Cholesterol Oxide.—Eight-tenths of a gram of cholesterol (Eastman Kodak C. P. product) was mixed with a large excess of camphoric acid peracid in 200 cc. of chloroform and the mixture allowed to stand at 0° for five days. The mixture was then shaken twice, each time with 200 cc. of 1 *N* sodium hydroxide solution, then with water and dried over calcium chloride. It was filtered and the chloroform removed by distillation. The residue, a white solid (m. p. 125–130°), was recrystallized three times from ethyl acetate, giving a constant melting point of 141–142°. Westphalen[6] gives a melting point of 140–141° for cholesterol oxide.

Hydrolysis of Cholesterol Oxide.—To prove definitely that our product was the oxide, 0.4 g. of the latter was heated with 4 cc. of water in a sealed tube at 115° for twelve hours. The resulting white solid was recrystallized twice from ethyl alcohol, m. p. 239.3°. The melting point of cholestantriol has been reported by Pickard and Yates[7] and by Westphalen[6] to be 239°.

Summary

1. The stability of camphoric acid peracid and benzoperacid, in chloroform, has been measured at 0° and at 25°.
2. At 25° camphoric acid peracid is more stable, in chloroform solution, than benzoperacid, while at 0° the difference in stability is not significant.
3. Camphoric acid peracid was found to add quantitatively to certain types of unsaturated substances.
4. Pinene and cholesterol oxides have been definitely isolated from the interaction of camphoric acid peracid and *d*-pinene and cholesterol.

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[6] Westphalen, *Ber.*, **48**, 1064 (1915).

[7] Pickard and Yates, *J. Chem. Soc.*, **93**, 1684 (1908).

CAMBRIDGE A, MASSACHUSETTS

RECEIVED JULY 20, 1932
PUBLISHED JANUARY 11, 1933

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

The Action of Sodium Alcoholate and of Sodium Amalgam on Aromatic Pinacols

BY W. E. BACHMANN

Reaction of Pinacols with Sodium Alcoholate.—According to Schlenk and Thal[1] sodium ketyl radicals are formed when a suspension of benzopinacol in alcohol is treated with a concentrated alcoholic solution of sodium alcoholate. We found, in agreement with Schlenk and Thal, that the deep blue color of the ketyl is produced in the reaction, but we observed further that the color disappeared completely after a short time. At first this disappearance of color was attributed to oxidation of the ketyl by oxygen of the air. That this was not the case was definitely proved when the same disappearance of color occurred when air was excluded. Hydrolysis of the colorless solution gave a mixture of equal parts of benzophenone and benzohydrol.

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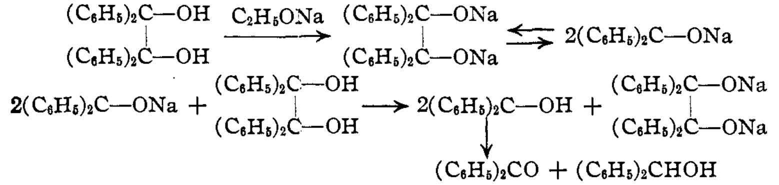
[1] Schlenk and Thal, *Ber.*, **46**, 2841 (1913).

An insight into the mechanism of the reaction was gained by the observation that a small amount (1% by moles) of sodium alcoholate suffices to produce exactly the same phenomena: formation of the blue color followed by disappearance of the color; moreover, it was found that all of the pinacol was converted to ketone and hydrol by this small amount of sodium alcoholate. The mechanism of the reaction is considered to be the following: sodium pinacolate is formed which partly dissociates into sodium ketyl radicals; the radicals so formed then react with unchanged pinacol or with alcohol



$$\begin{array}{l}(C_6H_5)_2C{-}OH\\ \quad |\\ (C_6H_5)_2C{-}OH\end{array} \xrightarrow{C_2H_5ONa} \begin{array}{l}(C_6H_5)_2C{-}ONa\\ \quad |\\ (C_6H_5)_2C{-}ONa\end{array} \rightleftarrows 2(C_6H_5)_2C{-}ONa \qquad (1)$$

$$2(C_6H_5)_2C{-}ONa + \begin{array}{l}(C_6H_5)_2C{-}OH\\ \quad |\\ (C_6H_5)_2C{-}OH\end{array} \longrightarrow 2(C_6H_5)_2C{-}OH + \begin{array}{l}(C_6H_5)_2C{-}ONa\\ \quad |\\ (C_6H_5)_2C{-}ONa\end{array} \qquad (2)$$

