it can be made to add more hydrogen to the latter compound is to change its surface by activation.

Summary

1. Curves are given for the reduction rate of furfural at 0, 20, 40 and 60°.

2. Activation of the catalyst is necessary to add more than 1 mole of hydrogen to furfural.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION OF MERCURY DIPHENYL[1] BY USE OF THE GRIGNARD REAGENT

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The reactions that may take place in the preparation of mercury diphenyl by the Grignard reagent are as follows

$$HgX_2 + 2C_6H_5MgBr = Hg(C_6H_5)_2 + 2MgBrX \qquad (1)$$
$$HgX_2 + C_6H_5MgBr = Hg(C_6H_5)Hal + MgBrX$$
$$Hg(C_6H_5)X + C_6H_5MgBr = Hg(C_6H_5)_2 + MgBrX$$
$$HgX_2 + Hg(C_6H_5)_2 = 2Hg(C_6H_5)X$$

HgX_2 may be the iodide, bromide or chloride. Laszczynski[2] measured the solubility of mercuric iodide and chloride in absolute ether at 0° and found it to be 0.62 and 5.98%, respectively. Measurements made on mercuric bromide at 0° gave the solubility as 4.82 g. per 100 g. of solution, using absolute ether. Due to the insolubility of the iodide experiments were made with the bromide and chloride only. The yields as given in Table I show some difference between the bromide and chloride for the same concentration but not sufficient to say that one is much better than the other.

Table I shows that 85 mole per cent. of mercuric halide gives the best yield with the methods used. From published data[3] the yield of the Grignard reagent from bromobenzene is about 94%, which gives an excess over the mercuric halide used of about 9%; this is not too much considering the fact that it must be transferred before using.

[1] For the different methods of preparation of mercury diphenyl see "Organic Syntheses," Vol. IX, John Wiley and Sons, Inc., New York, 1929, p. 54. One later method is described in *Ber.*, **62**, 1018 (1929). The method in "Organic Syntheses" uses a 3% sodium amalgam. Better yields can be obtained with an 8% amalgam (Michaelis and Loesner, *Ber.*, **27**, 264 (1894)) which has been checked by the authors. If a large quantity of mercury diphenyl is wanted this method is recommended over the Grignard. It should always be remembered that the vapors of mercury diphenyl are toxic.

[2] Laszczynski, *Ber.*, **27**, 2285 (1894).

[3] Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1584 (1929).

Hilpert and Grüttner[4] give the yield for Equation 2. They refluxed for four hours 0.16 *M* phenylmagnesium bromide and 0.20 *M* mercuric bromide with a yield of recrystallized mercury phenyl bromide of 93%, or nearly quantitative. They state that this was easily prepared but to go from it to mercury diphenyl as shown in Equation 3 required an excess of the Grignard reagent and then gave a poor yield with 40% as the highest (no experiments cited).

From experimental evidence given in this paper the yield in Equation 3 is very close in agreement with the mercury diphenyl formation from mercury dihalide itself and may be the controlling factor in its preparation. The reverse reaction of Equation 3 is probably not sufficient to affect the yield in the presence of the excess Grignard reagent.

Equation 4 shows that if there is once any excess of mercury dihalide and mercury diphenyl present without the Grignard reagent there will be a loss of mercury diphenyl. This was substantiated by experiment.

Fleck[5] studied the reaction between mercury diphenyl and magnesium metal and found a reaction at about 200° with the formation of magnesium diphenyl and free mercury. It may be that this same reaction occurs to a less extent at the boiling point of ether, for if any unreacted magnesium is allowed to remain in the reaction flask the yield is greatly reduced.

