The optical activity of these salts appears to be due to the asymmetry of the carbon atom carrying the nitro group.

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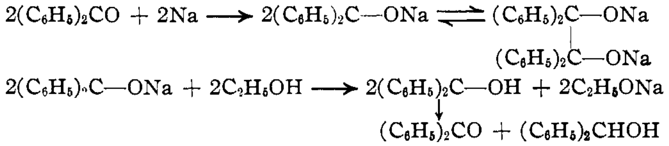
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# The Mechanism of Reduction by Sodium Amalgam and Alcohol. I. The Reduction of Aromatic Ketones to Hydrols

BY W. E. BACHMANN

During the reduction of benzophenone by 2% sodium amalgam and absolute alcohol two striking phenomena were observed. In the first place, the sodium amalgam is almost without action on the alcohol; when, however, benzophenone is added and the mixture is shaken, a vigorous reaction takes place with evolution of heat and in a few minutes all of the ketone is reduced to hydrol. Secondly, during the reduction the solution becomes blue, indicating the formation of the sodium ketyl $(C_6H_5)_2CONa$; the blue color rapidly disappears if shaking is discontinued. When all of the ketone has been reduced the blue color no longer reappears. When these facts are considered in conjunction with the fact that benzophenone reacts rapidly with sodium amalgam in absence of alcohol and gives the ketyl as the initial product, there can be no doubt that the reduction of the ketone is not effected by the hydrogen liberated by the action of the sodium amalgam on the alcohol; instead, the reduction occurs in virtue of the reactions



$$2(C_6H_5)_2CO + 2Na \longrightarrow 2(C_6H_5)_2C\text{—}ONa \rightleftharpoons \begin{array}{l}(C_6H_5)_2C\text{—}ONa\\ \qquad\ \ | \\ (C_6H_5)_2C\text{—}ONa\end{array} \qquad (1)$$

$$2(C_6H_5)_2C\text{—}ONa + 2C_2H_5OH \longrightarrow 2(C_6H_5)_2C\text{—}OH + 2C_2H_5ONa \qquad (2a)$$

$$\downarrow$$

$$(C_6H_5)_2CO + (C_6H_5)_2CHOH \qquad (2b)$$

The sodium attaches itself to the ketone and gives the sodium ketyl which associates to sodium pinacolate with which it establishes an equilibrium; the ketyl is converted by the alcohol into a mixture of benzohydrol and benzophenone; the ketone that is regenerated in this manner then in its turn goes through the cycle of reactions until benzohydrol is the sole product. Benzopinacol may be formed by reaction of the sodium pinacolate with alcohol, but since the reaction is reversible the pinacol, like the ketyls, will ultimately be converted rapidly to ketone and hydrol.[1]

If this mechanism be correct, then it should be possible to effect complete reduction by using only as much alcohol as is required by the formulation, since no loss of reducing agent occurs through evolution of hydrogen. This was found to be the case when the reduction was carried out in a mix-

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(1) Bachmann, THIS JOURNAL, **55**, 355 (1933).

ture of ether and benzene. Rapid and complete reduction takes place if a mixture of benzophenone and the theoretical amount of alcohol is shaken with 2% sodium amalgam in ether and benzene. Under these conditions it becomes even more apparent that the reduction proceeds through the intermediate formation of ketyl radicals, since the color phenomena are more pronounced; the solution becomes opaque dark blue and remains so until the end of the reaction when the solution becomes nearly colorless. The reaction is similar to the reduction of benzophenone by an equivalent amount of benzohydrol and sodium amalgam.[1] As a matter of fact, it was found that complete reduction can be effected by using only one-half the amount of alcohol required in the formulation since the benzohydrol can react in the manner of the alcohol.