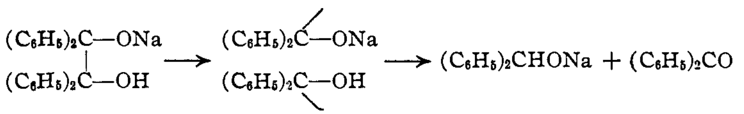
$$\downarrow$$

$$(C_6H_5)_2CO + (C_6H_5)_2CHOH \qquad (3)$$

The products are diphenylhydroxymethyl and sodium pinacolate. The diphenylhydroxymethyl immediately disproportionates into benzophenone and benzohydrol; the sodium pinacolate can dissociate into ketyls which in turn can react with more pinacol. This mechanism satisfactorily accounts for the production and the disappearance of the color as well as for the products of the reaction. Moreover, it is clear that only a small amount of sodium alcoholate is necessary; as soon as a small amount of sodium pinacolate is produced, decomposition of the remaining pinacol is assured.

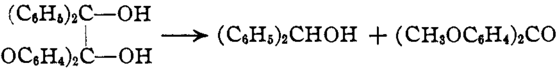
If this mechanism is correct, then according to Equation 2 a small amount of ketyl should be capable of promoting the decomposition of a large amount of pinacol. Such was found to be the case. When a small amount of ketyl was added to a solution of benzopinacol, the blue color remained for a time, then disappeared, and it was found that all of the pinacol had been converted to a mixture of ketone and hydrol. From this it follows that benzopinacol will be decomposed into a mixture of ketone and hydrol by the addition of a small amount of any sodium compound which is capable of replacing the hydrogen of the hydroxyl group by sodium.

It is not unlikely that the following reaction takes place in addition or in some cases exclusively: only one hydrogen is replaced by sodium and the mono-sodium pinacolate which results undergoes cleavage either with or without the intermediate formation of free radicals



$$\begin{array}{l}(C_6H_5)_2C{-}ONa\\ \quad |\\ (C_6H_5)_2C{-}OH\end{array} \longrightarrow \begin{array}{l}(C_6H_5)_2\overset{/}{C}{-}ONa\\ \\ (C_6H_5)_2\underset{\backslash}{C}{-}OH\end{array} \longrightarrow (C_6H_5)_2CHONa + (C_6H_5)_2CO \qquad (4)$$

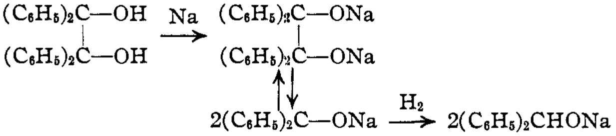
Support for this mechanism is found in the fact that the quantity of color seems less than that which would be expected if all of the pinacol passed through the ketyl stage. This second formulation would account for the results obtained with asymmetrical pinacols. When *as*-diphenyldianisylglycol reacts with sodium alcoholate the products are benzohydrol and dianisyl ketone exclusively



$$\begin{matrix}(C_6H_5)_2C-OH\\ |\\ (CH_3OC_6H_4)_2C-OH\end{matrix} \longrightarrow (C_6H_5)_2CHOH + (CH_3OC_6H_4)_2CO \qquad (5)$$

If the reaction proceeded according to the first formulation, one should expect the products to be benzophenone, benzohydrol, dianisyl ketone and dianisylcarbinol.

