

drated by the use of benzene or hexane azeotropes or distillation from metallic calcium or "drierite." Fractions distilling within 0.01° were obtained. Propanol was treated with bromine to remove allyl alcohol, which was found present in commercial c. p. product to the extent of $0.2 M$. The methods of Weissberger and Proskauer,¹ Rowe and Phelps,² and of Brunel³ for the purification of alcohols failed to remove the difficulty; neither did distillation in an atmosphere of nitrogen.

Tests for carbonyl derivatives in the anomalous cases using dinitrophenylhydrazine⁴ gave precipitates in propanol, 2-propanol and pentanol only; of all the tests tried this seems the most reliable providing the solutions are allowed to stand at least overnight to precipitate the hydrazone.

If the impurity x be an aldehyde which forms a compound with hydrocyanic acid of greater stability than acetone cyanohydrin, we may write

$$c = \frac{b}{c} \frac{(1 + Kc)}{(1 + K(c + x))} K_1 - K_1$$

where K is the equilibrium constant for the reaction between hydrocyanic acid and x , in original concentration x . In such a case the intercept in the above-mentioned plots would be $(1 + Kx)$, and the limiting slope at high values of c would be K_1 . This situation is duplicated in Fig. 1, which shows the normal case of acetone cyanohydrin in butanol and the effect of adding to it a trace of butyraldehyde. Knowing the approximate amount of butyraldehyde and finding from the plot that $Kx = 0.62$, then $K = 72$. If for the case of presumably pure propanol we assume K to have a value of 100 and observe Kx in Fig. 1 to be 0.30, then x is of the order of $0.003 M$, corresponding to about 0.2% propionaldehyde by weight. It is noteworthy that these certain alcohols could not be purified by the usual methods and that the impurity reacted reversibly (as shown by analysis for total cyanide) with the hydrocyanic acid. The aberration in these alcohols was found in the same degree when approaching the equilibrium by association of acetone and hydrocyanic acid. Amine used as catalyst did not affect the equilibrium.

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(1) Weissberger and Proskauer, "Organic Solvents," Oxford Press, New York, N. Y., 1935.

(2) Rowe and Phelps, *THIS JOURNAL*, **46**, 2078 (1924).

(3) Brunel, *ibid.*, **45**, 1338 (1923).

(4) "Book of Reagents for Spot Tests," The British Drug Houses, Ltd., 1936, pp. 32-34.

The Action of Grignard Reagents on Heavy Metal Salts. V. The Formation of Olefins in the Reaction with Silver Bromide¹

BY JOHN H. GARDNER AND CHARLES J. SNYDER

In a note published in September, 1939, the suggestion was made that in the reaction between aliphatic Grignard reagents and silver bromide, the low yield of coupling products might be explained by the formation of the alkene and alkane corresponding to the Grignard reagent as the result of a simultaneous reaction.² In order to have a system yielding products having properties making them suitable for isolation and identification, the reaction of n -hexylmagnesium bromide with silver bromide has been studied in detail. From this reaction, there were obtained a good yield of n -dodecane and a small quantity of a mixture boiling at $60-70^\circ$. The latter yielded after bromination 1,2-dibromohexane, leaving some material boiling at $66-68^\circ$, which must have been n -hexane, although the quantity obtained was too small to permit of its being completely purified.

Since it is well known that among the by-products in the formation of an aliphatic Grignard reagent are the corresponding alkane, alkene and coupling product, in one run the ethereal solution of n -hexylmagnesium bromide was distilled until all volatile material had been removed. Dry ether was then added, followed by silver bromide. The same products were obtained as before, showing that n -dodecane, n -hexane and hexene-1 were all formed as the result of the reaction between n -hexylmagnesium bromide and silver bromide.

Experimental

Procedure.—To the Grignard reagent prepared from 0.25 mole of n -hexyl bromide, cooled to 0° , there was added 0.25 mole of dry silver bromide, with efficient stirring, during a period of an hour. The mixture was then allowed to warm to room temperature and finally boiled for an hour. The ether solution of the products was separated, dried and distilled through a 75-cm. Vigreux column until the temperature reached 100° . On redistilling this distillate, there was obtained a small fraction boiling at $60-70^\circ$. The residue from the first distillation was distilled from a 50-cc. flask provided with a 37-cm. Vigreux column.

As the average of four runs using 0.25 mole of n -hexyl bromide in each, the hydroxyl-bromide ratio was 0.866, corresponding to 0.217 mole of n -hexylmagnesium bromide, assuming all of the bromide to have reacted. The average yields were 1.2 g. of the fraction of b. p. $60-70^\circ$

(1) Paper IV of this series, E. A. Bickley and J. H. Gardner, *J. Org. Chem.*, **5**, 126 (1940).

(2) J. H. Gardner and L. Joseph, *THIS JOURNAL*, **61**, 2551 (1939).

