filtered, and the solid was washed well with water followed by ether. This solid was shaken with 15% hydrochloric acid to give 9.6 g. (60%) of monoacetyl-β-diketone XI as red crystals; after recrystallization from hexane the compound melted at 97–97.5°, reported[12,20] m.p. 96–97°.

Anal. Calcd. for $C_{14}H_{14}FeO_2$: C, 62.25; H, 5.22. Found: C, 62.67; H, 5.30.

Cyclizations of bis-β-diketones with hydrazine to form pyrazoles. Pyrazole VI was prepared as previously described.[3]

To a solution of 1 g. of bis-β-diketones III or IV in 200 ml. of absolute ethanol was added 10 g. of 95% hydrazine in 20 ml. of absolute ethanol to produce a deep red color. After adding 1 drop of glacial acetic acid, the solution was boiled for a few minutes. The resulting bright-red solution was cooled overnight in the refrigerator.

Pyrazole VII was obtained in 89% yield as a pink powder, m.p. 300° dec. Some infrared bands occurred at 6.3, 6.85, 7.28, 7.7, and 8.65 μ.

Anal. Calcd. for $C_{18}H_{18}N_4Fe$: C, 62.44; H, 5.24; N, 16.18; Fe, 16.13. Found: C, 62.04; H, 5.41; N, 16.16; Fe, 16.38.

Pyrazole VIII was obtained in 99% yield as a pink powder, m.p. 300° dec. Some infrared bands occurred at 6.25, 6.35, 6.85, 7.25, 7.7, and 8.62 μ.

Anal. Calcd. for $C_{20}H_{22}N_4Fe$: C, 64.18; H, 5.93; N, 14.97; Fe, 14.92. Found: C, 64.18; N, 15.01; Fe, 14.96.

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(20) See L. Wolf and M. Beer, *Naturwiss.*, **44**, 442 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Ferrocenyl and 1,1'-Ferrocenylene Grignard Reagents[1a]

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Received July 28, 1960

Grignard reagents have been prepared by controlled reactions of magnesium with chloroferrocene, bromoferrocene, iodoferrocene, and 1,1'-dibromoferrocene, respectively, in tetrahydrofuran. Advantageous techniques involving methyl iodide and ethylene bromide have been developed. Ferrocenyl Grignard reagents decompose at elevated temperatures to give ferrocene and biferrocenyl; in the presence of cobaltous chloride, ferrocenylmagnesium bromide gives biferrocenyl in 80% conversion. These abnormal Grignard reactions apparently involve ferrocenyl radicals.

Lithio and sodioferrocenes are obtained by exchange of ferrocene with butyllithium[2] and phenyl- or amyl sodium,[3] respectively. These preparations often have disadvantages that mixtures of mono and dimetalloferrocenes are formed, and the excess metal alkyls or aryls required compete undesirably in many preparative sequences. Ferrocenyl Grignard reagents have not been previously described; efforts to prepare ferrocenylmagnesium iodide from iodoferrocene and magnesium in ethyl ether have been unsuccessful.[4] It is now reported that chloroferrocene, bromoferrocene, and iodoferrocene (Table I) react with magnesium powder in tetrahydrofuran under controlled conditions to give Grignard reagents in satisfactory yields. 1,1'-Dibromoferrocene has been converted to its di-Grignard reagent (59%). The yields of these reagents were determined by carbonation and isolation of the resultant carboxylic acids. The potential utility of ferrocenyl Grignard reagents in synthesis is indicated by the present results in conjunction with the elegant methods for preparing bromo- and chloroferrocenes from lithioferrocenes and butyl borate and subsequent reaction of ferrocenylboronic acids with cupric halides.[5]

Reactions of haloferrocenes and magnesium to give Grignard reagents occur under oxygen-free nitrogen when initiated with methyl iodide; an attempt to use iodine as an initiator was unsuccessful. The relative reactivities of haloferrocenes are typical: iodo> bromo> chloro. The rates of reaction and conversions to Grignard reagents are increased by use of methyl iodide or ethylene bromide as entrainers (Table I). Methylmagnesium iodide does not undergo exchange with bromoferrocene under conditions for preparing the ferrocenyl Grignard reagent.

