Krieg gives 76–78°. Mixed with tetralupine the mixture began to melt at 61° and was completely fluid at 79°. Other differences between the two compounds are: isolupinine is more strongly dextrorotatory than tetralupine, $[\alpha]^{15}_{D}$ 38.17°[14] and readily forms double compounds with gold and platinum chlorides that are insoluble in alcohol. The corresponding compounds of tetralupine are so soluble in water and alcohol that they cannot be isolated.

### Isolation of a New Alkaloid, Pentalupine

The highest boiling fraction was a deep yellow oil with a strong green fluorescence, $n^{25}_{D}$ 1.5252; in alcohol, $[\alpha]^{29}_{D}$ −3.197°. Its melting range at 2 mm. was 170–210°. To purify it the fraction was converted into hydrochloride but no crystalline compound could be isolated. The alkaloid was regenerated from this salt and was warmed under reduced pressure to remove solvent. The substance was then fractionated in vacuum. The first portions of distillate were discarded and the middle fraction, boiling 175 to 182° was taken. Ten grams of straw yellow oil with a strong greenish fluorescence was obtained, $n^{29.5}_{D}$ 1.5155. No crystalline compounds have been obtained from this substance.

*Anal.* Calcd. for $C_{16}H_{30}ON_2$: C, 72.12; H, 11.34; N, 10.52. Found: C, 72.07, 72.17; H, 11.49, 11.32; N, 10.47, 10.46, 10.49.

## Summary

*Lupinus palmeri*, S. Wats. contains three alkaloids: lupinine, $C_{10}H_{19}ON$, previously found in *L. luteus and in Anabasis aphylla;* tetralupine, a new alkaloid isomeric with lupinine and not identical with isolupinine; and pentalupine, provisionally given the formula $C_{16}H_{30}ON_2$, also a new alkaloid. Sparteine does not occur in this plant.

WASHINGTON, D. C.

RECEIVED JULY 21, 1934

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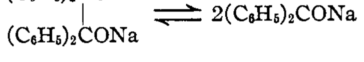
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

# The Structure of Metal Ketyls. II. The Dissociation of Alkali Metal Pinacolates to Metal Ketyls in Liquid Ammonia Solution

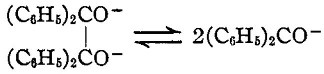
BY CHARLES BUSHNELL WOOSTER

Bachmann[1] has shown by isolating the pinacol formed on rapid hydrolysis with excess acetic acid, that the sodium derivatives of ketones, the so-called metal ketyls, *as prepared in ether by previous investigators*, are not monomolecular free radicals but sodium pinacolates or equilibrium mixtures of sodium-ketyl and sodium pinacolate in which the equilibrium is almost entirely in favor of the sodium pinacolate. However, a similar investigation of the solutions obtained from benzophenone and one equivalent of sodium in *liquid ammonia* leads to the conclusion that relatively high concentrations of the monomolecular ketyl are present under these conditions. Thus in a solution which is approximately 0.15 *N* (with respect to the pinacolate) the pinacolate is about 85% dissociated into the ketyl in accordance with Equation 1.



$$\begin{matrix}(C_6H_5)_2CONa \\ | \\ (C_6H_5)_2CONa\end{matrix} \rightleftharpoons 2(C_6H_5)_2CONa \qquad (1)$$

In addition to the direct influence of the solvent upon the dissociation equilibrium, two other clearly understandable reasons for the striking difference between the results of Bachmann and those of the present investigation may be pointed out. First, these sodium compounds are only moderately soluble in ether, and in Bachmann's experiments a large amount of the pinacolate was present as a precipitate. Thus his results are not an accurate measure of the state of the dissociation equilibrium *in solution*. Second, the pinacolate undoubtedly undergoes electrolytic dissociation in liquid ammonia[2] and the electrostatic repulsion between the two negative charges may well play a part in promoting dissociation of the pinacolate anion into ketyl anions.[3]



$$\begin{matrix}(C_6H_5)_2CO^- \\ | \\ (C_6H_5)_2CO^-\end{matrix} \rightleftharpoons 2(C_6H_5)_2CO^- \qquad (2)$$

As it is impossible to attribute the conductance values obtained by Kraus and Bien entirely to simple electrolytic dissociation of the small amount of pinacolate present, without ascribing ridiculously high values to the limiting equivalent conductance of the pinacolate anion, it is evident that the simple ketyl anion, $R_2CO^-$, actually exists in liquid ammonia. This anion is an interesting and unusual type of stable complex because it contains both an *odd* and an *extra* electron. Modern electronic theories of valence recognize,

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

(2) Kraus and Bien, *ibid.*, **55**, 3609 (1933).

