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HYDROBORATION OF ORGANOMETALLIC COMPOUNDS

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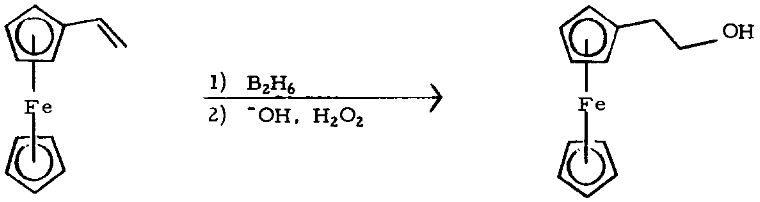
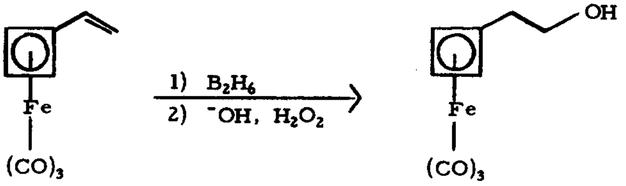
The hydroboration reaction is one of the most important and versatile reactions in synthetic organic chemistry; however, it has been applied to organometallic compounds only recently. The hydroboration of cobalt carbonyl complexes of ene-yne compounds[1] has been reported as well as the unusual formation of ethyl benzenetricarbonylchromium during the attempted hydroboration of styrenetricarbonylchromium.[2] We would like to now report some results of our study of the hydroboration reaction of several organo-iron compounds.

When vinylferrocene (I) is reacted with diborane followed by alkaline oxidation, the only detectable product (nmr analysis of crude reaction product) is 2-ferrocenylethanol (II). The product may be isolated by chromatography over alumina (86% yield). Similarly, hydroboration of vinylcyclobutadienetricarbonyliron (III, obtained by acidic alumina catalyzed dehydration of α-hydroxyethylcyclobutadienetricarbonyliron) produces only the terminal alcohol IV (54% yield) as a yellow liquid[3] [nmr (CS_2) τ 6.03 (s, 2H); 6.08 (s, 1H); 6.30 (s, 1H); 6.45 (t, 2H); 7.83 (t, 2H)] . The hydroboration reaction thus allows one to produce a variety of substituents at alkyl positions <u>beta</u> to the metallocene system. Substituents at alkyl positions <u>alpha</u> to the metallocene system are accessible by suitable modifications of the



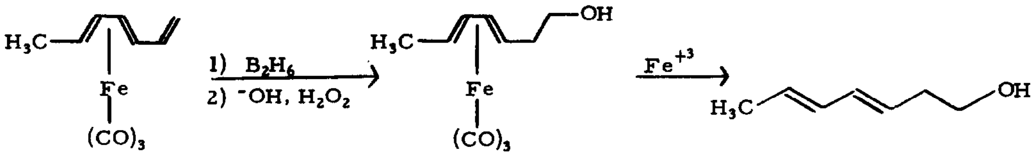
I II

readily available acyl derivatives.



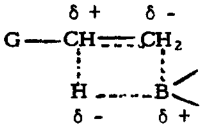
III IV

The triene complex V is prepared from the known 2,4-hexadienaltricarbonyliron by a Wittig reaction with methylenetriphenylphosphorane in ether at room temperature. Typical hydroboration and oxidation produces VI (73% yield) as a viscous orange oil [nmr (CS_2)τ5.08 (m, 2H); 6.20 (s, 1H); 6.58 (t, 2H); 8.30 (m, 2H); 8.90 (m, 5H)]. Treatment of VI with alcoholic $FeCl_3$ liberates <u>trans-trans</u>-3,5-heptadien-1-ol (VII) as a colorless liquid, bp 98° at 21 mm Hg. The nmr spectrum (CS_2) of VII exhibits signals at τ4.30 (complex multiplet, 4H); 6.40 (s, 1H); 6.52 (t, 2H); 7.80 (q, 2H); and 8.30 (d, 3H).

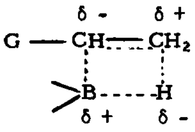


V VI VII

The selectivity of these reactions is quite marked. In contrast, hydroboration of styrene[4] produces, after alkaline oxidation, 2-phenylethanol (81% of product) and 1-phenylethanol (18%). The direction of addition of diborane is such that the boron atom usually becomes bonded to the least sterically hindered carbon atom. Since these organometallic systems have larger steric requirements than benzene, attack should predominate at the terminal position. A second factor which influences the direction of attack is electrical effects. Evidence[5] indicates that the addition of the boron-hydrogen moiety to olefins involves a four-centered transition state. Thus the effect of the substituent on the direction of the attack will be determined by its influence on the stabilization of the two possible transition states VIII and IX. The dramatic ability of ferrocene[6], cyclobutadienetricarbonyliron[7], and



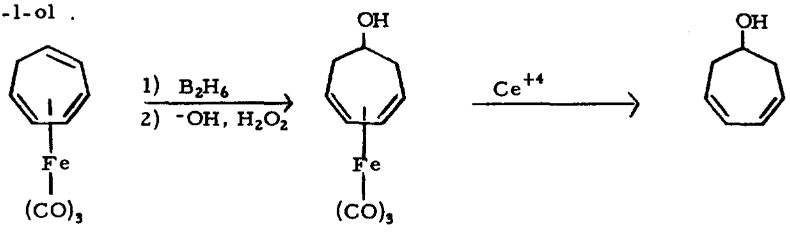
VIII



IX

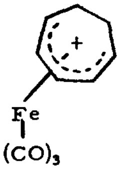
butadienetricarbonyliron[8] to stabilize an adjacent carbonium ion is well known. Electronic factors would then strongly favor a transition state such as VIII. A combination of steric and electrical factors could then account for the observed selectivity.

The cyclic triene complex, cycloheptatrienetricarbonyliron X, upon usual treatment with diborane and oxidation, produces the unsaturated alcohol complex XI as pale yellow needles, mp 108-109°. The nmr spectrum ($CDCl_3$) has signals at τ4.57 (multiplet, 2H); 6.33 (broad, 1H); 7.23 (multiplet, 2H); and 7.87 (multiplet, 5H). Treatment of XI with ceric ammonium nitrate in aqueous ethanol, followed by ether extraction and distillation affords a single alcohol, XII, which is identical in all respects to an authentic sample of 3,5-cycloheptadien-1-ol[9].



X XI XII

Since steric effects in complex X are apparently very small, the driving force for the exclusive formation of XI must be electrical in nature. Pentadienyltricarbonyliron cations are well known and are remarkably stable. For example, the cycloheptadienyl complex XIII can be isolated in 90% yield as a stable fluoroborate salt by reaction of X with HBF_4 in



XIII

propionic anhydride.[10] Therefore transition state VIII should be greatly stabilized in comparison to IX and thereby account for the formation of XI in this hydroboration reaction.

It can be seen that the presence of the tricarbonyliron moiety in V and X greatly simplifies the selective monohydroboration of these trienes. The ease of removal of the transition metal by oxidation with ferric or ceric salts thus makes this an attractive route for the preparation of these difficult-to-obtain alcohols. Interestingly, cyclooctatetraenetricarbonyliron is very resistant to attack by diborane. Only starting material may be isolated after 16 hours reaction at room temperature. This lack of reactivity may be due to the rapid valence tautomerism which this molecule is known to undergo.[11]

The scope of the synthetic applications of the hydroboration reaction in organometallic compounds is presently being investigated.

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