TABLE II

TETRASUBSTITUTED FERROCENES PREPARED FROM DIAROYLCYCLOPENTADIENES

Compound	Yield, %	M.P.	Formula	Calcd. C	Calcd. H	Found C	Found H
1,1′,2,2′-Tetrabenzylferrocene	13	154.5–155.5	$C_{38}H_{34}Fe$	83.51	6.27	83.20 83.44	6.22 6.33
1,1′,2,2′-Tetrakis(*p*-methylbenzyl)-ferrocene	25.5	101–102[a] 117–118	$C_{42}H_{42}Fe$	83.71	7.03	83.32	7.12
1,1′,2,2′-Tetrakis(*o*-chlorobenzyl)-ferrocene	10.7	163.5–164.5	$C_{38}H_{30}Cl_4Fe$	66.69	4.42	66.52	4.40
1,1′,2,2′-Tetrakis(*p*-chlorobenzyl)-ferrocene	25.7	169–171	$C_{38}H_{30}Cl_4Fe$	66.69	4.42	66.75 67.08	4.33 4.58
1,1′,2,2′-Tetrakis(*p*-fluorobenzyl)-ferrocene	30.5	142–143	$C_{38}H_{30}F_4Fe$	73.79	4.89	73.66	5.03
1,1′,2,2′-Tetrakis(*m*-bromobenzyl)-ferrocene	24.4	117.5–118	$C_{38}H_{30}Br_4Fe$	52.94	3.51	53.26	3.53
1,1′,2,2′-Tetrakis(*p*-bromobenzyl)-ferrocene	9.5	207–208	$C_{38}H_{30}Br_4Fe$	52.94	3.51	53.11	3.65

[a] Compound melts at 101°, resolidifies at 102°, and melts finally at 117–118°.

The other tetrabenzylferrocenes were prepared by almost identical procedures from diaroylcyclopentadienes prepared from the appropriately substituted benzoyl chlorides. The recrystallization solvents used with the substituted compounds were as follows: *p*-methyl, ethanol; *o*-chloro, ethyl acetate; *p*-chloro; acetone; *p*-fluoro, acetone-water; *m*-bromo, acetone; *p*-bromo, benzene.

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CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORIES, UNIVERSITY OF NORTH CAROLINA]

Preparation of Heteroannular Disubstituted Ferrocenes from Fulvenes

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Lithium aluminum hydride was added to the *exo* double bonds of dimethylfulvene and diphenylfulvene, followed by treatment with ferrous chloride to produce heteroannular diisopropylferrocene and dibenzhydrylferrocene, respectively. Addition of phenyllithium to dimethylfulvene, followed by treatment with ferrous chloride similarly gave heteroannular bis(α,α-dimethylbenzyl)ferrocene. Phenyllithium addition to diphenylfulvene, however, did not give the expected bis-triphenylmethylferrocene upon treatment with ferrous chloride. The structure of the product obtained was not determined. Bistriphenylmethylferrocene was, however, obtained from triphenylmethylcyclopentadiene and ferrous chloride.

The aromatic nature of a cyclopentadienide ion endows the ring with a stability that enables fulvenes to react with several reagents as pseudo ketones, the five-membered ring with its ability to accommodate a negative charge performing as the carbonyl oxygen. Figure 1 summarizes four reactions of fulvenes that are analogous to ketone reactions. Lithium aluminum hydride adds to the *exo* double bond of alkyl- and arylfulvenes to yield substituted cyclopentadienide ions[1]; phenyllithium likewise adds to fulvenes[2] in an analogous manner to carbonyl addition. With strong bases such as triphenylmethide or sodium amide, alkylfulvenes lose protons[3] in a manner analogous to enolization; and with sodium metal,[4] reductive coupling occurs, as in pinacol formation from ketones, to form dianions.

