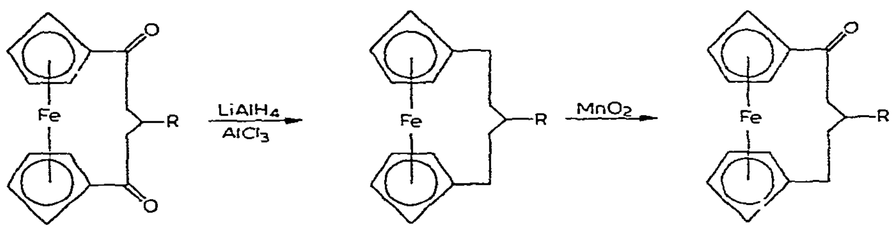
Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

PRELIMINARY NOTE

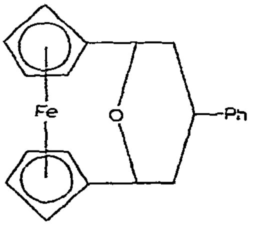
---

[5]Ferrocenophanes

In addition to the expected product of Claisen–Schmidt condensation, *viz.* 1,1'-dicinnamoylferrocene, Hauser *et al.* isolated from the base-catalysed reaction of benzaldehyde with 1,1'-diacetylferrocene a second compound for which several possible structures were suggested[1]. On the basis of infrared and ultraviolet spectral evidence, on the other hand, Furdik *et al.* reformulated[2] the structure as 3-phenyl[5]-ferrocenophane-1,5-dione (I; R = Ph)* and showed that a range of products of related structure could be prepared using other aromatic[2,4] as well as aliphatic aldehydes[5]. We wish to present conclusive evidence substantiating the bridged structure proposed by Furdik and to outline some of the chemistry of these compounds**.



(I) (II) (III)



(IV)

Thus, lithium aluminium hydride/aluminium chloride reduction of the diketone (I; R = Ph) affords 3-phenyl[5]ferrocenophane (II; R = Ph; m.p. 111–113°)† which can be selectively oxidised by manganese dioxide to the monoketone (III; R = Ph; m.p. 169–171°). The above diketone can also be converted by lithium aluminium hydride reduction followed by alumina dehydration to the novel tetrahydropyran derivative (IV) which has been obtained in two stereoisomeric modifications (m.p. 163–164.5° and 167–169°).

We have also reinvestigated the condensation between 1,1'-diacetylferrocene and formaldehyde in aqueous ethanolic sodium hydroxide solution. In addition to

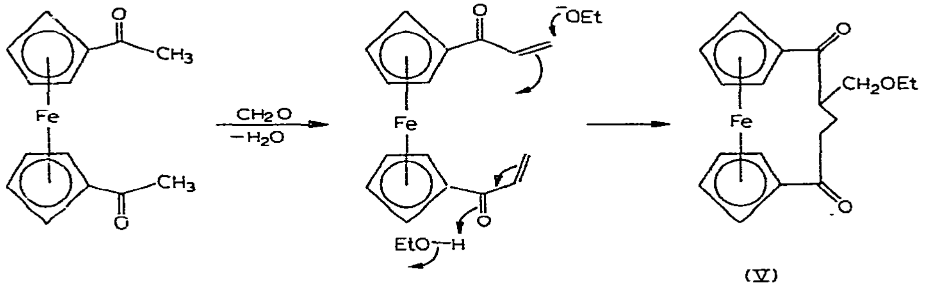
---

* The nomenclature system proposed by B. H. Smith[3] has been adopted throughout.

** Satisfactory analytical data have been obtained for all new compounds described.

† This reaction has apparently[6] been carried out by Schlögl who assigned to the product (m.p. 110–112°) the structure (II; R = Ph) on the basis of its molecular weight and lack of unsaturation.

the bridged diketone (I; R = H) described[5] by Furdik *et al.*, we have isolated as the main product of this reaction a compound (m.p. 140–142°) whose structure we formulate as 2-ethoxymethyl[5]ferrocenophane-1,5-dione (V). Since this compound can also be prepared by treatment of 1,1′-diacryloylferrocene with sodium ethoxide in ethanol, it seems probable that its formation in the condensation reaction follows a related course as shown below.



(V)

The assignment of the [5]ferrocenophane structure to these compounds follows directly from their PMR and mass spectra which in all cases were fully consistent with the proposed structures. For example, accurate mass measurement of the parent ion peak in the high resolution mass spectrum of (I) (R = H) established the molecular formula as $C_{15}H_{14}FeO_2$. The PMR spectrum ($CDCl_3$ solution, TMS internal standard) of this compound consisted of two triplets centred at τ 5.18 and 5.45 ($J \sim 2$ c/s; ring protons) and a singlet at τ 7.50 (methylene protons) in the ratio 2:2:3 respectively. Further structure proof was provided by lithium aluminium hydride/aluminium chloride reduction of the above diketone (I; R = H) to the known parent [5]ferrocenophane (II; R = H; m.p. 57–59°; lit.[7] m.p. 61–62°) which could be selectively oxidised by manganese dioxide to the monoketone (III; R = H; m.p. 116–117°).

The ready availability of simple [5]ferrocenophane derivatives makes possible the study of conformational mobility of the interannular bridge in this system and current research is directed to this end.

The authors thank Dr. P. Bladon and his staff for spectral determinations, the S.R.C. for a maintenance grant (to T.H.B.), and the Ethyl Corporation for supplies of ferrocene.

Department of Pure and Applied Chemistry,
University of Strathclyde, Glasgow (Great Britain)

T. Hugh Barr
William E. Watts

1 T. A. Mashburn, C. E. Cain and C. R. Hauser, *J. Org. Chem.*, 25 (1960) 1982.
2 M. Furdik, S. Toma and J. Suchy, *Chem. Zvesti*, 15 (1961) 45.
3 B. H. Smith, *Bridged Aromatic Compounds*, Academic Press, New York, 1964.
4 M. Furdik, S. Toma and J. Suchy, *Chem. Zvesti*, 15 (1961) 789; M. Furdik, M. Dzurilla, S. Toma and J. Suchy, *Acta Facultatis Rerum Naturalium Universitatis Comenianae, Chimia*, 8 (1964) 569.
5 M. Furdik, S. Toma and J. Suchy, *Chem. Zvesti*, 16 (1962) 449.
6 K. Schlögl, unpublished work reported in reference 3, p. 166.
7 A. Lüttringhaus and W. Kullick, *Angew. Chem.*, 70 (1958) 438; *Makromol. Chem.*, 44–46 (1961) 669.

Received April 7th, 1967