[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

Grignard Reagents of Sulfones. VII. Additional Reactions with Carbonyl Compounds[1]

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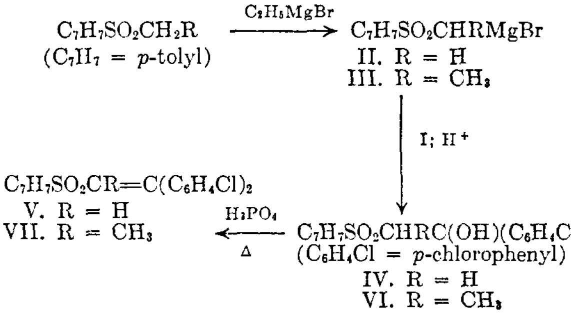
Reaction of *p,p'*-dichlorobenzophenone with typical Grignard reagents of sulfones, formulated as $C_7H_7SO_2CHRMgBr$, gave the expected carbinols, but only under unusually vigorous conditions. The carbinols were difficult to purify, but could be dehydrated without extensive purification to afford a useful synthesis of the unsaturated sulfones.

The product from treatment of a β-hydroxysulfone with two molar proportions of ethylmagnesium bromide failed to add to benzaldehyde. The favored explanation for the surprising nonoccurrence of addition is that the bromomagnesium alkoxide which first forms resists metalation.

In a continuing study of Grignard reagents of sulfones (substances such as II and III),[2] metalation of 1,5-bis(phenylsulfonyl)pentane and its homologs became of interest. A convenient means of determining the positions of metalation seemed to be by isolation of addition products with *p,p'*-dichlorobenzophenone(I). Use of the symmetrical ketone I for addition minimizes the number of stereoisomeric products; furthermore, the bulky products should crystallize nicely, and the chlorine atoms provide a tag of probable help in removing sulfone used as starting material. However, reactions of the ketone I proved to be considerably less straightforward than anticipated from those involving aldehydes and aliphatic ketones.[3,4]

Although Potter added *p*-tolylsulfonylmethylmagnesium bromide (II) to benzophenone and dehydrated the carbinol to 1,1-diphenyl-2-(*p*-tolylsulfonyl)ethene, he did not have occasion to report yields.[5] Accordingly, we have studied reactions of the ketone I with the simple Grignard reagents II and III in order to gain experience which would be applicable in subsequent use of the ketone I with other Grignard reagents of sulfones. This paper reports results related to reactions of the ketone I with Grignard reagents II and III.



$$\begin{tikzcd}
\begin{array}{l} C_7H_7SO_2CH_2R \\ (C_7H_7 = p\text{-tolyl}) \end{array} \arrow[r, "C_2H_5MgBr"] & \begin{array}{l} C_7H_7SO_2CHRMgBr \\ \text{II. } R = H \\ \text{III. } R = CH_3 \end{array} \arrow[d, "I;\ H^+"] \\
\begin{array}{l} C_7H_7SO_2CR{=}C(C_6H_4Cl)_2 \\ \text{V. } R = H \\ \text{VII. } R = CH_3 \end{array} & \begin{array}{l} C_7H_7SO_2CHRC(OH)(C_6H_4Cl)_2 \\ (C_6H_4Cl = p\text{-chlorophenyl}) \\ \text{IV. } R = H \\ \text{VI. } R = CH_3 \end{array} \arrow[l, "H_3PO_4"', "\Delta"]
\end{tikzcd}$$

Reaction of the ketone I with the Grignard reagent II at 72° for nine and a half hours gave the carbinol IV in 86% yield, but with a very low melting point, relative to pure IV. Although the melting point of pure IV showed peculiar variations, the low melting point of the reaction product undoubtedly resulted chiefly from contamination by the ketone I. Removal of unchanged ketone(I) was difficult; it could not be converted effectively to a water-soluble derivative with hydroxylamine-*O*-sulfonic acid or with Girard's "T" reagent. Numerous recrystallizations had little effect. Chromatography removed 23% of the original product as the ketone I, and recrystallization then gave fairly pure 1,1-di(*p*-chlorophenyl)-2-*p*-tolylsulfonyl-1-ethanol(IV) in an overall yield of 27%. Fractional crystallization still was required, however, for complete purification of the carbinol IV. Dehydration of IV, as obtained in 86% yield, nevertheless gave the unsaturated sulfone V in an overall yield of 35%, demonstrating that the yield of carbinol IV was reasonably good despite the difficulty of purifying it.

