

aration and upon saponification of the 3-chloro-diacetone-glucose to diacetone-glucose.

2. The neutral sulfite ester of diacetone-glucose is produced when thionyl chloride reacts with either diacetone-glucose or its sodium-salt at 0–20°. At higher temperatures, a mixture of the sulfite ester and the isomeric diacetone-glucose-sulfonate ester is produced.

3. The stability of the chlorine in the 3-chloro-diacetone-glucose, the stability of the sulfonate esters and the reaction of diacetone-glucose-toluenesulfonate with Grignard's reagent, all indicate "negative" properties for the third carbon atom in diacetone-glucose.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

NICKEL CARBONYL, CARBON MONOXIDE AND GRIGNARD REAGENTS¹

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It is well known that carbon dioxide reacts with Grignard reagents forming first the magnesium complexes that yield carboxylic acids on hydrolysis;² after prolonged treatment of the first product with excess of Grignard reagent the complex of tertiary alcohols is obtained.³

On the other hand, carbon monoxide does not ordinarily react with Grignard reagents. It is the purpose of this paper to show how we have succeeded in making carbon monoxide and Grignard reagents react freely when they are activated by a small amount of nickel carbonyl, yielding a series of compounds somewhat similar to the carbon dioxide series.

Some attempts have previously been made to prepare aldehydes and secondary alcohols from carbon monoxide. Zelinski⁴ reported the formation of aldehydes and ketones by the action of nickel carbonyl on propylmagnesium iodide. Vinay⁵ reported the formation of tertiary alcohols by the direct action of carbon monoxide on Grignard reagents of the types R_2CHMgX and R_3CMgX . Grignard, in a general address,⁶ makes a brief reference to the way in which the reaction with carbon monoxide might be expected to proceed and refers to some unpublished work of

¹ A part of a thesis presented by W. L. Gilliland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, at the Massachusetts Institute of Technology.

² Grignard, *Ann. chim. phys.*, [7] **24**, 433 (1901). Gilman and Parker, *This Journal*, **46**, 2816 (1924).

³ Grignard, *Compt. rend.*, **138**, 152 (1904).

⁴ Zelinski, *J. Russ. Phys.-Chem. Soc.*, **36**, 339 (1904).

⁵ Vinay, *Thesis*, Geneva, 1913.

⁶ Grignard, *Bull. soc. chim.*, [4] **13**, XX (1913).

his own on the subject. Jegorawa⁷ failed to check the results of Vinay and reported an action of carbon monoxide with *isopropylmagnesium bromide*, *tert.*-butylmagnesium chloride and *tert.*-amylmagnesium chloride. For example the hydroxyketone $(\text{CH}_3)_3\text{C}.\text{CHOH}.\text{CO}.\text{C}(\text{CH}_3)_3$ was obtained from *tert.*-butylmagnesium chloride; but carbon monoxide was found to be without action on triphenylmethylmagnesium chloride, *tert.*-heptylmagnesium bromide, methylmagnesium iodide and phenylmagnesium bromide.

In the course of our own studies of nickel carbonyl, its action with Grignard reagent was tested and a startlingly vigorous reaction was observed. H. O. Jones⁸ had made a similar observation during his attempts to work out the structure of nickel carbonyl and had succeeded in isolating diphenyl and benzoin from among the reaction products of phenylmagnesium iodide and nickel carbonyl. These substances have also been observed by us but we believe that all of the diphenyl is formed in the preparation of the Grignard reagent itself and we have been unable to isolate benzoin from the products of the reaction carried out according to our later procedure.

In our first experiment a clear ethereal solution of nickel carbonyl was added slowly to an ether solution of methylmagnesium iodide. A violent reaction took place and the liquid became filled with a voluminous black precipitate containing metallic nickel and basic magnesium salt. Similar superficial observations were made with phenylmagnesium bromide as the reagent and, furthermore, after hydrolysis and evaporation of the ether layer a high-boiling yellow oil was obtained.

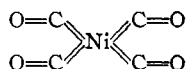
The difficulty of carrying out the hydrolysis in the presence of this black precipitate was great and the idea suggested itself that nickel carbonyl might be continuously regenerated from the precipitated nickel if carbon monoxide were steadily passed into a Grignard reagent to which a small portion of nickel carbonyl had been added. The first trial justified the suggestion, for carbon monoxide was freely absorbed and after hydrolysis a yellow oil was obtained resembling that obtained from the experiments with nickel carbonyl in quantity.

