have activation energies in the neighborhood of 20 kcal./mole[19] compared to values of at least 30 kcal./mole found for most O–O homolyses.[10] Electron-releasing groups substituted on the double bond enhance the rate and yield of epoxide formation in both reactions.[19] Both reactions are stereospecific in the sense that they give *cis* epoxidation.[20] The evidence presented speaks strongly in favor of a polar mechanism for hydroperoxide epoxidation with at least certain similarities to peracid epoxidation. It is consistent with the previously reported opinion that unbound free radicals are not significantly involved.[2] The conceivable advantages of hydroperoxide over peracid as epoxidizing agents are the potentially low cost of the reagent and the possibility of epoxidations in acid sensitive systems.

The Grignard Reagents of *p*- and *m*-Bromophenylferrocene[1a]

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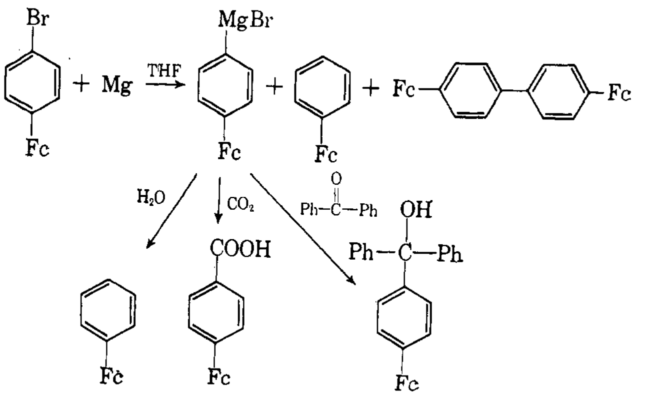
The Grignard reagent of *p*-bromophenylferrocene has been prepared in tetrahydrofuran, accompanied by the formation of phenylferrocene, and has been found to react normally with water, carbon dioxide, and benzophenone. Attempts to prepare the reagent at higher temperatures in dimethylcarbitol yielded only phenylferrocene and *p,p'*-diferrocenylbiphenyl. Similarly, *m*-bromophenylferrocene reacted with magnesium at high temperatures in dimethylcarbitol to yield only phenylferrocene and *m,m'*-diferrocenylbiphenyl, but even at lower temperatures in tetrahydrofuran only these two products could be obtained.

Ferrocene as a substituent on other aromatic systems has been of interest in these laboratories,[4,5] and in the course of these studies attempts have been made to prepare *m*- and *p*-ferrocenylphenylmagnesium bromides.

The Grignard reagent from *p*-bromophenylferrocene has been prepared in refluxing tetrahydrofuran, and in many ways the behavior of the system resembles the experiments reported by Shechter and Helling[6] on the preparation of ferrocenyl Grignard reagents. *p*-Bromophenylferrocene, like the haloferrocenes, reacts sluggishly with magnesium and requires, for a satisfactory reaction, tetrahydrofuran (THF) as a solvent and entrainment with alkyl halides, such as ethyl bromide.

Once formed, the Grignard reagent reacts normally with water, carbon dioxide, and benzophenone (see Scheme I); however, in all of these reactions phenylferrocene is a major product, despite rigorous precautions to exclude moisture. Of course deliberate hydrolysis of the Grignard reagent produced phenylferrocene (43%), but in the carbonation experiment phenylferrocene (25%) was produced along with *p*-ferrocenylbenzoic acid (44%). Upon addition of benzophenone to the Grignard reagent solution, phenylferrocene (58%) as well as *p*-ferrocenyltriphenylcarbinol (11%) was obtained. This behavior is quite analogous to the production of ferrocene accompanying the formation of ferrocenyl Grignard reagents[6] from haloferrocenes, and similarly this compound may arise from decomposition of the Grignard reagent to *p*-ferrocenylphenyl radicals, followed by abstraction of hydrogen from the solvent.

