

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 227]

## THE ACTION OF SODIUM ON BETA-CHLORO-ALPHA, ALPHA, ALPHA-TRIPHENYLETHANE IN LIQUID AMMONIA. REARRANGEMENT OF AN ORGANO-ALKALI COMPOUND

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RECEIVED AUGUST 13, 1929

PUBLISHED MARCH 6, 1930

When this investigation was undertaken no colored organo-alkali compounds had been reported except those in which one or more aromatic rings were attached to the same carbon atom as was the alkali metal.<sup>3</sup> A formula containing a quinonoid ring may be readily constructed for these compounds and the existence of tautomers so constituted had been suggested as the source of their color.<sup>4</sup> It appeared to be of interest, therefore, to investigate the influence upon the properties of the carbon-hydrogen and carbon-sodium bonds, in hydrocarbons and organo-alkali compounds, when aromatic rings are present only in the  $\beta$ -position with respect to the carbon atom in question. If organo-alkali compounds of this type were colored, the hypothesis just mentioned would require the assumption of a tautomeric quinonoid structure containing a trimethylene ring.

It has been shown that  $\alpha, \alpha, \alpha$ -triphenylethane does not react with potassium amide in liquid ammonia,<sup>5</sup> and attempts to prepare a nonaphenyl-*tert.*-butane were unsuccessful. However, since it had been observed<sup>6</sup> that sodium benzylide could be prepared from sodium and benzyl bromide in liquid ammonia, although potassium amide is also without action on toluene, it was suspected that an organo-alkali compound might be obtained when  $\beta$ -chloro- $\alpha, \alpha, \alpha$ -triphenylethane was treated with sodium. This proved to be correct but when the red compound which resulted was decomposed with ammonium chloride (which replaces the alkali metal with hydrogen) the product was  $\alpha, \alpha, \beta$ -triphenylethane. It is obvious that a rearrangement occurred<sup>6</sup> and a preliminary study which has been made of this rearrangement is the subject of this paper.

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<sup>3</sup> More recently, the preparation of colored alkali metal derivatives of purely aliphatic hydrocarbons has been described [Salzberg and Marvel, *THIS JOURNAL*, **50**, 1737 (1928); Schlenk and Bergmann, *Ann.*, **463**, 2-97 (1928)].

<sup>4</sup> (a) Gomberg, *Ber.*, **40**, 1875 (1907); (b) Schmidlin, "Das Triphenylmethyl," Stuttgart, 1914, p. 205; (c) Blicke, *THIS JOURNAL*, **46**, 2560 (1924); **47**, 229 (1925).

<sup>5</sup> Wooster and Mitchell, *ibid.*, **52**, 688 (1930).

<sup>6</sup> It has been shown recently by Ziegler and Crössmann [*Ber.*, **62**, 1768 (1929)] that the reaction between sodium and 1,1,3-triphenylindene, reported by Schlenk and Bergmann [*Ann.*, **463**, 125 (1928)], involves a similar rearrangement. The experiments which demonstrated the rearrangement of sodium triphenylethide were completed before the publication of Schlenk and Bergmann's paper.

### Experimental Part

**Apparatus and Materials.**—The apparatus employed in the experiments with liquid ammonia solutions has been described in previous communications.<sup>5,7</sup>

The method of preparing the two triphenylethanes has also been given.<sup>5</sup>  $\beta$ -Chloro- $\alpha, \alpha, \alpha$ -triphenylethane was obtained by the method of Cone and Robinson,<sup>8</sup> and purified by crystallization from petroleum ether.

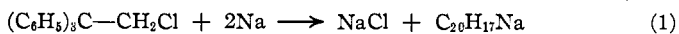
**Attempted Preparation of Nonaphenyl-*tert.*-butane.**—Three attempts to prepare this hydrocarbon directly by the interaction of potassium triphenylmethide and chloroform proved unsuccessful.