In further support of this mechanism may be cited the fact that the identical results are obtained if the two reactions (Equations 1 and 2) are carried out separately in succession. This is accomplished by allowing the benzophenone to react with sodium amalgam in a mixture of ether and benzene in the absence of alcohol; in this way the reaction represented in Equation 1 takes place. If alcohol is added to this blue reaction mixture, then the reaction represented by Equation 2 occurs; after being shaken for a short time the mixture gives a quantitative yield of benzohydrol.

Similarly to benzophenone, other aromatic ketones can be reduced nearly quantitatively to hydrols in ether and benzene by sodium amalgam and a small amount of alcohol. Indeed, the procedure has proved to be an excellent practical method for preparing hydrols, possessing certain advantages over other methods of preparation. In support of our theory of the mechanism of reduction it was found that in every case the solution becomes deeply colored, and the color corresponds with the color characteristic of the individual sodium ketyl. Investigation has shown that the excellent method of Fosse[2] for the reduction of xanthone to xanthydrol by sodium amalgam and alcohol depends upon the intermediate formation of the xanthone-sodium compound. We have confirmed Fosse's observation that a blue color is developed during the reaction and we have found that the color is the same as that of the ketyl formed by the action of sodium amalgam on xanthone in absence of alcohol.

Various investigators have postulated the formation of intermediates in reductions. Cohen[3] considered that pinacols are formed by association of two diphenylhydroxymethyl radicals, $(C_6H_5)_2C\text{-}OH$, formed as intermediates by addition of an atom of hydrogen to benzophenone. He believed that pinacols are initially formed in the reduction of ketones to hydrols, and then broken down by the alkali. Willstätter, Seitz and

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(2) Fosse, *Ann. chim.*, [9] **6**, 58 (1916). See also "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 88.

(3) Cohen, *Rec. trav. chim.*, **38**, 72, 113 (1919).

Bumm[4] recently pointed out that the mechanism by which reduction by sodium amalgam takes place is still obscure. These investigators found that although pure sodium amalgam liberates no hydrogen from water, nevertheless reduction by this system is rapid. From their study of the reduction of terephthalic acid by sodium amalgam and water under various conditions, they came to the conclusion that the initial step consists in an addition of sodium to the atoms having free affinity.

Reduction of benzophenone by lithium amalgam and by potassium amalgam and alcohol follows the same course taken by sodium amalgam. In the reactions the intense blue colors of $(C_6H_5)_2C\text{-}OLi$ and of $(C_6H_5)_2C\text{-}OK$ are present until reduction of the ketone is complete; the yields of benzohydrol are quantitative.

Preliminary experiments with aliphatic ketones, with aldehydes, and with other compounds indicate that in many cases reduction by sodium amalgam and alcohol takes place through the intermediate formation of sodium addition derivatives. The results of these investigations will appear in future communications.

## Experimental

**Preparation of Sodium Amalgam.**—Although many methods have been devised for preparing sodium amalgam, the following procedure proved to be most convenient for preparing 2% sodium amalgam rapidly in amounts necessary for our experiments. Sixty grams of mercury and 15 cc. of toluene are heated to the boiling point of the liquid in a 60-cc. Pyrex test-tube. One and two-tenths grams of sodium is cut into about a dozen pieces and added in portions to the hot mixture, shaking after each addition until reaction is complete. When all of the sodium has been added, the amalgam is cooled with shaking in order to prevent the amalgam adhering to the tube. The toluene is decanted from the solid amalgam and the latter is then removed from the tube, wiped clean with a cloth and broken into pieces.

**Reduction of Benzophenone by Sodium Amalgam and Alcohol.**—When a mixture of 60 g. of 2% sodium amalgam and 60 cc. of absolute alcohol was shaken, less than 1 cc. of hydrogen was evolved in the course of one hour. As soon as 3.64 g. of benzophenone was added and the mixture was shaken, a vigorous reaction ensued; the solid amalgam became liquid and heat was evolved, making it necessary to cool the flask. On being shaken vigorously the solution became blue; when shaking was stopped the blue color rapidly disappeared. Hydrolysis after one-half hour gave 3.56 g. (96%) of benzohydrol. When reduction by 40% sodium amalgam and alcohol was tried, a vigorous evolution of hydrogen occurred and the product was an oil that did not crystallize. Linnemann[5] obtained a 60% yield of benzohydrol by reducing benzophenone by solid sodium amalgam and 90% alcohol. Klages and Allendorff[6] found that benzophenone was reduced to diphenylmethane to the extent of 90% by the action of sodium and alcohol.

