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

# The Reaction between Aromatic Ketones and Sodium. II. Reactions of Sodium Pinacolates

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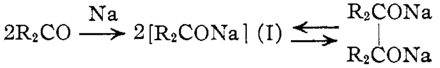
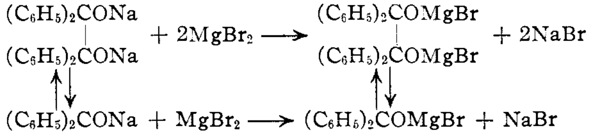
It was shown recently[1] that sodium ketyl radicals (I) which are initially formed in the reaction between aromatic ketones and sodium do not remain in the monomolecular state as has been supposed[2] but associate practically entirely to the dimolecular form, sodium pinacolate (II).



$$2R_2CO \xrightarrow{Na} 2[R_2CONa]\ (I) \rightleftarrows \begin{array}{c} R_2CONa \\ | \\ R_2CONa \end{array} \quad (II) \qquad (1)$$

Hydrolysis of the mixture by dilute acetic acid gives nearly quantitative yields of pinacol $R_2C(OH)(HO)CR_2$. If water alone is used for hydrolysis the pinacol that is formed is rapidly decomposed by the alkali into a mixture of ketone and hydrol, and it is the overlooking of this reaction that deceived previous investigators in their interpretation of the structure of the sodium compounds. Since pinacols are stable to magnesium hydroxide it occurred to us to add a magnesium salt to the ether–benzene solution of the sodium compounds so that on addition of water the sodium hydroxide would be converted to magnesium hydroxide and the decomposition of the pinacol would be avoided. We obtained excellent yields of pinacols by this procedure but, we believe, for a slightly different reason than for the one we had in mind. It was found that an exothermal reaction takes place when magnesium bromide is added to the compound obtained from benzophenone and sodium; the blue color of the sodium compound is immediately replaced by the red color of the bromomagnesium derivative;[3] addition of water gives a nearly quantitative yield of benzo pinacol. The following reactions appear to occur



$$\begin{array}{ccccc} \begin{array}{c}(C_6H_5)_2CONa\\ |\\ (C_6H_5)_2CONa\end{array} & + 2MgBr_2 \longrightarrow & \begin{array}{c}(C_6H_5)_2COMgBr\\ |\\ (C_6H_5)_2COMgBr\end{array} & + 2NaBr & (2) \\ \uparrow\downarrow & & \uparrow\downarrow & & \\ (C_6H_5)_2CONa & + MgBr_2 \longrightarrow & (C_6H_5)_2COMgBr & + NaBr & \end{array}$$

Magnesium iodide reacts in a similar manner. Two other representative ketones, phenyl *p*-biphenyl ketone and fluorenone, likewise gave excellent yields of the corresponding pinacols when the sodium derivatives were treated with magnesium bromide prior to hydrolysis (see Table I). Indeed, this procedure makes it possible to utilize the sodium derivatives to prepare pinacols. These results show clearly the close relationship between the sodium derivatives and the halogen-magnesium derivatives of ketones.

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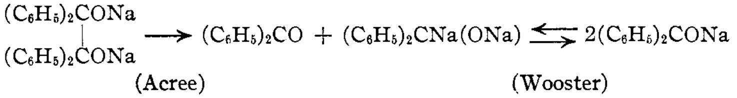
[1] Bachmann, THIS JOURNAL, **55**, 1179 (1933).

[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] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

**Reaction of Sodium Pinacolates with Grignard Reagents.**—Acree[4] believed that sodium benzopinacolate, produced in the reaction between sodium and benzophenone, breaks down spontaneously at room temperature into benzophenone and its disodium salt. A similar concept has been revived recently by Wooster[5] except that he considers that sodium ketyl may be in equilibrium with the ketone and the salt.

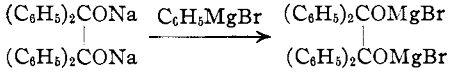


$$\begin{array}{c}(C_6H_5)_2CONa\\ |\\ (C_6H_5)_2CONa\end{array} \longrightarrow (C_6H_5)_2CO + (C_6H_5)_2CNa(ONa) \rightleftarrows 2(C_6H_5)_2CONa \quad (3)$$

(Acree) (Wooster)

Since our results have shown that the sodium compound is nearly entirely sodium pinacolate it follows that benzophenone and its disodium salt cannot be present except in very small amounts. We have now employed several reagents in order to determine whether benzophenone is present. Addition of a reagent such as sodium phenyl which is capable of combining rapidly with benzophenone should yield triphenylcarbinol if ketone is present and since the ketone is removed from the equilibrium by this reaction complete decomposition of the pinacolate should occur. Actually, no triphenylcarbinol was obtained when the reaction mixture from benzophenone and sodium was treated with sodium phenyl or with phenylmagnesium bromide.

