



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.

FRIEDRICH WILHELM UNIVERSITY
BERLIN, GERMANY

E. BERGMANN

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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

exists at the end of the reaction an equilibrium mixture of sodium ketyl and sodium pinacolate



in which the equilibrium is preponderantly in favor of the *right-hand* side of the formulation. In other words, the products obtained by addition of sodium to aromatic ketones are *not radicals existing in the monomolecular state, as has been commonly supposed for nearly twenty years*, but consist for the most part of the *dimolecular form*, namely, sodium pinacolate.

In addition, the forthcoming publication will point out the reason why Schlenk, E. Bergmann and others were misled in interpreting as they did the reaction and the structure of the compounds.

CHEMISTRY LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

W. E. BACHMANN

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THE ELECTRODEPOSITION OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

Sir:

The possibility of the electrodeposition of molybdenum and tungsten from aqueous solutions is suggested by their position below hydrogen in the electromotive series. Acidic solutions of these elements in various valence states may be prepared with citric acid, glucose or other hydroxyl compounds. Since the procedure for the electrodeposition of molybdenum and tungsten should resemble to a certain extent the methods applicable to chromium, some studies were first made using solutions of trivalent chromium salts and citric acid.

Britton and Westcott [*Trans. Faraday Soc.*, 27, 809 (1931)] have suggested, subsequent to the completion of these experiments, that chromium may be deposited from solutions containing chromium in the form of complexes with organic acids.

The following procedure was found to give bright, adherent deposits of chromium: 2 g. of hydrated chromic chloride and 4 cc. of 2.5 *M* monopotassium citrate solution are diluted in 20 cc., heated to boiling and cooled. A carbon anode is contained in a porous cup and a sheet of copper serves as cathode. Metal is deposited at a current density of 3 amp. per sq. dm. and a voltage drop of 4.5 to 7.5 volts. Too high current density and voltage will cause the deposition of black powder. Chromium was also deposited from a bath in which tartaric acid was employed.

Molybdenum may be deposited from an acid solution: 2 g. of molybdic acid and 15 cc. of 34% hydrobromic acid are evaporated almost to dryness. The dark red-brown residue is dissolved in 6 cc. of 2.5 *M* dipotassium citrate