All of these reactions offer routes to substituted ferrocenes, simply by treating the products with anhydrous ferrous chloride. The purpose of the present communication is to present the details of the use of the first two of these reactions for the production of ferrocenes. Concurrently, the authors[5] and Pauson[6] reported results of preparations of disubstituted ferrocenes by these routes in preliminary communication form. Pauson also reported the use of potassium amide on dimethylfulvene for preparation of dialkenylfulvenes, and Pruett[7] has found that the fourth reaction produced bridged ferrocenes whose

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[1] K. Ziegler, H. G. Gellet, H. Martin, and J. Schnider, *Ann.*, **589**, 91 (1954).

[2] K. Ziegler and W. Schafer, *Ann.*, **511**, 101 (1934).

[3] W. Schlenk and E. Bergmann, *Ann.*, **479**, 58 (1930).

[4] W. Schlenk and E. Bergmann, *Ann.* **463**, 63 (1928); **479**, 42 (1930).

[5] R. C. Koestler and N. F. Little, *Chem. & Ind. (London)*, 1589 (1958).

[6] P. L. Pauson and G. R. Knox, *Proc. Chem. Soc.*, 289 (1958).

[7] R. L. Pruett, personal communication.

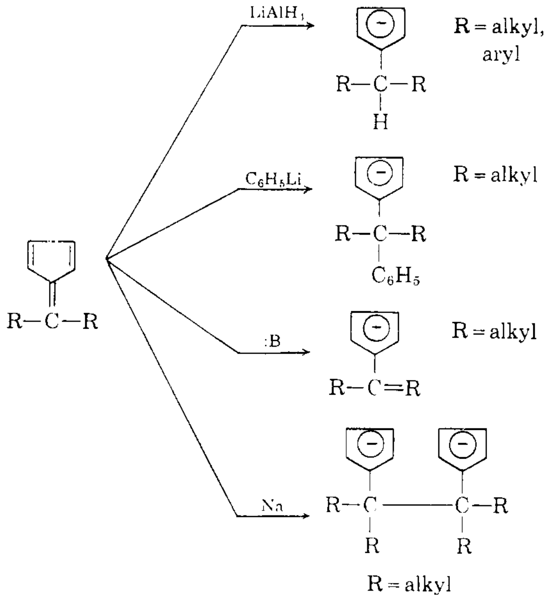

Figure 1

bridged structures have been recently demonstrated by use of NMR.[8]

The addition of lithium aluminum hydride to dimethylfulvene occurs readily in ether, and, upon addition of the product to ferrous chloride in tetrahydrofuran, 1,1′-diisopropylferrocene (I) (Fig. 2), was obtained as a red oil[9] in 24% yield. Inverse addition of ferrous chloride tetrahydrofuranate to the adduct of dimethylfulvene and lithium aluminum hydride improved the yield to 39%. Pauson[6] has reported a considerably higher yield from this reaction, but several variations of the conditions of our reaction failed to improve the yield. While lithium tri-*t*-butoxyaluminum hydride failed to add to dimethylfulvene, it was found that sodium trimethoxyborohydride, which does not normally add to carbon-carbon double bonds[10] does add to dimethylfulvene, though the yields of diisopropylferrocene were not improved by the use of this reagent. Diarylfulvenes are also converted by lithium aluminum hydride and ferrous chloride to substituted ferrocenes. 1,1′-Dibenzhydrylferrocene, III, was prepared in 45% yield from diphenylfulvene.

The smooth addition of phenyllithium to dimethylfulvene resulted in high yields of 1,1′-bis-(α,α-dimethylbenzyl)ferrocene, II; however, the addition of phenyllithium to diphenylfulvene was not so simple. A reaction does occur between diphenylfulvene and phenyllithium, and from treatment with ferrous chloride a product containing iron was obtained, but was difficult to purify. This product, IV, melting at 174–175° was originally thought[5] to be bistriphenylmethylferrocene, V, although carbon analyses, consistently about 1.5% high, cast doubt on the assigned structure.

