

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE BENZOHYDRYL RULE AND THE CONSTITUTION OF
ALKALI TRIPHENYLETHIDES WHICH ARE STABLE IN
LIQUID AMMONIA¹

BY CHARLES BUSHNELL WOOSTER AND JOHN F. RYAN

RECEIVED DECEMBER 11, 1931

PUBLISHED JUNE 6, 1932

It has been emphasized by Kraus² that although the systematic investigation of the chemistry of non-aqueous solutions cannot but lead to many valuable results, substantial progress will be achieved only when such a study is made a primary objective rather than a side line, incident to other investigations. An important division of this subject deals with organic reactions, particularly reduction reactions, in liquid ammonia solution. There is a good reason for beginning an investigation of this field with the hydrocarbons. These substances exhibit a greater reactivity toward alkali metal solutions than was originally recognized³ and some notion of the probable behavior of hydrocarbon radicals may be expected to facilitate a study of the reduction of the various types of organic compounds in which such radicals occur.

In general the reduction of hydrocarbons with alkali metals leads primarily to the formation of organo-alkali compounds which may be either stable or subject to ammonolysis in the presence of liquid ammonia. Some basis for predicting the result in particular instances has been obtained by a study of the reaction between hydrocarbons and alkali metal amides in liquid ammonia solution. This reaction is the reverse of ammonolysis



and its occurrence demonstrates the existence of a stable alkali metal derivative of the hydrocarbon in question.

The Benzohydril Rule.—The action of potassium amide on some phenylated methanes and ethanes has been reported previously.⁴ This study has now been extended using sodium amide and including some additional hydrocarbons.

The results obtained with the two alkali metal amides were the same. Reaction was observed with $(C_6H_5)_2CH_2$, $(C_6H_5)_3CH$, $(C_6H_5)_2CHCH_3$, $(C_6H_5)_2CHCH_2C_6H_5$, $(C_6H_5)_2CHCH(C_6H_5)_2$, $(C_6H_5)_2CHCH_2CH(C_6H_5)_2$ and tetrahydronaphthalene, but no reaction took place with $C_6H_5CH_3$, $(C_6H_5)_4C$, $C_6H_5CH_2CH_3$, $C_6H_5CH_2CH_2C_6H_5$, $(C_6H_5)_3CCH_3$, $(C_6H_5)_3CCH_2C_6H_5$ or $C_6H_5CH(CH_3)_2$.

¹ Paper presented at the Indianapolis meeting of the American Chemical Society, April, 1931.

² Kraus, *Chem. Rev.*, **8**, 263 (1931).

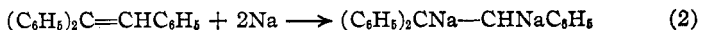
³ Kraus and White, *THIS JOURNAL*, **45**, 769 (1923).

⁴ Wooster and Mitchell, *ibid.*, **52**, 688 (1930).

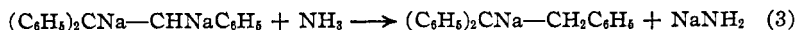
It may be seen that in the case of the *phenylated paraffins* reaction occurred when and only when the benzohydryl group, $(C_6H_5)_2CH-$, was present in the hydrocarbon molecule. This generalization, which has been established for all the phenylated methanes, most of the phenylated ethanes and two of the phenylated propanes (including one with a tertiary structure not involving two phenyl groups), is probably applicable to the other phenylated paraffins and may be conveniently termed the *benzohydryl rule*.

This rule is closely related to that of Vorländer,⁵ who pointed out that the reactivity of a hydrogen atom was increased by the presence of unsaturation in the β -position. The benzohydryl rule is more specific, however, in that it determines the amount of a particular type of unsaturation necessary to render the hydrogen atom reactive toward sodium or potassium amides in liquid ammonia at -33.5° . A comparison of the two rules furnishes two interesting suggestions. First, it indicates that the benzohydryl rule will not generally apply without modification to hydrocarbons containing other types of unsaturation than phenyl groups. This is true even when the additional unsaturation is that of a six-membered ring, as is shown by the behavior of tetrahydronaphthalene. Second, it suggests that the hydrogen atom which is replaced by alkali metal is the one attached to the aliphatic carbon atom of the benzohydryl group. This suggestion as well as other predictions based on the foregoing generalizations has been confirmed in the case of stable alkali triphenylethides prepared by various reactions including addition, substitution and molecular rearrangement. The remainder of this paper is devoted to these results which illustrate the value of the benzohydryl rule.

