

Behaviour of 1,3-Diferrocenylalkenes and 1,2-Diferrocenylethylene in Strong Acid. Apparent Intramolecular Reduction of α -Ferrocenyl Carbocations †

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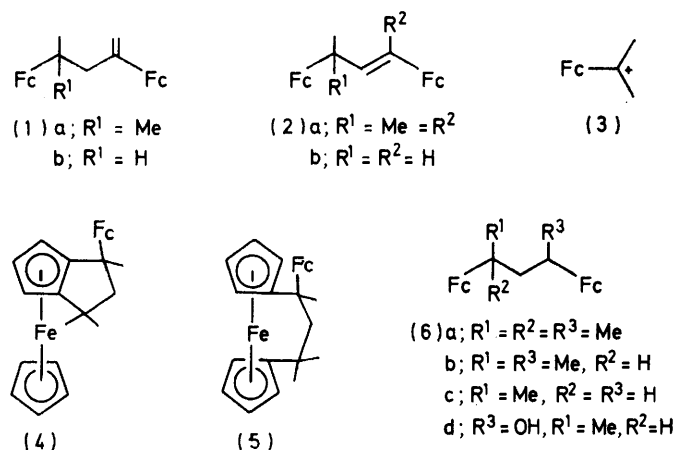
The reactions of 1,3-diferrocenylalkenes and 1,2-diferrocenylethylene in 98% sulphuric acid are described. Reduction of the alkene to an alkane occurs concomitant with oxidation of the two iron atoms to the Fe^{III} state. The reaction is considered to involve a novel intramolecular electron transfer from the iron to a carbocation centre in a ferrocene molecule. The behaviour of 2-ferrocenylpropan-2-ol in concentrated sulphuric acid yielding 2,4-diferrocenyl-2-methylpentane is rationalized by the same mechanism.

INTEREST in ferrocenyl carbocations has continued following the early observation that α -ferrocenyl cations exhibit remarkable stability.¹ Considerable attention has been directed towards the shape of the ions, particularly in relation to the involvement of the iron atom in the stabilisation. To this end X-ray² and n.m.r.³ spectral analysis have been especially useful. We have been interested in the behaviour of ferrocenyl systems towards strong acid,^{4a} and have used this medium for n.m.r. spectral studies of ferrocenyl olefins,⁵ ethers, and alcohols.⁶

In some instances the generated ion behaved differently depending upon which acid (trifluoroacetic or concentrated sulphuric) was employed. Thus an attempt to observe the ion generated by protonation of 2,4-diferrocenyl-4-methylpent-1- or -2-ene [(1a) or (2a)] in trifluoroacetic acid yielded the spectrum of the ion (3). Similar behaviour was observed for the two cyclic compounds [(4) and (5)] dissolved in the same acid.⁷ The degeneration of complex ions into simpler ions has been recognized⁸ for some time and the general concept of fragmentation has been reviewed.⁹ This process was not examined further by us but was studied by Abram and Watts,¹⁰ who established the scope of the process in ferrocenyl systems. Our investigations were concerned with diferrocenyl systems in concentrated sulphuric acid.

In particular the reactions of diferrocenyl olefins (1) and (2) and 1,2-diferrocenylethylene were studied, and a reaction path different from the fragmentation described above was uncovered. The olefins (1a) and (2a) dissolved readily in 98% sulphuric acid to yield blue-green solutions, as opposed to the dark brown expected for α -ferrocenyl carbocations in sulphuric acid. The colour and the absence of ¹H n.m.r. signals immediately sugges-

ted that ferricenium species had been formed. Quenching the sulphuric acid solution in water gave a blue-green aqueous phase which after reduction and conventional work-up yielded a hydrocarbon (6a) as the sole product. The identity of the hydrocarbon was readily established since the same product was obtained by catalytic hydrogenation of the olefin (1a) or (2a).¹¹ Thus no skeletal



change had been induced by the sulphuric acid treatment. The olefins (1b) and (2b), subjected to the same treatment in sulphuric acid, yielded, after work-up, the alkanes (6b) and (6c), respectively, readily identified by their spectra.

The reaction path envisaged for the reduction of the diferrocenyl olefins involves protonation of the olefin to afford the carbocation (7) (Scheme). It has been shown¹² that this ion can undergo intramolecular cyclisation to

† Studies in Ferrocene Derivatives, Part 20. Part 19, R. G. Sutherland, J. R. Sutton, and W. M. Horspool, *J. Organometallic Chem.*, 1976, **122**, 393.

