dicate that these compounds as a class are less effective than sulfanilamide against infections by beta hemolytic streptococci in mice.

BOUND BROOK, N. J. RECEIVED DECEMBER 13, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY AND UNIVERSAL OIL PRODUCTS COMPANY]

The Electrolysis of Some Higher Aliphatic Organomagnesium Halides in Ethyl Ether

BY WARD V. EVANS, DAVID BRAITHWAITE AND EDMUND FIELD

The electrolysis studies of the simple organomagnesium halides have been completed.[1] These studies indicated that the main course of the reaction was the liberation of the organic free radical, which then reacted by disproportionation to give the corresponding saturated and unsaturated hydrocarbons. In the electrolysis of *n*-propylmagnesium halide in ethyl ether[1d] it was found, however, that there was a marked tendency for the liberated free radical to combine to give the coupled product *n*-hexane. The isopropylmagnesium halide, on the other hand, showed very little or no tendency to couple upon electrolysis.

The present work is a continuation of this problem, electrolyzing some higher organomagnesium halides in ethyl ether, and attempting thereby to further our knowledge of the coupling tendency. To accomplish this the four isomeric butyl compounds were studied, as well as the *n*-hexyl compound.

Experimental

The same apparatus that has previously been described was used,[1b] and platinum electrodes were employed throughout the investigation.

***n*-Butylmagnesium Bromide.**—In this electrolysis the solution conducted the electric current so readily that even at 0.4 to 0.5 ampere there was not sufficient heat generated to cause the solvent to reflux. Since refluxing was the sole means of agitation, there was no great amount of disturbance in this electrolysis, and consequently the magnesium plated out and often bridged the gap between the electrodes. For the most part this was avoided by shaking the cell, but it undoubtedly accounts for the low efficiency found.

It was noted, however, that gas was liberated when the gap between the electrodes had nearly been closed, whereas otherwise no gas was liberated. Samples of this gas at different current densities were taken, and the analyses, made by the absorption method, are shown in Table I. Change in current density had no effect on the composition of the gas over a small range.

A quantity of 0.72 mole of Grignard reagent was decomposed during the electrolysis, and the efficiency was approximately 65% based on the number of coulombs passed through the solution. On the basis of the amount of octane isolated experimentally, approximately 85% of the butyl radicals liberated coupled. Because of loss in isolating and purifying the octane, the actual amount of coupling must be approximately 100%.

Isobutylmagnesium Bromide.—As in the case of *n*-butylmagnesium bromide, no gas was liberated except when magnesium nearly bridged the gap between the electrodes. There was not sufficient gas to fractionate, and all that could be done with this small amount of gas was to determine that the saturated hydrocarbon gas in the mixture was essentially C_4.

A 500-cc. sample of the original organomagnesium halide (1.36 *N*) was hydrolyzed and analyzed. About 5 cc. of diisobutyl was found, indicating a slight coupling during the formation of the Grignard reagent.

The efficiency of this electrolysis was found to be about 83% based on the number of coulombs passed through the solution. After electrolysis, 500 cc. (0.6 *N*) was hydrolyzed and analyzed. No alcohols were found, but approximately 35 cc. of diisobutyl was present. During the electrolysis 0.78 equivalent of Grignard compound was decomposed. Therefore, on the basis of the amount of diisobutyl found, approximately 96% of the liberated isobutyl free radical coupled.

***s*-Butylmagnesium Bromide.**—No gas was liberated during this electrolysis.

A 500-cc. sample (1.35 *N*) of the original Grignard was hydrolyzed and analyzed before electrolysis. A 2-cc. portion of this solution was identified as the coupled product, 3,4-dimethylhexane.

On the basis of the amount of 3,4-dimethylhexane found on analyzing the solution after electrolysis, about 43% of the liberated free radical coupled. This would appear to be a poor yield of the coupled product, but considerable difficulty was encountered in the isolation of the product. No alcohols were found.

On a second electrolysis of *s*-butylmagnesium bromide, the solution was prepared 0.588 *N* and 825 cc. electrolyzed until 0.165 equivalent had been decomposed. On the basis of the amount of coupled product isolated from the original solution and the electrolyzed solution, coupling took place to about 49%. In this experiment an external heater was used to keep the solution in the vicinity of the electrodes refluxing vigorously. This heater accomplished two things. It stopped the magnesium from bridging

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[1] (a) Evans and Field, THIS JOURNAL, 58, 720 (1936): (b) Evans and Field, *ibid.*, 58, 2284 (1936); (c) Evans and Lee, *ibid.*, 56 654 (1934); (d) Evans and Braithwaite, *ibid.*, 61, 898 (1939).