SCHEME I



Fc = ferrocenyl

Shechter and Helling also report the formation of biferrocenyl from the ferrocenyl Grignard reagents, especially at higher temperatures. The analogy was observed when *p*-bromophenylferrocene was treated with magnesium (with entrainment) at 100° in dimethylcarbitol (diethylene glycol dimethyl ether). Such a reaction mixture yielded only phenylferrocene (58%) and *p,p'*-diferrocenylbiphenyl[7] (15%) when carbonated, and phenylferrocene (58%) and *p,p'*-diferrocenylbiphenyl (18%) on treatment with benzophenone. Yields up to 57% of phenylferrocene were obtained on deliberate hydrolysis of the original reaction mixtures. It is most likely that at this higher temperature of formation the Grignard reagent does not survive to add to carbon dioxide or ketones.

m-Bromophenylferrocene also reacts with magnesium in refluxing tetrahydrofuran (with entrainment), but no addition products with carbon dioxide or benzophenone could be obtained. Hydrolysis yielded phenylferrocene (77%) and, in one attempted carbonation, a small amount *m,m'*-diferrocenylbiphenyl was obtained along with phenylferrocene (54%). Also in dimethylcarbitol, attempted preparations of the Grignard reagent, followed by addition to carbon dioxide

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(1) (a) Taken in part from the Ph.D. dissertation of A. K. Clark, The University of North Carolina, 1960; (b) Union Carbide Fellow, 1958–1959.

(2) Petroleum Research Fund Scholar, 1960–1961.

(3) National Science Foundation Undergraduate Research Participation Program participant.

(4) W. F. Little and A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1960).

(5) W. F. Little, R. A. Berry, and P. Kannan, *J. Am. Chem. Soc.*, **84**, 2525 (1962).

(6) H. Shechter and J. F. Helling, *J. Org. Chem.*, **26**, 1034 (1961).

(7) This compound has been prepared by an independent synthesis from the arylation of ferrocene with bisdiazonium salts of benzidine and will be described more fully in a later publication.

(Dry Ice), yielded only phenylferrocene (trace amounts) and *m,m'*-diferrocenylbiphenyl (58%), and attempted reaction with benzophenone yielded these same two products in yields of 63 and 11%, respectively.

It is likely then that the Grignard reagent of *m*-bromophenylferrocene decomposes to radicals at even lower temperatures than *p*-ferrocenylphenylmagnesium bromide and does not survive these conditions of formation long enough to add to substrates.

Experimental

Melting Points.—The melting points were obtained with a Fisher-Johns apparatus and are uncorrrected.

***p*-Bromophenylferrocene.**—*p*-Bromophenylferrocene, m.p. 121–123°, lit.[8] m.p. 125°, was prepared by the method of arylation described by Weinmayr.[9]

***m*-Bromophenylferrocene.**—*m*-Bromophenylferrocene was prepared from *m*-bromoaniline essentially according to the method of arylation described by Weinmayr,[9] m.p. 85–86°.

Anal. Calcd. for $C_{16}H_{13}BrFe$: C, 56.39; H, 3.84. Found C, 56.29; H, 3.96.

Preparation of *p*-Ferrocenylphenylmagnesium Bromide in Tetrahydrofuran.—A solution of 1.70 g. (0.005 mole) of *p*-bromophenylferrocene and 0.55 g. (0.005 mole) of ethyl bromide in 75 ml. of tetrahydrofuran was added dropwise under nitrogen to 0.365 g. (0.015 g.-atom) of magnesium turnings. After about 20% of the solution was added, the reaction mixture was brought to reflux, and a few drops of externally formed ethylmagnesium bromide (or in some cases a crystal of iodine) were added. The mixture was held at reflux throughout the addition of the remainder of the solution and for 2–4 hr. more.

Hydrolysis of the Grignard Reagents.—A solution of *p*-ferrocenylphenylmagnesium bromide was added with stirring to 360 ml. of 1 *N* H_2SO_4 at 0°. The mixture was allowed to come to room temperature and a yellow solid was collected. Chromatography on alumina [3:1 petroleum ether (b.p. 60–90°)-benzene] yielded 0.56 g. of phenylferrocene (43%), m.p. 109–111°, lit.[10] m.p. 112°. A mixture melting point was undepressed, and the infrared spectrum of the product was identical with that of an authentic sample.

Similar treatment of the reaction mixture of *m*-bromophenylferrocene with magnesium in tetrahydrofuran yielded phenylferrocene (77%), m.p. 110–112°.

