In the cobalt chloride experiment a solid residue remained after removal of the ether. The solid was leached with hot ligroin until half the substance had dissolved, and the remainder was then dissolved in hot 95% alcohol. The two portions were fractionally crystallized. All fractions from the alcohol produced benzopinacol, 178–180° (dec.). The first fractions from ligroin produced pinacol, succeeding fractions giving a mixture of pinacol and 1,2-addition product. The two compounds were separated by fractional crystallization from ligroin.

The product of the ferric chloride experiment was fractionally crystallized from 95% alcohol. Pure pinacol crystallized at first. A mixture of pinacol and carbinol appeared in the last fractions. The substances were separated by fractional crystallization from ligroin.

In the experiment in which magnesium was added to the Grignard reagent, a red to red-violet coloration appeared during and shortly after the addition of the benzophenone. However, only diphenylmethylcarbinol was obtained, although a careful search was made for benzopinacol.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

# Factors Determining the Course and Mechanisms of Grignard Reactions. IV. The Effect of Metallic Halides on the Reaction of Aryl Grignard Reagents and Organic Halides[1]

BY M. S. KHARASCH AND E. K. FIELDS

## Introduction

The interesting effects of metallic halides on the reaction between Grignard reagents and benzophenone[2,3] or isophorone[4] prompted us to extend our studies to other systems. This paper describes the results obtained when aryl Grignard reagents are treated with organic halides in the presence of small quantities (3–5 mole per cent.) of the halides of copper, manganese, nickel, chromium and cobalt.

## Previous Work

The coupling of Grignard reagents by metallic halides in accordance with scheme (I) has been

$$2RMgX + MX_2 \longrightarrow R{-}R + 2MgX_2 + M \qquad (I)$$

the subject of numerous investigations.[5] Chromic chloride, cupric chloride, aurous chloride carbonyl, and silver bromide are the halides most thoroughly investigated. The Grignard reagents studied are those of bromobenzene, benzyl chloride, bromonaphthalene, the bromotoluenes, *p*-bromoanisole, cyclohexyl bromide, and the butyl bromides. The yields of the R—R compounds vary from 25–100%.

In all cases, however, at least one mole of the metallic halide was used. Their function is best understood by assuming that they act as electron acceptors. In the reaction they are reduced, in some cases, to the metallic state.

**Arylmagnesium Halides with Organic Halides in the Presence of Metallic Halides.**—To appreciate the tremendous effect of small quantities of metallic halides on the reaction between aryl Grignard reagents and organic halides, the following facts must be borne in mind: (1) arylmagnesium halides do not react with monosubstituted aryl halides; (2) the metallic halides, such as cobaltous chloride, nickelous chloride, ferric chloride, etc., do not react with aryl halides; (3) arylmagnesium halides react with the above-mentioned metallic halides to yield the biaryl compounds. Thus, phenylmagnesium bromide reacts with cobaltous chloride to yield biphenyl. Furthermore, it follows from Scheme I that for each mole per cent. of the cobaltous chloride used, no more than two mole per cent. of the Grignard reagent can be utilized and no more than one mole per cent. of biphenyl (on the basis of the Grignard reagent) can be formed. A large number of our experiments has confirmed the validity of this principle. Similar results were obtained by Gilman and Lichtenwalter.[5]

However, when bromobenzene (one mole) is dropped into a mixture consisting of one equivalent of phenylmagnesium bromide and three mole per cent. of cobaltous chloride, a vigorous reaction ensues; considerable heat is liberated, and biphenyl is formed in excellent yield. Further-

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[1] The writers are indebted to Eli Lilly and Company for support which made this work possible.

[2] Kharasch, Kleiger, Martin and Mayo, THIS JOURNAL, **63**, 2305 (1941).

[3] Kharasch and Lambert, *ibid.*, **63**, 2315 (1941).

[4] Kharasch and Tawney, *ibid.*, **63**, 2308 (1941).