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¹ M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

² S. Lupan, M. Kapon, M. Cais, and F. H. Herbstein, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1025.

³ For leading references see S. Braun and W. E. Watts, *J. Organometallic Chem.*, 1975, **84**, C33; A. A. Koridze, *ibid.*, p. C26; G. A. Olah and G. Liang, *J. Org. Chem.*, 1975, **40**, 1849; T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177, 185, 189, 195; J. J. Dannenberg, M. K. Levenberg, and J. H. Richards, *Tetrahedron*, 1973, **29**, 1575.

⁴ (a) W. M. Horspool, B. J. Thomson, and R. G. Sutherland, *Chem. Comm.*, 1970, 729. (b) W. M. Horspool, B. J. Thomson, and R. G. Sutherland, *Synth. Inorg. Metal-Org. Chem.*, 1973, **3**, 149.

⁵ W. M. Horspool and R. G. Sutherland, *Chem. Comm.*, 1967, 786.

⁶ R. G. Sutherland, J. R. Sutton, and W. M. Horspool, *Tetrahedron Letters*, 1973, 3283.

⁷ B. J. Thomson, Ph.D. Thesis, University of Dundee, 1970, p. 142.

⁸ F. C. Whitmore and E. E. Stahly, *J. Amer. Chem. Soc.*, 1933, **55**, 4153; 1945, **67**, 2158.

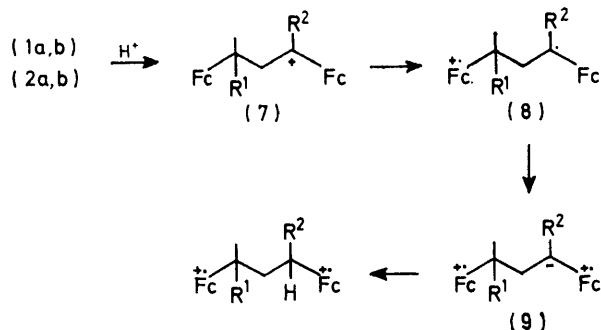
⁹ C. A. Grob and P. W. Schiess, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1.

¹⁰ T. S. Abram and W. E. Watts, *J.C.S. Perkin I*, 1975, 113.

¹¹ W. M. Horspool, P. Stanley, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc. (C)*, 1971, 1365.

¹² W. M. Horspool, R. G. Sutherland, and J. R. Sutton, *Canad. J. Chem.*, 1970, **48**, 3542.

afford compounds (4) and (5). This cyclisation occurred under a variety of conditions, including treatment with dilute sulphuric acid or in formic acid. However cyclisation, if it does occur in 98% sulphuric acid, is a reversible process, as was demonstrated for the cyclic compound (5) which gave the alkane (6a) when dissolved in sulphuric acid. The carbocation (7) is then oxidised to the free radical (8) by electron transfer from the more distant



iron in the ion, since the iron atom immediately adjacent to the cationic centre is intimately involved in the stabilization of that centre. [When both ferrocenes are involved in overlap with the electron-deficient centre reduction does not take place. Thus the attempted reduction of 1,3-diferrocenylbut-2-en-1-one in sulphuric acid, which when protonated yields an allylic cation, gave only starting material. The same result has been observed by Yamakawa and Moroe,¹³ who found that the same enone failed to undergo reduction when treated with ferrocene in hydrochloric acid.] A second electron transfer from the adjacent iron atom then affords the anion (9), which is rapidly protonated.*

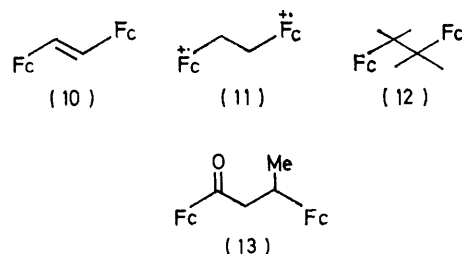
These steps (Scheme) reduce the double bond and oxidise both iron atoms to the Fe^{III} state. The formation of a bisferricenium species was demonstrated by the u.v. spectra of solutions of the olefin (10) in sulphuric acid, which show an absorption at 630 nm (ϵ 650). The full intensity of this absorption was developed in the time (ca. 30 s) it took to add the olefin to the acid, mix, and introduce the sample into the spectrometer. The peak must be due to a bisferricenium species since monoferricenium species have weaker absorptions [e.g. t-butyl-

