filtered, and the excess *p*-cymene was removed by distillation. Recrystallization of the residue from petroleum ether (60–80°) yield *o,p*-quaterphenyl (VI), (1.05 g.); m.p. 119–119.5°.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.34; H, 6.10.

4-Bromo-o-terphenyl. A solution of 2-phenyl-2-cyclohexenone (3 g.) in ether was added dropwise with stirring to a solution of *p*-bromophenyllithium prepared from the reaction of *p*-dibromobenzene with *n*-butyllithium. The reaction mixture was decomposed with dilute sulfuric acid. The ether layer was separated and submitted to steam distillation. An oily residue remained in the steam pot. The oil was extracted with ether and the ethereal solution was dried with magnesium sulfate. The ether was removed and the resulting oil was dissolved in 20 ml. of chloroform. To this was added an equivalent amount of bromine (2.8 g.) dissolved in 20 ml. of chloroform. Both solutions had been chilled in ice. The mixture was heated on a steam bath to remove the chloroform. (If, however, the mixture was held at ice-salt temperatures a precipitate of the presumed tribromide X was obtained; (m.p. 160–165°). The resulting oil was distilled. The distillate (180°/0.5–1 mm.) solidified and upon recrystallization from methanol, 4-bromo-*o*-terphenyl (2.5 g.; 46%) was obtained; m.p. 89–90.5°; λ_{max} 237 mμ (ϵ 3.3 × 10^4).

Anal. Calcd. for $C_{18}H_{13}Br$: C, 69.94; H, 4.24. Found: C, 69.96; H, 4.52.

Quinque[2.4.3]phenyl, (VII). The lithium derivative from 4-bromo-*o*-terphenyl (2 g.) was prepared by the interchange reaction with *n*-butyllithium in ether. To this solution 3-phenyl-2-cyclohexenone (2.2 g.) dissolved in ether was added. The addition complex was decomposed with dilute sulfuric acid and the ether layer was submitted to steam distillation. The residue in the steam pot was extracted with ether. The ether was evaporated and the resulting crude diene was dissolved in a minimum of *p*-cymene to which was added a small amount of palladium charcoal. This mixture was heated under reflux until the evolution of hydrogen ceased (about 0.5 hr.) and was then filtered. *p*-Cymene was removed by distillation and the residue was dissolved in petroleum ether (b.p. 60–80°) and passed through a chromatographic column of alumina. The earlier fractions contained residual *p*-cymene and some *o*-terphenyl. The subsequent eluant contained the quinquephenyl which upon concentration and chilling crystallized. The material was recrystallized from petroleum ether (b.p. 60–80°); yield: 1 g. (40%); m.p. 119.5–120°. No depression of melting point on admixture with earlier prepared sample.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.46; H, 6.07.

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College Park, Md.

[Contribution from the Chemical Laboratory of the University of Kansas]

Electrolysis of Bromobenzene in Pyridine Solutions[1]

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An investigation of the electrolysis of bromobenzene in pyridine solutions has been carried out between magnesium electrodes and also between a magnesium anode and a platinum cathode. Products isolated from the anolyte included benzene, 4,4′-dipyridyl, and the three isomeric phenylpyridines, with 4-phenylpyridine being the predominant isomer. Evidence is presented in support of mechanisms of reaction involving unipositive magnesium and phenyl radicals as intermediates.

When platinum was employed as cathode, benzene and the three isomeric phenylpyridines were obtained from the catholyte. The distribution of phenylpyridines corresponded very closely to that which results when pyridine is caused to react with a variety of reagents known to give rise to phenyl radicals. However, with a magnesium cathode the situation was much more complex. The electrode was corroded to a significant extent, and of the isomeric phenylpyridines isolated from the catholyte, the 4-isomer was predominant. Furthermore, 4,4′-dipyridyl was also found. The results indicate that here, as in the anolyte, the formation of unipositive magnesium exerts a profound influence on the course of reaction.

The results of this investigation and their interpretation, taken with previous observations, suggest a mechanism for the formation of Grignard reagents which involves a chain reaction with hydrocarbon radicals and unipositive magnesium serving as chain carriers.