Although no triphenylcarbinol is formed when phenylmagnesium bromide is added to the sodium compound, the Grignard reagent is not without action; a reaction occurs which is similar to that produced by magnesium bromide: the sodium pinacolate is converted to bromomagnesium pinacolate, and an excellent yield of benzopinacol is obtained on hydrolysis.



$$\begin{array}{c}(C_6H_5)_2CONa\\ |\\ (C_6H_5)_2CONa\end{array} \xrightarrow{C_6H_5MgBr} \begin{array}{c}(C_6H_5)_2COMgBr\\ |\\ (C_6H_5)_2COMgBr\end{array} \quad (4)$$

Other Grignard reagents such as ethylmagnesium iodide and even triphenylmethylmagnesium bromide react in a similar manner.

In Table I are given the results which were obtained when the sodium derivatives of benzophenone, phenyl $p$-biphenyl ketone and fluorenone were treated with a magnesium salt or with a Grignard reagent prior to hydrolysis.

## Experimental

**Reaction of Sodium Pinacolates with Magnesium Salts.**—A colorless solution of magnesium bromide prepared from 10 g. of mercuric bromide[3] was added to the bright blue sodium compound obtained from 5.0 g. of benzophenone in a mixture of anhydrous ether and benzene. The blue color of the sodium compound immediately gave way to a transparent cherry-red color which was like that obtained by reducing benzophenone by a mixture of magnesium and magnesium bromide;[3] at the same time a colorless pre-

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[4] Acree, *Am. Chem. J.*, **29**, 588 (1903).

[5] Wooster, THIS JOURNAL, **50**, 1388 (1928).

TABLE I

YIELDS OF PINACOLS FROM SODIUM DERIVATIVES OF KETONES

| Ketones | Reagent added to sodium derivative | Pinacols, yield, % |
|---|---|---|
| Benzophenone | $MgBr_2$ | 90 |
| Benzophenone | $MgI_2$ | 90 |
| Benzophenone | $C_6H_5MgBr$ | 90 |
| Benzophenone | $C_2H_5MgI$ | 94 |
| Benzophenone | $(C_6H_5)_3CMgBr$ | 80 |
| Phenyl *p*-biphenyl ketone | $MgBr_2$ | 80 |
| Phenyl *p*-biphenyl ketone | $C_2H_5MgI$ | 90 |
| Fluorenone | $MgI_2$ | 90 |
| Fluorenone | $C_2H_5MgI$ | 90 |
| Fluorenone | $MgBr_2$ | 95 |

cipitate of sodium bromide was formed. After fifteen minutes the solution was poured into water with stirring and the mixture was acidified with acetic acid. The benzopinacol which was obtained from the ether–benzene solution was recrystallized from a mixture of chloroform and alcohol; yield, 4.5 g.

A solution of magnesium iodide prepared from magnesium and iodine in a mixture of ether and benzene acted similarly. Hydrolysis gave 4.5 g. of benzopinacol from 5.0 g. of benzophenone.

The reactions between the sodium derivatives of phenyl *p*-biphenyl ketone and fluorenone and magnesium salts were carried out in a similar fashion. When the brilliant green compound obtained by the action of sodium on phenyl *p*-biphenyl ketone was treated with a solution of magnesium bromide the mixture became dark blue; hydrolysis gave 4,4′-diphenylbenzopinacol.[3]

The intense black–green color of the sodium derivative of fluorenone changed to a light orange-red color when a colorless solution of magnesium bromide or magnesium iodide was added. Hydrolysis after one hour gave yields of fluorenopinacol varying from 4.5 to 4.8 g. from 5.0 g. of fluorenone.

**Reaction of Sodium Pinacolates with Grignard Reagents.**—Addition of a filtered colorless solution of ethylmagnesium iodide to the sodium compound from 5.0 g. of benzophenone changed the bright blue color to the cherry-red color characteristic of solutions of iodomagnesium benzopinacolate. After one hour the mixture was poured into water; a considerable evolution of gas (ethane) occurred; 4.7 g. of benzopinacol was isolated.