The chief product of the reaction, in addition to potassium chloride, was a yellow mass which did not crystallize upon cooling and could not be recrystallized from alcohol, benzene and other solvents. When distilled<sup>9</sup> at 100–150° under 0.2-mm. pressure, a solid was obtained which, after purification by crystallization from alcohol, proved to be triphenylmethane. This result may have been due either to ammonolysis of the chloroform in liquid ammonia or to a decomposition of the reaction product in the course of vacuum distillation.

Another attempt was made involving the stepwise substitution of triphenylmethyl groups into methane. This was halted by the inactivity of  $\beta$ -chloro- $\alpha, \alpha, \alpha$ -triphenylethane, which would not react with potassium triphenylmethide in liquid ammonia.

**The Action of Sodium on  $\beta$ -Chloro- $\alpha, \alpha, \alpha$ -Triphenylethane in Liquid Ammonia.**—When this experiment was carried out in a small reaction tube in the usual manner, a red color was imparted to the solution and all the sodium ultimately reacted, even when large quantities of the metal were employed. Ammonium chloride decolorized the mixture rapidly but in several such experiments only a quantity of the unchanged chloride was recovered. In another of these experiments a very large excess of sodium was used and a liquid mixture was isolated from the reaction residue which solidified below 0°. It was partially frozen and pressed out between filter papers cooled between blocks of ice. Its melting point was raised in this manner to 47°, but at this point the quantity of material became too small for further manipulation.

Success was attained only when the procedure was modified so that the finely pulverized chloride was slowly "dusted" (in the course of about two hours) into a very concentrated solution of sodium contained in a large Dewar flask, the mixture being vigorously agitated by means of the combined action of a stream of gaseous ammonia and a rapidly rotating mechanical stirrer. The stirring was continued for four hours after all of the chloride had been introduced, fresh pieces of sodium being added from time to time. The action of ammonium chloride instantly decolorized the solution and a red precipitate was thrown down. The ammonia was allowed to evaporate completely and water added to the residue. The aqueous solution was filtered and the crystals remaining on the filter paper were crystallized once from alcohol. White needles were obtained which melted at 53.5–54.5°. The melting point remained unchanged upon further recrystallization and upon mixing this product with a sample of  $\alpha, \alpha, \beta$ -triphenylethane. The ultimate results of the reactions involved are probably those expressed in the following equations



**The Structure of the Red Sodium Compound.**—The product of the reaction with ammonium chloride shows that a rearrangement has taken

<sup>7</sup> Wooster, *THIS JOURNAL*, **51**, 1856 (1929).

<sup>8</sup> Cone and Robinson, *Ber.*, **40**, 2164 (1907).

<sup>9</sup> The apparatus employed has been described by Kraus and Foster, *THIS JOURNAL*, **49**, 460 (1927).

place, but it leaves the exact structure of the sodium compound in doubt, for it is impossible to tell which hydrogen atom in  $\alpha,\alpha,\beta$ -triphenylethane is the one which replaced the sodium atom. Accordingly, attempts were made to substitute some group other than hydrogen for the sodium atom and thus obtain a characteristic derivative. These attempts are reported below, but all were unsuccessful.

In a previous communication<sup>5</sup> the authors have shown that all the organo-alkali derivatives of phenylated methanes and ethanes which have been found to be stable in liquid ammonia apparently contain the grouping  $(C_6H_5)_2C(M)-$  ( $M =$  alkali metal). Since the sodium compound in question is stable in ammonia it probably contains this grouping. For this reason the constitution represented in the formula  $(C_6H_5)_2C(Na)-CH_2C_6H_5$ , may be accepted provisionally as its structure.

**The Action of Carbon Dioxide on the Red Sodium Compound.**—The only derivatives of such possible salts as  $(C_6H_5)_2C(Na)CH_2C_6H_5$  and  $(C_6H_5)_2CHCH(Na)C_6H_5$  which are known are the carboxylic acids, which might be expected to result from the action of carbon dioxide on these salts. Experiments showed that carbon dioxide could not be used in liquid ammonia solutions since ammonium carbamate was formed too rapidly.