Heating ketone I with the Grignard reagent III, prepared from ethyl *p*-tolyl sulfone, at 72° for five hours, conditions far more vigorous than those used in earlier reactions with aliphatic ketones,[4] seemed to result in incomplete reaction. A reaction period of twenty-one hours resulted in 1,1-di(*p*-chlorophenyl)-2-*p*-tolylsulfonyl-1-propanol (VI) in 56% yield and fair purity, and one of thirty-seven and a half hours gave VI in 66% yield; the melting point of VI showed some indication of the erratic behavior mentioned for the carbinol IV. The carbinol VI was purified much more easily than the carbinol IV. Dehydration of carbinol VI gave the fairly pure unsaturated sulfone VII in 76% yield (50% overall, based on ethyl *p*-tolyl sulfone). The unsaturated sulfone VII also showed erratic behavior in its melting point.

Results with the ketone I thus may be summarized by stating that its reactions with Grignard reagents such as II and III require unusually vigorous conditions. Because of the difficulty of removing unchanged ketone I [and perhaps also

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[1] Work supported by the Office of Ordnance Research U. S. Army. Abstracted from part of the Ph.D. dissertation of E. T. B., January, 1961.

[2] Paper VI, L. Field, J. R. Holsten, and R. D. Clark, *J. Am. Chem. Soc.*, 81, 2572 (1959).

[3] L. Field, *J. Am. Chem. Soc.*, 74, 3919 (1952).

[4] L. Field and J. W. McFarland, *J. Am. Chem. Soc.*, 75, 5582 (1953).

[5] H. Potter, *J. Am. Chem. Soc.*, 76, 5472 (1954).

ethyldi(p-chlorophenyl)carbinol, formed from ketone I and ethylmagnesium bromide], the reaction is not an appealing means of obtaining pure carbinols such as IV and VI, but it does afford a fairly satisfactory route to unsaturated sulfones such as V and VII.

Although unrelated to the study just described, a recently investigated aspect of the reaction of a Grignard reagent of a sulfone with an aldehyde also may be reported appropriately in this paper. In previous work, reaction products obtained using Grignard reagents like II with certain substances have undergone metalation by the Grignard reagent and then have reacted with a second mole of the substance.[2] For example, Grignard reagent II reacts with ethyl chloroformate (acting as an acyl halide) to give diethyl p-tolylsulfonylmalonate and with phenyl isocyanate to give p-tolylsulfonylmalonanilide.[6] Nitriles and esters, on the other hand, give (after hydrolysis) only monoketo sulfones; thus Grignard reagent II and methyl benzoate give α-(p-tolysulfonyl)acetophenone.[6] Whether mono or diacylation occurs depends to a considerable extent on the activity of the acylating agent.[2,6] The foregoing results are understandable, as reactivity toward conventional Grignard reagents decreases in the order isocyanates > acyl halides > esters > nitriles.[7]

Aldehydes and methyl ketones are more reactive than isocyanates, however,[7] and one would suppose that the following sequence should be possible:

$$\underset{\text{VIII}}{C_6H_5SO_2CH_2CH(OH)C_6H_5} \xrightarrow{\text{RMgBr}} \underset{\text{IX}}{C_6H_5SO_2CH_2CH(OMgBr)C_6H_5} + RH$$

$$\text{IX} \xrightarrow{\text{RMgBr}} \underset{\text{X}}{C_6H_5SO_2CH(MgBr)CH(OMgBr)C_6H_5} + RH$$

$$\text{X} + C_6H_5CHO \longrightarrow \underset{\text{XI}}{C_6H_5SO_2CH[CH(OMgBr)C_6H_5]_2}$$

Ordinarily only one mole of an aldehyde or ketone reacts with a Grignard reagent of a sulfone, such as the phenyl counterpart of II, giving products such as the carbinol VIII in good yield.[3,4] This fact can be explained by assuming that the aldehyde or ketone reacts so rapidly with a Grignard reagent of a sulfone that this Grignard reagent is consumed before it can metalate an adduct such as IX. In order to test this explanation, the carbinol VIII was treated with excess ethylmagnesium bromide (XII) in an effort to convert the carbinol first to IX and then to X. The product then was allowed to react with benzaldehyde and the diol which would be formed by hydrolysis of the adduct XI was sought.

