferrocenophanes were purified by chromatography on a Al_2O_3 column, petroleum ether being used as the eluent.

TABLE 3
 ATOMIC COORDINATES MULTIPLIED BY 10^4 (FOR Fe BY 10^5 , FOR H BY 10^3)

Atom	X	Y	Z	H ₁₁	H ₁₂	H ₁₃	H ₂₃
Fe	8678(6)	8743(2)	24481(6)	2.14(2)	2.28(2)	3.05(2)	0.09
O	-777(3)	1801(1)	-1174(3)	5.0(1)	4.9(1)	3.1(1)	0.44
C(1)	-685(4)	1650(1)	1402(3)	2.5(1)	2.5(1)	3.3(1)	0.4(1)
C(2)	152(4)	1788(1)	3001(4)	2.5(1)	2.5(1)	3.4(1)	-0.4(1)
C(3)	-443(4)	1298(1)	3875(3)	2.4(1)	3.5(1)	3.3(1)	-0.2(1)
C(4)	-1732(4)	868(2)	2801(4)	2.3(1)	3.7(1)	4.1(2)	0.0(2)
C(6)	-1890(4)	1082(2)	1297(4)	2.0(1)	3.6(2)	3.6(2)	-0.5(1)
C(1')	3289(4)	1018(1)	1962(3)	2.1(1)	3.0(1)	3.4(1)	0.2(1)
C(2')	3643(4)	868(1)	3565(2)	2.0(1)	2.5(1)	3.6(1)	0.0(1)
C(3')	2896(4)	222(1)	3651(4)	2.6(1)	2.5(1)	3.6(2)	0.4(1)
C(4')	2059(4)	-29(2)	2165(4)	3.2(1)	2.2(1)	4.5(2)	-0.6(1)
C(5')	2328(4)	455(2)	1125(4)	3.1(2)	3.6(2)	3.3(2)	-0.5(1)
C(6)	94(4)	1871(1)	185(4)	3.5(2)	2.3(1)	3.5(2)	0.2(1)
C(7)	2053(5)	2166(2)	690(4)	4.0(2)	2.7(1)	3.5(2)	0.4(1)
C(8)	3688(5)	1652(2)	1212(5)	3.0(2)	4.1(2)	4.4(2)	1.1(1)
C(9)	247(5)	1239(2)	5594(4)	3.5(2)	4.6(2)	3.7(2)	-0.0(1)
C(10)	2141(5)	1572(2)	6395(4)	4.6(2)	4.5(2)	3.0(2)	-0.6(1)
C(11)	3966(5)	1231(2)	6345(4)	3.2(2)	4.3(2)	3.4(2)	-0.3(1)
C(12)	4578(5)	1315(2)	4904(4)	2.6(2)	2.7(1)	4.0(2)	-0.1(1)
Atom	X	Y	Z	H			
H(2)	102(4)	211(1)	343(3)	2.0(6)	H(4)	-228(4)	3.8(7)
H(5)	-253(4)	89(1)	43(3)	3.1(7)	H(3')	290(4)	3.8(7)
H(4')	147(4)	-42(2)	194(4)	4.0(7)	H(6')	200(4)	3.6(7)
H(7)	217(4)	248(2)	145(3)	3.6(7)	H(7)	235(4)	3.5(7)
H(8)	408(4)	154(1)	32(4)	4.2(8)	H(8)	479(5)	4.7(8)
H(9)	19(4)	76(1)	58(3)	3.4(7)	H(9)	-62(4)	4.1(8)
H(10)	212(4)	202(2)	602(3)	3.7(7)	H(10)	223(5)	5.0(8)
H(11)	499(5)	141(1)	716(4)	4.3(8)	H(11)	386(4)	3.3(7)
H(12)	447(4)	176(2)	461(3)	3.6(7)	H(12)	597(3)	3.1(6)

Anisotropic temperature factors are given in the form $T = \exp[-1/4(h^2 a^2 + \dots + 2h_1 h_2 a^* b^* c^* R)]$

Interaction between ferrocenophanes and acryloyl chloride (general method)

