

Citation:

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Chemistry. — Dr. P. VAN ROMBURGH: „*On the action of nitric acid on alkylated amides of p.-toluenesulphonic acid*”. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of February 22, 1902).

Many years ago ¹⁾, I communicated the results of an investigation of the action of nitric acid on substituted amides of benzenesulphonic acid which not only revealed an easy way of preparing dimethylnitramide but also the peculiar fact that one of the ethyl groups of diethylamide became replaced by NO₂. FRANCHIMONT and KLOBBIE have afterwards demonstrated that the substituted amides of ethylsulphonic acid behave in quite an analogous manner. During the action of nitric acid on the amides of benzenesulphonic acid the benzene group remains intact. I now wanted to ascertain in how far the reaction would be affected by the introduction of a methyl group into the nucleus, just as I had done before in the case of substituted anilines, and I studied the reaction first of all with the amides of p.-toluenesulphonic acid.

These amides, like those of benzenesulphonic acid, are readily prepared by acting on the chloride with an aqueous solution of the amines.

Monomethyl- and ethylamides of p.-toluenesulphonic acid have already been described by REMSEN and PALMER, the first compound melting at 75° and the other at 58°. I found the respective melting points to be 76—77° and 64°.

I obtained dimethylamide as a beautifully crystallised substance melting at 76° while diethylamide melts at 59—60°.

If monomethylamide is dissolved in fuming nitric acid of sp. gr. 1.48 two products are formed which may be separated, although with difficulty, by recrystallisation from alcohol. The one melting at 116° proved to be a nitro p.-toluenesulphomethylnitramide, while the other melting at 60° was p.-toluenesulphomethylnitramide. When using a very concentrated acid of sp. gr. 1.52 we get exclusively nitramide nitrated in the nucleus; with an acid of a sp. gr. below 1.48 more of the readily melting substance is formed but the formation of the substance with the higher melting point is not entirely prevented. Nitric acid of sp. gr. 1.4 seems to be inert.

Monoethyl-p-toluenesulphamide behaves quite analogous towards concentrated nitric acid; with an acid of sp. gr. 1.52 a nitro-

¹⁾ Rec. Trav. Chim. Pays-Bas 3, 7.

p-toluenesulphoethylnitramide (m. p. 76°) is exclusively obtained. Strong sulphuric acid decomposes it with evolution of N₂O and a nitro-*p*-toluenesulphonic acid is formed, the barium salt of which crystallises with 2 mols. of water.

The dimethylamide of *p*-toluenesulphonic acid yields with nitric acid of sp. gr. 1.48 dimethylamide melting at 57° while diethylamide yields with an acid of sp. gr. 1.5, amidst oxydation phenomena, a product which is liquid at first but solidifies after some time. When recrystallised from alcohol a product is obtained which melts at 76° and appears to be identical with the above mentioned nitramide nitrated in the nucleus, as obtained from the monoethyl compound.

Nitric acid of sp. gr. 1.52 has scarcely any oxydising action on the diethylamide, the product being again nitrated nitramide. After pouring the mixture into water and distilling a liquid product is obtained which sinks in water (ethyl nitrate).

The properties of the said barium salt rendered it probable that the nitrogroup had occupied the ortho-position in regard to the CH₃ group. To make sure of this, I have endeavoured to prepare the nitrated nitramines by a method which showed with certainty the position of the nitrogroup in the nucleus. I first of all prepared a nitrotoluenesulphochloride by acting on nitrotoluene with HO-SO₂Cl; the product treated with ammonia yielded an amide melting at 140°, but the amount obtained left much to be desired. Even the action of PCl₅ on the potassium salt of a sulphonic acid prepared by acting with fuming sulphuric acid on nitrotoluene (which yielded two isomers) did not produce the chloride in sufficient quantity to prepare the substituted amides. The action of ammonia produced two amides one of which melted at 141°.

By acting on *p*-toluenesulphochloride with absolute nitric acid a nitroderivative was obtained which could be recrystallised from petroleum ether when the temperature of the surroundings was low, and melted at 45°. ¹⁾ With ammonia it yielded an amide melting at 143°.

¹⁾ FR. RÉVERDIN and P. CRÉPIEUX BB. 34 (1901) 2993 state that they have obtained the same substance by nitrating *p*-toluenesulphochloride with a mixture of nitric and sulphuric acids. It melted at 36° but could not be recrystallised. They found the melting point of its amide to be 144°, this confirming the result obtained by ANNA WOLKOW. In the literature at my disposal mention is only made of the wrong statements of OTTO and GRÜBER who found 128°. I had already obtained my results when the paper of RÉVERDIN and CRÉPIEUX appeared.

In this nitrated chloride the position of the nitrogroup is known, as it is also formed from o.-nitrotoluene.

I have prepared the corresponding amides by acting with mono-methyl- and monoethylamine on this. 2. nitrotoluene. 4. sulphochloride. By treatment with nitric acid the methylamide gave the above mentioned nitroparatoluenesulphomethylnitramide melting at 116° and the ethylamide gave the analogous ethyl compound melting at 76°.

During the action of nitric acid on the alkylated amides of paratoluenesulphonic acid, the reactions in regard to the amido-group are analogous to those observed in the case of benzenesulphonic acid; a nitrogroup, however, readily enters the nucleus and occupies the ortho position in regard to the CH₃. Consequently 2. nitrotoluene. 4. alkylnitramide sulphonates are also formed.

An extensive communication on the numerous compounds obtained during this investigation will shortly appear elsewhere. I intend to state on a future occasion the results of the action of nitric acid on the two other isomers of toluenesulphonic acid.

Chemistry. — Dr. P. VAN ROMBURGH: "*On some further constituents of the essential oil of Kaempferia Galanga L.*" (Communicated by Prof. FRANCHIMONT).

(Communicated in the meeting of February 22, 1902.)

On May 26th 1900, I had the honour to present to the Academy a communication on the ethyl ester of p.-methoxycinnamic acid, the chief constituent of the essential oil of *Kaempferia Galanga L.* (Kentjoer, Mal.). Since then, I have continued the investigation of the liquid portion of that oil and tried in the first place to identify the nature of the second acid which I had found in it. Its purification, when contaminated with p.-methoxycinnamic acid, is not an easy matter and it must be recrystallised many times from water and alcohol before obtaining a product with a constant melting point (133°) which proved to be cinnamic acid. The acid may be more readily obtained pure by distilling the liquid essential oil in vacuum and saponifying the fraction boiling at 155°—165° (at 30 m.m.). The acid thus obtained at once showed the right melting point.

The alcohol formed during the saponification of that fraction proved to be ethyl alcohol so that the Kentjoer oil consists to a large extent