is ordinarily allowed to stand overnight at 0°. The crystals are filtered off, washed successively with 75%, 95%, and absolute alcohol and dried in a vacuum oven. The sugar is in many cases colorless and pure and the yield is between 10 and 12%, depending upon the cobs that are used. If required, the crude xylose may be recrystallized from water or aqueous alcohol.

In conclusion, we would add that xylose is one of the most easily prepared members of the sugar group when either cottonseed hulls or preferably corn cobs are used as its source. There should no longer be any difficulty in obtaining a supply of this pentose sugar for chemical, bacteriological, medical or other scientific uses.

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[CONTRIBUTION FROM THE SANDERS CHEMICAL LABORATORY OF VASSAR COLLEGE.]

ON THE DINITRO DERIVATIVES OF *p*-DICHLOROBENZENE: 2,5-DICHLORO-1,4-DINITROBENZENE.

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Received July 19, 1918.

p-Dichlorodinitrobenzene was first prepared by Jungfleisch[1] by the nitration of mononitro-*p*-dichlorobenzene. He obtained two isomers, α and β, the melting points of which he gave as 87° and 107°, respectively. Englehardt and Latschinoff[2] repeated the process and isolated two compounds which corresponded in appearance to the two isomers obtained by Jungfleisch, but which melted at 104° and 101°, respectively. Later investigators confirmed these melting points and fixed the constitution of the 104° compound as 2,5-dichloro-1,3-dinitrobenzene, that of the 101° being left undetermined. Rütgers[3] studied the reactions of *p*-dichlorodinitrobenzene, prepared by the nitration of *p*-dichlorobenzene. He refers to the β (101°) compound, but states that the amount formed in his preparation was so small as to render its separation unnecessary.

Despite the fact that no reference is made to it by any of these investigators, it seemed probable that the third theoretically possible *p*-dichlorodinitrobenzene was also formed in the nitration of *p*-dichlorobenzene, particularly in view of the work of Jackson, Calhane and Wheeler,[4] who succeeded in isolating the 3 corresponding *p*-dibromodinitro derivatives. Careful recrystallization of the crude product has shown that all 3 isomers are in fact produced in the nitration of *p*-dichlorobenzene, the third, hitherto unnoticed, being formed in considerably larger proportion than either of the other two.

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[1] *Jahresber.*, 1868, 345.

[2] *Z. Chem.*, 6, 234 (1870).

[3] *Inaug. Diss.*, Basle, 1893.

[4] *Am. Chem. J.*, 22, 449 (1899); 28, 451 (1902).

The object of the present paper is to show that the constitution of this third isomer, which melts at 81°, is 2,5-dichloro-1,4-dinitrobenzene. As the constitution of the 104° isomer is already established, that of the 101° compound is fixed by implication as 2,5-dichloro-3,4-dinitrobenzene.

p-Dichloronitrobenzene, melting at 81°, gives on reduction with tin and hydrochloric acid, 2,5-dichloro-1,4-phenylenediamine, prepared by Mohlau[1] from nitrosodimethylanilin hydrochloride and conc. hydrochloric acid. Although the constitution was practically fixed by this reaction, confirmation was obtained by the oxidation of the diamine to the corresponding 2,5-dichloroquinone.[2]

Experimental Part.

Purification of *p*-Dichlorobenzene.—Commercial *p*-dichlorobenzene, obtained from E. C. Klipstein Sons & Co., contained a large amount of brown coloring matter. This crude product was dissolved in alcohol and filtered. A large amount of the impurity was left on the paper by this process, but the crystals which separated from the filtered solution still had a brownish tinge. They were dissolved in alcohol and the solution was boiled with animal charcoal, filtered and allowed to crystallize. The crystals were quite white, melting at 53–54°. Further treatment with animal charcoal did not improve them. An alternative method for purification is by sublimation, since *p*-dichlorobenzene sublimes readily on a steam bath.

Nitration of *p*-Dichlorobenzene.—The method used for nitration was that of Rütgers,[3] namely the nitration of *p*-dichlorobenzene. 100 g. of pure *p*-dichlorobenzene was added slowly to a mixture of 1000 g. of conc. sulfuric acid (sp. gr. 1.84) and 400 g. of fuming nitric acid (sp. gr. 1.52), and heated over a free flame for 5 hours in a flask with a large funnel inserted in the neck to act as condenser. The mixture was partially cooled and poured over cracked ice. A greenish yellow oil separated, which solidified on standing. This was washed free from acid and dried. The yield was 151 g. (94% theoretical).

Isolation of 2,5-Dichloro-1,4-dinitrobenzene.—The 104° compound is easily separated from the crude product by means of ethyl alcohol, in which it is sparingly soluble. The separation of the other two isomers is much more difficult owing to the fact that their solubilities in all common solvents seem to be almost identical. Ethyl alcohol was found to be the most satisfactory solvent, although it was far from ideal. By careful concentration of the filtrate from the 104° compound, successive crops of long needles, melting at 101°, and rosets or balls composed of microscopic needles melting at 81° may be obtained. The process of crystallization

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[1] *Ber.*, **19**, 2010 (1886).

[2] *Ann.*, **210**, 150 (1881).

