ment I for the material on the basis of infrared studies.[4]

We wish to report an unequivocal, convenient synthesis of biferrocenyl by means of the Ullmann reaction of haloferrocenes. For example, the reaction of iodoferrocene[5] and activated copper bronze at 150–160° produces biferrocenyl (Found: C, 64.99; H, 4.97; Fe, 30.09; mol. wt., 360), m.p. 239–240° (dec.), in 96–100% yield. The reaction can be carried out under very mild conditions, *viz.*, 60°, without any appreciable lowering in yield of the coupling product. Biferrocenyl prepared in this manner by the well-known Ullmann bi-aryl reaction is identical to biferrocenyl obtained previously, both in melting point and in a comparison of the infrared and ultraviolet spectra of the two products. Examples of quantitative Ullmann bi-aryl couplings are extremely rare in the chemical literature.[6,7] Moderate to high yields of bi-aryls from the Ullmann reaction usually require activation by strongly electron withdrawing substituents such as the nitro group.

We have also obtained biferrocenyl in reasonably good yield (47–61%), together with ferrocene, from the reaction of diferrocenylmercury[8,9] and powdered silver at 250–300°.[10] Moreover, the simultaneous heating of an equimolar mixture of diferrocenylmercury and diphenylmercury in the presence of silver has produced phenylferrocene, m.p. 111–112°, in 45% yield, accompanied by lesser amounts of biferrocenyl and ferrocene. Phenylferrocene prepared in this manner was identical to a sample obtained from the reaction of ferrocene and phenyldiazonium chloride.[11,12] The reaction of diferrocenylmercury with other arylmercury compounds in the presence of silver should constitute an alternate method for the synthesis of arylferrocenes.

Nesmeyanova and Perevalova recently have reported a similar reaction between diferrocenylmercury and palladium black at elevated temperatures.[13] The yields of biferrocenyl obtained by their method amounted to only 1–6%, however. Nesmeyanov and co-workers also have reported the isolation of biferrocenyl from the reaction of ferrocenylboronic acid with an ammoniacal solution of silver oxide.[14]

It is assumed tentatively that the reaction of diferrocenylmercury and silver proceeds via a homolytic mechanism involving ferrocenyl radicals, as has been suggested by Nesmeyanova and Perevalova in their studies. Experiments designed to elucidate the mechanism and determine the scope of the reaction are in progress.

The discovery of these facile syntheses of biferrocenyl from readily available starting materials[5,8,9,14] now permits studies of the chemical reactivity of this compound and a comparison of its properties with those of ferrocene. Thus, as in the case of ferrocene,[15,16] biferrocenyl reacts readily with acetyl chloride and aluminum chloride in the usual Friedel–Crafts manner to produce a mixture of isomeric diacetylbiferrocenyls: red needles, m.p. 147–147.5° (Calcd. for $C_{24}H_{22}Fe_2O_2$: C, 63.48; H, 4.88; Fe, 24.60. Found: C, 63.32; H, 5.10; Fe, 24.68); red needles, m.p. 191–192° (Found: C, 63.85; H, 4.98; Fe, 24.20). Benzoylbiferrocenyl, m.p. 124–125° (Calcd. for $C_{27}H_{22}Fe_2O$: C, 68.38; H, 4.68. Found: C, 68.03; H, 4.87), can be prepared by Friedel–Crafts benzoylation of biferrocenyl in a manner analogous to the benzoylation of ferrocene.[17] Studies of this nature and of related reactions of the haloferrocenes are being continued.

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[4] S. I. Goldberg and D. W. Mayo, *Chemistry and Industry*, 671 (1959).

[5] A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, *Doklady Akad. Nauk S.S.S.R.*, **99**, 539 (1954).

[6] P. A. Fanta, *Chem. Rev.*, **38**, 139 (1946).

[7] P. H. Gore and G. K. Hughes, *J. Chem. Soc.*, 1615 (1959).

[8] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954).

[9] M. D. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

[10] Our procedure was patterned after the method reported for the synthesis of biphenylene in 54% yield from biphenylenemercury; G. Wittig and W. Herwig, *Chem. Ber.*, **87**, 1511 (1954).

[11] G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

[12] M. Rosenblum, THIS JOURNAL, **81**, 4530 (1959).