[5] For an exhaustive series of references see Gilman and Lichtenwalter, *ibid.*, **61**, 957 (1939).

more, the bromobenzene takes part in the reaction, as can be demonstrated by a halogen titration of the aqueous solution obtained by hydrolysis of the reaction mixture after the reaction has ceased and by the fact that only a portion of the bromobenzene can be recovered. It is clear, therefore, that in the presence of cobaltous chloride, bromobenzene acts as an oxidizing agent in converting the phenylmagnesium bromide to biphenyl. That the biphenyl is formed exclusively from the phenylmagnesium bromide is proved by the fact that bromobenzene can be replaced by *p*-tolyl bromide, ethyl bromide, isopropyl chloride, etc. (Table I), without appreciably decreasing the yield of biphenyl. The organic radical of the bromobenzene is, however, responsible for the formation of a trace of biphenyl, terphenyl, quadriphenyl and other high boiling materials, since no such materials are found when aliphatic halides are used in place of phenyl bromide. In semiquantitative studies of the reaction just described it has been possible to account for more than 97% of the organic materials used. The result of one such representative experiment is as follows. A mixture of reactants composed of 0.54 mole of phenylmagnesium bromide in diethyl ether, 0.40 mole of phenyl bromide and 0.04 mole (7 mole %) of cobaltous chloride was heated for two hours. The following products were obtained: benzene 18 g. (0.23 mole), phenyl bromide 10.7 g. (0.068 mole), biphenyl 34.5 g. (0.224 mole), terphenyl (1.7 g.), quadriphenyl (0.8 g.), and a very high boiling material (17.5 g.). Similar results were obtained when as little as 3 mole per cent. of cobaltous chloride was used.

The above method of forming biphenyl from phenylmagnesium bromide, by the use of an organic halide and the halides of iron, nickel and cobalt (Table I), has yielded excellent results when extended to other aryl Grignard reagents. Thus, by this method, *p*,*p*-bitolyl, *o*,*o*-bitolyl, 4,4'-bianisyl, 2,2'-biphenetyl, uniformly were obtained in yields superior to those reported for other coupling reagents (Table II). Since in most of the condensations here reported (Table II), ethyl bromide was used as the oxidizing agent, no high boiling products (besides the diaryls) were found. However, phenyl bromide and *p*-tolylmagnesium bromide gave a 95% yield of *p*,*p*-bitolyl, and a quantity of very high boiling material. The weight of this material and of the benzene formed in the reaction accounted quantitatively for the phenyl radicals of the phenyl bromide which had reacted.

This reaction, whereby a biaryl is formed from an aryl Grignard reagent, in the presence of an organic halide and a metal halide (Table I), is most remarkable. Essentially it involves the transfer of an electron or electrons to the organic halide (*e. g.* bromobenzene or ethyl bromide) from the organic radical of the Grignard reagent. The metallic halide presumably acts as an oxidation–reduction catalyst in that it is reduced to a lower oxidation state by the Grignard reagent and oxidized back to its original oxidation state (or possibly to a higher state) by the organic halide. The resemblance of this mechanism to the action of metal ions in the oxidation–reduction reactions of biological systems is most striking.

The fact that only small quantities of metallic halides are used in bringing about the above coupling reaction of Grignard reagents suggests that it is a chain reaction. It is our belief that even smaller quantities of metallic halides would produce the same effect were it not for the fact that the reaction is heterogeneous and that appreciable quantities of the catalyst, say cobaltous chloride, become covered either with metallic cobalt (formed in the reaction) or with a tarry organic matter. Provisionally, we suggest the following chain mechanism.

$$C_6H_5MgBr + CoCl_2 \longrightarrow C_6H_5CoCl + MgBrCl \quad (1)$$

$$2C_6H_5CoCl \longrightarrow C_6H_5{\cdot}C_6H_5 + 2CoCl \quad (2)$$

$$CoCl + C_6H_3Br \longrightarrow CoClBr + C_6H_5{\cdot} \quad (3)$$

$$\begin{aligned} X(C_6H_5{\cdot}) \longrightarrow\ & C_6H_6, C_6H_5{:}C_6H_5(\text{trace}) + \\ & C_6H_5{\cdot}C_6H_4{\cdot}C_6H_5 + C_6H_5{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}C_6H_5 \\ & \text{and other polymers} \quad (4) \end{aligned}$$

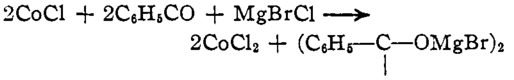
The essential feature of this scheme is that the reaction proceeds through the agency of a cobalt subhalide, the active chain carrier. The mechanism further indicates that the biaryls are formed exclusively from the aryl Grignard reagent, and that the bromine atom of the phenyl bromide is converted into bromide ion by the cobalt subhalide. The benzene, biphenyl (trace), terphenyl, quadriphenyl and the high molecular compounds result from disproportion of phenyl radicals, since similar substances have been found wherever reactions occur through the intermediate formation of free phenyl radicals in solution. Strictly speaking, complete identity of final products is not to be expected since, in the case under consideration, the reaction is heterogeneous, the free phenyl radical being formed on the surface of the cobalt subhalide.

