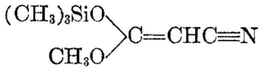
probable CH stretching vibration arising from the structural unit =CH—.

This evidence allows a probable assignment of the structure II to the compound. None of these



$$\left.\begin{matrix}(CH_3)_3SiO \\ CH_3O\end{matrix}\right> C{=}CHC{\equiv}N$$

II

data corresponds to the original structural assignment. We therefore wish to withdraw the assignments that we had previously made.[2,3]

EXPERIMENTAL

Reaction of trimethylchlorosilane with methyl cyanoacetate. To a solution of methyl cyanoacetate (49.5 g., 0.5 mole) and triethylamine (202 g., 2.0 moles) in benzene (264 g.) at −5° was added dropwise a solution of trimethylchlorosilane (54.5 g., 0.5 mole) in benzene (264 g.) over a period of 1.5 hr. During the addition, the temperature was held at 5° with an ice bath. The reaction mixture was filtered, and the filtrate was stripped and carefully distilled through a well dried 6-inch Vigreux column. After removal of unreacted cyanoacetic ester, the product (42.5 g., 50%) distilled as a colorless liquid, very sensitive to moisture, at 75–76°/0.65 mm., n_D^{25} 1.4465.

Anal. Calcd. for $C_7H_{13}O_2NSi$: C, 49.1; H, 7.6; N, 8.2. Found: C, 49.1; H, 7.6; N, 8.2.

Infrared spectra were carried out on films, using a Perkin-Elmer Model 21 spectrophotometer.

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Cleavage of Tetrahydrofuran by Triphenylmethylmagnesium Bromide

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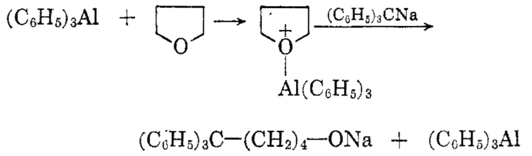
Most ethers, except strained cyclic ethers and allyl ethers, are not cleaved by Grignard reagents at temperatures below 175°.[1] For example, ethylene oxide reacts with Grignard reagents at room temperature,[2] trimethylene oxide is cleaved by Grignard reagents in refluxing benzene,[3] but anisole is cleaved by Grignard reagents at 200°. Cleavage of tetrahydrofuran, which is not highly strained, has not been generally found to occur, and tetrahydrofuran has been widely used as a solvent for the preparation and reaction of Grignard reagents.

In an attempt to prepare *t*-butylmagnesium bromide in tetrahydrofuran, Assarson[4] obtained a white precipitate which he assumed to be a product of the cleavage of tetrahydrofuran by the Grignard reagent, and was unable to find any gas evolved upon hydrolysis of the reaction mixture. However, in a reinvestigation of this reaction, Normant[5] was able to prepare *t*-butylmagnesium bromide in normal fashion in tetrahydrofuran, and obtained the normal addition product from further reaction with acetaldehyde. He proposed that the white precipitate was analogous to the precipitates obtained with dioxane.

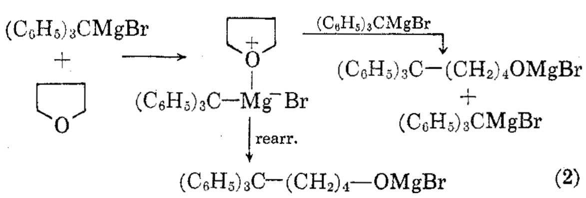
In a study of organometallic complexes, Wittig and co-workers[6] found that in the presence of triphenylaluminum and triphenylboron, triphenylmethylsodium reacts with tetrahydrofuran at room temperature to produce 5,5,5-triphenylpentanol-1 in good yield. Triphenylmethylsodium alone, however, was ineffective as a cleaving agent. These workers also found that 9-fluorenyllithium and 9-phenyl-9-fluorenyllithium also cleave tetrahydrofuran in good yield in the presence of triphenylaluminum.

