[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE RICE INSTITUTE.]

# THE REACTION BETWEEN PHENYL-MAGNESIUM BROMIDE AND THE ESTERS OR ANHYDRIDE OF PHTHALIC ACID.

BY LLOYD B. HOWELL.

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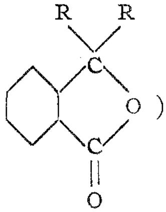
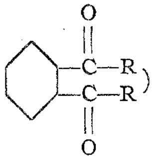
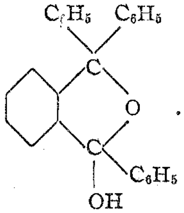
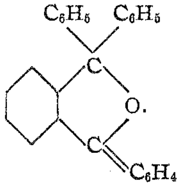
It is the commonly accepted fact that the so-called Grignard reagents, R–Mg–X, react with esters to give tertiary alcohols. But an examination of the literature concerning the condensation between the Grignard reagents and certain derivatives of phthalic acid, *viz.*, the methyl and ethyl esters and the anhydride, shows some discrepancies. All workers agree that the product of the reaction of 2 moles of a magnesium alkyl, or aryl, halide and phthalic anhydride, or phthalic esters, is a mixture[1] of a phthalide (general formula, ) and an *ortho* diketone (general formula, ). The reaction of Grignard reagents in yet higher molecular quantities, however, has been variously reported. In 1905 and 1906, Guyot and Catel[2] showed that phenyl-magnesium bromide in excess (over 3 moles) acted normally upon dimethyl phthalate, or phthalic anhydride, to give the tertiary alcohol triphenyl-hydroxy-$\alpha,\alpha'$-benzo-$\beta,\beta'$-dihydro-furfurane, . But in 1909 Shibata[3] reported that excess of the same Grignard reagent, reacting with diethyl phthalate, produced a phthalan derivative of the structure,  Shibata

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[1] *Ber.*, **38**, 240 (1905).

[2] Guyot and Catel, *Compt. rend.*, **140**, 254 (1905); *Bull. soc. chim.*, [3] **35**, 554 (1906).

[3] Shibata, *J. Chem. Soc.*, **95**, 1449 (1909).

for some reason failed to give any recognition to the previous work of Guyot and Catel and made the statement that no tertiary alcohol was formed, but instead, the dehydration product shown above. Both the French and Japanese workers claimed that a large excess of phenyl-magnesium bromide must be employed, and the latter claimed that it was this excess which brought about the dehydration of the expected product.

It has been found that the differences in the results obtained were due to the various methods of isolation employed. Guyot and Catel, after making the condensation between dimethyl phthalate and phenyl-magnesium bromide and hydrolyzing the product in the usual manner, crystallized their product from the ether or benzene solution. The solid obtained melted at 118°. Shibata made the condensation with the diethyl ester in practically the same manner, but found it necessary to isolate the product by distillation under diminished pressure after impurities had been expelled by distillation with steam. His product had a melting point of 194°.

The preparation of triphenyl-hydroxy-$\alpha,\alpha'$-benzo-$\beta,\beta'$-dihydro-furfurane from either dimethyl or diethyl phthalate has been found possible. It can be made also from phthalic anhydride, although with more difficulty. Furthermore, it has been shown that the compound of Shibata can be prepared from either the dimethyl or the diethyl ester. Moreover, it is found that if the tertiary alcohol obtained by Guyot and Catel be heated to a temperature required for distillation under diminished pressure (280° to 300°) it is dehydrated and yields the compound which was obtained by Shibata.

