[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Reaction of Aromatic Ketones with Sodium. I. The Structure of the So-called Metal Ketyls

BY W. E. BACHMANN

Beckmann and Paul[1] observed that aromatic ketones react with metallic sodium in anhydrous ether and give deeply colored sodium derivatives; they considered that the compounds were dimolecular and had the formula $(R_2)NaC—O—CONa(R_2)$. Twenty years later, Schlenk[2] and co-workers took up the study of these compounds. The intense colors of the compounds and the reactions with iodine and with oxygen indicated to them the presence of a radical analogous to the triarylmethyls and they came to the conclusion that the sodium compounds are free radicals of the type, R_2CONa, formed by addition of an atom of sodium to a molecule of ketone. According to Schlenk, these ketyls, as they were named, are monomolecular and do not associate to the dimolecular form, sodium pinacolate, $R_2C(ONa)(NaO)CR_2$. The strongest support for the monomolecular structure has been the observation of Schlenk and co-workers that hydrolysis of the compounds does not give pinacols but always a mixture of ketone and hydrol. They rightly remark that if the sodium derivative had the dimolecular structure of sodium pinacolate, then pinacols should result on hydrolysis; and it is noteworthy that in not a single instance did Schlenk obtain a pinacol. According to him the formation of ketone and hydrol can be explained only on the basis of ketyl radicals and they formulated the reaction as follows

$$2R_2C—ONa \xrightarrow{H_2O} 2R_2C—OH \longrightarrow R_2CO + R_2CHOH \qquad (1)$$

Schlenk's views regarding the structure of the ketone–sodium compounds have been generally accepted[3] or at least uncontested.[4] That these views are held at the present time is evident from the recent statements of Bergmann;[5] according to him "the ketyls are practically monomolecular" and "it is impossible to obtain pinacols from the sodio-ketyls." For the past twenty years it has been considered that the sodium derivatives are free radicals existing in the monomolecular state.

In 1927 it was shown with Professor M. Gomberg[6] that aromatic ketones react with a mixture of magnesium and magnesium iodide and are reduced

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(1) Beckmann and Paul, *Ann.*, **266**, 6 (1891).

(2) Schlenk and Weickel, *Ber.*, **44**, 1183 (1911); Schlenk and Thal, *ibid.*, **46**, 2840 (1913); Schlenk, Appenrodt, Michael and Thal, *ibid.*, **47**, 486 (1914).

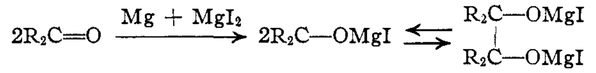
(3) See for example the articles on metal ketyls in Stewart's "Recent Advances in Organic Chemistry," London, 1932, Vol. II, p. 335; and in Walden's "Chemie der freien Radikalen," Leipzig, 1924, p. 100.

(4) Schmidlin's view ["Das Triphenylmethyl," Stuttgart, 1914, pp. 186–188] that the compounds are loose combinations of the type, $R_2C{=}O\ldots Na$, has been shown to be incorrect, at least in liquid ammonia. Wooster, THIS JOURNAL, **51**, 1856 (1929).

(5) Bergmann, *ibid.*, **54**, 3773 (1932).

(6) Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

to iodomagnesium pinacolates, $R_2C(OMgI)(IMgO)CR_2$. Although colorless in the solid state, these pinacolates give colored solutions; this fact led us to the conclusion that in solution the pinacolates dissociate to a slight extent into iodomagnesium-ketyl radicals, $R_2C{-}OMgI$, and this hypothesis was confirmed by the reactions of the solutions with iodine and with oxygen in the manner of the corresponding sodium compounds. The reduction of the ketones by the mixture of magnesium and magnesium iodide was, therefore, interpreted as taking place in the following manner



$$2R_2C{=}O \xrightarrow{Mg + MgI_2} 2R_2C{-}OMgI \rightleftarrows \begin{array}{l} R_2C{-}OMgI \\ \ \ | \\ R_2C{-}OMgI \end{array} \qquad (2)$$

That the latter equilibrium between the iodomagnesium-ketyl and the iodomagnesium pinacolate is nearly entirely ($>99\%$) in favor of the pinacolate is shown by the fact that hydrolysis of the mixture gives nearly quantitative yields of pinacol and none of the mixture of ketone and hydrol.