Evidence has been presented in previous communications from this laboratory[2] that lower valent magnesium and aluminum species are formed as intermediates in the anodic oxidation of the metals in various media. These lower valent forms of the elements are highly reactive and readily give up electrons either to the anode or to an oxidant present in solution. It has been shown that in the presence of bromobenzene in pyridine solutions containing suitable electrolytes both magnesium and aluminum enter solution with initial mean valence numbers significantly lower than their characteristic values.[3] Since it is well known that the reaction of bromobenzene with magnesium results in the formation of a Grignard reagent, it was thought that the "anodic reduction" of bromobenzene in sodium iodide–pyridine solutions between magnesium electrodes might provide valuable evidence regarding the mechanism of the formation of Grignard reagents. This would be true particularly if the products formed in the anolyte were capable of attacking massive mag-

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(1) Sponsored by the Office of Ordnance Research, U.S. Army.

(2) See T. T. Tsai, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.,* **82,** 3326 (1960) and papers cited therein.

(3) M. D. Rausch, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.,* **77,** 2093 (1955).

nesium by a free-radical chain mechanism similar to that shown to occur in previous "anodic reduction" studies,[4-6] and if the Grignard reagent were the product of this corrosion process.

A thorough investigation of the electrolysis of bromobenzene in sodium iodide–pyridine solutions between magnesium electrodes and also between a magnesium anode and a platinum cathode has now been completed and the results are given below.

In an electrolysis between magnesium electrodes in which the anode entered solution with an initial mean valence number (V_i) of 1.49, no evidence could be found for the presence of phenylmagnesium bromide in the anolyte after completion of electrolysis. However, following hydrolysis of the anolyte, there was obtained benzene (58.6% yield, based on oxidation by bromobenzene of the metal from its initial mean valence state to the common +2 state), 4-phenylpyridine (28.4%), 3-phenylpyridine (2.3%), 2-phenylpyridine (11.8%). An appreciable amount of 4,4′-dipyridyl (8.6%) was also obtained (see Discussion). From the catholyte, after hydrolysis, there was found benzene (35.6%), 4-phenylpyridine (14.5%), 2-phenylpyridine (4.3%), and 4,4′-dipyridyl (2.2%). Inasmuch as the magnesium was corroded appreciably during the course of electrolysis, the yields of reduction products cited above were calculated on the basis of the sum of the number of equivalents of electricity passed through the solution and the number of equivalents of magnesium entering the catholyte as a result of corrosion. A duplicate electrolysis gave substantially the same results as those noted above.

When a platinum cathode was employed in place of magnesium in order to eliminate corrosion and its resulting products, a marked difference was observed in the relative amounts of the various reduction products formed in the catholyte. In duplicate experiments the products found were benzene (38%), 4-phenylpyridine (0.7%), 3-phenylpyridine (1.6%), and 2-phenylpyridine (2.9%).

Although control experiments showed that there was no attack on massive magnesium by a sodium iodide–pyridine solution containing bromobenzene at 40° (the temperature at which the electrolysis experiments were carried out), at an initiating temperature of 100° magnesium turnings underwent reaction. In the reaction mixture, after hydrolysis, the percentage yields of the various basic products were found to be: 4-phenylpyridine (11.4%), 3-phenylpyridine (0.9%), 2-phenylpyridine (4.8%), and 4,4′-dipyridyl (3.4%).

It was of importance in arriving at an understanding of our electrochemical results to determine the predominant orientation in the nucleophilic substitution reaction which occurs when phenylmagnesium bromide is treated with pyridine. In several experiments 2-phenylpyridine proved to be the major substitution product.

EXPERIMENTAL

Materials. Magnesium in rod form of 8 mm. diameter from which electrodes were cut was obtained from the Aluminum Company of America, and it was of 99.8% purity. In some electrolyses the cathode consisted of sheet platinum, having dimensions of about 50 × 8 mm. The sodium iodide employed as electrolyte was Merck reagent grade, and it was dried at 110° before use. Pyridine, Mallinckrodt or Fisher analytical reagent, was fractionally distilled at atmospheric pressure from sodium through a 3-foot packed column and stored over anhydrous barium oxide until used. Bromobenzene was dried over anhydrous calcium chloride, then fractionally distilled.

