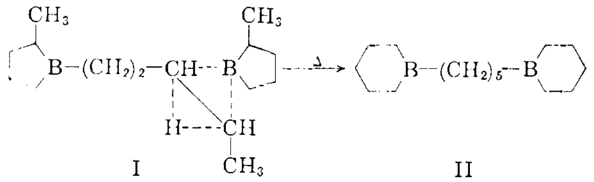
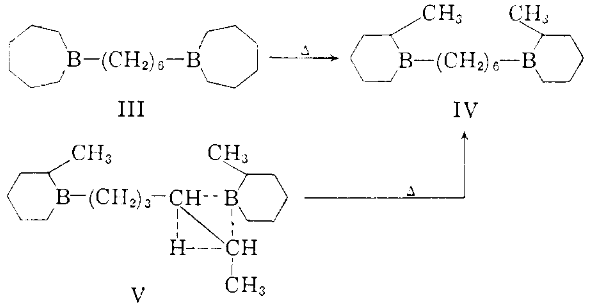


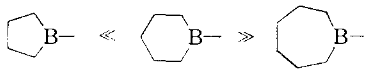
phase chromatographical analysis.[5] However, after heating I at 160–175° for six hours the product obtained on oxidation was essentially pure 1,5-pentanediol, yield 80%, b.p. 134–135° at 14 mm., $n^{25}\mathrm{D}$ 1.4489, bisphenylurethan, m.p. 171.5–172°,[6] indicating that isomerization of I to 1,5-bis-(1-boracyclohexyl)-pentane (II) had occurred.

Treatment of 1,5-hexadiene with diborane gave 1,6-bis-(1-boracycloheptyl)-hexane (III) in 82% yield (b.p. 131–132° at 1 mm.; *Anal.* Calcd. for $C_{18}H_{36}B_2$: C, 78.9; H, 13.2; B, 7.9. Found: C, 78.7; H, 13.2; B, 7.8) which was converted by alkaline hydrogen peroxide to essentially pure 1,6-hexanediol, b.p. 114–118° at 3 mm., m.p. 41–42°. On heating III at 160–175° for 6 hours



rearrangement to IV occurred as evidenced by an 82% yield of a 70:30 mixture (v.p.c. analysis) of 1,5- and 1,6-hexanediols (predicted: 67:33), b.p. 138–140° at 16 mm., $n^{25}\mathrm{D}$ 1.4485. Hydroboration of 1,4-hexadiene gave the mixture of organoboranes (V), which on oxidation produced a 78% yield of a 13:87 mixture (v.p.c. analysis)[4] of 1,4- and 1,5-hexanediol, b.p. 130–136° at 18 mm., $n^{25}\mathrm{D}$ 1.4496. On heating V at 160–175° for six hours thermal rearrangement to IV occurred, since on oxidation a 76% yield of a 69:31 mixture (v.p.c. analysis; predicted 67:33) of 1,5- and 1,6-hexanediols was isolated, b.p. 139.5–142° at 18 mm., $n^{25}\mathrm{D}$ 1.4480.

These results present excellent confirmatory evidence for the bis-(1-boracycloalkyl)-alkane structure for the diene-bishydroboration products[1] and indicate the thermodynamic control of the boracycloalkyl ring enlargement or contraction process, as would be predicted from the heats of



combustion of the analogous cycloparaffins.[7] In this light Brown's suggestion[2a] of the existence of a rapid equilibrium between organoborane, olefin and boron-hydrogen bonds in the thermal rearrangement reaction becomes highly reasonable. These results and others will be reported in greater detail in the near future.

CONTRIBUTION NO. 98
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(5) A 2.5 m. silicone rubber on Celite column operated at 190° was used.

(6) H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 3125 (1948); report b.p. 122–127° (7 mm.), $n^{25}\mathrm{D}$ 1.4490, phenylurethan, m.p. 171–172°.

(7) W. G. Dauben and K. S. Pitzer, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 4.

1,1-DIFERROCENYLETHANE. A FRIEDEL-CRAFTS REARRANGEMENT

Sir:

1,2-Diferrocenylethane[1] and 1,2-diferrocenyl-1,2-diphenylethane[2] (the latter in *meso* and *racemic* forms)[2,3] have been shown to be the products of the reactions of ferrocene and concentrated sulfuric acid with formaldehyde and benzaldehyde, respectively. 1,2-Diferrocenylethane has been prepared also by the coupling of ferrocenylcarbinol in concentrated sulfuric acid,[1] and this method now has been extended to the preparation of 2,3-diferrocenyl-2,3-dimethylbutane, m.p. 74–75° [*Anal.* Found: C, 68.47; H, 6.71], from isopropenylferrocene, m.p. 77.5–78.5° [*Anal.* Found: C, 68.74; H, 6.32], $\lambda_{\max}$ 275 mμ, $\epsilon_{\max}$ 9440.