Because of the similarities between the iodomagnesium derivatives and the sodium compounds in the matter of color formation and reaction with iodine and with oxygen, it has seemed incredible that an enormous difference exists between the two in the matter of structure. It seems impossible that the sodium pinacolates dissociate practically 100% to ketyl radicals, as is indicated by lack of pinacol formation, while the iodomagnesium pinacolates break down less than 1%, as shown by the yields of pinacol. In spite of the statements that pinacols are never formed on hydrolysis of the sodium compounds, we turned to this reaction in order to determine whether the sodium derivatives are actually monomolecular.[7] We followed the directions of Schlenk and co-workers and carried out about a dozen experiments with benzophenone and a number of other ketones. The colored mixtures which were obtained by the action of sodium on the ketones were hydrolyzed in an inert atmosphere either by pouring the mixtures into water or by adding alcohol to the mixture, a method frequently employed by Schlenk to replace the sodium by hydrogen, especially when using the apparatus recommended by him.[8] In every case a careful search failed to reveal even a trace of pinacol; the products consisted of mixtures of ketone and hydrol in agreement with Schlenk.

The clue to the solution of the problem was furnished by an observation, made during the investigation, that a small amount of alkali can rapidly effect the decomposition of a large amount of pinacol into a mixture of ketone and hydrol.[9] It occurred to us that pinacol *is* formed on hydrolysis

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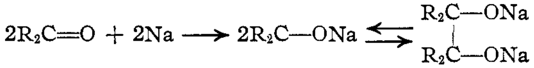
(7) We agree with Bergmann that the free ketyl itself would not give pinacol but ketone and hydrol on hydrolysis; if pinacol is formed it must come from sodium pinacolate. Although Schlenk mentioned that there might be ketones which would give pinacolates or mixtures of pinacolates and ketyls, he apparently never found such conditions in any case studied by him.

(8) See Schlenk and Thal, Ref. 2, for apparatus and methods of preparing and handling the metal ketyls.

(9) Bachmann, THIS JOURNAL, **55**, 355 (1933); see also *ibid.*, **55**, 770 (1933) for an application of the reaction.

of the ketone–sodium compounds and that the pinacol is subsequently broken down into ketone and hydrol by the action of the alkali liberated simultaneously on hydrolysis. It was thought that if the formation of alkali could be prevented, then pinacol would be obtained. With this thought in mind the mixtures were hydrolyzed by pouring them with vigorous stirring into dilute acetic acid. The results of the experiments fully substantiated the correctness of our idea. Hydrolysis with acetic acid gave pinacols in yields as high as 95%; practically no hydrol was formed. According to our theory it should be possible to get a quantitative yield of a pinacol that is not affected by alkali. Such a pinacol is 9,10-diphenyldihydrophenanthrenediol, and in confirmation of our theory it was found that this pinacol is obtained in 100% yield. These results show that the reaction between ketones and sodium proceeds in the following manner



$$2R_2C{=}O + 2Na \longrightarrow 2R_2C{-}ONa \rightleftarrows \begin{array}{l} R_2C{-}ONa \\ \mid \\ R_2C{-}ONa \end{array} \qquad (3)$$

From this it follows that *the sodium derivatives of ketones, the so-called metal ketyls, are not monomolecular free radicals but sodium pinacolates or equilibrium mixtures of sodium-ketyl and sodium pinacolate in which the equilibrium is nearly entirely in favor of the sodium pinacolate* (Equation 3).

It is now easy to see why Schlenk, Bergmann and others have been misled in interpreting the reactions and the structures as they did. If the reaction mixture is decolorized by adding alcohol, there is no chance for the pinacol to survive; as soon as it is formed it is converted to a mixture of ketone and hydrol by the action of the sodium alcoholate, a reaction that is remarkably rapid. In a similar manner, if the mixture is poured into water the alkali which is formed will decompose the pinacol. Since the ketone and hydrol are products of a secondary reaction, the conclusions that have been drawn in the past from their presence cannot be correct.

