2. The reactions are classified into three types, which (with examples) are as follows: (I) Unsaturates by Dissociation, Example—$C_3H_8 \longrightarrow C_3H_6 + H_2$; (II) Unsaturates by Oxidation, Example—$C_3H_8 + {}^1/_2O_2 \longrightarrow C_3H_6 + H_2O$; (III) Aldehyde Reaction, Example—$C_3H_8 + 2O_2 \longrightarrow CO + 2H_2O + CH_3CHO$.

3. Types I and II give evidence of being more or less normal homogeneous gas reactions which appear at 500–600°, but are subject to induction by Type III at lower temperatures in amount increasing with the temperature.

4. Type III may begin at temperatures of 300–350° and gives every indication of being a chain reaction. Its development is highly spontaneous, and at the same time it is sensitive to relatively minor variations in the conditions of reaction. In particular, it is subject to suppression by a broken-glass packing (especially when this is coated with potassium chloride), and by use of a reaction tube of small diameter. Lowering the pressure to a few millimeters has a like effect. Dilution with oxygen, methane, nitrogen, carbon dioxide or hydrogen depresses the reaction in amount increasing in the order named; this effect is the greater at higher temperatures. Under these conditions the reaction thus has a negative temperature coefficient, though eventually becoming explosive. Excess of hydrocarbon promotes the reaction.

5. Under suppression, there may be no reaction up to 500–600°. Types I and II then appear, accompanied by Type III in varying amount.

6. Considerations bearing on the isolation of particular reactions are set forth.

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THE STRUCTURE OF METAL KETYLS. I. THE SCHMIDLIN FORMULA

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The highly colored products formed by the addition of one atom of an alkali metal to one molecule of certain aromatic ketones were named "metal ketyls" by Schlenk and his co-workers,[2] who concluded that these substances comprised a new class of compounds containing trivalent carbon. This view was criticized by Schmidlin,[3] who contended that they should be regarded as molecular compounds analogous to those formed between

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[2] (a) Schlenk and Weikel, *Ber.*, **44**, 1182 (1911); (b) Schlenk and Thal, *ibid.*, **46**, 2840 (1913); (c) Schlenk, Appenrodt, Michael and Thal, *ibid.*, **47**, 486 (1914).

[3] Schmidlin, "Das Triphenylmethyl," Stuttgart, **1914**, pp. 186–188.

the ketones and metal chlorides[4] and could best be represented by the formula RR′C=O···Me.

Such a formula has little or no definite significance until the meaning of the symbols employed (particularly the dotted line) has been defined in terms of the properties to be expected of the substance represented. In his consideration of the reactions of these compounds Schmidlin gave a very clear definition of the meaning of his formula. In every case he assumed that a dissociation into the ketone and free metal occurred, and was immediately followed by interaction of the latter with the reagent employed. When the product of this interaction was capable of reacting further with the ketone, derivatives were obtained which were identical with those resulting from a mixture of the ketone, the reagent and the alkali metal. Otherwise, the entire amount of ketone was recovered at the end of the reaction.

The mechanism proposed by Schmidlin for the reaction between metal ketyls and alkyl halides may be subjected to a very exacting test by carrying out this reaction in the presence of some additional reagent capable of reacting with any intermediate organo-alkali products which might be formed. A suitable material is liquid ammonia and its influence upon this reaction has been studied under conditions permitting the collection of all gases formed in the process. Two trials gave identical results; only a negligible quantity of gas insoluble in water was collected. If sodium ethyl[5] had been formed as an intermediate step, reaction with the ammonia would be expected, resulting in the formation of ethane

$$C_2H_5Na + NH_3 \longrightarrow NaNH_2 + C_2H_6 \qquad (1)$$

Furthermore, if dissociation of the ketyl into ketone and free metal had occurred, as Schmidlin supposes, the formation of ethane might be expected in any event, for this gas has been shown to be a product of the action of ethyl iodide on sodium in liquid ammonia.[6]

The only assumption that can harmonize these results with the Schmidlin formula is that a competition occurs between the ketone and the solvent ammonia in their reactions with the product formed from sodium and ethyl bromide and that the reaction with the ketone preponderates because of its greater rapidity. The validity of this assumption was then tested by adding metallic sodium to a solution of benzophenone and excess ethyl bromide in liquid ammonia. Ethane, in an amount equivalent to the sodium used, was evolved in both of the experiments carried out.

The Schmidlin formula, as defined and interpreted by its author, requires that the action of ethyl bromide on the ketone–metal compound

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[4] (a) Pfeiffer, *Ann.*, **383,** 97 (1911); (b) K. H. Meyer, *Ber.*, **42,** 1149 (1909); **43,** 157 (1910).