**Reduction of Benzophenone in Ether and Benzene.**—To 60 g. of 2% sodium amalgam in a 50-cc. cylinder or 50-cc. Erlenmeyer flask was added 25 cc. of anhydrous ether, 25 cc. of dry benzene and 2.5 cc. of absolute alcohol and finally 3.64 g. (0.02 mole) of

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(4) Willstätter, Seitz and Bumm, *Ber.*, **61B**, 871 (1928).

(5) Linnemann, *Ann.*, **163**, 6 (1865).

(6) Klages and Allendorff, *Ber.*, **31**, 998 (1898).

benzophenone. The tube was corked and shaken. Almost immediately the solution became dark blue in color; it was necessary to cool the flask. After five minutes the solution was opaque blue; after ten minutes the color was less intense and after fifteen minutes the solution was transparent pale green. At the end of this time the mixture was poured into water contained in a separatory funnel, the mercury was drawn off and the solution was acidified. The ether–benzene solution was separated and evaporated; the residue was nearly pure benzohydrol. After recrystallization from petroleum ether the benzohydrol weighed 3.60 g. (98%).

**Reduction of Other Ketones.**—In Table I are given the results obtained by reducing a number of representative aromatic ketones, following the procedure described for benzophenone. In each case 0.2 gram-mole of ketone, 60 g. of 2% sodium amalgam and 2.5 cc. of absolute alcohol was shaken in 50 cc. of a mixture of ether and benzene. The mixtures were hydrolyzed as soon as the solution had only a pale color, which generally occurred in fifteen to thirty minutes. The yields given in the table are based on recrystallized product. Phenyl α-naphthyl ketone gave a number of products; this ketone is being studied further.

TABLE I

REDUCTION OF AROMATIC KETONES TO HYDROLS BY SODIUM AMALGAM AND ALCOHOL

| Ketone | Color during reduction | Hydrol yield, % |
|---|---|---|
| Benzophenone | Blue | 98 |
| 4-Methylbenzophenone | Blue | 98 |
| 4,4'-Dimethylbenzophenone | Blue | 96 |
| 4-Phenylbenzophenone | Green | 98 |
| 4,4'-Diphenylbenzophenone | Green | 99 |
| Fluorenone | Brown-green | 99 |

**4,4'-Diphenylbenzophenone and 4,4'-Diphenylbenzohydrol.**—We have found that the method of Adam[7] for preparing 4,4'-diphenylbenzophenone from biphenyl and phosgene in the presence of aluminum chloride gives excellent yields of the ketone. Because of the difficulty involved in obtaining phosgene on account of shipping regulations, a different method was devised Staudinger[8] found that oxalyl chloride and benzene react and give benzophenone and we have now applied the reaction to oxalyl chloride and biphenyl. A mixture of 70 g. of oxalyl chloride, 200 g. of biphenyl and 150 cc. of carbon disulfide was warmed to 40–50° in a 1-liter round-bottomed flask fitted with a reflux condenser. To the mixture 100 g. of anhydrous aluminum chloride was added in portions at such a rate as to keep the mixture boiling. After addition was complete the mixture was warmed for one hour on a steam-bath and was then allowed to stand overnight. The hydrolyzed mixture was warmed on a steam-bath in order to remove the carbon disulfide and the solid diphenylbenzophenone was filtered off, washed and dried. In order to remove biphenyl, the crude ketone was warmed with a large amount of alcohol and the mixture was filtered while hot. The ketone was obtained in the form of colorless leaflets by extracting it in a Soxhlet extractor with a mixture of equal parts of acetone and benzene; extraction took place at the rate of 2 g. of ketone per hour; yield, 155 g. (80%); m. p. 233°. Contrary to statements in the literature the ketone is very little soluble in hot alcohol or in hot benzene.