Comparison of Metal Pinacolates.—It was found that of the metals of the first group lithium, potassium, rubidium and cesium give colored derivatives of benzophenone which give benzopinacol on hydrolysis. Of the second group metals, beryllium (with beryllium iodide),[6] magnesium (with magnesium iodide or as amalgam) and calcium likewise react with benzophenone and give colored derivatives. The actions of these metals on benzophenone and the products that are formed are similar. In each case colors are produced in the reaction; if the color is that of the ketyl, then the various metal ketyls of the formula $(C_6H_5)_2C{-}OMe$, where Me is the group indicated, have the following colors: Li, blue; Na, blue; K, violet-blue; Rb, blue; Cs, blue; IBe, red; Mg/2, blue; IMg, red; Ca/2, green. In every instance it is considered that the ketyls are intermediate products and that they associate nearly completely to the metal pinacolates, so that an equilibrium mixture of the two is formed. The amount of dissociation of the pinacolate varies with the pinacolate; in no case is the dissociation great. All of the pinacolates react with iodine and with oxygen and give back the ketone in virtue of the slight dissociation of the pinacolates into the ketyl radicals; the individual ketyls may vary considerably in their reactivity with various reagents. If the pinacol is not decomposed by the alcoholate or hydroxide of the metal, no special precautions, except protection from oxygen, need be taken with regard to the manner of carrying out the hydrolysis; the chief reason why quantitative yields of pinacols are easily obtained from the iodomagnesium pinacolates is the fact that the pinacols are not affected by iodomagnesium hydroxide or alcoholate. Although the reaction of ketones with sodium may be employed as a method of preparing pinacols, it is hardly likely that the reaction will be used in place of the Mg + MgI_2 reaction because the latter method has so many advantages. It is clear that there are no real differences in the structures of the products obtained from ketones and different metals; there is simply a gradation of properties in the series of metal pinacolates that are formed.

Experimental

In all experiments moisture and air were rigorously excluded. All operations were carried out in a stream of nitrogen which was purified by being passed through concentrated sulfuric acid and through a solution of benzophenone-disodium. The latter reagent is able to react with oxygen, water and carbon dioxide and is, therefore, a convenient purifying agent. The mixture was prepared by shaking a solution of 5 g. of benzophenone in 50 cc. of ether and 50 cc. of toluene in a wash-bottle with 5 g. of 40% sodium amalgam until the mixture was violet-red in color; this reaction required several days.

The reactions were usually carried out in glass-stoppered graduated cylinders; the glass stopper was sealed with the new lubricant of Meloche and Fredrick,[10] the top was covered with paraffin and the stopper was tied down; the flask was shaken mechanically. In many experiments 2% sodium amalgam was used in place of the metal alone; the mercury prevents to a great extent the formation of the disodium derivative,[11] except in the case of fluorenone. Hydrolysis was carried out by forcing the mixture by a stream of nitrogen into 400 cc. of 10% acetic acid (freshly boiled) contained in a 1-liter, 3-necked flask which was fitted with an inlet tube, an outlet tube passing through a mercury trap and a mercury-sealed stirrer. The mixture is run into the acid slowly in order to avoid accumulation of the sodium compound, for it too can decompose the pinacol. One must constantly bear in mind that the decomposition of the pinacol by alkali is extremely rapid; only after dozens of experiments were carried out was it possible to obtain consistently high yields of pinacols. Best results were obtained if the ketone was not converted completely to the sodium derivative; excess of either ketone or metal was isolated at the end of the reaction and taken into account in calculating the yield of product. At times considerable amounts of ketone were obtained even when a sufficient amount of sodium had apparently reacted.

Reaction of Benzophenone with Sodium.—Five to ten gram portions of benzophenone in 120 cc. of ether were shaken with 100 g. of 2% sodium amalgam. The solution quickly became green and then dark blue; after several days a large amount of pale blue precipitate was present. The mixtures were hydrolyzed after being shaken for

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[10] Meloche and Fredrick, THIS JOURNAL, **54**, 3264 (1932).

