this procedure is followed by measuring the deuterium pressure above the inner charcoal. For example, in the course of one hour the deuterium pressure sank from an initial value of 6 mm. (at 60°K.) to 0.013 mm. When the pressure is slowly rising again the process is interrupted. The metal case and the outer vessel are detached quickly by admitting air into (S) and (Y) through taps 2 and 3. The deuterium is rapidly desorbed by blowing air at (N) and is collected in a reservoir. From 5 cc. of charcoal saturated with deuterium under 0.013 mm. pressure, about 300 cc. of gas (at S. T. P.) was desorbed. The desorption of the gas was practically completed in ten seconds. Its ortho-concentration was about 82%, corresponding to a temperature of 45°K.

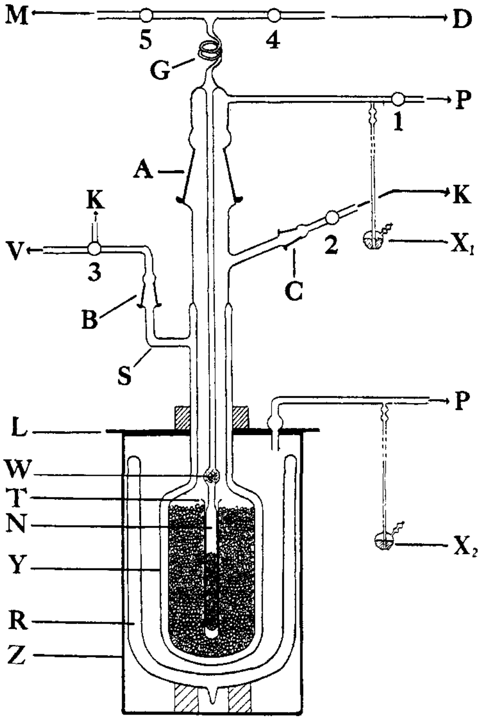

Fig. 1.—M, to high vacuum and McLeod gage; D, to deuterium reservoirs; G, glass spiral; P, to oil pump; K, to Kipp generator for hydrogen; V, to high vacuum; X_1, excess pressure valve 1; X_2, excess pressure valve 2; L, lid; W, glass wool; T, test-tube; N, inner charcoal vessel; Y, outer charcoal vessel; R, dewar flask; Z, metal case; 1, 2, 3, 4, 5, taps.

The equilibrium concentrations of p-H_2 and o-D_2 at different temperatures are listed in Table I.

TABLE I

Temp., °K.	Concn., % p-H_2	Concn., % o-D_2	Excess concn., % p-H_2	Excess concn., % o-D_2	Method by which obtainable
200	25.0	66.7	0.0	0.0	High temp. equil.
85	45.4	69.1	20.4	2.4	Liq. air
60	65.4	74.8	40.4	*8.1*	Solid air
45	82.9	82.1	57.9	*15.4*	Desorption
20	99.8	98.0	74.8	31.3	Liq. H_2

By using ortho-deuterium prepared by the desorption method, the concentration range available is nearly doubled and thus the accuracy of measurement of a conversion rate is much improved. This has been made use of lately in investigations concerning the paramagnetic conversion of hydrogen.[2]

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[2] L. Farkas and L. Sandler, *J. Chem. Phys.*, **8**, 248 (1940).

DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE RECEIVED FEBRUARY 27, 1940

An Effect of Carbonyl Derivatives as Impurities in Alcohols

BY B. J. FONTANA AND T. D. STEWART

In studying the equilibrium

$$(CH_3)_2C(OH)CN \overset{K_I}{\rightleftarrows} (CH_3)_2C{=}O + HCN$$

in various alcohols as solvents, the data were examined by plotting c against b/c, where b is the initial concentration of the cyanohydrin and c the equilibrium value of hydrocyanic acid and acetone. The usual equilibrium expression can be put in the form

$$c = K_I b/c - K_I$$

In the cases, methanol, ethanol, butanol, 2-methylpropanol and t-butyl alcohol, the plot gave straight lines with intercept of unity on the b/c axis; in propanol, 2-propanol, 2-butanol and pentanol the lines were straight (perhaps fortuitously) but the intercept greater than unity. The alcohols were purified in general by distillation through a three-meter (about 18-plate) column, with and without lime present. In some cases they were dehy-

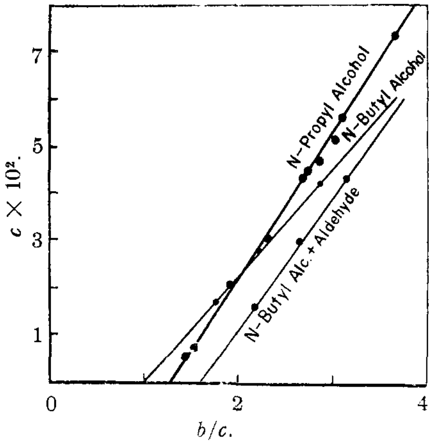

Fig. 1.—The effect of aldehyde impurity upon the dissociation of acetone cyanohydrin in propanol and butanol.

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 Brunel[3] 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 dinitrophenylhydrazine[4] 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

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

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_{I}. 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 Bromide[1]

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°. The latter yielded after bromination 1,2-dibromohexane, leaving some material boiling at 66–68°, 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°. 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°

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[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).