[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Structure of Metal Ketyls. IV. The Nature of the Intermediate Product in the Reaction with Alkyl Halides

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It has been shown[1] that the reaction between the metal ketyl, sodium benzophenone, and ethyl bromide involves at least two successive reactions which may be expressed by Equations 1 and 2, writing the formula of the ketyl as $C_{13}H_{10}ONa$ to avoid prejudice regarding its structure.

$$C_{13}H_{10}ONa + C_2H_5Br = NaBr + (C_{15}H_{15}O) \quad (1)$$

$$C_{13}H_{10}ONa + (C_{15}H_{15}O) = (C_6H_5)_2CO + (C_6H_5)_2C(C_2H_5)ONa \quad (2)$$

On the basis of the *customary formula* for the metal ketyl,[2] one is tempted to ascribe to the intermediate radical, $(C_{15}H_{15}O)$, the structure of diphenylethoxymethyl.

$$(C_6H_5)_2\underset{|}{C}ONa + C_2H_5Br = NaBr + (C_6H_5)_2\underset{|}{C}OC_2H_5 \quad (3)$$

The formation of the observed reaction products might then be explained by Equations 4 and 5

$$(C_6H_5)_2\underset{|}{C}ONa + (C_6H_5)_2\underset{|}{C}OC_2H_5 = (C_6H_5)_2CO + (C_6H_5)_2C(Na)OC_2H_5 \quad (4)$$

$$(C_6H_5)_2C(Na)OC_2H_5 = (C_6H_5)_2C(C_2H_5)ONa \quad (5)$$

the assumed rearrangement of diphenylethoxymethyl-sodium (Equation 5) being supported by observations of Schlenk and Bergmann[3] on diphenylmethoxymethyl-sodium. However, diphenylethoxymethyl-sodium and its potassium analog have now been prepared in liquid ammonia solution by cleavage of benzophenone diethyl acetal

$$(C_6H_5)_2C(OC_2H_5)_2 + 2Na = (C_6H_5)_2C(Na)OC_2H_5 + C_2H_5ONa \quad (6)$$

and by the action of potassium amide on benzohydryl ethyl ether

$$(C_6H_5)_2CHOC_2H_5 + KNH_2 = (C_6H_5)_2C(K)OC_2H_5 + NH_3 \quad (7)$$

and characterized by auto-oxidation to benzopinacol diethyl ether and diphenylethoxymethyl peroxide. It was found that neither of these organo-alkali compounds underwent appreciable rearrangement in the course of several hours and, furthermore, that the products of the reaction between ethyl bromide and the metal ketyl in liquid ammonia did not contain any significant amounts of ethoxy compounds. This proves conclusively that *diphenylethoxymethyl-sodium is not formed as an intermediate in the reaction between the metal ketyl and ethyl bromide.*

It is evident that the structure of the intermediate radical, $(C_{15}H_{15}O)$, should be inferred from the *known products of the reaction*, rather than the assumed formula for the ketyl; its formation, therefore, involves carbon alkylation which is most simply explained by the presence of a carbon–sodium bond in the metal ketyl.[4]

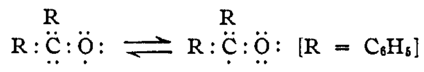
$$(C_6H_5)_2C(Na){-}O{-} + C_2H_5Br = NaBr + (C_6H_5)_2C(C_2H_5){-}O{-} \quad (8)$$

$$[(C_6H_5)_2CO]Na + (C_6H_5)_2C(C_2H_5){-}O{-} = (C_6H_5)_2CO + (C_6H_5)_2C(C_2H_5)ONa \quad (9)$$

All of the known reactions of the metal ketyls are in harmony with this interpretation, if the ketyls are considered to comprise an equilibrium between molecules of the "carbide" and "oxide" structures

$$(C_6H_5)_2C(Na){-}O{-} \rightleftharpoons (C_6H_5)_2\overset{/}{C}{-}ONa \quad (10)$$