Reaction of Pinacols with Sodium Amalgam.—Linnemann,[2] the discoverer of benzopinacol, reported that benzopinacol is converted to benzohydrol when its alcoholic solution is treated with sodium amalgam and he formulated the reaction as $C_{26}H_{22}O_2 + H_2 = 2C_{13}H_{12}O$. Thörner and Zincke[3] did not believe that the pinacol was reduced directly to the hydrol in this manner; they considered that reduction to hydrol occurred only after previous cleavage of the pinacol into a mixture of ketone and hydrol. More recently, Schlenk and Weickel[4] reported that an entirely different reaction takes place. According to these investigators, hydrogen is evolved and the product is sodium ketyl $(C_6H_5)_2C-ONa$. If this reaction is correct, then hydrolysis would give a mixture of benzophenone and benzohydrol and not benzohydrol alone as Linnemann had reported. We have now found that in the reaction between benzopinacol and sodium amalgam (1.5%) in a mixture of anhydrous ether and benzene, no hydrogen is evolved; the solution becomes dark blue but after a short time nearly colorless; hydrolysis gives benzohydrol in nearly quantitative yield. Several reactions seem to be involved. In the first place, the reaction may be assumed to proceed as follows



$$\begin{tikzcd} \begin{matrix}(C_6H_5)_2C-OH\\ |\\ (C_6H_5)_2C-OH\end{matrix} \arrow[r, "Na"] & \begin{matrix}(C_6H_5)_2C-ONa\\ |\\ (C_6H_5)_2C-ONa\end{matrix} \arrow[d, shift left] & \\ & 2(C_6H_5)_2C-ONa \arrow[u, shift left] \arrow[r, "H_2"] & 2(C_6H_5)_2CHONa \end{tikzcd} \qquad (6)$$

We believe that very little of this reaction takes place. Instead, as soon as a small amount of sodium pinacolate or sodium benzohydrolate is formed, decomposition of the pinacol rapidly takes place; the mixture of benzophenone and benzohydrol so produced then reacts with the amalgam and gives benzohydrol. In support of this view it was found that if the reaction is interrupted before reduction is complete, there is obtained a mixture of pinacol, benzophenone and benzohydrol. Moreover, separate experiments showed that a mixture of equal parts of benzophenone and benzohydrol in

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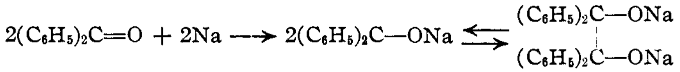
[2] Linnemann, *Ann.*, **133**, 28 (1865).

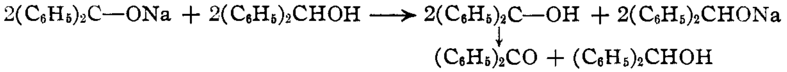
[3] Thörner and Zincke, *Ber.*, **10**, 1474 (1877).

[4] Schlenk and Weickel, *ibid.*, **44**, 1184 (1911).

ether and benzene reacts rapidly with sodium amalgam and gives benzohydrol; during the reduction the solution becomes dark blue in color and this color disappears when the reduction is complete. In all respects this reaction is like the reaction of the pinacol with amalgam. The deep blue color indicates that the reduction proceeds through the intermediate formation of sodium ketyl radicals and the reactions that occur are best expressed by the formulation



$$2(C_6H_5)_2C{=}O + 2Na \longrightarrow 2(C_6H_5)_2C{-}ONa \rightleftarrows \begin{array}{l}(C_6H_5)_2C{-}ONa\\ \quad\;\; | \\ (C_6H_5)_2C{-}ONa\end{array} \qquad (7)$$



$$2(C_6H_5)_2C{-}ONa + 2(C_6H_5)_2CHOH \longrightarrow \underset{\displaystyle (C_6H_5)_2CO + (C_6H_5)_2CHOH}{\underset{\downarrow}{2(C_6H_5)_2C{-}OH}} + 2(C_6H_5)_2CHONa \qquad (8)$$

It is possible that the ketyl is reduced to some extent by the hydrogen liberated by the action of the amalgam on the benzohydrol although experiment showed that the amalgam and hydrol react very slowly with each other. Forty per cent. sodium amalgam reacts with benzopinacol in a similar manner without liberation of hydrogen; the product is nearly pure benzohydrol.

