[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Nickel Carbonyl with Grignard Reagents[1]

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In a survey of the literature on the reaction of carbon monoxide or nickel carbonyl on various types of Grignard reagents no evidence of a single, primary reaction was found. When nickel carbonyl was used[2,3] the resulting reaction products were numerous and no one product was obtained in significant yield. When carbon monoxide under pressure was used the nature of the products and the yields varied with the type of Grignard reagent. Fischer and Stoffers[4] found, for example, that phenylmagnesium bromide gave high yields of benzoin; *n*-alkylmagnesium halides yielded unsaturated hydrocarbons; and some *iso*-alkylmagnesium halides produced both the acyloins and unsaturated hydrocarbons. In no previous work, however, has the reaction been studied under conditions where a positive excess of carbon monoxide or nickel carbonyl has been maintained.

Since it appeared probable that the various products reported by previous investigators were due to secondary reactions of excess Grignard reagent with the primary reaction product, a study of the reaction of Grignard reagents with excess nickel carbonyl was undertaken. Nickel carbonyl was chosen as a source of carbon monoxide since it is known to react readily with Grignards and because it could conveniently be maintained in excess. Several of the types of Grignards studied were found to follow a definite single course of reaction and to produce significant yields of one type of product.

Experimental

Preparation of Reagents.—Nickel carbonyl was prepared in some cases by the method of Mayer and Wibaut[5] and in others by the method of Gilliland and Blanchard.[6] Grignard reagents were prepared in the usual manner, using 300 ml. of absolute ether for one-half mole of Grignard. The *t*-butyl Grignard was prepared from the chloride; all others from the bromides.

Apparatus and Procedure.—The ether solution containing one-half mole of Grignard reagent was forced under positive pressure of dry nitrogen through a cloth filter into a 500-ml. separatory funnel. A weighed amount of nickel carbonyl was introduced, together with 200 ml. of absolute ether, into a 1-liter, 3-necked, reaction flask. The amount varied in different cases from the theoretical quantity to an excess of 100%, based on the assumption that one mole of carbon monoxide reacts with one of the Grignard reagent. The flask was fitted with a separatory funnel containing the solution of the Grignard reagent, a mercury-sealed stirrer, and a reflux condenser. The apparatus was protected from atmospheric moisture by sulfuric acid wash bottles.

To the contents of the reaction flask at ice-bath temperature the Grignard reagent was added from the separatory funnel in a dropwise fashion over a period of two hours with continuous stirring. With the exception of the acetylenic Grignard, which reacted very sluggishly, the reaction took place quite vigorously with the formation of a black solid insoluble in ether. After the addition of the Grignard reagent the mixture in the reaction flask was allowed to rise to room temperature over a period of an hour, after which time it was hydrolyzed by pouring into a slight excess of ice-cold, dilute hydrochloric acid. Considerable time was required for complete solution of the black solid which was attacked very slowly by hydrochloric acid. When hydrolysis was complete the ether layer was separated, washed with water, then with a solution of sodium bicarbonate, and finally dried over anhydrous magnesium sulfate. Ether was removed from the reaction product by distillation.

Purification and Identification of Reaction Products.—Benzoin, resulting from the reaction of phenylmagnesium bromide with nickel carbonyl, was obtained by crystallization from alcohol as a white, crystalline solid melting at 133°. It gave no depression in melting point when mixed with a sample of pure benzoin.

With the exception of benzoin the acyloins obtained were high-boiling liquids. The products were fractionally distilled under vacuum and the fractions of constant index of refraction combined. The physical constants and the molecular refraction of each product are summarized in Table I. These values were found to be in good agreement with those reported in the literature.[7]

Analysis of the Intermediate Product.—A weighed sample of the intermediate was dissolved in concentrated hydrochloric acid and analyzed for nickel by means of dimethylglyoxime. Magnesium was determined gravimetrically by weighing as $MgNH_4PO_4 \cdot 6H_2O$.

Results and Discussion

The products obtained, together with the yield and physical constants of each, are summarized in Table I.

These results are of special interest in that they demonstrate that a single, definite reaction between the carbon monoxide in nickel carbonyl and the Grignard reagent may be postulated provided that an excess of nickel carbonyl is always present. Thus, the Grignard reagent reacted mole for mole with carbon monoxide in nickel carbonyl to form an intermediate which hydrolyzed to the corresponding hydroxy ketone. The fact that an undistillable oil was obtained in the case of the reaction of the acetylenic Grignard reagent with the nickel carbonyl may possibly be attributed to polymerization induced by the unsaturated nature of the acetylene.

From the reaction mixture of excess nickel carbonyl with *t*-butylmagnesium chloride we were able to isolate only an insignificant quantity of a white crystalline solid which, however, did not have the melting point reported for pivaloin by Egorova.[8] Because the quantity of product obtained was so small further identification was considered to be of no value in this work. The result

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(1) Presented before the Organic Division of the American Chemical Society, April, 1943.

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

(3) Gilliland and Blanchard, THIS JOURNAL, **48**, 410 (1926).

(4) Fischer and Stoffers, *Ann.*, **500**, 253 (1933).

(5) Mayer and Wibaut, *Rec. trav. chim.*, **56**, 356 (1937).

