

grain more nitrogenous, it at the same time very materially reduces the yield per acre, the present figures indicating a loss in weight of about 50 per cent.

We have not as yet been able to complete the analysis of the milling products of this shriveled wheat, but we may rest assured until such time as the data are available that the proportion of bran to flour will be higher than from normally ripened wheat. We may, further, conjecture that this bran will be found slightly more nitrogenous than that from rust-free wheat. It is held by certain millers that the rust makes flour somewhat "stronger," but at the moment there are no data, I believe, to support this contention. The probabilities, from deduction, rather point to a deterioration or lack of "strength" in the gluten.

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THE PREPARATION AND NITRATION OF METETHYLTOLUENE.

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WHILE the three possible ethyltoluenes have been made synthetically, and their properties studied, comparatively few of their derivatives have been prepared. There are recorded some halogen,¹ some sulphonic acid,² some nitro³ derivatives and one amino⁴ derivative. On account of the greater difficulty in obtaining *m*-ethyltoluene, only one derivative, a sulphonic acid, is recorded.

Some work done by one of us with *m*-isocymene⁵ suggested the possibility of similar work with *m*-ethyltoluene.⁵ We have prepared the *m*-ethyltoluene and tried on it the action of nitric acid.

The preparation of *m*-ethyltoluene presents some difficulties. It is best prepared according to the Fittig synthesis. The most convenient starting-point is, of course, a halogen derivative of toluene and an ethyl haloid, rather than a halogen derivative

¹ *Ber. d. chem. Ges.*, 11, 225 (1878); 19, 3088 (1886); 28, 2651 (1895).

² *Ibid.*, 19, 3090 (1886); 28, 2649 (1895); *Ann. Chem.* (Liebig) 146, 85; 193, 199.

³ *Ber. d. chem. Ges.*, 7, 1513 (1874); 19, 3090; 27, 2084 (1894); 28, 2649 (1895); *Ann. Chem.* (Liebig), 136, 314.

⁴ *Ber. d. chem. Ges.*, 15, 1650 (1882).

⁵ *Inaug. Diss.*, Göttingen (1895).

of ethylbenzene and a methyl haloid. For our ethyl haloid we used ethyl bromide. For the halogen derivative of toluene we used, in part, *m*-chlortoluene from Kahlbaum, and in part *m*-bromtoluene prepared in this laboratory.

The *m*-bromtoluene must be prepared indirectly, since by action of the halogens on toluene only ortho and para compounds result. We find that there are several methods for its preparation, but the best are the two following: In one benzaldehyde is nitrated, forming *m*-nitrobenzaldehyde; this is treated with phosphorus pentachloride, making *m*-nitrobenzalchloride; this, by reduction, gives *m*-toluidine; *m*-toluidine by diazotizing and treating according to the method of Sandmeyer gives *m*-bromtoluene.

The second method depends on the bromination of *p*-toluidine and the removal of the amino group from the product. We prepared our *m*-bromtoluene by the second method. Our method was practically like that recommended by Wroblewsky,¹ but we find that sodium hydroxide in concentrated aqueous solution will serve as well as potassium hydroxide for saponifying *m*-brom-*p*-acetoluidine (compare Grete).²

In the Griess reaction when nitrous acid is led into an alcoholic solution of the *m*-brom-*p*-toluidine, we also find that a thick crystal broth, not noted by Wroblewsky, is formed. These crystals were purified and investigated by Bartow and Allen³ and found to have a composition and molecular weight corresponding to 2,2'-dibrom-4,4'-dimethyl diazoaminobenzene, $\text{CH}_3\text{BrC}_6\text{H}_3\text{N}_2\text{—NHC}_6\text{H}_3\text{BrCH}_3$ (melting-point, 111.4°–112.0°). These crystals were stable when the solution was neutral, and care was taken to cool the solution and the nitrous acid. A few drops of sulphuric acid causes almost immediate replacement of the amino group by hydrogen. The product, after washing with water, diluting with ether, and drying with calcium chloride, was used in the preparation of *m*-ethyltoluene by the Fittig synthesis.

PREPARATION OF *m*-ETHYLTOLUENE.

We used 30 per cent. more than the calculated amount of ethyl bromide, and 50 per cent. excess of sodium for a given amount of chlor- or bromtoluene. The reaction takes place with considerable violence, making it necessary to cool the re-

¹ *Ann. Chem.* (Liebig), **168**, 147.

² *Ibid.*, **177**, 231.

³ *Trans. Kan. Acad. Sci.*, **19** (1905).

action mixture with salt and ice. Once the reaction miscarried, giving *m*-ditolyl. This result was prevented when the sodium, covered with ether, was thoroughly cooled and the mixture of ethyl bromide and chlor- or bromtoluene was added slowly, 2 to 3 cc. every thirty minutes.

In our first experiments, after driving off the ether on a water-bath, we distilled the hydrocarbon from the sodium bromide and the excess of sodium. On fractionating the distillate the temperature rose gradually from 120° to 170° with no larger amount distilling at 158°—the boiling-point of *m*-ethyltoluene. By repeated fractionations with a Linnemann dephlegmator we obtained about 4 grams, boiling at 158°, representing the yield from 25 grams of *m*-chlortoluene.

