CHLORINE DERIVATIVES OF M-CRESOL

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Philip Stanley Chen

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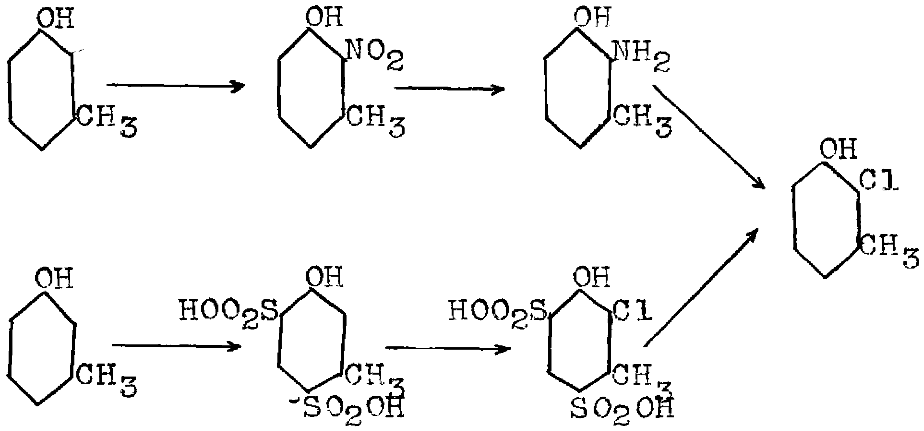
Introduction

This study had as its objective a survey of those chloro derivatives of m-cresol in which the chlorine atoms are ortho or para to the hydroxyl group. Information concerning these compounds is meager and often conflicting.

MONO CHLORO-M-CRESOLS

Gibson[1] describes 2-chloro-m-cresol, as prepared from its methyl ether, as massive ill-defined transparent crystals melting at 55-56°. When prepared by the following sequences it melted at 49-50°, its crystalline form being clusters of tetragons. ?



The preparation and properties of 4-chloro-m-cresol have been described by several investigators. A brief discussion of their work is given below:

The earliest work done on the chlorination of m-cresol was by Biedermann[2], who by chlorinating m-cresol

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(1) Gibson, J. Chem. Soc., 1926, 1424-8.
(2) Biedermann, Ber., 6, 325 (1873).

in the state of vapor obtained 4-chloro-m-cresol melting at 56°. — B.pt 235°

The preparation of 4-chloro-m-cresol by chlorinating an exceedingly cold solution of m-cresol in glacial acetic acid was described in a patent taken out by Kalle and Company[3]. The melting point of 66° given for 4-chloro m-creol has not been supported by experiment data.

The 4-chloro-m-cresol was later prepared by Peratoner and Condorelli[4] from m-cresol by the action of sulfuryl chloride. They gave the melting point as 52-53°.

Chlorination of a technical mixture of m- and p-cresols was tried by Raschig[5], who found that the action of sulfuryl chloride or chlorine on this mixture of cresols is selective. If only sufficient chlorine is introduced to react with the m-cresol this alone is attacked, and on subsequent distillation the p-cresol will pass over at 200° followed by pure 4-chloro-m-cresol.

The 4-chloro-m-cresol was also obtained by Liebrecht[6] from the mixed cresols by a modified method. The 4-chloro-m-cresol is separated from the isomers and the simultaneously produced o-chloro-p-cresol by sulfonating the chlorinated mixed cresols. While 4-chloro-m-cresol is converted into the sulfonic acid, o-chloro-p-cresol remains unchanged and can therefore be readily separated.

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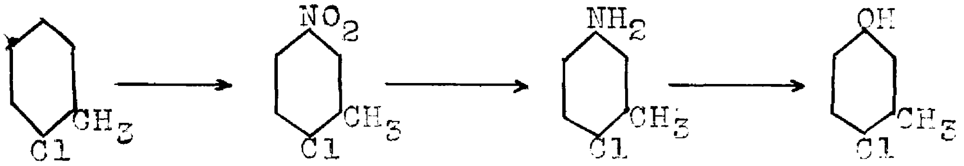
(3) Kalle and Co., D. R. P. 90847; 93694.
(4) Peratoner and Condorelli, Gazz. chim. ital., 28 I, 213 (1898).
(5) Raschig, D. R. P. 232071.
(6) Liebrecht, D. R. P. 233118.

