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

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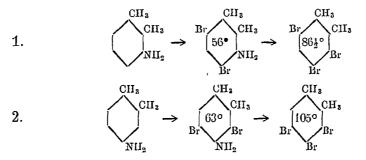
(153)

Chemistry. — "On the six isomeric tribromoxylenes." By Dr. F. M. JAEGER and J. J. BLANKSMA. (Communicated by Prof. A. F. HOLLEMAN).

The six isomeric tribromotoluenes were prepared in 1880 by NEVILE and WINTHER¹) and again in 1903 in a different manner by JAEGER²) with the object of studying the connection between molecular and crystallographic symmetry with isomeric benzene derivatives. In order to be able to extend this study to another series of compounds with an analogous chemical character we have now prepared the isomeric tribromoxylenes and give a short review of the mode of formation of these substances; we intend publishing a more extended report later on in the "Recueil".

Tribromo-o-xylenes.

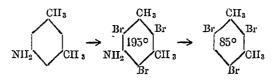
These substances are prepared by starting from the orthoxylidines 1-2-3 and 1-2-4 according to the subjoined scheme:

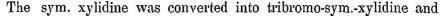


The orthoxylidines were treated in glacial acetic acid with the calculated amount of bromine and in the dibromoxylidines thus obtained the NH_2 -group was replaced by Br according to SANDMEYER's method. The tribromoxylenes thus obtained were purified by distillation in steam.

Tribromo-*m*-xylenes.

- 3. 2-4-6-tribromo-m-xylene was prepared in different ways.
- a. Starting from symmetrical xylidine,





¹) Ber. 13. 974.

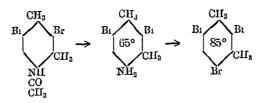
²) Dissertation, Leiden, 1903.

the NH₂-group was then eliminated by means of amylnitrite with addition of finely divided copper.

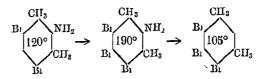
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b. Starting from 4-6-dibromo-2-amido-m-xylene prepared according to Auwers¹), we also obtain 2-4-6-tribromo-m-xylene m.p. 85° by replacing the NH_2 by Br according to SANDMEYER.

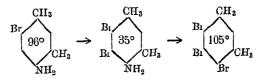
c. Acetoxylidide 1-3-4 yields on treatment with bromine and water dibromoacetoxylidide²). If this is boiled with hydrochloric acid, so that the acetyl group is eliminated and if in the dibromoxylidine so obtained the NH_2 -group is replaced by bromine 2-4-6-tribromo-m-xylene is also obtained.



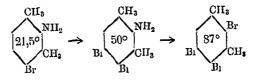
4. a. In order to arrive at 4-5-6-tribromo-m-xylene 4-6-dibromo-2-amido-m-xylene was converted by means of bromine into 4-5-6-tribromo-m-xylidine and from this substance the NH₂-group was eliminated by diazotation and boiling with alcohol.



b. Starting from 6-bromo-4-amido-*m*-xylene m.p. 96° we obtain by bromination 5-6-dibromo-4-amido-*m*-xylene m.p. 35° , which is converted by means of the SANDMEYER reaction into 4-5-6-tribromo*m*-xylene.



5. After many failures to prepare it differently, 2-4-5-tribromo-mxylene was finally made in the following manner.



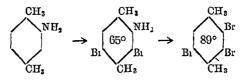
¹) Ber. **32**. 3313.

2) GENZ. Ber. 3 225,

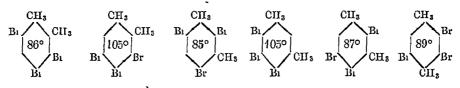
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Starting from 4-bromo-2-amido-*m*-xylene prepared according to Nolting¹), we obtained 4-5-dibromo-2-amido-*m*-xylene by bromination and from this 2-4-5-tribromo-*m*-xylene was prepared according to SANDMEYER.

6. Finally, tribromo-*p*-xylene was prepared according to the subjoined scheme.



Consequently all six tribromoxylenes had been obtained.



We wish here to express our thanks to Prof. FRANCHIMONT, who kindly presented us with the specimens for this research.

Zaandam, Amsterdam, Juni 1905.

Meteorology. — "Oscillations of the solar activity and the climate". (Second communication ²). By Dr. C. EASTON. (Communicated by Prof. C. H. WIND.)

(Communicated in the meeting of May 27, 1905).

At the end of the first communication on this subject the supposition was started, that the 11-year oscillation of temperature with regard to the eleven-year cycle of the sun's activity generally was accelerated in the cold, retarded in the warm part of the larger oscillation. In order to investigate this matter more thoroughly, I proceeded as follows:

Proceedings Royal Acad. Amsterdam. Vol. VIII.

¹) Ber. 34, 2261.

²) See for the First Communication: Proceedings of Nov. 26, 1904, p. 368. In that paper p. 372 read 89-years instead of 178-years. Furthermore strike out what has been said on p. 369 about the experiment of SAVÉLIEF.