theses of certain tetramethoxy-dianthraquinones by the method of Attree and Perkin.[17] The conversion to the corresponding helianthrones, supposedly a simple matter of suitable irradiation, has been most uncertain, and no satisfactory yield obtained.

## Summary

Hypericin, the photodynamic pigment from St. John'swort, is composed of at least six fractions. Two of these have the formulas $C_{29}H_{22}O_8$ and $C_{31}H_{28}O_9$. Six of these oxygens are in hydroxyl groups. A pale-yellow oil with a pure blue fluorescence is obtained on zinc dust distillation. Methods of extraction and purification are discussed and hypericin is compared with a group of pigments from the mold *Penicilliopsis clavariaeformis.* Previously suggested structures porphyrin, flavone, anthocyanin, *meso*-dianthrone, are inadequate to explain the properties of hypericin. It is tentatively suggested that hypericin is a partially reduced polyhydroxy derivative of helianthrone. Further synthetic work is obviously needed for final proof, but the observations of Oxford and Raistrick on penicilliopsin, the studies of Meyer and of Scholl and co-workers on helianthrones, together with our comparisons, and our hydrogenation of *meso*-dianthrone, all support the plausibility of the present suggestion.

BERKELEY, CALIFORNIA RECEIVED JUNE 23, 1941

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[17] G. F. Attree and A. G. Perkin, *J. Chem. Soc.*, 144 (1931).

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

# The Electrolysis of Arylmagnesium Bromides in Ethyl Ether: the Behavior of Short-lived Aryl Free Radicals

BY WARD V. EVANS, RALPH PEARSON AND DAVID BRAITHWAITE

The electrolyses of the simple aliphatic Grignard reagents have been reported.[1] It was found that organic free radicals are liberated at the anode and that these radicals may react (1) by coupling, (2) by disproportionation or (3) by the removal of hydrogen from the ether solvent. The present work presents the electrolyses of aromatic Grignard reagents more fully than was previously reported[2] in an effort to determine the behavior of short-lived aryl radicals. Phenyl, *p*-tolyl, *p*-chlorophenyl, and benzylmagnesium bromides were electrolyzed. The ionization of the Grignards may be represented as being[1c]

$$(RMgX)_2 \longrightarrow Mg^{++} + (R_2MgX_2)^=$$

The corresponding electrode reactions are

$$\text{at the anode: } (R_2MgX_2)^= \longrightarrow 2R\cdot + MgX_2 + 2e$$
$$\text{at the cathode: } Mg^{++} + 2e \longrightarrow Mg^0$$

The symbol R· stands for a free radical.

## Experimental

The same apparatus and general procedure previously described were used,[1b] with platinum electrodes and voltages varying from 100 to 600. The high voltages were necessary because of the lower conductivity of the aromatic Grignards. To make sure that the changes in voltage did not significantly change the course of electrolysis, check runs were made on aliphatic Grignards using 300 volts.

**Phenylmagnesium Bromide.**—Ether solutions of phenylmagnesium bromide about one molar were electrolyzed continuously at different current densities and voltages. The products found by analysis of the hydrolyzed solution after electrolysis were benzene, diphenyl, *p*-terphenyl, styrene, ethyl alcohol and an insoluble, high molecular weight hydrocarbon that formed upon the anode. The results are tabulated in Table I. Samples of the Grignard solution were hydrolyzed and analyzed before electrolysis as blanks. The diphenyl was separated from the *p*-terphenyl by fractional crystallization from hot alcohol. These solids were identified by their melting points. The styrene was identified by its dibromide (m. p. 72–73°) and the ethyl alcohol by its 3,5-dinitrobenzoate. Only small amounts of alcohol were found. The polymer found on the anode was insoluble in all common reagents. It did

TABLE I

PRODUCTS OF ELECTROLYSIS OF PHENYLMAGNESIUM BROMIDE

| Current density, amp./dm. | Voltage | Current efficiency, % | Moles elect. | Moles of phenyl radical found as | | | |
|---|---|---|---|---|---|---|---|
| | | | | Styrene | Diphenyl | Terphenyl | Polymer |
| 0.32 | 300 | 13 | 0.126 | 0.05 | 0.02 | 0.01 | 0.01 |
| .48 | 300 | 14 | .181 | .09 | .01 | .02 | .01 |
| .48 | 400 | 41 | .501 | .09 | .15 | .07 | .01 |
| .48 | 600 | 18 | .143 | .06 | .0 | .02 | .01 |
| .24 | 110 | 66 | .178 | .0 | .12 | .02 | .01 |

Small amounts of ethyl alcohol were found in all cases.

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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); (e) Evans, Braithwaite and Field, *ibid.*, **62**, 534 (1940).

[2] Gaddum and French, *ibid.*, **49**, 1295 (1927).

not melt but carbonized at high temperatures leaving no residue.