Gibson[1] obtained a mixture of three mono chloro-m-cresols by treating m-cresol in carbon tetrachloride with a saturated solution of chlorine in the same solvent. 4-chloro-m-cresol distilled over at 231-233° while the 2- and the 6- isomers distilled over at 196-197°. The benzoyl and p-toluene sulfonyl esters of 4-chloro-m-cresol melted at 86° and 98° respectively.

Chlorination of m-cresol with a mixture of both sulfuryl chloride and chlorine was described in a recent patent taken out by Laschinger[7]. M-cresol is treated with a mixture containing sulfurl chloride and a substantial amount of uncombined chlorine, the total amount of chlorine being substantially no greater than the amount required to convert the m-cresol into 4-chloro-m-cresol.

The following sequence of reactions ~~as~~ which we employed gave 4-chloro-m-cresol as clusters of very fine needles melting at 55.5°.



The first mention of 6-chloro-m-cresol was made by Raschig[5], who obtained it along with the 4-chloro-m-cresol in the chlorination of m-cresol by the action of sulfuryl chloride. He was unable to isolate it in the

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(7) Laschinger, U. S. 1847566.

solid form, and describes it as a colorless liquid boiling at 197° and with a camphor-like odor.

As has been mentioned before, 6-chloro-m-cresol was one of the three mono chloro-m-cresols formed when m-cresol in carbon tetrachloride was treated with a saturated solution of chlorine in the same solvent as described by Gibson[1]. The benzoyl ester prepared from it melted at 31° (from alcohol) and 40° (from petroleum ether), and the p-toluene sulfonyl ester at 98°.

The preparation of 6-chloro-m-cresol by diazotization has been described by Hodgson and Moore[8] who prepared it from 4-chloro-m-nitrotoluene by first reducing with tin and hydrochloric acid and then subjecting to diazotization and hydrolysis. The 6-chloro-m-cresol melted at 45°.

A method for preparing 6-chloro-m-cresol from o-dichloro benzene was described by Kraay[9]. It was prepared by substituting a methyl group in the para position of o-dichloro benzene and then treating the resulting product with sodium methoxide in methyl alcohol. The formation of 6-chloro-m-cresol was also checked by preparing it from 3-amino-4-chlorotoluene.

The preparation of 6-chloro-m-cresol in the present work was accomplished by the following sequences. It melted at 46°.

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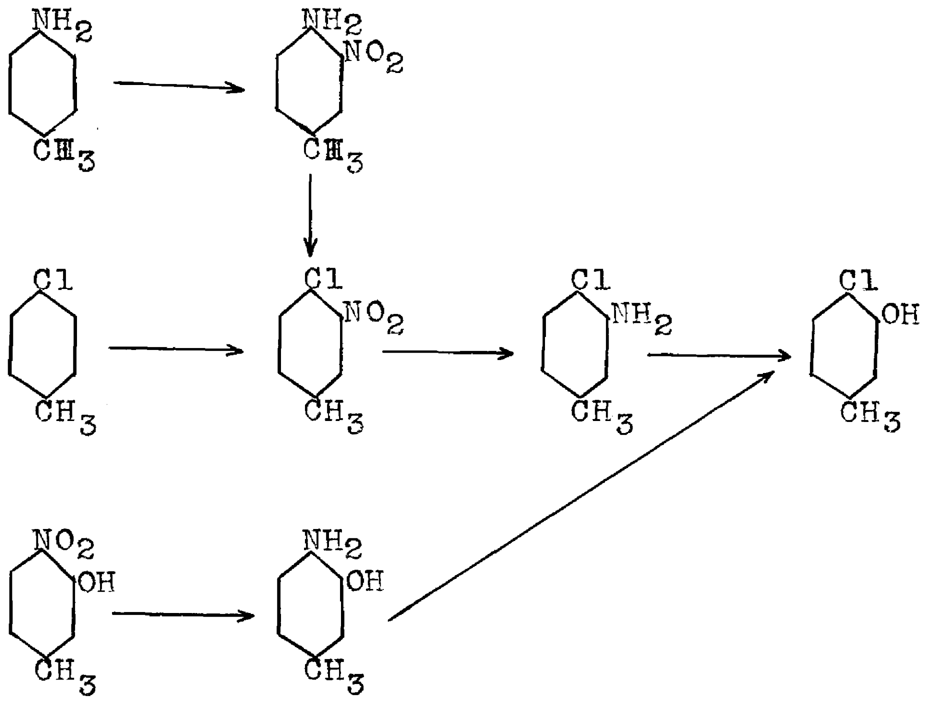
(8) Hodgson and Moore, J. Chem. Soc., 1926, 2036-40.
(9) Kraay, Rec. trav. chim., 49, 1082-92 (1930).