[3] *Loc. cit.*

is slow, as the separation of pure crystals from a mixture can only be effected by crystallizing from rather dilute solution at room temperature. Further concentration or cooling in ice invariably results in the separation of a mass of fine indistinguishable crystals of both kinds. In some cases separation can be hastened by alternate crystallization from carbon tetrachloride and from ethyl alcohol. When a rough separation has once been made the further purification of the two compounds by recrystallization from ethyl alcohol offers no difficulty. The relative proportions in which the 3 isomers were obtained are: 104° = 13.1%; 101° = 26.2%; 81° = 45.6%. Analysis of the compound melting at 81° shows it to be isomeric with the other two.

Subst., 0.2446 g. gave 25.8 cc. N at 742 mm. and 18.5°; 0.2129 g. gave 0.0185 g. H_2O, and 0.2372 g. CO_2.

Calc. for $C_6H_2Cl_2(NO_2)_2$: N, 11.82; C, 30.37; H, 0.85. Found: N, 11.86; C, 30.38; H. 0.96.

Properties of 2,5-Dichloro-1,4-dinitrobenzene.—The third isomer crystallizes from alcohol in very fine needles forming small yellow rosets, melting at 81°. It is very soluble in methyl alcohol, chloroform, benzene, acetone, ether and warm carbon tetrachloride, rather sparingly soluble in acetic acid, nitric acid, and ethyl alcohol, and very sparingly soluble in petroleum ether.

Reduction of 2,5-Dichloro-1,4-dinitrobenzene.—Seven grams of dichlorodinitrobenzene was treated with 150 cc. of 70% acetic acid and an excess of zinc dust. The mixture was allowed to stand overnight in a warm place (60°). In the morning the solution was rendered alkaline with a saturated solution of sodium hydroxide, which was added in a sufficient amount to redissolve the zinc hydroxide first formed. An ether extraction gave only a very little of impure dark brown diamine, melting near 164°. On testing the ether solution with hydrogen sulfide and ferric chloride, the purple color which is characteristic of the paradiamines appeared. Not enough of the impure diamine was obtained to recrystallize.

Since zinc and acetic acid appeared to be an unsatisfactory reducing agent, a second attempt was made, using tin and hydrochloric acid. Seven grams of dichlorodinitrobenzene was dissolved in alcohol and treated with 350 cc. of conc. hydrochloric acid and an excess of tin. The mixture was heated on a steam bath for 5 hours with a reflux condenser. The clear amber solution was filtered, heated to expel excess of acid, and allowed to stand overnight. A very few crystals of what was probably the tin double salt of the diamine separated. On adding sodium hydroxide a large amount of heat was generated and a grayish black precipitate formed. The mixture was made alkaline and filtered. Ether extraction of the filtrate gave no better results than before. The reduction was repeated once more and the tin was precipitated with hydrogen sulfide. Complete removal of the tin was very difficult and the results were even less satisfactory. A reduction with aluminum amalgam was also a failure. It seemed probable, therefore, that the difficulty was not in the method of reduction but in the recovery of the reduced compound. Another reduction was made, this time with tin, stannous chloride, and hydrochloric acid. Twenty grams of dichlorodinitrobenzene, 60 g. of stannous chloride, 200 g. of conc. hydrochloric acid and an excess of tin were heated for 5 hours on a steam bath with a reflux condenser. The clear solution was heated to expel excess of acid. Sodium hydroxide was then added until the usual black precipitate ceased to form. The mixture was filtered and the precipitate thoroughly dried and extracted with ether for 8 hours in a Soxhlet extractor. About two g. of the diamine were obtained in this way, a large part of which appeared as colorless prisms in the ether before evaporation, showing the sparing solubility of the diamine in that solvent. The filtrate from the black precipitate was distilled with steam. About two g. more of the diamine appeared in crystalline form in the receiver, and one g. more was obtained on concentrating the distillate. The product was purified by recrystallization from chloroform.

Subst., 0.2858 g. gave 30.6 cc. N at 754.5 mm., and 18.5°.
Calc. for $C_6H_2Cl_2(NH_2)_2$: N, 15.8. Found: 15.9.

Oxidation of 2,5-Dichloro-1,4-diamidobenzene.—Four grams of dichlorophenylenediamine was added to 130 cc. of dil. sulfuric acid cooled to 0°. Without waiting for the diamine to go completely into solution, 4 g. of powdered potassium dichromate was slowly added with constant stirring and the mixture was allowed to stand overnight. In the morning 4 g. more of potassium dichromate was added with the same precautions. After 3 or 4 hours the oxidation mixture was extracted with ether. On evaporation *p*-dichloroquinone crystallized out. Recrystallization from alcohol in a freezing mixture gave yellow crystals melting at 161°.

Subst., 0.1235 g. gave 0.0158 g. H_2O, and 0.1866 g. CO_2.
Calc. for $C_6H_2Cl_2O_2$: C, 40.7; H, 1.1. Found: C, 41.2; H, 1.4.

The investigation described above was carried out under the direction of Miss A. L. Macleod of Vassar College, to whom I wish to express my thanks. The further reactions of 2,5-dichlorodinitrobenzenes are being studied in this laboratory.

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