It is difficult to reduce 4,4'-diphenylbenzophenone by many reducing agents because of the insolubility of the ketone in most solvents. By our procedure the carbinol is prepared in quantitative yields. In one experiment 33.4 g. (0.1 mole) of diphenylbenzophenone was added to 300 g. of 2% sodium amalgam and 12.5 cc. of absolute

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[7] Adam, *Ann. chim. phys.*, [6] **15**, 258 (1888).

[8] Staudinger, *Ber.*, **41**, 3563 (1908).

alcohol in 150 cc. of ether and 150 cc. of benzene. The mixture was warmed to 40°, stoppered and shaken. The reaction was slow until the amalgam became liquid (two hours); then on being shaken vigorously so that the amalgam was dispersed into fine globules the mixture became dark green and all of the ketone was reduced in five minutes. The diphenylcarbinol which was obtained by hydrolysis of the nearly colorless solution was recrystallized from acetone (3.5 cc. of acetone per gram of carbinol) and was obtained in the form of large colorless needles; yield, 33 g.; m. p. 151–152°.

**Reduction of the System, Sodium Ketyl $\rightleftharpoons$ Sodium Pinacolate.**—A mixture of 3.64 g. of benzophenone and 60 g. of 2% sodium amalgam in ether and benzene was shaken for two days. To the blue mixture of sodium ketyl and sodium pinacolate was added 2.5 cc. of absolute alcohol and the resulting mixture was shaken for fifteen minutes. Hydrolysis gave a quantitative yield of benzohydrol. In like manner the ketyl-pinacolate mixtures obtained from 4-phenylbenzophenone and 4,4′-diphenylbenzophenone were reduced completely to the hydrol.

**Reduction of Benzophenone by Lithium Amalgam and by Potassium Amalgam.**—Lithium amalgam was prepared by keeping 0.35 g. of lithium, cut into several pieces, under 60 g. of heated mercury covered with toluene; several hours were often required for complete combination. The semi-solid amalgam was cleaned and added to a solution of 3.64 g. of benzophenone and 2.5 cc. of alcohol in 60 cc. of ether and benzene. The solution became dark blue in color; after being shaken for fifteen minutes the solution was nearly colorless. Hydrolysis gave a quantitative yield of benzohydrol.

In like manner an intense blue color resulted when 1.82 g. of benzophenone in ether and benzene was shaken with 1.3 cc. of alcohol and potassium amalgam that had been prepared from 0.88 g. of potassium and 50 g. of mercury. After half an hour little color remained; hydrolysis gave a quantitative yield of benzohydrol.

## Summary

Benzophenone and a number of other aromatic ketones are reduced in ether–benzene solution quantitatively to hydrols by 2% sodium amalgam and a small amount of alcohol.

The reduction of ketones to hydrols by 2% sodium amalgam and alcohol is not effected by hydrogen liberated by the action of the amalgam on the alcohol. It has been shown that the reduction proceeds through the intermediate formation of ketyl radicals: (a) $2(C_6H_5)_2CO + 2Na \longrightarrow 2(C_6H_5)_2CONa \rightleftharpoons (C_6H_5)_2C(ONa)(NaO)C(C_6H_5)_2$; (b) $2(C_6H_5)_2CONa + 2C_2H_5OH \longrightarrow (C_6H_5)_2CHOH + (C_6H_5)_2CO + 2C_2H_5ONa$. The ketone that is regenerated in this manner goes through the series of reactions until the hydrol is the sole product.

A study is being made of the mechanism of reduction of other types of ketones and of other compounds.

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