TABLE I

ANALYSIS OF GAS LIBERATED BY THE ELECTROLYSIS OF *n*-BUTYLMAGNESIUM BROMIDE

Amp./sq. dm.	CO_2	Other unsatd. hydrocarbons	O_2	H_2	CO	Unsatd. hydrocarbon (butylene)	Hydrocarbons	*n*
1.0	2.0	1.2	2.0	2.5	1.2	42	50	3.7
1.6	...	2.1	1.5	2.2	...	43	52	3.6
0.4 to 2.0 (range)	0.8	1.1	1.9	0.3	0.3	40	55	3.7

the gap between the electrodes, and also decreased the solubility of any gases formed during the electrolysis and aided them to escape by means of the refluxing. Gas was not liberated to the extent that it could be collected.

Two possible conclusions can be drawn from these results. First, the free radical liberated on electrolysis may be considered to couple 100% since no gas was given off. The explanation for the poor yield of the isolated coupled product could be offered on the basis that some of the product was lost in separating it from the large volume of ether used as a solvent. Second, the coupling can be considered to take place only to the extent indicated by the amount of coupled product isolated. The remainder of the products of the electrolysis, supposedly butane and butylene, could be thought of as dissolving in the ether solution and consequently being lost on analysis.

The first interpretation seems more plausible because of the ease of liberation of small amounts of butane and butylene in the *n*-butylmagnesium bromide electrolysis, and because of the unfavorable conditions for solution of the gases when the solution was in a state of reflux. On this basis, then, the *s*-butyl free radical takes its assigned place in Table II.

***t*-Butylmagnesium Bromide.**—In the electrolysis of this compound the gas liberated could not be analyzed by the absorption method due to the presence of ethyl ether vapors. Also, the coupled product, di-tertiary-butyl, is a very volatile hydrocarbon. Only approximations, therefore, could be made as to amounts present.

A 550-cc. sample (0.506 *N*) of the solution was analyzed before electrolysis, and about 1 g. of the coupled hydrocarbon estimated to be present. After electrolysis, upon hydrolyzing and analyzing the same quantity of solution (0.278 *N*), from 3 to 4 g. of di-tertiary-butyl was found.

No alcohols were found.

During this electrolysis gas was given off freely but, as has been stated, samples at different current densities could not be analyzed because of the nature of the mixture. Therefore, after the run was completed, a Podbielniak distillation was made on the gas collected. The fractionation was not very efficient, and the main result was merely the separation of the gaseous products from the ethyl ether vapors. With the elimination of the ethyl ether vapors, however, it was then possible to analyze the hydrocarbon mixture by means of absorption and combustion. The mixture was found to be essentially isobutylene and C_4 saturated hydrocarbon, probably isobutane.

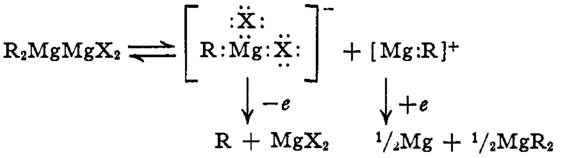
***n*-Hexylmagnesium Bromide.**—No gas was given off during this electrolysis.

On analysis of 500 cc. of original solution (0.916 *N*) 4 to 5 cc. of dodecane was found. During the electrolysis 0.364 equivalent of Grignard compound was decomposed. From 500 cc. of the final solution (0.507 *N*) 23 cc. of dodecane was isolated. The yield of the coupled product then, on the basis of the material isolated, was 82.5%. Since no other products were found, it can be assumed that the coupling reaction is the only one, and the obvious discrepancy between 82.5 and 100% is due to experimental methods of isolation.

Discussion

From all the data obtained thus far on the electrolysis of various aliphatic organomagnesium halides, we are able to draw certain conclusions.

1.—In all cases studied the ionization of the Grignard reagent and the liberation of the organic free radical at the anode may be represented as follows



$$\begin{array}{cccc} R_2MgMgX_2 \rightleftharpoons & \left[R{:}\underset{..}{\overset{:\ddot{X}:}{Mg}}{:}\ddot{X}{:} \right]^- & + & [Mg{:}R]^+ \\ & \downarrow -e & & \downarrow +e \\ & R + MgX_2 & & {}^1/_2Mg + {}^1/_2MgR_2 \end{array}$$

2.—The reactions of the free radical with the solvent as represented in earlier papers[1b,d] seem to disappear, or at least become negligible as higher molecular weight organomagnesium halides are used for electrolytes.