* A referee has pointed out that intramolecular electron transfer from a ferrocene group to a free radical as suggested for the formation of (9) from (8) (Scheme) is unusual. This we cannot deny. Indeed we have not found an analogy for such a transfer in the literature. It is tempting to suggest that such an electron transfer might be expected in the reduction by zinc-acetic acid of $\text{Fc}-\text{C}^+$ to $\text{Fc}-\text{C}^-$. However in this example (M. Cais and A. Eisenstadt, *J. Org. Chem.*, 1965, **30**, 1148) the radical can take part in several reactions among which are abstraction of hydrogen from the solvent (highly likely in acetic but not in sulphuric acid) or dimerization (a metal surface reaction?). Dimerization is also the fate of $\text{Fc}-\text{C}^-$ in 0.1M-perchloric acid in water-dioxan, when the radicals are formed at a mercury electrode in the reduction of $\text{Fc}-\text{C}^+$ (J. Tirouflet, E. Laviron, C. Moise, and Y. Mugnier, *J. Organometallic Chem.*, 1973, **50**, 241). In neither of the above examples was any evidence found for intramolecular electron transfer. Our mechanism can only be taken as an hypothesis until further information is obtained concerning the behaviour of the radical (8) in concentrated sulphuric acid.

ferricenium tri-iodide shows λ_{max} 626 nm (ϵ 360)]. Thus the bisferricenium compound (11) is formed immediately the olefin (10) is dissolved in sulphuric acid. It is also evident that the oxidation of the iron atoms in (10) occurs at the same time as the reduction of the double bond, since the oxidation of 1,2-diferrocenylethane to the ferricenium species (11) takes ca. 90 min under the same conditions as dissolution of the olefin (10) in sulphuric acid.

[Oxidation of 1,2-diferrocenylethane in concentrated sulphuric acid gives material showing a visible spectrum identical with that obtained from the solution of (10) in the same medium.]

The mechanism for the oxidation-reduction depends on the ability of ferrocenyl groups to undergo electron-transfer reactions. There are in the literature several examples of electron transfer in an intermolecular sense. Thus Hawthorne¹⁴ implicated intermolecular electron transfer in the reaction of ferrocene with the triphenylmethyl cation under aerobic conditions. Pauson *et al.*¹⁵ proposed a similar exchange in the formation of 1,1'-ditriptylferrocene from ferrocene and triphenylmethyl cation under anaerobic conditions. Another intermolecular electron-transfer reaction has been reported recently where ferrocene has been used in concentrated hydrochloric acid to reduce electron-deficient olefins to alkanes,¹³ e.g. the conversion of 1,2-bis(ferrocenecarbonyl)ethylene into 1,2-bis(ferrocenecarbonyl)ethane. Intramolecular electron-transfer reactions are not so well documented, although it has been suggested that the dimerisation of, for example, the ferrocenylmethyl cation



ion in sulphuric acid results from such a process.¹⁶ Other workers¹⁷ have examined the trapping of ferrocenylbenzyl cation by nitrosobenzene. The e.s.r. of the resultant solution exhibited a spectrum typical of a nitroxide radical. However such a species could arise by a mechanism other than the trapping of a radical formed by intramolecular electron transfer.

Other diferrocenyl systems undergo the reduction process. Thus the alcohol (6d) is reduced to the alkane (6c). This presumably involves the formation of a cation as in the case of the other compounds. The

¹³ K. Yamakawa and M. Moroe, *J. Organometallic Chem.*, 1973, **50**, C43.

¹⁴ M. F. Hawthorne, *J. Org. Chem.*, 1956, **21**, 363.

¹⁵ P. L. Pauson, M. A. Sandhu, and W. E. Watts, *J. Chem. Soc. (C)*, 1966, 251.

¹⁶ K. L. Rinehart, C. J. Michejda, and P. A. Kittle, *J. Amer. Chem. Soc.*, 1959, **81**, 3162.

¹⁷ P. Ashkenazi and M. Cais, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1027.

ketone (13) is also susceptible to this treatment and affords the alkane (6c), but only in low yield in contrast with the almost quantitative yields obtained in the other systems. However since four electrons are involved in the reduction it is likely that the yield cannot exceed 50%. (Such a reduction must have an intermolecular component.)

