value $[\alpha]_D^{20}$ = +59.2 in pure chloroform (1.0878 g. of substance, 25 cc. of chloroform solution; 5.154° rotation to the right in a 200mm. tube). The substance melted at 137–138° without decomposition but slowly decomposed with gas evolution in the range 155–165°. A chlorine estimation was made by heating 1.056 g. of substance with 0.4 g. of pure silver acetate in acetic anhydride solution for one hour on the steam-bath and weighing the silver chloride (0.2269 g.); 5.43% of chlorine was found as compared with 5.41% calculated for $C_{26}H_{35}O_{17}Cl$. A measurement by Bacon's directions for the Stepanoff method showed 5.40% of chlorine (0.1938 g. of substance gave 0.0414 g. of silver chloride), which proves that the substance contains only one chlorine atom in its molecule. The ease of removal of this atom by silver acetate corresponds with the behavior of chloro-acetyl derivatives of the sugars. The acid equivalent was found by saponifying in an ice-salt bath 0.2011 g. of substance dissolved in 50 cc. of acetone with 50 cc. of 0.1 $N$ potassium hydroxide aqueous solution for two hours; the alkali that was neutralized was 24.4 cc. as compared with the calculated value 24.5 cc. Chloro-acetyl celtrobiose is very soluble in chloroform or acetone, somewhat soluble in warm ether, nearly insoluble in cold ether, insoluble in petroleum ether or water. It reduces Fehling's solution on boiling. It is a stable halogeno-acetyl sugar derivative and may be kept in moist air without decomposition.
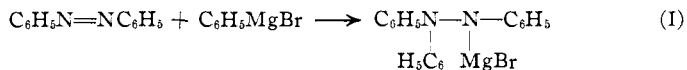
## Summary

The action of active aluminum chloride on a chloroform solution of cellobiose octa-acetate produces the well-known $\alpha$-chloro-acetyl cellobiose and in addition an isomeric substance that proves to be the chloro-heptaacetate of a new di-hexose to which the name celtrobiose is given.
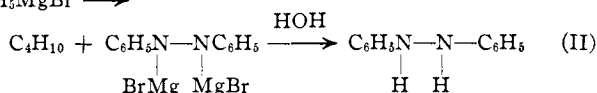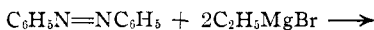
WASHINGTON, D. C.

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## NOTE

**The Mechanism of Reduction of Azobenzene by Organomagnesium Halides.**—Several theories have been proposed for the mechanism of reduction of azobenzene by organomagnesium halides. Busch and Hobein[1] suggested tentatively that phenylmagnesium bromide added to azobenzene as follows.

$$C_6H_5N{=}NC_6H_5 + C_6H_5MgBr \longrightarrow C_6H_5N{-}N{-}C_6H_5 \qquad (I)$$
$$\phantom{C_6H_5N{=}NC_6H_5 + C_6H_5MgBr \longrightarrow} H_5C_6 \ \ MgBr$$

This was proposed as a possible explanation for the formation of triphenylhydrazine from $\beta$-phenylhydroxylamine and phenylmagnesium bromide. Franzen and Deibel[2] interpreted the formation of hydrazobenzene as follows.
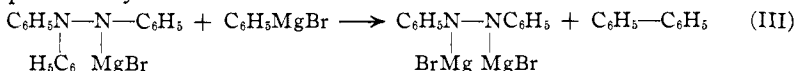
[1] Busch and Hobein, *Ber.*, **40**, 2099 (1907).

[2] Franzen and Deibel, *Ber.*, **38**, 2716 (1905).

$C_6H_5N{=}NC_6H_5 + 2C_2H_5MgBr \longrightarrow$

$$C_4H_{10} + \underset{\substack{| \quad | \\ BrMg \ MgBr}}{C_6H_5N{-}NC_6H_5} \xrightarrow{\text{HOH}} \underset{\substack{| \quad | \\ H \quad H}}{C_6H_5N{-}N{-}C_6H_5} \quad \text{(II)}$$

Gilman and Pickens[3] showed that the latter mechanism (II) is correct. This was done by replacing the —MgBr groups of the intermediate compound by groups that give known hydrazobenzene derivatives. For example, when the reaction product of azobenzene and an RMgX compound is treated with benzoyl chloride prior to hydrolysis, a good yield of dibenzoyl-hydrazobenzene is obtained, in addition to a corresponding amount of the expected R–R compound.

However, it is possible for both mechanisms (I and II) to be correct. In each experiment[3] a slight excess over two molecular equivalents of Grignard reagent was used with one equivalent of azo compound. Reactions I might first have taken place. Then the second equivalent of RMgX compound may have reacted as follows.

$$\underset{\substack{| \quad | \\ H_5C_6 \ MgBr}}{C_6H_5N{-}N{-}C_6H_5} + C_6H_5MgBr \longrightarrow \underset{\substack{| \quad | \\ BrMg \ MgBr}}{C_6H_5N{-}NC_6H_5} + C_6H_5{-}C_6H_5 \quad \text{(III)}$$

Experiment has shown that the mechanism postulated in (III) is incorrect. When triphenylhydrazine was treated with an excess of phenylmagnesium or ethylmagnesium bromide, under conditions that convert azobenzene to hydrazobenzene, no reaction occurs and practically all of the triphenylhydrazine is recovered. Accordingly Reaction I does not precede Reaction II.[4]

**Triphenylhydrazine and Ethylmagnesium Bromide.**—An ether solution of 5 g. (0.019 mole) of triphenylhydrazine and 0.1 mole of ethylmagnesium bromide was refluxed for eight hours, allowed to stand overnight, and then hydrolyzed by an ammoniacal ammonium chloride solution. The ether layer, when worked up in the customary manner, gave 4.6 g. of triphenylhydrazine.

**Triphenylhydrazine and Phenylmagnesium Bromide.**—Five g. (0.019 mole) of triphenylhydrazine was treated with 0.058 mole of phenylmagnesium bromide under the conditions described for ethylmagnesium bromide. Four g. of pure triphenylhydrazine was directly recovered as well as 0.3 g. of impure triphenylhydrazine from the mother liquors.

CONTRIBUTION FROM THE CHEMICAL
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[3] Gilman and Pickens, THIS JOURNAL, **47**, 2406 (1925).

[4] It has already been stated (Ref. 3, p. 2415) that diazonium salts do not show the reaction of $RN{=}NR$ compounds towards the Grignard reagent. However, diazosulfones appear to undergo the same type of reaction as azo compounds towards organomagnesium halides.

The *sym.*-diphenyl-tribenzoyl-triazane [$(C_6H_5)(C_6H_5CO)NN(COC_6H_5)N(COC_6H_5)(C_6H_5)$] obtained from diazo-aminobenzene, ethylmagnesium bromide and benzoyl chloride and described on p. 2411 of Ref. 3 has been analyzed by J. E. Kirby. Calcd. for $C_{33}H_{25}O_3N_3$: N, 8.22. Found: 8.37.