Haloferrocenes also react with magnesium in tetrahydrofuran to give biferrocenyl and ferrocene. Thus, reaction of iodoferrocene and magnesium at 25–30° for three hours in the presence of ethylene

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(1)(a) Abstracted from a portion of the Ph.D. Dissertation of J. F. Helling, The Ohio State University, 1960. (b) DuPont Company Fellow, 1958–1959; National Science Foundation Cooperative Fellow, 1959–1960. Present address, Chemistry Department, Massachusetts Institute of Technology, Cambridge, Mass.

(2)(a) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954). (b) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, 97, 459 (1954).

(3)(a) A. N. Nesmeyanov, E. G. Perevalova, and Z. A. Beinoravichute, *Doklady Akad. Nauk S.S.S.R.*, **112**, 439 (1957). (b) A. N. Nesmeyanov, E. G. Perevalova, Z. A. Beinoravichute, and I. L. Malygina, *Doklady Akad. Nauk S.S.S.R.*, **120**, 1263 (1958).

(4) A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, 100, 1099 (1955).

(5)(a) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Doklady Akad. Nauk S.S.S.R.*, **126**, 1004 (1959). (b) In the present research (see Experimental) preparation of lithioferrocenes in 1:1 tetrahydrofuran–ethyl ether and subsequent reaction with butyl borate in ethyl ether resulted in 44% conversion to ferrocenylboronic acid and 18% conversion to 1,1'-ferrocenylenediboronic acid; 29% ferrocene was recovered. (c) Iodoferrocene is prepared by reaction of chloromercuriferrocene and iodine (see Experimental).

TABLE I

REACTIONS OF HALOFERROCENES AND MAGNESIUM

Haloferrocene[a]	Reactant Ratio, Mole Haloferrocene	Mg	CH_3I	Temp., °	Time,[b] Hr.	Conv.,[c,d] %	Recovery, %; Haloferrocene[e]
Chloro	1	4	1	46–48[f]	4.0	15	79
Bromo	1	3	–[g]	38–42[f]	3.5	49[h]	34
Bromo	1	4	1	37–39[f]	2.0	84	11
Iodo	1	3	–[g]	11–12	2.5	47	44
Iodo	1	4	1	11–12	1.0	65	27
1,1′-Dibromo	1	5	2	33–34[f]	5.25	59[i]	Trace

[a] Reactions were performed with 0.5–1.0 g. of the haloferrocene and 15–20 ml. of tetrahydrofuran. [b] Time after dropwise addition of halide. [c] Conversion of haloferrocene to Grignard reagent; determined by addition of Dry Ice to give the carboxylic acid. [d] Optimum conditions for preparing the Grignard reagents were not determined. [e] The recovered haloferrocene, on the basis of melting points and infrared spectra, contained ferrocene. [f] The halides in tetrahydrofuran were added at room temperature. [g] Methyl iodide in trace amounts was used as the initiator. [h] Biferrocenyl was formed in 9% conversion. [i] *Conversion to 1,1′-ferrocenedicarboxylic acid; ferrocenecarboxylic acid was also obtained in 16% conversion.*

bromide as an entrainer yielded ferrocene (62%) and biferrocenyl (34%). Bromoferrocene, magnesium, and methyl iodide at 38–42° for three and a half hours gave biferrocenyl (9%), ferrocene, and the ferrocenyl Grignard reagent. At elevated temperatures the yields of Grignard reagents are substantially reduced by formation of ferrocene and biferrocenyl. Analogously, reaction of butyllithium and iodoferrocene in ethyl ether at 0° and subsequent carbonation gave biferrocenyl (20%), ferrocene (60%), and ferrocenecarboxylic acid (17%). Reaction of ferrocenylmagnesium bromide with cobaltous chloride gave biferrocenyl in 80% conversion.[6]

Formation of biferrocenyl and ferrocene in the present systems may indicate that ferrocenyl radicals are generated readily[6] (Equation 1); dimerization of ferrocenyl radicals (Equation 2) or exchange with the solvent (Equation 3) may thus give biferrocenyl and ferrocene.[7] The incursion

$$C_5H_5\text{—}Fe\text{—}C_5H_4\text{—}MgX \longrightarrow C_5H_5\text{—}Fe\text{—}C_5H_4\cdot + \cdot MgX \quad (1)$$

$$2C_5H_5\text{—}Fe\text{—}C_5H_4\cdot \longrightarrow C_5H_5\text{—}Fe\text{—}C_5H_4\text{—}C_5H_4\text{—}Fe\text{—}C_5H_5 \quad (2)$$

$$C_5H_5\text{—}Fe\text{—}C_5H_4\cdot + H\text{—}R \longrightarrow C_5H_5\text{—}Fe\text{—}C_5H_5 + \cdot R \quad (3)$$

of these abnormal Grignard reactions under relatively mild conditions to yield biferrocenyl and ferrocene appears to have much in common with reactions of diferrocenylmercury and silver[8] or palladium black,[9] iodoferrocene and copper bronze,[8] and ferrocenylboronic acid and ammoniacal silver oxide[5a] to give analogous products.[10]