Apparatus for electrolysis. The cell, rectifier, and coulometer were the same as described in a previous communication.[2] All electrolyses were carried out under an atmosphere of nitrogen and at a constant temperature of 39.5 ± 0.5°. In each case the anodic current density was 0.005 amp. per cm.^{2} and the initial cell voltage was 25.5 v.

Electrolyses between magnesium electrodes. In a typical electrolysis each compartment of the cell contained 50 ml. of 0.5 *M* sodium iodide–pyridine solution and 15 g. of bromobenzene, and current was passed through the solution for 10.5 hr. On completion of electrolysis, catholyte and anolyte were immediately separately hydrolyzed with saturated ammonium chloride solution and then treated with 250 ml. of 18% hydrochloric acid. The magnesium electrodes were washed with distilled water, then with acetone, and dried at 110°, the water washings being added to the respective compartment hydrolyzates. It was found that during electrolysis the anode lost 0.2167 g. and the cathode lost 0.1958 g. while 0.0133 faradays of electricity were passed through the solution.

The initial mean valence number with which the magnesium anode entered solution was calculated to be 1.49 by use of the following equation:

$$V_i = \frac{\text{no. of faradays} \times 24.32}{\text{wt. of Mg lost from anode}}$$

The hydrolyzed anolyte was continuously extracted with ether for 24 hr. The ether extract was washed with dilute sodium carbonate and dilute sodium sulfite solutions and then dried over anhydrous calcium chloride. The dried ether solution was subjected to distillation through a Vigreux column. The fractions having boiling points up to 154° were subjected to vapor phase chromatographic analysis for benzene, and 0.1039 g. of this material was found. This amounted to a 58.6% yield, based on oxidation by bromobenzene of the magnesium from its measured initial mean valence state of 1.49 to the familiar bipositive state.

The aqueous phase of the anolyte remaining after ether extraction was made basic with ammonia water and then extracted continuously with ether for 24 hr. The ether solution was dried over anhydrous barium oxide, and the ether and pyridine removed by distillation. The brown oily solid which remained was extracted with cold petroleum ether (b.p. 60–70°). Distillation of the petroleum ether left a white oily solid. Inasmuch as exploratory experiments had indicated that the basic fractions of both anolyte and catholyte hydrolyzates consisted of a mixture of the three isomeric phenylpyridines and 4,4′-dipyridyl, the quantitative determination of the basic anolyte components was made by infrared analysis.

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(4) D. L. Burdick, A. V. Santoro, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, 79, 5467 (1957).

(5) J. Y. Yang, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, 80, 4300 (1958).

(6) W. D. Hoffman, W. E. McEwen, and J. Kleinberg, *Tetrahedron*, 5, 293 (1959).

The three isomeric phenylpyridines were prepared by the method of Haworth, Heilbron, and Hey.[7] 4,4′-Dipyridyl was made by the procedure of Wibaut and Arens[8] and Dimroth and Heene.[9] It was shown that infrared spectra of known artificial mixtures of the four compounds in chloroform solution could not be used to construct calibration curves for the quantitative determination of the components, owing to overlap of regions of relatively intense absorption and also to the effects of interactions on the positions of absorption peaks. Neither was it possible to establish experimentally the amounts of the four components in known mixtures by solution of simultaneous equations utilizing the Beer-Lambert law and the absorption curves of the individual compounds. However, with the aid of an analysis for nitrogen in the basic fraction from the anolyte and the selection of four wave numbers for measurement of absorption, it was possible to assemble an artificial mixture giving an infrared spectrum in chloroform which matched that of the unknown. Specifically, with small fixed concentrations of 4,4′-dipyridyl and 3-phenylpyridine in chloroform, the percentages of 2-phenylpyridine and 4-phenylpyridine were systematically varied and infrared spectra taken. First, the peaks at 1570 cm.$^{-1}$ (characteristic of 2- and 3-phenylpyridine) and at 1548 cm.$^{-1}$ (characteristic of 4-phenylpyridine) were matched with those found in the spectrum of the basic anolyte product in chloroform solution (5% by weight). Secondly, the quantity of 4,4′-dipyridyl was adjusted to the correct value by matching the absorption at 1437 cm.$^{-1}$ with that of the unknown. Finally, the quantity of 3-phenylpyridine was similarly adjusted by use of absorption at 1160 cm.$^{-1}$ In analyses of this type it generally required the preparation of between twelve and twenty mixtures before the appropriate spectrum was obtained. Of the basic material isolated from the anolyte 55.6% consisted of 4-phenylpyridine, 4.4% of 3-phenylpyridine, 23.1% of 2-phenylpyridine, and 16.8% of 4,4-dipyridyl. The infrared spectra are available.[10] The total yield of basic material, based on oxidation of magnesium from V_i of 1.49 to the +2 state by bromobenzene was 42.5%. The 4,4′-dipyridyl isolated does not represent an "anodic reduction" product. (See Discussion.)

