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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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.

fram[5] isolated ethylbenzene, styrene and its polymers, and the pinacolone of acetophenone. They suggested the likelihood of alcohol formation followed by dehydration and reduction, and postulated that (1-chloroethyl) benzene might take part in the reaction. Therefore, a study was undertaken to clarify the mechanism of the Clemmensen reduction of acetophenone with the help of gas chromatography to detect the intermediates and products of the reaction.

Experimental observations. Anticipating the possible intermediates to be ethylbenzene, styrene and α-methylbenzyl alcohol, synthetic mixtures of these with acetophenone were prepared for analysis by gas chromatography to establish the efficiency of this method of analysis. It was found that a 10-foot column of 30% Harflex 370 plasticizer[6] on Burrell carrier, operated at 175°, with He at 40 ml. per min, successfully separated all of the components of such a mixture, and that as little as 1% of the alcohol could be detected with a filament current of 105 ma. in the conductivity cell detector.[7]

The reduction of acetophenone was faster than expected, only 15–20% of it remaining after 20 min refluxing. The ratio of ethylbenzene to styrene found was about 7:1, changing only slightly as the reaction progressed. After one hour, only traces of the ketone remained, but thereafter the styrene slowly changed to ethylbenzene, especially in the presence of a large excess of acid. At no time could the alcohol be detected in the reaction mixture, even at lower acid concentrations and lower temperatures.

α-Methylbenzyl alcohol cannot long exist in the reducing medium. After 5 minutes it was completely changed to styrene and a little ethylbenzene, after which the styrene was gradually converted to ethylbenzene. Using 21% HCl, the amount of ethylbenzene in the total hydrocarbons was 70, 80, 83, and 88% after 15, 25, 35, and 60 min. respectively. As the acid concentration was reduced the ethylbenzene content dropped, after 15 min. reaction time, to 67 and 52% for 15 and 12.5% HCl respectively, 21% HCl alone quickly changed the alcohol to the corresponding chloride, which gradually dehydrated to styrene. Reduction of the alcohol by HCl with zinc instead of its amalgam gave only styrene and its polymer.

Styrene was reduced slowly by the usual Clemmensen medium. After 15, 30, 45, 60, 90, and 120 minutes the yields of ethylbenzene were 25, 45, 58, 63, 70, and 79% respectively. Omitting the zinc amalgam, styrene was partly changed to (1-chloroethyl) benzene, which was proved to be identical with that obtained from the alcohol with HCl.

(1-Chloroethyl)benzene was readily reduced by the C. procedure to ethylbenzene, with the formation of only traces of styrene.

Inasmuch as the experiments indicated that the chloride is an important intermediate, a few experiments were tried in which 20% sulfuric acid was substituted for HCl. Acetophenone was reduced in this way to ethylbenzene and styrene but more slowly, and the styrene/ethylbenzene ratio was greater than before. Again, no alcohol could be detected at any time. Although the alcohol was reduced by the amalgam in HCl to ethylbenzene, styrene was the chief product when sulfuric acid was employed, and was formed very rapidly. Even after 6 hours in 20% sulfuric acid at reflux temperature, only traces of ethylbenzene were detected. Likewise, styrene was not appreciably reduced to ethylbenzene in the sulfuric acid medium.

It should be mentioned in passing that whenever styrene was formed in the presence of HCl small deposits of polystryene were also detected among the products.

Interpretation and conclusions. Contrary to much of the literature, α-methylbenzyl alcohol is reduced by the Clemmensen method to ethylbenzene, the rate of this reaction decreasing with lower concentrations of HCl. These facts, together with the fact that the alcohol is very rapidly changed to the corresponding chloride and styrene, make it reasonable to suppose that the alcohol can be an intermediate, even though it could not be detected by gas chromatographic methods. Furthermore, since the chloride is reduced more rapidly than styrene to ethylbenzene, and the change from styrene to the chloride is a reversible one under the conditions of the Clemmensen reduction, it seems likely that acetophenone is reduced to ethylbenzene primarily by way of the alcohol and the chloride, and secondarily *via* the alcohol-styrene-chloride route. This theory is supported by the fact that in sulfuric acid the alcohol, as well as acetophenone, gave much more styrene and much less ethylbenzene in a given time, and styrene was hardly at all reduced to ethylbenzene. In the presence of HCl the chloride–styrene equilibrium is established as fast as the chloride is formed, and the ethylbenzene is derived mainly from the reduction of the chloride.

EXPERIMENTAL

Preparation of amalgam. Fifty grams of zinc, Baker's 20-mesh granules, were etched a few minutes with dilute HCl, rinsed well with water, and then stirred with 100 ml. aq. 5% mercuric chloride containing 3 ml. concd. HCl. After 15 min., the liquid was decanted and the amalgam thoroughly washed with water.