[13] O. A. Nesmeyanova and E. G. Perevalova, *Doklady Akad. Nauk S.S.S.R.*, **126**, 1007 (1959).

[14] A. N. Nesmeyanov, V. A. Sazenova and V. N. Drozd, *ibid.*, **126**, 1004 (1959).

[15] M. Rosenblum and R. B. Woodward, THIS JOURNAL, **80**, 5443 (1958).

[16] J. H. Richards and T. J. Curphey, *Chemistry and Industry*, 1456 (1956).

[17] M. D. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).

[18] We gratefully acknowledge valuable discussions with Prof. Henry Gilman, Prof. Georg Wittig and Dr. Harold Rosenberg during the course of this investigation.

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THE ISOMERIZATION OF BIS-(1-BORACYCLOALKYL) ALKANES VIA THE HYDROBORATION OF DIENES

Sir:

We wish to report that the position of the boron atom in the thermal rearrangement of bis-(1-borocycloalkyl)-alkanes, prepared by the hydroboration of dienes,[1] has been found to be determined by the size of the hetero ring. This result is in contrast to earlier reports[2] on the isomerization of acyclic secondary or tertiary alkylboranes at 100 to 160° in which migration of the boron atom down a long carbon chain to the terminal position was observed.[2a]

1,3-Pentadiene was allowed to react with diborane[3] (diene: B_2H_6::3:1) at 25° to give a mixture of bis-1,3- and bis-1,4-(1-bora-2-methylcyclopentyl)-pentane (I), which on oxidation with alkaline hydrogen peroxide[3b] gave an 84% yield of a 10:90 mixture[4] of 1,3- and 1,4-pentanediols, b.p. 107–114° at 9 mm., n^{25}_{D} 1.4450, as shown by vapor

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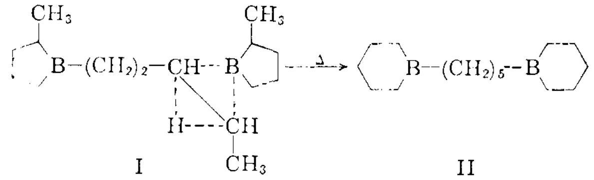
[1] R. Köster, *Angew. Chem.*, **71**, 520 (1959); K. A. Saegebarth, to be published.

[2] (a) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957); THIS JOURNAL, **81**, 6434 (1959); (b) G. F. Hennion, *et al.*, *ibid.* **79**, 5190, 5194 (1957); **80**, 617, 3481 (1958).

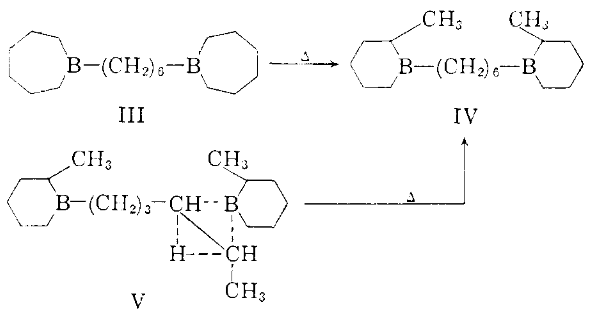
[3] (a) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); (b) THIS JOURNAL, **81**, 6428 (1959); (c) H. C. Brown and G. Zweifel, *ibid.*, **81**, 5832 (1959).

[4] Brown and Subba Rao[3a] report hydroboration–oxidation of pentene-2 yields a 50:50 mixture of 2- and 3-pentanol, thus a 17:83 mixture of 1,3- and 1,4-pentanediol would be predicted on the basis of Structure I.

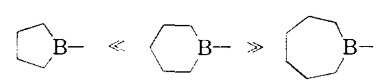


phase chromatographical analysis.[5] However, after heating I at 160–175° for six hours the product obtained on oxidation was essentially pure 1,5-pentanediol, yield 80%, b.p. 134–135° at 14 mm., $n^{25}\text{D}$ 1.4489, bisphenylurethan, m.p. 171.5–172°,[6] indicating that isomerization of I to 1,5-bis-(1-boracyclohexyl)-pentane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



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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.), $n^{25}\text{D}$ 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).