The catholyte hydrolyzate was worked up in the same manner as just described for the anolyte. The yield of benzene was 35.6% based on the sum of the number of equivalents of electricity passed through the solution and the number of equivalents of magnesium lost from the cathode as a result of corrosion. The yield of basic material amounted to 21.0%, of which 68.8% was 4-phenylpyridine, 20.7% 2-phenylpyridine, and 10.6% 4,4′-dipyridyl. The infrared spectra are available.[10]

Electrolysis between a magnesium anode and a platinum cathode. Two electrolysis were carried out in the same manner as described for electrolysis between magnesium electrodes. Only the catholyte was worked up, the procedure already described being employed. Benzene was obtained in 38% yield and basic material in 5.2% yield. Of the basic material, 13.3% was 4-phenylpyridine, 30.5% 3-phenylpyridine, and 56.2% 2-phenylpyridine. No 4,4′-dipyridyl appeared to be present. The infrared spectra are available.[10]

Corrosion experiments. When a magnesium rod was placed for 24 hr. in sodium iodide–pyridine solution containing bromobenzene in the amount used in the electrolysis experiments, no corrosion occurred at 40°. However, after electrolysis between magnesium electrodes for 21 hr., two fresh magnesium rods weighing 3.4886 g. and 3.5317 g., respectively, were placed in the catholyte and anolyte and allowed to remain for 23 hr. The rod in the anolyte lost 0.0156 g. and that in the catholyte 0.0122 g.

Miscellaneous control reactions. (a) In a 500-ml. three-necked flask there was placed 30 g. of bromobenzene, 0.4000 g. of magnesium turnings, 150 ml. of anhydrous ether, and a small crystal of iodine. The Grignard reagent was prepared in the usual way and kept under a nitrogen atmosphere. One hundred milliliters of anhydrous pyridine was added and as much ether as possible removed by vacuum distillation. The flask was then placed in a water bath and maintained at 39.5° for 24 hr. The contents were hydrolyzed with 500 ml. of 18% hydrochloric acid, and the hydrolyzate was extracted with ether. From the ether layer 0.45 g. of biphenyl was obtained after removal of bromobenzene. The aqueous layer was made basic with ammonia water, extracted with ether, and the ether extract dried over anhydrous barium oxide. Distillation of the ether and any pyridine present gave 0.1170 g. of oily material. The infrared spectrum taken of this material in chloroform showed that 2-phenylpyridine was the major component.

(b) A mixture of 0.4000 g. of magnesium turnings, 30 g. of bromobenzene, a small crystal of iodine, and 100 ml. of 0.5*M* sodium iodide–pyridine solution was heated under nitrogen on a steam bath. When the magnesium was completely dissolved, the dark solution was maintained at 39.5° for 24 hr. The solution was then hydrolyzed and worked up as in (a). The basic fraction amounted to 0.53 g. and the infrared spectrum in chloroform matched that of the mixture of 55.6% 4-phenylpyridine, 4.4% 3-phenylpyridine, 23.1% 2-phenylpyridine, and 16.8% 4,4′-dipyridyl. The infrared spectra are available.[10]

(c) A mixture of 30 g. of bromobenzene, 0.4000 g. of magnesium turnings, and a small crystal of iodine was heated under nitrogen until almost all of the magnesium had dissolved. The mixture was allowed to cool to room temperature and 100 ml. of 0.5*M* sodium iodide–pyridine solution added. The resulting mixture was maintained at 39.5° for 24 hr. After hydrolysis and work-up as described above, the basic fraction weighing 0.1100 g. was obtained. Its infrared spectrum in chloroform showed it to contain mainly 2-phenylpyridine.

