# CONDENSATION BY SODIUM INSTEAD OF BY THE GRIGNARD REACTION.   IV.   THE PROBABLE EXISTENCE OF A NEW INTERMEDIATE, "METAL HALYL," IN THE REACTION

BY AVERY A. MORTON AND JOSEPH R. STEVENS

The action of an alkali metal on a halogenated hydrocarbon has commonly been explained by assuming the intermediate formation of either a metal alkyl or aryl,[1] or a free hydrocarbon radical.[1e,2]   The idea of an earlier stage in which the metal is attached to the organic halide in a complex has received scant attention.[3]   Having made a study on this point we shall present herein experiments for which a reasonable interpretation lies in the assumption of such an intermediate compound.   As examples we have observed the behavior of sodium with chlorobenzene, bromobenzene, and butyl chloride.   The complexes assumed to occur may be designated as chlorobenzene sodium,[4] bromobenzene sodium, and butyl chloride sodium, respectively.   Because of certain analogies with the metal ketyls, to be pointed out in the following paragraphs, we shall consider these complexes as belonging to a new class of compounds to be called "Metal halyls."

Evidence for the above is found in the action of sodium on triphenylchloromethane carried out, on the one hand, in the presence of benzophenone or tetraphenylethylene and, on the other, in the presence of chloro- or of bromobenzene.   When sodium is allowed to stand with triphenylchloromethane in benzene or ether solution no reaction occurs, but if benzophenone is added, the sodium first combines with the ketone, as shown by the color change, forming the metal ketyl, which in turn reacts with triphenylchloromethane to produce triphenylmethyl, sodium chloride and benzophenone.   In other words, the benzophenone has acted as a carrier of sodium to triphenylchloromethane.   A similar result is obtained

[1] For example see (a) Acree, *Am. Chem. J.*, **29**, 588 (1903);   (b) Schorigin, *Ber.*, **41**, 2717 (1908);   (c) Goldschmidt and Schön, *ibid.*, **59**, 948 (1926);   (d) Ziegler and Colonius, *Ann.*, **479**, 135 (1930);   (e) Schlubach and Goes, *Ber.*, **55**, 2889 (1922).

[2] For example see (a) Marvel, Hager and Coffman, THIS JOURNAL, **49**, 2323 (1927);   (b) Bachmann and Clarke, *ibid.*, **49**, 2089 (1927).

[3] The formation of the blue color in the Wurtz–Fittig reaction has received considerable attention from investigators.   Among others Krafft and Göttig, *Ber.*, **21**, 3187 (1888), discuss the formation of a complex.   Schlubach and Goes[1e] find no evidence for organic matter in the blue compound.   Wooster, THIS JOURNAL, **51**, 1856 (1929), interprets certain statements by Schmidlin in "Das Triphenylmethyl" as referring to the formula $C_2H_5NaBr$.   Staudinger, *Z. Elektrochem.*, **31**, 549 (1925), has advanced the idea of a "Mol-Halogenide" as an intermediate product to account for the explosive nature of mixtures of alkali metals and certain halides.

[4] In naming the organic metal compounds we have adopted the recent practice of putting the metal last.