It seems reasonable that triphenylaluminum forms an etherate complex with tetrahydrofuran, and the complex then undergoes attack by triphenylmethylsodium to lead eventually to the product obtained. The decreased complexing ability of sodium accounts for the fact that no cleavage was observed in the absence of triphenylaluminum.



(1)

We have found that triphenylmethylmagnesium bromide also cleaves tetrahydrofuran to produce 5,5,5-triphenylpentanol-1 in excellent yield. In this case, the Grignard reagent complexes strongly with the ether, and the complex can then undergo either further attack by another molecule of Grignard reagent, or intramolecular rearrangement to form the product:



(2)

Triphenylmethylmagnesium bromide is ionized in solution to a sufficient extent to impart the dark red color of the triphenylmethylcarbanion[6] to the solution. Since most Grignard reagents are not highly ionized in solution and do not cleave tetrahydrofuran, it is not unlikely that the cleavage occurs by way of the carbanion.

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(1) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, 1954, pp. 961–1022.

(2) For example, see R. C. Huston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

(3) S. Searles, *J. Am. Chem. Soc.*, **73**, 124 (1951).

(4) L. O. Assarson, *Acta Chem. Scand.*, **10**, 1510 (1956).

(5) H. Normant, *Bull. soc. chim. France*, **11-12**, 1444 (1957).

(6) G. Wittig and A. Ruckert, *Ann.*, **566**, 111 (1950); G. Wittig and O. Bub, *Ann.*, **566**, 127 (1950).

There exists considerable evidence indicating that the addition of magnesium halides increases the rate of cleavage of ethers by Grignard reagents.[1–3] In the present case, because of the size of the group attached to magnesium, the Schlenck equilibrium should lie almost completely toward the monoalkylmagnesium compound and the concentration of magnesium bromide in solution should be very low. This does not preclude the possibility that magnesium bromide, even though present in very low concentration, is the effective complexing agent instead of triphenylmethylmagnesium bromide.

Triphenylmethylmagnesium bromide was prepared in normal fashion in tetrahydrofuran. The resulting dark red color disappears when reaction is complete. After 24 hr. at room temperature, the red color still persisted but upon analysis the products were 29.6% triphenylmethane, and 62.9% 5,5,5-triphenylpentanol-1. After 5 hr. reflux the red color had disappeared and the products were 13.0% triphenylmethane and 73.5% 5,5,5-triphenylpentanol-1.

In order to ascertain whether the results were due to possible cleavage of the tetrahydrofuran during formation of the Grignard reagent, the Grignard reagent was also prepared in 2:1 benzene-ethyl ether solution, and tetrahydrofuran was then added to the solution. After 10 hr. reflux the red color had disappeared, and upon hydrolysis, a 94.6% yield of 5,5,5-triphenylpentanol-1 was obtained.

EXPERIMENTAL

Triphenylmethyl bromide was prepared using the method of Bachmann[7] by reacting triphenyl carbinol with acetyl bromide. The product was subjected to further purification by recrystallizing from 3:1 methylene chloride–benzene under a nitrogen atmosphere, m.p. 155.1–155.5° (lit.,[8] m.p. 153–155°). The tetrahydrofuran was purified by redistilling from potassium hydroxide pellets until the pellets remained white after distillation, then distilling from calcium hydride, and finally distilling from 0.1*M* solution of triphenylmethylmagnesium bromide under an atmosphere of nitrogen.

Reactions in tetrahydrofuran as solvent. The triphenylmethylmagnesium bromide was prepared by adding a solution of 22.7 g. (0.0703 mole) triphenylmethyl bromide in 200 ml. tetrahydrofuran to 2.30 g. (0.096 mole) magnesium shavings, which were covered with tetrahydrofuran, under a nitrogen atmosphere at 25°. The reaction began immediately and the solution turned deep red. After the reaction was complete the contents of the flask were diluted with tetrahydrofuran to a total volume of 270 ml.

