Grignard Reactions with *in Situ* Trimethylchlorosilane.—In a three-necked flask equipped with dropping funnel, stirring rod, and condenser, was placed 58.8 g. (2.42 g.-atoms) of magnesium. The apparatus was dried by heating under a stream of dry nitrogen. To the flask was added 262 g. (2.42 moles) of trimethylchlorosilane and 600 ml. of tetrahydrofuran. This was heated to reflux, external heat was removed, and, at a rate to maintain reflux, 200 g. (0.603 mole) of carbon tetrabromide in 200 ml. tetrahydrofuran were added. After the addition which required 2.5 hr. and 2 hr. reflux, the mixture was poured over cracked ice and filtered. The unchanged magnesium weighed 3.2 g. Solvent and hexamethyldisiloxane were removed from the organic layer at atmospheric pressure. From the crude products 36 g. of precipitate was filtered. The filtrate was fractionated at reduced pressures yielding the products that follow: (1) 20.2 g. of 4-trimethylsilybutanol (see ref. 4 for origin of this product), b.p. 125° at 100 mm.; $n^{25}\mathrm{D}$ 1.4332, lit.[5] $n^{25}\mathrm{D}$ 1.4315; d^{25}_{4} 0.833, lit.[5] d^{25}_{4} 0.830. $r\mathrm{D}$ Calcd.: 0.3121. Found: 0.3122. (2) 4.7 g. (4.9%) of bis(trimethylsilyl)methane, b.p. 71° at 100 mm.; $n^{25}\mathrm{D}$ 1.4134, lit.[6] $n^{20}\mathrm{D}$ 1.4170; d^{25}_{4} 0.750, lit.[6] d^{20}_{4} 0.752. $r\mathrm{D}$ Calcd.: 0.3347. Found: 0.3328. (3) 55.7 g. (39.8%) of tris(trimethylsilyl)methane, b.p. 101° at 20 mm.; $n^{25}\mathrm{D}$ 1.4605, lit.[7] $n^{20}\mathrm{D}$ 1.4630; d^{25}_{4} 0.8275, lit.[7] d^{20}_{4} 0.836. $r\mathrm{D}$ Calcd.: 0.3320. Found: 0.3313.

From the residue, 16.5 g. of solid was extracted with benzene. After removal of the benzene, this was combined with the precipitate filtered from the crude products above and recrystallized from absolute ethanol, yielding 50.5 g. (27.6%) of tetrakis(trimethylsilyl)methane, melting point, sublimes.

Anal. Calcd. for $C_{13}H_{36}Si_4$: C, 51.20; H, 11.90; Si, 36.86; mol. wt., 304.8. Found: C, 51.40; H, 11.81; Si, 36.60; mol. wt. (ebullioscopic), 323.

The H^1 n.m.r. spectrum consists of a single peak at $\tau = 9.8$ p.p.m. using cyclohexane as the internal reference. Grignard reactions of bromotrichloromethane and dibromodichloromethane were run in the way described above for carbon tetrabromide. A trace of iodine was used to initiate reaction with the bromotrichloromethane. Products were characterized as above; yields are given in Table I.

Reaction with *in Situ* Dimethylchlorosilane.—To 56.8 g. (2.34 g.-atoms) of magnesium, 276 g. (2.92 moles) of dimethylchlorosilane, and 600 ml. of tetrahydrofuran was added at a rate to maintain reflux 200 g. (0.603 mole) of carbon tetrabromide in 200 ml. of tetrahydrofuran. The addition period of 2.75 hr. was followed by 5-hr. reflux. The mixture was poured over crushed ice, neutralized with sodium bicarbonate, and the organic layer was washed with water. The crude products, after the addition of 500 ml. of methanol, were cooled to the temperature of Dry Ice–acetone and 63.1 g. of precipitate was filtered off. The filtrate was distilled and in fractions boiling at about 160° at 50 mm. an additional 28.6 g. of solid crystallized. The two crystalline products were mixed and recrystallized from 95% methanol–5% ethanol, yielding 88.7 g. (59.5%) of tetrakis(dimethylsilyl)methane, m.p. 115°.

Anal. Calcd. for $C_9H_{28}Si_4$: C, 43.46; H, 11.34; Si, 45.19. Found: C, 43.60; H, 11.43; Si, 45.27.

The H^1 n.m.r. spectrum consists of two peaks, a doublet at $\tau = 9.8$ p.p.m. and a septet at $\tau = 5.9$ p.p.m. with a coupling constant of 4 c.p.s. The intensity ratio of the doublet to the septet is approximately 6:1 and tetramethylsilane is the internal reference.