Chlorination of m-cresol in chloroform at 0° gave a mixture of the three isomers. These were separated by fractional distillation and seeding. As seen from above, chloroform has never been used as a solvent in the chlorination of m-cresol.

DICHLORO-M-CRESOLS

The properties of 4,6-dichloro-m-cresol which we prepared by four different methods did not agree with those described in the literature. v. Walther and Zipper[10], who prepared it by passing a calculated amount of chlorine into a warm solution of 4-chloro-m-cresol in aqueous sodium hydrogen carbonate, gave it a melting point of 45-46°; while Tanaka and Morikawa[11], who obtained it by

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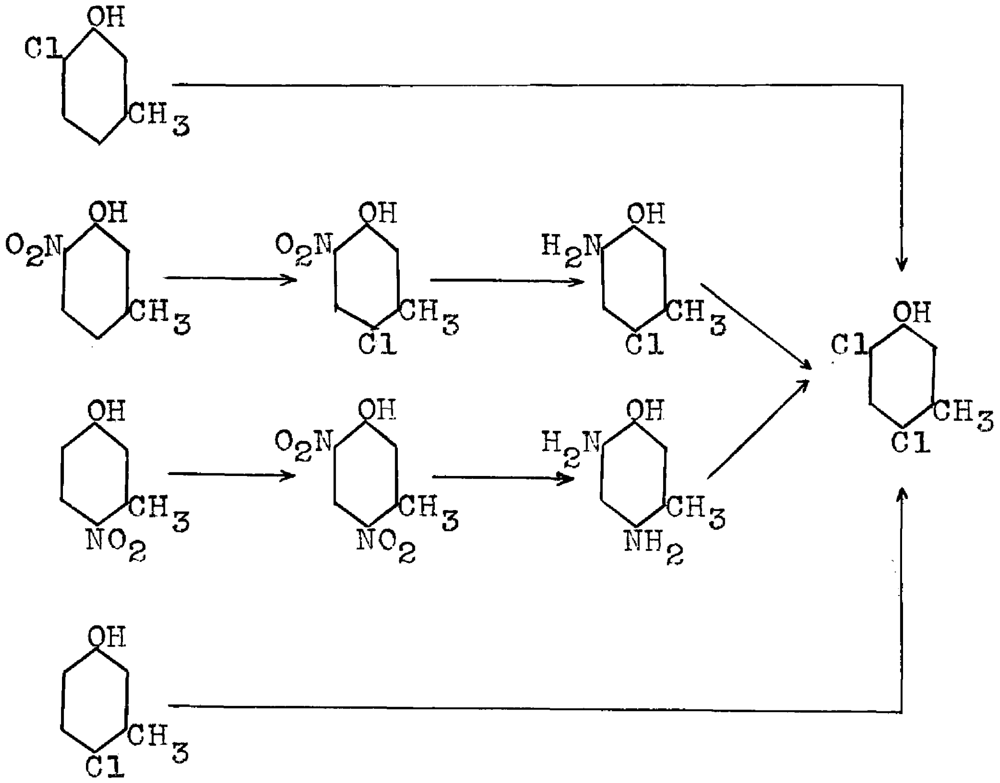
(10) v. Walther and Zipper, J. prakt. chem., (2) 91, 374 (1864).

(11) Tanaka and Morikawa, J. Chem. Soc. Japan, 51, 275-7 (1930).

chlorinating m-cresol in barbon tetrachloride in an ice bath, reported the melting point as 58°. We obtained a constant melting point of 71.5-72.5° and a boiling point of 235-236°. The four methods we used for the preparation of 4,6-dichloro-m-cresol are represented by the following sequences:



The preparation of 2,4-dichloro-m-cresol has also been reported. Tanaka and Morikawa[11] obtained it by chlorinating m-cresol in carbon tetrachloride at room temperature and gave its melting point as 44°. Datta and Mitter[12], who prepared it by replacing the corresponding sulfonic acid groups in the m-cresol with chlorine, gave