Isopropyl chloride or even phenyl chloride may be employed instead of phenyl bromide or ethyl bromide as the oxidizing agents. It was expected and confirmed by experiment, that phenyl chloride because of the stronger carbon to chlorine bond would give lower yields of biphenyl. Actually, phenyl chloride gave a 37% and phenyl bromide an 85–90% yield.

From the standpoint of the chain reaction mechanism here suggested for the catalytic effect of cobaltous (or nickel or iron) chloride, it is easy to understand why Kharasch and Lambert[3] found that methylmagnesium bromide reacts with benzophenone in the presence of one mole per cent. of cobaltous chloride to give exclusively benzopinacol, rather than diphenylmethylcarbinol, the product formed in the absence of the metallic halide.

$$CH_3MgBr + CoCl_2 \longrightarrow CH_3CoCl + MgClBr \quad (1)$$

$$2CH_3CoCl \longrightarrow C_2H_6 + 2CoCl \quad (2)$$



$$2CoCl + 2C_6H_5CO + MgBrCl \longrightarrow 2CoCl_2 + (C_6H_5\text{—}\underset{|}{C}\text{—}OMgBr)_2 \quad (3)$$

The cobalt subhalide by donating an electron to the benzophenone is regenerated in a higher oxidation state and participates again in the reaction. The organic free radical captures the $[MgBr]^{++}$ positive ions, to neutralize its negative charge, and is converted into the metal ketyl. The dimerization of the metal ketyl results in the formation of the benzopinacol.

However, it is not to be supposed that all Grignard reagents would react with benzophenone in the presence of cobaltous chloride to yield benzopinacol even though the primary requirements, namely, the reaction of the Grignard reagent with cobaltous chloride, be fulfilled. For the success of the reaction the second step, namely, the decomposition of the compound RCoCl into $R_2$ and a cobalt subhalide must be sufficiently rapid. Otherwise, the normal addition of the Grignard reagent to the benzophenone may take place exclusively. It is, therefore, not surprising to find that phenylmagnesium bromide, unlike methylmagnesium bromide, reacts with benzophenone in the presence of cobaltous chloride to yield a tertiary alcohol.

In our estimation these results imply that there is a great difference in stability, under the conditions of the experiment, between the intermediate products formed from the phenyl- and methylmagnesium bromides and cobaltous chloride. The former intermediate is much more stable. The following experiments confirm this view. When cobaltous chloride is added to an ether solution of phenyl- or methylmagnesium bromide, a vigorous reaction takes place and the solution acquires a deep brown to black color. When phenyl bromide or ethyl bromide is added to this mixture a vigorous reaction ensues, as indicated by a large heat evolution. However, if the mixtures of the respective Grignard reagents and cobaltous chloride are heated for 1.5 hours prior to the addition of the aryl halide, their behavior shows significant differences. The phenyl Grignard reagent still liberates a great deal of heat when treated with phenyl bromide and the yield of biphenyl and of the high molecular weight materials is about 50% of that obtained without preliminary heating. The methyl Grignard reagent mixture, however, when treated with phenyl bromide liberates scarcely any heat. Here none of the reagent is utilized and consequently hardly any high molecular weight material is formed. If the same mixture is used without previous boiling about 80% of the aryl halide is converted into benzene, a trace of biphenyl, terphenyl, quadriphenyl and high molecular material.

In attempting to alter the normal course of the reaction between a Grignard reagent and an organic molecule by the use of a metallic halide, the rate of the normal condensation as well as the stability of the intermediate formed must be considered. If the normal condensation is fast and the intermediate fairly stable, the metallic halide exerts hardly any effect. On the other hand, if the normal reaction is slow and the intermediate somewhat more stable the metallic halide has a pronounced effect. But if the reaction of the Grignard reagent and the metallic halide yields an exceedingly unstable intermediate, the metallic halide has no effect because the subhalide is quickly reduced to the metal.

