[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY]

REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION. VI. A. THE REDUCTION OF BENZOPHENONE. B. THE HYDROLYSIS OF METAL KETYLS[1]

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In 1891 E. Beckmann and T. Paul[2] found that certain aromatic ketones reacted with sodium in the proportion of one atom of metal to one molecule of ketone, forming highly colored addition products. Later, Schlenk and his co-workers[3] confirmed this result. A molecular weight determination by the ebullioscopic method enabled them to prove that the potassium derivative of phenylbiphenyl ketone was monomolecular in solution. Schlenk, therefore, proposed the name "metal ketyls" for this new class of substances represented by the general formula, $R_2{=}\overset{/}{C}{-}ONa$. **He also** found that disodium derivatives could be prepared by further action of the metal.

These reactions, which were carried out in benzene or ethereal solutions and in a nitrogen atmosphere, took place rather slowly. Following an observation of Kraus and White,[4] an investigation was undertaken of the reaction of sodium with benzophenone in liquid ammonia solution. It was found that this reaction occurred readily and rapidly. Either a mono- or disodium derivative could be obtained at will by merely adding the correct proportion of sodium. The compound containing two atoms of metal yields deep purple solutions in liquid ammonia and a considerable difference in the relative reactivity of the two sodium atoms was observed. Naturally, the sodium atom directly attached to a carbon atom is far more readily removed than that attached to oxygen, but this difference is enhanced by the fact that the latter atom exhibits even less reactivity than would be expected. This is evident in the reaction with excess ethyl bromide in which only one of the metal atoms is directly substituted.

$$(C_6H_5)_2CNaONa + C_2H_5Br \longrightarrow (C_6H_5)_2C(ONa)C_2H_5 \qquad (1)$$

$$(C_6H_5)_2C(ONa)C_2H_5 + C_2H_5Br + NH_3 \longrightarrow (C_6H_5)_2COHC_2H_5 + C_2H_5NH_2 + NaBr \qquad (2)$$

The second reaction probably takes place through the intermediate formation of ethylammonium bromide.

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[1] A portion of this material was submitted in a thesis for the degree of Master of Arts at Clark University, 1925.

[2] Beckmann and Paul, *Ann.*, **266,** 1 (1891).

[3] (a) Schlenk and Weickel, *Ber.*, **44,** 1182 (1911); (b) Schlenk and Thal, *ibid.*, **46,** 2840 (1913).

[4] Kraus and White, THIS JOURNAL, **45,** 771 (1923).

An entirely different type of reaction occurred when disodium benzophenone was treated with phenyl iodide.

$$(C_6H_5)_2CNaONa + C_6H_5I + NH_3 \longrightarrow (C_6H_5)_2C(NH_2)ONa + C_6H_6 + NaI \quad (3)$$

One product, sodium α-aminobenzhydrolate, is decomposed by water.[5]

$$(C_6H_5)_2C(NH_2)ONa + H_2O \longrightarrow NaOH + NH_3 + (C_6H_5)_2C{=}O \quad (4)$$

All of the final products indicated were actually obtained.

The partition of a molecule of ammonia between two radicals is a very common occurrence in liquid ammonia solution. In the present instance, the novel feature is that the partition takes place exclusively between two *different* groups, all the hydrogen reducing phenyl groups and all the amino radicals combining with metal ketyl groups rather than with some of the phenyl radicals to form aniline, diphenylamine or triphenylamine as always occurs when only the latter are present.[6]

A potassium derivative of benzophenone which is similar to the disodium compound results not only upon interaction of metal and ketone but also when benzhydrol is treated with potassium amide.

$$(C_6H_5)_2CHOH + KNH_2 \longrightarrow (C_6H_5)_2CHOK + NH_3 \quad (5)$$

$$(C_6H_5)_2CHOK + KNH_2 \longrightarrow (C_6H_5)_2CKOK + NH_3 \quad (6)$$

The second reaction demonstrates the acidic character of the methane hydrogen atom in potassium benzhydrolate. It is analogous to the action of potassium amide on triphenylmethane.[7]

In accordance with the views of Schlenk, the monosodium derivative appears to be a typical free radical. It is noteworthy that its reactions are predominately of the addition type, and in the second section of this paper evidence is presented to indicate that the general, if not exclusive, occurrence of such reactions is a characteristic of this substance. It appears that even the decomposition of these extremely unstable alkali metal compounds by water and strong acids (ammonium chloride in liquid ammonia solution) is preceded by the formation of addition compounds.