An assessment of methods for the formation of the ion (3) was one of the main reasons for our interest in this area. We established beyond reasonable doubt that the most efficacious way of forming such ions is by protonation of the corresponding olefin⁵ in strong acid. In weaker acids, problems arise such as deprotonation of the ions or equilibration between the olefin and the ion. We have reported such behaviour in formic acid¹² and it is likely that the same behaviour was encountered in the treatment of 2-ferrocenylpropene in acetic acid with platinum and hydrogen.¹⁸ The product from this reaction was claimed to be the symmetric dimer, 2,3-diferrocenyl-2,3-dimethylbutane (12), but this was disproved by our synthesis^{4b} of compound (12). The n.m.r. spectrum of the compound isolated by Ellis¹⁸ is identical with that recorded by us for the alkane (6a). Ellis' compound probably arises by alkylation of 2-ferrocenylpropene by the ion (3) followed by deprotonation to the olefins (1a) and (2a). This olefinic mixture would be readily hydrogenated catalytically to give the alkane.

A further source of the ion (3) is the treatment of 2-ferrocenylpropan-2-ol with strong acid.^{19a} This method has been popular for ferrocenyl carbocation formation. A re-examination of the reaction of 2-ferrocenylpropan-2-ol with sulphuric acid has confirmed that the ion (3) is formed, and a ¹H n.m.r. spectrum of the ion (3) can be recorded. However work-up of solutions used for n.m.r. studies provides evidence for the oxidation of the iron. Indeed the compound isolated from the aqueous phase was the alkane (6a), contrary to the proposal of Rinehart *et al.*^{19b} who suggested that 2,3-diferrocenyl-2,3-dimethylbutane was formed. It is reasonable to assume that the genesis of compound (6a) is the same as that adumbrated above, but the mode of formation of an ion such as (7), which is the obvious precursor of the alkane, from 2-ferrocenylpropan-2-ol is not immediately apparent. The most likely explanation is that as the alcohol is dissolved in the sulphuric acid there is local dilution of the acid, permitting the establishment of equilibrium between the cation (3) and 2-ferrocenylpropene. Consequently alkylation can take place and the reduction of the ion (7) will follow as the acid strength returns to the higher value.

It is conceivable that such a reaction could occur with other ions susceptible to deprotonation; consequently the use of ferrocenyl alcohols in sulphuric acid as a source of α -ferrocenyl carbocations should be treated with caution.

¹⁸ A. F. Ellis, Ph.D. Dissertation, University of Illinois, 1963.

¹⁹ (a) J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, 1969, **91**, 4324; (b) K. L. Rinehart, P. A. Kittle, and A. F. Ellis, *ibid.*, 1960, **82**, 2082.

²⁰ P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1962, 3880.

EXPERIMENTAL

1,3-Diferrocenylbutan-1-ol and -but-1-ene.—1,3-Diferrocenylbutan-1-ol (m.p. 106–108°; lit.,²⁰ 109–111°) was obtained (66% yield) from 1,3-diferrocenylbut-2-en-1-one²⁰ (2.2 g) by reduction with sodium borohydride in dioxan-ethanol followed by chromatography (alumina; benzene-ether, 1:1); τ (CDCl₃) 5.90br(s) and 5.95br(s) (18 H, ferrocenyl), 7.0–7.4 (1 H, m), 7.9–8.4 (3 H, m), 8.20br (1 H, s, disappears on addition of D₂O), and 8.75 and 8.77 (3 H, dd, *J* 8.0 Hz). Benzene eluted the minor product 1,3-diferrocenylbut-1-ene (0.35 g, 16%) as an oil, τ (CDCl₃) 4.0–4.2 (2 H, m), 5.80(t), 5.95br(s), and 6.02 (18 H, ferrocenyl), 6.8–7.2 (1 H, m), and 8.70 (3 H, d, *J* 8.0 Hz).