when tetraphenylethylene is substituted for benzophenone. The sodium first adds to the ethylenic linkage from which position it reacts with triphenylchloromethane forming triphenylmethyl, and regenerating tetraphenylethylene. It is clear that the initial step in each of these cases has been the addition of sodium to a polar atom, after which the metal is able to act upon the triarylchloromethane.
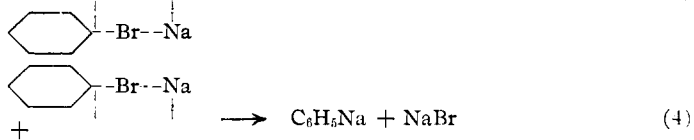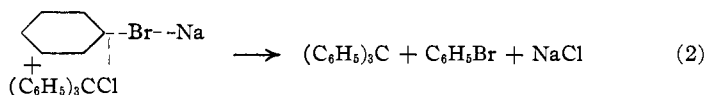
Chloro- or bromobenzene acts similarly to benzophenone or tetraphenylethylene in causing sodium to attack triphenylchloromethane.[5] We can assume, therefore, that sodium first attaches itself to the polar atom in chlorobenzene, forming a "Sodium Halyl," but before sufficient time has elapsed to remove completely the halogen from the phenyl radical, as in a Fittig synthesis, the complex meets a molecule of triphenylchloromethane and reacts with the latter forming triphenylmethyl. The only difference between benzophenone and tetraphenylethylene on the one hand, and chloro- or bromobenzene on the other, is that the former substances have no atoms which can be removed readily by sodium, whereas the latter will, if given time, lose their halogens completely to the alkali metal. Let us express the action of sodium on bromobenzene as in equation (1). "B" illustrates the complex designated as a "Sodium halyl." The dotted lines
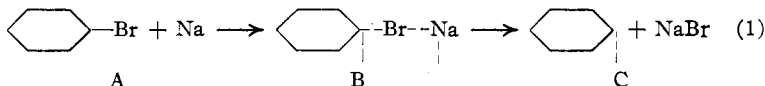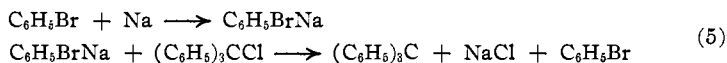


represent partial valences, some of which serve to bind the phenyl radical and the sodium to the polar atom, bromine, and others are unsaturated, representing unused combining power.[6] These free partial valences enable the complex to react either with a molecule of triphenylchloromethane forming triphenylmethyl, equation (2); or with another complex of the same kind forming diphenyl, equation (3); or with an atom of sodium forming phenylsodium, equation (4). If left to itself the complex will eventually form the free radical, phenyl, and sodium bromide as shown in stage C, equation (1).

[5] We wish to acknowledge our indebtedness to Professor Norris for calling to our attention the fact that Norris and Sanders, *Am. Chem. J.*, **25**, 58 (1901), observed the formation of triphenylmethyl from triphenylchloromethane and bromobenzene in the presence of sodium. This fact has been the basis for the experiments described in this paper.

[6] We recognize that it is possible to picture the complex by an associated molecule, a quinoid compound, or some electronic idea. One might also think of the complex as in a dormant state, awaiting the acquisition of sufficient energy to change to the state C; or as in a continual state of change due to the pulling action of the phenyl radical and the sodium atom for the bromine, as if in a tug of war. These interesting speculations are beyond the scope of this paper. We have adopted a form of writing this complex which expresses in the simplest manner possible the reactions and resemblances to the metal ketyls.

$$\text{(benzene ring)}\text{-Br--Na} + (C_6H_5)_3CCl \longrightarrow (C_6H_5)_3C + C_6H_5Br + NaCl \tag{2}$$

$$\text{(benzene ring)}\text{-Br--Na} + \text{(benzene ring)}\text{-Br--Na} \longrightarrow C_6H_5C_6H_5 + 2NaBr \tag{3}$$

$$\text{(benzene ring)}\text{-Br--Na} + Na \longrightarrow C_6H_5Na + NaBr \tag{4}$$

If such a picture of the role of the halide as a carrier of sodium is correct, the chloro- or bromobenzene should be recovered at the end practically unchanged. We have been able to test this hypothesis quantitatively by comparing the amounts of sodium chloride and bromide formed in the reaction of sodium on triphenylchloromethane in the presence of bromobenzene. If the reaction proceeds by the intermediate formation of the "Sodium halyl" which later gives up its sodium as shown in equation (5), sodium chloride will be formed exclusively. If, on the other hand,

