Table VI.—Angles of 1 : 1-Tetraethyl Ammonium Mercuric Iodide.
Tetragonal. $a : c = 1 : 1.1577$.

Number, letter.		Symbols.		Description.	Angles observed.	
		Gdt.	Mill.		φ.	ρ.
1	*c*	0	001	Dominant form (absent on prismatic crystals)	. . .	0° 00′
2	*a*	∞ 0	100	Narrow, but always present	90° 00′	90° 00′
3	*m*	∞	110	Prominent form	45° 00′	90° 00′
4	*p*	1	111	Narrow on plates; prominent on prismatic crystals	45° 00′	58° 35′

The chloride corresponding to this in formula has been described by Topsöe[1] as triclinic, with all three axial angles near 90°, and tabular on *b*; but if the tabular form is made *c* a certain degree of resemblance is shown between the two compounds. The pole distances of forms in pyramidal positions are then 51° 04′, 61° 17′ and 70° 53′, average 61° 05′, as against the 58° 35′ observed for the tetragonal pyramid on the iodide. The approach of these values is sufficiently marked to indicate at least a similarity in the structures underlying the two substances. Under the microscope the plates are practically isotropic, and in convergent light yield a uniaxial positive interference figure; and the double refraction is very strong.

Summary.

The new compounds dimethyl and diethyl ammonium mercuric iodide have been prepared and described. The amount of these compounds which can be detected by precipitation with Mayer's reagent has been determined. The crystallography and optical properties of di-, tri-, and tetramethyl and ethyl ammonium mercuric iodides have been described.

Washington, D. C.

[Contribution from the Laboratory of Organic Chemistry of the State University of Iowa.]

SOME DERIVATIVES OF *p*-DICHLOROBENZENE.[2]

By Joyce H. Crowell and L. Chas. Raiford.

Received October 22, 1919.

The use of monochlorobenzene in the manufacture of both phenol[3] and picric acid,[4] and the fact that the preparation of the starting material always involves the production of considerable amounts of the dichlorinated compounds show that the latter are relatively plentiful by-products. In accord with the best technical practice,[5] more than 4%

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[1] *Loc. cit.*

[2] This report represents a part of a thesis presented by Joyce H. Crowell to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Master of Science, July, 1919.

[3] *C. A.*, **11**, 868 (1917).

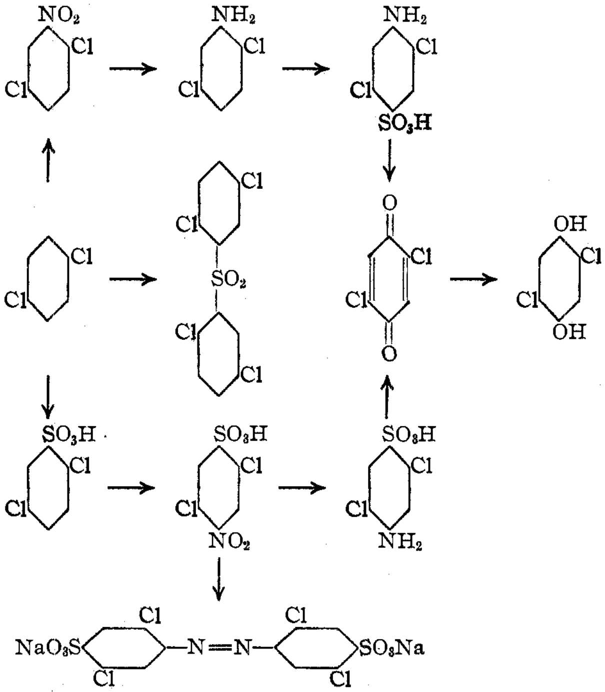
[4] Marshall, *Explosives*, **1**, 278 (1917).

[5] Ullman, *Enzyklop. tech. Chem.*, **11**, p. 370.

of the benzene used for this work is converted into *p*-dichlorobenzene, which is said to have practically no industrial value except that *p*-phenylenediamine[1] can be produced from it on a semi-technical scale. It seemed, therefore, a matter of interest to study more carefully than had been done before some of the derivatives of *p*-dichlorobenzene.

Among the reactions that suggested themselves in this connection, the following were considered: (*a*) The removal of one or both chlorine atoms and their replacement by hydroxyl or other radicals; (*b*) the preparation of some of the possible nitrosulfonic acids and their derivatives.