DISCUSSION

In the "anodic reduction" of bromobenzene in pyridine solution between magnesium electrodes the following significant observations were made. (1) The initial mean valence number with which the magnesium entered solution was significantly less than two, a fact consistent with the interpretation that at least some of the metal enters solution in the unipositive state.[2] (2) Reduction products—benzene and the three isomeric phenylpyridines—were isolated from the anolyte following hydrolysis in amount substantially corresponding to that expected from oxidation by bromobenzene of the magnesium from its initial mean valence state to the normal bipositive state. (3) No biphenyl was isolated from the anolyte hydrolyzate. (4) No evidence for the presence of phenylmagnesium bromide in the anolyte could be obtained; addition of the anolyte to Dry Ice, followed by acidification of the mixture, yielded no benzoic acid. (5) The ratio of phenylpyridines produced was 5.25 parts of 2-phenylpyridine to 1.00 part of 3-phenylpyridine to 12.64 parts of 4-phenylpyridine. (6) The anolyte, following electrolysis, was capable of corroding massive magnesium, whereas the original solution was not.

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[7] J. W. Haworth, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 372 (1940).

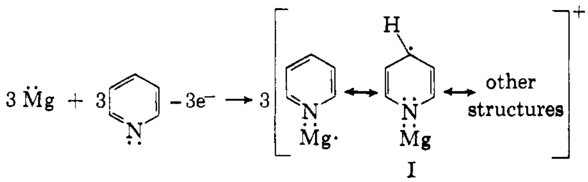
[8] J. P. Wibaut and J. F. Arens, *Rec. trav. chim.*, **61**, 59 (1942).

[9] O. Dimroth and R. Heene, *Ber.*, **54**, 2934 (1921).

[10] A photographic copy of these spectra will be supplied on request to the authors.

Before consideration of a detailed mechanism for the formation of the products noted above, it is necessary to take into account two apparently reasonable ways by which the isomeric phenylpyridines might have been produced One possibility which suggests itself is that phenyl radicals are produced in the anolyte (by a means which will be discussed below) and attack the solvent. However, data are available to prove that this could not have been the exclusive mode of production of the phenylpyridines in the anolyte in our experiments. Specifically, pyridine has been treated with five different reagents capable of yielding phenyl radicals as intermediates, and in each case the ratio of phenylpyridines produced was very close to 1.58 parts of 2-phenylpyridine to 1.00 part of 3-phenylpyridine to 0.42 part of 4-phenylpyridine.[11] Although these values were obtained for experiments carried out at 105°, whereas our results (see above) arise from electrolyses at 40°, it is inconceivable that this relatively small difference in temperature could account for the very large difference in product ratios. A second conceivable manner in which phenylpyridines might have been formed consists of the attack by an organometallic reagent (phenylmagnesium bromide or phenylsodium) on the solvent. This possibility is excluded as the sole source of the isomeric phenylpyridines in our experiments for four reasons. (1) It is known that phenyllithium attacks pyridine in a nucleophilic substitution reaction to produce 2-phenylpyridine apparently exclusively.[12,13] (2) No evidence for the formation of hydride ion in the anolyte was found (hydride ion *would* be formed in a nucleophilic substitution reaction). (3) It would not be anticipated that 3-phenylpyridine would be produced at all in a nucleophilic attack on pyridine. (4) We have caused phenylmagnesium bromide to react with pyridine under varying conditions and found that 2-phenylpyridine is the major isomer of the phenylpyridines produced. It is also clear that the isomer distribution found in the anolyte in the electrolysis experiments cannot be explained on the basis of a suitable combination of the two alternatives cited above, each of which yields 2-phenylpyridine as the major isomer.