The Constitution of the Stable Sodium Triphenylethide.—The initial step in the reaction between sodium and triphenylethylene in liquid ammonia is the addition of sodium to the double bond



as is shown by the fact that hydrolysis of the reaction product yields 1,1,2-triphenylethane.⁴ The initial product is, therefore, a 1,2-disodium-1,1,2-triphenylethane and falls within the province of the benzohydryl rule. Only one of the sodium atoms is attached to the aliphatic carbon atom of a benzohydryl group and consequently the other sodium atom is susceptible to ammonolysis.⁶



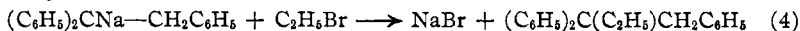
⁵ Vorländer, *Ber.*, **34**, 1632 (1901).

⁶ The benzohydryl rule requires that *under equilibrium conditions* the system represented in Equation 3 would consist principally of the substances on the right-hand side of the arrow. Consequently, the statement made above involves the assumption that equilibrium is attained under the conditions of the experiment. In all the cases thus far investigated the ammonolysis of an unstable *organo-alkali* compound has been found to proceed rapidly.

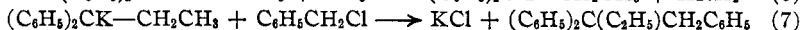
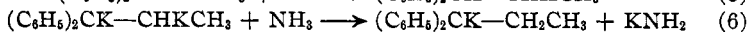
The structure of the stable sodium compound was established by the preparation of its ethyl derivative. Ammonia was condensed on a 3-g. sample of triphenylethylene in a reaction tube,⁷ and sodium was added in tenth-gram portions until a permanent blue color was obtained. After stirring for two hours, ethyl bromide diluted with dry ether was added until the color of the liquid ammonia solution was discharged. The reaction residue was washed with water and crystallized from alcohol. Rod-like crystals melting at 79–79.5° were obtained.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.31; H, 7.69. Found: C, 91.94, 92.30; H, 7.17, 7.02.

If the sodium compound actually possessed the structure tentatively assigned, the product of its reaction with ethyl bromide should be 1,2,2-triphenylbutane.



This hydrocarbon is unknown, but its independent synthesis from 1,1-diphenylpropylene-(1)⁸ was accomplished by the method expressed in Equations 5, 6 and 7.



The occurrence of the reaction expressed in Equation 5 was demonstrated by an experiment in which the propylene was slowly added to a concentrated solution of potassium in liquid ammonia so that the alkali metal was always present in large excess. The resulting organo-alkali compound was decomposed with ammonium chloride and the ammonia allowed to evaporate. The residue was a colorless oil, which was washed, dried and distilled under reduced pressure. Its properties were then compared with those of a sample of 1,1-diphenylpropane prepared by the method of Klages and Heilmann.⁹ These two substances were found to be identical; both boiled at 152° under 18 mm., the density of both was 0.9783 ± 0.0001 at 25° and the refractive index (white light) was 1.5743 ± 0.0001 at 17°. It is evident, therefore, that the double bond in 1,1-diphenylpropylene is attacked by a *concentrated* solution of *excess* potassium in liquid ammonia.

The procedure described is essential, however, because in one experiment in which ammonia was condensed on a sample of the propylene and then potassium was slowly added until it was present in slight excess, the reaction with benzyl chloride produced a hydrocarbon melting at 122–124° which decolorized a solution of bromine in carbon tetrachloride and was suspected to be 1,1,4-triphenylbutylene-(1).