The "oxide" structure may dimerize to the pinacolate and is the initial product of the dissociation of the pinacolate; the "carbide" structure is more reactive and plays the predominant part in the metathetical reactions of the ketyls. Since the metal ketyls are ionized,[5] the equilibrium may be expressed in terms of anions



$$R:\underset{\cdot\cdot}{\overset{\overset{R}{\cdot\cdot}}{C}}:\underset{\cdot}{\overset{\cdot\cdot}{O}}: \rightleftharpoons R:\underset{\cdot}{\overset{\overset{R}{\cdot\cdot}}{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}: \quad [R = C_6H_5] \quad (11)$$

and consists essentially of an oscillation between two electronic structures.[6]

This interpretation also suggests an explanation for an unusual feature of the electrolytic conductance of the metal ketyl, sodium benzophenone. Kraus and Bien[5] commented, "It is a remarkable fact that monosodium ketyl is a

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[1] Wooster and Holland, This Journal, **56**, 2438 (1934).

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

[3] Schlenk and Bergmann, *Ann.*, **464**, 35–42 (1928).

[4] A non-committal formula for the metal ketyl, $[(C_6H_5)_2CO]Na$, is used in Equation 9, since the behavior of the ketyl in this step gives no evidence regarding its structure beyond the well-known fact that when the metal is removed from the ketyl, the keton results.

[5] Kraus and Bien, This Journal. **55**, 3609 (1933).

[6] A structure in which the extra electron is *shared* by the oxygen and carbon, $R:\overset{\overset{R}{\cdot\cdot}}{C}.\overset{\cdot}{:}.\overset{\cdot\cdot}{O}:$, is conceivable. Similar structures also involving three-electron bonds have been proposed by Pauling [Pauling, This Journal, **53**, 3225 (1931)] for organic nitroso compounds.

much better conductor than sodium benzohydrolate. The only difference between the two salts is that a hydrogen atom is associated with the aliphatic carbon atom in the one case and not in the other. It seems evident that constitutional factors play a large part in the dissociation phenomenon in the case of these salts." Since the ionization of the carbon–sodium bond as exemplified by triphenylmethyl-sodium[7] is greater than that of the oxygen–sodium bond (in sodium phenolate and sodium benzohydrolate[5]), the presence of a carbon–sodium bond in a portion of the metal ketyl molecules might well be expected to increase the average ionization of the ketyl above that of the analogous sodium benzohydrolate in which the possibility of a carbon–sodium bond is excluded.

The chief obstacle to the earlier suggestion and acceptance of this simple and straightforward explanation of the behavior of the metal ketyls was doubtless a rather general prejudice that a competition between carbon and oxygen for sodium (*i. e.*, for the charge on the ketyl anion) would always favor the oxygen exclusively. This prejudice is actually without foundation for triphenylmethyl is able to remove sodium from sodium benzophenone in accordance with Equation 12 to the extent of approximately 39%.

$$[(C_6H_5)_2CO]Na + (C_6H_5)_3C— \rightleftharpoons (C_6H_5)_2CO + (C_6H_5)_3CNa \quad (12)$$

Obviously, *the attachment of the sodium in the metal ketyl is such that the alkali metal may be shared to a very appreciable extent with a tervalent carbon atom.* On this basis alone, a similar sharing of the alkali metal (*i. e.*, of the anionic charge) within the ketyl molecule appears highly probable.

Experimental Part

The Action of Alkali Metals on Benzophenone Diethyl Acetal.—Ammonia was condensed on weighed samples of the acetal in a liquid ammonia reaction tube[8] and two atomic equivalents of sodium or potassium were added in small pieces. A rapid reaction occurred and a bright red solution was formed. The organo-alkali compounds were decomposed by bubbling a stream of dry oxygen through the solutions which caused decolorization and the deposition of a white precipitate. Two products were obtained from the benzene–ether extracts of the reaction residue which were separated by crystallization from alcohol, ether and benzene mixtures. One, very slightly soluble in ether and readily obtained in fine white crystals from alcohol–benzene mixtures, melted at 162.5° and proved to be benzopinacol diethyl ether.

Anal. Calcd. for $C_{26}H_{20}(OC_2H_5)_2$: OC_2H_5, 21.33. Found: OC_2H_5, 22.37, 21.64.