[11] Schlenk and Bergmann, *Ann.*, **464**, 25 (1928).

periods of time ranging from two days to two months. The ether solutions were separated from the aqueous solution, dried, filtered and evaporated. The benzopinacol obtained in this manner was stirred with 20 cc. of 80% alcohol in order to remove benzohydrol.[12] if any were present, and after filtration the pinacol was warmed with 20 cc. of petroleum ether (60–90°) in order to remove benzophenone. The pinacol was then recrystallized from a mixture of chloroform and alcohol. From the alcohol and petroleum ether extracts small amounts of pinacol were isolated. In an experiment in which 7.5 g. of benzophenone had reacted during two weeks of shaking there was obtained 6.5 g. (86%) of benzopinacol; m. p. 188–190°. From the experiments with sodium amalgam over 200 g. of benzopinacol has been isolated. Dioxane can be used in place of ethyl ether; the color phenomena and the products are similar to those produced in ordinary ether. When the reaction mixture was hydrolyzed by adding alcohol until no more color remained, no pinacol was obtained; the products were benzophenone and benzohydrol.

Benzopinacol was also obtained by hydrolyzing the mixture resulting from the action of mercury on benzophenone-disodium. The reaction between the mercury and benzophenone-disodium must be

$$2(C_6H_5)_2C\text{—}Na(ONa) + Hg \longrightarrow NaHg + 2(C_6H_5)_2C\text{—}ONa \leftrightarrows (C_6H_5)_2C(ONa)(NaO)C(C_6H_5)_2$$

The reaction with sodium metal was like that with amalgam. The theoretical amount or a slight excess of sodium in the form of wire was shaken with a solution of benzophenone in ether; glass beads aided in carrying the reaction to completion. At the start of the reaction the sodium wire became red and then quickly changed to blue. After an hour the solution was violet-blue in color and after several days a large amount of precipitate was present. The color obtained with sodium metal was darker than the color formed with sodium amalgam and always had a violet shade even when the ketone was present in excess. The yields of pinacol were usually somewhat smaller than those obtained by using sodium amalgam.

A search of the literature revealed that the formation of benzopinacol had at times been observed by several investigators. Thus, Beckmann and Paul reported that hydrolysis of the sodium derivative of benzophenone gave either a mixture of benzophenone and benzohydrol or else a mixture of these two products in addition to benzopinacol. They made the curious statement that the formation of benzopinacol depends upon the amount of water used for hydrolysis and upon the time taken to isolate the products; only when a large amount of water and a short period of time are employed is it possible to isolate pinacol. We are now in a position to explain this strange statement. If a small amount of water is used, then the great concentration of alkali formed on hydrolysis can decompose the pinacol; this decomposition is favored if the pinacol is allowed to remain in contact with the alkaline solution for a long time. By employing a large amount of water, a weak solution of alkali is obtained and some pinacol remains. The results of Beckmann and Paul[13] and especially of Acree,[14] who reported a 60% yield of benzopinacol, have been neglected in formulating the ketyl theory.

Reaction of Benzophenone with Lithium, Potassium, Rubidium and Cesium.— In like manner, benzopinacol was obtained by hydrolysis of the reaction mixtures obtained from benzophenone and lithium and potassium, free and in the form of amal-

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[12] Cohen [*Rec. trav. chim.*, **38**, 72 (1919)] found that 10 cc. of 80% alcohol can dissolve 3.5 g. of benzohydrol. We have found that it is also capable of dissolving 3.5 g. of benzophenone in addition to the benzohydrol already present.

[13] Schlenk originally considered that small amounts of pinacol might be formed by association of the diphenylhydroxymethyl radicals formed on hydrolysis of the ketyl radicals.

[14] Acree, *Am. Chem. J.*, **29**, 588 (1903). See also Tingle and Gorsline, THIS JOURNAL, **30**, 1880 (1908), who obtained a 5.5% yield of pinacol.

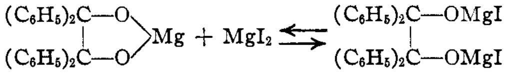
gams. The color of the lithium compound was pale green and at times it seemed to be nearly colorless.

For the reaction with rubidium a liquid amalgam was prepared from 1.0 g. of rubidium and 20 g. of mercury; with benzophenone in ether an intense blue color was produced. Hydrolysis of the solution yielded benzopinacol. Similarly an intense blue color was formed when the liquid amalgam from 0.25 g. of cesium and 25 g. of mercury was shaken with benzophenone in ether; benzopinacol was isolated from the hydrolyzed mixture.