A mechanism which is capable of explaining the formation of 4-phenylpyridine as the predominant isomeric phenylpyridine produced in our experiments involves the following steps: (1) anodic generation of unipositive magnesium;

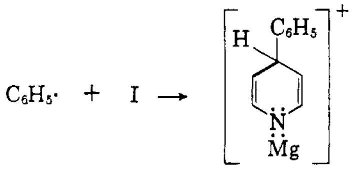


I

(2) formation of phenyl radicals by reaction of I and bromobenzene;

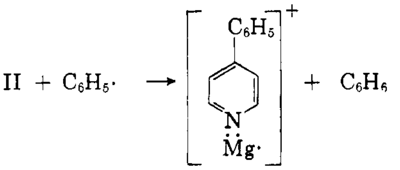
$$2I + 2C_6H_5Br \longrightarrow 2Mg^{2+}(\text{solvated}) + 2C_6H_5\cdot + 2Br^-$$

(3) addition of a phenyl radical to I;

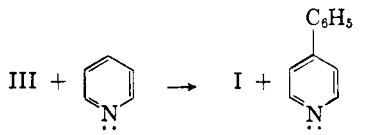


II

(4) abstraction of a hydrogen atom from II by the action of a phenyl radical



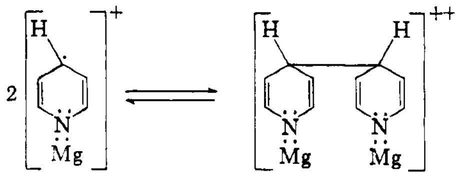
III (a)



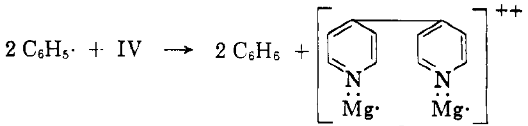
(b)

Although the mechanism proposed shows the formation only of 4-phenylpyridine, an analogous mechanism may be depicted for the production of 2-phenylpyridine. It is probable that the small amount of 3-phenylpyridine produced arises by attack of phenyl radicals directly on pyridine. Indeed a portion of all three isomers might very well be formed in this manner.

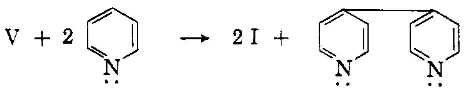
It should be emphasized that, in addition to the isomeric phenylpyridines and benzene, 4,4′-dipyridyl is also formed in the anolyte. This result is particularly striking in that the latter compound has never before been obtained as a product in the anolyte in electrolyses carried out in pyridine. We believe that in the current work this product arises in the following manner.



I IV (5)



V (6)



(7)

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(11) D. H. Hey, C. J. H. Stirling, and G. H. Williams, *J. Chem. Soc.*, 3963 (1955).

(12) J. C. W. Evans and C. F. H. Allen, *Org. Syntheses*, Coll. Vol. II, 517 (1943).

(13) K. Ziegler and H. Zeiser, *Ber.*, **63**, 1847 (1930).

Although the equilibrium shown in equation (5) undoubtedly exists in any solution of unipositive magnesium anodically generated in pyridine, 4,4′-dipyridyl is not obtained unless a sufficiently reactive radical, such as the phenyl radical, is present to abstract hydrogen from species IV, as shown in equation (6). Thus, no 4,4′-dipyridyl was obtained in "anodic reduction" reactions in which relatively stable radical-ions, such as the ketyl radical-ions obtained from benzophenone,[4,14] 4,4′-dimethylbenzophenone,[4,15] and 1,3-dibenzoylpropane,[6] and the radical-ions derived from azobenzene, azoxybenzene, and nitrosobenzene,[5,15] were formed as intermediates.

Strong support for the mechanisms cited above is afforded by our data. These mechanisms require a correspondence between the amount of benzene and the quantities of basic materials found in the anolyte. For each molecule of a phenylpyridine produced the mechanism requires a molecule of benzene, and for each molecule of 4,4′-dipyridyl formed two molecules of benzene should be produced. In the typical experiment cited earlier in the paper the yields of basic materials as determined from the apparent amount of unipositive magnesium generated (calculated from the V_1 value and the number of faradays passed through the solution) were: 4-phenylpyridine, 28.4%; 3-phenylpyridine, 2.3%; 2-phenylpyridine, 11.8%; and 4,4′-dipyridyl, 8.6%. Thus, the yield of benzene to be expected is 59.7%. Actually, 58.6% was found.

According to the mechanisms proposed 4,4′-dipyridyl is not an "anodic reduction" product. Thus the total amount of benzene and the isomeric phenylpyridines should correspond to that calculated on the basis of oxidation of magnesium from its initial mean valence state to the bipositive state by bromobenzene. The experimental correlation was excellent, the sum of the yields of reduction products being equal to 101%.