To secure material for the work indicated it was necessary to prepare a quantity of the well-known mononitro compound, 2,5-dichloronitrobenzene, for which we have determined the optimum conditions and recorded the yield.[2] This material was reduced to 2,5-dichloroaniline, which was then sulfonated in accordance with the method of Noelting and Kopp,[3] after which the acid (or its sodium salt) was oxidized to 2,5-dichloroquinone, and the latter reduced to its hydroquinone, in order to secure material with which to compare the derivatives of our new nitro-



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[1] *Chem. Centr.*, 1908, II, 1221.

[2] Though this compound has been prepared by several chemists, no one whose data is accessible to us has recorded either the yield or the details of the method by which the maximum yield can be obtained.

[3] *Ber.*, 38, 3513 (1905).

sulfonic acid (see experimental part). This was obtained through the nitration of 2,5-dichlorobenzene sulfonic acid, which was prepared by Holleman and van der Linden's method[1] modified in such a way as to enable us to isolate and recognize as 2,2′-5,5′-tetrachloro-diphenylsulfone, the insoluble body mentioned but not isolated by Lesimple.[2] The identity of this acid was established by the study of several of its salts and other derivatives, while its consitution was determined by the reduction of its sodium salt and the oxidation of the corresponding amino compound to 2,5-dichloroquinone. These reactions may be briefly indicated by the formulas given above.

Experimental.

Starting Material.—The *p*-dichlorobenzene with which this research was begun was obtained from the Dow Chemical Company, and consisted of white, massy, transparent crystals that melted sharply at 53°.[3] It was free from the *ortho* and *meta* isomers, which are liquids at ordinary temperatures, and was used without further purification.

Nitration of *p*-Dichlorobenzene.—The mononitro compound was obtained in almost theoretical yield by a modification of the method published by Morgan,[4] special care being taken to avoid the formation of isomers[5] through the introduction of more than one nitro group. We found it more satisfactory to add the mixed acids in 4 or 5 portions during half an hour, and to shake the flask during the entire period, after which the mixture was heated for an hour or so on the water bath. The product was separated and purified in the usual manner, and had the melting point and other properties recorded by Morgan.

The Sulfonation of *p*-Dichlorobenzene.—Lesimple[6] studied the action of sulfuric acid on a dichlorobenzene, evidently the *para* compound, as early as 1868, and described a dichloro-benzenesulfonic acid and several of its salts. Beilstein and Kurbatow[7] found later that *p*-dichlorobenzene reacts with sulfuric acid with much difficulty, and then only incompletely

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[1] *Rec. trav. chim.*, **30**, 305 (1911).

[2] *Bull. soc. chim.*, [2] **10**, 266 (1868).

[3] All melting points reported in this paper are uncorrected.

[4] *J. Chem. Soc.*, **81**, 1382 (1902).

[5] Morgan found that the introduction of a second nitro group gave two isomers, 2,5-dichloro-1,4-dinitrobenzene and 2,5-dichloro-1,3-dinitrobenzene, and that the first was formed in largest amount, though he did not record the yield of either. Hartley and Cohen (*J. Chem. Soc.*, **85**, 865 (1904)), also, found that two isomers were formed, and that the quantity of the *meta* compound (the second one named above) was about 6 times that of the *para* isomeride, but no yields were given; while Nason (THIS JOURNAL, **40**, 1602 (1918)) has recently found that when two nitro groups are introduced the product is a mixture of all 3 of the possible isomers. The relative yields were determined, the *para* compound being present in largest amount.

[6] *Loc. cit.*

[7] *Ber.*, **7**, 1760 (1874).