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(12) Datta and Mitter, This Journal, 41, 2033 (1919).

it a melting point of 45° and state that their compound is identical with the dichloro-m-cresol prepared by Claus and Schweitzer[13] who gave its melting point as 46°. As was pointed out by Crowther and McCombie[14], and also supported by the work of Raiford[15], Claus and Schweitzer's dicholoro compound was most probably the 2,4,6-trichloro-m-cresol of the same melting point. The same might be said of the 2,4-dichloro-m-cresol prepared by Tanaka and Datta and their coworkers. The 2,4-dichloro-m-cresol we prepared by careful chlorination of a cold chloroform solution of 2-chloro-m-cresol or 4-chloro-m-cresol boiled at 234° and melted at 58°.

Attention might also be called to the fact that in Datta and Mitter's work of converting the disulfonic acid into the corresponding dichloro compound, chlorine was passed in to "saturation" and the resulting product not analyzed. Furthermore, they state that 2,4-dichloro-m-cresol was also the sole product of chlorinating m-cresol-p-sulfonic acid. It is hard to see why the second atom of chlorine should enter the 2-position more readily than the 6-position, while the reverse is more probable.

A comparison of melting points might indicate that the 4,6-dichloro-m-cresol prepared by v. Walther and Zipper was also the trichloro-m-cresol, while on the other hand the 4,6-dichloro-m-cresol prepared by Tanaka

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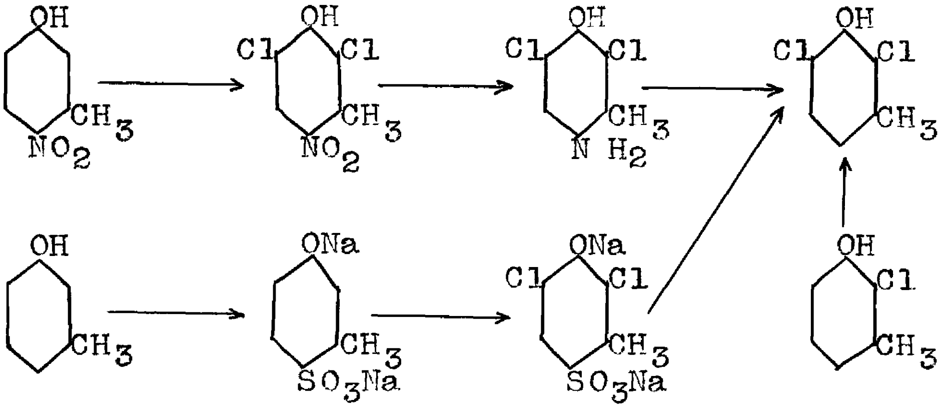
(13) Claus and Schweitzer, Ber., 19, 930 (1886).
(14) Crowther and McCombie, J. Chem. Soc., 103, 545 (1913).
(15) Raiford, Am. Chem. J., 46, 424 (1911).

and Morikawa might be the 2,4-dichloro-m-cresol.

The literature gives no description of 2,6-dichloro-m-crespl[13]. As prepared by the following sequences it boiled at 240.5-242.5° and crystallized from petroleum ether in prisms melting at 27°.



Chlorination of a cold chloroform solution of m-cresol with two mols of chlorine gave a mixture of the three dichloro-m-cresols. From this, 4,6-dichloro-m-cresol and 2,4-dichloro-m-cresol were separated by careful fractionation, cooling, and seeding. The fraction boiling at 240.5-242.5° analyzed for two atoms of chlorine and gave 2,4,6-trichloro-m-cresol when further chlorinated. We believe it consisted of 2,6-dichloro-m-cresol which failted to crystallize because of the presence of small amounts of its isomers.

Each dichloro-m-cresol gave upon further chlorination in cold chloroform the same 2,4,6-trichloro-m-cresol (fine prisms, m.p. 46°). This was also the only product formed when m-cresol was chlorinated in chloroform with three mols of chlorine.

Experimental

The chloro-m-cresols described below were purified by recrystallization from petroleum ether and their esters from ethyl alcohol. All cases of identity were established by the method of mixed melting points.

