sult of this increased interionic distance is that the magnitude of the charge on each ion becomes much less significant and the effect is determined by the total charge. As a result those principles which indicate a large variation with the charges of individual ions now become invalid. It is essential that a quantitative theory of these relations be developed.

In a qualitative sense the amount of lowering of the critical concentration of a detergent depends upon the tendency of that detergent to form aggregates. In Table VI are plotted the critical concentrations of several detergents together with the ratio of this concentration to the critical concentration in the presence of 0.05 molar sodium chloride.

TABLE VI

CRITICAL CONCENTRATIONS FOR MICELLE FORMATION IN 0.05 MOLAR SODIUM CHLORIDE

Detergent	Crit. concn. pure detergent	Crit. concn. pure detergent / Crit. concn. in 0.05 *M* NaCl
Decyltrimethylammonium bromide	6.36×10^{-2}	1.13
Dodecylammonium chloride	1.31×10^{-2}	1.91
Sodium decyl sulfonate	4.00×10^{-2}	1.33
Potassium laurate	2.33×10^{-2}	2.01
Sodium dodecyl sulfate	6.11×10^{-3}	2.87

It is apparent, in the cases considered, that the lower the critical concentration, *i.e.*, the greater the tendency toward aggregation, the greater is the lowering of the critical concentration by equal amounts of salt. As might be expected, this correlation is true only within each class of detergents.

Summary

It is shown that the behavior of the colloidal aggregates of long chain electrolytes cannot be described in terms of the principle of ionic strength or the related Debye–Hückel relationships. The depression of the critical concentration of such electrolytes, as measured by the spectral change of a dye, is related only to the concentration of that ion of an added salt which bears a charge opposite to that on the colloidal aggregate. The nature of the other ion is without effect.

The logarithm of the critical concentration of a colloidal electrolyte is a linear function of the logarithm of the total concentration of the ion opposite in charge to that on the aggregate. Urea, a non-electrolyte, is found to have a negligible effect in lowering the critical concentration.

Within each class of detergents, *i.e.*, anionic or cationic, the depression of the critical concentration brought about by equal amounts of salt is, in the cases investigated, greater the lower the critical concentration of the detergent.

The above relationships, and the fact that the form of the mass law usually applied to colloidal electrolytes is found to be invalid, indicate that they form *a new type of electrolyte in which salt ions of the same charge as the colloidal aggregate are repelled to such a distance as to give independence of the magnitude of the charge per ion*, with dependence upon only the sum of the charges on all such ions, in the formation of the aggregate. With ions of ordinary salts these ions are sufficiently close together to give the well-known high dependence on the charge per ion.

CHICAGO, ILLINOIS RECEIVED JUNE 26, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXII. The Reaction of the Sodium Derivatives of Allyl or Propenylbenzene with Proton Donors[1]

BY TOD W. CAMPBELL[2] AND WILLIAM G. YOUNG

The recent synthesis of the sodium derivative of allylbenzene $[C_6H_5CH{=}CH{-}CH_2]^-Na^+$ by Levy and Cope[3] suggests an interesting extension of our work on allylic organo-metallic compounds. Since this compound should be more ionic in nature than the corresponding Grignard reagent, it might be expected to give a greater opportunity for determining the reaction products to be expected from a resonating carbanion than with the corresponding Grignard reagent, which may be largely covalent in nature. In spite of the fact that the sodium derivatives might be expected to behave differently than the Grignard reagent, Levy and Cope found that the allylic sodium compound reacted at the secondary position in coupling reactions with allylic halides, just as has been reported from the reaction of cinnamylmagnesium chloride with carbon dioxide, phenyl isocyanate, ethyl chlorocarbonate[4] and acetaldehyde.[5]

On the other hand, we have found that proton donating agents give entirely different mixtures of products from cinnamylmagnesium chloride[6] and the sodium derivatives of allyl- and propenylbenzene. Preliminary work with carbon dioxide, ketones and α-haloacetic acids has also revealed differences in the products of the reactions

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[1] Presented before the Organic Division at the Chicago Meeting of the American Chemical Society, September 10, 1946.

