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Chemistry. — "*The Addition of Hydrogenbromide to Allylbromide*".
By Prof. A. F. HOLLEMAN and B. F. H. J. MATTHES.

(Communicated in the meeting of May 25, 1918).

In the many cases that in my laboratory I had trimethylene-bromide prepared by the introduction of HBr gas into allyl-bromide, I was struck with the fact that now an almost quantitative yield was obtained, now a much smaller yield, without our being able to indicate the cause of this varying yield. When now my assistant, Mr. DEN HOLLANDER, had obtained almost exclusively trimethylene-bromide in this addition in a very brightly lighted room, whereas a few years ago Mr. WUITE observed by the side of it considerable quantities of a product that boiled at a lower temperature (propylene bromide) in the ordinary work-room, the supposition suggested itself that daylight exerts an influence on this. Mr. MATTHES undertook to inquire more closely into this matter.

For this purpose a quantity of allyl-bromide was divided into two equal parts; one part was poured into an ordinary bottle, the other in a bottle that had been perfectly blackened on the outside with lacquer. The liquid in the ordinary bottle was exposed as much as possible to the sunlight during and after the introduction of HBr. Every time that no HBr was absorbed any more, it was closed, and left to itself till the next day. After some days no further HBr was absorbed. The blackened bottle was treated in the same way. The absorption of HBr took place a great deal more slowly here, so that the process had to be continued for some weeks, before complete saturation had been attained.

When the contents of the two bottles was afterwards subjected to distillation, the preparation from the ordinary bottle almost entirely went over at constant temperature and at the boiling point of trimethylene bromide. After distillation in vacuum its boiling point amounted to 167°.1 for 760 mm.

The contents of the other bottle, on the other hand, presented a very considerable boiling range, viz. from 100—190°. On fractionated distillation a fraction of about 7 gr., going over between 140°—150°, was obtained, while between 155° and 165° a fraction of 22 gr. went over. The former had about the specific gravity of propylene

bromide, viz. 1.9259 at 23°.2; the latter had the spec. gr. of trimethylene bromide, viz. 1.9801 at 23°.2. Between 100° and 105° a few drops had also been distilled, which were still unchanged allyl-bromide, as appeared from this boiling point. Hence the conclusion is that on addition of HBr to allyl-bromide in bright daylight trimethylene bromide is almost exclusively formed; in the dark, beside this compound as chief product, also pretty much propylene bromide.

Amsterdam, May 1918. Org. Chem. Lab. of the University.