(3) Electrolytic dissociation of the pinacolate in ether solution is, of course, not excluded, but this ionization would be much greater in liquid ammonia in accordance with the well-known differences in the suitability of these two liquids as electrolytic solvents.

among others, three important factors in molecular stability (1) electron octets, (2) electron pairs, (3) electrical neutrality. It is well known that all of these factors are not necessary. Thus free organic radicals are examples which lack the first two factors and all ions lack the third, but the metal ketyl anions are very exceptional because they lack all three. Consequently, a careful study of these substances may be expected to throw some new light on fundamental valence problems.

From the foregoing, it is evident that liquid ammonia possesses unique advantages as a solvent in which to study the behavior of the metal ketyls and an investigation of their reactions with a variety of reagents has been under way in this Laboratory for some time. Evidence has been obtained that none of the previously published interpretations of these reactions is wholly satisfactory.[4] These results will be reported in subsequent papers, but it is first necessary to dispose of one disconcerting possibility, namely, that the reactions attributed to the metal ketyls might actually be those of the corresponding disodium compounds formed in accordance with Equation 3

$$2R_2CONa \rightleftharpoons R_2CO + R_2CNaONa \qquad (3)$$

It has already been pointed out[5] that this hypothesis would suffice to explain all of the reactions of the metal ketyls (excluding those attributable to the pinacolates) which had been observed previously.

However, the disodium and dipotassium derivatives of benzophenone react rapidly and completely (five minutes) with benzyl alcohol and benzohydrol

$$(C_6H_5)_2CNaONa + C_6H_5CH_2OH = (C_6H_5)_2CHONa + C_6H_5CH_2ONa \qquad (4)$$

whereas the same reagents require several hours to discharge the color of the corresponding metal ketyls.

If the equilibrium expressed in Equation 3 actually existed it would necessarily be displaced to the right by the action of benzyl alcohol (or benzohydrol) since the reaction between this reagent and the disodium compound is not reversed by benzophenone. Only *slow displacement of this equilibrium* could then prevent rapid decomposition of the ketyl. Accordingly, such rapid reactions as that between the metal ketyl and ethyl bromide must involve a different mechanism unless it can be assumed that ethyl bromide exerts a positive catalytic influence upon the displacement of the equilibrium *or* that benzyl alcohol (and benzohydrol) exert a negative catalytic influence upon it.

Both of these assumptions have been shown to be invalid by experiments in which ethyl bromide was added shortly after the addition of benzyl alcohol. When the amount of ethyl bromide was approximately one equivalent a rapid reaction occurred and decolorization was complete in less than five minutes, showing that the presence of benzyl alcohol did not appreciably retard the reaction with ethyl bromide. On the other hand, when only about one-tenth equivalent of the alkyl halide was used, five to seven hours elapsed before the blue solution became transparent and a much longer time was required for substantially complete decolorization. This shows that the presence of ethyl bromide does not promote appreciably the reaction with benzyl alcohol.

Consequently, displacement of Reaction 3 to

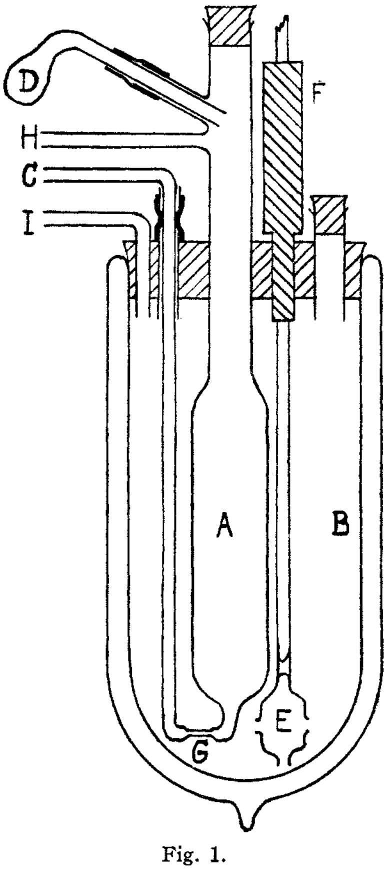

Fig. 1.

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[4] This includes the hypotheses of the present author regarding the hydrolysis of the metal ketyls [Wooster, THIS JOURNAL, **50**, 1392–1394 (1928)], which are hereby withdrawn.