Experimental Part

The reactions were carried out in an apparatus similar to that which has already been described in an earlier number of this series.[6]

The Disodium Derivative of Benzophenone.—Both reacting constituents are soluble, as is also the product. Reaction appears to follow the equation

$$(C_6H_5)_2C{=}O + 2Na \longrightarrow (C_6H_5)_2CNaONa \quad (7)$$

The sodium atoms may be replaced with hydrogen through the action of either ammonium chloride or water. In the first case, immediate decolorization occurs, whereas when water is employed, a transient greenish coloration is evident. Benzhydrol, $(C_6H_5)_2CHOH$, was obtained in both experiments and was characterized by its melting

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[5] Haller and Bauer, *Ann. chim. phys.*, 16, 145 (1909).

[6] White, This Journal, 45, 779 (1923).

[7] Kraus and Rosen, *ibid.*, 47, 2741 (1925).

point, by the deep red coloration given with sulfuric acid and also by oxidation to benzophenone. In one hydrolysis the sodium compound obtained from 3.95 g. of benzophenone yielded 3.90 g. of benzhydrol, indicating practically quantitative transformation.

Oxygen and sulfur act readily upon disodium benzophenone with regeneration of the free ketone.

Action of Ethyl Bromide on Disodium Benzophenone.—Ethyl bromide reacts with disodium benzophenone in liquid ammonia, giving a white precipitate and a light yellow solution. The residue was extracted with anhydrous organic solvents and a substance was obtained which melted at 92.5° after recrystallization. This was identified as diphenylethyl carbinol by analysis. Calcd.: C, 84.9; H, 7.55; mol. wt., 212. Found: C, 81.3; H, 7.54; mol. wt., cryoscopic in benzene, 210.8.[8] and by means of a reaction described by Hell and Bauer,[9]

$$(C_6H_5)_2COHC_2H_5 + (CH_3CO)_2O \longrightarrow 2CH_3COOH + (C_6H_5)_2C{=}CHCH_3 \qquad (8)$$

2.2 g. of compound yielded 0.53 g. of pure α,α-diphenylpropene, melting at 52°.

Prolonged action of ethyl bromide in large excess did not form an ether, $(C_6H_5)_2$-$C(C_2H_5)OC_2H_5$, but only the free alcohol. Hydrolysis of the intermediate product, $(C_6H_5)_2CONaC_2H_5$, was excluded by analysis of the inorganic residue, which proved to be pure sodium bromide. (0.5554 and 0.3724 g. samples required 54.87 and 37.67 cc. of 0.09974 *N* silver nitrate, equivalent to 0.5637 and 0.3897 g. of sodium bromide, respectively.) 3.95 g. of benzophenone was then treated with 1.0 g. of sodium and 3.53 cc. of ethyl bromide. The ammonia was distilled under dilute hydrochloric acid. This solution was evaporated to dryness and the residue (350 g.) extracted with 95% alcohol. The residue from this extract was extracted with absolute alcohol. From this solution 0.81 g. of ethylamine hydrochloride was isolated (calcd.: 1.78 g.).

The reaction expressed in Equation 2 was confirmed with potassium diphenylethyl carbinolate. This was prepared from 3.59 g. of the alcohol in liquid ammonia.

$$(C_6H_5)_2COHC_2H_5 + KNH_2 \longrightarrow (C_6H_5)_2COKC_2H_5 + NH_3 \qquad (9)$$

It appeared as a white precipitate but was readily dissolved by ethyl bromide; 3.1 g. of the free alcohol was recovered but no trace of an ether was found.

