monochromatic X-radiation, accurate measurements of resolved diffraction rings have been obtained.

2. Evidence is cited which indicates that the diffractions are those of a single major component of the starch granules, and that there is ring-for-ring correspondence between the extreme (A and B) types of pattern.

3. From analysis of potato (B) patterns, it is possible to set up a unit cell and arrive at indices of planes responsible for the individual diffractions. These assignments can be carried over to the corn (A) starch patterns with comparatively slight changes in unit cell dimensions and angles, thus providing confirmation. The number of maltose residues per cell seems to be two. Starch granule crystallites are apparently built on triclinic lattices whose axes are, however, very nearly orthogonal.

4. The validity of the chosen unit cells and the relation of the results to straight, branched and spiral chain models for starch are discussed briefly.

AMES, IOWA RECEIVED APRIL 28, 1941

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

Factors Determining the Course and Mechanisms of Grignard Reactions. I. Preliminary Study: The Effects of Metallic Compounds on Some Grignard–Carbonyl Interactions

BY M. S. KHARASCH, SARAH C. KLEIGER, JAMES A. MARTIN AND FRANK R. MAYO

In an earlier study in this Laboratory[1] it was found that when pure, magnesium-free, ethereal Grignard reagents are used, the nature of the Grignard-carbonyl interaction (whether reduction or addition) is determined (for some carbonyl compounds, at least) by the nature of the organic radical of the Grignard reagent. As a preliminary and a supplement to more extensive investigation in this field the catalytic effects of several metallic compounds have been examined in the present study.

It is well-known that various metals (including magnesium) and metallic compounds significantly affect the yields, the nature of the products obtained, and the rates of reaction in various Grignard reactions, and, further, that some interactions that do not otherwise take place may be effected in the presence of metallic catalysts.[2] Accordingly, the purest supply of reagent magnesium available was sought for these studies. A sample of sublimed magnesium, kindly donated by the Dow Chemical Company, was found to be spectrographically free of manganese, copper, tin, iron, and silver.[3] The only heavy metal detected, lead, was estimated to be present to the extent of approximately 0.01%.

Initial studies were made on the benzophenone–isobutylmagnesium bromide interaction, which normally gives high yields of a single product (benzohydrol). Cuprous chloride in concentrations up to 1.0 mole % was substantially without effect on the course of the reaction and the yields obtained. In the presence of manganous chloride, however, the addition of the first few drops of ketone solution to the Grignard solution gives rise to the deep cherry-red coloration characteristic of the magnesium ketyls, and the reaction product upon hydrolysis yields benzopinacol as well as benzohydrol. The proportion of benzopinacol in the product varies directly with the concentration of manganous chloride up to 2.0 mole %. The effect of chromic chloride is similar to that of manganous chloride, but less pronounced. A single experiment with 2 mole % of ferric chloride indicated activity similar in kind and degree to that of chromic chloride (71% benzopinacol). Experimental data are summarized in Figs. 1 and 2. The total yields of the hydrol and pinacol can be computed easily from the two curves.

The observations recorded show that benzophenone may undergo either a two-electron or a one-electron Grignard reduction, the former leading to benzohydrol, and the latter to benzopinacol.

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[1] Kharasch and Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

[2] See, *e. g.*, Gilman, *et al.*, (a) *Rec. trav. chim.*, **48**, 155 (1929); (b) **50**, 578 (1936); (c) THIS JOURNAL, **53**, 1581 (1931); (d) Young, Prater and Winstein, *ibid.*, **55**, 4908 (1933); Johnson and Adkins, (e) *ibid.*, **53**, 1520 (1931); (f) **54**, 1943 (1932); Job, *et al.*, (g) *Bull. soc. chim.*, [4] **41**, 814 (1927); (h) [4] **47**, 279 (1930).

[3] The writers are indebted to Dr. W. C. Pierce and Mr. W. W. Marshall for spectrographic analyses of several magnesium samples.