In the isolation of the triphenyl-hydroxy-$\alpha,\alpha'$-benzo-$\beta,\beta'$-dihydro-furfurane much difficulty is commonly experienced. Even if crystallization is attempted after driving off such volatile impurities as benzene, bromobenzene or diphenyl, an amorphous jelly or a glass-like mass is apt to be the only result. This was found to be true in many trials. In one case crystals failed to form in the viscous mother liquor until it had stood for over 2 years, notwithstanding the use of all ordinary means of starting such processes. When a few crystals have been obtained and purified, the process of "seeding out" is very advantageous. It was no doubt because of such discouraging results, not mentioned by Guyot and Catel, that Shibata had recourse to distillation.[1]

## Experimental Part.

**1. Preparation of Triphenyl-hydroxy-$\alpha,\alpha'$-benzo-$\beta,\beta'$-dihydro-furfurane from Diethyl Phthalate.**—In a 1000-cc. round-bottom flask provided with an efficient reflux condenser, 19.2 g. (8 moles) of dry magnesium turnings, covered by a large excess of anhydrous and alcohol-free ether, was slowly treated with 125.6 g. (8 moles) of dry monobromo-

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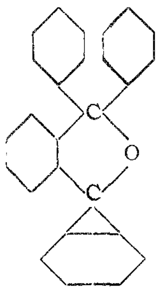
[1] Professor Roger Adams, of the University of Illinois, has called the attention of

benzene. After the resulting "Grignard" solution had been refluxed for $^1/_2$ hour it was cooled and 23 g. (one mole) of freshly prepared diethyl phthalate in 50 cc. of anhydrous and alcohol-free ether was added very slowly from a separatory funnel (total time, one hour) while the mixture was shaken constantly and the flask was cooled by ice-water. Each addition caused a yellow solid to form, but this dissolved instantly in the ether. The solution gradually darkened from yellow to brown.

When the condensation was complete, the magnesium-ether complex was hydrolyzed as usual, by pouring it into slightly more than the calculated amount of hydrochloric acid dissolved in a large volume of well iced water while the solution was stirred. The ether was then removed, dried over anhydrous sodium sulfate for a few hours, then decanted and allowed to evaporate spontaneously in a loosely covered dish. The ether solution thus obtained passed through a remarkable series of color changes. At first it was light orange in color and fluorescent. Then it changed in 12 hours to a deep purple hue and finally, after 24 hours, the color faded to reddish-purple with a remarkable green fluorescence.

When practically all of the ether had evaporated, the resulting viscous yellow oil was allowed to stand for several weeks. After about a month, slow crystallization commenced. From time to time the crude crystals were separated from the semi-fluid, jelly-like mass, washed with a trace of ether on a porous plate and allowed to stand overnight in a thin layer. When, subsequently, they were recrystallized twice from a mixture of equal volumes of toluene and chloroform, they gave a sharp melting point of 118° (corr.). From nearly all other common solvents, such as ether, alcohol, acetone and benzene, the material failed to emerge in crystalline condition but reverted to the original jell or amorphous glassy mass.

2. **Preparation of a Compound ($C_{26}H_{18}O$ m. p. 192-3°) from Dimethyl Phthalate.**—The Grignard reagent (slightly more than 5 moles) was

the writer to the fact that the structure, , assumed for the product by Shibata, involves the peculiarity of a 3-membered ring and a 6-membered (aromatic) ring with one side in common. Such a structure is entirely unprecedented elsewhere in the literature, and work undertaken at both the University of Illinois and The Rice Institute, indicates the possibility of an entirely different structure for the dehydration product of triphenyl-hydroxy-$\alpha,\alpha'$-benzo-$\beta,\beta'$-dihydro-furfurane.

prepared as described above with 12.8 g. of magnesium turnings and 83.7 g. of monobromo-benzene. This product was condensed with 18 g. (one mole) of freshly prepared dimethyl phthalate in a manner similar to that used with the diethyl ester.

To isolate the product after hydrolysis, the oil obtained from the ether was transferred at once to a large flask and distilled in a slow current of steam until about 5 liters of distillate (water, some bromo-benzene, benzene and diphenyl) had passed over. The deep yellow oil, after it cooled, set to a dark and brittle cake. It was broken up and subjected to distillation under 26 mm. pressure in a 50-cc. Claisen flask. The dark oil "bumped" badly, and distilled, with violent foaming, between 290° and 300°. The distillate showed little tendency to crystallize when cold, but it was found that the addition of a little ether was very effective in causing crystallization to start.

After the crude light-brown product was crushed and "worked" with a little ether on a porous plate, it was recrystallized 3 times from toluene. The crystals were nearly white (slightly grayish) and melted sharply at 192–193° (stem immersed).

