From a second preparation of α-phenylbutyronitril with sodium amide, in which 48 g. of benzyl cyanide was used, a yield of 49 g. of distillate boiling at 70–110°, at 10 mm., was obtained, all but a few drops of which distilled above 100°.

The distillate (6.4 g.) from the ethylation of 12 g. of benzyl cyanide with metallic sodium was hydrolyzed and a yield of about 4 g. of α-phenylbutyric acid obtained, of melting point 41–42°.

An attempt to substitute calcium carbide for sodium amide and sodium in the action with benzyl cyanide was made, but proved unsuccessful, because the carbide was not attacked appreciably.

Summary.

The successful preparation of *p*-ureido-phenyl-acetylurea is described as the first of a series of ureidophenyl acyl derivatives of urea which are intended to form the basis for a study of their physiological activity, particularly as hypnotics. Intermediate products and their preparation are described. The preparation of other derivatives of the series, such as ureido-phenylethyl-acetylurea, and ureido-phenylethyl-barbituric acid, is well under way in this laboratory and will be reported on at a later date.

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

METHYL AND ETHYL AMMONIUM MERCURIC IODIDES: THEIR PREPARATION, CRYSTALLOGRAPHY, AND OPTICAL PROPERTIES.

BY GEORGE S. JAMIESON AND EDGAR T. WHERRY.

Received October 22, 1919.

The compounds described in this paper were obtained by adding potassium mercuric iodide (Mayer's reagent) to aqueous solutions of the amines which had been acidified with hydrochloric acid. Woodward and Alsberg[1] discovered that minute quantities of tertiary methyl and ethyl amines could be precipitated and detected by means of Mayer's reagent in the presence of the primary amines as well as the secondary amines provided the latter were present in small amounts. However, when one cc. of solution contains more than 20 mg. of diethylamine or more than 4 mg. of dimethyl amine, these compounds are precipitated with Mayer's reagent. In addition to the trimethyl and triethyl ammonium mercuric iodides described by Woodward and Alsberg, Woodward prepared tetramethyl ammonium mercuric iodide, which was recently found

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[1] A paper on "A New Reagent for Volatile Tertiary Amines," was presented September, 1916, at the New York meeting of the American Chemical Society, and will be published later.

to melt at 236°, and the corresponding ethyl compound, which melts at 155°.

All of the substituted ammonium mercuric iodides were bright yellow in color and had the common property of being decomposed by water with the separation of red mercuric iodide. It was also observed that all of the compounds investigated were readily soluble in potassium iodide. It is of great importance, therefore, to prepare Mayer's reagent exactly as described below in order to avoid an excess of potassium iodide which would prevent the detection of small quantities of the tertiary amines as proposed by Woodward and Alsberg.

The methyl and ethyl ammonium mercuric iodides have been submitted to detailed crystallographic and optical investigation in order to obtain means for their identification.

Experimental Part.

Dimethyl Ammonium Mercuric Iodide, $(CH_3)_2NH.HI.HgI_2$.—This compound was prepared by adding a distinct excess of Mayer's reagent to a slightly acidified solution of dimethyl amine hydrochloride. The Mayer's reagent employed in this investigation was made of 45 g. of mercuric iodide and 33 g. of potassium iodide in water so as to make exactly 100 cc. of solution. It is important to weigh both of the iodides with care in order to avoid an excess of the potassium iodide in which all the substituted ammonium mercuric iodides are readily soluble. When Mayer's reagent was added to the dimethyl amine hydrochloride solution at room temperature, a heavy oil separated which was readily changed to a bright yellow crystalline meal by shaking the solution and cooling it to about 15°. The crystals were filtered with suction, washed twice with small portions of cold water, and thoroughly pressed on filter paper. Further washing must be avoided in order not to decompose the compound. The appearance of red mercuric iodide indicates decomposition. The filtrate was allowed to remain in an ice box for a day and a small crop of somewhat larger crystals was obtained. This compound was found to have an extraordinary solubility in alcohol and acetone. On the other hand it was almost completely insoluble in ether and chloroform. Many futile attempts were made to recrystallize this compound by dissolving it in alcohol or acetone together with various quantities of ether or chloroform. The compound was found to melt at 122°. An analysis for mercury gave the following result:

Subs., 0.3160: HgS, 0.1173.
Calc. for $(CH_3)_2NH.HI.HgI_2$: Hg, 32.02. Found: 32.08.

