trichloride (3.76 g., 0.032 mole) in 20 ml. of methylene chloride at −80°. After allowing the mixture to warm, the solvent was removed at the pump. The yellow-orange solid residue was recrystallized from benzene and then from carbon disulfide. Infrared analysis indicated that the compound was triphenylchloromethane. This was confirmed by hydrolyzing a weighed sample in aqueous acetone and titrating the hydrochloric acid liberated.

Anal. Calcd. for $C_{19}H_{15}Cl$: Cl, 12.7. Found: Cl, 11.9.

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Bromination of Dichlorophenylborane[1]

KURT NIEDENZU AND JOHN W. DAWSON

Received July 14, 1960

The direct bromination of aryldihalogenoboranes has not been investigated; this note describes the direct bromination of dichlorophenylborane.

The phenyl-attached —BCl_2 grouping should be considered as a second order substituent due to an electron deficiency on the boron atom. In the case of electrophilic substitution, the inductive effect should thus favor *m*-substitution of the aromatic ring.

At room temperature and in the presence of a catalyst, the addition of bromine to dichlorophenylborane results in substitution of the ring along with a small amount of a B—C cleavage. The brominated arylboron derivative was isolated and identified after hydrolysis as B-tri(*m*-bromophenyl)boroxine.

In contrast, bromination of aryldihydroxyborane rather than affording ring bromination results in cleavage of the B—C bond accompanied by replacement of the boron containing moiety by bromine,[2] unless the exchange of the $B(OH)_2$-group by bromine is hindered, due to an electron deficiency of the B-attached carbon atom.[3]

EXPERIMENTAL[4]

About 2 g. of iron filings and a few crystals of iodine were added to 198 cc. (1.5 mole) of dichlorophenylborane and 64 cc. (1.25 moles) of bromine were added with stirring over a period of 30 min. The reaction mixture warmed slightly and stirring was continued for 8 hr. After standing overnight, the product was distilled at normal pressure. A small amount of an unidentified forerun, b.p. 35–70°, was discarded. Unchanged dichlorophenylborane was collected at 165–180°, and the main product distilled at 187–250°. This high boiling fraction was shaken with mercury to remove free halogen, subjected to redistillation, and 174 g. of material, b.p. 205–228° was collected. The material, which crystallized on prolonged standing, showed a melting range (in a sealed tube) of 68–72°. It consists of dibromobenzene (isolated after alcoholysis of the mixture) and a boron-containing substance, which was isolated after hydrolysis in the following manner: 10 g. of the distillate was hydrolyzed with 100 cc. of water; the reaction was most vigorous. A white precipitate was collected and dried *in vacuo* over phosphorus pentoxide for 2 hr. Recrystallization from *n*-heptane afforded 4.1 g. of B-tri(*m*-bromophenyl)boroxine, m.p. 176–178°.

Anal. Calcd. for $B_3O_3C_{18}H_{12}Br_3$: B, 5.9; C, 39.4; H, 2.2; Br, 43.7; mol. wt. 548.5. Found: B, 6.1; C, 39.1; H, 2.4; Br, 43.4; mol. wt. (cryoscopically in benzene) 563.

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DUKE UNIVERSITY
DURHAM, N. C.

(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) H. F. Kuivala and A. R. Hendrickson, *J. Am. Chem. Soc.*, **74**, 5068 (1952).

(3) K. Torssell, *Svensk Kem. Tidskr.*, **69**, 34 (1957).

(4) Analysis by the Schwarzkopf Micoanalytical Laboratory, Woodside 77, N. Y. M.p. taken on a Mel-Temp Block.