Not only benzopinacol but also substituted benzopinacols react with sodium alcoholate and with sodium amalgam. In each case the solution assumes the color characteristic of the ketyl corresponding to the ketone. In the following table are presented the results obtained by treating a number of pinacols with sodium alcoholate and with sodium amalgam.

TABLE I

ACTION OF SODIUM ALCOHOLATE AND SODIUM AMALGAM ON PINACOLS

Pinacol	Sodium ethylate Color of solution	Yield, % Ketone	Hydrol	Sodium amalgam Color of solution	Yield, % hydrol
Benzopinacol	Blue	50	50	Blue	98
4,4'-Diphenylbenzopinacol	Green	50	50	Green	95
4,4',4'',4'''-Tetraphenylbenzopinacol	Green	50	50	Green	98
Fluorenopinacol	Brown-green	50	50	Brown-green	95
4,4',4'',4'''-Tetramethylbenzopinacol				Blue	95
as-Diphenyldianisylglycol	Blue	50	50		

Experimental

Benzopinacol (1 Mole) + Sodium Ethylate (0.1 Mole).—Although the reaction between benzopinacol and sodium ethylate takes place in alcoholic solution, the rate of reaction is slow because the pinacol is not very soluble in alcohol. As a rule a mixture of equal volumes of anhydrous ether and benzene was used. In all experiments air was excluded; this was usually accomplished by having the mixture completely fill the flask. The rate of reaction depends upon the concentration of sodium ethylate. When 0.01 mole of sodium ethylate was used for each mole of pinacol about two hours was required for decomposition of twenty grams of pinacol. This time was shortened to a few minutes when 0.1 mole of alcoholate was used.

To 1 cc. of absolute alcohol contained in a 150-cc. Erlenmeyer flask was added 0.12 g. of sodium. The sodium alcoholate was dissolved in ether and benzene, 20 g. of benzopinacol was added, and the flask was then filled with solvent, stoppered and shaken. Almost immediately the solution became green and then dark blue in color; the large amount of solid pinacol disappeared; after a few minutes the color became lighter and after ten minutes the solution was colorless. Hydrolysis with dilute acid gave an oil which consisted of equivalent quantities of benzophenone and benzohydrol. It is difficult to separate this mixture quantitatively into its two components. The proportion of benzophenone in the mixture was determined by treating a portion of the oil with phenylhydrazine and estimating the amount of benzophenone-phenylhydrazone that was formed. In another portion the amount of benzohydrol was estimated in the form of the urethan formed with phenyl isocyanate.

Experiments with a number of alcoholates were carried out in a similar manner. Sodium methylate, sodium isopropylate, sodium benzohydrolate, potassium ethylate and lithium methylate induced decomposition of the pinacol. Neither magnesium methylate nor calcium methylate reacted with benzopinacol. The magnesium methylate was prepared by allowing 0.03 g. of magnesium ribbon to react with 1 cc. of methyl alcohol; the alcoholate was dissolved in 30 cc. of ether and benzene and 1 g. of benzopinacol was added. No color developed in the course of twenty-four hours and the pinacol was recovered practically unchanged. In like manner no reaction occurred when 1 g. of benzopinacol was shaken for twenty-four hours with a solution of calcium methylate which had been prepared from 0.05 g. of calcium and 1 cc. of methyl alcohol in ether and benzene.

It is now easy to interpret the results that have been reported in the past on the behavior of pinacols in the presence of alkali. Thus, Thörner and Zincke found that benzopinacol is cleaved into a mixture of ketone and hydrol by the action of a boiling alcoholic solution of potassium hydroxide. We found that the reaction between benzopinacol and an alcoholic solution of potassium hydroxide takes place readily at room temperature; in the reaction the blue color of the ketyl radicals is visible. Cohen[5] observed that complete decomposition of pinacol occurred even when small amounts of alcoholic potassium hydroxide were employed. A number of investigators have followed the directions of Thörner and Zincke; of these only Montagne and Koopal[6] report that colors are visible during the reaction. They report that benzopinacol gave a feeble blue color only when it was heated with an alcoholic solution of potassium hydroxide; tetrachlorobenzopinacol gave a blue color even at room temperature and this color disappeared on shaking the solution and then reappeared. Their failure to obtain a color with benzopinacol at room temperature as well as the loss of color on shaking the solution are attributed to oxidation of the ketyl radicals by oxygen of the air.