Reaction of Benzophenone with Calcium Amalgam.—Mixtures of 5 to 6 g. of benzophenone and 80 g. of 1% calcium amalgam in 125 cc. of ether were shaken for two weeks. The solution became dark green in color and after several days deposited a large amount of dark green crystals; after two weeks the solid was reddish-brown in color. Hydrolysis gave an 87% yield of benzopinacol.

Reaction of Benzophenone with Magnesium Amalgam.—Magnesium amalgam was prepared from 0.24 g. of magnesium ribbon and 36 g. of mercury heated under toluene; about twenty minutes was required for complete combination. The amalgam of this concentration is semi-liquid. The amalgam was added to a solution of 3.0 g. of benzophenone in 60 cc. of ether. After fifteen minutes of shaking the solution was blue and this color remained for a week; after twelve days the color was red. The yields of pinacol obtained after two days of shaking were 80% of the theoretical amount. Longer shaking seemed to decrease the yield. Perhaps the failure to obtain benzopinacol in our first experiments[6] with magnesium amalgam was due to the solid amalgam which was used; the amalgam probably became coated with magnesium oxide and the reaction was prevented. The low yields (6–7%) of pinacol obtained by Gilman and Brown[15] are explainable on the same basis. By employing the semi-liquid amalgam and shaking the mixture to expose fresh surfaces good yields of pinacol are obtained.

If a colorless solution of magnesium iodide is added to the blue solution obtained from benzophenone and magnesium amalgam, the blue color immediately changes to a cherry-red color which is like that obtained by the action of magnesium and magnesium iodide on benzophenone. The reaction is considered to be



$$\begin{matrix}(C_6H_5)_2C{-}O\\ |\\ (C_6H_5)_2C{-}O\end{matrix}\!>\!Mg + MgI_2 \rightleftarrows \begin{matrix}(C_6H_5)_2C{-}OMgI\\ |\\ (C_6H_5)_2C{-}OMgI\end{matrix} \qquad (4)$$

followed by a slight dissociation of the iodomagnesium pinacolate into the red iodomagnesium-ketyl radicals, $(C_6H_5)_2C{-}OMgI$. Furthermore, the same red color and no blue color results when benzophenone is reduced by a mixture of magnesium amalgam and magnesium iodide.

On the basis of color Bergmann and Schuchardt[16] decided that the red color of solutions of iodomagnesium pinacolate cannot be attributed to iodomagnesium-ketyls but to a magnesium compound, $(C_6H_5)_2COMg$, similar to benzophenone-disodium. Contrary to this view is the fact that the red color is formed from the start of the reaction; this means that the red compound is stable in the presence of a large excess of ketone, a circumstance that would be highly improbable if the red compound is like benzophenone-disodium and is similar to a Grignard reagent. Bergmann's prediction that if the compound, R_2COMgI, were formed it would remain in the monomolecular state like the sodium-ketyls and not associate to the pinacolate no longer has any weight since we have shown that even the sodium compounds are dimolecular.

The entire amount of iodomagnesium pinacolate can be converted by iodine to ketone and not only an amount corresponding to the quantity of colored material present

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[15] Gilman and Brown, THIS JOURNAL **52**, 1128 (1930).

[16] Bergmann and Schuchardt, *Ann.*, **487**, 285 (1931).

as Bergmann supposed. If the color were due to the presence of a small amount of magnesium compound, and if the color is destroyed by the action of iodine, then the solution should become colorless and remain so. As a matter of fact the red color continues to reappear *throughout* the solution; this occurs even after 90% of the pinacolate has been converted to ketone by the action of iodine, a fact explainable only by assuming that the colored compound is derived continuously from the pinacolate.

Finally, Bergmann's supposition that the formation of the red color when a Grignard reagent is added to a solution of pinacol is due to metallic magnesium that cannot be removed completely from the Grignard reagent is far from correct. By filtration of a Grignard reagent through hardened filter paper a solution can be obtained which is entirely free of suspended particles. This is especially easy to accomplish if one uses, as we do, pure, distilled magnesium[17] either in the form of rods or heavy ribbon. By means of this pure magnesium it is possible to prepare a *colorless* solution of ethylmagnesium iodide. If this colorless solution is filtered onto a solution of benzopinacol, a red colored solution is obtained which contains the equilibrium mixture: $R_2C(OMgI)\text{-}(IMgO)CR_2 \rightleftarrows 2R_2C\text{—}OMgI$.