Although the structure of 1,2-diferrocenylethane was proved by unequivocal synthesis,[1] an apparent residual contradiction has lingered from the earlier reported preparation of a compound of this structure (reported m. p. "about 135°")[5] from the reaction of ferrocene with 1,2-dichloroethane and aluminum chloride.[5,6] The point now has been resolved by the demonstration that this product is in reality 1,1-diferrocenylethane (I).

Under the conditions employed by the previous workers,[5] a crude product isolated in the present study indeed melted 132–134°. However, after chromatography or vacuum sublimation, the pure material obtained had m.p. 147–149° [*Anal.* Found: C, 66.11; H, 5.86; C-CH_3, 3.51]. Its n.m.r. spectrum [τ 5.86 (ferrocene rings), 6.58 (α-H), 8.86 (aliphatic CH_3)] was quite distinct from that of 1,2-diferrocenylethane and was in accord with the 1,1-diferrocenylethane structure.

The structure of the compound was corroborated

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(1) K. L. Rinehart, Jr., C. J. Michejda and P. A. Kittle, THIS JOURNAL, **81**, 3162 (1959).

(2) K. L. Rinehart, Jr., C. J. Michejda and P. A. Kittle, XVIIth International Congress of Pure and Applied Chemistry, Munich, August, 1959; *cf. Angew. Chem.*, **72**, 38 (1960).

(3) No evidence was obtained for an intermediate hydroxy compound ("$C_6H_5CHOH\text{-}C_{10}H_8Fe\text{-}CHC_6H_5\text{-}C_{10}H_9Fe$, m.p. 268–270°"), reportedly isolated by Nesmeyanov and Kritskaya [*Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 253 (1956)]. Since the mode of formation of these compounds[1] renders an alcohol of this nature extremely improbable, the compound was presumably the higher melting diferrocenyldiphenylethane isomer in impure form. This isomer, m.p. 280–281°,[2,4] exhibits the solubility properties ascribed to the "alcohol" in the earlier publication.

(4) *Cf.* also A. Berger, W. E. McEwen and J. Kleinberg, *Chem. and Ind.* (*London*), 204 (1960).

(5) A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk S.S.S.R.*, **109**, 543 (1956).

(6) Although the compound is described in the original paper only as "diferrocenylethane," the 1,2-diferrocenylethane structure implied is stated explicitly in subsequent papers and reviews by the same authors; *cf.*, *inter alia*, A. N. Nesmeyanov and E. G. Perevalova, *Uspekhi Khim.*, **27**, 3 (1958), and ref. (10).

by independent synthesis. Diferrocenyl ketone, m.p. 210–211°,[7] was treated with methylmagnesium iodide and the product dehydrated to give *unsym*-diferrocenylethylene, m.p. 162–164° [*Anal.* Found: C, 66.70; H, 5.18], λ_{max} 252 mμ, ϵ_{max} 18,700. The olefin then was hydrogenated to authentic 1,1-diferrocenylethane, whose m.p. (144–146°) showed no depression with the dichloroethane–aluminum chloride product, and whose infrared spectrum was identical to that of the Friedel–Crafts material.

The rearrangement presumably proceeds by the path shown, involving the very stable intermediate cation (II),[8] and is unusual in that the reaction of benzene with 1,2-dichloroethane is reported to proceed, without rearrangement, to give bibenzyl.[9] The great stability of the cation (II) presumably supplies the driving force for the different path taken in the present study.