MONO CHLORO-M-CRESOLS

2-Chloro-M-Cresol

From 2-nitro-m-cresol: 2-Nitro-m-cresol was prepared from m-cresol by nitration in fuming sulfuric acid in the cold and reduced to the corresponding amino compound according to Hodgson and Beard[16]. Forty-four grams of 2-amino-m-cresol was treated with hydrochloric acid, diazotized, and converted into the corresponding chlorine compound by the Sandmeyer method as modified by Marvel and McAlvain for the preparation of o- and p-chlorotoluene[17]. The 2-chloro-m-cresol thus obtained boiled at 198-199° and melted at 49-50°. Yield 32 g.

Anal. Calcd. for C_7H_7OCl: Cl, 24.91. Found: Cl, 24.77.

By chlorination in fuming sulfuric acid: The method here used is similar to the one given above for the preparation of 2-nitro-m-cresol, except that in the place of nitric aicd, one mol equivalent of chlorine[18]

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(16) Hodgson and Beard, J. Chem. Soc., 127, 498 (1925).
(17) "Organic Syntheses", Wiley and Sons, Vol. III, 33.
(18) Houben, "Die Methoden der organischen Chemie", Leipzig, 1924, Vol. III, 799.

was passed in the fuming sulfuric acid solution. Chlorine was not readily absorbed. When the resulting oil separated from the distillate was fractionated five times, it gave a small fraction boiling at 198-199° and a larger fraction at 199-205° which consisted mostly of the unreacted m-cresol. The 198-199° fraction was set in the ice box and seeded with 2-chloro-m-cresol prepared from 2-nitro-m-cresol. The crystals that separated out from the oil were suction filtered and recrystallized from petroleum ether. The purified product melted at 49-50°.

By Chlorination of the sodium disulfonate: One mol of m-cresol was heated for three hours with 1.5 mols of concentrated sulfuric acid. The mixture was cooled and made alkaline with 5 mols of sodium hydroxide in 500 cc. of water. It was then chlorinated with two mols of chlorine generated from the calculated amount of potassium permanganate and concentrated hydrochloric acid[18], while the solution was stirred and its temperature maintained at 40-50°. The alkaline reaction mixture was distilled with steam, the flask being set in an oil bath kepl at 150°. When no more oil distilled over, steam distillation was stopped and the content in the flask evaporated to a thick paste. It was allowed to cool and then acidified with 600 cc. of concentrated sulfuric acid. Steam was again passed in and the oil bath raised to 200-210°. The oil was separated from the distillate and fractionated. It gave after seven distillations a

15 g. fraction boiling at 195-200° and a larger fraction (22 g.) at 235-245° which consisted of 2,6-dichloro-m-cresol to be described later. The 195-200° fraction was set in the ice box and seeded with 2-chloro-m-cresol. The crystals that separated out were filtered at the pump and purified, m. p. 49-50°.

4-Chloro-M-Cresol

From o-chlorotoluene: O-chlorotoluene prepared according to Marvel and McAlvain's method[17] was nitrated according to Goldschmidt and Honig[19]. The resulting nitro compound was reduced with tin and hydrochloric acid. After heating for half an hour to complete the reduction, the mixture was cooled, made alkaline with sodium hydroxide, and steam distilled. The amine which solidified in the distillate was recrystallized from ligroin, m. p. 83.5°[20].

Eleven grams of the 3-amino-6-chlorotluene was treated with hydrochloric acid and diazotized in the usual manner. The diazotized solution was heated on a steam bath for half an hour during which time a dark oil separated on top of the liquid. After steam distillation, the distillate was salted out and extracted with ether. Five and one half grams of 4-chloro-m-cresol distilled over at 228-233°. Upon purification it came down in clusters of fine needles melting at 55.5°.

Anal. Calcd. for C_7H_7OCl: Cl, 24.91. Found: Cl, 24.74.

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(19) Goldschmidt and Honig, Ber., 19, 2440 (1886).
(20) Bamberger, Ber., 35, 3701 (1902).

6-Chloro-M-Cresol

From p-toluidine: The p-toluidine was acylated, nitrated, and hydrolyzed according to the method of Gattermann[21]. The hydrochloride was diazotized and poured into a cold solution of cuprous chloride prepared by Marvel and McAlvain's method[17]. After stirring for one hour, the mixture was steam distilled. The distillate was extracted with ether. The 3-nitro-4-chlorotoluene distilled over at 258-262°[22]. When reduced with tin and hydrochloric acid it gave the amine boiling at 228-232°[22].