In the first experiment, the reaction was carried out essentially in the manner used for adding methyl phenyl sulfone, *via* its Grignard reagent, to benzaldehyde,[3] except for use of the carbinol VIII and sufficient excess Grignard reagent (XII) to react with its hydroxyl group. Chromatography gave only two significant peaks. One contained the carbinol VIII (40% recovery), and the other a small amount of material which was not a carbinol. No indication could be found of the diol.

In order to determine the nature of reaction of the carbinol VIII itself with ethylmagnesium bromide, VIII was heated with the same molar proportion of ethylmagnesium bromide used before. Evolution of 82% of one molar proportion of ethane suggested that only the hydroxyl group had reacted, with formation of the monomagnesium derivative IX, but it was possible that reaction had occurred with formation of the dimagnesium derivative X, even though incompletely. Hydrolysis returned all of the carbinol VIII.

In a concluding experiment the carbinol VIII was heated with one molar poıportion of ethylmagnesium bromide (XII). Again 82% of one molar proportion of ethane was evolved, consistent with formation of the monomagnesium product (IX), since the hydroxyl group of VIII should react more readily than the methylenic hydrogens. An additional amount of XII then was added to bring its total amount to the same proportion previously used, and the mixture was heated until gas evolution ceased, in the hope of generating another molar proportion of gas which would indicate conversion of the monomagnesium compound IX to the dimagnesium compound X. Relatively little additional gas appeared, and a total volume of 58% of two molar equivalents ultimately resulted. As about this proportion of expectation may result when methyl phenyl sulfone is metalated, probably because of partial solution of gas in solvent,[8] reaction of the product with benzaldehyde was attempted. After hydrolysis, 88% of the carbinol VIII was recovered.

The most reasonable explanation of these facts seems to be that the carbinol VIII reacts rapidly with the Grignard reagent XII to give the monomagnesium product IX. Reaction then ceases for all practical purposes. If this explanation is tenable, the reason for the resistance of IX to further metalation is of considerable interest, as alkyl sulfones ordinarily can be metalated with relative ease. We suspect that the monomagnesium compound IX may exist as a quasicyclic coordination compound in which the MgBr moiety associates with the sulfonyl group in such a way that the electron-withdrawing power of the sulfonyl group required for further metalation is markedly reduced. An alternative explanation of the facts, but a less attractive one, is that although some of the di-

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[6] L. Field, J. E. Lawson, and J. W. McFarland, *J. Am. Chem. Soc.*, **78**, 4389 (1956).

[7] C. E. Entemann, Jr., and J. R. Johnson, *J. Am. Chem. Soc.*, **55**, 2900 (1933).

[8] L. Field, *J. Am. Chem. Soc.*, **78**, 92 (1956).

magnesium derivative X may form, it fails to react with benzaldehyde (in certain Grignard reagents of sulfones, only one of two geminal MgX residues reacts).[8]

EXPERIMENTAL[9]

1,1-Di(p-chlorophenyl)-2-p-tolylsulfonyl-1-ethanol (IV). (a) *Preparation.* A solution of 15.98 g. of *p,p'*-dichlorobenzophenone (I) in 200 ml. of dry benzene was added with good stirring during 20 min. to a suspension of *p*-tolylsulfonylmethylmagnesium bromide (II) prepared in the usual way[3,10] from 8.50 g. of methy *p*-tolyl sulfone and 0.063 mole of ethereal ethylmagnesium bromide (XII). The mixture was heated at 72° (reflux temperature) for 9.5 hr. and then was hydrolyzed by addition of cold 1*N* hydrochloric acid. A benzene extract was washed until neutral with water and dried. Removal of solvent left 24.1 g. (115%) of material, m.p. 92–105°, which after one recrystallization from carbon tetrachloride amounted to 18.1 g. of crude carbinol IV (86%), m.p. 105.5–107.5°. Recrystallization of a sample seven times using ethanol, carbon tetrachloride, and 1:1 benzene-hexane resulted in material melting at 111–118°. The melting point was essentially unchanged after a sample had been heated at 125° for 2.5 hr., indicating that dehydration during the determination of melting point was not the cause of the broad melting point.