[5] Wooster, *ibid.*, **51**, 1858 (1929).

the right, if it occurs at all, must be very slow and can play no significant part, if any, in the rapid reactions of the metal ketyls.[6]

## Experimental Part

**The Dissociation of Sodium Benzopinacolate into the Metal Ketyl in Liquid Ammonia.**—In the experiments with liquid ammonia solutions, the aqueous acetic acid used by Bachmann was replaced by solutions of ammonium chloride or bromide in liquid ammonia. Under these conditions the ammonium salts function as strong acids, reacting instantaneously with the alkali metal compounds with formation of alkali metal halides. By means of trial experiments it was shown that benzopinacol was not decomposed by ammonium hydroxide, liquid ammonia or liquid ammonia solutions of ammonium or alkali metal halides.

The hydrolyses were carried out in the apparatus shown in Fig. 1. The metal ketyl solution was prepared in the reaction tube A. The ammonium halide was dissolved in the bath of liquid ammonia contained in the Dewar flask B and vigorously stirred with the stirrer E. By twisting the inlet tube C, which passed through a slip-joint, it was possible to snap it off at the capillary G. The metal ketyl solution was then forced through the openings into the bath under a slight pressure of ammonia vapor. The residue after evaporation of the ammonia was washed out with ether and water, and the benzopinacol was isolated from the ether extract. In a series of six experiments using 2 to 5 gram samples of ketone, 5 to 15% yields of benzopinacol were obtained (average 10.9%).

A crucial point in connection with these experiments is the fact that the sodium compound is capable of destroying the pinacol. This has been emphasized by Bachmann, who stated that the mixture must be run into the acid slowly in order to avoid accumulation of the sodium compound. Although the reaction between ammonium salts and the ammonia solutions of the sodium compound is extremely rapid, every effort was made to make the experiments with ammonia solutions as comparable with Bachmann's procedure as possible. Furthermore, additional experiments were carried out to make certain that none of the pinacol initially formed in the bath was subsequently destroyed. Weighed amounts of benzopinacol were added to the bath just before the solution of the sodium compound was run in. All of this pinacol was recovered in addition to the usual amount from the hydrolysis of the sodium compound.

## Summary

1. It has been shown that sodium benzopinacolate is largely dissociated into the corresponding metal ketyl in liquid ammonia solution.

2. It has been shown that intermediate formation of the corresponding disodium compound plays no significant part, if any, in the rapid reactions of the metal ketyl.

3. It has been pointed out that the metal ketyls apparently exhibit more exceptional valence relationships than other tervalent carbon compounds.

PROVIDENCE, RHODE ISLAND RECEIVED JULY 24, 1934

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[6] This result is in agreement with the observations of Bachmann [THIS JOURNAL, **55**, 2828 (1933)], who was unable to detect any benzophenone in ether solutions of sodium benzopinacolate by the use of sodium phenyl.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

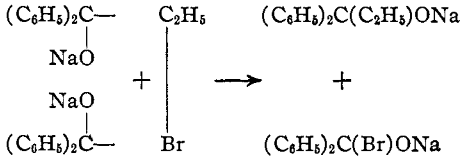
# The Structure of Metal Ketyls. III. Mechanism of the Reactions with Alkyl Halides

BY CHARLES BUSHNELL WOOSTER AND WILLIAM E. HOLLAND

The reactions between alkyl halides and the metal ketyls ordinarily yield the corresponding ketone and alkyl carbinolate in approximately equimolecular proportions as may be illustrated by the following equation for the over-all reaction between ethyl bromide and sodium benzophenone.

$$2(C_6H_5)_2CONa + C_2H_5Br = NaBr + (C_6H_5)_2CO + (C_6H_5)_2C(C_2H_5)ONa \quad (1)$$

In order to account for the carbon alkylation, Schlenk[1] interpreted these transformations as trimolecular reactions in which the metal ketyl molecules, by virtue of their tervalent carbon atoms, cleaved the alkyl halide molecules and combined with the resulting fragments.



$$\begin{matrix}(C_6H_5)_2C- \\ | \\ NaO \\ \\ NaO \\ | \\ (C_6H_5)_2C-\end{matrix} + \begin{matrix} C_2H_5 \\ | \\ | \\ | \\ | \\ Br\end{matrix} \longrightarrow \begin{matrix}(C_6H_5)_2C(C_2H_5)ONa \\ + \\ (C_6H_5)_2C(Br)ONa\end{matrix} \quad (2)$$

$$(C_6H_5)_2C(Br)ONa \longrightarrow (C_6H_5)_2CO + NaBr \quad (3)$$

There are a number of reasons for questioning the validity of this hypothesis. It is difficult to understand why the sodium atom in the metal ketyl molecule would not react directly with alkyl halides, for it is highly reactive toward iodine, oxygen, sulfur, carbon dioxide and hydrolytic reagents. Furthermore, the extraordinary cleavage power attributed by Schlenk to the tervalent carbon atom is not exhibited by any

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[1] Schlenk and Weickel, *Ber.*, **44**, 1182 (1911).