Benzopinacol + Sodium Ketyl.—A solution of 0.1 g. of benzophenone in 20 cc. of ether and benzene was shaken with a small amount of 40% sodium amalgam which was wrapped in a piece of filter paper. As soon as the solution showed the blue color of the sodium ketyl, the amalgam was withdrawn and 1.0 g. of benzopinacol was introduced. The blue color remained as long as pinacol was present. After five minutes the colorless solution was hydrolyzed; it was found that all of the pinacol was converted to a mixture of benzophenone and benzohydrol.

Substituted Pinacols + Sodium Ethylate.—A stock solution of sodium ethylate was prepared by dissolving the alcoholate from 0.23 g. of sodium and 5 cc. of alcohol in a mixture of ether and benzene to make 100 cc. of solution. Enough of this solution was used for 1 g. of pinacol to correspond to 0.1 mole of alcoholate per mole of pinacol.

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[5] Cohen, *Rec. trav. chim.*, **38,** 72, 113 (1919).

[6] Montagne and Koopal, *ibid.*, **29,** 148 (1910).

One gram of pinacol was suspended in 30 cc. of ether and benzene mixture in a test-tube and the sodium ethylate solution (3–5 cc.) was added. The solution became colored as soon as the mixture was shaken; as a rule the color disappeared after a few minutes. In most cases the mixture of ketone and hydrol was resolved into the two components by making use of the differences in solubilities of the two compounds. The yields of pure ketone and of pure hydrol which were isolated always corresponded to more than 90% of that theoretically possible.

The mixture of 4-phenylbenzophenone and 4-phenylbenzohydrol was separated by recrystallization from *n*-propyl alcohol; the ketone crystallizes out while the more soluble hydrol can be isolated from the liquid. 4,4′-Diphenylbenzohydrol can be easily separated from the corresponding ketone by warming the mixture with enough *n*-propyl alcohol to dissolve the hydrol (6 cc. per gram); the ketone is practically insoluble in the hot alcohol.

Fluorenone is readily separated from fluorenol by dissolving the mixture of the two in hot benzene; on cooling, fluorenol crystallizes out in the form of the insoluble addition compound with benzene. The mixture of benzohydrol and 4,4′-dimethoxybenzophenone which was obtained from *as*-diphenyldianisylglycol was treated with 10 cc. of 80% alcohol; this solution dissolves all of the hydrol but only a trace of the ketone. In this manner from 1 g. of pinacol there was obtained 0.55 g. (96%) of 4,4′-dimethoxybenzophenone and 0.45 g. (96%) of benzohydrol. Erdmann[7] reported that *as*-diphenyldi-*p*-tolylglycol was decomposed into a mixture of benzohydrol and di-*p*-tolyl ketone when it was heated with an alcoholic solution of potassium hydroxide.

When xanthopinacol was treated with a solution of sodium ethylate the solution became intensely blue in color. From the mixture xanthone but not xanthydrol was isolated in a pure state.

Benzopinacol + Sodium Amalgam (1.5%).—Three grams of benzopinacol was shaken with 65 g. of 1.5% sodium amalgam in a mixture of 30 cc. of ether and 30 cc. of benzene. In a short time the mixture was dark blue in color. After one-half hour most of the color had disappeared; after two hours the solution was nearly colorless. Hydrolysis gave 2.95 g. (98%) of pure benzohydrol. It was found that the greater part of the reaction is over in a short time. Thus, in one experiment the mixture though still colored was hydrolyzed after fifteen minutes of shaking and there was obtained a 95% yield of benzohydrol.