The carbon monoxide molecule probably possesses the same structure and to some degree it has the same sort of stability as the nitrogen molecule. In order to satisfy an electron sheath of eight around each atom we should have to regard three electron pairs as being held in common, that is, carbon monoxide would possess a triple bond. The stability of such a carbon monoxide molecule may well be so great that no reaction takes place directly between it and the Grignard reagent. According to

⁷ Jegorawa, *J. Russ. Phys.-Chem. Soc.*, **46**, 1319 (1914); *Chem. Zentr.*, [1] **86**, 1055 (1915).

⁸ Jones, *Chem. News*, **90**, 144 (1904).

the theory advanced in another paper⁹ nickel carbonyl is formed in virtue of a shifting of electrons to give a structure in which eight electron pairs in the nickel sheath are held in common with the carbonyl groups, the triple bond of C≡O having changed to a double bond =C=O and the molecule having the structure

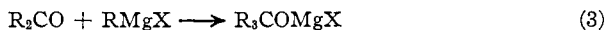
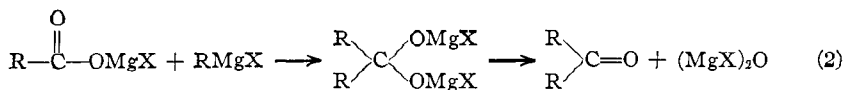
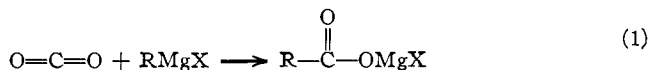


The bond, in accordance with Langmuir's theory of valence, represents a pair of electrons held jointly in the sheaths of two atoms. It is to be noted that the assumed triple bond of C≡O imposes a strained condition which is shared by the oxygen and carbon atoms. The rearrangement during the formation of the carbonyl group alters the strain and leaves the oxygen in its ordinary divalent condition when the valence of the carbon atom rises to four. Thus the carbon is effectively divalent in carbon monoxide with two latent valences.

G. N. Lewis has particularly noted¹⁰ that the so-called triple bond is less unstable than the double bond. We should expect the double bond between nickel and carbon of the group Ni=C=O to be more readily attacked than the double bond between carbon and oxygen, and much more readily than the triple bond of C≡O.

When the Grignard reagent attacks the =C=O group of ketones, or of carbon dioxide, the organic radical adds to the carbon atom, and the MgBr group to the oxygen atom.

Thus Grignard has followed the reaction of carbon dioxide.



Schroeter¹¹ and Bodroux¹² have been able to isolate benzophenone and *p*-dichlorobenzophenone from the second step, but the reaction is difficult to control and to stop at this point. Grignard⁸ treated cold phenylmagnesium bromide rapidly with carbon dioxide until the first step was complete. He then added two molecular equivalents of ethylmagnesium bromide and refluxed the mixture for 50 hours. Upon hydrolysis at the end of this time the chief product was the tertiary alcohol as indicated.

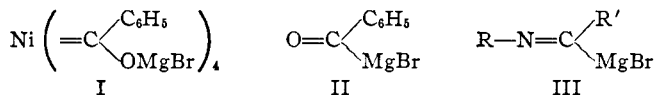
⁹ To be published later.

¹⁰ Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., 1923, pp. 93, 126.

¹¹ Schroeter, *Ber.*, **36**, 3004 (1903); **40**, 1584 (1907).

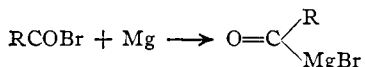
¹² Bodroux, *Compt. rend.*, **137**, 710 (1903).

In the reaction of phenylmagnesium bromide with nickel carbonyl we might expect either an addition in the orthodox Grignard fashion to give I,

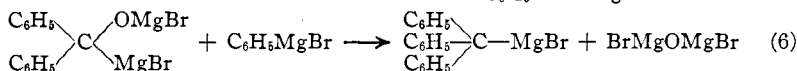
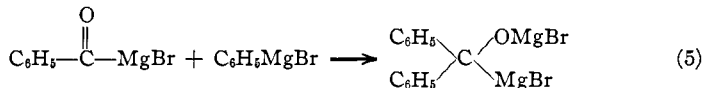
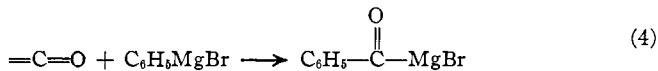


or an addition of both the C_6H_5 and MgBr groups to the same carbon atom to give II, if the nickel at the same time dropped out of combination. Sachs and Loevy¹³ have indeed noted that in the reaction with isonitriles such an addition as the latter takes place to give III.