We conclude that in the reaction between sodium benzopinacolate and ethylmagnesium iodide the products are iodomagnesium pinacolate, sodium iodide and magnesium diethyl; the latter compound furnishes the ethane on hydrolysis. Analogous reactions take place when the sodium benzopinacolate is treated with a solution of phenylmagnesium bromide and with a solution of triphenylmethylmagnesium bromide. In the latter case, the solution became intense red, indicative of the formation of some triphenylmethyl sodium; hydrolysis gave 3.5 g. of triphenylmethane and 4.0 g. of benzopinacol from 5.0 g. of benzophenone originally taken. In none of these reactions was there found any tertiary alcohol corresponding to the action of the Grignard reagent on benzophenone.

Addition of a solution of ethylmagnesium iodide to the green sodium derivative from 5.0 g. of phenyl *p*-biphenyl ketone gave a blue colored mixture; hydrolysis gave 4.5 g. of 4,4′-diphenylbenzopinacol. In a similar fashion the black-green color of the sodium derivative of fluorenone was changed to an orange-red color by ethylmagnesium iodide; hydrolysis gave 4.5 g. of fluorenopinacol from 5.0 g. of ketone.

**Sodium Pinacolate + Sodium Phenyl.**—Mercury diphenyl was prepared by interaction of phenylmagnesium bromide and mercuric bromide. Borgstrom and Dewar,[6] who studied this reaction recently, obtained yields of 37–54% of mercury diphenyl. Using the same relative amounts of reagents employed by those investigators we have obtained an 81% yield of recrystallized product by the following procedure. Phenylmagnesium bromide was prepared from 61 g. of bromobenzene and excess of magnesium in 200 cc. of ether; the Grignard reagent was decanted, 200 cc. of benzene was added and then 60 g. of dry mercuric bromide. After the mixture had been refluxed for three days on a steam-bath it was poured onto water; dilute hydrochloric acid was added, the ether–benzene solution was filtered from insoluble material and the solvent was evaporated. The crude mercury diphenyl was recrystallized by adding alcohol to a saturated solution of the compound in chloroform; yield, 48 g.; m. p. 122–124°.

Sodium phenyl was prepared in the following simple manner: 4.0 g. of mercury diphenyl was added to 2.0 g. of sodium ribbon suspended in 100 cc. of benzene in a 100-cc. flask. The flask was stoppered and shaken mechanically for several hours; the reaction began at once and appeared to be at an end in less than one hour. The amount of sodium that was employed furnished a liquid sodium amalgam as the by-product; after being allowed to settle, the amalgam was frozen by placing the flask in cold water; the suspension of sodium phenyl was then decanted. A trial experiment with 2.5 g. of benzophenone gave a 93% yield of triphenylcarbinol when the reaction with the ketone was allowed to proceed for fifteen minutes.

When a suspension of sodium phenyl in benzene from 4.0 g. of mercury diphenyl was added to the blue sodium derivative obtained from 5.0 g. of benzophenone, no visible reaction took place. The mixture retained the blue color; had reaction taken place then the color would have been changed to an intense red as more and more benzophenone-disodium was produced (Equation 3). The mixture was allowed to stand for twenty-four hours and was then hydrolyzed; an excellent yield of benzopinacol but no triphenylcarbinol was obtained. Although the sodium phenyl is gradually decomposed by the ether, it was found that on addition of a certain amount of benzophenone to the mixture an equivalent quantity of triphenylcarbinol was found when the mixture was hydrolyzed. We are now studying the action of lithium phenyl, which is stable in ether.

## Summary

The sodium derivatives of ketones are converted by magnesium bromide or magnesium iodide into halogen-magnesium pinacolates; the latter compounds can be hydrolyzed readily to pinacols. This reaction makes it possible to obtain pinacols without difficulty from the sodium derivatives.

Grignard reagents react with the sodium compounds in the manner of magnesium salts and give the corresponding halogen-magnesium pinacolates.

The results reported in this paper are in complete agreement with our recent findings that the sodium derivatives of aromatic ketones are sodium pinacolates $R_2C(ONa)(NaO)CR_2$, presumably in equilibrium with a very small amount of sodium ketyl radicals $R_2CONa$.

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RECEIVED JANUARY 20, 1933
PUBLISHED JULY 6, 1933

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[6] Borgstrom and Dewar, THIS JOURNAL, **51**, 3387 (1929).