The analysis was made by dissolving the weighed portion in about 20 cc. of 20% sodium sulfide solution and the mercury sulfide was precipitated by adding a slight excess of 1 : 3 sulfuric acid. After heating for 5 minutes on the steam bath, the solution was allowed to stand until the mercury sulfide had settled. The precipitate was collected in a Gooch crucible, washed with water, then with absolute alcohol, and the precipitated sulfur was extracted with carbon disulfide. The mercury sulfide was then dried at 100° and weighed.

A series of experiments was made in order to ascertain how small a quantity of dimethyl amine could be detected by Mayer's reagent, and it was found that no precipitate was obtained when less than 20 mg. of the amine per cc. was present.

Trimethyl Ammonium Mercuric Iodide, $(CH_3)_3N.HI.HgI_2$.—This compound, which was first prepared by Woodward and Alsberg, was obtained in the same manner as the previous one described above, except that it is not necessary to cool the solution because it separates at once in a crystalline form. After filtering the crystalline precipitate and pressing it on filter paper, it was dissolved in warm 95% alcohol and as the solution gradually cooled, long, slender, yellow prisms separated. It is very easy to grow crystals 5 cm. long. The recrystallized compound melted sharply at 136°, which is identical with the melting point found by Woodward and Alsberg. Since none of the crystals from alcohol had any definite end faces, some of them were dissolved in acetone, in which they are very soluble, and after adding 3 volumes of chloroform, the solution was placed in the ice box to crystallize. Beautiful needle-like prisms with well developed end faces were obtained. These crystals were employed for the crystallographic work described below. An analysis for mercury gave the following result:

Subs., 0.2832: HgS, 0.1025.
Calc. for $(CH_3)_3N.HI.HgI_2$: Hg, 31.28. Found: 31.29.

Diethyl Ammonium Mercuric Iodide, $(C_2H_5)_2NH.HI.HgI_2$.—This compound was obtained in the form of a dark yellow oil by adding Mayer's reagent to a slightly acidified solution of diethyl amine. The solution was agitated while it was being cooled to 10° and the oil solidified into a bright yellow crystalline meal. This compound like the corresponding dimethyl derivative described above was found to be exceedingly soluble in alcohol and acetone and difficultly soluble in ether and chloroform. Some of the product was dissolved in acetone, and chloroform was added in a sufficient quantity to produce a slight turbidity. A gentle current of air was directed across the surface of the solution and when it became cold, due to evaporation of some of the volatile solvent, small crystals were formed. Also some well developed crystals were obtained from the aqueous solution from which the precipitated compound had been filtered by allowing it to remain for two days in the ice box. These crystals, as well as those obtained from the acetone and chloroform solution, melted at about 114°.

A series of experiments was made in order to determine how small a quantity of diethyl amine could be detected by Mayer's reagent and it was found that no precipitate was formed when less than 4 mg. of the amine per cc. was present. An analysis gave the following results:

Subs., 0.2752: HgS, 0.0977.
Calc. for $(C_2H_5)_2NH.HI.HgI_2$: Hg, 30.60. Found: 30.69.