$$C_6H_5Br + Na \longrightarrow C_6H_5BrNa$$
$$C_6H_5BrNa + (C_6H_5)_3CCl \longrightarrow (C_6H_5)_3C + NaCl + C_6H_5Br \tag{5}$$
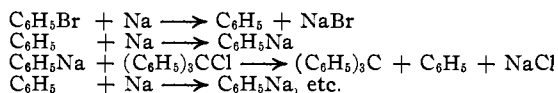
the reaction occurs through the formation of phenylsodium as shown in equation (6), sodium chloride and sodium bromide must be formed in equivalent quantities. Ideal conditions, naturally, will never exist as some

$$C_6H_5Br + 2Na \longrightarrow C_6H_5Na + NaBr$$
$$C_6H_5Na + (C_6H_5)_3CCl \longrightarrow (C_6H_5)_3C + \frac{1}{2}C_6H_5C_6H_5 + NaCl \tag{6}$$
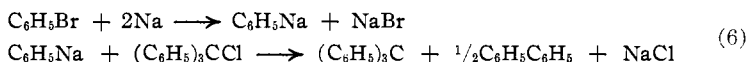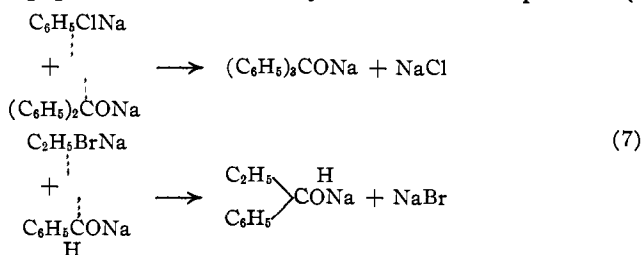
sodium bromide will result from a Fittig reaction. As we increase the concentration of triphenylchloromethane, however, the ratio of chloride to bromide formed will approach 100% sodium chloride if the "Sodium halyl" is the intermediate, and will approach only 50% sodium chloride if phenylsodium is the agent. It is apparent from the analyses of the halides (see Fig. 1), that the quantity of sodium chloride is well above the 50% line demanded by equation (6) and under favorable conditions reaches nearly 88% of the total halides formed. This result shows conclusively that the two are not formed in equivalent quantities and suggests that the probable[7] course is through the formation of a "Sodium halyl."

[7] It is still possible, of course, to write the changes using a free phenyl radical as an intermediate. Thus

$$C_6H_5Br + Na \longrightarrow C_6H_5 + NaBr$$
$$C_6H_5 + Na \longrightarrow C_6H_5Na$$
$$C_6H_5Na + (C_6H_5)_3CCl \longrightarrow (C_6H_5)_3C + C_6H_5 + NaCl$$
$$C_6H_5 + Na \longrightarrow C_6H_5Na, \text{ etc.}$$

However, it is exceedingly unlikely that a free phenyl radical would continue such a role

Application of these ideas to some of the reactions which we have discussed in previous papers[8] of this series may be made as in equations (7).

$$C_6H_5ClNa$$
$$+ \qquad\qquad \longrightarrow \quad (C_6H_5)_3CONa + NaCl$$
$$(C_6H_5)_2CONa$$

$$C_2H_5BrNa$$
$$+ \qquad\qquad \longrightarrow \quad \begin{array}{c} C_2H_5 \\ \diagdown \\ C_6H_5 \end{array}\!\!\!\!>\!\!CONa + NaBr \tag{7}$$
$$C_6H_5CONa$$
$$H$$

In drawing conclusions as to the mechanism of reactions in which sodium is involved, it will be necessary in the future to distinguish more closely
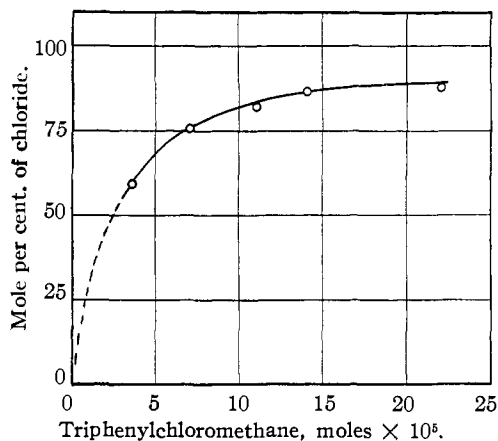


