liquor permitted the recovery of 5 g. of L-mannonic lactone. The over-all yields thus represent the production of 49.6% L-gluconic and 14.9% of L-mannonic acid by the use of sodium cyanide.

Obviously the procedure can be used advantageously for the preparation of D-gluconic acid and D-glucose labeled at carbon atom 1 from D-arabinose and labeled sodium cyanide.

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RECEIVED AUGUST 6, 1951

MECHANISM OF THE LOW TEMPERATURE CHLORINATION OF ISOBUTYLENE

Sir:

Chlorine reacts practically instantaneously with excess isobutylene at 0° to form the unsaturated monohalide, methallyl chloride, in 83% yield, based on the chlorine consumed.[1] We have studied the reaction of chlorine with 1-C^{14}-2-methyl-1-propene to determine whether the mechanism of this reaction involves an attack by an electrophilic chlorine atom on the terminal unsaturated carbon atom with a subsequent elimination of a proton from the carbonium ion thus formed or, alternatively, a direct attack by chlorine on one of the methyl groups without the double bond entering into the reaction.

1-C^{14}-2-Methylpropionic acid was prepared by the carbonation of isopropylmagnesium bromide[2]; this was esterified, reduced to isobutyl alcohol, converted to the iodide with phosphorus and iodine, and dehydrohalogenated to isobutylene with potassium hydroxide. A sample of this was shown to have all the C^{14} in the one position by ozonolysis and the examination of the formaldehyde and the acetone thus formed. The dimedone derivative of the formaldehyde gave 1400 counts per minute; the 2,4-dinitrophenylhydrazone derivative of the acetone was inactive. The reaction with chlorine involved mixing 30% excess isobutylene with the chlorine in a 0.8-mm. glass capillary flow system immersed in an ice-bath. The methallyl chloride (4.2 g., 60% yield based on the total isobutylene) was purified by distillation, b.p. 72 to 74° (760 mm.). It probably contained 1 to 3% of isocrotyl chloride ((CH_3)$_2$C=CHCl) which boils at 68.1°.[1] The methallyl chloride was ozonized, and the ozonide decomposed in the presence of an excess of platinized zinc to convert the chloroacetone to acetone. The formaldehyde and acetone were examined as their dimedone and 2,4-dinitrophenylhydrazone derivatives, respectively. The former had little activity (50 counts/min.) possibly due to the isocrotyl chloride ozonide giving formaldehyde under our experimental conditions. The acetone derivative had an estimated 97% of the radioactive carbon (1760 counts/min.).

The above clearly shows that the chlorination of isobutylene near 0° involves as the first step an attack by an electrophilic chlorine atom at the

(1) J. Burgin, W. Engs, H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939).

(2) The carbon dioxide was prepared from barium carbonate-C^{14} supplied by the Clinton Laboratories on allocation from the U. S. Atomic Energy Commission.

number one carbon atom. This is followed by the loss of a proton to form the methallyl chloride, the double bond now being in a new position. It is thus apparent that the first step in the chlorination of isobutylene is much like that in the case of ethylene. Unlike the case of ethylene, however, the intermediate postulated loses a proton before the usual final step can occur, namely, the addition of a nucleophilic chlorine atom at the positive center.

The procedure for preparing the isobutyl alcohol was worked out by Mrs. Claudia Sebeste Prickett. Dr. Carl Rollinson's apparatus was used in making the counts.

DEPARTMENT OF CHEMISTRY   WILKINS REEVE
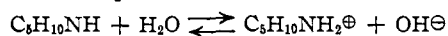UNIVERSITY OF MARYLAND   D. HARRY CHAMBERS
COLLEGE PARK, MARYLAND
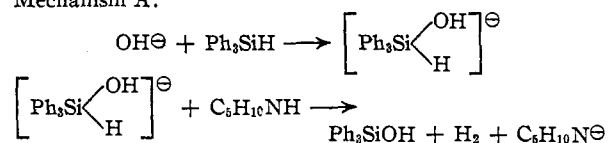RECEIVED JULY 23, 1951
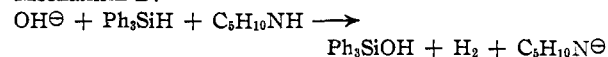
AN UNUSUAL ISOTOPE EFFECT

Sir:

We have observed an unusual isotope effect in connection with a study of the hydrolysis of triphenylsilane in moist piperidine.[1] The reaction is first order in silane, half order in water, and has a positive value of ρ in the Hammett equation, leading to the conclusion that one of the two following mechanisms is operative.

$$C_5H_{10}NH + H_2O \rightleftharpoons C_5H_{10}NH_2^{\oplus} + OH^{\ominus}$$

Mechanism A:

$$OH^{\ominus} + Ph_3SiH \longrightarrow \left[Ph_3Si\!\!\begin{array}{c} OH \\ H \end{array}\!\! \right]^{\ominus}$$

$$\left[Ph_3Si\!\!\begin{array}{c} OH \\ H \end{array}\!\! \right]^{\ominus} + C_5H_{10}NH \longrightarrow$$
$$Ph_3SiOH + H_2 + C_5H_{10}N^{\ominus}$$

Mechanism B:
$$OH^{\ominus} + Ph_3SiH + C_5H_{10}NH \longrightarrow$$
$$Ph_3SiOH + H_2 + C_5H_{10}N^{\ominus}$$

In an attempt to learn whether or not the silicon-hydrogen bond is broken in the rate-determining step of the reaction, we prepared triphenyldeutero-silane and compared its rate of hydrolysis with that of the compound having the normal deuterium content. It was anticipated that, if the bond in question were broken in the rate-controlling step, the protium-rich compound would react more rapidly than the deutero compound. This would be in accord with previous work,[2] and with the view that the zero-point vibrational energy of a bond in the process of being broken decreases as the system passes from its resting state to the transition state. Since zero-point energies are always smaller for deuterium compounds than for analogous protium compounds, it would follow that the activation energy for breaking bonds to hydrogen should be decreased by the larger increment. We were, therefore, surprised to find that *the deuterium compound reacted almost six times faster than its protium analog.* Abnormal isotope effects have been both predicted[3]

(1) The experimental procedures used are similar to those described by H. Gilman and G. E. Dunn, THIS JOURNAL, **73**, 3404 (1951).

(2) F. H. Westheimer and N. Nicolaides, *ibid.*, **71**, 25 (1949); O. Reitz, *Z. physik. Chem.*, **A184**, 429 (1939); **A179**, 119 (1937); **A176**, 363 (1936).

(3) M. Polanyi, *Nature*, **133**, 26 (1934); B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934).