EXPERIMENTAL

Iodoferrocene. Iodoferrocene[4] was prepared advantageously in the present study by reaction of chloromercuriferrocene and iodine in partial solution in methylene chloride. After the mixture had been stirred 30 min. at room temperature, methylene chloride was evaporated and the iodine complexes destroyed with aqueous sodium thiosulfate. The product was dissolved in petroleum ether, passed through an alumina column, and concentrated. Vacuum sublimation[11] of the red oily residue gave iodoferrocene (70% conversion), m.p. 43–45°; lit.[4] m.p. 44–45°.

Ferrocenylboronic acid and 1,1′-ferrocenylenediboronic acid. Ferrocenylboronic acid and 1,1′-ferrocenylenediboronic acid were obtained by an improved modification of a previous procedure.[5a] Ferrocenyllithium was prepared in tetrahydrofuran–ethyl ether[12] (1:1 by volume, 220 ml.) from butyllithium (~0.27 mole) and ferrocene (16.7 g., 0.09 mole). The mixture was filtered through glass wool and then added dropwise in 2 hr. to butyl borate (72.5 g., 0.315 mole) in ethyl ether (50 ml.) at −70°. A solid formed. The mixture was warmed to room temperature (1.5 hr.), decomposed with 10% aqueous sodium hydroxide (100 ml.) and filtered. The ether solution was extracted nine times with 10% aqueous sodium hydroxide (total vol., 400 ml.). Acidification of the basic solution with 10% sulfuric acid at 0° gave a yellow precipitate which was washed with water. Soxhlet extraction of the precipitate with ethyl ether for 4 days removed ferrocenylboronic acid (9.02 g., 0.039 mole, 44%)

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(6) Related homolytic decomposition reactions of Grignard reagents are summarized and discussed by M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances,* Prentice-Hall, New York, 1954, pp. 116–137.

(7) Reaction of iodoferrocene and magnesium at room temperature (see Experimental) and subsequent carbonation of the mixture gave only biferrocenyl and ferrocene. The absence of ferrocenecarboxylic acid indicated that the Grignard reagent had been completely destroyed before carbonation and hydrolysis, and thus ferrocene was formed by radical exchange with the solvent rather than by hydrolysis. As stringent precautions were always taken to avoid hydrolysis of the Grignard reagents before carbonation, formation of ferrocene by radical-exchange with the solvent appears to be a general competitive process.

(8) M. D. Rausch, *J. Am. Chem. Soc.,* 82, 2080 (1960).

(9) O. A. Nesmeyanova and E. G. Perevalova, *Doklady Akad. Nauk S.S.S.R.,* 126, 1007 (1959).

(10)(a) Other reactions of ferrocenyl Grignard reagents are being investigated. (b) Lithioferrocene and dinitrogen tetroxide in ethyl ether at −70° give nitroferrocene, m.p. 124–125°, in 2% yield. The melting point of nitroferrocene was previously reported incorrectly (96–97°); J. F. Helling and H. Shechter, *Chem. & Ind.,* 1157 (1959). Reaction of ferrocenylmagnesium bromide and dinitrogen tetroxide in ethyl ether–tetrahydrofuran at −70° does not yield nitroferrocene.

(11) Vacuum sublimation is a convenient method for purifying iodoferrocene, bromoferrocene, and chloroferrocene.

(12) D. W. Mayo, P. D. Shaw, and M. Rausch, *Chem. & Ind.,* 1388 (1957).

which was obtained as a yellow powder after evaporation of solvent, m.p. 136–140° dec.; lit.[5a] m.p. 143–148°. Remaining as an insoluble yellow powder from the Soxhlet extraction was 1,1′-ferrocenylenediboronic acid (4.42 g., 0.016 mole, 18%), dec. ~200°; lit.,[5a] dec. 180°.

The ether solution which had been washed with alkali was concentrated; filtration and vacuum sublimation of the precipitate gave crude ferrocene (4.93 g., 29%).