Reaction with *in Situ* Phenyldimethylchlorosilane.—To 14.6 g. (0.60 g.-atoms) of magnesium, 102.2 g. (0.60 mole) of phenyldimethylchlorosilane, and 150 ml. of tetrahydrofuran was added dropwise 50 g. (0.15 mole) of carbon tetrabromide in 50 ml. of tetrahydrofuran. The reaction mixture was treated as described above. Distillation yielded 28.8 g. (67.5%) of bis-(phenyldimethylsilyl)methane, b.p. 131° at 1 mm.; $n^{25}\mathrm{D}$ 1.5404, lit.[8] $n^{25}\mathrm{D}$ 1.5426; d^{25}_{4} 0.960, lit.[8] d^{25}_{4} 0.961. $r\mathrm{D}$ Calcd.: 0.3285. Found: 0.3270.

Acknowledgment.—The authors are grateful to P. C. Lauterbur and J. J. Burke for the H^1 n.m.r. spectra and their interpretation.

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(5) J. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

(6) L. Sommer, G. Goldberg, J. Gold, and F. Whitmore, *ibid.*, **69**, 980 (1947).

(7) R. Müller and G. Seitz, *Chem. Ber.*, **91**, 22 (1958).

(8) J. T. Goodwin, U. S. Patent 2,544,079 (1951).

Hydrogenolysis of the Grignard Reagent

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In the course of some studies on the Grignard reagent, we had occasion to investigate the hydrogenolysis reaction. While hydrogenolysis of organometallic compounds is not new, there has been no report of hydrogenolysis of the Grignard reagent.

We found that ether solutions of the Grignard reagent react readily and cleanly with hydrogen without a catalyst according to the following equation.

$$2RMgX + 2H_2 \longrightarrow 2RH + MgX_2 + MgH_2$$

This reaction is general for a large number of Grignard reagents. The reaction conditions and results obtained with a variety of Grignard reagents are summarized in Table I. Runs of shorter duration with ethylmagnesium chloride at 100° showed that the reaction was 28% complete in 1 hr. and 43% complete in 3 hr.

It is obvious from Table I that some Grignard reagents react with hydrogen more readily than others. There appears to be no simple correlation of relative reactivity with the structure of the alkyl group. Such factors as the molecular aggregation of the Grignard reagent and the equilibria among the various species, monomer, dimer, dialkylmagnesium, and magnesium halide could affect the rate of the hydrogenolysis reaction. Furthermore, the system is heterogeneous and even the relative solubilities of the Grignard reagents at elevated temperatures are unknown.

We have found further that Grignard reagents are stable with respect to olefin elimination. Deuterium reacted with isopropylmagnesium chloride at 75° and at 125°. In both cases mass spectrometer analysis of the gaseous products showed that the propane produced contained only one deuterium atom. Hydrolysis of the ether-insoluble product with H_2O produced HD. The deuterium reaction can thus be written as shown.

$$2\ i\text{-PrMgCl} + 2D_2 \longrightarrow 2\ i\text{-PrD} + MgD_2 + MgCl_2$$

These experiments also show that hydrogenolysis does not proceed by an olefin elimination mechanism.

Experimental

Fisher certified reagent grade ethyl bromide, ethyl iodide, allyl bromide, *n*-butyl chloride, phenyl chloride, phenyl bromide, and benzyl chloride were used as received. Isopropyl chloride and *sec*-butyl chloride (Eastman) and neopentyl chloride (Matheson, Coleman and Bell) also were used as received. Eastman *t*-butyl chloride was distilled prior to use, and both methyl chloride and ethyl chloride (Ethyl Corporation) were vaporized through a calcium chloride drying tube. Mallinckrodt anhydrous ether and Domal high purity sublimed magnesium granules (Dominion Magnesium Co., Ltd., Haley, Ont.) were used without purification.

Grignard Preparation.—In general the Grignard reagents were prepared in 1-mole quantities from 27 g. of magnesium, 300 ml. of ether, and 1 mole of halide. A three-necked, 1-l. creased flask equipped with an air-driven stirrer, Dry Ice condenser, and addition funnel served as the reaction vessel. A blanket of argon was maintained on the reaction mixture at all times. The

TABLE I

HYDROGENOLYSIS OF GRIGNARD REAGENTS[a]

Grignard	Hydrogenolysis (based on insoluble Mg), % 50°	75°	100°	125°	150°
CH_3MgCl	0	0	0	76	
C_2H_5MgCl	0	7, 14	100, 100	100	
C_2H_5MgBr		15	53	100	
C_2H_5MgI	10, 17	50, 60			
$(CH_3)_2CHMgCl$	80, 100	100	100	100	
$CH_2{=}CHCHMgBr$	10	89			
$CH_3CH_2CH_2CH_2MgCl$		0	85		
$CH_3CH_2CH(CH_3)MgCl$	0, 24[b]	79, 81	93	100	
$(CH_3)_3CMgCl$	0, 0	6, 13	47, 47	100	
$(CH_3)_3CCH_2MgCl$		0[c]	0[c]	60[c]	95[c]
C_6H_5MgCl			0[d]	44[d]	100[d]
C_6H_5MgBr		0	0, 15	53, 67	100
$C_6H_5CH_2MgCl$		0	0		

[a] 150 ml. of 2 *M* solutions in ether were used except where noted. Reactions were run 12 hr. at 5000-p.s.i.g. hydrogen. [b] Temperature rose to 70° momentarily. [c] Concentration was 1 *M*. [d] Concentration was 1.3 *M*.

superiority of argon or helium over nitrogen was demonstrated by Owens, *et al.*[1]

Usually the reaction was initiated by simply warming a concentrated ether solution of halide in the presence of magnesium. Once the reaction started, more ether was added, after which a 50% halide solution in ether was added dropwise over a period of several hours. The neopentyl Grignard could not be initiated in this manner but addition of 1 ml. of ethyl bromide led to quick initiation.