(6) Gilliland and Blanchard, "Inorganic Syntheses," Vol. II, in press.

(7) Corson, Benson and Goodwin, THIS JOURNAL, **52**, 3993 (1930).

(8) Egorova, *J. Russ. Phys.-Chem. Soc.*, **46**, 1319 (1913).

TABLE I

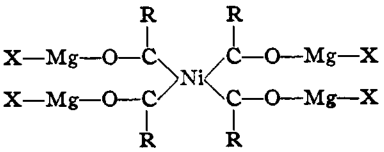
DATA ON PRODUCTS OBTAINED

R of Grignard reagent, R—Mg—X	Product	Yield, %	B. p., °C.	B. p., Mm.	d^{20}_4	n^{20}_D	*MR*D Calcd.	*MR*D Obs.
C_6H_5	Benzoin	70						
n-C_3H_7—	*n*-Butyroin	50	53–55	5	0.9231	1.4290	40.4	40.4
n-C_4H_9—	*n*-Valeroin	50	100–101	8	.9031	1.4357	49.6	49.7
iso-C_3H_7—	*iso*-Butyroin	35	108–109	82	.9116	1.4266	40.4	40.2
t-C_4H_9—	Unidentified	Trace						
n-C_4H_9—C≡C—	Undistillable oil							

obtained with the *t*-butylmagnesium chloride was unexpected in view of the earlier report of Egorova[8] that this Grignard reagent was the only one which reacted under normal pressure with carbon monoxide and that it gave the hydroxy ketone, which is the uniform product observed in our work with other types of Grignard reagents. It should be noted, however, that neither Egorova[8] nor Fischer and Stoffers,[4] who reported confirmation of Egorova's results on *t*-butylmagnesium chloride, stated the yield obtained.

For the purpose of obtaining some information on the mechanism of the reaction the solid intermediate formed during the reaction was studied. The intermediate precipitated as a voluminous black solid of an amorphous, tarry appearance. Crystallization of the solid mass was never observed, although in some cases small portions of the solid took on a definitely crystalline appearance. Previous workers[3] have postulated the presence of nickel and basic magnesium halide in this intermediate, but no analyses have been reported. Samples of the black solid, washed thoroughly with dry ether and freed of ether in a current of dry nitrogen, were analyzed for nickel and magnesium. Analyses on several different products varied by too great an amount to enable a positive identification of the complex to be made. In all cases, however, the nickel and magnesium content approximated the values calculated for a complex in which 4 moles of Grignard are combined with 1 mole of nickel carbonyl. A representative analysis for the intermediate from the *n*-propylmagnesium bromide gave the following values: calculated for $Ni(C_3H_7—C—O—Mg—Br)_4$, Ni 7.7, Mg 12.8; found Ni 7.7, Mg 10.7. These results do not indicate that a pure intermediate was isolated, but do demonstrate that the nickel and magnesium content correspond to a complex in which the organic material is still present in appreciable quantities. The probable composition of the intermediate enables a mechanism for the reaction to be proposed

(1) $4R—Mg—X + Ni(CO)_4 \longrightarrow$



The probable existence of a carbon-to-carbon bond in the intermediate is indicated by the high yield of hydroxy ketone obtained as the product on hydrolysis.[9]

The hydrolysis of the intermediate proceeds slowly with dilute hydrochloric acid and more rapidly with concentrated hydrochloric acid with the evolution of hydrogen. The amount of hydrogen evolved corresponds to the nickel content as analyzed. The reaction may then be considered to involve the breaking of the loose nickel-to-carbon bonds by the action of the hydrochloric acid and the normal hydrolysis of the remainder of the molecule to yield nickel chloride and hydroxy ketone. As evidence for the retention in the intermediate of nickel-to-carbon bonds, of a type similar to the bonds in nickel carbonyl, may be cited the fact that complete solution of the black intermediate is necessary in order to obtain good yields of hydroxy ketone. If uncombined nickel and organo-magnesium halide were present as a mixture it would be expected that the hydrolysis of the organo-magnesium halide would occur more rapidly than the solution of the free nickel in hydrochloric acid.

Summary

1. The reaction of Grignard reagents with an excess of nickel tetracarbonyl has been studied.
2. Phenylmagnesium bromide, *n*-propylmagnesium bromide, *i*-propylmagnesium bromide, and *n*-butylmagnesium bromide with nickel carbonyl yielded benzoin, *n*-butyroin, *i*-butyroin and *n*-valeroin, respectively.
3. *t*-Butylmagnesium chloride gave only traces of an unidentified product; *n*-butylethynylmagnesium bromide produced an undistillable oil.
4. The approximate composition of the intermediate has been shown by analysis and a simple mechanism has been proposed for the reaction.

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[9] A Referee has suggested that the results of the analysis of the black intermediate may be interpreted as indicating a mixture of metallic nickel and an organo-magnesium compound rather than a complex in which the nickel is combined. The analyses would be consistent with either interpretation. However, the appearance of some crystalline material in the intermediate and the fact that it appears completely homogeneous suggest an actual chemical combination. Repeated washings with dry ether cause no change in the homogeneous appearance of the solid. Further work would, however, be necessary to establish, without question, the existence of nickel-to-carbon bonds in the intermediate.