Ferrocenylmagnesium bromide (Methyl iodide as entrainer). Anhydrous tetrahydrofuran (5 ml.) was added to magnesium powder (0.36 g., 0.0148 g.-atom, 80–200 mesh) flamed briefly under oxygen-free dry nitrogen.[13] After the magnesium had been activated with a drop of methyl iodide, a solution of bromoferrocene (1.00 g., 0.0038 mole) and methyl iodide (0.53 g., 0.0037 mole) in tetrahydrofuran (10 ml.) was added dropwise with stirring at 31–33°. The mixture was then stirred at 37–39° for 2 hr. under nitrogen, cooled to 0°, and Dry Ice was added.[14] After the mixture had been acidified with hydrochloric acid and diluted with ether, the organic layer was extracted with excess aqueous sodium hydroxide (10%). The orange basic solution was cooled to 0° and neutralized with cold hydrochloric acid. A voluminous yellow precipitate formed which was extracted with ether. After the ether solution had been evaporated to dryness, ferrocenecarboxylic acid (0.73 g., 0.0032 mole, 84%) was obtained, m.p. 194–197° dec. after crystallization from ether-petroleum ether (b.p. 30–60°), lit.[2b] m.p. 192–205° dec.; lit.[15] m.p. 219–225° dec. The infrared spectrum of the acid was identical with that of an authentic sample.

The initial organic layer, after the extraction with sodium hydroxide, was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. Vacuum sublimation of the residue gave a mixture of bromoferrocene and ferrocene (0.11 g., 11% calculated as bromoferrocene, 15% calculated as ferrocene),[16] m.p. 75–125°.

Ferrocenylmagnesium bromide (Methyl iodide as initiator). Ferrocenylmagnesium bromide was prepared as previously described with the exceptions that no entrainer was used and the reaction was effected at 38–42° for 3.5 hr. Bromoferrocene (0.96 g., 0.0036 mole), magnesium powder (0.26 g., 0.0108 g.-atom) and initiator amounts of methyl iodide in tetrahydrofuran (15 ml.) gave ferrocenecarboxylic acid (0.41 g., 0.0018 mole, 49%), m.p. 194–197° dec. after crystallization from ether–petroleum ether.

Vacuum sublimation of the nonacidic products gave a mixture of ferrocene and bromoferrocene (0.33 g., 34% calculated as bromoferrocene). Remaining as a nonsublimable residue was biferrocenyl (0.06 g., 0.00016 mole, 9%), m.p. 233–237° after recrystallization from benzene-ligroin; lit.[8] m.p. 239–240° dec. Identification of biferrocenyl was confirmed by its infrared spectrum.[17]

Attempted reaction of bromoferrocene and methylmagnesium iodide. Methylmagnesium iodide was prepared under oxygen-free, dry nitrogen from methyl iodide (0.88 g., 0.0062 mole) and magnesium powder (0.13 g., 0.0056 g.-atom) in tetrahydrofuran (15 ml.) at 27° for 1.5 hr.; only traces of magnesium remained. Bromoferrocene (0.50 g., 0.00187 mole) in tetrahydrofuran (5 ml.) was added dropwise with stirring at 27°. The mixture was stirred at 37–40° for 2 hr., cooled to 0°, and Dry Ice was added. Isolation of products by methods previously described gave bromoferrocene (0.38 g., 76%) m.p. 29–30°; no ferrocenecarboxylic acid was detected.

Reaction of iodoferrocene and magnesium (Reduction and coupling). Magnesium turnings (0.57 g., 0.0233 g.-atom) in tetrahydrofuran (10 ml.) were activated with a small quantity of ethylene bromide. Iodoferrocene (2.34 g., 0.0075 mole) in tetrahydrofuran (20 ml.) was added dropwise with stirring under oxygen-free, dry nitrogen at room temperature. After ethylene bromide (2.82 g., 0.0150 mole) in tetrahydrofuran (25 ml.) had been added slowly, the mixture was stirred 3 hr., cooled to 0°, and Dry Ice added.

Following treatment of the mixture with hydrochloric acid, dilution with ether, and filtration, the organic layer was extracted with excess aqueous sodium hydroxide. The colorless alkaline extract contained no ferrocene derivatives. The ether solution was washed with water, dried, and evaporated. Vacuum sublimation of the residue gave ferrocene (0.86 g., 0.0045 mole, 62%), m.p. 168–174°; lit.[18] m.p. 173–174°. Remaining as a nonsublimable residue was biferrocenyl (0.47 g., 0.0012 mole, 34%), m.p. 236.5–237.5° after recrystallization from benzene-ethanol; lit.[8] m.p. 239–240°.