Chromatography of 4.00 g. of material (m.p. 105.5–107.5°) on 275 g. of acid-washed alumina with elution by carbon tetrachloride, first pure and then containing 3 parts of ethanol, resulted in three major fractions: A, 0.91 g., m.p. 145–148°; B, 2.24 g., m.p. 103–120°; and C, 1.77 g., m.p. 112–120°. The melting point of A was undepressed by the authentic ketone I (the melting point of pure IV is depressed to *ca.* 120° by I). Infrared spectra of B and C were identical, except for presence of a weak peak at 1670 cm.$^{-1}$ in the spectrum of B, and showed medium absorption at 3600 cm.$^{-1}$ (in Nujol mull). Recrystallization of B from ethanol gave 1.69 g. of material, m.p. 116–130°. Recrystallization of C from ethanol gave 1.27 g. (27% overall of carbinol IV) of material, m.p. 131–147°.

Fractional crystallization of 0.60 g. of C from ethanol resulted in three fractions: 0.12 g., m.p. 146–147° (depressed by I); 0.26 g., m.p. 120–147°; and 0.17 g., m.p. 129–146°. The first fraction after several more recrystallizations from ethanol gave the carbinol IV (6 mg.); IV at first had a constant m.p. of 147–148° but later in the recrystallizations the m.p. became 132–132.5° (unchanged by drying).

Anal. Calcd. for $C_{21}H_{18}Cl_2O_3S$: C, 59.86; H, 4.31. Found: C, 60.00; H, 4.55.

(b) *Dehydration.* Essentially according to the procedure of Field,[3] 3.00 g. of carbinol IV (m.p. 105.5–107.5°) was heated in 85% phosphoric acid (35 ml.) at the reflux temperature for 3 hr. The reaction mixture was poured onto ice and a benzene extract was washed until neutral with water and dried. Removal of solvent left 2.60 g. (91%) of crude 1,1-di(*p*-chlorophenyl)-2-*p*-tolylsulfonylethene (V), m.p. 119–140°. Recrystallization from ethanol and then from ethyl acetate gave 1.17 g. (41% from crude IV, 35% overall from methyl *p*-tolyl sulfone) of V, m.p. 153–155°. Further recrystallization (ethyl acetate) gave V with a constant m.p. of 155–155.5°.

Anal. Calcd. for $C_{21}H_{16}Cl_2O_2S$: C, 62.53; H, 4.00. Found: C, 62.76; H, 4.24.

1,1-Di(p-chlorophenyl)-2-p-tolylsulfonyl-1-propanol (VI). (a) *Preparation.* The ketone I (15.98 g.) in dry benzene (200 ml.) was added with vigorous stirring to the 1-(*p*-tolylsulfonyl)ethylmagnesium bromide (III) prepared as usual[4] from ethyl *p*-tolyl sulfone (9.20 g.) and 0.063 mole of ethereal XII. The mixture was heated at 72° for 5 hr., cooled to 25°, and hydrolyzed with cold 1*N* hydrochloric acid. Removal of solvent from a washed and dried benzene extract gave 23.0 g. of material, m.p. 85–160°. A small sample of the product when recrystallized from dimethylformamide had m.p. 136.5–160°, undepressed by the ketone I.

In an identical experiment except with a reflux period of 21 hr., there was obtained 19.7 g. (91%), of crude VI, m.p. 79–157°. One recrystallization from benzene-hexane gave 15.15 g. (70%), m.p. 156.5–159.5° and a second crop of 0.55 g. of I, m.p. and mixture m.p. 145.5–147.5°. Another recrystallization of the carbinol VI from benzene-hexane left 12.23 g. (56%), m.p. 151–153°.

When the heating period was increased to 37.5 hr., the usual extraction of the acidified reaction mixture with benzene left behind 6.04 g. of material, m.p. 179.5–190.5°, which was insoluble in both benzene and water. The benzene-soluble product amounted to 17.5 g. (81%), m.p. 111–169.5°. Recrystallization of this 17.5 g. of crude VI from benzene-hexane gave 9.46 g. (43%), m.p. 158.5–160°; after the product was ground and redried under vacuum, the m.p. was 151–153°. A second crop (2.39 g., m.p. 135–140°) and a third crop (1.63 g., m.p. 143–146.5°) were undepressed in melting point by mixture with I (the m.p. of pure VI is depressed to *ca.* 137° by I). When the original benzene-insoluble material was dissolved in boiling benzene, filtered and adjusted to incipient turbidity with *n*-hexane, there was obtained 4.80 g. more of VI, m.p. 151–153°. The total yield of the carbinol VI thus was 14.26 g. (66%). Fractional crystallization of a 4.00 g. portion of the dried VI (m.p. 151–153°) from ethyl acetate gave, in order: 0.45 g., m.p. 153.5–155°; 1.17 g., m.p. 153.5–155.5°; 1.15 g., m.p. 154.5–155.5°; and 0.86 g., m.p. 155.5–157°. The first fraction, recrystallized several times from ethyl acetate and from *n*-butyl chloride, had m.p. 157.5–158.5°.

