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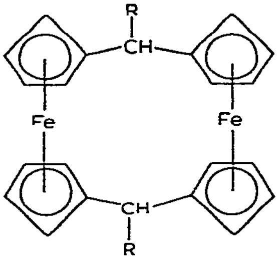
SHORT COMMUNICATION

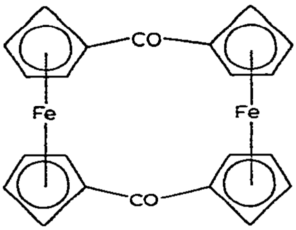
The Friedel–Crafts route to the [1.1]ferrocenophane system

It has recently been demonstrated[1] that [1.1]ferrocenophanes* (I) can be synthesised from bisfulvenes derived from 1,1′-diacylferrocenes. We now report an alternative approach involving an intramolecular Friedel-Crafts cyclisation in the key step.

Thus, aluminium chloride-catalysed reaction between ferrocene and 1,1′-bis-(chlorocarbonyl)ferrocene in dilute chloroform solution affords a mixture of products from which [1.1]ferrocenophane-1,12-dione (II) can be readily separated on account of its poor solubility in organic solvents. The compound crystallises from chloroform in fine maroon needles, m.p. >350°.



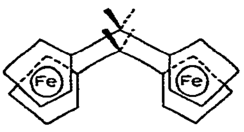
(I)



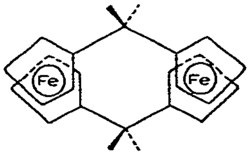
(II)

Alternatively, the same diketone can be prepared by treatment of dilute chloroform solutions of either (chlorocarbonyl)ferrocene or 1-(chlorocarbonyl)-1′-ferrocenoylferrocene** with aluminium chloride suggesting that the Lewis acid complex of the latter is an intermediate common to these synthetic routes. Reduction of the diketone in ether with lithium aluminium hydride/aluminium chloride affords the parent [1.1]ferrocenophane (I; R = H), m.p. 254–256°.

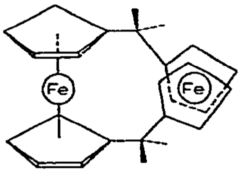
Assignment of the [1.1]ferrocenophane structure to these compounds follows from their analyses and mass spectra. The diketone, for example, gives rise to the expected (*cf.* ref. 4) intense group of molecular ion peaks around *m/e* 424 (for ^{56}Fe) with doubly charged counterparts at *m/2e* 212. The main fragmentation pathways involve successive loss of two molecules of carbon monoxide or elimination of a C_6H_4O fragment.



(III)



(IV)



(V)

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* The systematic nomenclature proposed by Smith[2] has been adopted throughout.

** The synthesis of this and related compounds will be described in a future publication[3].

The PMR spectrum of (I) ($R = H$) at 40 Mcps. in $CDCl_3$ solution consists of two triplets ($J \sim 2$ cps.) centred at τ 5.61 and 5.82 (ring protons) and a singlet at τ 6.45 (methylene protons) of relative intensity 2:2:1 respectively. Inspection of models* reveals that, of the two possible ligand arrangements, the "eclipsed" configuration (III) is much more flexible than the "staggered" form (IV). Further, by mutual rotation of the ferrocene nuclei about the ring-methylene bonds, structure (III) can easily be converted to its mirror image, by which process the *exo*- and *endo*-hydrogens of each methylene group change position. [The halfway stage in this interconversion is given by the conformation (V)]**. The magnetic equivalence of the methylene protons can be accounted for by the operation of such a process which would also render equivalent on time average the pairs of ring protons α- (and β-) to the bridges and hence produce the observed A_2B_2 pattern.

In this connection, it is significant that the ring protons in the PMR spectrum of 1,12-dimethyl[1.1]ferrocenophane (I; $R=CH_3$)[1a] appear as complex multiplets of relative intensity 1:3. Crystal structure determination[5] has established an "eclipsed" stereochemistry for this compound with the methyl groups *exo*. A rotational interconversion process such as described above is thus highly improbable since it would lead to an "eclipsed" structure in which there would be severe steric interaction between *endo*-methyl groups.

Further research in progress is designed to investigate the possibility of rotational interconversion of [1.1]ferrocenophane derivatives.

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* Dreiding ferrocene stereomodels, supplied by W. Büchi Glasapparatefabrik, Flawil, Switzerland, were used.

** Models also indicate that interconversion of the "eclipsed" and "staggered" configurations can occur only at the expense of gross deformation of preferred bond angles and distances and is therefore considered improbable.