[5] Schmidlin actually suggested a complex of the type C_2H_5NaBr.

[6] Lebeau, *Compt. rend.*, **140,** 1043 (1905).

and that of the metal itself on the ethyl bromide–ketone mixture be identical. The fact that these two reactions lead to quite different results in the presence of liquid ammonia demonstrates conclusively that *the Schmidlin formula is incorrect.*

However, the interpretation of the reactions of these compounds proposed by Schlenk and his co-workers is not the only alternative to be considered. For instance, it has been observed that monosodium benzophenone results from the action of benzophenone upon its disodium derivative in liquid ammonia

$$(C_6H_5)_2C(Na)ONa + (C_6H_5)_2C{=}O \longrightarrow 2\ (C_6H_5)_2CONa \qquad (2)$$

If it is assumed that this reaction is to some extent reversible and that under the influence of any reagent which attacked the very reactive sodium atom in the disodium compound, the transformation could be caused to proceed to completion in the sense of Equation 2 as read from *right* to *left;* it would be expected that the products would consist of the ketone and of the equivalent of an equimolecular quantity of the di-metallic derivative in the form of the materials ordinarily resulting from the action of the reagent upon it. It is a noteworthy fact that the substances actually isolated and identified after decomposition of the ketyls with numerous reagents have been identical with those which are thus predicted, with the single exception that in certain instances the products of hydrolysis of the solid also contained a quantity of the pinacol; this may be ascribed to partial polymerization of the ketyl to the pinacolate. These considerations are of particular significance since they suggest that none of the reagents hitherto employed attack the ketyls *directly* and consequently such reactions scarcely reveal the structure of the ketyls themselves.

Experimental Part

Apparatus.—A diagram of the apparatus used in these experiments appears in Fig. 1. A pyrex reaction tube A fitted with two ground-in introduction tubes B was attached to the system with de Khotinsky cement. It could be evacuated by means of a mercury vapor pump and ammonia introduced from a cylinder attached at C. This cylinder, which is not shown, was filled with liquid ammonia from a commercial fifty-pound tank, a few pieces of sodium metal having been previously introduced. Ammonia thus dried was always used as the solvent for the reacting materials and was transferred from the cylinder by distillation. A manometer D permitted the pressure within the tube to be regulated so that pure ammonia could be condensed therein when it was surrounded by a cylindrical Dewar flask containing a bath of commercial liquid ammonia. The ammonia which was allowed to evaporate at the end of a reaction was permitted either to escape through outlet E into a carboy of water, or could be passed into the gas-collection tube F. This tube contained water for the absorption of ammonia and the volume of any insoluble gas which collected in the tube could be measured. Fresh water could be introduced through a tube which led to the upper part of the collection tube. Since the density of aqua ammonia is less than that of water, it was very convenient to be able to lead the fresh water to the upper surface of the absorbing column. The collected gas could also be transferred into the drying system G and the density of a sample determined by removing and weighing the bulb H. Liquid or solid products were examined after the reaction tube had been removed from the system. The addition of a liquid reagent was accomplished by replacing one of the introduction tubes B with the small buret I. A two-way stopcock J permitted a gaseous reagent to be bubbled through the solutions and, when necessary, the entire system could be filled with a gas other than air or ammonia by means of the inlet K.

The Action of Ethyl Bromide on Monosodium Benzophenone.—The ketone was put in the reaction tube, which was then connected to the apparatus and evacuated. The reaction tube was then filled with ammonia gas, the ground-in fitting B removed and the sodium in the form of spherical pellets dropped into it. It was replaced at once and the apparatus again evacuated, after which the condensation of ammonia in the reaction tube was carried out. The sodium pellets were obtained by cutting the metal into small pieces, melting it under paraffin, washing with petroleum ether and weighing under "Nujol," which was removed by a second washing in petroleum ether. After a suitable quantity of ammonia had been condensed, the sodium was added by turning the fitting in its socket and tapping it gently until the pellets dropped in. They could thus be added one at a time or all at once, as desired. When the formation of the ketyl was completed and the entire line connecting the reaction tube with the collection tube thoroughly swept out with ammonia gas, the ethyl bromide was added through the buret I and the evolved gases were collected. In two experiments employing 1.82 and 1.92 g. of ketone, 0.26 and 0.25 g. of sodium and about 6 cc. of ethyl bromide only about 4 cc. of gas was collected. This might well have been hydrogen, since the ammonia had been dried with sodium, which slowly reacts with the solvent forming sodamide and hydrogen. The possibility that air dissolved in the water might be displaced from solution as the ammonia dissolved and the absorbing liquid became warm was