Anal. Calcd. for $C_{22}H_{20}Cl_2O_3S$: C, 60.69; H, 4.63. Found: C, 60.65; H, 5.08.

(b) *Dehydration.* 1,1-Di(*p*-chlorophenyl)-2-*p*-tolysulfonyl-1-propene (VII) was prepared by dehydration of 3.00 g. of the dried carbinol VI (m.p. 151–153°) with 85% phosphoric acid (30 ml.) in the manner described for the preparation of V from the carbinol IV. Removal of solvent from the dried benzene extract gave 2.40 g. (83%) of VII, m.p. 126.5–130°. One recrystallization from ethanol left 2.18 g. (76% from the carbinol VI, 50% overall) of white needles, m.p. 128–129.5°. Repeated recrystallization of a sample of VII alternately from ethyl acetate and from ethyl alcohol gave material with constant m.p. 133–134° which suddenly increased in one more crystallization to 135–136° (unchanged by drying; similar behavior occurred with the product of another experiment).

Anal. Calcd. for $C_{22}H_{18}Cl_2O_2S$: C, 63.31; H, 4.35. Found: C, 63.34; H, 4.43.

Reaction of phenyl 2-hydroxy-2-phenylethyl sulfone (VIII) *with* XII *and then with benzaldehyde.* The carbinol VIII (5.00 g., m.p. 92–94°)[3] was dissolved in dry benzene (50 ml.) and 0.05 mole of ethereal XII was added over 10 min. Gas was evolved and a gray precipitate formed. The mixture was heated at the reflux temperature for 5 min., cooled to 25°, and 2.65 g. of purified benzaldehyde in 20 ml. of dry benzene was added over 10 min. The originally gummy mass balled up and became very difficult to stir. It was necessary to spread out the gum with a spatula from time to time, care being taken to avoid access of moisture. After 2 hr. of stirring, the original dark ball had been replaced by a yellow oil. The mixture was stirred for 3 hr. more at 25° and then was hydrolyzed with iced 1*N* hydrochloric acid. Removal of solvent from a benzene extract gave 7.1 g. (93% of starting materials) of yellow oil. Chromatography of 3.80 g. of this

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(9) General procedures followed are summarized in footnote 19 of Ref. 6. However, infrared spectra were determined using a Perkin-Elmer Model 137 spectrophotometer and analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(10) W. M. Ziegler and R. Connor, *J. Am. Chem. Soc.*, 62, 2596 (1940).

oil on 275 g. of acid-washed alumina using elution by 6:1 chloroform–carbon tetrachloride gave forty fractions (3.72 g.) of gummy solid with an overall melting range of 56–92.5°; only two significant peaks resulted. The last sixteen fractions (2.20 g., m.p. 61–92.5°) when combined and recrystallized from carbon tetrachloride gave 1.30 g. of material, m.p. 77–91°. Recrystallization from benzene-hexane gave 1.08 g. (40% recovery of the carbinol VIII), m.p. 87.5–91°, undepressed by authentic VIII; the infrared spectrum was essentially identical with that of VIII. A second crop amounted to 0.22 g., m.p. 62–70°.

The first twenty-four fractions (1.52 g.) when combined and recrystallized from carbon tetrachloride amounted to 0.45 g., m.p. 68–73°, which was not a carbinol (no infrared absorption in excess of 3130 cm.$^{-1}$) and was not studied further.

In the study simply of metalation of the carbinol VIII, 1.00 g. in 35 ml. of dry benzene was treated at *ca.* 25° with 0.004 mole of XII in apparatus attached through a Dry Ice trap to a wet test meter. No gas evolution occurred after addition of this first portion of XII. An additional 0.006 mole of XII was added and the mixture was heated rapidly to the reflux temperature. In 5 min., 0.07 l. of gas was collected (82% of theory for replacement of one hydrogen atom of VIII; the volume of gas reported here and subsequently is corrected to standard conditions); there was no further evolution during an additional heating period of 55 min. The mixture was cooled to 25°, hydrolyzed, and extracted with benzene. Removal of solvent gave 1.00 g. (100%) of material, m.p. 81–92°, undepressed by authentic VIII; the infrared spectrum was essentially identical with that of VIII.