Triethyl Ammonium Mercuric Iodide, $(C_2H_5)_3NH.HI.HgI_2$.—For the preparation of this compound pure triethyl amine was made by L. Mikeska of this Bureau. A slight excess of Mayer's reagent was added to 4 g. of triethyl amine which had been acidified with hydrochloric acid and diluted to 30 cc. with water. The compound separated in the form of a dark yellow oil and solidified to a bright yellow crystalline powder when the solution was cooled to —10°. After filtering off the crystals, the filtrate was allowed to stand for two weeks in the ice box, but no further separation of crystals or oil took place. This compound was found to melt at 59 to 60°. However, it should be observed that when Mayer's reagent is added to a 0.01 *N* solution of the triethyl amine hydrochloride and allowed to remain in the ice box overnight, the compound separated in the form of very small crystals instead of an oil as mentioned above which is in agreement with the observations of Woodward and Alsberg, who first prepared it. These crystals melted at 77° to 78°. This compound is extremely soluble in alcohol and acetone and insoluble in chloroform and ether. Many experiments were made to recrystallize it but all were unsuccessful.

An analysis was made with the following results:

Subs., 0.3132: HgS, 0.1057.
Calc. for $(C_2H_5)_3N.HI.HgI_2$: Hg, 29.34. Found: 29.17.

Crystallography and Optical Properties.

In order to obtain means for the identification of the above described compounds, they have been submitted to detailed crystallographic and optical investigation. The crystallographic measurements were made on a Goldschmidt two-circle goniometer, and the angles are given in the coördinate system, as meridian-distance (longitude, azimuth) φ and pole-distance ρ. When an attempt was made to study the optical properties by the immersion method, the difficulty was encountered that these compounds are decomposed by all immersion liquids approaching them in refractive indices. The indices are extremely high, in the neighborhood of 1.9–2.0, and the only liquids available are solutions of metallic iodides or of arsenic sulfide in methylene iodide. Even though approximate determinations of indices were possible in some cases by working rapidly, the values obtained were too uncertain to be of any value in the practical identification of the substances, therefore, only optical properties other than indices are recorded. In fragments under the microscope the compounds all agree in being faintly yellow in color, without noticeable pleochroism; and their features agree in every case with the theory for the system indicated by the crystallographic measurements.

1 : 1-Dimethyl Ammonium Mercuric Iodide, $(CH_3)_2NH.HI.HgI_2$.—The crystals of this substance obtained on allowing the mother liquor from the first crop to stand are only about 2.5 mm. in length, but are well suited to crystallographic measurement. They have the aspect of distorted square pyramids, and are often cavernous or again built up by subparallel intergrowth of several individuals. By working over the material, 6 crystals yielding fairly good reflections were finally picked out. They proved to belong to the rare class of the monoclinic system known variously as clinohedral, domatic, or No. 3. They were oriented so that the large square face became the lower base, and the two-faced form lying most nearly at right angles to this base the front unit prism. The other prominently developed two-faced form then became the back upper unit pyramid; and the minute faces of other forms sometimes present had the positions of the upper base, the front clinopinacoid, and front lower unit pyramid. A diagram of a crystal exhibiting all these forms is shown as Fig. 1. Most of the crystals are bounded only by the 5 faces of *C*, *m* and *p*.

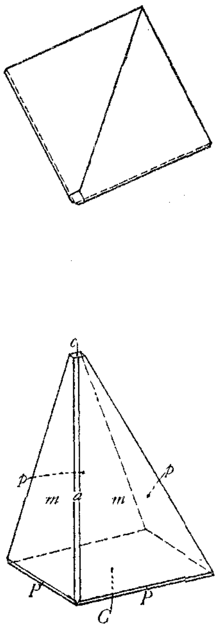

Fig. 1.

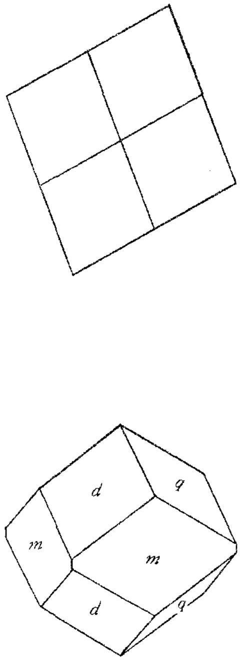

Fig. 2.