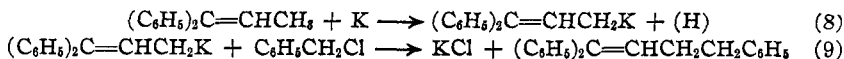
⁷ The apparatus employed in these investigations has been described previously [Wooster, *THIS JOURNAL*, **51**, 1858 (1929)].

⁸ Prepared by the method of Hell and Bauer, *Ber.*, **37**, 232 (1904).

⁹ Klages and Heilmann, *ibid.*, **37**, 1450 (1904).

Anal. Calcd. for $C_{22}H_{16}$: C, 92.96; H, 7.04. Found: C, 93.63; H, 7.96.

This might have been formed by reactions of the type expressed in Equations 8 and 9.



Similar substitution reactions have been observed by Schlenk and Bergmann, and Ziegler and Schäfer.¹⁰

Accordingly, another sample of diphenylpropylene was added to a *concentrated* solution of *excess* potassium in liquid ammonia and after stirring the mixture for one hour just enough benzyl chloride was added to discharge the red color which appeared after the excess free potassium had reacted. The product was difficult to purify, probably because it was contaminated with low melting products of the reaction between benzyl chloride and the excess of free potassium. After three crystallizations, the substance possessed a melting point of 77–79° and was then compared with the product of the action of ethyl bromide on sodium triphenylethide.

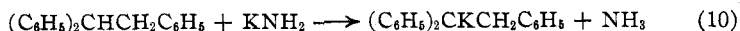
The identity of the two hydrocarbons was shown by mixed melting points. This evidence established their constitution as that of 1,2,2-triphenylbutane, but since this conclusion is to be applied to the molecular rearrangement of an organo-alkali compound one point deserves emphasis. *The possibility of molecular rearrangements involving the carbon skeleton during the preparation of these organo-alkali compounds is excluded* by the fact that upon decomposition with ammonium chloride the sodium derivative of triphenylethylene (Reactions 2 and 3) yielded 1,1,2-triphenylethane and the potassium diphenylpropide prepared from diphenylpropylene and a *concentrated* solution of potassium in liquid ammonia yielded 1,1-diphenylpropane.

The only ethyl substitution product of 1,1,2-triphenylethane which is identical with a benzyl substitution product of 1,1-diphenylpropane is 1,2,2-triphenylbutane.¹¹ Therefore, the single hydrocarbon prepared by these two methods must be 1,2,2-triphenylbutane and *the tentative structure proposed for the stable sodium triphenylethide on the basis of the benzohydril rule has been independently confirmed.*

The Constitution of the Stable Potassium Triphenylethide.—From considerations regarding the benzohydril rule it may be predicted that the reaction between 1,1,2-triphenylethane and potassium amide follows the course indicated in Equation 10

¹⁰ (a) Schlenk and Bergmann, *Ann.*, **479**, 78 (1930); (b) Ziegler and Schäfer, *ibid.*, **479**, 154 (1930).

¹¹ It can be readily seen that identical products could not be obtained in any case if more than one ethyl or benzyl group were introduced. Also, it will be shown presently that the sodium triphenylethide yields a *monobenzyl* derivative with benzyl chloride.

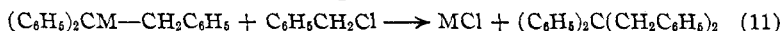


yielding a substance analogous in constitution to that resulting from the action of sodium on triphenylethylene. This prediction was verified by the preparation of benzyl derivatives of the two organo-alkali compounds as follows. 1,1,2-Triphenylethane was treated with potassium amide in liquid ammonia,⁷ and benzyl chloride was added to the red solution. Rapid decolorization occurred and the residue after evaporation of the ammonia was extracted with ether, the ether evaporated and the product recrystallized from alcohol. Transparent needles melting at 125–127° were obtained.