between the various possibilities. It is reasonable to consider that all three, *viz.*, the "Metal halyl," the metal alkyl or aryl, and the free radical may, on superficial examination, appear to bring about identical reactions. We have shown, as a matter of fact, that phenylsodium, prepared separately, will cause the formation of triphenylmethyl from triphenylchloromethane and it is very likely that a free phenyl radical, if it could be isolated as such, would also form triphenylmethyl. Further studies are being made.

Fig. 1.

Mole per cent. of chloride.

Triphenylchloromethane, moles $\times 10^5$.

## Experiments

The Action of Sodium on Triphenylchloromethane in the Presence of Benzophenone.—Triphenylchloromethane, 2 g., and benzophenone, 1 g., dissolved in 25 cc. of anhydrous ether were put into a closed tube with a small lump of sodium. The surface of the sodium became coated with the blue color of benzophenone ketyl but the solution was yellow from the formation of triphenylmethyl. When air was admitted triphenylmethyl peroxide precipitated. It was identified by means of a mixed melting point. When a similar reaction mixture was allowed to stand for three days it went through the stages of formation of benzophenone sodium ketyl which was blue on the surface of the sodium, triphenylmethyl which was yellow in solution, triphenylmethyl sodium as the solution became red, and finally the blue of benzophenone sodium in solution. All of these changes were clearly evident. After treating the reaction mixture with water

as a carrier of sodium when it could even more readily react with triphenylchloromethane and with itself.

    [8] This Journal, **53,** 2244, 2769, 4028 (1931).

and evaporating the ether, the residue was dissolved in benzene and shaken with concentrated sulfuric acid several times to remove all of the peroxide and carbinol present. A mixture of hydrocarbons was obtained from the benzene layer. This mixture was washed twice with hot acetone to remove any triphenylmethane present. The mixture melted up to 185°. The amount present was very small but it is possible that some hydrocarbon was formed other than triphenylmethane and $p$-benzhydryltetraphenylmethane.

The observation of Schlenk and co-workers,[9] that benzophenone sodium added to triphenylchloromethane should cause the formation of triphenylmethyl, was confirmed. The blue color of the ketyl was instantly discharged and the yellow color of triphenylmethyl appeared. From the mixture the peroxide was precipitated when air was admitted.

The Action of Sodium on Triphenylchloromethane in the Presence of Tetraphenylethylene.—To a solution of 0.25 g. of triphenylchloromethane in 10 cc. of ether in contact with 0.25 g. of sodium was added 0.25 g. of tetraphenylethylene.[10] The solution became yellow, indicating the formation of triphenylmethyl. When air was admitted triphenylmethyl peroxide was precipitated. It was identified by a melting point and a mixed melting point.

The Action of Sodium on Triphenylchloromethane in the Presence of Chlorobenzene, Bromobenzene or Butyl Chloride.—To a solution of triphenylchloromethane, 0.2 g. in 20 cc. of anhydrous benzene in contact with 1 g. of sodium, was added 5 g. of chlorobenzene. The yellow color of triphenylmethyl formed easily. When air was let into the tube triphenylmethyl peroxide precipitated. Similar experiments with bromobenzene and with $n$-butyl chloride gave the same results. A blank experiment of triphenylchloromethane with sodium in benzene showed that no triphenylmethyl had formed after the mixture had stood for sixty days.

The Action of Phenylsodium on Triphenylchloromethane.—Two grams of triphenylchloromethane in benzene was added to a suspension of phenylsodium in benzene, made from 2 g. of diphenyl mercury and an excess of sodium wire. Heat was evolved and a strongly colored solution of triphenylmethyl was formed. When air was admitted the peroxide precipitated and was identified by means of a mixed melting point. On evaporation of the mother liquors a small amount of a gummy material remained in which no evidence of tetraphenylmethane could be found. Our original purpose in this experiment was to observe if a different product was formed when the metal aryl was an intermediate in the reaction. The failure to find tetraphenylmethane led to an investigation of the relative quantities of chloride and bromide formed when triphenylchloromethane reacts with sodium in the presence of bromobenzene.