The substituted pinacols were allowed to react with sodium amalgam in the same manner. As a rule the mixture was hydrolyzed after being shaken for two hours. The results of these experiments are recorded in Table I.

Benzophenone + Benzohydrol + Sodium Amalgam (1.5%).—Sixty-five grams of 1.5% sodium amalgam was added to a solution of 1.50 g. of benzophenone and 1.52 g. of benzohydrol in 60 cc. of ether and benzene. After less than a minute of shaking the solution was blue in color; after one-half hour most of the color had disappeared and after two hours the solution was nearly colorless. Hydrolysis gave 2.90 g. (97%) of benzohydrol. In another experiment the solution was hydrolyzed after fifteen minutes of shaking; the yield of benzohydrol was nearly quantitative.

Benzopinacol + Sodium Amalgam (40%).—One gram of benzopinacol was added to 2.5 g. of 40% sodium amalgam in 15 cc. of ether and 15 cc. of benzene in a test-tube. On being shaken the mixture became dark blue in color; no hydrogen was evolved. After five minutes the blue color changed to violet and after ten minutes to violet-red. Hydrolysis gave a 94% yield of benzohydrol. Although the solution had the violet-red color characteristic of benzophenone-disodium $(C_6H_5)_2CNaONa$, only a trace of this compound was present. This was shown by passing carbon dioxide into the solution

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[7] Erdmann, Thesis, Rostock, 1910.

prior to hydrolysis; only a trace of benzilic acid was formed. Other pinacols were converted to hydrols by 40% sodium amalgam in the same manner.

When a solution of 0.50 g. of benzophenone and 0.51 g. of benzohydrol was shaken with 2.5 g. of 40% sodium amalgam in a mixture of ether and benzene, no hydrogen was evolved; the solution became dark blue and later violet-red in color. Hydrolysis after fifteen minutes gave a 95% yield of benzohydrol.

The formation of the violet-red color was an indication that benzophenone is converted to benzophenone-disodium by 40% sodium amalgam. This was surprising in view of the work of Schlenk and Bergmann,[3] who showed that mercury removes one sodium from benzophenone-disodium and gives sodium ketyl. We find that a small amount of mercury removes little or no sodium and consequently 40% sodium amalgam can be used to prepare disodium derivatives of ketones. We have prepared a number of disodium derivatives by this method; in one instance, fluorenone, the disodium derivative is formed when 1% amalgam is used. The amalgam has certain advantages over the free metal and the method promises to be a convenient way of making these derivatives. Details of these experiments will be published in a future communication.

Summary

Benzopinacol and substituted benzopinacols are converted by a small amount of sodium alcoholate into a mixture of equivalent parts of ketone and hydrol. Free ketyl radicals are formed as intermediate products; these radicals are then converted by unreacted pinacol into the ketone and hydrol.

The pinacols are reduced quantitatively to hydrols by sodium amalgam in anhydrous ether–benzene solutions. This reaction, likewise, takes place through the intermediate formation of free ketyl radicals.

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[3] Schlenk and Bergmann, *Ann.*, **463**, 1 (1928).

ANN ARBOR, MICHIGAN

RECEIVED JULY 22, 1932
PUBLISHED JANUARY 11, 1933

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Tertiary Aliphatic Alcohols and Chlorides Containing Normal Butyl Groups

BY FRANK C. WHITMORE AND H. MILTON WOODBURN[1]

While most alcohols are capable of rearrangement,[2] those which show this tendency to the greatest degree contain the grouping, $R_3C\overset{|}{\underset{|}{C}}OH$. Tertiary alcohols and their halides are needed for the preparation of these substances. To make such tertiary alcohols available for this work and to gain experience in handling them, this research was undertaken. The alcohols studied contain only normal aliphatic groups, including in each case at least one *n*-butyl group but no groups higher than butyl. All ten alcohols of this type were made and their boiling points, densities and

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree. This study was completed in July, 1930.

[2] Whitmore, THIS JOURNAL, **54**, 3274, 3431 (1932).