Too much weight must not be placed on mere color phenomena in interpreting the structures of the metallo compounds. It is generally considered that the color of the sodium compounds is the color of the ketyl radicals; in fact the colors have been cited as proof of the radical nature of the compounds. In view of our results, may not the color be attributed to a quinonoid form of sodium pinacolate? The whole question of the origin of the color of the compounds is obscure; how little we know of the cause of the color is exemplified by the fact that the ketone-disodium compounds are likewise intensely colored.

Reaction of Fluorenone with Sodium.—Fluorenone was allowed to react with the calculated amount of sodium wire in the same manner as described for benzophenone. After a short time a heavy dark green precipitate was formed; this appeared to be a complex formed between the ketone and the sodium derivative because the solid disappeared as the reaction proceeded further. After twenty-four hours a large amount of muddy green solid was present; after three days the solution was dark green and contained a green precipitate. From the reaction between 5.0 g. of fluorenone and 0.64 g. of sodium wire there was obtained by hydrolysis after ten days a pale yellow solid which was found to consist of fluorenopinacol and a small amount of fluorenone. The fluorenopinacol was obtained in the form of colorless prisms by recrystallization of the mixture from benzene and alcohol; yield, 4.8 g. (95%); m. p. 188–190°. The compound was identical with the pinacol prepared from fluorenone by reduction by magnesium and magnesium iodide.[6]

In one experiment 6.0 g. of fluorenone was allowed to react with 1.0 g. (30% excess) of sodium. After thirteen days of shaking the mixture was hydrolyzed; it yielded 75% pinacol, 24% fluorenol and 1% of fluorenone; calculated, 70% pinacol and 30% fluorenol. When the crude product was recrystallized from alcohol two kinds of crystals were obtained; one kind was pinacol, the other form melted at 151°. This latter compound was found to be a complex produced by combination of fluorenol and fluorenopinacol and is similar to the complex which is formed between fluorenone and fluorenopinacol.[6] The proportions of each constituent present in the complex were determined by treating 1.08 g. of the compound with a solution of sodium ethylate; under these conditions the pinacol was converted to a mixture of fluorenone and fluorenol. The mixture of ketone and hydrol was separated by recrystallization from benzene, from which the fluorenol crystallizes with benzene of crystallization. The weights of fluore-

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[17] This magnesium, which is 99.7% pure, is made by the Aluminum Company of America, Niagara Falls, N. Y. This pure magnesium is recommended for making Grignard reagents having a high degree of purity.

none (0.38 g.) and of fluorenol (0.72 g.) obtained by this method indicated that the complex consists of one mole of pinacol to one mole of fluorenol. This result was confirmed by recrystallizing mixtures of different proportions of pinacol and fluorenol from benzene. From the mixture of two parts by weight (one mole) of pinacol to one part (one mole) of fluorenol, only the complex of melting point 151° was obtained; other proportions gave mixtures of the complex and one of the components.

Reaction of 2,2'-Dibenzoylbiphenyl with Sodium.—A mixture of 1.5 g. of 2,2'-dibenzoylbiphenyl and 80 g. of 2% sodium amalgam in 70 cc. of ether was shaken for four days. In this time no trace of color developed; a large amount of the sodium pinacolate was present as a colorless solid. The product which was obtained on hydrolysis of the mixture consisted of 1.1 g. (73%) of 9,10-diphenyldihydrophenanthrenediol of m. p. 202° and 0.4 g. (27%) of the stereoisomer of m. p. 178–179°. The mixture was separated by repeated recrystallization from methyl alcohol in which the lower melting isomer is more soluble than the other. The same products in similar proportions are obtained by reducing dibenzoylbiphenyl by a mixture of magnesium and magnesium iodide.[18] It is clear that the reductions by sodium and by the binary system are of the same nature.

It was found that the pinacol is unaffected by sodium alcoholate, unlike most pinacols. When 0.5 g. of pinacol was shaken with a solution of sodium alcoholate in ether and benzene no decomposition of the pinacol occurred in three hours. The stability of the pinacol is shown by the fact that it can be prepared from dibenzoylbiphenyl by reduction by zinc dust in potassium hydroxide solution.