Half of the crystals were mounted with the obtuse end up, and served to measure the coördinate angles of the base and the unit prism. The balance were mounted in the opposite manner, the prism being put in polar position, and the angles of the unit pyramid were then obtainable. The results of these measurements are presented in Table I; the probable error of the angles is about ±5′, and the axial ratio accordingly certain to 5 units in the third decimal place.

TABLE I.—ANGLES OF 1 : 1-DIMETHYL AMMONIUM MERCURIC IODIDE.
Monoclinic, domatic. $a : b : c = 0.9687 : 1 : 1.3406$; $\beta = 78° 20'$.

Number, letter.		Symbols.		Description.	Angles observed.	
		Gdt.	Mill.		φ.	ρ.
1	*c*	0	001	Minute, rarely present	90° 00′	11° 40′
2	*C*	—0	$00\bar{1}$	Prominently developed	90° 00′	11° 40′
3	*a*	∞0	100	Minute line face	90° 00′	90° 00′
4	*m*	∞	110	Prominently developed	46° 30′	90° 00′
5	*p*	—11	$\bar{1}11$	Prominently developed	42° 00′	61° 00′
6	*P*	1–1	$\bar{1}1\bar{1}$	Minute, rarely present	42° 00′	61° 00′

No other compound approaching this in composition, with which comparison of crystal form might be made, appears to have been measured, although it may be noted that a cesium mercuric iodide, with a somewhat different formula type, $2CsI.3HgI_2$, has been observed to crystallize in the same class.[1] Under the microscope double refraction is extremely strong, extinction is oblique, optical class biaxial, axial angle large, and sign negative.

1 : 1-Diethyl Ammonium Mercuric Iodide, $(C_2H_5)_2NH.HI.HgI_2$.—The crystals obtained from a mixture of acetone and chloroform are nearly equidimensional, with the aspect of somewhat flattened rhombic dodecahedrons. On setting up and measuring several crystals it was found that the system is rhombic, with the 3 axes not differing greatly in length, thus peri-cubic. Flattening may occur in the direction of any of the three forms present, but after a few trials the orientation of any of the crystals can be readily found. It was decided to make the axes $a>b>c$, and on this basis the following angle table has been prepared. The probable error of the angles is ±2′, and the axial ratios certain to a few units in the fourth place.

TABLE II.—ANGLES OF 1 : 1-DIETHYL AMMONIUM MERCURIC IODIDE.
Rhombic, peri-cubic. $a : b : c = 1.1572 : 1 : 0.9102$.

Number, letter.		Symbols.		Description.	Angles observed.	
		Gdt.	Mill.		φ.	ρ.
1	*m*	∞	110	All forms	40° 50′	90° 00′
2	*q*	01	011	equally	0° 00′	42° 19′
3	*d*	10	101	developed	90° 00′	38° 11′

There appears to be no relation whatever between the crystal form of this and the dimethyl compound, but it is interesting to compare the diethyl mercuric iodide with the corresponding chloride, which was de-

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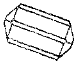
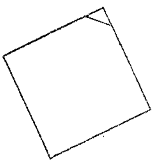
[1] Penfield, *Am. J. Sci.*, [3] 44, 311 (1892).

scribed by Topsöe[1] as rhombic pseudotetragonal (peritetragonal as here used) with $a:b:c = 0.9853:1:0.4624$. If in the present compound the a and b axes should be interchanged, and the domes taken as 021 and 201, respectively, the ratio obtained would be 0.8642 : 1 : 0.3933, which is fairly close to the value for the chloride. The habits of the two are so different, however, that no close isomorphism is to be inferred to exist between them. Under the microscope the double refraction is extreme, extinction symmetrical, optical class biaxial, axial angle very large and sign positive.