TABLE II

GRADATION OF TENDENCY TO COUPLE WITH CHANGE OF STRUCTURE

Free radical		Coupling tendency
Ethyl	H H HC^2—$^1C\cdot$ H H	Trace
Isopropyl (mono-methyl substitution on C 1 of ethyl radical)	H H HC^2—$^1C\cdot$ H | CH_3	Trace
t-Butyl (dimethyl substitution on C 1 of ethyl radical)	CH_3 H | HC^2—$^1C\cdot$ H | CH_3	Slight
n-Propyl (mono-methyl substitution on C 2 of ethyl radical)	H H HC^2—$^1C\cdot$ | H CH_3	Approximately 50%
s-Butyl (dimethyl substitution on C 1 and 2 of ethyl radical)	CH_3 | H HC^2—$^1C\cdot$ H | CH_3	Approximately 100%
Isobutyl (dimethyl substitution on C 2 of ethyl radical)	CH_3 | H HC^2—$^1C\cdot$ | H CH_3	Approximately 100%

3.—As higher molecular weight compounds are electrolyzed the main reaction seems to be one of coupling.

Certain generalizations can be made regarding structures necessary for nearly complete coupling.

A.—Straight chain free radicals of four carbon atoms or more will have approximately a 100% tendency to couple.

B.—Substituted *n*-propyl free radicals will have nearly a 100% tendency to couple.

It is interesting to consider the free radicals as substituted ethyl radicals, and it can be shown that there is a gradual increase in the tendency to couple as the ethyl radical becomes substituted with methyl groups. This is shown in Table II.

If we consider isopropyl and *t*-butyl as monomethyl and dimethyl substituted ethyl radicals, respectively, the effect of substitution on carbon number one is comparatively slight. If we consider *n*-propyl and isobutyl as mono-methyl and dimethyl substituted ethyl radicals, the effect on carbon number two is very marked. This analogy cannot be carried further, because, as has been stated, the higher molecular weight aliphatic radicals tend toward 100% coupling.

Summary

The products of electrolysis of the four butylmagnesium halides have been reported.

The products of the electrolysis of *n*-hexylmagnesium bromide in ethyl ether have been reported.

The relation between the structure of the free aliphatic radical liberated upon electrolysis and its tendency to couple has been presented.

EVANSTON, ILL. RECEIVED AUGUST 12, 1939

[COMMUNICATION NO. 752 FROM THE KODAK RESEARCH LABORATORIES]

Surface Conditions of Silver Halides and Rate of Reaction. I. Rate of Reduction of Precipitated Silver Chloride

BY T. H. JAMES

The effects of adsorption during and subsequent to the preparation of silver halide precipitates and sols are clearly shown, in both the physical and in the chemical behavior of the resulting product. The very important role played by adsorption of sensitizing dyes and gelatin in the photochemistry of the silver halides has been demonstrated by the work of several investigators.[1] The effects of adsorption on the chemical reduction of silver halide are less well understood, and the problem is clouded by lack of concrete evidence on the mechanism of the reduction process. The fact that gelatin markedly retards the reduction of unexposed silver halide by developing agents has been known since the early days of the gelatin dry plate, but the manner in which the gelatin acts has been the subject of conflicting views. Reinders and van Nieuwenburg[2] found that the reduction of silver chloride by ferrous citrate was definitely retarded by as little as 0.0012% gelatin in the solution, and an increase in the gelatin concentration resulted in a further decrease in the reaction rate. They assumed that three steps were involved in the over-all process: (1) solution of the silver chloride, (2) reduction of the silver ions in solution; and (3) crystallization of the silver. They attributed the effect of gelatin to a retardation of the crystallization process. Sheppard, however, viewed the protective action of gelatin as an adsorption effect, and showed that a layer of gelatin of approximately molecular thickness is tenaciously held to silver bromide grains which have been prepared in the presence of gelatin.

A decision between the conflicting points of view evidently rests upon a knowledge of the mechanism of the reduction process. Hydroxylamine is a reducing agent well adapted to an experimental investigation of the problem. The reaction between hydroxylamine and silver ions has been studied.[3] Reduction of silver chloride proceeds with quantitative formation of nitrogen, and this allows a convenient method of following the reaction. In addition, hydroxylamine is a photographic developing agent and results ob-

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[1] *Cf.* review of G. Kornfeld, *J. Phys. Chem.*, **42**, 795 (1938); also, S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **7**, 265, 426 (1939); S. E. Sheppard, R. H. Lambert and R. L. Keenan, *J. Phys. Chem.*, **36**, 174 (1932).

[2] W. Reinders and C. J. van Nieuwenburg, *Kolloid Z.*, **10**, 36 (1912).

[3] T. H. James, THIS JOURNAL, **61**, 2379 (1939).