Reaction of 4-Phenylbenzophenone and 4,4'-Diphenylbenzophenone with Sodium.—Five to ten gram portions of 4-phenylbenzophenone and 100 g. of 2% sodium amalgam in 120 cc. of ether were shaken for three weeks. In a short time an intensely colored blue-green solid appeared (complex). After some time this solid disappeared and a bright emerald-green mixture resulted which contained a light green precipitate. When the mixture was run into dilute acetic acid a large amount of pinacol precipitated. This was filtered off, washed with acetone and recrystallized from a mixture of chloroform and acetone, from which it was obtained in the form of colorless needles; m. p. 198°. In one experiment in which 6.0 g. of ketone had reacted, 5.5 g. (90%) of the pinacol was obtained. The product was found to be identical with 4,4'-diphenylbenzopinacol that is formed by reduction of the ketone by magnesium and magnesium iodide.[6] The result is of especial interest since the potassium derivative of this ketone was used by Schlenk in molecular weight determinations and was interpreted as being monomolecular.

In a similar manner 4,4',4'',4'''-tetraphenylbenzopinacol was obtained in 70% yields by hydrolysis of the sodium derivative of diphenylbenzophenone. When the solid pinacol was treated with a solution of sodium ethylate a green color was produced and the pinacol was cleaved into a mixture of ketone and hydrol.

Although Schlenk and Weickel stated that benzene solutions of the sodium derivatives of the ketones are unfortunately colloidal so that the structures could not be determined by molecular weight determinations but only from the reactions of the compounds, nevertheless, Schlenk and Thal made use of determinations of the molecular weight in ether to prove that the compounds are monomolecular. In addition to the probability that the ether solutions are likewise colloidal there arises the question whether the reaction between the ketone and the metal was complete. This is important when one considers that a difference of less than one-tenth of a degree elevation in the boiling point determined whether the compound was completely monomolecular or entirely dimolecular. We have carried out an experiment which shows that the results of the determinations are of doubtful value. We have shaken in a sealed tube in an atmos-

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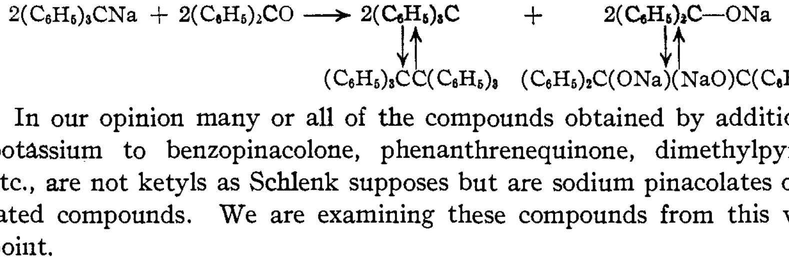
[18] Bachmann, THIS JOURNAL, 54, 1969 (1932).

phere of nitrogen a mixture of 0.2144 g. of 4-phenylbenzophenone and 0.035 g. of potassium in 17.5 g. of ether, the exact proportions used by Schlenk in a molecular weight determination. After the mixture had been shaken for a few days a considerable amount of potassium pinacolate was present as an insoluble precipitate. This precipitate did not dissolve when the mixture was warmed to the boiling point of the solution. These results show that Schlenk and Thal either had not carried out the reaction to completion or else had supersaturated solutions. In either case the determinations would have no value.

Conclusion

All of the reactions of the sodium derivatives of the ketones that have been studied so far are in harmony with our view that the compounds are chiefly sodium pinacolates. We are now examining the reactions of the compounds with a variety of reagents and we shall publish the results in the near future. It is not unlikely that the structures of the compounds formed by the action of sodium on ketones in liquid ammonia[19] are likewise dimolecular; at any rate a reëxamination of the products from this point of view may prove of value.

The reaction between sodium triphenylmethyl and benzophenone must now be considered to be analogous to the reaction between triphenylmethylmagnesium bromide and benzophenone[20] which yields triphenylmethyl and bromomagnesium pinacolate; the sodium triphenylmethyl reaction should now be written



$$\begin{array}{cccc} 2(C_6H_5)_3CNa + 2(C_6H_5)_2CO \longrightarrow & 2(C_6H_5)_3C & + & 2(C_6H_5)_2C\text{—}ONa \\ & \downarrow\uparrow & & \downarrow\uparrow \\ & (C_6H_5)_3CC(C_6H_5)_3 & & (C_6H_5)_2C(ONa)(NaO)C(C_6H_5)_2 \end{array}$$

In our opinion many or all of the compounds obtained by addition of potassium to benzopinacolone, phenanthrenequinone, dimethylpyrone, etc., are not ketyls as Schlenk supposes but are sodium pinacolates or related compounds. We are examining these compounds from this viewpoint.