Therefore the ideal condition for a large yield for the preparation of mercury diphenyl is as follows: have Grignard reagent in excess, have no magnesium metal present, do not let the mercury diphenyl formed stand with mercuric halide without the presence of the Grignard reagent and use about 85 mole per cent. of mercuric salts.[6]

TABLE I

YIELD OF MERCURY DIPHENYL WITH VARYING CONCENTRATIONS OF MERCURIC HALIDES

	Mercuric chloride			Mercuric bromide		
Runs	3	1	2	1	2	1
HgX_2, moles	0.375	0.425	0.45	0.188	0.415	0.225
C_6H_5Br, moles	1	1	1	0.5	1	0.5
$Hg(C_6H_5)_2$, moles	0.177	0.217	0.174	0.070	0.226	0.096
$Hg(C_6H_5)_2/HgX_2 \times 100$	47.2	51.0	38.7	37.2	54.6	42.6

Experimental

Preparation of Mercury Diphenyl.—To the Grignard reagent, which was poured into a dry two-liter flask to separate it from the unreacted magnesium, was added the dried mercuric halide. After the slight reaction had subsided, it was refluxed for seventy-two hours. At the end of the reaction there was usually a gray residue in the flask

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[4] Hilpert and Grüttner, *Ber.*, **46**, 1675 (1913).

[5] Fleck, *Ann.*, **276**, 138 (1893).

[6] These experiments were made without the use of mechanical stirrers, Soxhlet [see Gilman and Brown, THIS JOURNAL, **51**, 928 (1929)], etc., which are now used. The yield should be improved by their use.

with some unreacted mercuric halide. The ether layer was then poured while warm onto ice. White needles separated which were washed and dried. The contents of the flask were washed with 500 cc. of wet ether and the ether extract was washed with a very little dilute hydrochloric acid. The ether was evaporated and crystals of mercury diphenyl separated. The crude mercury diphenyl was dissolved in warm chloroform to which was added an equal volume of warm alcohol; it then was allowed to crystallize. The residue in the flask contained some mercury phenyl halide which could be extracted with hot xylene. The yields are given in Table I.

In one run using 0.75 mole quantity of mercuric chloride and 1.0 mole of bromobenzene, the Grignard reagent was not poured from the magnesium residues. The procedure was the same as with the others. The yield was reduced 15%.

In one run using 0.9 mole quantity mercuric chloride and 1 mole of the Grignard reagent, the experiment was conducted as usual except that the ether was cooled before pouring off from the residues. Crystals of mercury diphenyl separated. Then more ether was added and the contents of the flask was refluxed for several hours. On separation and evaporation of the ether no further mercury diphenyl was recovered and the yield was reduced over 5%. This decrease was probably due to the reaction between mercury diphenyl and the excess mercuric chloride to form mercury phenyl chloride.

Mercury Phenyl Chloride and Phenylmagnesium Bromide.—To 0.1 *M* Grignard (made and poured from the magnesium residues) was added 26.5 g. (0.085 mole) of recrystallized mercury phenyl chloride. There was a slight reaction on addition. This was gently refluxed for seventy-two hours as usual. The reaction product was handled as in the typical case; yield, 15.7 g. of recrystallized mercury diphenyl or 52.2% conversion based on the mercury phenyl chloride used.

Mercury Diphenyl and Mercuric Bromide.—Eighteen grams of recrystallized mercuric bromide and 17.7 g. of mercury diphenyl were gently refluxed in 250 cc. of dry ether for seventy-two hours. The ether was poured off and evaporated. A few tenths of a gram of mercury diphenyl was recovered. There is practically complete conversion to mercury phenyl bromide.

Mercury Diphenyl and Anhydrous Magnesium Bromide.—One hundredth mole of mercury diphenyl in 50 cc. of dry ether was refluxed with anhydrous magnesium bromide for several days. Then dried Michler's ketone was added and it was again refluxed. No color developed with the ketone on decomposition with water, showing no appreciable amount of the Grignard reagent present.[7]

Summary

The preparation of mercury diphenyl by the Grignard reagent and mercuric halides has been discussed. Some factors influencing the yield are given.

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[7] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925), give the test with Michler's ketone as a qualitative one for the Grignard reagent, but point out that the Grignard reagent might be present in small quantities and still be negative. The results here were either negative or at best a trace. As the magnesium bromide used was prepared by heating $MgBr_2 \cdot 6H_2O$ and NH_4Br in an atmosphere of dry carbon dioxide, it may not have been absolutely pure. This reaction is being studied further.