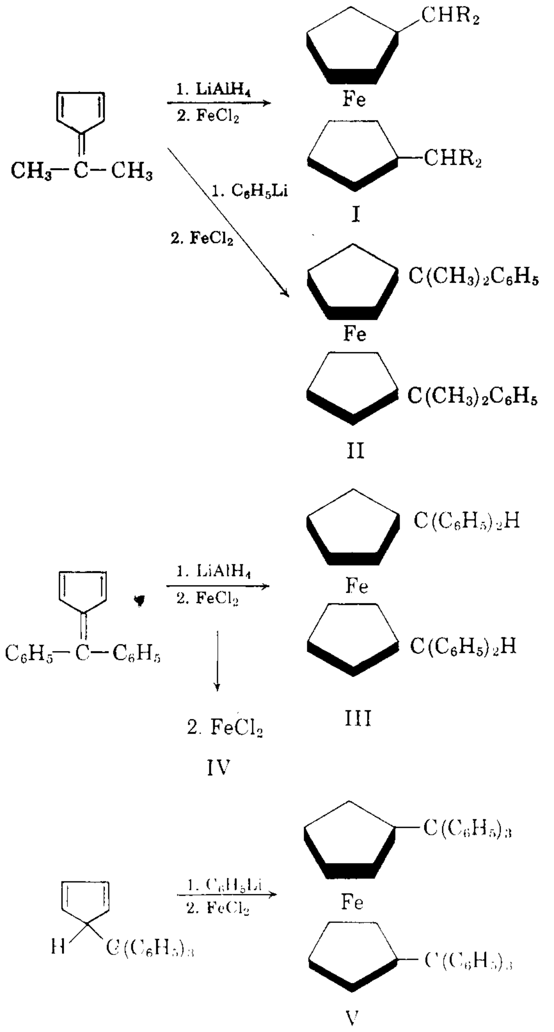

Figure 2

In an attempt to verify or discredit this structure, another approach to the synthesis of 1,1′-bistriphenylmethylferrocene was employed. Triphenylmethylcyclopentadiene was prepared by the method of Hartman and Flenner.[11] Using phenyllithium to generate the triphenylmethylcyclopentadienide ion, addition to anhydrous ferrous chloride yielded a compound, V, melting at 280°, which was not identical to the product IV. Compound V gave carbon and hydrogen analyses that were in agreement with the bistriphenylmethylferrocene structure, and the correct assignment was facilitated by the timely report of Nesmeyanov[12] that mono(triphenylmethyl)ferrocene can be prepared from diferrocenylmercury and triphenyl-

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(8) K. L. Rinehart, Jr., A. K. Fredricks, P. A. Kittle, L. F. Westman, D. H. Gustafson, R. L. Pruett, *J. Am. Chem. Soc.*, **82**, 4111 (1960).

(9) K. L. Rinehart, Jr., K. L. Motz, and S. Moon, *J. Am. Chem. Soc.*, **79**, 2750 (1957).

(10) H. C. Brown and E. J. Mead, *J. Am. Chem. Soc.*, **75**, 6263 (1953).

(11) H. Hartman and K. H. Flenner, *Z. Phys. Chem.*, **194**, 278 (1950).

(12) A. N. Nesmeyanov and E. G. Perevalova, *Doklady Akad. Nauk, S.S.S.R.*, **119**, 215 (1958).

methyl chloride. Rosenblum[13] has called attention to the useful rule that the infrared spectrum of a heteroannular disubstituted ferrocene is identical to that of the corresponding monosubstituted ferrocene, except that the peaks at 9 and 10 μ, characteristic of an unsubstituted ring, are absent in the disubstituted derivative. Application of this rule to the infrared spectrum of Nesmeyanov's triphenylmethylferrocene and compounds IV and V showed that while the spectrum of IV was very similar to that of triphenylmethylferrocene, there were differences between 7 and 13 μ and that the spectrum of V was identical to that of triphenylmethylferrocene except for the absence of peaks at 9 and 9.95 μ. Thus, the structure of V is confirmed as bistriphenylmethylferrocene.