[2] Abbott Laboratories Research Fellow 1944–1945.

[3] Levy and Cope, THIS JOURNAL, **66**, 1684 (1944).

[4] Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927); **53**, 3541 (1931).

[5] Ou Kuin-Houo, *Ann. chim.*, **13**, 175 (1940).

[6] Young, Ballou and Nozaki, THIS JOURNAL, **61**, 12 (1939).

of the sodium and magnesium derivatives in the propenyl–allylbenzene system, which will be discussed in forthcoming papers.

Experimental

Allylbenzene was prepared in the usual way[7] from phenylmagnesium bromide and allyl bromide, b. p. 156–157° (uncor.), $n^{25}D$ 1.5132.

Propenylbenzene was prepared by refluxing allylbenzene with an equal volume of 20% potassium hydroxide in butyl alcohol for about three hours. The alkali was washed out with several portions of water, and the product distilled, after drying over anhydrous magnesium sulfate, b. p. 176–177° (uncor.), $n^{25}D$ 1.5491.

Sodium Derivatives of Allyl- and Propenylbenzene.—Those derivatives were prepared from the corresponding hydrocarbon by the method of Levy and Cope.[3] In general approximately 0.25 mole of the appropriate hydrocarbon was added dropwise over a period of about ten minutes to an equivalent amount of sodamide in about 300 ml. of anhydrous liquid ammonia. However, in a few experiments, 30–50% excess of sodamide was employed. A one-liter three-necked flask equipped with dropping funnel, stirrer and a large outlet tube for the escape of ammonia was employed. The apparatus was protected by drying tubes containing potassium hydroxide.

Decomposition of the Sodium Compounds. Method I.—The liquid ammonia solution of the sodium salt was treated with slightly more then the theoretical amount of methyl alcohol. The intense red color of the sodium compound was discharged at once. Immediately a large excess of powdered anhydrous ammonium chloride was added (cautiously!), and the mixture stirred vigorously until the ammonia had completely evaporated and the system had attained room temperature.

Method II.—The sodium salt was decomposed directly by the *cautious* addition of powdered anhydrous ammonium chloride, and the mixture was stirred as above until the ammonia had evaporated.

Method III.—An excess of phenylacetylene was added to the liquid ammonia solution. The red color of the sodium derivative was almost completely destroyed. The color remaining indicated the presence of only a small amount of sodium allylbenzene in the equilibrium mixture. After about fifteen minutes, the sodium derivatives were decomposed with ammonium chloride, and the ammonia allowed to evaporate.

Analysis of the C_9 Hydrocarbon Fraction from the Above Reactions.—The reaction product from Methods I or II, after removal of the liquid ammonia, was treated with enough water to dissolve solid salts, and then filtered, to remove traces of solid matter. The hydrocarbon layer was taken up in ether, the ethereal solution was washed with dilute sulfuric acid to remove traces of amines, and dried. It was distilled through a column packed with a 90-cm. metal spiral. The fraction boiling between 150–178° was cut, and refractionated into several fractions. Since the refractive indices of allylbenzene ($n^{25}D$ 1.5132) and propenylbenzene ($n^{25}D$ 1.5491) differ widely, each of the above fractions was analyzed by comparing its refractive index with a plot of refractive index *versus* per cent. propenylbenzene and allylbenzene, obtained from known mixtures. From those data, the percentage composition of the C_9 hydrocarbon fraction was determined.

The mixture obtained by method III was analyzed by a study of the distillation curve obtained when the reaction mixture was carefully distilled through a precision column similar to that described by Bower and Cook,[8] except the packing was platinum rather than nichrome gauze.

Allylbenzene in the above reaction mixtures was characterized in the low-boiling fractions as its dibenzoate,[7] and propenylbenzene in the higher-boiling fractions as its dibromide.