Tistchenko¹⁴ has succeeded in obtaining a compound of the same structure in a totally different way, namely, through the carefully regulated action of magnesium on acid bromides.



Proceeding on the basis of the second alternative we would formulate, in analogy to the carbon dioxide series, the following train of reactions if an excess of the Grignard reagent were present.



The products of these steps would on hydrolysis yield (4) benzaldehyde, (5) benzhydrol, (6) triphenylmethane. In the actual experiments the products of Reactions 4 and 5 have never been isolated, but triphenylmethane has been produced abundantly under some conditions.

In the present discussion we shall use the term complex to designate the direct product formed by the addition of a Grignard reagent. Thus the products of Reactions 4, 5 and 6 before hydrolysis are complexes.

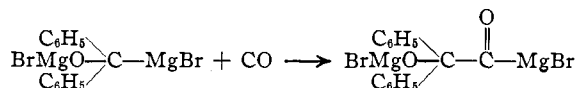
It is to be noted that the carbon monoxide series of products differs from the carbon dioxide series in that the complexes of the former may contain $\text{C}-\text{MgBr}$ as well as $\text{C}-\text{O}-\text{MgBr}$ groups. Complexes of the type formed in (5) containing both OMgBr and MgBr groups are unusual and their behavior was found to be markedly different from that of the corresponding complexes from carbon dioxide, $\text{R}_2\text{C}(\text{OMgBr})_2$. Grignard boiled the complex RCOOMgBr with fresh reagent for 50 hours to effect the formation of the complex of diethylphenyl carbinol and the elimination of magnesium oxybromide, whereas in the present research the analogous

¹³ Sachs and Loevy, *Ber.*, **30**, 874 (1904).

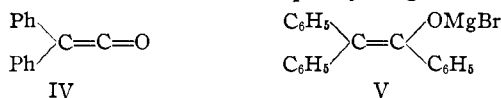
¹⁴ Tistchenko, *Bull. soc. chim.*, **37**, 623 (1925).

result was obtained by simply allowing the reaction mixture to stand for a few hours. This points to the conclusion that the C—MgBr bond labilizes the other groups attached to the carbon atom.

The complex formed in Reaction 5 contains the C—MgBr group of a Grignard reagent and it may react with fresh carbon monoxide as well as with fresh Grignard reagent. With the former it would yield

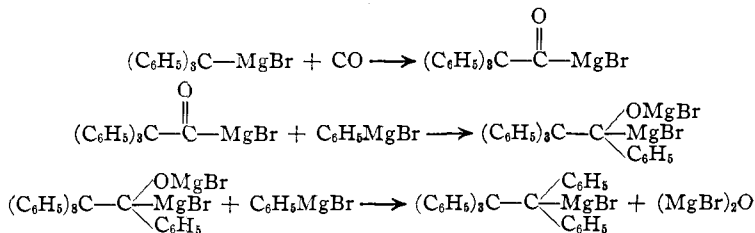


The latter on splitting out magnesium oxybromide would yield diphenylketene IV, which is known to react with phenylmagnesium bromide, yield-



ing V, the complex of triphenyl-vinyl alcohol,¹⁵ (C₆H₅)₂C=C(C₆H₅)OH. This alcohol is another of the substances which have been isolated in the present research.

The third product of the carbon dioxide series, R₃C—OMgBr, is non-reactive toward either carbon monoxide or Grignard reagents, but the corresponding complex (C₆H₅)₃C—MgBr of the carbon monoxide series is itself a Grignard reagent and can undergo all the additions and transformations of the original C₆H₅MgBr. Pentaphenylethane is the next compound in the series if carbon monoxide were to react with this new Grignard reagent.



