tane.[4] Ethylene, which was observed to be an impurity before fractionation, could not have been present in more than a very small percentage after fractionation. Moreover, the rate was not altered appreciably by the addition of ethylene (Table I).

TABLE I

Sample I, vap. press. at 0° = 467 mm. compared with 466.5 mm. calculated by Heisig's equation; Ia, refluxed with freshly distilled sodium; Ib, refluxed over silver oxide; IIa, passed over concd. sulfuric acid, vap. press. at −7.7° = 338.5 mm. compared with 337 mm. calculated by Heisig's equation. $t_{1/4}$ = time for the pressure increase to reach 25% of the maximum pressure increase. C_3H_6 = propylene.

Temp., °C.	$P^0_{C_4H_8}$, mm.	Sample	Added subst.	$P_{A.S.}$ mm.	$t_{1/4}$, min.
438	125	I	...	0	18.9
438	124	Ib	...	0	18.8
438	106	I	C_2H_4	23	19.3
438	112	IIa	...	0	18.6
449	33	I	...	0	10.6[a]
449	106	Ia	...	0	9.7
449	129	I	...	0	9.8
449	406	I	...	0	9.8
459	68	I	C_3H_6	43	5.4
459	88	I	...	0	5.3
459	110	I	NO	3.3	5.2

[a] Average of three runs; for all runs at 449° the time for 24.4% pressure increase (cor. for dead space) has been taken as $t_{1/4}$.

The fact that the ratios of the maximum final pressure to the initial pressure are 2.00, 1.98 and 1.97 (corrected for dead space) at 482, 459 and 438°, respectively, indicates that two molecules are formed from each cyclobutane molecule. There are indications that a subsequent reaction of the products which produces a very slow pressure decrease may be at least partly responsible for the difference in P_f/P_0 at the lower temperatures where the attainment of the final pressure is slow. The infrared absorption curve for the products at complete decomposition indicates that ethylene is practically the sole product. This finding is in agreement with the observations that 99% of the mixture in the reaction zone at maximum pressure increase is condensable at −196°, not more than 3% is condensable at −78°, and about 95% is absorbable in activated sulfuric acid.[5] The over-all reaction appears to be $C_4H_8 = 2\ C_2H_4$.

During the decomposition the pressure increases in the manner expected for a first order reaction (with no induction period). By calculation of the amount of reaction from the pressure measurements and the observed over-all pressure increase, the ratio of $t_{1/2}/t_{1/4}$ averaged 2.39 in comparison with 2.41 for a first order reaction and a linear plot of log $P_{C_4H_8}$ *vs.* time was obtained over essentially the entire reaction. For the experiments at 449° shown in Table I the fractional times appear to be approximately the same for the range 100–400 mm. The reaction has been carried out in an unpacked Pyrex vessel with and without potassium chloride coating, in a packed Pyrex vessel, and in a silica vessel.[6] The results have shown that the decomposition does not depend to a significant extent upon the nature or the amount of the surface. No evidence for a chain reaction has been obtained yet, but this matter will be investigated. Preliminary data indicate the activation energy is about 61 kcal./mole.

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[4] T. P. Wilson, *J. Chem. Phys.*, **11**, 369 (1943); J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949); G. B. Heisig, *ibid.*, **63**, 1698 (1941).

[5] W. J. Gooderham, *J. Soc. Chem. Ind. (London)*, **57**, 388T (1938).

[6] D. A. Bittker and H. D. Batha have assisted in these studies.

THE USE OF SODIUM CYANIDE WITH L-ARABINOSE IN THE KILIANI SYNTHESIS

Sir:

When hexonic acids are synthesized from L-arabinose by the Kiliani method, using aqueous hydrocyanic acid, L-mannonic acid is the principal product with only a minor amount of L-gluconic acid.[1] We have observed that if the cyanide addition is carried out in a cold aqueous solution of sodium cyanide L-gluconic acid is the principal product with only a minor amount of L-mannonic acid. This reversal of proportions of diastereoisomers does not occur, however, with all reducing sugars; thus D-glucose yields about the same ratio of D-gluco-D-*gulo*-heptonic acid to D-gluco-D-*ido*-heptonic acid with either hydrocyanic acid or sodium cyanide. Since it thus becomes evident that any generalization relating the configuration of an aldose with that of the next higher aldonic acid diastereoisomer that is favored in the cyanide synthesis must specify the method of addition, it is emphasized that the Maltby rule which I have discussed[2] is to be understood as applying to syntheses in which aqueous hydrocyanic acid reacts with aldoses.

The experimental procedure for preparing L-gluconic acid (as its barium salt) from L-arabinose and sodium cyanide involves only one major change from the directions of E. Fischer for L-arabinose and hydrogen cyanide; this consists in the removal of sodium ions at the proper stage by an ion-exchange column. An ice-cold solution containing 30 g. of pure L-arabinose and 13 g. of sodium cyanide in 300 ml. of water was kept near +5° in a refrigerator until the Fehling test became faint (4 days). Barium hydroxide (10 g. of octahydrate) was added and the solution was boiled with renewal of water to expel all ammonia (3 to 4 hours). The barium was then removed as carbonate after addition of activated carbon and the sodium ions were adsorbed by passing the solution through an ion-exchange column. Concentration to a sirup, lactonization and solution of the residue in methyl cellosolve led to only 2.5 g. of crystalline L-mannonic γ-lactone. Removal of solvent from the mother liquor, conversion of the acidic residue to its neutral barium salt and crystallization from aqueous ethanol[3] produced 26.1 g. of barium L-gluconate (anhydrous basis). Its $[\alpha]^{20}\text{D}$ was −6.4° (*c* 8.7 g./100 ml. aqueous soln.) in agreement with the value for barium D-gluconate (+6.1). (Kiliani found that even pure barium L-mannonate would not crystallize and our experience confirms this observation.) Removal of barium ions from the mother

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[1] E. Fischer, *Ber.*, **23**, 2611 (1890).

[2] C. S. Hudson, *Advances in Carbohydrate Chem.*, **1**, 26 (1945).

[3] H. Kiliani, *Ber.*, **58**, 2350 (1925); **59**, 1470 (1926).

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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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 ($(CH_3)_2C{=}CHCl$) 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 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.

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[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.

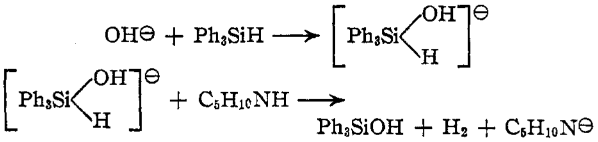
AN UNUSUAL ISOTOPE EFFECT

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:



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

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

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 triphenyldeuterosilane 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]

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[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).