Its constitution was confirmed by the recovery of β-benzopinacolin after the decomposition with hydriodic acid.

$$(C_6H_5)_2C(OC_2H_5)—C(OC_2H_5)(C_6H_5)_2 + 2HI \longrightarrow$$
$$2C_2H_5I + (C_6H_5)_2COHCOH(C_6H_5)_2 \xrightarrow{HI}$$
$$H_2O + (C_6H_5)_3CCOC_6H_5 \quad (13)$$

The second product was readily separated from the first due to its solubility in ether and was also crystallized from an alcohol–benzene solution. The white crystals of m. p. 138° appeared to be a peroxide of the formula

$$(C_6H_5)_2C(OC_2H_5)—O—O—C(OC_2H_5)(C_6H_5)_2$$

Anal. Calcd. for $C_{26}H_{20}O_2(OC_2H_5)_2$: C, 79.29; H, 6.61; OC_2H_5, 19.82; mol. wt., 454. Found: C, 80.81, 80.40, 79.85; H, 7.15, 6.98, 6.88; OC_2H_5, 20.05, 19.88; mol. wt. (cryoscopic in benzene), 423.5, 414.2.

After the ethoxyl determinations, the hydriodic acid was diluted with water and extracted with ether. The ethereal extract was washed with a solution of potassium hydroxide, dried, and evaporated and the presence of benzophenone in the oily residue was detected by converting it into the oxime. Its formation under these conditions might be expected as a result of reactions of the following type.

$$(C_6H_5)_2C(OC_2H_5)—O—O—C(OC_2H_5)(C_6H_5)_2 + 2HI \longrightarrow$$
$$2C_2H_5I + (C_6H_5)_2C(OH)—O—O—C(OH)(C_6H_5)_2 \longrightarrow$$
$$2(C_6H_5)_2CO + H_2O_2 \quad (14)$$

These oxidation products may be taken as evidence of the presence of diphenylethoxymethyl-sodium and -potassium in the red liquid ammonia solutions, for their formation is analogous to the behavior observed on oxidation of other typical organo-alkali compounds.[9]

The cleavage of benzophenone diethyl acetal proceeds in accordance with Equation 15 as well as Equation 6.

$$(C_6H_5)_2C(OC_2H_5)_2 + 4Na = (C_6H_5)_2CNa_2 + 2C_2H_5ONa \quad (15)$$

Since only two equivalents of sodium were actually used, reaction according to Equation 15 would leave an excess of unchanged acetal equal to the amount doubly cleaved. The extent of the double cleavage under these conditions was measured by hydrolyzing with acid the excess acetal in the reaction residue and determining the resulting benzophenone in the form of its oxime by the method described in a previous paper.[1] The average of the results of four experiments indicates that approximately 14.4% of the acetal was doubly cleaved, an equal amount was unchanged and the remainder, 71.2%, was singly cleaved in accordance with Equation 6.

The Action of Potassium Amide on Benzohydryl Ethyl Ether.—Solutions of potassium amide were prepared in liquid ammonia by ammonolysis of the metal under the influence of an iron oxide catalyst and then a sample of the benzohydryl ethyl ether was added and the mixture stirred. A rapid reaction took place forming a deep red solution

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(7) Wooster, *Chem. Rev.*, **11**, 26 (1932).

(8) Wooster, THIS JOURNAL, **51**, 1859 (1929).

(9) Ref. 7, pp. 14, 21

which was subsequently decolorized with a stream of oxygen after which benzopinacol diethyl ether and diphenylethoxymethyl peroxide were isolated and identified as described previously. The reaction apparently went to completion in accordance with Equation 7 without any side reactions.

The Stability of Diphenylethoxymethyl-Sodium and -Potassium.—The sodium compound was prepared by cleavage of benzophenone diethyl acetal and a Zeisel ethoxyl analysis was performed on the dry reaction residue immediately after evaporation of the ammonia. The analysis was carried out in the liquid ammonia reaction tube, itself, after adding the constant boiling hydriodic acid and connecting the absorption flasks. The reaction tube was constructed with a uniform diameter so that a condenser could be slipped on it during the ethoxyl analysis. Experiments showed that undecomposed benzohydryl ethyl ether was likely to be carried over by the stream of carbon dioxide unless *cold* water was circulated through the condenser. This prolonged the time required for sweeping over the ethyl iodide slightly, but yielded much more accurate results. The results obtained in this way, together with those of similar experiments using potassium in place of sodium, gave an average value of 98.3% of the theoretical ethoxyl content of the acetal used. Experiments were also carried out with diphenylethoxymethylpotassium prepared from potassium amide and benzohydryl ethyl ether. In this case the potassium compound was hydrolyzed before the ethoxyl analysis. It was found necessary, however, to use ammonium chloride instead of water as the hydrolytic agent because even a slight excess of water diluted the hydriodic acid enough to render the decomposition of benzohydryl ethyl ether incomplete. The results of these experiments gave an average value of 95.9% of the theoretical ethoxyl content of the ether used.