The data on hand point a definite relation between the electronegativity of the organic radical, the stability of the intermediate organometallic compound, and the rate of the normal addition. These factors have been taken into account in an hypothesis which permits the effect of metallic halides to be predicted in the reactions of Grignard reagents with many types of organic molecules. It is hoped to treat this subject in a forthcoming publication.

## Experimental Part

**Preparation of the Grignard Reagents.**—Phenylmagnesium bromide was prepared from freshly distilled bromobenzene and an excess of sublimed magnesium. To ensure the absence of unreacted bromobenzene the Grignard solution was heated for two hours after addition of this reagent. The normalities of various solutions varied from 2.264 to 3.44 (determined by a bromide titration of 30-cc. samples of solution). The amount of biphenyl in the Grignard reagent was determined by working up the samples used for standardization. The yield of biphenyl was fairly constant (6–8%).

The other Grignard reagents used in our study (Tables I and II) were prepared and standardized in the same manner. The normalities of these reagents varied from 1.1 to 1.3.

TABLE I

REACTION OF PHENYLMAGNESIUM BROMIDE WITH ORGANIC HALIDES IN THE PRESENCE OF METALLIC SALTS

| Moles of $C_6H_5MgBr$ | Moles of organic halide | | Mole per cent. of metallic salt | | Yield of diaryl,[a] % |
|---|---|---|---|---|---|
| 0.09 | 0 | | 0 | | 8[b] |
| .14 | 0 | | 9 | $CoCl_2$ | 27 |
| .54 | 0.4 | $C_6H_5Br$ | 7 | $CoCl_2$ | 83 |
| .113 | .1 | $C_6H_5Br$ | 2.5 | $CoCl_2$ | 86 |
| .11 | .1 | *p*-$BrC_6H_4CH_3$ | 9 | $CoCl_2$ | 86 |
| .12 | .1 | $C_6H_5Br$ | 4 | $CoCl_2$ | 44[c] |
| 0 | .1 | $C_6H_5Br$ | 100 | Co | 0[d] |
| .127 | .1 | $C_2H_5Br$ | 7 | $CoCl_2$ | 81 |
| .131 | .1 | $C_6H_5Cl$ | 4 | $CoCl_2$ | 37 |
| .113 | .1 | *i*-$C_3H_7Cl$ | 5 | $CoCl_2$ | 58 |
| .11 | .1 | $C_6H_5Br$ | 9 | $Cu_2Cl_2$ | 6 |
| .13 | .1 | $C_6H_5Br$ | 4 | $MnCl_2$ | 21 |
| .106 | .1 | $C_6H_5Br$ | 5 | $FeCl_3$ | 47 |
| .134 | .1 | $C_6H_5Br$ | 4 | $NiCl_2$ | 72 |
| .113 | .1 | $C_6H_5Br$ | 4 | $CrCl_3$ | 7 |
| .11[e] | None | | 28 | $CoCl_2$ | 64[f] |
| .117[e] | .1 | $C_6H_5Br$ | 4 | $CoCl_2$ | 86 |

[a] Based on $C_6H_5MgBr$. [b] Control; amount of biphenyl in control experiments was 6–8%. [c] Grignard reagent and cobalt chloride refluxed for one hour, then $C_6H_5Br$ added and mixture refluxed another hour. [d] Pyrophoric cobalt stirred with $C_6H_5Br$ at 40° for one hour. [e] Phenylmagnesium iodide was used. [f] In ether–benzene solution at 0° for three hours.

**Preparation of the Metallic Salts.**—Ferric chloride was prepared from iron wire and chlorine. The other chlorides were prepared from their hydrates by dehydration in a stream of hydrogen chloride gas. They were finally dried *in vacuo* at 100–150°.