Action of Phenyl Iodide on Disodium Benzophenone.—Bromobenzene was inactive but phenyl iodide reacted readily. The residues from three reactions when severally treated with water and extracted with organic solvents yielded *only* benzophenone and in amounts suggesting it as a principal product. Formation of aniline, di- or triphenylamine was excluded by separate qualitative tests of the aqueous extract and by proving nitrogen absent from the ether extract. When the solvent ammonia was distilled under water a little benzene was collected.

The reaction residue was then examined directly. The product from 1.5 g. of sodium, 5.77 g. of benzophenone and excess phenyl iodide was thoroughly washed with hot toluene, hot benzene and petroleum ether and then dried in a vacuum desiccator. When a portion was boiled with water, benzophenone separated and ammonia was detected in the escaping vapors with mercurous nitrate paper. After complete expulsion of ammonia, the solution still reacted alkaline and also gave a test for iodide ions.

The Action of Potassium Amide on Benzhydrol.—One and 68 hundredths g. of potassium was converted into potassium amide in liquid ammonia and treated with 2 g. of benzhydrol. The solution of the potassium alcoholate was light orange in color and transparent but began to turn greenish after ten to fifteen minutes, finally becoming deep purple and opaque at the end of twenty hours. A stream of dry air decolorized

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[8] Buxton, *Thesis*, Clark University, 1924; Everett H. Gibbs, unpublished observations.

[9] Hell and Bauer, *Ber.*, 37, 231 (1904).

the mixture but upon standing the purple color characteristic of dipotassium benzophenone was regenerated.

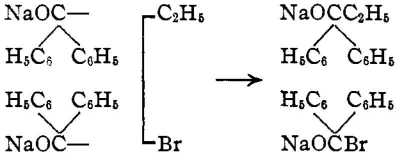
The Monosodium Derivative of Benzophenone.—When one equivalent of sodium was added to a solution of benzophenone in liquid ammonia, reaction occurred and a deep blue solution resulted. The presence of a definite monosodium compound was demonstrated by an experiment employing 3.95 g. of benzophenone and 0.5 g. of sodium. The residue was repeatedly extracted with hot petroleum ether. This extract was filtered in an atmosphere of ammonia and evaporated. The amount of benzophenone resulting represented the quantity present as such in the reaction product plus that formed by inadvertent oxidation during the extraction. Only 0.06 g. was obtained.

Excess ammonium chloride immediately decolorized the blue solution. Extraction of the residue with benzene yielded a product which was resolved by fractional crystallization from petroleum ether into benzhydrol (m. p. 67°) and benzophenone (m. p. 48°). No trace of benzopinacone was detected. When water was employed, a transient green color appeared but the same products resulted.

These products are analogous to those obtained from monopotassium phenylbiphenyl ketone and other metal ketyls.[3a]

Beckmann and Paul[2] reported that benzopinacone is also produced by hydrolysis of monosodium benzophenone. That it was formed in liquid ammonia, even as an intermediate product, is very improbable since it should be stable under these conditions and those prevailing during purification.

The Action of Ethyl Bromide on Monosodium Benzophenone—This reaction yields sodium bromide, a yellow solution and a separate, orange-colored liquid phase. The benzene extract of the reaction residue gave upon evaporation a yellow liquid that did not solidify when cooled in a mixture of ice and salt. Qualitative tests showed the absence of nitrogen and halogen. It was twice distilled under reduced pressure. The residue in the distilling flask deposited, upon standing, some crystals of diphenylethyl carbinol (m. p., 93°). The apparent molecular weight (cryoscopic in benzene) of the distillate was 182, indicating that benzophenone was the principal constituent. This was obtained in crystalline form and identified after cooling the liquid to −33.5° and inocculating with the ketone. The reaction probably follows the equations[3a]



(10)

$$(C_6H_5)_2C(Br)ONa \longrightarrow (C_6H_5)_2C{=}O + NaBr \qquad (11)$$

$$(C_6H_5)_2CONaC_2H_5 + C_2H_5Br + NH_3 \longrightarrow (C_6H_5)_2COHC_2H_5 + C_2H_5NH_2 + NaBr \qquad (12)$$

B. The Hydrolysis of Metal Ketyls

A Sodium Ammonium Derivative of Benzophenone.—Kraus and Kawamura[10] observed that the reaction between sodium triphenylmethide and ammonium chloride in liquid ammonia yields the corresponding ammonium compound as a pinkish precipitate. It slowly decomposes, even at −33.5°, to form triphenylmethane and ammonia.