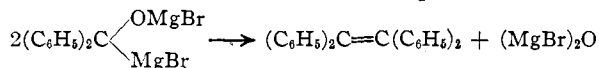
The hydrolysis of the last complex yields the pentaphenylethane, a product which also has actually been isolated in our work. If such action were to be continued a whole series of phenylated hydrocarbons would be built up, each by the insertion of the (C₆H₅)₂C group into the preceding member.

When the addition of carbon monoxide has been slow, and particularly when nickel carbonyl without carbon monoxide has been slowly added, the hydrocarbons are found most abundantly in the products. On the other hand, when the addition of carbon monoxide has been rapid and accompanied by violent stirring, the hydrocarbon fraction is less in amount and triphenyl-vinyl alcohol is found more abundantly.

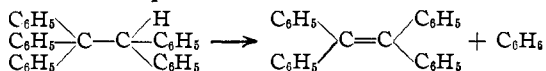
Another substance which has been isolated from the distilled oil is

¹⁵ Gilman and Heckert, *THIS JOURNAL*, **42**, 1010 (1920).

tetraphenyl-ethylene, $(C_6H_5)_2C=C(C_6H_5)_2$. This may be accounted for by the interaction of two molecules of the complex formed in Reaction 5,



but it seems more likely that it is produced by the decomposition of more complex substances during the distillation. For example, it is known that pentaphenylethane decomposes as follows.



When it is taken into account that in all the complexes formed by the addition of Grignard reagents to carbon monoxide, the MgBr group is bound directly to carbon and the substances so formed are new Grignard reagents that can react with more carbon monoxide, and that all the intermediate complexes containing the $=C=O$ or the $\equiv C-O-MgBr$ group may react with any of the Grignard complexes present, the variety of possible products is almost unlimited.

For example, two molecules of the complex formed in Reaction 4 by reacting with each other would yield the complex of benzoin. That this substance is not found under the procedure usually followed would indicate either that its complex is not formed at all or that it reacts further. With another molecule of phenylmagnesium bromide it would give a complex which would split out a molecule of magnesium oxybromide, leaving the complex of triphenyl-vinyl alcohol.

Actually the definite substances that have been isolated are (1) triphenylmethane, (2) triphenyl-vinyl alcohol, (3) pentaphenylethane and (4) tetraphenylethylene, but these all together do not in most cases form even the major part of the total reaction product. The hydrolysis of the complexes yields an ethereal layer which leaves a yellow oil after the ether is evaporated. Crystalline products, that is, one or more of the four just mentioned, often but not invariably separate from this oil. After vacuum distillation crystalline products usually separate from some of the fractions, but there is always a large amount of the oil that is non-crystallizable. Furthermore, distillation always leaves a large amount of tarry residue which stiffens and becomes brittle when cold. The oil and tar must contain a number of unidentified substances. Further research upon this material is considered.

Experimental Part

After much preliminary work in which nickel carbonyl was added in quantity to various Grignard reagents, and the discovery was made that carbon monoxide itself was activated by a small initial amount of nickel carbonyl, it was decided to confine the work to the study of the reaction of carbon monoxide with phenylmagnesium bromide. This reagent was

prepared by allowing an ethereal solution of bromobenzene to descend through a column of magnesium shavings, the solution being highly diluted; before reaching the column, by the ether condensed from the vapors of the solution boiling in the receiving flask. By this device large quantities of concentrated reagent can be prepared and yet allow only very dilute bromobenzene to come into the reacting column. Furthermore, the apparatus being filled with ether vapor, air is excluded and an entirely unoxidized reagent is obtained when no interruptions in the process have occurred.

The reagent was placed in the flask of the apparatus, Fig. 1. The flask was swept out with carbon monoxide which alone was without action.