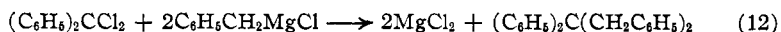
Sodium was added to a mixture of triphenylethylene and liquid ammonia until the metal was present in slight excess as shown by the blue color of the solution. Enough benzyl chloride in absolute ethereal solution was added to just discharge the color of the reaction mixture. A substance crystallizing from alcohol in needles melting at 124–126° was isolated from the ethereal extract of the reaction residue. When mixed with the product of the previous experiment, a melting point of 125–127° was found showing that the two substances are identical. The analysis also shows that only *one* benzyl radical was introduced, proving that the stable organo-alkali compounds were both *mono*-alkali triphenylethides.

Anal. Calcd. for $\text{C}_{27}\text{H}_{24}$: C, 93.10; H, 6.90; mol. wt., 348. Found: C, 92.57; 92.12; H, 6.87, 7.00; mol. wt., cryoscopic in benzene, 337.

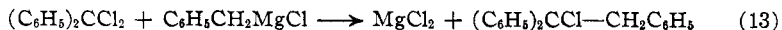
This hydrocarbon is doubtless diphenyldibenzylmethane



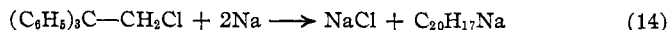
but attempts to prepare it, independently, from benzophenone chloride and benzylmagnesium chloride



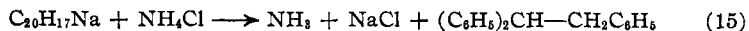
were unsuccessful, the results indicating that the reaction did not proceed smoothly beyond the first step



The Sodium Triphenylethide Rearrangement.—Sodium reacts with 2-chloro-1,1,1-triphenylethane to give a red-colored organo-alkali compound which is stable in liquid ammonia solution¹²



When this was treated with ammonium chloride the product recovered proved to be 1,1,2-triphenylethane, showing that a molecular rearrangement had occurred.



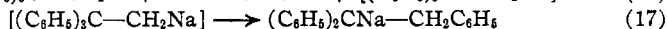
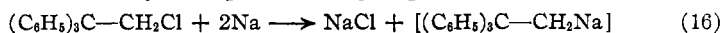
Attempts to prepare derivatives of the sodium compound by the use of phenyl halides or carbon dioxide proved unsuccessful, but in view of its

¹² Wooster and Mitchell, *THIS JOURNAL*, **52**, 1042 (1930).

stability in liquid ammonia a tentative formula, $(C_6H_5)_2CNa-CH_2C_6H_5$, was assigned¹² on the basis of the benzohydryl rule. It is evident that this formula is identical with that of the sodium triphenylethide previously mentioned (Equations 2 and 3) and accordingly experiments were undertaken to prove the identity of the two compounds.

The product of Reaction 14 was first treated with benzyl chloride. However, five recrystallizations of the product failed to yield a satisfactorily purified substance. The material obtained melted at 115–117°; it was shown to be a hydrocarbon and its melting point was not decreased by admixture with the diphenyldibenzylmethane prepared previously. The product is probably diphenyldibenzylmethane but the evidence is obviously inconclusive.

Consequently the experiment was repeated using ethyl bromide. The apparatus and procedure was essentially similar to that formerly described.¹² The product was obtained after a single crystallization from alcohol in the form of transparent rod-like crystals melting sharply at 79–79.5° and was shown to be identical with 1,2,2-triphenylbutane by a mixed melting point, *thus confirming the tentative structure for this sodium compound* and showing that the reaction between 2-chloro-1,1,1-triphenylethane and sodium may be represented by Equations 16 and 17.



Summary

1. It has been noted that reaction between sodium or potassium amides and phenylated paraffins in liquid ammonia at its boiling point occurs only when the benzohydryl group is present in the hydrocarbon. This generalization may be conveniently termed the *benzohydryl rule*.

2. It appears probable that the alkali metal derivatives of phenylated paraffins which are stable in liquid ammonia may be prepared by the action of the alkali metal amides on the corresponding hydrocarbons and that in these reactions the alkali metal replaces hydrogen which is attached to the aliphatic carbon atom of a benzohydryl group.

3. Predictions based on the foregoing generalizations have been confirmed in the case of stable alkali triphenylethides prepared by various reactions including addition, substitution and molecular rearrangement.

PROVIDENCE, RHODE ISLAND