Reaction of ferrocenylmagnesium bromide and cobaltous chloride. Magnesium powder (0.33 g., 0.0135 g.-atom) under oxygen-free, dry nitrogen was activated with a drop of methyl iodide. A solution of bromoferrocene (0.72 g., 0.0027 mole) and ethylene bromide (0.51 g., 0.0027 mole)[19] in tetrahydrofuran (10 ml.) was added in 30 min. at 29–30°. After the mixture had been stirred for 2.5 hr. at 37–39°, anhydrous cobaltous chloride (0.23 g., 0.0018 mole)[20] was added all at once at 0°.

The mixture was warmed to room temperature, allowed to stand overnight, decomposed with hydrochloric acid, and worked up in the usual manner. Vacuum sublimation of the residue gave a mixture of ferrocene and bromoferrocene (0.13 g., 18% calculated as bromoferrocene[16]), m.p. 35–95°. Remaining as a red-orange residue was biferrocenyl (0.40 g., 0.0011 mole, 80%) which melted at 230–234° after recrystallization from benzene-ethanol.

Reaction of butyllithium and iodoferrocene. Butyllithium was prepared under nitrogen from butyl bromide (0.96 g., 0.007 mole) and lithium wire (0.0972 g., 0.014 g.-atom) in ethyl ether (10 ml.). Iodoferrocene (1.09 g., 0.0035 mole) in ethyl ether (15 ml.) was added dropwise with stirring at 0°. The mixture was stirred 1 hr. at 0° and then Dry Ice was added. After having been washed with hydrochloric acid, the mixture was extracted with aqueous sodium hydroxide. The ether layer was washed with water, dried, and evaporated. Vacuum sublimation of the residue gave impure ferrocene (0.39 g., 0.0021 mole, 60%), m.p. 140–165°; lit.[18] m.p. 173–174°. Biferrocenyl (0.13 g., 0.00035 mole, 20%) remained as a red-orange residue, m.p. 236–237° from benzene-petroleum ether; lit.[8] m.p. 239–240°.

Acidification of the basic extract gave a yellow precipitate which was extracted with ether. After the extract had been dried, ferrocenecarboxylic acid (0.14 g., 0.00060 mole, 17%) crystallized upon addition of petroleum ether, m.p. 194–197° dec.

Reaction of 1,1′-dibromoferrocene and magnesium. A solution of 1,1′-dibromoferrocene (0.55 g., 0.0016 mole) and methyl iodide (0.45 g., 0.0032 mole) in tetrahydrofuran (10 ml.) was added dropwise to stirred magnesium powder (0.20 g., 0.0080 g.-atom; activated with a drop of methyl iodide) in tetrahydrofuran (5 ml.) at 29–32° under nitrogen. The mixture was stirred at 33–34° for 5.25 hr. and cooled to 0°;

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(13) L. F. Fieser, *Experiments in Organic Chemistry*, Third Edition, D. C. Heath and Co., Boston, Mass., 1957, p. 299.

(14) The techniques in preparing ferrocenylmagnesium chloride and iodide were similar to those presently described.

(15) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).

(16) The percentage composition was not determined because of the difficulty in separating ferrocene from haloferrocenes.

(17) S. I. Goldberg and D. W. Mayo, *Chem. & Ind.*, 671 (1959)

(18) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(19) D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

(20)(a) A. R. Pray, *Inorganic Syntheses*, Vol. V, McGraw-Hill, New York, 1957, p. 153. (b) M. S. Kharasch and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941).

Dry Ice was added. After the mixture had been treated with hydrochloric acid and diluted with ether and tetrahydrofuran, the organic layer was extracted with excess aqueous sodium hydroxide. The basic solution was cooled to 0° and neutralized with cold hydrochloric acid. The yellow precipitate which formed was extracted with tetrahydrofuran with the aid of added saturated aqueous sodium chloride and then recrystallized by addition of petroleum ether. The solid obtained was filtered and washed with ether. Evaporation of the ether washings and recrystallization of the residue from benzene and ether–petroleum ether gave ferrocenecarboxylic acid (0.06 g., 0.00026 mole, 16%) which was identified by comparison with an authentic sample.