2,4-Diferrocenylpent-1-ene.—Methyltriphenylphosphonium bromide²¹ (3.0 g) was added to sodium methylsulphinylmethanide [from sodium hydride (0.37 g) in dimethyl sulphoxide] in dry dimethyl sulphoxide (100 ml) under nitrogen. 1,3-Diferrocenylbutan-1-one²⁰ (2.2 g) was added. The mixture was stirred for 12 h before quenching in water. Conventional work-up with ether gave a residue, which was chromatographed on alumina (Spence grade H). Elution with light petroleum-benzene (1:1) gave 2,4-diferrocenylpent-1-ene (1.53 g, 70%) as brown rosettes (from pentane), m.p. 69.5–71°; ν_{\max} (Nujol) 1620 and 900 cm⁻¹; τ (CDCl₃) 4.76 (1 H, d, *J* 1.7 Hz), 5.20 (1 H, d, *J* 1.7 Hz), 5.91(s) and 5.98br(s) (18 H, ferrocenyl), 7.1–7.9 (3 H, m), and 8.77 (3 H, d, *J* 7.0 Hz) (Found: C, 68.15; H, 6.1. C₂₅H₂₆Fe₂ requires C, 68.55; H, 6.0%).

1,2-Diferrocenylethylene.—(Ferrocenylmethyl)triphenylphosphonium iodide²² (6.5 g) was added to a cool solution of sodium methylsulphinylmethanide [from sodium hydride (0.6 g)] in dimethyl sulphoxide (75 ml). The solution turned red after 2 min and formylferrocene²³ (2.15 g) was added. The mixture was stirred for 1 h and then quenched with water and worked up in the conventional manner. Chromatography on alumina (Spence grade H) with light petroleum-benzene (1:1) gave ferrocene (0.3 g) and 1,2-diferrocenylethylene (0.77 g, 39%) as a mixture of *cis*- and *trans*-isomers, m.p. 146° (lit.,²² *cis* 195–198°, *trans* 265–267°), τ (CDCl₃) 3.88 (1 H, s), 5.69 (2 H, t), 5.86 (2 H, t), and 5.93 (5 H, s).

Reactions in Sulphuric Acid (AnalaR).—(a) *Reduction of 2,4-diferrocenyl-4-methylpent-1- and -2-enes.* A mixture of the alkenes (1a) and (2a) (0.29 g) was dissolved in sulphuric acid (98%; 20 ml) at room temperature. A deep blue colour resulted immediately. The solution (either left overnight at ambient temperatures or worked up immediately) was quenched in ice-water (100 g), treated with ascorbic acid to reduce the ferricenium species, and extracted with ether. The extract was washed (H₂O, sat. NaHCO₃), dried (MgSO₄), filtered, and evaporated to dryness. The residue was dissolved in benzene and chromatographed on alumina with the same solvent as eluant. Only one component was present, as a yellow band. This yielded 2,4-diferrocenyl-2-methylpentane (0.26 g, 88%), m.p. 79–80°, identical with that obtained from the catalytic reduction of the olefins (1a) and (2a).¹¹

(b) *Reduction of 2,4-diferrocenylpent-1-ene.* 2,4-Diferrocenylpent-1-ene (0.44 g) was dissolved in sulphuric acid (98%; 10 ml). After 0.5 h the blue solution was worked up as above to yield 2,4-diferrocenylpentane (0.43 g, 98%),

²¹ A. Maercker, *Org. Reactions*, 1965, **14**, 270 and references contained therein.

²² P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1963, 2990.

²³ D. Bublitz and K. L. Rinehart, *Org. Reactions*, 1969, **17**, 1.

m.p. 80—85° (from benzene–light petroleum) as a mixture of diastereoisomers, τ (CDCl₃) 6.00br(s) and 6.06br(s) (18 H, ferrocenyl), 7.60 (2 H, sext, *J* 6.9 Hz), 8.49 (2 H, d, *J* 6.9 Hz), and 8.77 and 8.80 (6 H, two d, *J* 6.9 Hz). Fractional crystallization gave one pure stereoisomer as *granules*, m.p. 116—118° (from benzene–petroleum), τ (CDCl₃) 6.06br (18 H, s, ferrocenyl), 7.60 (2 H, sext, *J* 6.9 Hz), 8.49 (2 H, d, *J* 6.9 Hz), and 8.77 (6 H, d, *J* 6.9 Hz) (Found: C, 68.4; H, 6.65. C₂₅H₂₈Fe₂ requires C, 68.2; H, 6.4%).