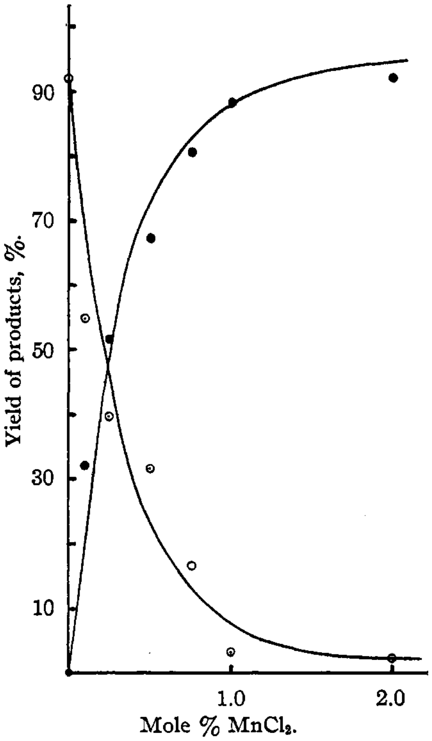

Fig. 1.—Effect of manganese chloride on the interaction of benzophenone and isobutylmagnesium bromide: ⊙, hydrol; ●, pinacol.

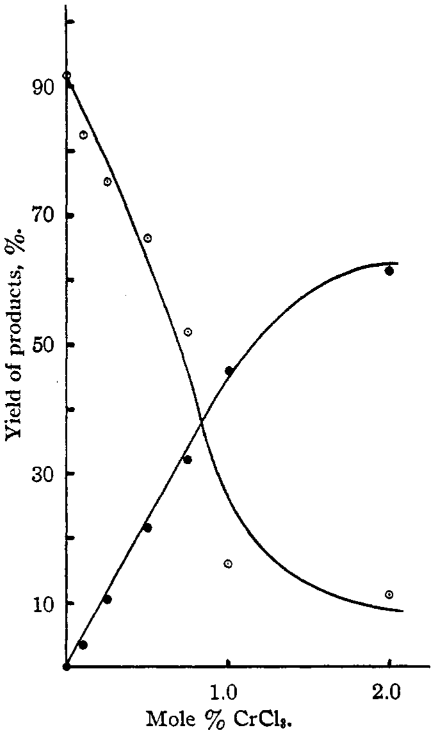

Fig. 2.—Effect of chromic chloride on the interaction of benzophenone and isobutylmagnesium bromide: ⊙, hydrol; ●, pinacol.

The latter reaction presumably has a chain mechanism, for small quantities of metallic halide are sufficient to induce comparatively high yields of pinacol.

The interaction of chloral and methylmagnesium bromide gives rise to considerable quantities of tar, and the results of a similar study of this reaction are less striking. Both in the absence and in the presence of metallic substances, the isolable product is essentially trichloroisopropanol (the normal addition product), contaminated with trichloroethanol (the reduction product). In the control reaction the yield of trichloroisopropanol was 40%; in the presence of 0.1 mole % of cuprous chloride, 31%; with 0.1 mole % ferric chloride, 10%; 0.1 mole % manganous chloride, 50%; one mole % metallic manganese, 60%. The manganous chloride and manganese products were thus relatively high in trichloroisopropanol, while ferric chloride inhibited the normal addition reaction as well as the reduction to trichloroethanol.

Experimental

The organic compounds used were obtained from the Eastman Kodak Company and were distilled or crystallized before use. The cuprous chloride was freshly made; the manganous chloride was prepared from the hydrated form by heating in an oven for eight hours at 120°; the chromic chloride and ferric chloride were the usual anhydrous salts of reagent grade. Only sublimed magnesium was used in the preparation of the Grignard reagent. Two other samples of magnesium examined for us by Dr. Pierce and Mr. Marshall were estimated to contain impurities as follows: (Kahlbaum) manganese 0.1%, copper 0.01%, tin 0.01%, iron 0.001%, silver 0.001%; (Mallinckrodt), manganese 0.05–0.1%, copper 0.01%, tin 0.01%, iron 0.01%.

Preparation of the Grignard Reagents.—The Grignard reagents were prepared in a three-necked flask equipped with mercury-sealed stirrer, reflux condenser, and dropping funnel, the latter two fitted with calcium chloride tubes. A small-bore tube filled with glass wool and provided with a stopcock was sealed into the side of the flask.