In the reaction of disodium benzophenone with excess ammonium chloride, decolorization was practically instantaneous and any interme-

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[10] Kraus and Kawamura, This Journal, **45**, 2758 (1923).

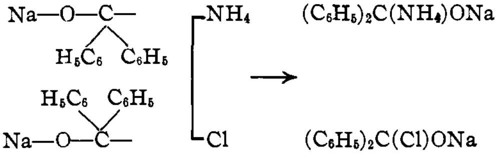
diate compound, if formed, must have been very unstable. This result is to be expected, since the compound formed under these conditions would contain two ammonium groups and would in consequence be much less stable than ammonium triphenylmethide. If it were possible to replace but one of the sodium atoms with an ammonium group, a more stable product could be expected. For this purpose, the disodium compound prepared from 1.82 g. of ketone and 0.46 g. of sodium was treated with 0.54 g. of ammonium chloride, this amount being equivalent to one-half of the sodium. The purple solution immediately became nearly blue in color and the reflected light was no longer green. If the reagent had reacted with all of the sodium in one-half the total amount of compound present, the color of the remaining solution should then be that of disodium compound at one-half the original concentration; but a previous experiment had shown this to be purple and quite stable for at least twenty-seven hours. Apparently, the more active sodium atoms were all replaced with ammonium groups

$$(C_6H_5)_2C(Na)ONa + NH_4Cl \longrightarrow NaCl + (C_6H_5)_2C(NH_4)ONa \qquad (13)$$

After a lapse of eight and one-half hours, the solution became light yellow and transparent. This confirmed Equation 13, for disappearance of the blue color was caused by decomposition of the unstable sodium ammonium compound

$$(C_6H_5)_2C(NH_4)ONa \longrightarrow (C_6H_5)_2CHONa + NH_3 \qquad (14)$$

Intermediate Reactions of Monosodium Benzophenone and Ammonium Chloride.—Since excess ammonium chloride immediately decolorized solutions of monosodium benzophenone, the monoammonium derivative, if formed, must also be very unstable. Other explanations of this reaction may be given. Immediate replacement of the sodium atom by hydrogen might take place, followed by reaction with the solvent ammonia or by the intermolecular oxidation and reduction suggested by Schlenk and Weickel.[3a] On the other hand *addition* of ammonium chloride might occur, so that the sodium ammonium compound would be formed



(15)

$$(C_6H_5)_2C(Cl)ONa \longrightarrow (C_6H_5)_2C{=}O + NaCl \qquad (16)$$

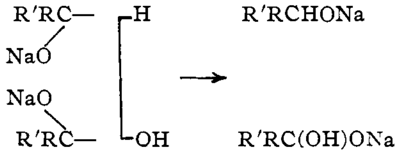
$$(C_6H_5)_2C(NH_4)ONa + NH_4Cl \longrightarrow NaCl + (C_6H_5)_2CHOH + 2NH_3 \qquad (17)$$

It is evident from Equations 15, 16 and 17 that the sodium ammonium compound should result if the third reaction was eliminated by using an amount of ammonium chloride equivalent to but one-half of the sodium. Accordingly, an experiment was made with 0.23 g. of sodium, 1.82 g. of ketone and 0.27 g. of ammonium chloride. A small quantity of dry ether was added to hold any regenerated benzophenone in solution; otherwise it separates as a gummy mass and retards the color changes. The blue color of the solution remained apparently unchanged immediately after the addition of ammonium chloride, but then slowly faded until it had entirely disappeared at the end of seven hours. The theory expressed in Equations 15, 16 and 17 was thus confirmed, for the other explanations predict an abrupt and marked diminution of color due to decreased concentration of monosodium compound, after which the color should be stable for at least twenty-seven hours, as has been proved in a separate experiment. The reaction expressed in Equation 15 is particularly noteworthy since ammonium chloride behaves as a strong acid in liquid ammonia solution.