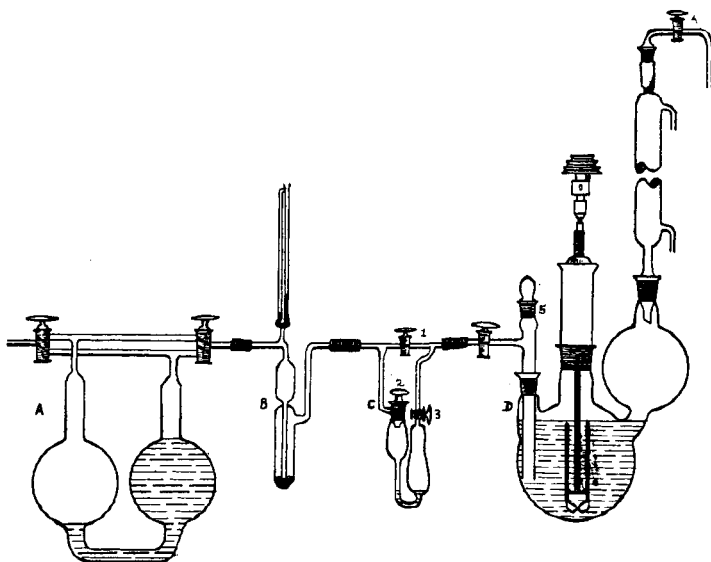


Fig. 1.—*A*, bulbs for metering carbon monoxide (the liquid is concd. H_2SO_4); *B*, pressure gage and valve; *C*, by-pass for introducing nickel carbonyl; *D*, reaction flask with mercury-sealed stirrer (capacity of main flask, 2 liters; of side flask, 1 liter).

The incoming carbon monoxide was then diverted through the by-pass in which a small amount of nickel carbonyl (usually less than 1 g. per mole of Grignard reagent) had been placed. The nickel carbonyl vapor was carried along to the reaction flask and very quickly a dark brown, almost black color spread through the solution and the reaction started. The by-pass and the exit tube were closed and the gas was allowed to pass into the solution as fast as it was absorbed. More nickel carbonyl vapor could be introduced by again opening the by-pass, but this was usually unnecessary. With the flask in a cooling-bath the initial absorption of gas was at the rate of 20 to 25 liters per hour per mole of reagent

and persisted until perhaps 7 to 8 liters had been absorbed, when it diminished markedly. The color had meanwhile become chocolate brown and then deep wine-red. Fine, red crystals began to separate as the absorption rate diminished. When the mixture was not stirred, the crystals were beautifully formed, clear, red prisms with edges about 1.5 mm. long. After the crystals had deposited, the rate of absorption increased somewhat.

In several runs the following practice was adopted.

When the rate of gas absorption fell to 1 liter per hour or less the cooling-bath was removed, the inlet was closed, the outlet opened and the solution was boiled for 20 to 120 minutes. This caused a partial solution of the crystals, but they separated more abundantly as the solution cooled. As soon as boiling was stopped the outlet was closed, the inlet opened, and the ice-bath placed around the flask. The gas absorption began again at a rapid rate, 8 to 12 liters per hour, and 3 to 5 liters per mole in addition was absorbed. This could be repeated and a maximum of 14 to 16 liters per mole of reagent absorbed.

The red crystals were basic magnesium bromide with ether of crystallization. Exposed to air they quickly turned white and powdery. With water they evolved a great deal of heat, ether vapor was expelled and a residue of flocculent magnesium hydroxide was left. No accurate analysis was made, but it was ascertained that these crystals contained no organic material other than the ether.

When the gassing was long continued a sticky, black, tarry material separated in small amount and adhered to the inside of the flask. Other than this, all of the organic fraction of the reaction products remained in the ether solution.

The contents of the flask were then hydrolyzed, usually without removal of the red crystals, by the very cautious addition of water. A great deal of heat was produced and the reflux condenser came into active service. A heavy, light yellow, granular precipitate of hydrated basic magnesium bromide was formed. Enough water was then added to give a lower aqueous layer and, lastly, the residue was completely dissolved by running in an excess of 50% of sulfuric acid. The two layers were separated. The aqueous layer was not found to contain any organic constituents except sometimes small amounts of phenol which were attributed to oxidation of the Grignard reagent.

The ethereal layer was allowed to stand for several hours, and very frequently it deposited on the sides of the flask a thin layer of fine, yellow crystals. In exceptional cases these crystals were found floating in the ether layer just above the boundary of the aqueous layer before separation and, in such cases, more deposited on standing. The total weight of this material was generally less than 1 g. It was identified as pentaphenyl-ethane.

The ethereal solution was filtered from these crystals and dried with anhydrous copper sulfate; then it was filtered into a flask with a distilling

head and the ether distilled. The oil which remained was yellow to reddish amber to brown; sometimes crystals deposited from it on standing and sometimes not. Such crystals were either triphenylmethane or triphenyl-vinyl alcohol or a mixture of both.