The analyses of the products obtained from methods I, II and III showed an average composition of 15% allylbenzene, and 85% propenylbenzene, with an average deviation not greater than ±5%. The results appear to be independent of the hydrocarbon used in forming the sodium salt and the method of decomposition. An excess of sodamide had no effect on the composition of the hydrocarbon mixtures.

The yield of C_9 hydrocarbons averaged about 70%. The remainder was a dimer of allylbenzene, with a molecular weight of 236 (bromine titration, see below. The compound was assumed to have one double bond.); b. p. 141–145° (2 mm.), $n^{25}D$ 1.5455. This same dimer was obtained in about 65% yield when an attempt was made to isolate solid sodium allylbenzene, by allowing the liquid ammonia solvent to evaporate overnight under anhydrous conditions.

Preparation and Hydrolysis of Cinnamylmagnesium Chloride.—This Grignard reagent was prepared as described by Young, Ballou and Nozaki,[6] and by Gilman and Harris.[4] The Grignard reagent was obtained in about 70% yield, as determined by titration. It was hydrolyzed with ice and dilute sulfuric acid. The ether layer was separated, dried and distilled. The fraction boiling from 150–180° was collected, and redistilled through a 100-plate Podbielniak column. From the distillation data the C_9 fraction was adjudged to be 75% allylbenzene and 25% propenylbenzene. These values agree with those in the literature[6] based on oxidation of the hydrocarbon fraction with permanganate to a mixture of benzoic and phenylacetic acids.

Determination of the Percentage Unsaturation of the Various Hydrocarbon Fractions.—Percentage unsaturation was determined essentially after the method described by Winstein and Lucas,[9] except that glacial acetic acid was used as the solvent. A weighed sample of unsaturated hydrocarbon was introduced into a 250-ml. glass-stoppered flask containing 50 ml. of pure glacial acetic acid. A measured volume of standard bromate–bromide solution was added, followed by 3 ml. of 10% sulfuric acid in glacial acetic acid. The mixture was allowed to stand in the dark for about five minutes, and then 3 ml. of saturated potassium iodide solution was added, and the liberated iodine titrated with standard sodium thiosulfate solution, using starch paste near the end-point. The color change for starch in glacial acetic acid was noted to be yellow-brown to colorless. All of the fractions analyzed showed an unsaturation of better than 99%, except the propenylbenzene fraction obtained by hydrolysis of cinnamylmagnesium chloride. This fraction contained 11.0% of propylbenzene.[6]

Discussion of Results

Three reagents were chosen for the liberation of hydrocarbon mixtures from the sodium derivatives of allyl- and propenylbenzene by addition of a proton. One was methanol, an oxygen-containing proton donor; the second was an ammonium salt, which must operate as a direct proton donor, since unshared electrons are not available to enter into a preliminary coördination complex, and the third was phenylacetylene.

Early experiments on the decomposition of sodium allylbenzene with methanol gave only propenylbenzene. However, this substance did not necessarily have to be the only product of the reaction, since allylbenzene was found to be readily converted into propenylbenzene by methoxide ion produced from the methanol. The procedure was modified to avoid this rearrangement by neutralizing the methoxide ion with ammonium chloride soon after the addition of the methanol. Blank runs showed that sodium chloride or am-

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(7) Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934).

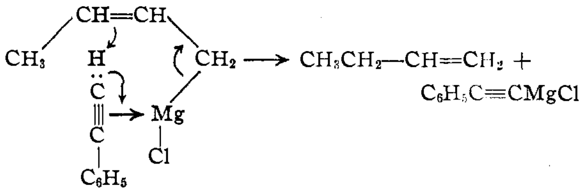
(8) Bower and Cook, *Ind. Eng. Chem., Anal. Ed.*, **15**, 291 (1943).

(9) Winstein and Lucas, THIS JOURNAL, **59**, 1461 (1937).

monium chloride in liquid ammonia produced no rearrangement of allylbenzene after three days. All later runs with the modified procedure produced some allylbenzene. This was not the result of incomplete conversion of the original allylbenzene, since an excess of sodamide and longer reaction times had no appreciable effect on the composition of the reaction mixture.