The changes in the concentration of the Grignard reagent were found by Gilman's acid titration method. The current efficiencies, based on the moles of Grignard decomposed per faraday, were low, between 66 and 14%. The magnesium that plated out on the cathode was black, finely divided and very reactive in all cases where the current efficiencies were below 50%. Styrene was formed in large amounts whenever the black magnesium was deposited. When the current efficiency was high, diphenyl was the chief product found.

**$p$-Tolylmagnesium Bromide.**—This compound was electrolyzed at 300 volts and a current density of 0.16 amp./sq. dm. Since 0.07 mole of Grignard was decomposed for 0.233 faraday, the current efficiency was 31%. About 0.5 g. of polymer formed on the anode. No ditolyl was formed as a result of electrolysis, but 6 g. of $p$-methylstyrene was found. The dibromide of this compound did not crystallize out, so a portion was oxidized to $p$-toluic acid (m. p. 170–172°) with dilute nitric acid. The magnesium that plated out was black and powdery.

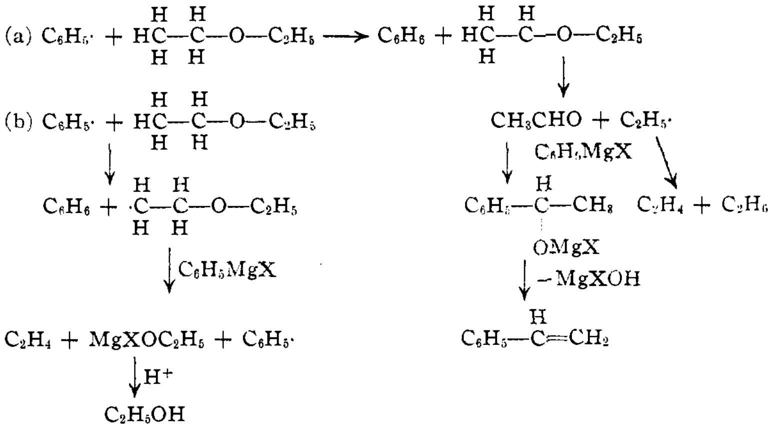
**$p$-Chlorophenylmagnesium Bromide.**—This Grignard was electrolyzed at 300 volts and 0.24 amp./sq. dm. Since 0.96 faraday was used and 0.194 mole was decomposed, the efficiency was 20%. No coupled product was found, but a polymer formed on the anode and 7.4 g. of $p$-chlorostyrene (m. p. 43–44°, dibromide) was found. The magnesium was black and reactive.

**Benzylmagnesium Bromide.**—A 0.6 molar solution was electrolyzed at 0.24 amp./sq. dm. and 300 volts. The current efficiency was high, about 80%. Some polymerized product formed on the anode, but no unsaturated compounds were formed. From the amount of dibenzyl that was found, practically all of the benzyl radicals coupled. The magnesium that came out was gray and crystalline. Benzylmagnesium bromide behaved like an aliphatic Grignard upon electrolysis.

## Discussion

The results show clearly that neither coupling nor disproportionation is the chief reaction of the aryl free radicals liberated upon electrolysis. Alkyl free radicals under the same conditions couple or disproportionate. The products found, however, can be explained if the reactions are assumed to be (1) coupling, followed by an attack by radicals upon the coupled product, or (2) an attack by radicals upon the ether solvent.

Considering (2), a mechanism has already been proposed by Evans and Field[1b] for the decomposition of ethyl ether by free radicals. Either an alpha or a beta hydrogen can be removed from the ether by a free radical, the reactions being



$$\text{(a)}\ C_6H_5\cdot + \underset{H}{\overset{H}{HC}}—\underset{H}{\overset{H}{C}}—O—C_2H_5 \longrightarrow C_6H_6 + \underset{H}{\overset{H}{HC}}—\overset{H}{C}—O—C_2H_5 \longrightarrow CH_3CHO + C_2H_5\cdot$$

$$CH_3CHO \xrightarrow{C_6H_5MgX} C_6H_5—\underset{OMgX}{\overset{H}{C}}—CH_3 \xrightarrow{-MgXOH} C_6H_5—\overset{H}{C}{=}CH_2 \qquad C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6$$

$$\text{(b)}\ C_6H_5\cdot + \underset{H}{\overset{H}{HC}}—\underset{H}{\overset{H}{C}}—O—C_2H_5 \longrightarrow C_6H_6 + \cdot\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—O—C_2H_5 \xrightarrow{C_6H_5MgX} C_2H_4 + MgXOC_2H_5 + C_6H_5\cdot \xrightarrow{H^+} C_2H_5OH$$

The reaction with the beta hydrogen is far less common. Secondary alcohols were found in the case of aliphatic Grignards which reacted with the acetaldehyde formed from the ether.[1b] The phenylmethylcarbinol which might be looked for evidently lost water to form styrene. Klages[3] found that an excess of Grignard reagent can act as a dehydrating agent for the magnesium salts of secondary and tertiary alcohols. Considering (1) above, some coupling takes place to form diphenyl in the case of the phenyl radical. However, the diphenyl seems to be a ready source of hydrogen for other phenyl radicals, so that a diphenyl free radical is formed

$$C_6H_5\cdot + C_6H_5—C_6H_5 \longrightarrow C_6H_6 + C_6H_5—C_6H_4\cdot$$

The diphenyl radical could couple with a phenyl radical to give a terphenyl

$$C_6H_5—C_6H_4\cdot + C_6H_5\cdot \longrightarrow C_6H_5—C_6H_4—C_6H_5$$

The terphenyl might lose a hydrogen to another phenyl radical and the process be repeated until a long chain of phenyl radicals was formed. This could happen best at the anode where the concentration of free radicals was greatest. The final product would be an insoluble, high melting organic solid exactly as found. Since $p$-terphenyl was found as an intermediate, the para hydrogen seemed the most easily removed. However, blocking the para position did not prevent the polymerization process.

