

a negative carbon atom, with two unshared electrons, a condition similar to that supposed above for the aliphatic diazo compounds. Gibson suggests that ionization may have rendered the activity too fugitive to be observed. This indicates that active compounds of this type are difficult to isolate but, in the light of the evidence given above, is not conclusive against the possibility of such structures.

### Summary

1. Amino-*d*-camphor, which had not previously been resolved, has been separated into two amines with specific rotations  $[\alpha]_D$  17.5 and 55.5°, respectively.

2. The diazocamphors prepared from the two amines were proved to be identical.

3. The theoretical aspect of this fact is discussed.

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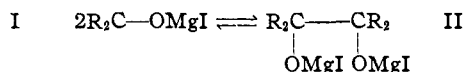
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## COMMUNICATIONS TO THE EDITOR

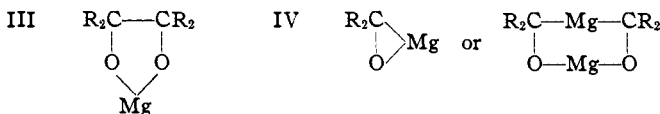
### THE MECHANISM OF THE PINACOL SYNTHESIS BY THE SYSTEM $Mg + MgI_2$

Sir:

In a recent paper [THIS JOURNAL, 54, 2112 (1932)] Bachmann criticizes adversely the arguments brought by Bergmann and Schuchardt [*Ann.*, 487, 225 (1931)] in favor of their interpretation of the reduction of aromatic ketones by  $Mg + MgI_2$ . In the considerations advanced by Bachmann, there are two erroneous assumptions to which I intend to draw attention. In the first place, it is impossible to ascribe to the equation



more than only a formal meaning, because the ketyls—and the left-hand compound belongs, to all appearances, to the ketyls—are practically monomeric, as was pointed out by Schlenk and Thal [*Ber.*, 46, 2840 (1913)]. In contrast to Bachmann's opinion, we are far from denying that the iodomagnesium pinacolate (II) is capable of dissociation into radicals, but we may almost deny that it is capable of existence in its dimeric form. It is very probable that molecules of the formula I can be formed, for instance by the action of a Grignard reagent on a pinacol, and come in equilibrium with the five-membered compound (III), but as it is impossible to obtain pinacols from the sodio-ketyls, we shall not make the "MgI-ketyls" responsible for the formation of the pinacols. In the paper criticized by Bachmann it was assumed, therefore, that the five-membered ring compound III is formed and, on hydrolysis, yields the pinacols.



Secondly, it is impossible to attribute the colors formed in the Gomberg-Bachmann reaction to the ketyl-like compound I. The colors observed are never those of the ketyls, but of the di-alkali or analogous compounds. In a great number of experiments we have verified this statement. When on addition of a Grignard reagent to the solution of a pinacol the color in question appears, we must conclude that by any means the compound IV is formed, for instance because it is very difficult to free a Grignard solution from finely divided magnesium. It is a well-known fact that not only the ketyls, but also the ketone disodium compounds, regenerate the ketones under the influence of oxygen in iodine. These reactions also, therefore, do not prove the formation of ketyls (I). I may believe that the mechanism proposed by Bergmann and Schuchardt for the excellent method of Gomberg and Bachmann is right.

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#### THE REDUCTION OF KETONES BY MAGNESIUM + MAGNESIUM IODIDE AND BY SODIUM

*Sir:*

In the preceding communication, E. Bergmann has presented a defense of his criticisms of the mechanism proposed by Gomberg and Bachmann, according to which reduction of ketones by  $\text{Mg} + \text{MgI}_2$  to pinacols involves the intermediate formation of iodomagnesium ketyls,  $\text{R}_2\text{C}-\text{OMgI}$ . He insists that a vast difference exists between the sodium ketyls and our proposed equilibrium system,  $2 \text{R}_2\text{C}-\text{OMgI} \rightleftharpoons \text{R}_2\text{C}(\text{OMgI})(\text{IMgO})\text{CR}_2$ ; and he concludes that we cannot be dealing with iodomagnesium pinacولات in equilibrium with a very small amount of iodomagnesium ketyls because ketyls are practically monomolecular.

I shall not stop now to point out why Professor Bergmann has arrived at erroneous conclusions, although the reasons are indicated partly in what follows. At this time I wish to say only that in a communication which will appear shortly in THIS JOURNAL, I shall present experimental evidence which will show definitely not only that our interpretation with respect to the magnesium compounds is correct, but also that the corresponding sodium compounds are like the magnesium derivatives. To be more specific, in the reaction between sodium and aromatic ketones, the sodium ketyl radicals persist as such *to a small extent only*, so that there