In the second reaction with benzaldehyde, 5.00 g. of VIII was dissolved in 75 ml. of dry benzene at the reflux temperature, and 0.02 mole of XII was added rather rapidly. Gas evolution began almost immediately. The mixture was heated at the reflux temperature for 1 hr. and cooled to 25°. The gas evolved amounted to 0.35 l. (82% of theory for the replacement of one hydrogen atom), nearly all of which appeared in the first 5 min. of reflux. A second portion of the XII (0.03 mole) was added and the mixture was heated again to the reflux temperature and maintained at this temperature until gas evolution ceased (1.5 hr.). The additional gas evolved amounted to 0.15 l. (total evolution, 58% of theory for replacement of two hydrogen atoms). The mixture was cooled to 25° and 2.65 g. of purified benzaldehyde in 25 ml. of dry benzene was added. A gummy mass was formed which had to be dislodged occasionally from the sides and bottom of the flask. The mixture was stirred for 4.5 hr. at 25°. After hydrolysis, extraction with benzene, and removal of the solvent, there remained 7.1 g. of material, m.p. 78–88°. A portion of this material (3.00 g.) when triturated with cold carbon tetrachloride and twice recrystallized from carbon tetrachloride gave 1.86 g. of the original carbinol VIII, m.p. 91.5–93°, undepressed by authentic VIII; the infrared spectrum of the recrystallized VIII was identical with that of authentic material. Based on the total amount of product, the recovery of VIII was 88%.

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[CONTRIBUTION FROM THE RESEARCH DIVISION, WYANDOTTE CHEMICALS CORP.]

Ferrocenes. II. Silicon-Substituted Ferrocenes with Hydrolyzable Functional Groups[1,2]

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Silicon-substituted ferrocenes containing hydrolyzable functional groups were prepared from cyclopentadienyldimethylethoxysilane, cyclopentadienylmethyldiethoxysilane, cyclopentadienyldimethyl(1-piperidyl)silane, and 1-cyclopentadienyl-5-ethoxyhexamethyltrisiloxane. Hydrolysis of ethoxysilylferrocenes yielded bridged ferrocenes. Bridged compounds were also isolated when two bis(cyclopentadienyl)siloxanes were converted to ferrocenes.

A number of silicon-substituted ferrocenes are described in the literature,[3] but none contain hydrolyzable functional groups. In view of the importance of difunctional silanes for the preparation of silicones, it was of interest to prepare and hydrolyze compounds such as 1,1′-bis(dimethylethoxysilyl)ferrocene (II).

The preparation of cyclopentadienyldimethylethoxysilane (I), cyclopentadienylmethyldiethoxysilane, and 1-cyclopentadienyl-5-ethoxyhexamethyltrisiloxane was accomplished in 82–86% yields by treatment of the corresponding chloro compounds[4] with the required amount of ethanol in the presence of pyridine.

For the conversion of cyclopentadienyldimethylethoxysilane (I) to the corresponding ferrocene, II, conditions found to be effective were addition of isopropylmagnesium chloride to the cyclopentadienyl compound in tetrahydrofuran at 0°, and, after one hour, treatment of the resulting chloromagnesium derivative with ferrous chloride (62% yield). When *n*-butyllithium or phenyllithium was used in place of isopropylmagnesium chloride, the yield was low and the reaction less straightforward. With butyllithium, analysis of the product indicated that some replacement of ethoxy groups by butyl groups had occurred, a side reaction anticipated in view of the ready attack of ethoxysilanes by organolithium compounds.[5]

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[1] Presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 1959.

[2] This investigation was conducted under contract with Materials Laboratory, Wright Air Development Center, Dayton, Ohio.

[3] See R. L. Schaaf, P. T. Kan, C. T. Lenk, and E. P. Deck, *J. Org. Chem.*, 25, 1986 (1960), and references cited therein.

[4] Schaaf *et al.*, *J. Org. Chem.*, 25, 1986 (1960), and references cited therein.

[5] H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, 68, 1675 (1946).