of 5-*p*-toluenesulfonyl-2,3-acetone methylrhamnofuranoside. A comparison of the properties of the free sugar and its derivatives prepared by Muskat with those of the newer substances reported above shows clearly that the product obtained by this author is not *d*-gulo-methylose.

It may be added that Dr. A. L. Raymond of this Laboratory has failed to observe a Walden inversion in the cases of 3-*p*-toluenesulfonyl diacetone glucose and 3-*p*-toluenesulfonyl-5-methyl monoacetone xylose.

THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH
NEW YORK, N. Y.
P. A. LEVENE
JACK COMPTON

RECEIVED MARCH 11, 1935

6-DESOXY-*d*-GULOSE*

Sir:

In the preceding note P. A. Levene and Jack Compton [THIS JOURNAL, **57**, 777 (1935)] present some data on a supposed 6-desoxy-*d*-gulose which they have prepared. The properties of this substance seem to differ from an inverted compound previously obtained by this author.

While at the Rockefeller Institute as a National Research Council fellow, I studied, independently, the mechanism of Walden inversion of sugars. As a result of theoretical considerations it was decided to investigate the alkaline hydrolysis of two *p*-toluenesulfonyl esters of rhamnose. It was definitely established that an inversion occurred during the hydrolysis of both sugars. No effort was made to determine the structure of the inverted product, for neither of the sugars nor derivatives isolated in this work had been previously prepared. Insufficient material was available to determine the structures by other than empirical and, therefore, unreliable means. The inverted sugar obtained from the rhamnofuranoside was *assumed* to be 6-desoxy-*d*-gulose since it was not clear how any other product could be formed under the particular conditions of the experiment. I may mention here that in the original paper as sent to the Journal this fact was clearly stated, but due to the necessity of limiting its size, it was inadvertently omitted in the final paper. Consequently, it is true that the author did not definitely establish the identity of the inverted product as 6-desoxy-*d*-gulose.

An examination of the evidence presented by Levene and Compton for the structure of their product reveals the following facts. Their starting material, 5-desoxy-*d*-xylose, is a sirup. This was treated with hydrogen cyanide, hydrolyzed to a lactone, and then reduced to the aldose sugar. It may be well to point out that two different sugars, each having two forms (furanose and pyranose) may result from such reactions. In other words, any or all of *four* different compounds may have composed the final product. Levene and Compton must have overlooked this simple fact, since they present no evidence that the sugar they have obtained is a 6-desoxy-*d*-gulose. Of course the rotations of the lactone and of its bromophenylhydrazide may be taken as indications of such a structure, but insufficient work has been done on these particular sugars to use such empirical rules as anything but supporting data. Consequently, Levene and Compton do not know the structure of their sugar and their criticism is therefore invalid. From the data they present it may be that they have an entirely different sugar or simply an impure form of 6-desoxy-*d*-gulose.

Levene and Compton state that "A. L. Raymond of this Laboratory has failed to observe a Walden inversion in the cases of 3-*p*-toluenesulfonyl diacetone glucose and 3-*p*-toluenesulfonyl-5-methyl-monoacetone xylose." The author wishes to call their attention to page 2653 of his article in which it is stated "It is not suggested that a Walden inversion will necessarily occur in all reactions of type (II)," and on page 2654, "Whether an inversion will or will not occur, and if it will, to what extent, will depend on the steric effects in the sugar molecule and the experimental conditions." It may be that no inversion has occurred in these two sugars or, as Levene and Compton so aptly put it, "Raymond has *failed* to observe it."

MELLON INSTITUTE
PITTSBURGH, PA.
IRVING E. MUSKAT

RECEIVED MARCH 21, 1935

THE ALLEGED ISOTOPIC INTERCHANGE BETWEEN WATER AND ACETYLENE

Sir:

It has recently been reported [L. H. Reyerson and S. Yuster, THIS JOURNAL, **56**, 1426 (1934)] that an isotopic interchange takes place between water and acetylene in alkaline solution. Experiments in this Laboratory have failed to give any in-

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* This letter was received prior to the addition of items six and seven to the table in the preceding communication—EDITOR.

dication of such an interchange, even under conditions more drastic than those previously employed.

