Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

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A.P.N. Franchimont, Sulpho-isobutyric acid and some of its derivatives, in: KNAW, Proceedings, 7, 1904-1905, Amsterdam, 1905, pp. 275-277

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bable, he now, to judge from the above quotation, definitely adopts the oxide-ring 1).

The results of my researches, I may draw up in the following rule:

In the transformation of the 1.2 glycols into aldehydes, a real intramolecular atomic rearrangement takes place, which cannot be explained by any normally-proceeding intermediate reaction; it has not, however, been decided as yet whether this atomic migration takes place with the 1.2 glycols themselves or whether the oxides are formed first and then undergo an intramolecular rearrangement.

I am now making experiments in that direction with Dr. MEERBURG.

Chemistry. — Prof. A. P. N. FRANCHIMONT presents to the Library of the Academy a dissertation from Dr. J. MOLL VAN CHARANTE, entitled: "Sulpho-isobutyric acid and some of its derivatives" and offers the following explanation.

(Communicated in the meeting of September 24, 1904).

Dr. MOLL VAN CHARANTE has commenced at my instigation to thoroughly investigate sulpho-isobutyric acid. He prepared it according to the process which I had published many years ago for the preparation of those aliphatic sulphocarboxylic acids in which the sulphonic acid group is attached to the same carbon atom as the carboxyl group (namely from the acid anhydrides with sulphuric acid). These acids are not only important from the fact that they are bibasic acids, of which our knowledge leaves generally much to be desired, but also because the two acid functions are of themselves, and not merely on account of their position, of different strength, and are situated together more closely than in the case of the aromatic acids, and can therefore, exert a greater influence on each other. The difficulties experienced in the case of sulphoacetic acid, sulphopropionic acid etc. caused by the mobility of the hydrogen atoms which are placed at the same carbon atom could not present themselves here, because the atom to which the two acid functions are linked, does not carry hydrogen.

The said method of preparing, which had never been fully elucidated, in which two mols. of acid anhydride react with one mol. of sulphuric acid to yield one mol. of sulphonic acid is thus explained by Dr. MOLL VAN CHARANTE: a diacylsulphuric acid is formed which

¹⁾ At least if the quotation is meant for all the 1.2 glycols.

on being warmed is converted into monacylsulphonic acid, which in contact with water yields sulphonic acid and carboxylic acid:

 $C_n H_{2n+1}$ CO.O.SO₂.O.CO.C_n H_{2n+1} passing into $C_n H_{2n+1}$ CO.O. SO₂.C_n H_{2n} CO.OH and then by H₂O into C_n H_{2n+1} CO.OH and HO.SO₂. C_n H_{2n}.CO.OH.

Specially undertaken experiments led him to this conclusion and also taught him that when the acid chloride was used instead of the acid anhydride also two mols. of the latter are required to one mol. of sulphuric acid. The action of chlorosulphonic acid on carboxylic acids, which is also given as a method of preparing sulphonic acids, is understood by him to first yield the acid chloride and sulphuric acid, which then react on each other with formation of the sulphonic acid.

Sulpho-isobutyric acid itself is a very hygroscopic substance containing two mols. of water of crystallisation. The barium salt contains three mols. of water, the sodium salt half a mol. The neutral silver salt is anhydrous like the acid salt, which latter can only be obtained in the presence of a large excess of the acid.

When acting on the sodium salt with phosphorus pentachloride Dr. MOLL VAN CHARANTE obtained, according to circumstances, either the dichloride or a chloro-anhydride, which is the chloride of the carboxylicand the anhydride of the sulphonic acid function. The dichloride is a colourless liquid, which distils at about 55° under a pressure of $1-\frac{1}{2}$ m.m. mercury, with a sp. gr. $d\frac{20}{4} = 1.4696$ and a refractive power $n_D = 1.4887$; it solidifies at -10° . The sulpho-anhydridecarboxy-chloride is solid, crystallises from ligroin and melts at 61°.

With a little water the dichloride yields sulpho-chloride-isobutyric acid, which is crystalline and melts at 134°. With more water, sulpho-isobutyric acid is formed. With methyl alcohoi the ester of the carboxylic function is generated whilst the sulpho-chloride function remains. This ester sulpho-chloride is a liquid, which passed over at a pressure of $1^{1}/_{2}$ m.m. at about 60° and solidified at 21°.5; the sp. gr. was $d\frac{20}{4} = 1.3436$, the refractive power $n_{D} = 1.46658$. Treatment with sodium methoxide dissolved in methyl alcohol yielded

not the dimethyl ester but the ester sodium salt of the sulphonic acid. The dimethyl ester prepared from the neutral silver salt with methyl iodide was a liquid which passed over at a pressure of $1-\frac{1}{2}$ m.m. between $82^{\circ}-78^{\circ}$, solidified on cooling and then melted at 4° ; the sp. gr. was $d\frac{20}{4} = 1.2584$, the index of refraction $n_D = 1.44481$.

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The neutral ester is saponified by methyl alcohol and then yields an acid one like all sulphonic esters. With ammonia it yields an ammonium salt of the sulphonic ester function, which is also an ester of the carboxylic acid.

The acid ester, namely the carboxylic ester of the sulphonic acid, was also obtained from the sodium salt of sulpho-isobutyric acid by means of hydrogen chloride and methyl alcohol and is hygroscopic. Its isomer, the carboxylic acid of the sulphonic ester, which was prepared from the acid silver salt with methyl iodide, is not hygroscopic, it crystallises from benzene and melts at 90°. Dr. MOLL VAN CHARANTE's experiences with the esters of sulpho-isobutyric acid agree fairly well with those of WEGSCHEIDER with metasulphobenzoic acid.

The melting points of the compounds obtained behave as might be expected; those of the sulphonic acid chlorides are more elevated than those of the sulphonic esters; those of the carboxylic chlorides are lower than those of the carboxylic esters. The melting points of the esters as well as those of the chlorides of the carboxylic acids are lower than those of the carboxylic acids themselves.

Mathematics. — "The relation between the radius of curvature of a twisted curve in a point P of the curve and the radius of curvature in P of the section of its developable with its osculating plane in point P." By W. A. VERSLUYS. (Communicated by Prof. P. H. SCHOUTE).

(Communicated in the meeting of September 24, 1904.)

§ 1. THEOREM. For each twisted cubic C^{3} the ratio is constant of the radius of curvature in any point P to the radius of curvature of the section of the osculating plane in the point P with the developable O_{4} belonging to C^{3} .

PROOF. If we take P to be origin of coordinates and the tangent, principal normal and binormal of the curve C^3 in the point P to be the axes of coordinates, then C^3 is the cuspidal curve of the surface O_4 enveloped by the plane

$$A t^3 - 3 B t^2 + 3 C t - D = 0,$$

where

$$D = z,$$

$$C = c_2 y,$$

$$B = b_1 x + b_2 y + b_3 z,$$

$$A = a_1 x + a_2 y + a_3 z + a_4.$$