In a representative run, a 10% excess of sublimed magnesium was placed in the flask and approximately one-third (0.8 mole) of the anhydrous ether to be used was added. The alkyl halide (0.4 mole) was dissolved in the remainder of the ether (1.6 mole). After the addition of a few drops of the halide solution, the reaction mixture was warmed with a micro burner until reaction started. The remainder of the halide solution was then added at such a rate as to keep the ether refluxing gently. After addition of the halide was complete, the reaction mixture was refluxed for an additional half-hour with continuous stirring, and was then allowed to cool. The solutions when pure magnesium was used were beautifully clear as contrasted with the opaque dark solutions when Eastman or Kahlbaum magnesium was used.

The Grignard reagent was then filtered (to remove excess of magnesium) through the glass wool plug into a graduated dropping funnel, and a two-milliliter aliquot was removed for titration. The remaining Grignard reagent was divided into three equal parts and transferred to three-necked flasks, each fitted with a reflux condenser, mercury-sealed stirrer, dropping funnel and calcium chloride tubes.

To two of the three portions of the solution weighed quantities of anhydrous metal halide were added; the third lot was used as a control. Upon addition of the heavy metal salt, a vigorous exothermic reaction occurred and the solution turned black.

Reaction with Benzophenone.—One mole equivalent of ketone in six times its weight of benzene was added dropwise to each portion of the Grignard reagent over a period of one and one-half hours while the reaction mixture was kept cold in a bath of ice and water. After all the ketone had been added, the temperature was allowed to rise to that of the room, and stirring was continued for an additional hour.

Isolation of Product.—The precipitated magnesium-benzhydrol product was collected on a filter, washed with benzene, dried, weighed, and then hydrolyzed with 10% sulfuric acid. The benzhydrol was crystallized from dilute alcohol and was found to melt at 65–67°.

The ether–benzene filtrate was treated at 0° with ice-cold 10% sulfuric acid, and dried over anhydrous potassium carbonate. The solvent was then removed on a steam-bath. Only a small amount of oil was obtained at this point from those experiments in which either no metal halide or cuprous chloride had been used. When, however, manganous chloride or chromic chloride was the added catalyst, a residue of benzopinacol remained. After crystallization from alcohol the product melted at 176–178° with decomposition.

Chloral–Methylmagnesium Bromide Reaction.—The experiments were carried out in the same way as described for isobutylmagnesium bromide and benzophenone. The reaction mixtures were hydrolyzed with dilute sulfuric acid under ice-water cooling. The ethereal layer was separated, and to it were added three ethereal extracts of the water layer. The ether was removed by evaporation, and the product was steam distilled. The ethereal extract of the water layer of the steam distillate was added to the organic layer, and the whole was dried with anhydrous sodium sulfate and fractionally distilled. After removal of the ether, the fraction passing over up to 150° at atmospheric pressure consisted of unchanged chloral and chloral hydrate. The fraction distilling at 62–66° at 22 mm. pressure consisted of the alcohols. These were separated by distillation at ordinary pressures. In each case there was about 2 g. of residue.

Summary

1. The benzophenone–isobutylmagnesium bromide interaction, which normally yields benzohydrol, is substantially unaffected by the presence of cuprous chloride in concentrations up to 1.0 mole %.

2. Manganous chloride leads to the production of benzopinacol in proportions varying directly with the concentration of the halide (up to 2 mole %).

3. The effects of chromic and ferric chlorides on this interaction are similar to but less pronounced than that of manganous chloride.

4. The yield of isolable product (trichloroisopropanol and trichloroethanol) from the chloral–methylmagnesium bromide interaction is somewhat reduced by cuprous chloride, and increased by manganous chloride and metallic manganese.

5. Ferric chloride (0.1 mole % on the basis of magnesium) inhibited the normal addition of methylmagnesium chloride to chloral and the production of the reduction product (trichloroethanol).

6. Investigations of the effect of metal catalysts on the reaction of Grignard reagents with other compounds are under way in this Laboratory.

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