In one experiment the residue after evaporation of the ammonia from a preparation of the sodium compound was treated with anhydrous ether but no solution was formed and the treatment with carbon dioxide under these conditions was also unsuccessful. It is not certain whether the salt is actually insoluble in ether or whether it was coated with a layer of the excess sodium. Unfortunately, the use of a large quantity of this metal is necessary, since its reaction with ammonia to form the amide is apparently catalyzed by some of the reacting materials or products.

**Attempts to Prepare Reference Compounds.**—The use of such reagents as methyl iodide, ethyl bromide, etc., is an obvious resort, but before such reactions could yield the desired information the expected derivatives must be synthesized independently for comparison with the actual reaction products. Attempts to obtain the corresponding halides from diphenylethylcarbinol and diphenylbenzylcarbinol for use in an independent synthesis of such reference compounds were also unsuccessful. Only the corresponding ethylene derivatives were obtained when the reagents were thionyl chloride or hydrogen chloride gas.

The sole preparation of these chlorides mentioned in Beilstein's "Handbuch" is that of Klages and Heilmann.<sup>10</sup> Since these investigators obtained liquids which they assumed to be the chlorides merely because the corresponding ethylene derivatives could be isolated after the liquids

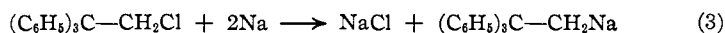
<sup>10</sup> Klages and Heilmann, *Ber.*, **37**, 1450, 1455 (1904).

were boiled with pyridine, it is somewhat doubtful whether they actually obtained such chlorides.<sup>11</sup>

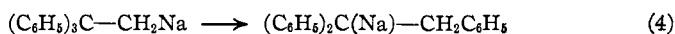
**The Mechanism of the Rearrangement.**—Although, as has just been noted, the constitution of the red compound is still somewhat uncertain, some study has been devoted to the possible mechanism of the rearrangement. Since the action of ammonium chloride upon a liquid ammonia solution of an organo-alkali salt is that of simple hydrolysis by a strong acid, it is probable that the rearrangement occurred at an earlier stage in the process.

Furthermore, the structure of the original chloride seems to be in little doubt. Its properties agree with those described by Cone and Robinson<sup>8</sup> and are distinctly different from those of the isomeric  $\alpha$ -chloro- $\alpha, \alpha, \beta$ -triphenylethane as described by Klages and Heilmann.<sup>10</sup> It has just been stated that it is somewhat doubtful whether these investigators actually obtained this compound. However, the evidence indicates that such a chloride if it exists at all is very unstable and would differ markedly from the very stable one assumed to be  $\beta$ -chloro- $\alpha, \alpha, \alpha$ -triphenylethane. There is no reason to suspect that the halogen is in a phenyl nucleus and the reaction with sodium is not of the type to be expected of such a compound.<sup>12</sup> Finally, the presence of halogen in the ring would not account for the rearrangement observed. It is very likely, in consequence, that the rearrangement occurs during the reaction with sodium.

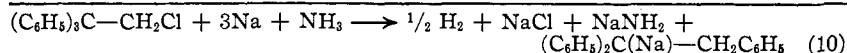
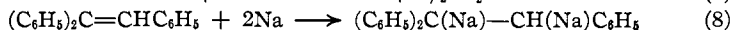
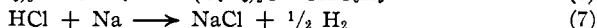
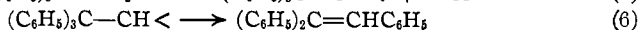
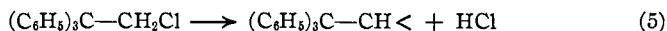
Two very different mechanisms may be suggested; I—that the normal sodium salt was first formed



and this then rearranged in some such manner as that indicated.



II. Another mechanism would assume an initial loss of hydrogen chloride



The rearrangement itself is expressed by Equations 5 and 6 and is analogous to that observed upon heating  $\beta$ -chloro- $\alpha, \alpha, \alpha, \beta$ -tetraphenylethane or treating this halide with water, phenylmagnesium bromide or benzene

<sup>11</sup> In this connection it is interesting to note that three attempts by one of us (N. W. M.) to obtain triphenylethylene by dehydration of diphenylbenzylcarbinol with acetic anhydride were all unsuccessful. This suggests that the dehydrations reported by us may have involved the intermediate formation of a very unstable chloride.