The structure of IV is yet unassigned. Attempted molecular weight determinations (camphor) resulted in decomposition. Carbon and hydrogen analyses correspond to a structure containing two more phenyl groups than bistriphenylmethylferrocene. The determination of the structure of this compound will be the subject of a future investigation.

Several attempts to prepare fulvenes from acetylferrocene and cyclopentadiene were unsuccessful; starting materials were recovered.

EXPERIMENTAL

All melting points are uncorrected.

Analyses were performed by Microtech Laboratories, Skokie, Ill., and by Kenneth L. Shephard in this department.

1,1'-Diisopropylferrocene. To a stirred mixture of 3.9 g. of lithium aluminum hydride in 100 ml. of ether was added 10 g. (0.039 mole) of dimethylfulvene[14] under nitrogen. The reaction immediately gave a white precipitate, and the slurry was added, with exclusion of air, to a cold mixture of anhydrous ferrous chloride (0.0464 mole) in 100 ml. of tetrahydrofuran. The ensuing reaction brought the mixture to reflux, and the dark-colored mixture was stirred for 3 hr. Methanol was added to decompose the excess hydride, and filtration and stripping of the solvent yielded a residue which was distilled at 3 mm. to collect the fraction boiling over the range 101–125°. Redistillation at 124–125° and 3 mm. yielded 3.0 g. of a red oil (24%), $n^{25.5}_{D}$ 1.5596.

Anal. Calcd. for $C_{16}H_{22}Fe$: C, 71.12; H, 8.21. Found: C, 71.53; H, 8.19.

Addition of ferrous chloride tetrahydrofuranate, prepared by evaporation of the tetrahydrofuran from the usual preparation of ferrous chloride,[15] to the reaction product of dimethylfulvene with lithium aluminum hydride, followed by a similar work-up was found to give a somewhat improved yield (35%). Use of sodium trimethoxy borohydride in the place of lithium aluminum hydride was equally successful, but offered no advantage.

Diisopropylferrocene on standing, even in the dark, slowly decomposes to a dark amorphous solid and a red fluid supernatant that retains the same refractive index.

1,1'-Dibenzhydrylferrocene. To a solution of 1.62 g. (0.427 mole) of lithium aluminum hydride in ether was added 10 g. (0.0427 mole of diphenylfulvene[16] in 200 ml. of dry ether with stirring under nitrogen. The reaction was held at reflux for 2 hr., and the solvent was evaporated under nitrogen. The spongy yellow solid that remained was taken up in 100 ml. of tetrahydrofuran. This solution was slowly added under nitrogen to ferrous chloride (0.0213 mole) in 100 ml. of tetrahydrofuran. The black mixture was heated at reflux for 45 min., and after destroying the excess hydride with methanol the solvent was removed. The residue was extracted with acetone, and the extract upon removal of the solvent yielded 5 g. of a yellow crystalline solid (45%). After two recrystallizations from acetone, the product melted at 162–163.5°, lit.[17] 162–163°.

1,1'-Bis(α,α-dimethylbenzyl)ferrocene. Phenyllithium (0.187 mole) in ether was added under nitrogen to a solution of 13.9 g. (0.130 mole) of dimethylfulvene in 100 ml. of dry ether. The reaction immediately yielded a white precipitate, and the slurry was added to a mixture of anhydrous ferrous chloride (0.065 mole) in 100 ml. of tetrahydrofuran. The orange mixture was stirred overnight without heat and was filtered. Evaporation of the solvent yielded a solid, which was washed with cold acetone. Recrystallization from acetone gave 20 g. (73%) of orange crystals, m.p. 133.5–136°.

Anal. Calcd. for $C_{28}H_{32}Fe$: C, 79.62; H, 7.16. Found: C, 79.64; H, 7.04.