(c) *Reduction of 1,3-diferrocenylbutan-1-ol*. 1,3-Diferrocenylbutan-1-ol (1.45 g) was dissolved in sulphuric acid (98%; 50 ml). After 0.5 h the blue solution was worked up as before to yield 1,3-diferrocenylbutane (1.16 g, 83%) as golden prisms, m.p. 78—79.5° (from acetone–water), τ (CDCl₃) 6.02 and 6.07 (18 H, ferrocenyl), 7.4—7.85 (3 H, m), 8.12—8.55 (2 H, m), and 8.75 (3 H, d, *J* 7.0 Hz) (Found: C, 67.5; H, 6.35. C₂₄H₂₆Fe₂ requires C, 67.65; H, 6.15%).

(d) *Reduction of 1,3-diferrocenylbut-1-ene*. 1,3-Diferrocenylbut-1-ene (0.35 g) gave 1,3-diferrocenylbutane (0.2 g, 58%) as the sole product under conditions identical with those of (c).

(e) *Reduction of 1,3-diferrocenylbutan-1-one*. 1,3-Diferrocenylbutan-1-one (0.34 g) was dissolved in sulphuric acid (98%; 7 ml) and the initially purple mixture was kept at ambient temperature overnight, after which it had turned grey-blue. The residue obtained by conventional work-up was chromatographed on alumina. Benzene eluted 1,3-diferrocenylbutane (0.11 g, 33%) and starting material (0.2 g, 59%).

(f) *Attempted reduction of 1,3-diferrocenylbut-2-en-1-one*. 1,3-Diferrocenylbut-2-en-1-one (0.54 g) in sulphuric acid (98%; 10 ml) gave only starting material (0.34 g, 63%), with considerable decomposition.

(g) *Reduction of 1-ferrocenyl-1,3,3-trimethyl[3]ferrocenophane (5)*. The ferrocenophane (5) (0.10 g) was dissolved in sulphuric acid (98%; 5 ml) and the blue solution set aside for 12 h. Conventional work-up gave a quantitative yield of 2,4-diferrocenyl-2-methylpentane. The trimethyleneferrocene (4) was inert under the same conditions.

(h) *Reduction of 1,2-diferrocenylethylene*. 1,2-Diferrocenylethylene (0.3 g) was dissolved in sulphuric acid (98%; 7 ml). After 5—20 min the blue-green solution was worked up as previously to give a quantitative yield of 1,2-diferrocenylethane, m.p.: 199.5—200° (lit.,²² 193—195°; lit.,²⁴ 200—200.5) as pale orange plates (from benzene), identical with a sample prepared by catalytic (Pd–C) hydrogenation of the olefin; τ (CDCl₃) 5.92(s) and 5.95(s) (9 H) and 7.48 (2 H, s).

Reactions of 2-Ferrocenylpropan-2-ol in Sulphuric Acid.

(a) 2-Ferrocenylpropan-2-ol (0.5 g) was added to stirred sulphuric acid (98%; 10 ml) pre-cooled to –10 °C. The brown solution was stirred for 1 h and poured into water. The ferricenium species were reduced with ascorbic acid and the mixture was extracted into ether. Conventional treatment of the extract gave a brown crystalline residue which was chromatographed on alumina. Benzene–petroleum (3:25) eluted isopropenylferrocene (0.12 g, 26.1%). Benzene eluted 2,4-diferrocenyl-2-methylpentane (0.042 g, 9.1%) and a mixture (3.2:1) of 2,4-diferrocenyl-4-methylpent-1- and -2-enes (0.21 g, 44.9%).

(b) The above experiment was repeated with the same quantities but with the sulphuric acid at room temperature. Chromatography gave isopropenylferrocene (0.2 g, 43.0%), 2,4-diferrocenyl-2-methylpentane (0.15 g, 32%), and 2,4-diferrocenyl-4-methylpent-1-ene (0.10 g, 21.4%).

(c) The experiment was repeated on twice the scale with sulphuric acid preheated to 50 °C. The mixture was maintained at 45—50° for 1 h before work-up. There was considerable charring of the organic material. Chromatography gave isopropenylferrocene (0.04 g, 4.3%), 2,4-diferrocenyl-2-methylpentane (0.48 g, 51.4%), and 2,4-diferrocenyl-4-methylpent-1-ene (0.12 g, 12.9%).

We thank the S.R.C. for a research studentship (to B. J. T.)

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²⁴ A. N. Nesmeyanov, E. G. Perevalova, and Yu. A. Ustynyuk, *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, 1105 (*Chem. Abs.*, 1960, **54**, 24 616f).