It is significant that a predominance of propenylbenzene is produced at all times. Since these results represent a complete reversal of the results from the hydrolysis of cinnamylmagnesium chloride,[4] using permanganate oxidation for analysis, the hydrolysis of the Grignard reagent was repeated, using precision fractional distillation for analysis of the hydrocarbon mixture. However, the results were in agreement with the previous analysis (75% allylbenzene and 25% propenylbenzene).

The observation that all three of the proton donors used give the same mixture of hydrocarbons with the sodium derivatives of allyl- and propenylbenzene is of considerable interest. With butenylmagnesium chloride, phenylacetylene gives virtually 100% 1-butene,[10] while hydroxylic substances give about 50% 1-butene and 50% 2-butene. This would not be surprising if the initial step in the reaction of the Grignard reagent with phenylacetylene involves a coördination of the magnesium atom with the triple bond of phenylacetylene and this coördination compound then decomposes through the only cyclic process available to give nearly pure 1-butene



Apparently the complex formed from coördination of hydroxylic substances with the magnesium may donate a proton at either the first or the third carbon atom.

This mechanism is substantiated by the observation that sodium allylbenzene, which would not be expected to form coördination complexes, since it is ionic, gives the same mixture of hydrocarbons with both hydroxylic substances and phenylacetylene, as well as with ammonium ion.

Summary

1. The sodium salts of allyl- and propenylbenzene have been prepared and decomposed with methanol, ammonium chloride and phenylacetylene.

2. Addition of a proton to these sodium salts has been shown to give predominantly propenylbenzene.

3. Cinnamylmagnesium chloride, the Grignard reagent analogous to the above salts has been prepared and hydrolyzed. The analysis of the hydrocarbon fraction agrees with values in the literature.

4. A mechanism for the reaction of phenylacetylene with allylic Grignard reagents has been postulated.

LOS ANGELES, CALIF. RECEIVED AUGUST 31, 1946

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[10] Young and Roberts, THIS JOURNAL, 68, 1472 (1946).

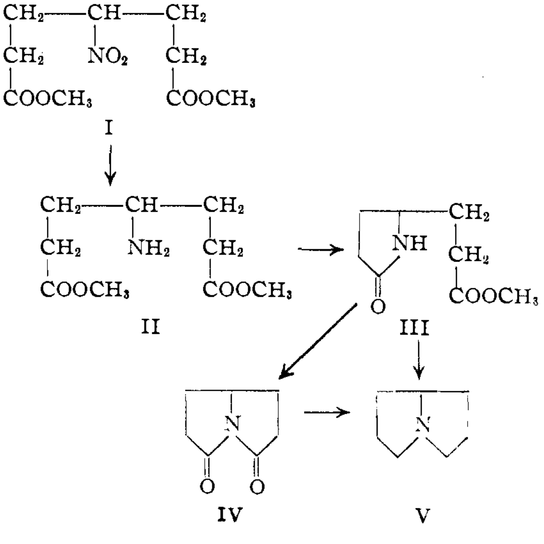
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of Pyrrolizidines[1]

BY NELSON J. LEONARD, LILLIAN RUTH HRUDA[2] AND FRANK W. LONG[3]

One method for the synthesis of pyrrolizidine (V) would appear to be a reductive ring-closure of dimethyl γ-aminopimelate (II), which should be readily available from the γ-nitro compound (I). At the outset, the following compounds were regarded as probable intermediates in the course of the reaction: dimethyl γ-aminopimelate (II), 5-β-carbomethoxyethyl-2-pyrrolidone (III), and 3,5-diketopyrrolizidine (IV).

Experiment has shown that the method is not only feasible but also very practical, since pyrrolizidine can be made by a two-step catalytic hydrogenation of dimethyl γ-nitropimelate (I), without necessity for the isolation of intermediates. The



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[1] Presented before the Division of Organic Chemistry at the 110th meeting of the American Chemical Society, Chicago, Illinois, September 12, 1946.

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