even after long heating in a sealed tube at 230°, using massy, fuming acid, while Holleman and Van der Linden[1] state that sulfuric acid containing more than 0.3% of free sulfur trioxide will sulfonate it. For more satisfactory results they recommend an acid containing 10% sulfur trioxide, at ordinary temperature, and acting for 24 hours' time. We obtained the highest yields of product by the use of an acid containing 10–12% of sulfur trioxide, when the reaction was carried out as follows: A mixture of 150 g. of dichlorobenzene and 225 g. of the sulfuric acid specified was placed in a suitable flask and heated to 140–150°, while the material was kept in constant motion with a mechanical stirrer. After about 45 minutes the two layers had disappeared and the mixture, which was quite dark in color, was cooled somewhat and poured into a large volume of cold water. This caused the separation of any unchanged material present together with some of the tetrachloro-diphenylsulfone already referred to. About 35 g. of solid was filtered off at this point and the filtrate concentrated, after which, upon cooling, the sulfonic acid separated out in long, colorless needles. Recrystallization from water removed practically all the sulfuric acid. A yield of 85–90% was obtained. A second portion of the sulfonic acid solution, prepared as indicated above, was poured into saturated salt solution, and the sodium sulfonate precipitated out. On recrystallization from hot water this separated out in glittering, hexagonal plates, or in long, silky needles. The plates contained one molecule of water of crystallization, and had a tendency toward efflorescence. A sample heated to constant weight at 110° gave the following figures:

Subs., 0.5233: H_2O, 0.0338.
Calc. for $C_6H_3Cl_2SO_3Na.H_2O$: H_2O, 6.74. Found: 6.46.

2,2′-5,5′-Tetrachloro-diphenylsulfone, $(C_6H_3Cl_2)_2SO_2$.—In his report on the sulfonation of *p*-dichlorobenzene, Lesimple[1] refers to an insoluble product that separated as the reaction proceeded, and suggested that this might be a sulfobenzid, though he did not purify the material or study it further. In our work about 30 g. of this substance was formed during the sulfonation of 150 g. of dichlorobenzene. The product is not very soluble in cold alcohol, but much more soluble in the hot liquid, out of which, on cooling, it crystallizes in colorless, small, thick, diamond-shaped crystals whose sides are parallelograms. It is quite soluble in hot benzene, and insoluble in water. It melts at 179°. Analysis for halogen gave figures that agree with the formula assigned.

Subs., 0.5262: AgCl (Carius), 0.8438.
Calc. for $(C_6H_3Cl_2)_2SO_2$: Cl, 39.84. Found: 39.67.

2,5-Dichloro-4-nitrobenzene-sulfonic Acid, $C_6H_2Cl_2NO_2SO_3H$.—So far as far as we are aware no mononitrosulfonic acid derived from *p*-dichloro-

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[1] *Loc. cit.*

benzene has heretofore been reported in the literature, although similar derivatives from the *ortho* and *meta* isomers are known.[1] On this account it seemed a matter of interest to us to investigate the action of fuming nitric acid on 2,5-dichloro-benzenesulfonic acid. It may be stated here, at once, that this is probably the only method by which a nitrosulfonic acid can be prepared from the *para* isomer, for all attempts to sulfonate 2,5-dichloro-nitrobenzene were unsuccessful. Many experiments with varying concentrations of acid showed that no sulfonation took place below 150°, but above that temperature violent decomposition, with almost complete carbonization, occurred. The action of fuming nitric acid alone or in the presence of sulfuric acid gave, under the conditions we imposed, a mononitrated product. A quantity of the sulfonic acid weighing about 75 g. was treated with a mixture of 54 cc. of nitric acid (sp. gr. 1.6) and 32 cc. of sulfuric acid (sp. gr. 1.84). Such a mixture approximates that one found by Saposchinikoff[2] to have the maximum vapor pressure which, according to his results, contains nitric acid, sulfuric acid and water very nearly as represented by the formula $5HNO_3.2H_2SO_4.3H_2O$. The reaction mixture was then boiled down until a sample crystallized on cooling. This compound was also prepared by mixing 35 g. of the sulfonic acid with 50 cc. of nitric acid (sp. gr. 1.6), and then concentrating the mixture until a sirupy condition was produced. On standing for a day or two this liquid deposited bushy, burr-like crystals composed of flat, yellow needles. Repeated crystallization from water gave a compound that is quite hygroscopic and apparently has a melting point near 150°. The acid is not soluble in organic solvents to any appreciable degree, and this behavior, in addition to the properties already named, has prevented the preparation, thus far, of a perfectly pure sample of our product. Nevertheless, since several of its salts and other derivatives have been prepared and analyzed, the composition and structure of the acid are fixed without doubt.

The Salts of 2,5-Dichloro-4-nitrobenzene-sulfonic Acid, $C_6H_2Cl_2NO_2SO_3Me$.