Attempted reduction of the phenyl groups in bis(α,α-dimethylbenzyl)ferrocene with rhodium on alumina at 60 p.s.i. gave no change. The reduction was allowed 24 hr.

Attempted preparation of bistriphenylmethylferrocene from diphenylfulvene and phenyllithium. A solution of phenyllithium (0.064 mole) in ether was added dropwise under nitrogen to a refluxing solution of 15 g. (0.064 mole) of diphenylfulvene in 200 ml. of dry ether. The dark red solution was stirred for 1 hr. after the addition and was added slowly to ferrous chloride (0.032 mole) in a mixture of 100 ml. of tetrahydrofuran and 200 ml. of ether. The mixture turned yellow slowly, then brown and finally black. After stirring 30 min., dilute hydrochloric acid was added, and an additional 200 ml. of ether was added. The organic layer was separated and washed three times with water, dried over magnesium sulfate, and the solvent was stripped. The tarry residue was extracted with acetone in a Soxhlet extractor, and from the extract was obtained 17 g. of an amorphous yellow powder, m.p. 150–155°, that was soluble in benzene and in methylene chloride, but insoluble in most other organic solvents. Chromatography in benzene on alumina failed to effect purification, but with difficulty, part of the powder was extracted and recrystallized with acetone to yield 4.3 g. of yellow crystals, m.p. 174–175°. This product, originally thought to be bistriphenylmethylferrocene, did not analyze correctly for bistriphenylmethylferrocene, and its infrared spectrum did not correspond to that of triphenylmethylferrocene prepared by the method of Nesmeyanov.[12] Attempted molecular weight determinations (Rast) resulted in decomposition.

Anal. Calcd. for $C_{48}H_{38}Fe$: C, 85.96; H, 5.71. Found: C, 87.49, 87.20; H, 6.07, 5.85.

The structure of this compound remains unassigned.

1,1'-Bistripenylmethylferrocene. To a solution of phenyllithium (0.0179 mole) in 50 ml. of ether was added, under nitrogen, 5 g. (0.0179 mole) of triphenylmethylcyclopentadiene[11] in 350 ml. of dry ether. The resulting light yellow solution was added rapidly to ferrous chloride (0.0875 mole) in 50 ml. of tetrahydrofuran. The mixture turned dark and was allowed to stand overnight. Ice and dilute hydrochloric acid were added, and the mixture was extracted with ether. After drying with magnesium sulfate, the extract was stripped

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[13] M. Rosenblum, *Chem. & Ind. (London)*, 953 (1958).

[14] G. Crane, C. E. Boord, and A. L. Henne, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

[15] G. Wilkinson, *Org. Syntheses*, **36**, 31 (1956).

[16] J. Thiele, *Ber.*, **33**, 672 (1900).

[17] P. L. Pauson, *J. Am. Chem. Soc.*, **76**, 2187 (1954).

and the residue taken up in benzene and chromatographed on alumina. Recrystallization from benzene yielded one gram of yellow crystals, 18%, m.p. 279–281°.

Anal. Calcd. for $C_{43}H_{32}Fe$: C, 85.96; H, 5.71. Found: C, 85.59; H, 5.96.

The infrared spectrum of this product was identical with that of triphenylmethylferrocene prepared by the method of Nesmeyanov,[12] except for the absence of the monosubstitution bands at 9 and 9.95 μ.

Spectra. The spectra used in this work were obtained with a Perkin-Elmer Model 137 Infracord instrument with sodium chloride optics, employing potassium bromide pellets.

