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

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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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[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

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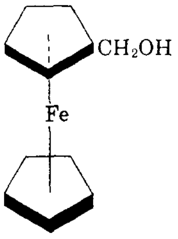
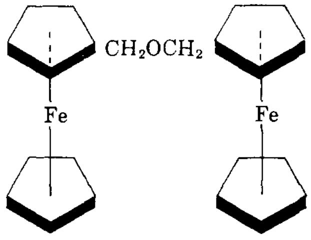
Several workers have observed that hydroxymethylferrocene (I) is readily converted to ether II. This reaction has occurred on treatment of I with 5% acetic acid in ethanol-water,[2] with acidified oxidizing agents,[2] and with phosphorus trichloride.[3] The hydrogenation of formylferrocene over Raney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

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[1] Union Carbide Corporation Fellow, 1958–1960.

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

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[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.