The Sodium Salt, $C_6H_2Cl_2NO_2SO_3Na$.—This compound was prepared by salting out the nitration mixture, and also by nitration of the sodium salt of the sulfonic acid. A quantity of the sodium salt weighing about 50 g. was mixed with 50 cc. of fuming nitric acid (sp. gr. 1.6), and heated for several hours under a return condenser, after which 40 cc. more of the acid was added and the heating continued for some time. On evaporating off the excess of nitric acid the sodium nitrosulfonate was left as a pale yellow, amorphous powder. It was purified by recrystallization

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[1] *Chem. Centr.*, **1906**, II, 1537; *Ibid.*, **1908**, I, 726.

[2] *J. Russ. Phys. Chem. Soc.*, **36**, 518 (1904); *J. Chem. Soc. Abs.*, **86**, II, 558 (1904). We regret that the original of this paper was not accessible to us.

from water, from which it separated in thin, wing-like scales or leaflets that showed a tendency to clump together, and contained one molecule of water of hydration. It is not easily soluble in organic solvents. By the second method indicated about 90% of the salt was nitrated. Analyses for water of hydration for halogen and for sodium gave results that are in agreement with the requirements of a mononitro compound.

Subs., 2.5005, 0.8124: H_2O, 0.1386, 0.0455.

Subs., 0.5464: AgCl (Carius), 0.5434.

Subs., 0.8273: Na_2SO_4, 0.2013.

Calc. for $C_6H_2Cl_2NO_2SO_3Na.H_2O$: H_2O, 5.77; Cl, 24.12; Na, 7.82. Found: H_2O, 5.54, 5.61; Cl, 24.57; Na, 7.87.

With the exception of the first analysis for water, the analyses here recorded were made upon portions of the same sample.

The Potassium Salt, $C_6H_2Cl_2NO_2SO_3K$.—This substance was prepared by salting it out from a saturated solution of potassium chloride, by addition of the free nitro acid, in the manner used to obtain the sodium salt. The product has practically the same solubilities as the sodium salt, crystallizing out of water in pale yellow, flat, bushy needles that tend to cluster in the form of nodules containing one molecule of water of hydration. Analyses for water and for potassium gave the following figures:

Subs., 1.0454: H_2O, 0.0553.

Subs., 0.7354: K_2SO_4, 0.2081.

Calc. for $C_6H_2Cl_2NO_2SO_3K,H_2O$: H_2O, 5.47; K, 12.61. Found: H_2O, 5.29; K, 12.69.

The Ammonium Salt, $C_6H_2Cl_2NO_2SO_3NH_4$.—This salt was prepared by the addition of aqueous ammonia in excess to the solution of free nitro acid, and concentration of the resulting liquid. The product was further purified by crystallization from water from which it separated in lemon-yellow tufts of flat, grass-like needles, sometimes clustering together to form hard balls. It is easily soluble in water. Analysis for the ammonium radical gave results that agree with the formula assigned.

Subs., 0.7552: NH_3, 0.0446.

Calc. for $C_6H_2Cl_2NO_2SO_3NH_4$: NH_3, 5.88. Found: 5.91.

The Barium Salt, $(C_6H_2Cl_2NO_2SO_3)_2Ba$.—This compound was made by the action of barium nitrate on the sodium salt, and was obtained as a precipitate by mixing solutions of these salts. It is but sparingly soluble in water, and from a hot solution it separates, upon cooling, in the form of thin, sharp-pointed leaflets having the appearance of peach leaves, and clustering together in roset-like forms. It was analyzed for barium.

Subs., 0.2553: $BaSO_4$, 0.0882.

Calc. for $(C_6H_2Cl_2NO_2SO_3)_2Ba$: Ba, 20.22. Found: 20.32.

Proof of the Constitution of the Acid, $C_6H_2Cl_2NO_2SO_3H$.—A portion of the sodium salt was reduced with tin and hydrochloric acid in the usual manner, and the resulting sodium dichloro-sulfanilate crystallized from the mixture. It separated in the form of colorless, shining leaflets. Its water solution turned red slowly on standing exposed to the air. Analysis for halogen gave results consistent with the formula below.

Subs., 0.4230: AgCl (Carius), 0.4600.
Calc. for $C_6H_2Cl_2NH_2SO_3Na$: Cl, 26.85. Found: 26.89.