This compound was identified as that prepared by Shibata, by a mixed m. p. determination with analyzed material made from diethyl phthalate according to his procedure.

3. **Dehydration of Triphenyl-hydroxy-$\alpha,\alpha'$-benzo-$\beta,\beta'$-dihydro-furfurane upon Heating.**—A few g. of recrystallized triphenyl-hydroxy-$\alpha,\alpha'$-benzo-$\beta,\beta'$-dihydro-furfurane was slowly heated under reduced pressure (26 mm.) in a Wood's metal bath. The crystals melted to yield a colorless oil at 119°. This oil slowly darkened to a yellow color at 160°, to deep yellow with a green fluorescence at about 170°, to red-brown at 200° and to dark amber, with fluorescence persisting, above 350° (temperature of bath). The bath was then heated slowly to nearly 400°, while the behavior of the oil was closely watched. When the temperature of the vapor had reached 280° (uncorr.), a very noticeable condensation of moisture occurred in the cool parts of the apparatus. No moisture had previously been evident in the apparatus. At 295°, distillation of a pale greenish-yellow fluorescent liquid began.

At this stage, the heating was discontinued, the residue in the flask was cooled and removed as a coarse dark-brown crystalline powder. It was dissolved in toluene and crystallized. The crude product thus obtained was freed from oily impurities by pressing it on a clay plate and then recrystallized twice from toluene and dried at 130° for 2 hours. The crystals were nearly pure white, and melted at 192–193°.

Subs., 0.1618: $CO_2$, 0.5305; $H_2O$, 0.0781.

Calc. for $C_{26}H_{18}O$: C, 90.17; H, 5.24. Found: C, 89.36; H, 5.36.

## Summary.

1. The reaction of an excess of phenyl-magnesium bromide upon the methyl or ethyl ester of phthalic acid gives a mono-hydric tertiary alcohol which is a derivative of furfurane.

2. If the product of the reaction of an excess of phenyl-magnesium bromide upon the esters of phthalic acid is heated to about 300°, it loses a molecule of water and gives the compound $C_{26}H_{18}O$ of m. p. 192–193° which Shibata[1] claimed to be a derivative of phthalan and the direct product of the original condensation.

Houston, Tex.

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[Contribution from the Chemical Laboratory of Harvard University.]

# ADDITION REACTIONS OF PHOSPHORUS HALIDES. I. THE MECHANISM OF THE REACTION OF THE TRICHLORIDE WITH BENZALDEHYDE.

By James B. Conant and Alexander D. Macdonald.

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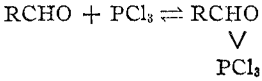
## I. Introduction.

It has been shown in a previous paper[2] that phosphorus trichloride adds to the ends of the conjugated system of certain unsaturated ketones. This addition takes place with an increase in valence of the phosphorus atom from 3 to 5. The chlorine atoms in the addition product are very active and are readily replaced by hydroxyl or oxygen when the reaction mixture is treated with acetic acid or acetic anhydride. The product thus formed is a phosphonic acid or an intermediate cyclic compound. An exactly similar reaction takes place when simple aldehydes or ketones are treated with phosphorus trichloride. In this case, however, the primary addition product is formed by the 1,2-addition of the phosphorus atom.



$$\mathrm{RCHO} + \mathrm{PCl_3} \rightleftharpoons \underset{\underset{\mathrm{PCl_3}}{\vee}}{\mathrm{RCHO}}$$

(I).

Benzaldehyde was chosen as a suitable aldehyde for studying the mechanism of this reaction and only the results obtained with this substance are presented here. The reaction, however, takes place readily with most aldehydes and ketones and the limits of the reaction will be discussed in a subsequent paper.

### The Primary Reversible Reaction.

When benzaldehyde and phosphorus trichloride are brought together considerable heat is evolved and the addition reaction (Equation I) proceeds to a definite equilibrium. If equimolecular amounts of the 2 sub-

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[1] *Loc. cit.*

[2] This Journal, 42, 830 (1920).