dipole moment measurements ($\mu_{II} = 6.4 \pm 0.5D$ and $\mu_I = 4.6 \pm 0.5D$).[6]

The compositions and structures of the products of the systems based upon Me_3Al and $isoBu_3Al$ apparently are not known, but the formulations $Cp_2TiCl_2AlR_2$, where R = alkyl, may well apply. For R = Me, the e.s.r. spectrum is consistent with this assumption, whereas the large width of the spectrum observed in the case R = iso-Bu cannot be explained in this way, if the treatment used to explain the widths of the other spectra is correct. The hyperfine pattern given by the $iso\text{-}Bu_3Al$ product is consistent with the interaction of the electron spin with the Al^{27} nuclear moment and with two equivalent protons which have equal coupling constants.[1] The e.s.r. results suggest that the final paramagnetic product of this reaction is not of the same structural type as given by the other aluminum alkyls which we have studied.

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RECEIVED JUNE 2, 1960

1,1'-(TETRAMETHYLETHYLENE)-FERROCENE. OBLIQUITY AND N.M.R. IN BRIDGED FERROCENES

Sir:

We wish to report the preparation and properties of 1,1'-(tetramethylethylene)-ferrocene (I), containing an unusual two-carbon bridge linking the two cyclopentadienyl rings.

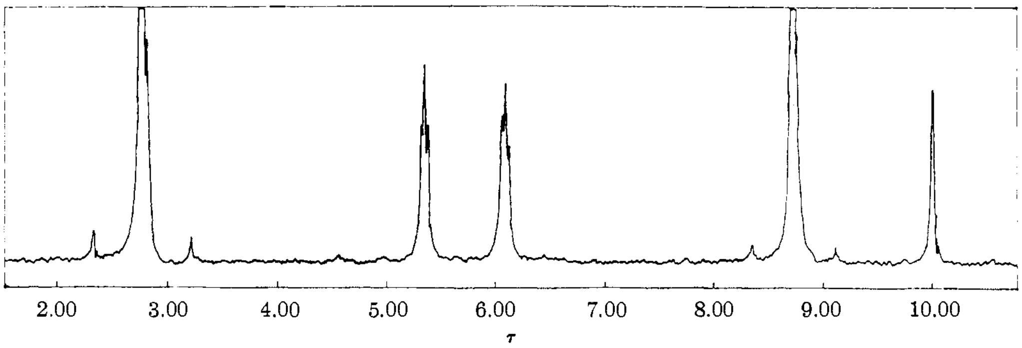

Fig. 1.

Treatment of 6,6-dimethylfulvene[1] with sodium metal dispersed in tetrahydrofuran, and then ferrous chloride, gave a mixture in which the major product (albeit in low yield) was the bridged compound (I); red crystals, sublimes 130° (8 mm.), m.p. 168–169° (crystal modification 129–130°) [*Anal.* Found: C, 71.83; H, 7.62; Fe, 20.68; mol. wt. (cryoscopic), 285].

The infrared spectrum of I is generally similar to that of 1,1'-diisopropylferrocene,[2] with bands at 3100, 917 and 850 cm.$^{-1}$ (alkylferrocene),[2] 1451, 1377 and 1367 cm.$^{-1}$ (*gem*-dimethyl).[3] Its ultraviolet spectrum is very similar to that of 1,1'-dimethylferrocene,[2] containing a weak maximum at 320 mμ (ϵ_{max} 492), a shoulder at 250 mμ (ϵ 4,920), and high end absorption (ϵ_{210} 13,600).

Although the ultraviolet and infrared spectra of I are characteristic of alkyl ferrocenes, the n.m.r. spectrum is not.[4] The n.m.r. spectrum of the close analog, 1,1'-diisopropylferrocene contains a single peak due to the ferrocene ring protons ($\tau = 5.97$),[5] together with the expected doublet ($\tau = 8.86$) and multiplet[4] ($\tau = 7.36$) due to methyl and methine protons, respectively. Similarly the spectrum of 2,3-diferrocenyl-2,3-dimethylbutane[6] contains three singlet peaks at $\tau = 8.69$ (methyl), 5.94 (unsubstituted ring) and 5.86 (substituted ring). The spectrum of I contains the expected methyl proton singlet ($\tau = 8.74$), but the ring protons are found in two widely separated triplets ($\tau = 6.11$ and 5.37; $J = 1.6$ c.s.). The considerable chemical shift is best explained as arising from the ring protons' unequal distance from the iron nucleus in a molecule where the rings are tilted; this interpretation is thus in accord with the mono-iron molecular weight above.