1 : 1-Trimethyl Ammonium Mercuric Iodide, $(CH_3)_3N.HI.HgI_2$.—The crystals obtained from alcohol consist of rods grouped into flat clusters without definite terminal planes, but from a mixture of 3 parts chloroform and one of acetone terminated needles fairly well adapted to crystallographic measurement were obtained. The results are presented in Table III, the measurements having, because of the minute size of the crystals, a probable error of ±5′, so that the axial ratio is not certain beyond the third place. The prism angle deviates but a few minutes from 60°, so the substance is markedly perihexagonal.

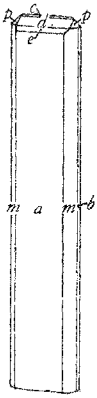


Fig. 3.

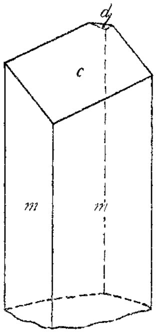


Fig. 4.

TABLE III.—ANGLES OF 1 : 1-TRIMETHYL AMMONIUM MERCURIC IODIDE.
Rhombic, perihexagonal. $a:b:c = 1.7262:1:0.9569$.

Number,	letter.	Symbols. Gdt.	Mill.	Description.	Angles observed. φ.	ρ.
1	c	0	001	Very narrow but definite	. . .	0° 00′
2	b	0 ∞	010	Narrow but well marked	0° 00′	90° 00′
3	a	∞ 0	100	Prominent	90° 00′	90° 00′
4	m	∞	110	The dominant form	30° 05′	90° 00′
5	d	10	101	The principal termination	90° 00′	29° 00′
6	e	20	201	A small terminal form; ρ calcd. 47° 57′	90° 00′	48° ±
7	p	1	111	Minute but definite; ρ calcd. 47° 53′	30° ±	48° ±

The chloride corresponding to this was measured by Topsöe[2] and found to be monoclinic, pseudo or perihexagonal with $a:b:c = 1.6165:1:1.6538$ and $\beta = 97°\ 18'$. If the vertical axis of the iodide is doubled, the corresponding values for it are $1.7262:1:1.9138$ and $\beta = 90°$. A cer-

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[1] *Oversigt Danske, Videnskabernes Selskabs, Copenhagen,* 1882; *Z. Kryst. Mineralog.,* 8, 246 (1883); and Groth's *Chem. Kryst.,* 1, 371 (1906).

[2] *Loc. cit.*

tain degree of similarity, though no definite isomorphism, is thus shown between the chloride and iodide compounds. Under the microscope double refraction is extremely strong, extinction is parallel, optical class biaxial, axial angle large, and sign negative.

1 : 1-Triethyl Ammonium Iodide, $(C_2H_5)_3N.HI.HgI_2$.—In spite of repeated trials it was found impossible to obtain well developed crystals of this compound. In the crystalline mass obtained by solidification of the oil first obtained, however, there could be found occasional individuals with definite though rough bounding planes. These yielded measurements sufficient to show the system to be monoclinic, peritetragonal although the angles were in no case measurably closer than ±30′, and the axial ratio is accordingly uncertain beyond the second place. Crystals earlier prepared by Mr. Woodward were too rounded for satisfactory measurement, but appeared to be about the same as those here described, except for tabular development on a pinacoid (*a* or *b*).

TABLE IV.—ANGLES OF 1 : 1-TRIETHYL AMMONIUM MERCURIC IODIDE.

Monoclinic, peritetragonal. $a : b : c = 1.15 : 1 : 1.08$; $\beta = 62° 30'$.

Number, letter.		Symbols.		Description.	Angles observed.	
		Gdt.	Mill.		φ.	ρ.
1	*c*	0	001	Chief terminations	90° 00′	27° 30′
2	*m*	∞	110	Dominant form	44° 30′	90° 00′
3	*d*	—10	107	Minute	90° 00′	28° 30′

The chloride corresponding to this does not appear to have been prepared, but it is curious to note that the form of the triethyl iodide is similar to that of the diethyl chloride compound. The latter was described as rhombic, with $a : b : c = 0.9853 : 1 : 0.4624$ but with only one face of the brachydome usually developed. If the iodide should be so oriented that the forms here taken as the base and orthodome together make up a brachydome (distorted), the axial values would be $0.98 : 1 : 0.53$. Too much significance should not, however, be attached to this similarity. Under the microscope, the double refraction is extreme, extinction oblique, class biaxial, and axial angle large.