This compound was further identified by the preparation of its acetyl derivative, which was carried out by heating the salt with acetic anhydride in the usual way. The product is easily soluble in water, from which it was crystallized in the form of colorless masses made up of long, thin needles having the appearance of cotton. A determination of nitrogen gave the following figures:

Subs., 0.2985: 6.95 cc.; HCl, 0.1427 *N*.
Calc. for $C_6H_2Cl_2SO_3NaNHCOCH_3$: N, 4.58. Found: 4.65.

The relative positions of the nitro and sulfonic acid groups in the acid under consideration were determined by oxidation of the sodium salt of the corresponding amino compound. Five g. of this product, purified as indicated above, was slowly mixed with a solution containing 9 g. of sodium dichromate dissolved in 35 cc. water and 14 cc. of conc. sulfuric acid dissolved in 80 cc. water. The temperature was kept below 10°, and the mixture was constantly agitated by means of a mechanical stirrer. The resulting quinone separated in the form of yellow needles which, after recrystallization from alcohol, melted sharply at 160°. To show that in this compound the chlorine atoms occupy Positions 2 and 5, and that the substance in hand was identical with 2,5-dichloroquinone, obtained by Noelting and Kopp,[1] a sample of the latter was prepared by the method described by these chemists. This product, also, melted at 160°, and a mixture of it and the quinone obtained by the oxidation of our sulfanilic acid melted at the same temperature as either of them separately, which indicates their identity. The nitro and the sulfonic acid groups in our new acid are, therefore, in the *para* positions with respect to each other.

Sodium Salt of 2,2′-5,5′-Tetrachloro-azobenzene-4,4′-disulfonic Acid, $(SO_3NaC_6H_2Cl_2)_2N_2$.—This was formed by the alkaline reduction of the sodium salt of the nitrosulfonic acid, and also by reduction in weakly acid solution. Ten g. of the recrystallized sodium salt was mixed with a solution of sodium hydroxide containing one g. of the alkali in 10 cc. of water, and this was treated with 15 g. of zinc dust, added in 3 portions. The mixture was warmed and the reaction completed by boiling until the liquid became faintly brown or nearly colorless On filtering it rapidly turned red, and dark brownish red on boiling. When the solution had become very dark colored and no further change seemed to take

[1] *Loc. cit.*

place, it was allowed to crystallize. On recrystallization from 95% alcohol the product was obtained in the form of long, double wedge-shaped yellowish red crystals with thin, pointed ends. It contains some water of hydration, the amount of which was not determined, and on complete dehydration it forms a dark grayish brown, amorphous powder, which is quite soluble in water, giving a deep red solution. Analysis of the dehydrated product for sodium gave figures that agree with formula below.

Subs., 0.2970: Na_2SO_4, 0.0800.
Calc. for $(SO_3NaC_6H_2Cl_2)_2N_2$: Na, 8.77. Found: 8.72.

Summary.

1. The details of a method for obtaining practically a quantitative yield of *p*-dichloro-nitrobenzene have been worked out on a laboratory scale.
2. The results obtained by Holleman and Van der Linden in the sulfonation of *p*-dichlorobenzene have been confirmed, and the details of a convenient method for purification of the resulting sulfonic acid have been described.
3. A new tetrachloro-diphenylsulfone, separating as a by-product in the sulfonation of *p*-dichlorobenzene, has been isolated and its composition determined.
4. One of the nitrosulfonic acids of *p*-dichlorobenzene, the 2,5-dichloro-4-nitrobenzene-sulfonic acid, has been prepared and its structure established.

IOWA CITY, IOWA.

[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY OF THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE COMPOSITION OF HUBBARD SQUASH SEED OIL.

BY WALTER F. BAUGHMAN AND GEORGE S. JAMIESON.

Received November 3, 1919.

Hubbard squash (*Cucurbita maxima*) belongs to the same family in which pumpkin and watermelon are classified. Extensive examinations have been made of both pumpkin seed oil and watermelon seed oil by Power and Salway.[1] However, no report of an examination of squash seed oil has been found in the literature. The object of the investigation, reported in this paper, was to determine the constituents of a specimen of the expressed oil of Hubbard squash seed.

Seeds.—The seeds were examined with the following results:[2]

	%.
Moisture	5.72
Ether extract	36.66

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[1] THIS JOURNAL, 32, 347, 360 (1910).

[2] Analysis made by J. M. Johnson, formerly of This Laboratory.