That 4-phenylpyridine is the predominant isomeric phenylpyridine found in the anolyte and that orientation in the formation of dipyridyl is at the 4- and 4′-positions require comment. It has been observed previously[16,17] that reactions in which pyridine is attacked successively by two radicals lead to the formation of 1,4-disubstituted 1,4-dihydropyridines. When two metal-pyridyl radicals couple or when another radical couples with a metalpyridyl radical, a 1,4-dihydropyridine derivative would more likely be formed than a 1,2-derivative inasmuch as *para*-quinoid structures are generally more stable than *ortho*-quinoid structures.[18]

The nature of the electrode had a profound effect on the distribution of reduction products formed at the cathode. When platinum was employed as cathode, no 4,4′-dipyridyl was isolated and the ratio of isomeric phenylpyridines was 0.44 part of 4-phenylpyridine to 1.00 part of 3-phenylpyridine to 1.8 parts of 2-phenylpyridine. It should be noted that this ratio corresponds very closely to that obtained by Hey and coworkers[11] on treatment of pyridine with a variety of agents which give rise to phenyl radicals. In addition to the isomeric phenylpyridines, benzene and material believed to be a mixture of polypyridyls were also found in the catholyte.

The picture is a much more complicated one at a magnesium cathode, primarily because the electrode is corroded significantly during electrolysis. Besides benzene and 4,4′-dipyridyl, 4-phenylpyridine and 2-phenylpyridine were produced, the latter two compounds in a ratio of 3.4 parts to 1. Thus, for the reasons cited in the discussion of the formation of anolyte products, the phenylpyridines cannot arise predominantly by either a simple radical or nucleophilic substitution reaction. Corrosion of the magnesium is undoubtedly caused by the attack of phenyl radicals; the latter are produced in part by cathodic reduction of bromobenzene. It is postulated in line with the results of corrosion studies presented in a previous communication[4] that solvated unipositive magnesium is formed in the corrosion process. As a consequence of this 2-phenylpyridine and 4-phenylpyridine can be produced by reactions (2) through (4).

It is inescapable that there should be some relationship between the mechanism of corrosion of the magnesium cathode in pyridine solution and the mechanism of formation of Grignard reagents. The latter process also involves the corrosion of magnesium but in ether medium. A case can also be made that the formation of a Grignard reagent in ether is a free radical chain reaction. For example, many reactions leading to the formation of Grignard reagents take place only when an initiator magnesium(I) iodide formed by reaction between magnesium and a limited amount of iodine] is present, and then the reaction proceeds with gradually increasing vigor. Thus, in line with our proposed corrosion mechanism for attack of massive magnesium by a radical-ion,[4] we propose that Grignard reagents are formed by the following mechanism.

Initiation step:

$$\dot{\mathrm{M}}\mathrm{g} + {}^1/_2\mathrm{I}_2 \longrightarrow \dot{\mathrm{M}}\mathrm{g}^+ + \mathrm{I}^- \qquad (8)$$

Propagation steps:

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[14] M. D. Rausch, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **76**, 3622 (1954).

[15] W. E. McEwen, J. Kleinberg, D. L. Burdick, W. D. Hoffman, and J. Y. Yang, *J. Am. Chem. Soc.*, **78**, 4587 (1956).

[16] R. L. Frank, F. Pelletier, and F. W. Starks, *J. Am. Chem. Soc.*, **70**, 1767 (1948).

[17] M. S. Kharasch, D. Schwartz, M. Zimmermann, and W. Nudenberg, *J. Org. Chem.*, **18**, 1051 (1953).