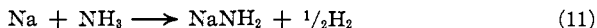
<sup>12</sup> White, *THIS JOURNAL*, **45**, 779 (1923).

and aluminum chloride.<sup>13</sup> Similar equations have been suggested for other rearrangements involving "unilateral" abstraction of hydrogen halides by Tiffeneau, Stieglitz and others.<sup>14</sup> The remaining reactions are those expected as a consequence of the presence of sodium and ammonia.

That expressed in Equation 8 has been shown to take place by separate experiments employing sodium and also potassium. In the latter case, triphenylethylene<sup>15</sup> was treated with excess potassium and after reaction had occurred the color of the free metal was discharged by adding an iron oxide catalyst to convert the metal into its amide. This left a deep red solution and from the amount of hydrogen evolved in the process it was calculated that two atoms of potassium had reacted with the hydrocarbon. Ammonium chloride decomposed the salt and  $\alpha,\alpha,\beta$ -triphenylethane was obtained from the residue.

Reaction 9 is suggested as a result of the information reported in a previous communication<sup>5</sup> that only those potassium derivatives of phenylated methanes and ethanes which contain the  $(C_6H_5)_2C(K)^-$  group resist ammonolysis in liquid ammonia. This suggestion is supported by the fact that the action of benzyl chloride upon the product of potassium and triphenylethylene yields the same substance that is produced when this halide is added to the reaction product of potassium amide and  $\alpha,\alpha,\beta$ -triphenylethane.<sup>16</sup>

Since the reaction



always occurred during the actual experiment, it is impossible to distinguish between the two alternative mechanisms by a study of the final products, for these are the same. This is evident when Equation 11 is added to 3 and 4, for the sum is identical with 10.

**The Action of Sodium on  $\beta$ -Chloro- $\alpha,\alpha,\alpha$ -triphenylethane in Indifferent Solvents.**—If the rearrangement could be carried out in the absence of ammonia or other reactive solvent, Reactions 9 and 11 could be eliminated and the final products predicted by the two mechanisms would differ. (The influence of employing an excess concentration of the halide instead of the metal might lead to a synthesis of the Wurtz-Fittig type but would not invalidate this statement.) Unfortunately, this test was defeated by the inertness of the halide.

When 2.0 g. was treated with sodium in dry ether for two days (the solvent was refluxed for five hours during this period), 1.985 g. was recovered unchanged and the aqueous solution of the residue insoluble in

<sup>13</sup> Ref. 4 b, p. 146.

<sup>14</sup> (a) Tiffeneau, *Bull. soc. chim.*, [4] 1, 1205 (1907); (b) Stieglitz and Leech, *THIS JOURNAL*, 36, 272 (1914); Stieglitz and Vosburgh, *Ber.*, 46, 2151 (1913); Vosburgh, *THIS JOURNAL*, 38, 2081 (1916).

<sup>15</sup> Prepared by the method of Hell and Wiegandt, *Ber.*, 37, 1431 (1904).

<sup>16</sup> These reactions are being studied further and details will be published later.

ether gave no test for halogen, proving that no reaction had occurred. A similar experiment employing boiling toluene as a solvent was continued for ten hours but precipitation of silver chloride from the aqueous extract indicated that but 1.88% of the material had reacted.