Phenylmagnesium chloride was prepared by refluxing a mixture of 40 g. of magnesium, 400 ml. of chlorobenzene, and 1 g. of aluminum chloride overnight. A high speed stirrer was used to agitate the refluxing mixture. Excess chlorobenzene was removed by vacuum pumping at 130°. The residue was washed thoroughly with hexane and filtered in a nitrogen box. Ether was added to the dried residue, and this mixture was then filtered. The filtrate was 2 *M* in phenylmagnesium chloride.

Both methyl chloride and ethyl chloride were used as ether solutions. In order to prevent loss of halide from these solutions by evaporation, a Dry Ice condenser was simply placed on top of the addition funnel. The Grignard preparation proceeded in the normal manner.

Standardization.—All Grignard reagents were filtered in a nitrogen box and then standardized. Initially, the method of Gilman[2] was used; later on, most of the magnesium analyses were done by Versene titration. Halogen was determined by the Volhard method. In most cases the magnesium and halogen analyses agreed to within 1%. Where appreciable Wurtz coupling occurred, notably with the allyl and *t*-butyl Grignard reagents, excess magnesium halide was present.

Hydrogenolysis Procedure.—In general the standardized Grignard solution was diluted with ether to a concentration of 2.00 *M*. A 150-ml. aliquot was charged into a 250-ml. Magne-Dash autoclave. This mixture was heated at 50, 75, 100, 125, or 150° for 12 hr. under 5000-p.s.i.g. hydrogen.

After the reaction mixture had been cooled and vented, it was filtered in a nitrogen box. Both precipitate and filtrate were analyzed for magnesium by Versene titration, for halide by the Volhard method, and by gas evolution, where applicable, by measuring the gas evolved upon hydrolysis of a weighed sample. The vent gas, where applicable, was analyzed by a mass spectrometer. The per cent hydrogenolysis was calculated on the basis of the magnesium present in the precipitate. In the case of the bromides and iodides the precipitate was predominantly magnesium hydride but did contain a small amount of halide. In the case of the reaction product from ethylmagnesium bromide, for example, the amount of halogen present was 11.6 wt. %. This was reduced to 4.1% by extraction with tetrahydrofuran overnight. The purity of the magnesium hydride is thus 95 wt. %, or 99.8 mole %.

For chlorides a mixture of magnesium chloride and magnesium hydride was obtained. The product from the hydrogenolysis of ethylmagnesium chloride at 100° was extracted with tetrahydrofuran. The magnesium chloride was extracted out, leaving the insoluble magnesium hydride in the precipitate.

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[1] F. H. Owens, R. P. Fellman, and F. E. Zimmerman, *J. Org. Chem.*, **25**, 1808 (1960).

[2] H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

A Convenient Laboratory Preparation of Pure $\Delta^{9,10}$-Octalin

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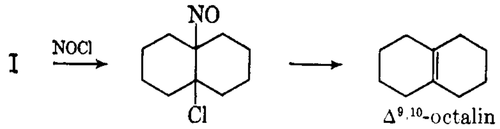
Numerous preparations for $\Delta^{9,10}$-octalin have been described.[1] It generally seems conceded[2,3] that the best method for making the pure compound involves the following four-step sequence.

$$\text{2-Naphthol} \xrightarrow[\text{cat.}]{H_2} \text{2-decalol} \xrightarrow[\Delta]{H^+} \text{octalin mixture (I)}$$



While purity of product by this method is excellent, some of the steps are tedious.[4] An optimistic estimate of over-all yield would be 50% based on 2-naphthol.

We demonstrated earlier[5] that lithium dissolved in methylamine effectively reduces naphthalene to a

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[1] See Elsevier ["Encyclopedia of Organic Chemistry," Vol. 12, Elsevier Publishing Co., Houston, Tex., 1948, p. 76] for a compilation of these methods.

[2] W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, **23**, 1205 (1958).

[3] A. S. Hussey, J. F. Sauvage, and R. H. Baker, *ibid.*, **26**, 256 (1961).

[4] For example, high pressure hydrogenation equipment has been used in the first step [see W. P. Campbell and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 2721 (1941)]. A hydrogen pressure of 2000 p.s.i. and temperatures of 150-170° are recommended.

[5] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1955).