(6.7%, calculated as an equimolar mixture of *n*-hexane and hexene-1) and 15.3 g. (82.9%) of *n*-dodecane, b. p. 213–216°, n_{20}^{25D} 1.4214. Egloff gives for *n*-dodecane, b. p. (760 mm.) 216.2 and n_{20}^{25D} 1.42182.³

Identification of the Fraction of b. p. 60–70°.—All of the material of b. p. 60–70° collected in the series of runs was combined and cooled to –5° in a mixture of ice and salt. Bromine in carbon tetrachloride was added in drops until a faint bromine color persisted for a few minutes. The carbon tetrachloride was distilled off and the residue distilled under reduced pressure; yield, 4.8 g. of 1,2-dibromohexane, b. p. (38 mm.) 103–106°, $n_{20}^{18.2D}$ 1.5006, $d_{20}^{22.5_{22}}$ 1.5498. Dykstra, Lewis and Boord give for 1,2-dibromohexane, b. p. (36 mm.) 103–105°, $n_{20}^{18.5D}$ 1.50601, d_{20}^{20} 1.56322.⁴

After redistilling the lower boiling material through a 75-cm. Vigreux column three times, there was obtained a small fraction, b. p. 66–68°, n_{20}^{25D} 1.4072. A Beilstein test showed the presence of halogen. The properties indicate that this material was *n*-hexane contaminated with a little carbon tetrachloride. Egloff gives for *n*-hexane, b. p. (760 mm.) 68.8°, n_{20}^{25D} 1.37506.⁵ The amount of material was too small to permit further purification.

Reaction after Elimination of the By-products in the Formation of the Grignard Reagent.—*n*-Hexylmagnesium bromide was prepared in the usual manner. The ether and all volatile products were removed by distillation and then 4 g. of *n*-dodecane was added and the distillation continued until no more liquid came over. The residue was taken up in 200 cc. of dry ether and caused to react with silver bromide as described above. There were obtained in this way 1.9 g. of the fraction b. p. 60–70° and 4.7 g. of *n*-dodecane, b. p. 213–216°.

(3) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Company, New York, N. Y., 1939, p. 80.

(4) H. B. Dykstra, J. F. Lewis and C. E. Boord, *THIS JOURNAL*, **52**, 3401 (1930).

(5) G. Egloff, ref. 3, p. 36.

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Solubilizing and Detergent Action in Non-Ionizing Solvents

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Now that it has been established that insoluble materials may dissolve in dilute aqueous solutions of solubilizers or detergents, to form stable colloidal solutions as distinguished from mere suspensions or emulsions, it becomes evident that this must be a general possibility for all solvents. Many indications of this are to be found in technical literature¹ and Freundlich² adduces a number of probable examples. Strict proof that such

(1) For example, U. S. Patents 2,097,773 and 2,147,713 for imparting fluorescence to petroleum products; possibly also the anti-bloom agents mentioned by Clayton, Black, Johnson and Morse, *Nature*, **138**, 801 (1936); and soaps used in dry cleaning.

(2) H. Freundlich, "Kapillarchem.," Akad. Verlagsges., Leipzig, 1932, 4th edition, Vol. II, p. 532.

solubilization is possible would be of great scientific as well as technical significance. It would then remain to find appropriate solubilizers for taking up and reorganizing given materials in various media.

It is a cognate but different phenomenon that, as McBain and Woo³ showed, spontaneous emulsification may occur, either of oil into water or of water into oil, without mechanical effort. Solubilizers, however, produce true reversible equilibria in contrast to temporary emulsions or mere protected particles.

The present note adduces a series of upwards of two hundred qualitative observations which serve the purpose of demonstrating that solubilizing does occur in non-aqueous solvents. Many solubilizers or detergents that operate in water are likewise effective in other solvents, provided that they are themselves soluble therein. Many are not soluble and a very few, even if soluble, do not exhibit solubilizing action in certain non-aqueous solvents. Solubilizers include substances that are not aqueous detergents such as rubber in benzene.

The experimental procedure has been to take approximately 1% solutions of pure or commercial detergents as supplied by the makers and add solid dye. Solubilization is indicated by the almost immediate coloration of the liquid. It is well known that admixture with a second solvent of 1% only slightly affects the solvent power of an ordinary solvent,^{3a} whereas here it is affected by orders of magnitude. Likewise a solid dye cannot as such yield emulsions. The use of crystalline dye avoids mere suspension of colloidal particles of dye. The subject of solubilization is best discussed in connection with aqueous systems with regard to which there is now a good deal of information and in which we have conducted some critical experiments, whereas this note refers to most of what is available with regard to non-aqueous systems. It is sufficient here to point out that the dye is not dissolved as single molecules of dye, but that the colloidal particles must be organized from both dye and detergent. Direct X-ray evidence for this has been presented for benzene in the lamellar micelles of ordinary aqueous soap solutions.⁴

(3) J. W. McBain and T.-M. Woo, *Proc. Roy. Soc. (London)*, **A163**, 182 (1937).

(3a) For example, in the present case, alcohol is not appreciably effective until 15–20% is added to toluene, or glacial acetic acid 4–8%; whereas lauryl sulfonic acid is highly effective with only 0.2% used.

(4) H. Kiessig and W. Philippoff, *Naturwiss.* **27**, 593 (1939).