Since protons close to a transition metal nucleus have been shown to give n.m.r. peaks at relatively higher field in similar compounds (*cf.* cyclopentadienylcyclopentadienecobalt),[7] the ring 2-protons are assigned to the higher field peak ($\tau = 6.11$) and the ring 3-protons to the lower ($\tau = 5.37$).

Similar two-carbon bridged ferrocenes are formed from other fulvenes[8]; however, an alternative reaction path can predominate. Thus, the major product from treatment of cyclopentylidenecyclopentadiene (6,6-tetramethylenefulvene)[9] with sodium, then ferrous chloride, is 1,1'-di-(1-cyclopentenyl)-ferrocene (II), m.p. 108–109° [*Anal.*

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[1] G. Crane, C. E. Boord and A. L. Henne, THIS JOURNAL, **67**, 1237 (1945).

[2] K. L. Rinehart, Jr., K. L. Motz and S. Moon, *ibid.*, **79**, 2749 (1957).

[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, New York, N. Y., 1958, p. 13.

[4] Additional differences between bridged and non-bridged alkyl ferrocenes, to be discussed in the complete paper, are lower stability (standing, as crystals or in solution) and decreased reactivity (toward Friedel–Crafts acylation) of the bridged compounds. Detailed discussion of n.m.r. spectra, in particular of splitting, is also deferred to the full report.

[5] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[6] K. L. Rinehart, Jr., P. A. Kittle and A. F. Ellis, THIS JOURNAL, **82**, 2082 (1960).

[7] *Cf.*, *e.g.*, G. Wilkinson and F. A. Cotton, *Progr. in Inorg. Chem.*, **1**, 1 (1959), and Ref. I.3 therein.

[8] R. L. Pruett and J. E. McMahon, unpublished results.

[9] E. P. Kohler and J. Kable, THIS JOURNAL, **57**, 917 (1935).

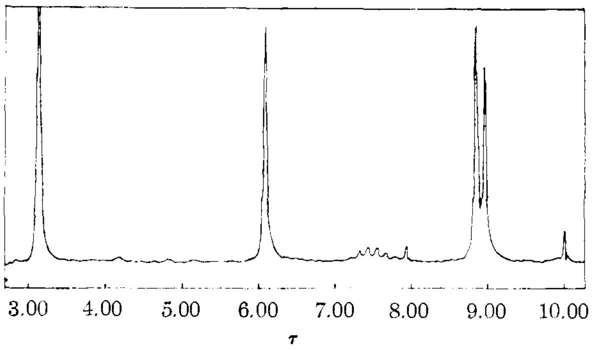
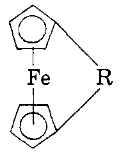


Fig. 2.

Found: C, 75.50; H, 7.16; Fe, 17.54]. In this reaction sodium presumably functions as a base to give the alkenyl cyclopentadienyl anion from the fulvene much as does sodium amide in an alternative preparation of alkenyl ferrocenes.[10,11] The structure II may be assigned on the basis of its infrared spectrum (conjugated C=C stretching band at 1630 cm.$^{-1}$) and ultraviolet absorption (λ_{max} 275 mμ, ϵ_{max} 13,700).[1] Conclusive evidence is derived from the n.m.r. spectrum, which contains an olefinic proton (triplet) at (τ = 4.33).[4]

While the rings are sufficiently canted when spanned by a two-carbon bridge to cause chemical shift of the ring protons, this is apparently not the case with simple saturated three-atom bridges. Thus, the ring protons appear as a singlet in both 1,1′-(trimethylene)-ferrocene (III)[12] (τ = 6.05) and 1,1′-(dimethyleneoxy)-ferrocene (IV)[13] (τ = 5.88), m.p. 148° (sinters 100°) [*Anal.* Found: C, 63.34; H, 5.44; mol. wt. (isothermal distillation), 233].



I, R = $-C(CH_3)_2C(CH_3)_2-$
III, R = $-(CH_2)_3-$
IV, R = $-CH_2OCH_2-$

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(10) P. L. Pauson, G. R. Knox, J. D. Munro and J. M. Osgerby, XVIIth International Congress of Pure and Applied Chemistry, Munich, August-September, 1959, *cf. Angew. Chem.*, **72**, 37 (1960).