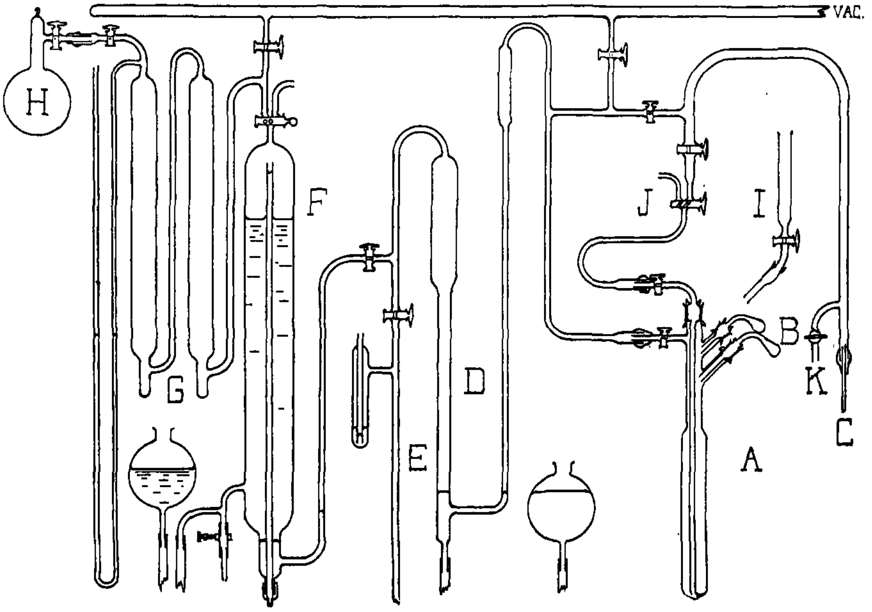

Fig. 1.—Apparatus for studying reactions in liquid ammonia.

largely eliminated by using at all times water which had been previously boiled and cooled in a closed vessel.

The non-volatile products of this reaction were examined in a previous investigation[7] and sodium bromide, benzophenone and diphenylethyl carbinol were identified, but since a quantitative separation of the organic materials was not accomplished the additional formation of gaseous products was not excluded.

The Action of Sodium on Ethyl Bromide and Benzophenone.—These experiments were carried out in a manner similar to that just described except that the ethyl bromide was added before the sodium. It dissolved the ketone and held it in solution in the presence of the liquid ammonia used. The sodium reacted vigorously with this mixture and considerable quantities of gas were evolved. In the two experiments 0.348 and 0.381 g. of sodium added to solutions containing 1.90 and 1.92 g. of ketone and about 6 cc. of ethyl bromide yielded 171 and 189 cc. of gas (under standard conditions); calcd., 170 and 186 cc. of ethane from the equation

$$C_2H_5Br + 2\ Na + NH_3 \longrightarrow NaBr + NaNH_2 + C_2H_6 \qquad (3)$$

The density of the gas was determined by collecting and weighing a dried sample in the density bulb: 339.3 cc. of gas at 24.6° and 223 mm. weighed 0.1317 g., at 25° and 239 mm., 0.1413 g.; mol. wt., 32.3, 32.4; calcd. for ethane, 30.06.

The excess ethyl bromide and ethylamine (formed from ethyl bromide and sodamide) distilled out when the ammonia was allowed to evaporate. The residue was extracted with water to remove sodium bromide and was then soluble in ether. Evaporation of the ether left a residue which was completely converted into benzophenone oxime (m. p. 140°) by treatment with hydroxylamine hydrochloride and sodium hydroxide in dilute alcohol solution. Thus it is evident that the benzophenone remained unchanged in this reaction.

The Action of Benzophenone on Disodium Benzophenone.—The disodium compound was prepared by treating the ketone with two equivalents of sodium in liquid ammonia and an equal amount of ketone was then added. The presence of a definite monosodium compound and the absence of an appreciable amount of ketone in the reaction product were demonstrated by the procedure previously employed[7] for a similar purpose.

Summary

1. It has been shown that the reaction of ethyl bromide with monosodium benzophenone in liquid ammonia is not identical with that between sodium and a solution of ethyl bromide and benzophenone in the same solvent. This fact furnishes conclusive evidence that the Schmidlin formula for the metal ketyls is incorrect.

2. It has been pointed out that the interpretation of the reactions of these compounds proposed by Schlenk and his co-workers is not necessarily the only alternative to be considered.

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[7] Wooster, THIS JOURNAL, **50**, 1391 (1928).