Acknowledgment. The authors would like to acknowledge financial assistance from the University of North Carolina Research Council, the Du Pont Co., and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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[CONTRIBUTION FROM THE MOORE LABORATORY, ROYAL HOLLOWAY COLLEGE, UNIVERSITY OF LONDON]

Boron Ring Compounds. A New Series

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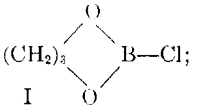
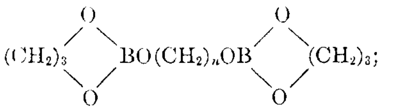
The preparation and characterization of the boron-containing heterocycle, 2-chloro-1,3,2-dioxaborinane, and of related compounds are described. Isolation of the mixed ester, 2-(3′-chloropropyl)-1,3,2-dioxaborinane, in addition to the expected tris(3-chloropropyl) borate and boric oxide, from the pyrolysis of 2-chloro-1,3,2-dioxaborinane, is discussed.

Cyclic esters of chloroboronic acid are of interest because they are thermodynamically more stable than noncyclic esters, and yet contain a reactive center, the B—Cl bond. Both the susceptibility of this B—Cl link to nucleophilic attack, and its chlorinating function, enable the synthesis and study of new boron-containing heterocycles. In this paper, a survey of reactions of 2-chloro-1,3,2-dioxaborinane and its pyrolytic decomposition is made.

The reaction of boron trichloride and trimethylene glycol at low (*ca.* −80°) temperatures, and in various proportions, has been investigated. 2-Chloro-1,3,2-dioxaborinane I and diborate IIa were obtained using appropriate ratios of glycol to boron trichloride. A further excess of glycol produced IIa but no tris-(3-hydroxypropyl) borate III was isolated.



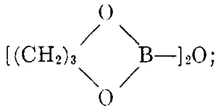
I



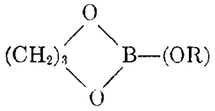
IIa. $n = 3$
b. $n = 2$

$B[O(CH_2)_3OH]_3$
III

I was further characterized by the preparation of the anhydride IV, several esters V, and another diborate IIb.



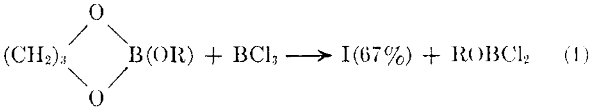
IV



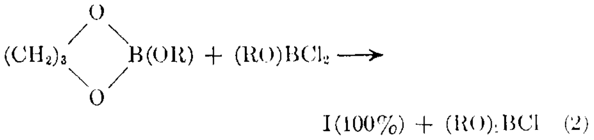
V

R is a. n-C_3H_7 c. $Cl(CH_2)_2$
b. n-C_4H_9 d. $Cl(CH_2)_3$

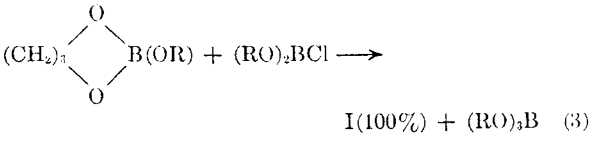
The ester 2-(3′-chloropropyl)-1,3,2-dioxaborinane Vc is of special interest, as it was isolated from the pyrolysis of I. The reactions of this ester with the chlorinating species boron trichloride, (3-chloropropyl) dichloroborinate, and di(3-chloropropyl) chloroboronate led to high yields of I, in accordance with the following equations:



$$(CH_2)_3O_2B(OR) + BCl_3 \longrightarrow I(67\%) + ROBCl_2 \quad (1)$$



$$(CH_2)_3O_2B(OR) + (RO)BCl_2 \longrightarrow I(100\%) + (RO)_2BCl \quad (2)$$



$$(CH_2)_3O_2B(OR) + (RO)_2BCl \longrightarrow I(100\%) + (RO)_3B \quad (3)$$

These reactions presumably take place *via* a 4-center bridge complex involving the (vacant) boron P_z orbital. For example, the transition state in Equation 3 is represented as shown below, with the direction of subsequent disproportionation towards removal of the comparatively volatile I and simultaneous production of the thermodynamically stable ester, tris(3-chloropropyl) borate VI.

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(1) Holder of an I.C.I. Research Fellowship.

(2) Holder of a D.S.I.R. Postgraduate Studentship.