

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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