The Determination of the Amount of Sodium Bromide and Sodium Chloride Formed in Mixtures of Triphenylchloromethane and Bromobenzene.—A number of experiments were made in which mixtures of triphenylchloromethane and bromobenzene in 10 cc. of benzene were allowed to stand in contact with very nearly enough sodium to combine completely with all of the bromine in bromobenzene. The quantity of triphenylchloromethane was varied. When the sodium had disappeared the tube was opened and the solid material filtered. After washing the solid twice with considerable anhydrous warm benzene to remove any triphenylchloromethane present, it was washed with anhydrous petroleum ether and dried. The halides were then dissolved in water and filtered through the same filter to remove the small quantity of organic insoluble material which was present. After acidification with nitric acid, a portion of the filtrate

[9] Schlenk and Thal, *Ber.*, **46**, 2854 (1913); Schlenk and Ochs, *ibid.*, **49**, 612 (1916).

[10] Schlenk and Mark [*ibid.*, **55**, 2289 (1922)] added tetraphenylethylene sodium to triphenylchloromethane forming triphenylmethyl.

was treated with an excess of standard silver nitrate solution. The mixture of silver halides was filtered, washed, and weighed. The excess of silver nitrate was titrated with potassium thiocyanate solution using ferric alum as an indicator. From the volumetric results the number of moles of silver halides precipitated could be determined, which value, with the grams of silver halides from the gravimetric analysis of the same sample, enabled one to calculate the moles of chloride and of bromide present. Table I summarizes the results of these calculations.

TABLE I

GRAM ATOMS OF SODIUM, 0.004; MOLES OF BROMOBENZENE, 0.0048; CC. OF BENZENE, 10

| Triphenyl-chloro methane, mole | Silver nitrate equivalent to silver halide precipitated, cc. of 0.0918 $N$ solution | Silver halide, grams | Moles of bromide $\times 10^5$ | Moles of chloride $\times 10^5$ | Mole per cent. of chloride |
|---|---|---|---|---|---|
| 0.0036 | 19.93 | 0.2951 | 74.2 | 108.8 | 59.4 |
| .007 | 20.74 | .2935 | 45.5 | 144.9 | 76.0 |
| .011 | 24.38 | .3392 | 40.3 | 183.5 | 82.1 |
| .014 | 23.09 | .3166 | 29.0 | 183.0 | 86.3 |
| .022 | 20.76 | .2836 | 23.2 | 167.4 | 87.9 |

In order to make sure that triphenylchloromethane did not react with the sodium bromide formed during the reaction, a blank test was made by allowing a mixture of 0.0061 mole of triphenylchloromethane to remain in contact with 0.009 mole of sodium bromide under conditions comparable to those in which the action of sodium has been observed. From this mixture the halides obtained by the method given above were found in two separate determinations to be 99.8 and 100.6% sodium bromide.

## Conclusions

Chlorobenzene, bromobenzene and butyl chloride have been shown to act as carriers of sodium to triphenylchloromethane, in which respect they are similar to benzophenone and tetraphenylethylene.

Analyses of the halides formed in the reaction of sodium with triphenyl-chloromethane in the presence of bromobenzene shows that sodium chloride is formed to a greater extent than sodium bromide.

The above facts are interpreted as indicating the formation of a complex between sodium and bromobenzene. Complexes of this type are designated as "Metal halyls" because of their similarity to metal ketyls.

The position of the "Metal halyl" as an intermediate first step in the formation of a free hydrocarbon radical and metal alkyls or aryls is discussed.

CAMBRIDGE, MASSACHUSETTS