1 : 1-Tetramethyl Ammonium Mercuric Iodide, $(CH_3)_4NI.HgI_2$.—Crystals of this substance prepared by Mr. Woodward several years ago, and preserved in the Bureau, were found to be minute needles, closely resembling the trimethyl compound, though differing in important respects. The system is rhombic, but the angles are perihexagonal, as in the preceding. In the present case, however, the crystals are oriented so that the front-back axis *a* is shorter than *b*, to bring out the relationship with the corresponding chloride. The angles are not measurably closer than ±30′, so that the axial ratio is uncertain beyond the second place.

TABLE V.—ANGLES OF 1 : 1-TETRAMETHYL AMMONIUM MERCURIC IODIDE.

Rhombic, perihexagonal. $a : b : c = 0.59 : 1 : 0.52$.

Number, letter.		Symbols.		Description.	Angles observed.	
		Gdt.	Mill.		φ.	ρ.
1	*b*	0 ∞	010	Distinct	0° 00′	90° 00′
2	*a*	∞ 0	100	Distinct	90° 00′	90° 00′
3	*m*	∞	110	Dominant prism form	59° 30′	90° 00′
4	*d*	10	101	Distinct	90° 00′	41° 30′
5	*p*	1	111	Chief termination	59° 30′	45° 30′

The tetramethyl ammonium mercuric chloride, as described by Topsöe[1] is monoclinic, but perihexagonal, its axial values not diverging much from those of the iodide: $a : b : c = 0.5657 : 1 : 0.4813$ and $\beta = 93° 33'$ as against $0.59 : 1 : 0.52$ and 90° here obtained. The two are thus isomorphous to the extent that their underlying structures are probably closely similar. The tetramethyl iodide is also close to the trimethyl iodide described previously; if the orientation is changed so that the long horizontal axis is *a*, then the axial ratio would become: 1.69 : 1 : 0.88, as against 1.73 : 1 : 0.96 for the trimethyl compound. Isomorphism is again shown here. Under the microscope double refraction is extreme, extinction is parallel, and class is biaxial, the acute bisectrix apparently running lengthwise of the needles, so that interference figures are difficult to obtain.

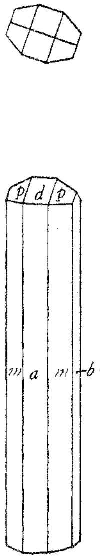

Fig. 5.

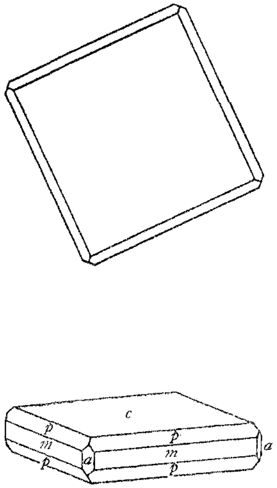

Fig. 6.

1:1-Tetraethyl Ammonium Mercuric Iodide, $(C_2H_5)_4NI.HgI_2$.—The specimen of this substance prepared by Mr. Woodward, and preserved in the Bureau of Chemistry collections, proved to consist of crystals of two habits. The bulk of the material is in tabular crystals, about 0.5 mm. in diameter (Fig. 6), but scattered through these there are occasional prismatic crystals one mm. or more long, but less than 0.2 mm. thick. The angles on these two types of crystals are identical, and they evidently merely represent two crops of the same substance. The system proved to be tetragonal, with a positive axial ratio, as shown in the table, the probable error of the measurements ±3′ rendering the value of the axial ratio certain to about one unit in the third place.

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[1] *Loc. cit.*

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.