Hydrolysis of Metal Ketyls.—Hydrolysis of the sodium compounds in liquid ammonia may be considered analogous to the reaction with ammonium chloride. However, since ammonium hydroxide is more weakly acidic than ammonium chloride, the reaction of the sodium ammonium compound with excess reagent would be expected to proceed somewhat slowly and decolorization would be retarded. In fact, a green coloration was observed in all cases. This indicates the presence of sodium ammonium compound which would appear green at low concentration, since the final reaction mixture is always light yellow.

Some inferences may also be drawn regarding the course of hydrolysis under other conditions. Schlenk and Weickel[3a] have already suggested that immediate replacement of the sodium by hydrogen occurs, followed by polymerization or intermolecular oxidation and reduction, or both, depending upon the nature of the metal ketyl. However, it is difficult to understand why the radical, $R'R\overset{/}{C}—OH$, should undergo intermolecular oxidation and reduction instead of simple polymerization when the polymer is stable under the conditions of the experiment and no other factor, such as reaction with solvent, is involved. Yet no polymer was obtained by Schlenk and his co-workers from any of the numerous metal ketyls which they prepared and hydrolyzed. The only exceptions were observed by Beckmann and Paul, as has been previously mentioned.

Since it appears that intermediate addition products result between the metal ketyls and either moderately electropositive groups (NH_4) or weakly amphoteric radicals (C_2H_5), there is little reason to believe that the hydrogen atom, occupying an intermediate position, would not behave similarly. Consequently, the following general reaction scheme may be proposed



(18)

$$R'RC(OH)ONa \longrightarrow R'RC{:}O + NaOH \qquad (19)$$
$$R'RCHONa + H_2O \longrightarrow R'RCHOH + NaOH \qquad (20)$$

Formation of a pinacone, as observed by Beckmann and Paul, would imply that the sodium compound was itself partially polymerized under the conditions of their experiment and that direct hydrolysis of this polymer occurred to some extent.

The author wishes to acknowledge his deep obligation to Dr. George F. White, at whose suggestion this research was initiated, and to thank the other members of the Faculty of the Department of Chemistry of Clark University for their aid.

Summary

1. Both mono- and disodium derivatives of benzophenone may be prepared readily by the action of sodium in liquid ammonia. Dimetallic derivatives may also result from the action of amides on the corresponding alcohol.

2. The reactions of ethyl bromide and phenyl halides with sodium compounds of benzophenone have been studied. Both substitution and reactions involving the solvent have been observed.

3. Evidence has been presented to show that the occurrence of addition reactions is a more general property of the metal ketyls than has been previously supposed. Even their decomposition by strong acids may be preceded by the formation of addition products.

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[Contribution from the Chemical Laboratory of Hamline University]

ALIPHATIC-AROMATIC ARSENO COMPOUNDS. II. β-HYDROXYETHYLARSONIC ACID AND SOME ARYL ARSENO-ETHANOLS[1]

By R. Herbert Edee

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A complete series of unsymmetrical aliphatic-aromatic arseno compounds has been described in the literature.[2] In this series it was found that all of the members were soluble because of the presence of a carboxyl group in the aliphatic part of the molecule. Most of the compounds contained additional solubilizing groups in the aromatic part. It was thought desirable to prepare a series of aliphatic-aromatic arseno compounds whose solubilities would be due to the presence of certain groups in the aromatic portion of the molecule. The series to be described contains the hydroxy-ethyl group, $-CH_2CH_2OH$, as the aliphatic portion and various aryl groups as the aromatic part of the arseno molecule.

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[1] This paper is the result of an investigation which was begun at the suggestion of Dr. Charles Shattuck Palmer, formerly of Northwestern University.

[2] Palmer and Edee, This Journal, 49, 998 (1927).