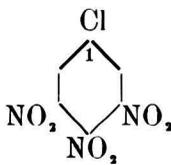
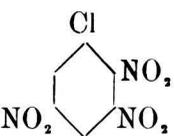
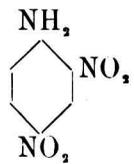


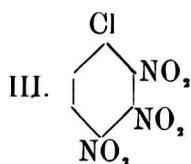
**Chemistry.** — “*Monochloro-trinitrobenzenes.*” By Prof. A. F. HOLLEMAN.

(Communicated at the meeting of June 24, 1922.)

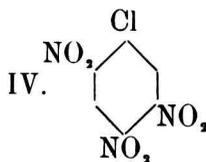
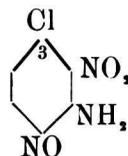
So far only two of the six possible isomers were known, viz. picrylchloride and a product obtained by NIETZKI (see below). For an inquiry into the replaceability of substituents it was required to prepare also the other four isomers. I have only been able so far to lay hands on three, and without doubt I should have waited with the publication of my results till the whole investigation had been completed, if I had not happened to hear that also others are engaged in a study of the same subject.

I.  *1-chloro-3, 4, 5-trinitrobenzene.* This compound is easily accessible; it is indeed surprising that it has not been known long since. The starting-point for its preparation is chlorodinitraniline 1, 4, 2, 6, in which  $\text{NO}_2$  was substituted for the  $\text{NH}_2$  group according to the method of KÖRNER and CONTARDI. The yield of raw compound amounts to 70% of the theory, and there is only little loss in the purification. The substance may be recrystallized from benzene. It then melts at 168°. Large yellow crystals.

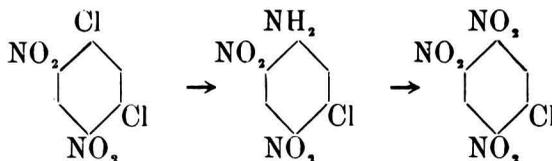
II.  *1-chloro-2, 3, 5-trinitrobenzene.* This compound is formed on very energetic nitration of 1-chloro-2,3-dinitrobenzene with a mixture of fuming nitric acid and oleum of 50%. The heating of 160—170° is continued for 5 hours. When the mixture is poured out into water, an oil is obtained, in which crystals are formed after some time. By centrifugation these are separated and then recrystallized from alcohol. Melting-point 106°. The structure of this compound was verified by a treatment with alcoholic ammonia, through which 2-chloro-4,6-dinitraniline is obtained, melting-point 159°. This compound is known. Much more easily, however, than according to the methods used up to now it could be prepared by chlorination of  2-4-dinitraniline with  $\text{KClO}_3$ . The entrance of a  $\text{NO}_2$ -group chloro-2,3-dinitrobenzene is group takes a position at *m* with regard to a nitro-group.



*1-chloro-2,3,4-trinitrobenzene.* In the nitration of 1-chloro-2,3-dinitrobenzene by the method given under II, the oil from which II was crystallized contains this third isomer. When the oil stands for a long time, the isomer crystallizes out of it in colourless needles of the melting-point of 69°. They are purified by recrystallization from alcohol. The structure of this compound can also be determined by treatment with alcoholic ammonia. If the action of the ammonia is allowed to last only for a short time, only one of the nitro-groups is replaced by NH<sub>2</sub>. The aniline formed is 3-chloro-2,6-dinitraniline for 1-chloro-2,4-dinitrobenzene is obtained from it by deamidation. This aniline has the melting-point 112°; it was unknown up to now.



*1-chloro-3,4,6-trinitrobenzene.* This compound was already prepared by NIETZKI by nitration of 1-chloro-3,4-dinitrobenzene. On repetition of his experiments it appeared to me that the yield was small, and especially very uncertain, because either the nitration remains incomplete, or the reaction is so violent that total destruction ensues. It is therefore, better to proceed as follows :



The substitution of NH<sub>2</sub> for Cl takes place in alcoholic solution on the waterbath with addition of gaseous ammonia, till a test-sample shows the correct melting-point of 174°. According to KÖRNER and CONTARDI NO<sub>2</sub> can then be substituted for NH<sub>2</sub>. The crude product is coloured black. It can be purified by boiling with nitric acid 1.4, followed by recrystallisation from alcohol. The melting-point is 116°, as has been given by NIETZKI.

No method of preparation has as yet been found for the last isomer, the 1-chloro-2,3,6-trinitro-benzene; probably it is also present in the oil obtained in the nitration of 1-chloro-2,3-dinitrobenzene.

*Amsterdam, June 1922. Org. Chem. Lab. of the University.*