After allowing the solution to stand at room temperature, a 42.5-ml. aliquot was hydrolyzed with dilute hydrochloric acid, ether was added to extract the organic material, the ether extraction was dried with calcium chloride, the drying agent removed by filtration, and the ether was removed. The material thus obtained was dissolved in pentane-benzene (5%) and this solution was placed on an alumina column. Elution with pentane gave 0.828 g. triphenylmethane (29.6%), m.p. 92.4–94.5° after recrystallization from hexane (lit.,[9] m.p. 94.5–95.5°). Elution with carbon tetrachloride gave 0.33 g. unidentified material. Elution with ether gave 2.28 g. 5,5,5-triphenylpentanol-1 (62.9%), m.p. 119–119.7° after recrystallization from cyclohexane and sublimation (lit.,[6] m.p. 118–119°).,

Anal. Calcd. for $C_{23}H_{24}O$: C, 87.34; H, 7.59. Found: C, 87.23; H, 7.77.

p-Nitrobenzoate, m.p. 107.2–108.5°.

Anal. Calcd. for $C_{30}H_{27}O_4N$: C, 77.42; H, 5.81; N, 3.01. Found: C, 77.33; H, 5.87; N, 3.00.

A 50-ml. aliquot of the Grignard solution was refluxed 5 hr. and the solution was worked up as before. The products found were: 0.431 g. triphenylmethane (13.0%); 0.11 g. unidentified material; 3.14 g. 5,5,5-triphenylpentanol-*1* (73.5%).

The reaction of triphenylmethylmagnesium bromide with tetrahydrofuran in benzene-ether solution. The Grignard reagent was prepared by mixing 16.42 g. (0.0508 mole) triphenylmethyl bromide, 1.23 g. (0.0513 mole) magnesium shaving, 60 ml. dry benzene and 30 ml. anhydrous ether and then refluxing the mixture for 30 min.[9] A 25-ml. portion of tetrahydrofuran was added and the mixture was refluxed for 10 hr. The products were isolated as before. The yields of crude materials were 15.2 g. 5,5,5-triphenylpentanol-1 (94.6%) and a small amount of triphenylmethane.

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[7] W. E. Bachmann, in *Org. Syntheses*, **Coll. Vol. III**, 841 (1955).

[8] C. G. Swain, C. B. Scott, and K. H. Lohman, *J. Am. Chem. Soc.*, **75**, 137 (1953).

[9] M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **52**, 2455 (1930).

Clemmensen Reduction of Acetophenone

MARVIN POUTSMA AND ENNO WOLTHUIS[1]

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The Clemmensen reduction of a carbonyl to a methylene group has been applied to a large variety of aldehydes and ketones. An excellent review has been published by Martin.[2] When applied to the more complex compounds, *e.g.* bifunctional, this reduction often leads to rearrangements, and this aspect of it has been studied fairly extensively in recent years. However, little work has been done to clarify the mechanism by which relatively simple compounds like acetophenone are reduced. It seemed likely that gas chromatography as an analytical tool might be useful in identifying the intermediates involved in such a reduction.

Literature references on the mechanism are confusing. While one[3] states that the alcohol cannot be an intermediate because alcohols are not reduced by the Clemmensen medium, another[4] assumes the alcohol to be formed but consumed as rapidly as formed. In a study on the Clemmensen reduction of acetophenone, Steinkopf and Wol-

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[1] Calvin College, Grand Rapids, Mich.; Sr. author.

[2] E. L. Martin, *Org. Reactions*, I, 155–209 (1942).

[3] F. Royals, *Advanced Organic Chemistry*, Prentice-Hall, Englewood Cliffs, N. J., 1954, p. 110.

[4] C. Weygand, *Organic Preparations*, Heath and Co., Boston, 1954, p. 51.