Each experiment was carried out with 10–15 cc. of water containing about 1.5 mole per cent. of deuterium. The density was determined pycnometrically with an accuracy of 0.002%, so that interchange of hydrogen to an extent of 2% could have been detected with certainty. The acetylene was prepared from calcium carbide and purified by passing through solutions of sodium hydroxide and chromic acid; it was passed continuously through the solutions being investigated at about 500 cc. per hour. In the experiments at 76° the evaporation loss was reduced to less than 5% by a reflux condenser. After removing the acetylene by a current of air or carbon dioxide the solutions were distilled at least twice *in vacuo* at 40–50°, and the density determined. The density was in each case unchanged by repeated distillation, provided that the whole of the water was distilled over. The following experiments were carried out:

N NaOH	Acetylene passed 11 hours at 0°
Pure water	Acetylene passed 5 hours at 76°
N NaCl	Acetylene passed 5 hours at 76°
0.01 *N* $Ba(OH)_2$	Acetylene passed 3.5 hours at 76°
0.1 *N* $Ba(OH)_2$	Acetylene passed 5 hours at 76°
0.5 *N* $Ba(OH)_2$	Acetylene passed 9.5 hours at 76°

In no case was any change in isotopic composition observed. (The hydrogen contained in the hydroxides was taken into account in calculating the original composition.)

These results are completely at variance with those of Reyerson and Yuster, who obtained about 50% interchange on treating *N* sodium hydroxide with acetylene for eight hours at 0°. It is difficult to suggest an explanation for this discrepancy.

PHYSICAL CHEMISTRY LABORATORY R. P. BELL
BALLIOL COLLEGE AND TRINITY COLLEGE
OXFORD, ENGLAND

RECEIVED MARCH 8, 1935

THE ISOTOPIC INTERCHANGE BETWEEN ACETYLENE AND HEAVY WATER

Sir:

Dr. R. P. Bell was kind enough to send me a copy of the communication to the Journal concerning his failure to obtain the isotopic interchange between acetylene and heavy water which we previously had reported. In answer to the question raised by Dr. Bell, I wish to report that under the conditions of our experiments there is no question but that the isotopic exchange takes place. Since our previous publication several equilibrium studies of this reaction have been completed in this Laboratory. They have been carried out at 0, 25 and 100° in closed systems using various pressures of acetylene which was prepared by the action of carefully distilled water on very pure calcium carbide, the acetylene being further purified. The concentrations of deuterium in the water used varied from about 9 to 18%. Except for a small temperature coefficient the equilibrium constants checked excellently. This work is being written up for a lengthier publication on the subject. In addition to the above evidence Mr. A. O. Nier working in Professor J. T. Tate's laboratory in physics has completed an analysis of the products of one of our equilibrium studies by means of the mass spectrograph. He reports that about 10% of the gas submitted for analysis consisted of C_2HD. This checks very well the value calculated from the density change in the water as determined in this Laboratory.

Dr. Bell states in his communication that his experiments were carried out under more drastic conditions than those reported by us. This does not seem to be borne out by the facts. The concentration used in our solutions was from six to eight times as great, and the rate of passage of the acetylene through the solution was approximately seven times as great as that reported by Dr. Bell. Since all but one of his reported experiments were carried out at 76° it must be he considered this to be more drastic treatment. However, in order for the exchange to occur the acetylene must dissolve in the solution and then ionize. The solubility of acetylene is much less at 76° than at zero so that the chance for exchange is thereby reduced. A simple calculation from our equilibrium constant values obtained for the reaction

$$C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O \text{ at } 0°C.$$

shows that the amount of exchange with 1.5% deuterium should be very small, even under equilibrium conditions, conditions which are obviously not reached by bubbling the gas through the solution for the length of time reported. It seems therefore that Dr. Bell did not lose sufficient deuterium from the water to detect it by the technique he employed. Dr. Yuster in a private communication to the author suggested a further possibility for Dr. Bell's failure to observe the