

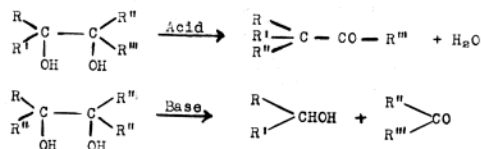
## SOME STUDIES IN THE PINACOL SERIES

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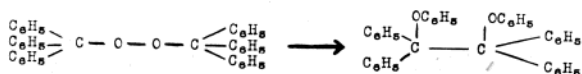
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The pinacols are ditertiary alcohols of the type  $RR'C(OH)C(OH)R''R'''$ , where the R groups may be alike or different. These compounds show several interesting properties, among them the sensitivity to acids and bases. Upon treatment with acids, most pinacols undergo rearrangement to  $\beta$ -pinacolones; bases tend to split the molecule into a secondary alcohol and a ketone:

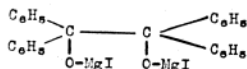


These two reactions have been the subjects of many investigations—other aspects of the chemistry of the pinacols have been but little studied. On account of the sensitivity of the pinacols to acids and bases, very few derivatives have been prepared. The only ether which is reported in the literature is the phenyl ether of benzo-pinacol, which Wieland<sup>1</sup> has shown to be formed when triphenylmethyl peroxide is heated:



Esters seem to be entirely unknown.

There is one derivative of benzopinacol, however, which is well known. This is the iodomagnesium pinacolate,

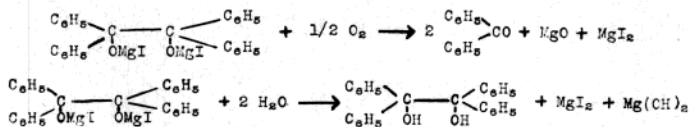


It may be prepared by the action of a Grignard reagent upon benzopinacol, benzil, esters of benzoyl formic acid, or esters of oxalic acid. Gomberg and Bachmann<sup>2</sup> have recently shown that it may be obtained

<sup>1</sup> Wieland, Ber. 44: 2550 (1911).

<sup>2</sup> Gomberg and Bachmann, J. Amer. Chem. Soc. 49: 236 (1927).

by the action of a mixture of magnesium and magnesium iodide upon benzophenone in anhydrous ether or benzene. The corresponding bromo-compound may also be prepared by either of the above methods. These halomagnesium pinacolates are slowly oxidized by the air to the corresponding ketone, and are converted by water to the pinacol:



Whether these pinacolates are subject to rearrangement and to splitting is not known with certainty. Acree<sup>3</sup> has reported that the distillation of bromomagnesium benzopinacolate at 400° gives  $\beta$ -benzopinacolone, but it may well be that the rearrangement takes place after the decomposition of the magnesium compound. Certainly we should not expect the halo-magnesium derivatives to rearrange as easily as the pinacol itself. With this in mind, I have attempted to prepare other pinacol derivatives from the iodomagnesium pinacolate.

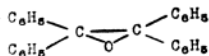
I have succeeded in preparing the methyl ether of benzopinacol by the action of dimethyl sulfate upon the iodomagnesium pinacolate. Twice the calculated amount of dimethyl sulfate was added to a benzene solution of the pinacolate. A white gelatinous precipitate formed at once. After the mixture was shaken for several hours, the liquid was separated from the precipitate by filtration, was washed several times with water to remove the excess dimethyl sulfate and the magnesium. The crystalline residue which remained was purified by recrystallization from alcohol, in which it is quite soluble. Analysis showed it to be the methyl ether of benzopinacol. The substance is unstable—even boiling the alcoholic solution causes some decomposition. There is no definite melting point—at about 150° the material sinters and at 166° it melts with the evolution of a gas. These temperatures may be varied somewhat by changing the rate of heating.

In an attempt to prepare the chloride of benzopinacol a solution of the pinacolate was treated with phosphorus pentachloride. A precipitate at once formed, and iodine was liberated. After shaking over night, the solution and precipitate were separated by filtration and the filtrate was washed with water and allowed to evaporate. The crystalline residue was entirely  $\beta$ -benzopinacolone—no pinacol chloride could be detected.

<sup>3</sup> Acree, Am. Chem. J. 33: 187 (1905).

The liberation of iodine can doubtless be laid to the dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine, which displaced iodine from the magnesium iodide. The free iodine oxidized part of the pinacolate to benzophenone. This forms an insoluble double salt with magnesium iodide—hence the benzophenone precipitated as fast as it formed, and was later recovered from the precipitate.

An attempt was made to prepare the benzoyl ester of benzopinacol by the action of benzoyl chloride on the iodomagnesium pinacolate. In this case, as in the previous one, the desired product was not obtained. Instead of the ester,  $\alpha$ -benzopinacolone, was formed in very good yield.



Both phosphorus pentachloride and benzoyl chloride have the power of removing magnesium oxide and magnesium iodide from the iodomagnesium pinacolate—phosphorus pentachloride alone has the power of effecting a rearrangement. This would indicate that the magnesium oxide and iodide are removed before the rearrangement takes place.

These studies are being continued at the present time.