A previously prepared solution of $\text{CH}_2=\text{CHCOCl}/\text{AlCl}_3$ in CH_2Cl_2 was added dropwise for 0.5 h with stirring to a solution of ferrocenophane in the same solvent at -78°C with an approximate reagent ratio of 3 : 2.8 : 1. The mixture was stirred at the same temperature for 30 h and decomposed with dilute HCl containing $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The organic layer was separated, while the aqueous layer was extracted with CH_2Cl_2 . After washing and drying over Na_2SO_4 the solvent was evaporated and the unreacted ferrocenophane, usually in a yield of 40–50%, was removed from the residue by chromatography with petroleum ether on an Al_2O_3 column. The mixture of ketones remaining in the column was fractionated with a petroleum ether/benzene mixture, the amount of benzene in the mixture being gradually increased. The fractions eluted in this manner were additionally separated by preparative thin layer chromatography on Al_2O_3 (neutral activity grade II according to Brockman, produced by Roanal (Hungary)) or silica gel (40/100 or 100/160 produced by Chemapol (Czechoslovakia) with benzene/ether = 4/1 or chloroform/ether = 8/1 eluent. Chromatograms revealed a number of other substances in trace amounts, whose structures were not studied.

[3](1,1)[3](3,3') ferrocenophane-6-one. 9.2 g (0.04 mol) of [3]-ferrocenophane, 9.5 g (0.105 mol) of $\text{CH}_2=\text{CHCOCl}$, and 13.3 g (0.1 mol) of AlCl_3 yielded 1.8 g (34%) of (Ia); 4.8 g of [3]-ferrocenophane were recovered.

[3](1,1')[4](3,3')- and [3](1,1')[4](3,2')-ferrocenophane-6-ones. 12.2 g (0.05 mol) of 4-ferrocenophane, 13.6 g (0.15 mol) of $\text{CH}_2=\text{CHCOCl}$, and 17.6 g (0.13 mol) of AlCl_3 yielded 1.4 g (12%) of Ib and 1.2 g 11% of IIb; 3.0 g of [4]-ferrocenophane were recovered.

[3](1,1')[5](3,3')- and [3](1,1')[5](3,2')-ferrocenophane-6-ones. 8.9 g (0.35 mol) of [5]-ferrocenophane, 9.5 g (0.105 mol) of $\text{CH}_2=\text{CHCOCl}$ and 13.0 g (0.097 mol) of AlCl_3 yielded 1.2 g (15.5%) of Ic and 0.2 g (2.5%) of IIIb; 2.6 g of [5]-ferrocenophane were recovered.

References

- 1 T.D. Turbitt and W.E. Watts, *J. Organometal. Chem.*, 46 (1972) 109.
- 2 W. Crawford, T.D. Turbitt and W.E. Watts, *J. Organometal. Chem.*, 105 (1976) 341.
- 3 M. Hisatome, T. Sakamoto and K. Yamakawa, *J. Organometal. Chem.*, 107 (1976) 87.
- 4 M. Hisatome, N. Watanabe, T. Sakamoto and K. Yamakawa, *J. Organometal. Chem.*, 125 (1977) 79.
- 5 A.D. Brown, Jr. and J.A. Winstead, *J. Org. Chem.*, 36 (1971) 2832.
- 6 T.N. Salmnikova, V.G. Andrianov and Yu.T. Struchkov, *Koord. Khimiya*, 3 (1977) 768.
- 7 T.N. Salmnikova, V.G. Andrianov, M.Yu. Antipin and Yu.T. Struchkov, *Koord. Khimiya*, 3 (1977) 939.
- 8 J.D. Dunitz, L.E. Orgell and A. Rich, *Acta Crystallogr.*, 9 (1956) 373.
- 9 O. Bastiansen and M. Traetteberg, *Tetrahedron*, 17 (1962) 147; L.E. Sutton (Ed.), *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement*, Chem. Soc., Special Publication No. 18, London, 1965.
- 10 T.H. Barr, E.S. Bolton, H.L. Lenzner and W.E. Watts, *Tetrahedron*, 25 (1969) 5245.
- 11 T.H. Barr and W.E. Watts, *Tetrahedron*, 24 (1968) 3219.
- 12 A.N. Nesmeyanov, G.B. Shulpin, M.V. Tolstaya and M.I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, 232 (1977) 1319.
- 13 A.Z. Kreindlin and M.I. Rybinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1980) 2120.
- 14 G.H. Stempl, Jr., R.P. Gross and R.P. Mariella, *J. Amer. Chem. Soc.*, 72 (1950) 2299.
- 15 K.L. Rinehart, Jr., D.E. Bublitz and D.H. Gustafson, *J. Amer. Chem. Soc.*, 85 (1963) 970.