However, even these facts may have some bearing upon the mechanism of the reaction. Since there is no doubt that sodium could react readily and completely with any hydrogen chloride liberated under the conditions described, any loss of hydrogen chloride from the halide must be very slight in ether at 35° and toluene at 111°. If reaction is assumed to take place according to Mechanism II, it is also necessary to make the doubtful assumption that the cleavage of the halide, which is sufficient for complete reaction in ammonia at -33.5°, is decreased to almost nil by raising the temperature to +35° and then increased again by further raising the temperature to 111°. On the other hand, Mechanism I permits the differences in reactivity of the halide to be ascribed to variations in the influences favoring the reaction of the sodium. This is in accordance with the facts, for the conditions become progressively more favorable to reaction of the sodium in passing from ether at 35°, where the metal is solid and readily coated with insoluble crusts, to toluene at 111°, where the sodium is molten and continuously presents a fresh surface for reaction, and to ammonia at -33.5° where the metal dissolves and may be used at high concentrations.

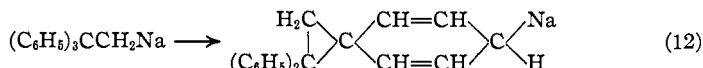
**The Action of Pyridine on  $\beta$ -Chloro- $\alpha, \alpha, \alpha$ -triphenylethane.**—It has just been noted that the variation in reactivity of the chlorotriphenylethane toward sodium under different conditions casts doubt upon the validity of Mechanism II. Further light upon this problem might be expected from a study of the reactivity of this halide toward a reagent which would combine readily with any liberated hydrogen chloride but which had very little tendency to remove the halogen alone.

Such a reagent is pyridine and at its boiling point (115°) the conditions for cleavage of the halide would appear to be as favorable as in toluene solution. Yet when two grams of the chlorotriphenylethane was dissolved in pyridine and the solution boiled under a reflux condenser for ten hours, little evidence of reaction was obtained. A quantity of the unchanged halide was recovered and treatment of the aqueous extracts with silver nitrate produced only a barely perceptible opalescence.

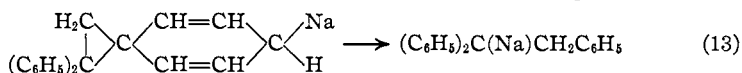
It is scarcely probable that pyridine inhibits, or that toluene in any special way promotes cleavage of hydrogen chloride from the chlorotriphenylethane. Consequently, the reaction with sodium in toluene must consist of direct halogen removal and the rearrangement in liquid ammonia solution very probably proceeds according to Mechanism I.

**A Possible Interpretation of Mechanism I on the Basis of the Quinonoid Hypothesis.**—The mechanism which has just been shown to be in

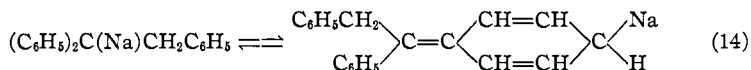
best accord with the experimental evidence assumes the preliminary formation of an organo-alkali compound which then rearranges. Some reasons for predicting such a rearrangement might be based upon the assumption that such organo-alkali compounds tend to exist in equilibrium with a tautomeric quinonoid form.<sup>4</sup> As pointed out in the introduction, the only type of quinonoid tautomer possible in this instance is one involving the formation of a trimethylene ring.



This structure could evidently revert to a benzenoid form in two ways, one being the reverse of Equation 12 and the other that represented below.



The stability of such organo-alkali compounds appears to be increased by the presence of phenyl groups upon the carbon atom to which the alkali metal is attached<sup>5,6,17</sup> and, therefore, it might be predicted that the process represented by Equation 13 would predominate over the reverse of that expressed in Equation 12. The fact that the rearranged compound could conceivably form a normal quinonoid tautomer



would perhaps also hinder the reversal of Reaction 13. Thus the sum of Reactions 12 and 13, proceeding in the direction which has just been suggested as the most probable, would constitute the rearrangement as expressed in Equation 4.

### Summary

1. The action of sodium on  $\beta$ -chloro- $\alpha,\alpha$ -triphenylethane in liquid ammonia leads to a molecular rearrangement.
2. Two very different mechanisms are suggested for this rearrangement and evidence is presented to discriminate between them.
3. A possible interpretation of the more probable mechanism on the basis of the quinonoid hypothesis is outlined.

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<sup>17</sup> Schlenk, Appendrot, Michael and Thal, *Ber.*, **47**, 473 (1914).