Reduction procedure. Two hundred milliliters of 21% HCl were heated to reflux temperature in a 500-ml. 3-neck flask,

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(5) W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113–161 (1922).

(6) Obtained from Harchem Div., Wallace and Tiernan, Belleville, N. J.

(7) The authors are indebted to R. S. Gohlke of the Dow Chemical Co. for assistance in assembling the apparatus.

fitted with a thermometer, a reflux condenser, and an agitator for vigorous agitation. The amalgam was then added, followed by 30 g. of the compound to be reduced, added through the condenser. Vigorous agitation was maintained at reflux temperature. Samples were taken at timed intervals by stopping the agitator, allowing the layers to separate, drawing off some of the top layer, and washing it well with water to remove all acid. Each sample was then analyzed by gas chromatography as described here.

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Pyrolysis of 2-Butyl Acetate

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In conjunction with the study of the stereoselective dehydration of butanols over alumina catalysts[1,2] the pyrolytic decomposition of 2-butyl acetate was reinvestigated. It was reported in the literature[3,4] that the pyrolysis of acetates gives exclusively the least substituted olefins following the Hoffmann rule. Contrary to the above reported findings and in accordance with recently published results on the pyrolytic decomposition of 2-heptyl acetate,[5] it was found that the pyrolysis of 2-butyl acetate yields a mixture composed of 1- and 2-butenes. The concentration of 1-butene in the reaction product varied from 55 to 69%, depending upon the experimental conditions used. The remainder of the product was composed of *cis*-2- and *trans*-2-butene in an approximate ratio of *cis/trans* = 0.5. The percentage of 1-butene produced approximates that expected from statistical elimination of the neighboring hydrogen atoms.

TABLE I

PYROLYSIS OF 2-BUTYL ACETATE

Temp., °C.	Flow Rate, Ml./hr.	Nitrogen Added	Packing Kind	Conversion, %	Butenes 1-	*cis*-2-	*trans*-2	*cis/trans*
410	5	–	Glass	12	61.5	25.9	12.6	0.49
450	5	–	Glass	100	57.8	27.4	14.8	0.54
450	10	–	Glass	54	62.0	24.2	13.8	0.57
450	50	–	Glass	9	69.1	20.7	10.2	0.49
450	5	+	Glass	47	55.4	28.4	16.2	0.57
490	14	+	Quartz	82	55.4	28.6	16.0	0.56
510	5	–	Glass	81	58.3	27.0	14.7	0.54
510	20	–	Glass	69	58.2	27.1	14.7	0.54
510	40	–	Glass	65	61.6	25.2	13.2	0.52
525	12	+	Quartz	71	57.5	26.7	15.8	0.58

The experimental results are summarized in Table I. The flow rate of 2-butyl acetate in the experiments carried out at 450° and 510° was varied and in the case of 450° experiments the composition of the butenes produced was plotted against the percentage of 2-butyl acetate which underwent pyrolysis. By extrapolating the plot to zero conversion, the composition of the primary products of the pyrolysis could be established. They were composed of 71% 1-butene, 9% *cis*-2- and 20% *trans*-2-butene (Fig. 1). The ratios of *cis*- to *trans*-2-butene approximate the thermodynamic equilibrium mixture.[6] Butenes *per se* do not undergo isomerization under the experimental conditions used for the pyrolysis of the acetate. The reason therefore for the change of the composition of the butenes with change in the extending of 2-butyl acetate decomposition is not immediately apparent

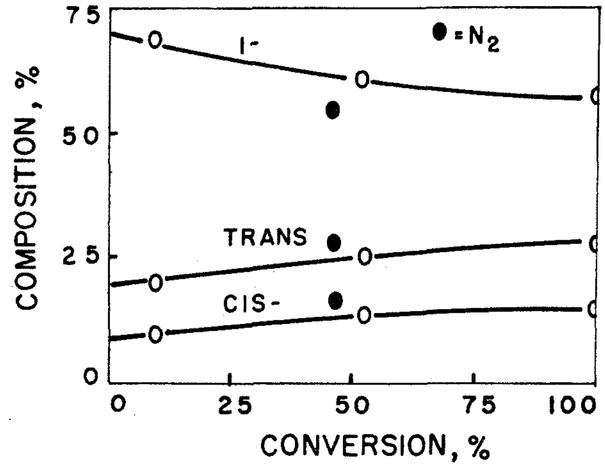

Fig. 1. Pyrolysis of 2-butyl acetate at 450°. Primary products: 71%. 1-butene, 20% *trans*-2-, 9%, *cis*-2-

n-Butyl acetate on pyrolysis formed only 1-butene.

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