(11) A cyclopentenylferrocene has been prepared previously by reaction of ferrocene with hot hydrogen fluoride under pressure [V. Weinmayr, THIS JOURNAL, **77**, 3009 (1955)]. While this reference does not assign the position of the double bond, its ultraviolet spectrum, (λ_{max} 275 mμ, ϵ_{max} 10,400) allows the double bond to be located in conjugation with the ferrocene ring, as in the di-substituted II.

(12) A. Lüttringhaus and W. Kullick, *Angew. Chem.*, **70**, 438 (1958).

(13) Compound IV was prepared by treatment of 1,1-di-(hydroxymethyl)-ferrocene (V) with *p*-toluenesulfonyl chloride in refluxing benzene. Compound V, m.p. 107–108° [*Anal.* Found: C, 58.85; H, 5.77], in turn, was prepared by lithium aluminum hydride reduction of dimethyl 1,1-ferrocenedicarboxylate, a method employed previously [A. N. Nesmeyanov, E. G. Perevalova and Z. A. Beinoravichute, *Doklady Akad. Nauk S. S. S. R.*, **112**, 439 (1957)] the earlier authors reported m.p. 85-86°.

(14) Undergraduate Research Participant, supported by a grant NSF G-8521) from the National Science Foundation.

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ACYL- FROM ALKYL-FERROCENES BY MANGANESE DIOXIDE OXIDATION. FERROCOBENZOQUINONE

Sir:

Alkyl ferrocenes frequently may be prepared directly from alkyl cyclopentadienes[1] and could provide useful starting materials for the preparation of functionally substituted ferrocenes if the alkyl groups could be oxidized selectively without concomitant or preferential oxidation of the ferrocene nucleus to ferricinium ion. In the present, initial studies toward this end manganese dioxide (which usually selectively oxidizes allylic or benzylic alcohols to the corresponding conjugated carbonyls,[2] and which has been used for conversion of hydroxymethylferrocene to ferrocenecarboxaldehyde)[5b] was selected as a mild, heterogeneous oxidant and shown to oxidize readily alkyl ferrocenes to the corresponding acyl compounds.

Methylferrocene[3] was heated for two days with a large excess of activated manganese dioxide (commercial, Beacon Labs.) in refluxing methylcyclohexane.[4] Chromatography of the product gave 55% of recovered methylferrocene and a 52% yield (based on unrecovered methylferrocene, *i.e.*, a 23% conversion) of ferrocenecarboxaldehyde,

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(1) (a) P. L. Pauson, THIS JOURNAL, **76**, 2187 (1954); (b) K. L. Rinehart, Jr., K. L. Motz and S. Moon, *ibid.*, **79**, 2749 (1957); (c) R. E. Benson and R. V. Lindsey, *ibid.*, **79**, 5471 (1957); (d) K. L. Rinehart, Jr., and K. L. Motz, *Chem. and Ind.* (*London*), 1150 (1957); (e) R. C. Koestler and W. F. Little, *ibid.*, 1589 (1958); (f) G. R. Knox and P. L. Pauson, *Proc. Chem. Soc.*, 289 (1958); (g) L. T. Reynolds and G. Wilkinson, *J. Inorg. and Nucl. Chem.*, **9**, 86 (1959); (h) P. L. Pauson, G. R. Knox, J. D. Munro and J. M. Osgerby, *Angew. Chem.*, **72**, 37 (1960).

(2) For recent reviews of manganese dioxide oxidations, *cf.* R. M. Evans, *Quart. Revs.* (*London*), **13**, 61 (1959), and C. D. Robeson, *Org. Chem. Bull.*, **32**, No. 2 (1960). Other oxidations by manganese dioxide, though less common, have been reported. For example, toluene and *o*-nitrotoluene gave the corresponding benzaldehydes and/or benzoic acids with manganese dioxide in sulfuric acid [F. Raschig, *Chemiker Ztg.*, **24**, 446 (1900)], while the allylic ring methylene group of vitamin A_1 and of reinene was oxidized to the corresponding allylic alcohol or to the α,β-unsaturated ketone, or unattacked, depending on the manganese dioxide employed [H. B. Henbest, E. R. H. Jones and T. C. Owen, *J. Chem. Soc.*, 4909 (1957)].

(3) A. N. Nesmeyanov, E. G. Perevalova, L. S. Shilovtseva and Z. A. Beinoravichute, *Doklady Akad. Nauk S.S.S.R.*, **121**, 117 (1958).

(4) The conditions described are not considered optimum, experimental results in this direction will be treated in the full paper.