[18] W. A. Waters, *Physical Aspects of Organic Chemistry*, 4th ed., D. Van Nostrand Company, Inc., New York, 1950, p. 481.

$$RX + \dot{M}g^{+} \longrightarrow R\cdot + Mg^{++} + X^{-} \qquad (9)$$

$$R\cdot + Mg{:} \longrightarrow R{:}^{-} + \dot{M}g^{+} \qquad (10)$$

The question now arises why no Grignard reagent is formed in either the anolyte or catholyte in our electrolysis experiments. The evidence for nonformation of Grignard reagent is two-fold. No benzoic acid is isolated following carbonation and acidification of either solution, and of the isomeric phenylpyridines produced the 4-isomer rather than the 2-isomer predominates. The answer to the question posed at the start of the paragraph is that pyridine functions as an inhibitor of the free radical chain reaction leading to Grignard reagent. As a matter of fact, when bromobenzene is heated with magnesium in pyridine solution containing a small amount of iodine and sodium iodide, 4-phenylpyridine is the predominant isomer formed (see Experimental) and the composition of the basic fraction is identical with that of the anolyte following electrolysis of bromobenzene in pyridine solution between magnesium electrodes.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Pentachlorophenyl Derivatives. VI.[1] The Preparation and Methanolysis of Pentachlorostyrene Oxide

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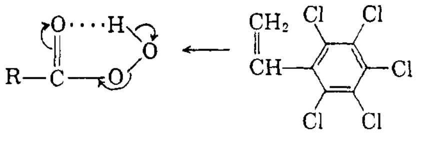
Pentachlorostyrene oxide reacts with methanol in the presence of acid to form 1-pentachlorophenyl-1-methoxy-2-hydroxyethane. In the presence of base, the attack by methoxide ion is on the β-position to give 1-pentachlorophenyl-1-hydroxy-2-methoxyethane. A second product, probably 4-methoxy-2,3,5,6-tetrachlorostyrene oxide, is also formed in this latter reaction. These reactions are discussed.

Pentachlorophenyl derivatives have been of interest because of the frequency with which they react to give atypical products. Some examples which may be cited are the predominant β-chlorination of ethylpentachlorobenzene,[3] the alcoholysis of pentachlorobenzal chloride to give an acetal of a 4-alkoxy-2,3,5,6-tetrachlorobenzaldehyde[4] and the ability of pentachlorostyrene to add hydrogen bromide by a radical mechanism to give β-bromoethylpentachlorobenzene coupled with the complete absence of any evidence for ionic addition in the same system.[5]

For the most part, these abnormal reactions have been attributed to the steric effects rather than the polar effects of the chlorine substituents. In this connection both the preparation and alcoholysis of pentachlorostyrene oxide appeared to be of interest. The failure of pentachlorostyrene to add hydrogen bromide by an ionic mechanism[5] might lead to difficulty in the preparation of the oxide, and the direction of opening of the oxide ring, once formed, might be influenced by polar factors as much as by steric factors.

In actual fact, the preparation of pentachlorostyrene oxide proved to be straightforward, good yields being obtained with either perbenzoic or peracetic acid in chloroform. The success of this reaction, in contrast to the failure of the ionic addition of hydrogen bromide, may be due to the fact that ionic intermediates are probably not involved. One possible rationalization: The reaction involves a π-complex, as depicted below, between the vinyl double bond and an internally hydrogen-bonded form of the peracid, which then collapses to give the final products. This is the mechanism proposed by Overberger and Cummins[6] for the oxidation of p,p'-dichlorobenzyl sulfide by perbenzoic acid.



The opening of the oxide ring with methanol proceeds smoothly in the presence of an acid catalyst to give a single methoxyalcohol (I) in good yield. The methanolysis product (I) reacts with thionyl chloride to form a chloro ether and readily forms an acetate and p-toluenesulfonate. The structure of I was established by the sequence of reactions shown:

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[1] For the previous paper in this series, see S. D. Ross, W. A. Leach, and I. Kuntz, *J. Am. Chem. Soc.*, **74**, 2908 (1952).

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[3] S. D. Ross, M. Markarian, and M. Nazzewski, *J. Am. Chem. Soc.*, **69**, 1914, 2468 (1947); **71**, 396 (1949).

[4] S. D. Ross and M. Markarian, *J. Am. Chem. Soc.*, **71**, 2756 (1949).

[5] S. D. Ross, M. Markarian, H. H. Young, Jr., and M. Nazzewski, *J. Am. Chem. Soc.*, **72**, 1133 (1950).

[6] C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953). See also S. Medvedev and O. Blokh, *J. Phys. Chem.* (*U.S.S.R.*), **4**, 721 (1933); *Chem. Abstr.*, **29**, 6492 (1935).