It was noted particularly that the efficiency of electrolysis of the aromatic Grignards was very low, and that the magnesium was black and powdery. In contrast, the aliphatic Grignards, except methyl,[1a] gave approximately 100% current efficiency and a gray crystalline type of magnesium. The difference between these two types

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(3) Klages, *Ber.*, **37**, 1447 (1904).

of magnesium is very marked. The simplest explanation is that, in the case of the aromatics, the anion is sometimes discharged to give an aryl halide instead of the free radicals

$$(R_2MgX_2)^{=} \longrightarrow RX + RMgX + 2e$$

The RX would then diffuse over to the cathode and react with the magnesium deposited there to produce more Grignard reagent, so that the net result of the electrolysis would be zero. The eating away of the magnesium by aryl halide would account for its appearance.

In order to test the above mechanism, phenylmagnesium bromide was electrolyzed in a transference cell where diffusion was avoided. As would be predicted, the magnesium in the cathode portion was gray and unreactive. The anode portion was drained off and found to contain appreciable amounts of bromobenzene. A portion of the Grignard before electrolysis contained no unreacted bromobenzene.

The increased tendency of aryl Grignards to give this secondary reaction, where a halide is formed, may be due to the greater strength of the carbon to halogen bond. It is significant that this reaction is not found in the cases where the Wurtz–Fittig type of reaction occurs

$$RX + RMgX \longrightarrow R—R + MgX_2$$

The observed vigorous attack on hydrogen bearing substances by the aryl radicals is probably related to the fact that the concentration of free radicals at any instant is very low due to the secondary anode reaction outlined above. Both the coupling and disproportionation of phenyl free radicals in the absence of a solvent have been reported.[4] In general, the evidence indicates that the aryl radicals are more difficult to form and once formed, are more reactive than the aliphatic free radicals of simple nature.

## Summary

1. The products of electrolysis of phenyl-, *p*-tolyl-, *p*-chlorophenyl- and benzylmagnesium bromides are reported.

2. The alternative discharge of aryl halides as an anode reaction is shown to occur with aromatic Grignard reagents.

3. The behavior of short-lived aryl free radicals in ether solution is discussed and mechanisms advanced for their reactions.

4. The marked difference between aliphatic and aromatic Grignards upon electrolysis is brought out.

[4] Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927).

EVANSTON, ILLINOIS RECEIVED JULY 14, 1941

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

# Studies on High Molecular Weight Aliphatic Amines and their Salts. III. Behavior of the Acetates of Dodecylamine and Octadecylamine in Water

BY A. W. RALSTON, CHARLES W. HOERR AND EVERETT J. HOFFMAN

The behavior of the acetates of dodecylamine and octadecylamine in water is qualitatively similar to the behavior of the corresponding hydrochlorides in water.[1]

A study of the cooling curves coupled with visual observations of both the dodecylamine acetate–water system and octadecylamine acetate–water system show that they both exhibit colloidal properties over a wide range of temperature and concentration. Determination of the osmotic coefficient *g* and dew-point data further substantiate the colloidal behavior of these systems. Dodecylamine acetate is more soluble in water than octadecylamine acetate. A metastable region was observed in the case of octadecylamine acetate and water but not in the dodecylamine acetate–water system. This differs from the corresponding hydrochlorides where the metastable region was observed only in the dodecylamine hydrochloride–water system.

## Experimental

**Preparation of Materials.**—Lauronitrile and stearonitrile were prepared by the action of ammonia upon the respective acids.[2] The lauronitrile was purified by fractional distillation *in vacuo*[3] ($n^{25}D$ 1.4342–1.4344) and the stearonitrile by crystallization from 95% ethanol (m. p. 42.0–43.0°). The nitriles were hydrogenated to the corresponding amines, and the amines were fractionally distilled *in vacuo*.[4] The amines were then converted to the acetates which were then crystallized from the appropriate

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[1] Ralston, Hoffman, Hoerr and Selby, THIS JOURNAL, **63**, 1598 (1941).

[2] Ralston, Harwood and Pool, *ibid.*, **59**, 986 (1937).

[3] Ralston, Selby and Pool, *Ind. Eng. Chem.*, **33**, 682 (1941).

[4] Ralston, Selby, Pool and Potts, *ibid.*, **32**, 1093 (1940).