Ethers of Bis(1-hydroxyethyl)ferrocene and 1-Hydroxybenzylferrocene

T. ARTHUR MASHBURN, JR.,[1]
AND CHARLES R. HAUSER

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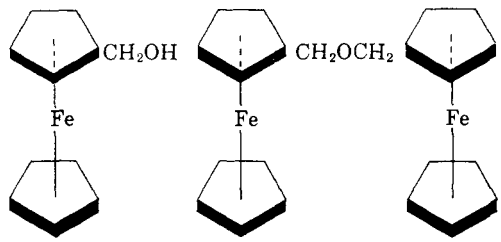
Several workers have observed that hydroxymethylferrocene (I) is readily converted to ether II. This reaction has occurred on treatment of I with 5% acetic acid in ethanol-water,[2] with acidified oxidizing agents,[2] and with phosphorus trichloride.[3] The hydrogenation of formylferrocene over Raney nickel has produced II[4]; I may have been an intermediate.



I II

Somewhat similarly, we have apparently obtained ether IV on treatment of benzoylferrocene (III) with sodium borohydride in methanol, which is one of the common methods of reduction of ketones or aldehydes to the corresponding carbinols.[5]

Structure IV was supported by analysis and by its infrared spectrum, which showed a strong band

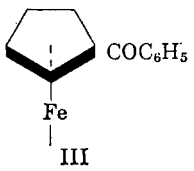
(1) Union Carbide Corporation Fellow, 1958–1960.

(2) C. R. Hauser and C. E. Cain, *J. Org. Chem.*, **23**, 2007 (1958).

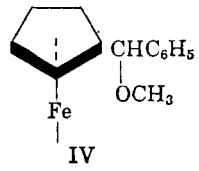
(3) K. Schögel, *Monatsh. Chem.*, **88**, 601 (1957).

(4) P. J. Graham, R. V. Lindsay, G. W. Parshall, M. W. Peterson, and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

(5) See N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience, New York, 1956, p. 118ff and 283ff.



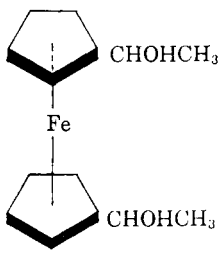
III



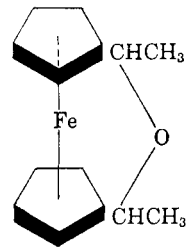
IV

at 9.25 μ attributable to the ether linkage[2,6]; also IV gave bands at 9.0 and 9.93 μ which may be attributed to an unsubstituted cyclopentadiene ring.[7] This compound, however, had no absorption in the region of 2.8 μ[8] for the hydroxyl group, as should have been present had the product been the corresponding carbinol. Like diphenylmethane[9] and especially benzhydrylmethyl ether,[10] ether IV reacted with potassium amide in liquid ammonia to produce a deep purple-red color, which may be ascribed to the corresponding benzhydryl type carbanion.

More significantly, we have synthesized cyclic ether VI through an intramolecular cyclization of glycol V with 2% acetic acid in ethanol-water. V was prepared by reducing bisacetylferrocene by means of lithium aluminum hydride.[4]



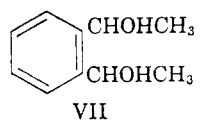
V



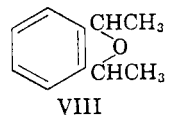
VI

That the product had structure VI was supported by analysis, molecular weight, and infrared spectrum, which showed a band at 9.25 μ[2,6] attributable to a benzyl type ether group. Whereas the spectrum of glycol V showed a strong band at 2.86 μ for the hydroxyl group,[8] that of the product VI gave no such band.

The analogous intramolecular cyclization in the benzene series has long been known.[11] Thus dicarbinol VII, prepared from phthaldehyde and excess methylmagnesium iodide, was cyclized by means of acid to form ether VIII.