Attempts to effect a separation of the part of the oil still uncrystallized, on the basis of fractional solubility in petroleum ether, were not successful. Distillation was resorted to as the most direct and easiest method, but this offered difficulties. The very high boiling point of the oil made it necessary to use a good vacuum to avoid excessive decomposition. The first fraction of the distillate was diphenyl. The amount of diphenyl did not appear to be greater than that which frequent tests upon the Grignard reagent showed to be present there. The possibility that any of it might have been formed by a reaction between the reagent and nickel salt after the manner in which it has been found by Job and Reich,¹⁶ Reich,¹⁷ Gilman and Parker¹⁸ to be formed by reactions of types more or less resembling $2\text{CuCl}_2 + 2\text{C}_6\text{H}_5\text{MgBr} \longrightarrow \text{Cu}_2\text{Cl}_2 + 2\text{MgClBr} + \text{C}_6\text{H}_5\text{—C}_6\text{H}_5$, appears to us to be extremely small. This diphenyl solidified in the apparatus; the highest-boiling fractions of the distillate were thick and gummy when cold. Finally, a considerable portion of the oil was non-volatile and remained as a tar.

Before distillation the oil was allowed to stand for several days to crystallize partially, then filtered into the distilling flask connected with a vacuum train so arranged that the succeeding liquid fractions could be removed without interrupting the distillation. The first distillate began to come over at about 60° (3 to 4 mm.). This was a thin, yellow oil but very soon the distillate began to solidify in the receiver and tubes and the latter had to be warmed with a free flame. The temperature rose to 80–90°, when the distillate became less in amount and began to be permanently liquid. The pump was shut off, air admitted and the receiving flask with contained diphenyl and light oil removed.

A new fractional receiving flask was inserted and at 90–100° the distillation begun again, when a light yellow oil distilled and the temperature slowly rose to about 135°. A considerable fraction was obtained in this range and was collected separately; it amounted to 15–20% of the total oil.

The second fraction was collected from 135° to 200°. This was amber in color and somewhat more viscous than the first fraction. Above 200° there was no sharp break in fractions, but the oil became more and more viscous and finally solidified to a gum when cold. This was at about 300° and it was evident that extensive decomposition was taking place.

The residue in the flask was poured out while still hot and solidified to a

¹⁶ Job and Reich, *Compt. rend.*, **174**, 1358 (1922).

¹⁷ Reich, *ibid.*, **177**, 322 (1923).

¹⁸ Gilman and Parker, *THIS JOURNAL*, **46**, 2823 (1924).

brittle tar. While still warm this could be drawn out into fine threads. This material was soluble in chloroform, acetone and carbon disulfide. Extraction with ether in a Soxhlet apparatus removed a tarry fraction and left a brown solid that was very slightly soluble in solvents.

Identification of Triphenylmethane.—This substance is obtained most abundantly in runs in which the gas is slowly added, or in which nickel carbonyl alone is slowly added. In one run carbon monoxide was passed into the boiling reagent for 12 hours without mechanical stirring, and at this temperature the absorption was not very rapid. After hydrolysis and removal of the ether the oil, without being distilled, soon solidified to a waxy mass through separation of crystals of triphenylmethane.

Samples for identification after four recrystallizations from ethyl alcohol melted at 92°. Mixed melting points with triphenylmethane from Eastman were sharp at 91–92°. A sample gave the fuchsin color reaction described by Mulliken.¹⁹

Identification of Triphenyl-vinyl Alcohol.—In the case of one rapidly gassed reagent prepared from 300 g. of bromobenzene, 105 g. of light brown oil was obtained after hydrolysis, and after several days it had deposited crystals until it became a solid wax. The mass was drained by suction and washed with a little ether, alcohol and then petroleum ether, and 43 g. of crude crystals melting at 120° was obtained. This material was further purified by six recrystallizations and distillation in a vacuum, after which it melted sharply at 135–136°. The mixed melting point with known triphenyl-vinyl alcohol was 134–135°.

An acetate, prepared from the unknown formed prisms melting at 103–104°; the acetate of triphenyl-vinyl alcohol is reported as melting at 104°.

The most characteristic property of triphenyl-vinyl alcohol is the intense green color that its solution in concd. sulfuric acid develops when it is heated to 180–200°. Our known and unknown samples behaved identically in this respect.

