

resembles natural rubber in the fact that when it is stretched its x-ray diffraction pattern shows a point diagram.

The transformation of chloroprene into μ -polychloroprene occurs very rapidly in aqueous emulsion. The resulting product constitutes a synthetic (vulcanized) latex. It has a much smaller particle size than natural latex and it penetrates porous materials more readily.

Chloroprene can also be polymerized in the pores of porous or bibulous materials. The materials thus become intimately impregnated with synthetic rubber.

Compared with natural rubber the new synthetic rubber is more dense, more resistant to absorption or penetration by water, less strongly swelled by petroleum hydrocarbons and less permeable to many gases. It is much more resistant to attack by oxygen, ozone, hydrogen chloride, hydrogen fluoride and many other chemicals.

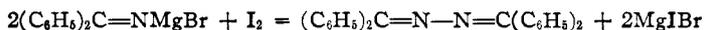
WILMINGTON, DELAWARE

COMMUNICATIONS TO THE EDITOR

A NEW METHOD FOR THE PREPARATION OF KETO-CHLORIMINES

Sir:

Recently, Morton and Stevens [THIS JOURNAL, 53, 2769 (1931)] have prepared diphenylketazine, in good yield, by heating with iodine the magnesium compound obtained from phenylmagnesium bromide and benzonitrile. The reaction is represented by the equation



When bromine was used instead of iodine, a small yield of the ketazine was obtained.

Since the corresponding reaction with chlorine has been carried out in this Laboratory [G. J. Haus, Master's Thesis, Duke University, May, 1931], it seemed desirable to make a preliminary report of our work at this time.

In the hope of developing a new method for the preparation of chlorimines [see Peterson, *Am. Chem. J.*, 46, 325 (1911)] the above magnesium compound was treated in the cold with an equivalent quantity of chlorine. A product was obtained which contained about 60% benzophenone-chlorimine as calculated from its active chlorine content. Although attempts to isolate the pure chlorimine have thus far failed, we have obtained further evidence that the crude product consists partly of benzophenone-chlorimine. Thus the fact that the chlorine content changed only a small amount even after standing in an open vessel at room temperatures for several weeks indicates the presence of a rather stable chlorine compound. Furthermore, when the crude product in anhydrous ether or benzene is

treated with dry hydrogen chloride a precipitate is obtained which with water yields benzophenone.

When the corresponding magnesium compound, prepared from *p*-chlorobenzonitrile, was treated with chlorine, a chlorimine, m. p. 103–104°, was obtained. Bromine instead of chlorine apparently yields a bromimine. These and other reactions of this type are being further studied and we hope to be able to publish our results within a short time.

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ACETYL DERIVATIVES OF THE LACTONES OF MONOBASIC SUGAR ACIDS

Sir:

Acetyl derivatives of several lactones of monobasic sugar acids have been prepared in this Laboratory using either zinc chloride or pyridine as the catalyst. Among others we have prepared the 2,3,4,6-tetraacetyl- δ -*d*-gluconolactone. So far as we are aware this lactone has not been converted previously into any derivative by a direct method. The only recorded work which we have found on these acetyl derivatives is by J. Mikšič [J. Mikšič, *Vestnik Kral.-Ces. Spal.-Nauk* Cl. II, 18 pp. (1929)], who reports the acetylation of γ -*d*-gluconolactone by acetic anhydride in the presence of pyridine. The crystalline product melted at 103° and the specific rotation was +13.46° in chloroform solution. We have been unable to repeat the work of Mikšič. Only a sirupy product was obtained using his methods. We have acetylated γ -*d*-gluconolactone in the presence of zinc chloride. The product is a liquid and the analysis indicates a tetraacetyl derivative. The rotation in 4% solution in an 80% acetone water mixture was +60.29° six minutes after solution. Two hours after solution it was +58.17°. This slow diminution in rotation is characteristic of γ -lactones. We conclude that this compound is 2,3,5,6-tetraacetylgluconolactone. On account of the low rotation +13.46° reported by Mikšič, it is possible that his product was the tetraacetylgluconic acid.

On acetylation of the δ -*d*-gluconolactone a crystalline product was obtained. The melting point was 114–117° and the specific rotation was –1.21°. Analysis showed it to be a tetraacetylgluconic acid monohydrate. On heating in vacuum at 100° the substance became liquid and moisture was given off. After several hours' heating there remained a colorless glassy solid, which analyzed correctly for a tetraacetylgluconolactone. In sharp contrast to that of the γ -lactone derivative is the rotational behavior of this substance. Six minutes after solution the specific rotation was +64.35°. In the course of twenty minutes the value had diminished

to $+47.95^\circ$; in forty-three minutes to $+38.91^\circ$; in two hours to $+27.4^\circ$ and after forty-two hours the rotation had become 0° . On evaporation of the acetone-water solution there crystallized again the tetraacetylgluconic acid monohydrate.