Finally we are studying the action of metals, free and in the form of amalgams, on aldehydes, esters and other compounds in the hope of clearing up the reactions undergone by these compounds.

Summary

The products obtained by the action of sodium on aromatic ketones in anhydrous ether are chiefly sodium pinacolates, $R_2C(ONa)(NaO)CR_2$, and not free ketyl radicals, $R_2C\text{—}ONa$, existing in the monomolecular state as has been supposed up to this time.

Hydrolysis of the sodium pinacolates with dilute acid gives pinacols in excellent yields. In order to account for the reactions of the pinacolates with certain reagents it is assumed that the pinacolate is in equilibrium

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(19) Wooster, THIS JOURNAL, **50**, 1388 (1928), concluded that in liquid ammonia the monosodium derivative appears to be a typical radical in accordance with the views of Schlenk.

(20) Bachmann, *ibid.*, **53**, 2758 (1931).

with small amounts of ketyl radicals, $2R_2C—ONa \rightleftarrows R_2C(ONa)(NaO)CR_2$. The ketyl radicals are intermediates in the reduction of the ketone to the pinacolate.

Other metals such as lithium, potassium, rubidium, cesium, beryllium, magnesium and calcium react in the manner of sodium. In all cases the products are metal pinacolates which differ from the sodium pinacolate and from each other only in degree.

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RECEIVED SEPTEMBER 12, 1932
PUBLISHED MARCH 7, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

Quinazolines. V. The Partial Hydrolysis of 2,4-Dialkoxyquinazolines with the Formation of 2-Alkoxy-4-ketodihydroquinazolines

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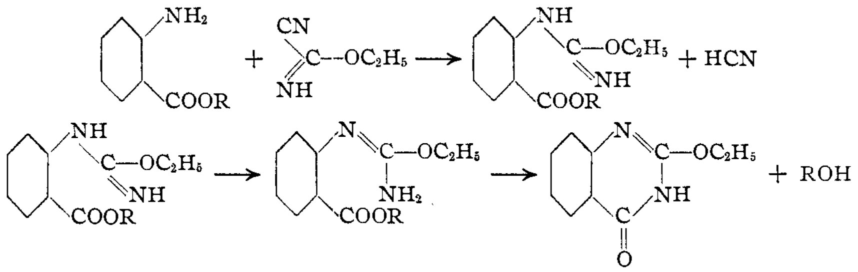
The earliest derivatives of quinazoline on record were prepared by Peter Griess in 1869. By the action of cyanogen on anthranilic acid in alcoholic solution he obtained 2-ethoxy-4-ketodihydroquinazoline, and from this, through hydrolysis with hydrochloric acid, benzoylene urea.[1] In 1910 Finger and Zeh[2] condensed cyanimidocarbonic acid ethyl ester with methyl and ethyl anthranilates, and found that the products were the same in both cases. Their compound was subsequently shown to be identical with the 2-ethoxy-4-ketodihydroquinazoline of Griess, and the reactions leading to its formation were explained as follows[3]



Griess' reaction probably follows a similar course, the addition product, $(CN)_2NH_2C_6H_4COOH$, first formed losing HCN to form a N-cyanoanthranilic acid, which then adds alcohol and rearranges as indicated, the 3,4-dihydro structure[4] being preferred since the substance, on methylation followed by hydrolysis, is transformed into 3-methylbenzoylene urea.[5]

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(1) Griess, *Ber.*, **2**, 415 (1869).
(2) Finger and Zeh, *J. prakt. Chem.*, [2] **81**, 468 (1910).
(3) Finger and Günzler, Berichtigung, *ibid.*, [2] **83**, 198 (1911).
(4) See also Bogert and Gortner, THIS JOURNAL, **32**, 123 (1910).
(5) Finger, *J. prakt. Chem.*, [2] **81**, 470 (1910).