Before the triphenyl-vinyl alcohol had been isolated from the oil prior to distillation it seemed probable that it might be a dehydration product of triphenyl-ethylene glycol. Furthermore, conflicting statements in the literature gave the melting point as 129° and as 165°.

In order to make a comparison some triphenyl-ethylene glycol was made by allowing benzoin to react with phenylmagnesium bromide. A sample twice crystallized from ethyl alcohol melted at 166° and showed the identical color reactions given by triphenyl-vinyl alcohol. The color in this case was probably due to the formation of triphenyl-vinyl alcohol by dehydration in the sulfuric acid.

The Identification of Pentaphenylethane.—This substance is never obtained in any distilled fractions of the oil. It is obtained from the hydrolyzed ether solution where it is precipitated as a fine, yellow powder; in exceptional cases a little separates from the undistilled oil. As first obtained it melts at 165–175°. It is difficultly soluble in most solvents but it can be recrystallized from benzene, when the melting point is 179°.

A sample of pentaphenylethane was prepared from triphenylmethylmagnesium chloride and diphenylmethyl bromide and the mixed and the simple melting points were all at 178–180°. There was obtained in each case a red-brown melt that did not solidify but became gummy when cold. This indicates decomposition and shows the reason why pentaphenylethane never occurs in any materials that have been distilled.

Identification of Tetraphenyl-ethylene.—This substance was rarely found, but when it was obtained, it separated as a finely granular precipitate from the higher boiling distillates. It is so insoluble that it can be purified by simply washing it with solvents,

¹⁹ Mulliken, "Identification of Pure Organic Compounds," Wiley and Sons, 1904, vol. 1, p. 177.

after which it melts at 218–221°. A sample was crystallized by extraction in a Soxhlet apparatus with ether; a fine, white powder melting at 220° was obtained. A known sample of tetraphenyl-ethylene melted at 221° and the mixed melting point was 218°.

In conclusion the authors take pleasure in acknowledging their deep obligation to Dr. Henry Gilman of Iowa State College for the friendly way in which he has aided them in preparing this paper for publication, giving freely of his extensive knowledge and understanding of Grignard reactions.

Further studies are being made by one of us (W. L. G.) under a grant from the National Research Council.

Summary

Carbon monoxide has been made reactive with Grignard reagents, but only as a constituent of nickel carbonyl. The nickel carbonyl is, however, continuously regenerated from the liberated nickel and fresh carbon monoxide.

With phenylmagnesium bromide as the reagent the identified products are triphenylmethane, triphenyl-vinyl alcohol, pentaphenylethane and tetraphenyl-ethylene. Reactions for the formation of these compounds have been formulated on the assumption of a structure $\text{Ni}(\text{C}=\text{O})_4$, the double bond $\text{Ni}=\text{C}$ being the first point of attack, both the MgBr and C_6H_5 groups adding to the carbon atom. The $\text{C}=\text{O}$ double bond may still be attacked in the normal way and the new $\text{C}-\text{MgBr}$ grouping is capable of reacting as a new Grignard reagent, thus giving a great number of possible substances, a mixture of which is probably contained in the non-crystallizable oil which comprises rather more than one-half of the entire product.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE JESSE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

A STUDY OF THE PREPARATION OF QUINIZARIN¹

BY HARRY H. REYNOLDS WITH LUCIUS A. BIGELOW

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Introduction

Quinizarin, or 1,4-dihydroxy-anthraquinone, is an important dye intermediate. The substance has been made by many methods² but there

¹ Abstract of a thesis submitted to the Faculty of the Graduate School of Brown University in partial fulfillment of the requirements for the Degree of Master of Science.

² (a) Grimm, *Ber.*, **6**, 506 (1873). (b) Baeyer and Caro, *Ber.*, **8**, 152 (1875). (c) Liebermann, *Ann.*, **212**, 11 (1882). (d) Wacker, *J. prakt. Chem.*, [2] **54**, 90 (1896). (e) Friedländer, "Die Fortschritte der Teerfarbenfabrikation," **4**, 296 (1895); Ger. pat., 81,245; **4**, 301 (1896); Ger. pat., 86,630; **4**, 274 (1895); Ger. pat., 81,960; **11**, 588 (1912); Ger. pat., 255,031.