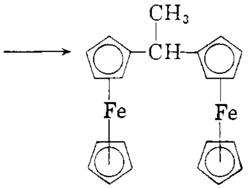
This demonstration of the structure (I) of the simple Friedel–Crafts product renders still more implausible the recently proposed[10] structure (III) for the polycondensate from the same reaction.

$$C_{10}H_{10}Fe + ClCH_2CH_2Cl \xrightarrow{AlCl_3}$$

$$C_{10}H_9Fe—CH_2CH_2Cl \xrightarrow{AlCl_3}$$

$$C_{10}H_9Fe—CH_2CH_2{}^+AlCl_4{}^- \longrightarrow$$

$$\underset{II}{C_{10}H_9Fe—C^+HCH_3AlCl_4{}^-} \longrightarrow$$



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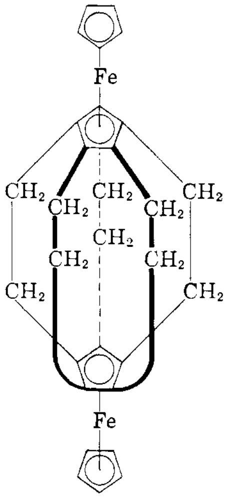

III

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[7] Prepared in 31% yield by an earlier method (R. B. Woodward and E. Csendes, personal communication), from ferrocene, phosgene and aluminum chloride. Woodward and Csendes found m.p. 206–208°.

[8] J. H. Richards and E. A. Hill, This Journal, **81**, 3484 (1959).

[9] (a) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941, pp. 110, 815; (b) G. S. Kolesnikov, V. V. Korshak and T. V. Smirnova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk,* 172 (1955).

[10] A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk S.S.S.R.,* **126**, 307 (1959).

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

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THE π-π^* PHOSPHORESCENCE OF CHLOROPHYLLS *a* AND *b*[1]

Sir:

Although the phosphorescence of chlorophyll *b* has been obtained,[2,3] attempts to photograph the phosphorescence spectrum of chlorophyll *a* have not been successful.

Recently, Fernandez and Becker[4] observed the long-lived emission spectra of solutions of dry chlorophylls *a* and *b* at 7550 Å. and 7330 Å., respectively. On the basis of solvent studies concerning both the absorption and emission spectra, the emissions were assigned as phosphorescences arising from transitions from n-π^* triplet states.

The present investigation employed both 3-methylpentane and ether–ethanol–hydrocarbon (EPA) solvents. The 3-methylpentane was purified by distillation and chromatography but not dried as by Fernandez and Becker.[4] The chlorophylls *a* and *b* were crystalline, spectroscopically pure samples[5] prepared and analyzed according to Stoll and Wiedemann.[6] The concentrations employed were approximately 2×10^{-5} *M.* All samples were degassed and sealed *in vacuo* to prevent air or photoöxidation. Studies were carried out at 77°K. employing two different spectrographs and hyper-sensitized Kodak spectroscopic plates, types M, N and Q. Special attention was given to hyper-sensitization of the plates regarding temperature and ammonia concentration. That is, the temperatures of all solutions were kept at or below 4° and the percentage ammonia was approximately 0.5. This procedure both improves plate sensitivity and decreases background. The improvement is particularly noticeable in plate types M and Q. Light sources were either a high pressure 1 kw. Xe–Hg lamp or a 500-watt projection lamp. Excitation light was selected by means of glass and solution filters or a grating monochromator.

The emission spectrum of chlorophyll *b* consists of two rather poorly resolved bands in the near-infrared region. One band occurs at 8750 ± 50 Å. and the other at 9150 ± 50 Å. The location of the first band differs by approximately 100 Å. from that previously reported.[2] The second band is a new one. The emission extends to approximately 9800 Å. The lifetime of the emission has been determined to be $\geqslant 5 \times 10^{-4}$ second.

The emission spectrum of chlorophyll *a* also appears to consist of two bands but these are even less resolved than for chlorophyll *b*. The first band occurs at 8850 ± 50 Å. and the second band at 9250 ± 50 Å. The emission extends to approximately 10,000 Å. The lifetime of the emission has been determined to be $\geqslant 5 \times 10^{-4}$ second.

It has not been possible to decide whether the two band system represents transitions between different electronic states or between different vibrational states. However, the low energy spacing strongly indicates that the bands are vibrational in origin. The emission intensity of the

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[1] Supported by the Robert A. Welch Foundation.

[2] R. S. Becker and M. Kasha, This Journal, **77**, 3669 (1955).

[3] N. Calvin and G. Dorough, *ibid.*, **70**, 699 (1948).

[4] J. Fernandez and R. S. Becker, *J. Chem. Phys.*, **31**, 467 (1959).

[5] Kindly provided by Sandoz Ltd., Basle, Switzerland.

[6] A. Stoll and E. Wiedemann, *Helv. Chim. Acta*, **42**, 679 (1959).