The product though not crystalline is without doubt the 2,3,4,6-tetraacetyl- δ -*d*-gluconolactone. The rotational behavior of these two acetylated lactones parallels very closely that of the γ - and δ -gluconolactones as reported by Nef [*Ann.*, **403**, 322 (1914)] and also by Hedenburg [THIS JOURNAL, **37**, 345 (1915)]. Of special interest is the fact that δ -gluconolactone may be acetylated to give the 2,3,4,6-tetraacetyl derivative. To our knowledge all derivatives of this lactone hitherto reported have been obtained by the oxidation of the corresponding sugar derivatives. Thus attempts to methylate δ -*d*- and *l*-mannonolactones in this Laboratory have resulted in the formation of 2,3,5,6-tetramethyl- γ -lactones, change in the position of the lactone bridge occurring during the process.

In addition to the above we have prepared the following acetylated lactones: tetraacetyl- α -*d*-glucoheptonolactone (γ), m. p. 128° , $[\alpha]_D^{20} -23.83^\circ$ (six minutes) and -21.58° (four days); tetraacetyl- γ -*d*-mannonolactone m. p. 119° , $[\alpha]_D^{20} +52^\circ$ (six minutes), and $+51.2$ (three days); tetraacetyl- γ -*l*-mannonolactone, m. p. 119° , $[\alpha]_D^{20} -52.2^\circ$ (nine minutes) and -51.2° (three days).

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CONCERNING THE EXPLOSION METHOD FOR THE DETERMINATION OF SPECIFIC HEATS OF GASES AT HIGH TEMPERATURES¹

Sir:

Values of the specific heats of gases above 2000°C . are due mainly to the investigations of Pier, Bjerrum, Siegel and Wohl. The explosion method was used and the maximum temperature and specific heat were calculated from the maximum pressure developed in the explosion.

It has always been assumed that at the instant maximum pressure is established, the reaction inside the chamber is complete or has reached an equilibrium state; that little or no energy has been lost in the meantime, or whatever is lost is corrected for. Consider the explosion of hydrogen and oxygen and the determination of the specific heat of water vapor. The reaction which is started at the center of a chamber spreads in all directions with an accelerating velocity. Coincidentally the pressure in the flame front increases, increasing the percentage combustion in each succeeding

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unburned layer of gas. Somewhere between ignition and the wall, detonation sets in. The detonation wave is reflected from the wall and returns toward the center, compressing the partially burned gases and completing the combustion. Two questions arise: (1) Does the impact of the detonation wave on the diaphragm pressure indicator contribute to the maximum pressure and thus modify an otherwise static recording? (2) Is the magnitude of the maximum pressure affected by the location and therefore speed of the detonation wave at the moment it is recorded?

Information on these points may be obtained in the following way. It is known that the velocity of the detonation wave in a mixture $2\text{H}_2 + \text{O}_2 + 5\text{He}$ is about twice as great as in a mixture $2\text{H}_2 + \text{O}_2 + 5\text{A}$ [Bernard Lewis and J. B. Friauf, *THIS JOURNAL*, **52**, 3905 (1930)]. Argon and helium have the same specific heats and they do not affect the equilibria at explosion temperatures. If the explosion method is yielding correct results under all conditions, the explosion of argon and helium mixtures should give identical maximum pressures and therefore the same specific heat of water vapor.

It would be desirable to obtain specific heat measurements in various mixtures of hydrogen and oxygen in all of which the velocity of the detonation wave is the same. This can be realized by the addition of suitable amounts of argon or helium, or mixtures of the two inert gases. It is also desirable to study the effect on specific heats of varying the type, size and material of the diaphragm pressure indicator and the explosion chamber.

In view of the importance of high temperature specific heats and the fact that the explosion method is the only one available for their determination, such fundamental studies are now in progress in this Laboratory.

EXPLOSIVES SECTION
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BERNARD LEWIS²

NEW BOOKS

A *Quarter Century of Learning, 1904-1929*, as Recorded in Lectures Delivered at Columbia University on the Occasion of the One Hundred and Seventy-Fifth Anniversary of its Founding. Columbia University Press, 2960 Broadway, New York, 1931. vi + 380 pp. 15.5 × 23 cm. Price, \$3.50.

In this book, eighteen professors of Columbia University "survey the progress of learning during the past twenty-five years"; each professor contributes a chapter on his own special field of learning.

The subjects discussed are the following: history, economics, sociology, government, jurisprudence, psychology, education, college administra-

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