Carbonation of *p*-Ferrocenylphenylmagnesium Bromide.—The Grignard reagent solution in tetrahydrofuran was added to a large excess of a powdered Dry Ice slurry in diethyl ether. After 1 hr. of stirring, the mixture was hydrolyzed with 150 ml. of 3 *N* HCl and the ether layer was extracted with dilute aqueous NaOH. The residue from evaporation of the ether was chromatographed on alumina (3:1 petroleum ether–benzene) and 0.34 g. (25%) of phenylferrocene, m.p. 104–110°, was obtained. The alkaline extract was acidified with concentrated HCl and 0.58 g. (44%) of *p*-ferrocenylbenzoic acid was collected. Recrystallization from benzene gave a product melting at 255–265° dec., lit.[11] m.p. 253–257° dec. The infrared spectrum of the product was identical with that of an authentic sample of *p*-ferrocenylbenzoic acid, prepared by alkaline hydrolysis of ethyl *p*-ferrocenylbenzoate.[11]

Addition of *p*-Ferrocenylphenylmagnesium Bromide to Benzophenone.—A solution of 1.82 g. (0.01 mole) of benzophenone in 75 ml. of tetrahydrofuran was added dropwise (1 hr.) to a solution of *p*-ferrocenylphenylmagnesium bromide at 0°. The mixture was then heated to reflux for 7 hr. and was allowed to stand overnight at room temperature. The reaction mixture was added to crushed ice and was acidified with dilute HCl. Ether extraction yielded a red oil, which was chromatographed on alumina. The first fraction, 0.76 g., eluted with 3:1 petroleum ether–benzene was phenylferrocene (58%), m.p. 105–109°; and the second fraction, eluted with benzene–methanol, was rechromatographed on Florisil (benzene) to give 0.23 g. (11%) of *p*-ferrocenyltriphenylcarbinol as yellow crystals, m.p. 129–131°.

Anal. Calcd. for $C_{29}H_{24}FeO$: C, 78.38; H, 5.44. Found: C, 78.24; H, 5.38.

The infrared spectrum showed an O–H stretching frequency at approximately 3590 cm.$^{-1}$ (KBr).

Attempted Preparation of *m*-Ferrocenylphenylmagnesium Bromide in Tetrahydrofuran.—The procedure used was identical with that described for *p*-ferrocenylphenylmagnesium bromide, except that *m*-bromophenylferrocene was the starting material. Upon treatment with water, as described for *p*-ferrocenylphenylmagnesium bromide, 1.1 g. of of phenylferrocene (77%) was obtained, m.p. 110–112°. However, carbonation of the original reaction mixture was unsuccessful. In one attempted carbonation, 0.70 g. (54%) of phenylferrocene was obtained with a small amount of *m,m'*-diferrocenylphenyl (*vide infra*); none of the *m*-ferrocenylbenzoic acid was obtained.

Reaction of Bromophenylferrocenes with Magnesium in Dimethylcarbitol.—Both *m*- and *p*-bromophenylferrocene were treated with magnesium (ethyl bromide entrainment) as in the preparation of *p*-ferrocenylphenylmagnesium bromide above, except for a change in the solvent to dimethylcarbitol (diethylene glycol dimethyl ether). The temperature was held at 100° for 7 hr. Both reaction mixtures after treatment with dilute acid and chromatography on alumina gave approximately 57% yields of phenylferrocene, but carbonation attempts and the addition of benzophenone produced none of the expected addition products. The carbonation mixture from the reaction with *p*-bromophenylferrocene was chromatographed on alumina. Elution with 3:1 petroleum ether–benzene yielded 0.75 g. of phenylferrocene (58%), m.p. 110–111°, and elution with benzene–methanol gave after recrystallization from heptane 0.20 g. (15%) of orange crystals of *p,p'*-diferrocenylbiphenyl,[7] which decomposed around 300°. The infrared spectrum showed no carbonyl group nor an OH stretch.

Anal. Calcd. for $C_{32}H_{26}Fe_2$: C, 73.59; H, 5.02. Found: C, 73.33; H, 5.12.

The same procedure for attempted carbonation of the reaction mixture of *m*-bromophenylferrocene with magnesium in dimethylcarbitol yielded a small amount of phenylferrocene and 0.75 g. (58%) of *m,m'*-diferrocenylbiphenyl, m.p. 238–239°

Anal. Calcd. for $C_{32}H_{26}Fe_2$: C, 73.59; H, 5.02. Found: C, 73.46; H, 5.21.

Treatment of the original reaction mixtures with benzophenone also yielded only *p,p'*-diferrocenylbiphenyl (18%) and phenylferrocene (58%) in the one case, and *m,m'*-diferrocenylbiphenyl (11%) and phenylferrocene (63%) in the other.

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