It is evident from these values, particularly when they are compared with those obtained by direct analysis of the acetal and the ether (98.0 and 96.1%, respectively), that no rearrangement of the organo-alkali compounds actually took place during the period of several hours which elapsed between their preparation and their decomposition.

Ethoxyl Content of the Reaction Products from Ethyl Bromide and the Metal Ketyls.—The reactions and subsequent analyses were carried out as follows. A weighed sample of benzophenone was placed in a liquid ammonia reaction tube[8] and pure dry ammonia was condensed on it. The calculated quantity of sodium or potassium was then added from a side arm and the solution was stirred with a stream of ammonia gas for fifteen minutes to ensure complete reaction. The ethyl bromide was then added and after a time interval of from fifteen minutes to sixteen hours, the reaction products were hydrolyzed and the ammonia allowed to evaporate. The ethoxyl content of the residue was then determined, the decomposition with hydriodic acid being carried out in the reaction tube, itself, as described previously. The results of seven experiments gave an average ethoxyl content of 2.9% of the theoretical based on Equations 3 and 4 (limits 2.0 to 3.8). The reaction residue, therefore, contained only unimportant quantities of ethoxyl compounds which may probably be ascribed to a direct reaction between the ethyl bromide and sodium benzopinacolate[10] to form ethyl ethers of benzopinacol.

The Reaction between Triphenylmethyl and Sodium Benzophenone.—The existence of an equilibrium of the type expressed in Equation 12 was suggested by Schlenk and Ochs[11] to explain the greenish color of the reaction mixture in ether solution. The reaction has been investigated further by determining the amount of benzophenone formed when the mixture was decomposed, as by ethyl bromide or ammonium bromide. It has been shown[1] that not more than 50% of the ketone is regenerated from the metal ketyl alone under similar conditions. Accordingly, any excess over this quantity recovered measures the extent of reaction in the sense of Equation 12 from left to right. Equivalent quantities of benzophenone and carefully purified triphenylchloromethane were placed in a reaction tube with about 10 cc. of dry toluene to promote solution of the organic materials. After liquid ammonia had been condensed in the tube, two atomic equivalents of sodium were added piece by piece. The first equivalent reacted with the triphenylchloromethane yielding sodium chloride and leaving a mixture of triphenylmethyl, benzophenone and one equivalent of sodium to interact as desired. The mixture was stirred for one hour and then decomposed, the ammonia was allowed to evaporate, the residue treated with water and ether, the ether extract separated and evaporated and the amount of benzophenone present in this residue determined in the form of its oxime as described previously.[1] The values obtained are approximate only, for the equilibrium may have been displaced somewhat by the ethyl bromide and ammonium bromide, but the average value of 39.2% for the extent of reaction in the sense of Equation 12 shows clearly that such an equilibrium exists.

Summary

1. It has been shown that the primary reaction between ethyl bromide and the metal ketyls, sodium and potassium benzophenone, results in carbon alkylation which is most simply explained by the presence of a carbon-sodium or carbon-potassium bond in the ketyls.

2. The chemical reactions and the electrolytic properties of the metal ketyls are all consistent with the assumption that the alkali metal (*i. e.*, the anionic charge) is shared between oxygen and carbon in the ketyl molecule (or anion).

3. It has been shown that the attachment of the alkali metal in the metal ketyl is such that the metal atom may be shared to a very appreciable extent with a tervalent carbon atom.

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[10] Wooster, THIS JOURNAL, **56**, 2436 (1934).

[11] Schlenk and Ochs, *Ber.*, **49**, 612 (1916).