As we used the sodium and the ethyl bromide in large excess, we were at a loss to account for the small yield of *m*-ethyltoluene and for the large quantity of by-products formed. We thought it not unlikely that the high temperature required to distil the hydrocarbon from the excess of sodium, as well as the presence of metallic sodium, might tend to break down the ethyltoluene. We therefore attempted, by means of water, to destroy the blue compound and remove the excess of sodium by means of water, using a sufficient amount of ether to prevent any great rise in temperature. Accordingly, after the completion of the reaction and the formation of a blue compound, a considerable quantity of commercial ether was added to the mixture and a reversed condenser was connected to the flask containing the mixture. Then water was added drop by drop. The color quickly changed from blue to white, and as more water was added from time to time the sodium was dissolved. Though the ether was raised to boiling, no trouble was experienced in the removal of the sodium.¹

When the sodium was used up the ethereal solution of the hydrocarbon and the water solution of sodium bromide were separated, and the former evaporated and fractionated. Without a dephlegmator 7 grams of *m*-ethyltoluene, boiling at 158°, were obtained. This represented the yield from 25 grams of *m*-chlor-

¹ Before carrying out the above experiment in the preparation of *m*-ethyltoluene, we tried with success the effect of the method in making ethylbenzene from brombenzene and ethyl bromide. Several students have since successfully applied this method for the removal of the excess of sodium. It is certainly much easier than the method recommended by Gattermann's "Praxis d. organ. Chem."

toluene, whereas only 4 grams were obtained when the hydrocarbon was distilled from the sodium.

The crude product thus obtained by means of water contains very few impurities. We have used it successfully in the preparation of nitro derivatives. We obtained better yields of ethyl toluene from bromtoluene than from chlortoluene.

NITRATION OF *m*-ETHYLTOLUENE.

Of the five known nitro ethyl toluenes two are derivatives of *o*-ethyltoluene and three of *p*-ethyltoluene. We have prepared two of the possible nitro derivatives of *m*-ethyltoluene, a dinitro and a trinitro derivative. Our attempts to isolate a mono-nitro derivative have not been successful.

Dinitro-m-ethyltoluene.—One part of *m*-ethyltoluene was slowly added, drop by drop, to seven parts of fuming nitric acid cooled by a freezing-mixture of salt and ice. After all the *m*-ethyltoluene was added the mixture was kept surrounded by ice water for fifteen hours, or until a test in water would sink completely. The whole reaction mixture was then poured into water. The oil which separated out was taken up with ether, washed free from acid, and the ethereal solution dried over calcium chloride. The ether was then evaporated and the residue placed in a vacuum over sulphuric acid. The product would not distil without decomposition, but could be distilled with steam. Analysis gave: C, 51.23; H, 5.03. Calculated for $C_9H_{10}O_4N_2$: C, 51.4; H, 4.8.

Reduction of the Dinitro-m-ethyltoluene.—By leading dry hydrochloric acid gas into a solution of dinitro-*m*-ethyltoluene in alcohol, containing the required amount of tin to reduce both nitro groups and then removing the tin with hydrogen sulphide, a diamine was obtained. We did not obtain enough for an analysis. A small amount with nitrous acid gave a compound analogous to Bismark-brown, indicating the meta position of the amino groups and hence of the nitro groups. There may be, however, a mixture of dinitro compounds.

S-Trinitro-m-ethyltoluene.—For the preparation of the trinitro derivative 1 part of *m*-ethyltoluene was added to 7 parts of fuming nitric acid in the same manner employed in making the dinitro compound. Without separating it from the nitric acid the mixture was poured into 15 parts of a mixture of equal volumes of fuming nitric and concentrated sulphuric acids. After

warming for an hour the whole mixture was poured on to cracked ice. A solid was obtained. After three crystallizations from absolute alcohol nearly colorless crystals were obtained, which melted at 86°.

Analysis gave: C, 42.63; H, 3.99. Calculated for $C_9H_9O_6N_2$: C, 42.3; H, 3.5.

Therefore, we conclude that the compound is 2,4,6-trinitro-3-ethyltoluene, because we would expect the three nitro groups to take the symmetrical position with reference to each other by direct nitration. Furthermore, we were able to obtain a crystalline compound when equal molecules of the substance and aniline were mixed in alcoholic solution.

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THE DECOMPOSITION OF AMMONIA AT HIGH TEMPERATURES.

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THE fact is well known that ammonia gas decomposes at a red heat into nitrogen and hydrogen, which recombine to only a very slight extent, if at all, on cooling. Deville and Troost¹ showed this very clearly. Ramsay and Young² in addition showed the very marked influence exerted by the character and extent of surface in contact with the gas, particularly at the higher temperatures. Their method of work was to pass dry ammonia gas through heated tubes of various materials and filled with various solid substances. Under circumstances to which some reference will be made later, decomposition became practically complete as the gas flowed through the hot tube. Recently Perman and Atkinson³ have studied the decomposition of ammonia in a different manner. They used a porcelain globe placed in a constant temperature oven and keeping the volume constant, measured the decomposition by the increase in pressure. They found that at high temperatures, such as 1100° C., decomposition was practically complete in their apparatus in twenty minutes. They consider that the volume of the cold stem of their globe is suffi-

¹ *Compt. Rend.*, **56**, 895.

² *J. Chem. Soc.*, **43**, 88.

³ *Proc. Roy. Soc.*, 1904, p. 110.