VII



VIII

EXPERIMENTAL[12]

Reduction of benzoylferrocene (III) *to form ether IV.* To a stirred, cold solution of 5.0 g. (0.0159 mole) of benzoylferrocene in 50 ml. of methanol was slowly added 5.0 g. of sodium borohydride in 15 ml. of water. After stirring for 1 hr., the resulting yellow solution was treated with excess acetone to destroy the unchanged sodium borohydride, and then poured into water. The solution was extracted several times with ether and the combined ethereal extracts were dried over drierite. The solvent was removed and the resulting crude solid recrystallized from absolute ethanol to give 2.5 g. (48%) of the methyl ether IV as yellow plates, m.p. 107–108°.

Anal. Calcd. for $C_{17}H_{14}FeO$: C, 70.65; H, 5.93; Fe, 18.23. Found: C, 70.62, 70.57; H, 6.04, 5.92; Fe, 18.21, 18.11.

Infrared bands: 3.46, 6.26, 7.60, 8.25, 9.0, 9.15, 9.25, 9.95, 10.5, 12.4, and 14.2 μ.

Bis(1-hydroxyethyl)ferrocene (V). This glycol was prepared from 15.0 g. (0.0555 mole) of bisacetylferrocene[13] and 1.5 g. of lithium aluminum hydride in 120 ml. of dry tetrahydrofuran by a modification of an earlier procedure.[4] After stirring and refluxing for 1.5 hr.; ethyl acetate was added to destroy the excess reagent. A mixture of 3.5 ml. of water, 25 ml. of ethanol, and 50 ml. of ether was then cautiously added and the resulting yellow suspension was filtered through Hi-flo supercell, which was washed well with ether. The yellow filtrate was combined with the ether washings and dried over Drierite. The solvents were removed under reduced pressure to give an amber oil which was taken up in hot hexane. Cooling of the hexane solution in a Dry Ice bath gave 10.5 g. (69%) of glycol V as yellow needles, m.p. 69–72°; reported[4] m.p. 69–72°. Infrared bands: 2.86, 3.42, 7.24, and 7.55 μ.

Cyclization of glycol V *to form cyclic ether* VI. A solution of 1.77 g. (0.0065 mole) of glycol V in 75 ml. of 2% acetic acid in 1:1 ethanol-water was stirred and refluxed for 1.5 hr. The reaction mixture was then poured in 150 ml. of water and then extracted three times with 150-ml. portions of ether. The ether extracts were combined and washed several times with 75-ml. portions of saturated sodium bicarbonate. The ether was dried over Drierite and removed on the steam bath to yield an amber oil. This was chromatographed on an alumina column; put on the column in benzene–petroleum ether (b.p. 30–60°) and eluted with petroleum ether. The eluate gave 0.96 g. (60%) of the cyclic ether as yellow needles, m.p. 110–111°.

Anal. Calcd. for $C_{14}H_{16}FeO$: C, 65.65; H, 6.30; Fe, 21.81. Found: C, 65.93; H, 6.61; Fe, 21.62.

Mol. wt. (Rast Method) Calcd. for $C_{14}H_{16}FeO$: 256.12. Found: 280, 289, 276, 276. Avg. 280 ± 10%.

Infrared bands: 3.42, 7.20, 7.55, 8.74, and 9.26 μ.

In a blank experiment, a sample of the glycol V was passed through an alumina column as described above. As very little of the ether VI was obtained, at least most of the ether VI must have arisen through cyclization by means of the acetic acid treatment.

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(6) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley and Sons, New York, 1958, p. 116.

(7) P. L. Pauson, *Quart. Revs. (London)*, **9**, 391 (1955).

(8) See Ref. 6, p. 96.

(9) See C. R. Hauser and P. J. Hamrick, Jr., *J. Am. Chem. Soc.*, **79**, 3142 (1952).

(10) C. R. Hauser and M. T. Tetenbaum, *J. Org. Chem.*, **23**, 233 (1958).

(11) F. Necker and H. Simonis, *Ber.*, **41**, 987 (1908).

(12) Analyses are by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 21 recording infrared spectrophotometer.

(13) We are indebted to Dr. R. L. Pruett, Union Carbide Chemicals Co., South Charleston, W. Va. for a sample of this compound.