

1,4-(Ferrocen-1,1'-ylene)pentan-1-one[1-Methyl-4-oxo-(4)-ferrocenophane]¹—a Novel Cyclisation Reaction

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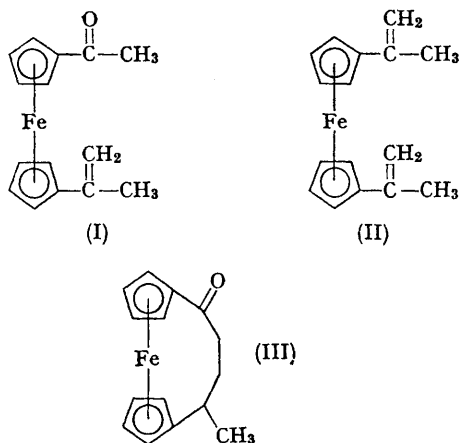
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IN connection with our work on ferrocenylethylenes² we required the mono- and di-olefins (I) and (II) which were synthesised, in fair yield, by the reaction of methylenetriphenylphosphorane with 1,1'-diacetylferrocene. We observed, however, that an excess of the base used (dimethylsulphinyl anion in dimethyl sulphoxide) led to the formation of a third product which was assigned the structure 1,4-(ferrocen-1,1'-ylene)pentan-1-one (III) on the basis of the following evidence. The analysis was correct for the formula $C_{15}H_{16}FeO$. The infrared spectrum (liquid film or Nujol mull) showed a carbonyl absorption at 1650 cm^{-1} while that of 1,4-(ferrocen-1,1'-ylene)butan-1-one³ is at 1647 cm^{-1} and that of 1,3-(ferrocen-1,1'-ylene)propan-2-one at 1680 cm^{-1} . The n.m.r. spectrum (CCl_4) is also consistent with (III) showing absorptions at τ 5.41, 5.60, 5.90, 6.03, and 6.13 as multiplets for the ferrocene ring protons, two multiplets at τ 7.42 and 7.82 for the bridge protons and a doublet at τ 8.83 ($J = 6\text{ c./sec.}$) for the methyl substituent, the three groups being in the ratio of 8:5:3.

Since it appeared that (III) must be formed from (I), by a novel base-catalysed cyclisation, (I) (15 mmole) was stirred overnight with dimethyl sodium (15 mmole) in dimethyl sulphoxide (10 ml.) at room temperature under an atmosphere of nitrogen. Subsequent work-up gave the ketone,

m.p. $81-83^\circ$, recrystallised from aqueous ethanol, in virtually quantitative yield.

The synthesis of (III) constitutes the first practical route to 1,4-(ferrocen-1,1'-ylene)butan-1-one since other routes to this system give only poor yields³ and the synthesis of the parent 1,4-(ferrocen-1,1'-ylene)butane gives only 0.05% of the desired product.⁴



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¹ Nomenclature suggested by B. H. Smith in "Bridged Aromatic Systems," Academic Press, 1964.

² W. M. Horspool and R. G. Sutherland, *Chem. Comm.*, 1966, 456.

³ M. Rosenblum, A. K. Banerjee, W. Danieli, R. W. Fish, and V. Schlatter, *J. Amer. Chem. Soc.*, 1963, **85**, 316.

⁴ A. Lutteringhaus and W. Kullick, *Angew. Chem.*, 1958, **70**, 438; *Makromol. Chem.*, 1961, **44-46**, 669.