Remaining as a residue from the ether washing was 1,1'-ferrocenedicarboxylic acid (0.26 g., 0.0016 mole, 59%) which did not melt or decompose below 280°; lit.,[2b] no melting or decomposition below 250°. The infrared spectrum of the 1,1'-ferrocenedicarboxylic acid obtained was identical with an authentic sample. The identity of the dicarboxylic acid was confirmed by esterification with methanol catalyzed by hydrochloric acid; chromatography on alumina and vacuum sublimation of the product gave dimethyl 1,1'-ferrocenedicarboxylate (73% conversion), m.p. 112–113°; lit.[2b] m.p. 114–115°.

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[CONTRIBUTION FROM THE DOW CORNING CORP.]

Reaction of 3,3,3-Trifluoropropylmagnesium Bromide with Carbonyl Compounds

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Received August 18, 1960

The reaction of 3,3,3-trifluoropropylmagnesium bromide with methyl trifluoroacetate and 1,1,1,5,5,5-hexafluoro-2-pentanone in both ether and tetrahydrofuran has shown the Grignard to be only a weak reducing agent. In the case of methyl trifluoroacetate, the principal product was a solid which on hydrolysis yielded the hydrate of 1,1,1,5,5,5-hexafluoro-2-pentanone. Evidence for the structure of this solid intermediate, $CF_3CH_2CH_2C(OCH_3)(OMgBr)CF_3$, and a reaction mechanism involving this intermediate are presented.

Fluorine-containing Grignard reagents have been studied extensively and, in particular, the preparation and reactions of the perfluoroalkylmagnesium halides have received much attention.[1] However, derivatives of the type $R_fCH_2CH_2MgX$ (R_f = CF_3, C_2F_5, etc.) have been studied only briefly in reactions of limited scope.[2,3] In this laboratory a study was undertaken to ascertain the differences between a Grignard of the above type and a nonhalogenated Grignard in reactions in which reduction by the Grignard reagent generally occurs. For this purpose, the reaction of 3,3,3-trifluoropropylmagnesium bromide (I) with fluorine-containing carbonyl compounds was chosen.

The tendency of fluorine-containing esters to undergo reduction in preference to addition with certain Grignard reagents has been extensively discussed.[2,4–8] In this study, the reaction of I with methyl trifluoroacetate in ether solution formed an insoluble material which on hydrolysis and further treatment with phosphorus pentoxide gave 1,1,1,5,5,5-hexafluoro-2-pentanone (II). No reduction was observed. A similar reaction conducted in tetrahydrofuran indicated no formation of a solid precipitate and yielded II as well as 1,1,1,7,7,7-hexafluoro - 4 - (trifluoromethyl) - 4-heptanol (III) and 1,1,1,5,5,5-hexafluoro-2-pentanol (IV). The last compound, resulting from reduction by the Grignard, was formed in only 12% yield. In an effort to increase the yield of reduction product (IV), the reaction was conducted in the presence of an excess of isopropylmagnesium bromide in ether solution.[8] The principal product of this reaction was 1,1,1-trifluoro-3-methyl-2-butanol (V) as well as lesser amounts of II, III and IV. In contrast to the poor reducing action of I, the reaction of methyl trifluoroacetate with *n*-propylmagnesium bromide in ether was found to give only 1,1,1-trifluoro-2-pentanol (VI), the reduction product.

Addition of magnesium bromide to the methyl trifluoroacetate prior to the addition of I in tetrahydrofuran solution changed the product distribution markedly. The principal product was the ketone (II) with only trace amounts of III and IV. A similar reaction conducted in ether solution gave only II, as was the case in the absence of magnesium bromide.

The reaction of II with trifluoropropyl Grignard in ether formed the addition product (III) in good yield together with a small yield of the reduction product (IV). Addition of magnesium

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[1] J. J. Lagowski, *Quart. Rev.*, Vol. XIII, No. 3, 233 (1959).

[2] O. R. Pierce, E. T. McBee, and R. E. Cline. *J. Am. Chem. Soc.*, **75**, 5618 (1958).

[3] E. T. McBee and A. Truchan, *J. Am. Chem. Soc.*, **70**, 2910 (1948).

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[7] E. T. McBee, O. R. Pierce, and M. C. Chen, *J. Am. Chem. Soc.*, **75**, 2324 (1953).

[8] O. R. Pierce, J. C. Siegle, and E. T. McBee, *J. Am. Chem. Soc.*, **75**, 6324 (1953).