**Coupling of Grignard Reagents by Organic Halides in the Presence of Metallic Salts.**—Unless otherwise indicated most of the experiments were conducted in the manner described for the interaction of phenylmagnesium bromide, bromobenzene and cobalt chloride. To bromobenzene (0.1 mole), anhydrous cobalt chloride (0.01 mole), and 10 cc. of anhydrous ether contained in a 200-cc. 3-necked flask equipped with mercury seal stirrer, reflux condenser and dropping funnel, 60 cc. of 2.264 *N* phenylmagnesium bromide was added at such a rate as to maintain a slow refluxing of the ether. The mixture was thoroughly agitated throughout the addition. Toward the end of this operation, and for an hour thereafter, the mixture was heated on a water-bath. The whole was then poured on a mixture of ice and water, 10 cc. of acetic acid added and the layers separated. The ether layer was washed with sodium bicarbonate solution and twice with water. The water layer and washings were made up to 500 cc. in a volumetric flask and aliquots withdrawn for analysis.

*Anal.* 5.52 cc. of solution required 19.28 cc. of 0.1674 *N* KCNS solution for back-titration of 1.000 g. of $AgNO_3$. This gives a total of 240.7 mm. of bromide ions in solution. If we subtract the 155.8 mm. of bromide ions (135.8 from Grignard and 20 from $CoCl_2$), 84.9 mm. of bromide ion becomes available from the bromobenzene, *i. e.*, 84.9% of the bromobenzene has reacted.

The ether layer was dried over anhydrous sodium sulfate, filtered, and fractionated. The following products were isolated: (I) benzene 4.8 g.; (II) bromobenzene (15.7%) 2.5 g.; (III) biphenyl 9.0 g.; (IV) residue 4.6 g. By correlation of figures from various experiments using ethyl bromide, phenyl bromide, and *p*-tolyl bromide, we conclude that in this experiment the 84.9% of bromobenzene which reacted gave approximately 20% benzene, 5% biphenyl, and 60% higher boiling material.

The products of all experiments (Tables I and II) were separated by distillation except in the case of *p,p'*-dianisole, which was crystallized from 95% alcohol after removal of the anisole.

**Reaction of Phenylmagnesium Iodide with Cobaltous Chloride.**—To 0.11 mole of phenylmagnesium iodide con-

TABLE II

COUPLING OF ARYL GRIGNARD REAGENTS IN THE PRESENCE OF METAL SALTS

| Grignard reagent | Mole, % $CoCl_2$ | Organic halide | Product | Yield, % | Yield reported, % | Metal salts used |
|---|---|---|---|---|---|---|
| *p*-Tolyl-MgBr | 10 | $C_6H_5Br$ | *p,p'*-Bitolyl | 95 | 80–85[a] | $CrCl_3$[a] |
| | | | | | 25–72[b] | AgBr[b] |
| | | | | | 91.5[c] | AuCl·CO[c] |
| *o*-Tolyl-MgBr | 7 | $C_2H_5Br$ | *o,o'*-Bitolyl | 75 | 0[a] | $CrCl_3$[a] |
| | | | | | 61.3[c] | AuCl·CO[c] |
| | | | | | 30[d] | $CuCl_2$[d] |
| *p*-Anisyl-MgBr | 5 | $C_2H_5Br$ | 4,4'-Bianisole | 76 | 48[b] | AgBr[b] |
| *o*-Phenetyl-MgBr | 5 | $C_2H_5Br$ | 2,2'-Biphenetole | 74 | | |

[a] Bennett and Turner, *J. Chem. Soc.*, **105**, 1057 (1914). [b] Gardner and Borgstrom, THIS JOURNAL, **51**, 3375 (1929). [c] Kharasch and Isbell, *ibid.*, **52**, 2919 (1930). [d] Turner, *J. Proc. Royal Soc. N. S. Wales*, **54**, 37 (1920); *C. A.*, **15**, 669 (1921).

tained in a mixture of ether and benzene and kept at 0°, 0.03 mole (28 mole per cent.) of cobalt chloride was added, and the treatment continued according to the directions given in the literature.[5] A 63% yield of biphenyl was obtained, on the basis of the Grignard reagent used. Since a blank on the phenylmagnesium iodide showed 7% biphenyl, the agreement between the calculated yield of biphenyl (56%) and that actually formed in the reaction (56%) is excellent. Our results are probably accurate within 2–3%.

### Summary

1. Excellent yields of biaryl are obtained when an aryl Grignard reagent is treated with an organic halide, preferably a bromide, in the presence of 3–10 mole per cent. of the halides of iron, nickel and cobalt (the metals are arranged in order of their increasing effectiveness). The halides of copper and chromium are ineffective, while manganous chloride has a slight effect.

2. It has been indicated that the metallic halides act in the above reaction as oxidation-reduction catalysts, and a chain reaction, involving the subhalides of the effective metals, is postulated.

3. The study of the effect of metallic halides on the reaction of Grignard reagents and organic molecules containing functional groups is under way in this Laboratory.

CHICAGO, ILLINOIS RECEIVED APRIL 16, 1941

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[CONTRIBUTION FROM THE ANIMAL CHEMISTRY AND NUTRITION SUBSECTION OF IOWA STATE COLLEGE]

# The Formation of the Molecular Compound of *allo*- and *epi-allo*-Cholesterol from $\Delta^{3,5}$-Cholestadiene[1]

BY J. C. ECK AND E. W. HOLLINGSWORTH

In a further study of the rearrangement of $\Delta^{4,6}$-cholestadiene (I) to $\Delta^{3,5}$-cholestadiene (II) by the action of hydrogen chloride in chloroform solution,[2] it was found that the molecular compound of *allo*- and *epi-allo*-cholesterol (III) could be isolated from the crude reaction product. This compound was isolated by the ether elution of an activated alumina column through which had been passed a petroleum ether solution of the reaction product.

The molecular compound of *allo*- and *epi-allo*-cholesterol was likewise isolated from the reaction products formed by the action of hydrogen chloride in chloroform on $\Delta^{3,5}$-cholestadiene which had been prepared by (a) the hydrogen chloride rearrangement of $\Delta^{4,6}$-cholestadiene, (b) the copper sulfate dehydration of cholesterol in xylene[3] and (c) the alcoholic hydrochloric acid dehydration of the molecular compound of *allo*- and *epi-allo*-cholesterol.[4] Since the molecular compound of *allo*- and *epi-allo*-cholesterol was isolated from the action of hydrogen chloride in chloroform on $\Delta^{3,5}$-cholestadiene which had been obtained from three different sources, it could not have been formed from an impurity but from the $\Delta^{3,5}$-cholestadiene itself. Furthermore, a twice repeated treatment of the $\Delta^{3,5}$-cholestadiene recovered from the reaction product obtained by the action of hydrogen chloride in chloroform on $\Delta^{3,5}$-cholestadiene resulted in a combined conversion of most of the $\Delta^{3,5}$-cholestadiene to the molecular compound of *allo*- and *epi-allo*-cholesterol.

The molecular compound of *allo*- and *epi-allo*-cholesterol was also isolated from the reaction product obtained by the action of hydrogen chloride in chloroform on $\Delta^{2,4}$-cholestadiene (IV) which has been shown to be rearranged to $\Delta^{3,5}$-cholestadiene by the action of alcoholic hydrochloric acid.[5] It is probable that $\Delta^{2,4}$- and $\Delta^{4,6}$-cholestadienes are rearranged to $\Delta^{3,5}$-cholestadiene which is then partially converted to the molecular compound of *allo*- and *epi-allo*-cholesterol. Thus (a) the molecular compound of *allo*- and *epi-allo*-cholesterol is formed by the action of hydrogen chloride in chloroform on $\Delta^{2,4}$-, $\Delta^{3,5}$- and $\Delta^{4,6}$-cholestadienes, (b) hydrogen chloride in chloroform rearranges $\Delta^{4,6}$-cholestadiene to $\Delta^{3,5}$-cholestadiene and (c) $\Delta^{3,5}$-cholestadiene is undoubtedly present in the reaction product resulting from $\Delta^{2,4}$-cholestadiene. It is of interest to note that hydrogen chloride in chloroform rearranges both $\Delta^{2,4}$- and $\Delta^{4,6}$-cholestadienes to $\Delta^{3,5}$-cholestadiene, whereas $\Delta^{2,4}$-cholestadiene is rearranged to $\Delta^{3,5}$-cholestadiene by the action of alcoholic

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[1] Journal Paper No. J-893 of the Iowa Agricultural Experiment Station, Project No. 506.

[2] Eck and Hollingsworth, THIS JOURNAL, 63, 107 (1941).

[3] Eck and Hollingsworth, *Iowa State Coll. J. Sci.*, 13, 329 (1939).

[4] Eck, Van Peursem and Hollingsworth, THIS JOURNAL, 61, 171 (1939).

[5] Stavely and Bergmann, *J. Org. Chem.*, 1, 575 (1937).