The diazotization and hydrolysis of 3-amino-4-chlorotoluene was accomplished under the same conditions used in the preparation of 4-chloro-m-cresol from 3-amino-6-chlorotoluene. The 6-chloro-m-cresol came down in rhombohedrons melting at 46°.

Anal: Calcd. for C_7H_7OCl: Cl, 24.91. Found: Cl, 24.69.

From -p-chlorotoluene: The p-chlorotoluene[17] was nitrated according to the method of Goldschmidt and Honig[19] and the isomeric nitro chlorotoluenes were separated by repeated distillation and filtration. The liquid 3-nitro-4-chlorotoluene was reduced, diazotized, and hydrolyzed as in the preseeding experiment. The 6-chloro-m-cresol melted sharply at 46° and was checked by ester formation.

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(21) Gattermann, Ber., 18, 1483 (1885).
(22) Gattermann and Kaiser, Ber., 18, 2600 (1885).

From 6-nitro-m-cresol: Thirty one grams of 6-nitro-m-cresol prepared by Staedal and Kobb's method[23] was reduced with stannous chloride according to the method given by Raiford[24]. The hydrochloride was filtered and recrystallized to free from the tin. 6-Chloro-m-cresol was prepared from it by the Sandmeyer method as described above. 10 g. were obtained, boiling at 195-200° and melting at 46°.

Mono Chloro-M-Cresols by Direct Chlorination

One mol of m-cresol chlorinated in 400 cc. of chloroform at 0° with one mol of chlorine[18] gave after six distillations 33 g. boiling at 196-199°; 20 g. at 199-230°; and 70 g. at 230-238°. The 199-230° fraction consists mostly of the unreacted m-cresol. The 230-238° fraction gave upon purification 32 g. of 4-chloro-m-cresol in fine needles, m. p. 55.5°.

The 196-199° fraction gave upon further distillation 18.5 g. boiling at 197-198°. When cooled to -10° and seeded with 6-chloro-m-cresol prepared from p-chlorotoluene, it partially solidified. The crystals were filtered at once by suction. The purified product melted at 46°.

The oil that remained after the complete removal of 6-chloro-m-cresol was again chilled and seeded with 2-chloro-m-cresol prepared from 2-nitro-m-cresol. The crystals which separated out were filtered by suction.

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(23) Staedal and Kobb, Ann., 259, 210-211 (1890).
(24) Raiford, Am. Chem. J., 46, 419 (1911).

They recrystallized in clusters of tetragonal crystals, m. p. 49-50°.

DICHLORO-M-CRESOLS

4,6-Dichloro-M-Cresol

From 6-nitro-m-cresol: Chlorination of 6-nitro-m-cresol in cold chloroform or acetic acid solution with two mols of chlorine gave only the 4-chloro-6-nitro-m-cresol (m. p. 131-133°)[25]. This was reduced with stannous chloride and hydrochloric acid[24]. The resulting hydrochloride was diazotized and treated with a cold solution of cuprous chloride[17]. Upon steam distillation, 4,6-dichloro-m-cresol separated out from the distillate as an oil. When separated and purified, it melted at 71.5-72.5°. Its p-toluene sulfonate melted at 104-105°.

Anal. Calcd. for $C_7H_6OCl_2$: Cl, 40.11. Found: Cl, 40.39.

From 4,6-dinitro-m-cresol: The 4,6-dinitro-m-cresol was obtained from 4-nitro-m-cresol[23] by nitration in acetic acid solution according to Gibbs and Robertson[26]. After standing overnight, the reaction mixture was poured into water and the oil that separated out was purified by distillation under vacuum. The product was separated from unchanged 4-nitro-m-cresol by fractional crystallization from benzene. Further recrystallization from dilute

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(25) Kenner, Tod, and Witham, J. Chem. Soc., 127, 2349 (1925); v. Walther and Zipper, J. prakt. chem., (2) 91, 411 (1864).

(26) Gibbs and Robertson, J. Chem. Soc., 105, 1889 (1914).

acetic acid gave a product melting at 71°[27]. After reduction with stannous chloride and hydrochloric acid[24], both amino groups were diazotized and replaced with chlorine by the Sandmeyer method[17]. This method gave a smaller yield of 4,6-dichloro-m-cresol than the preceding method.

2,6-Dichloro-M-Cresol

From 4-nitro-m-cresol: The 4-nitro-m-cresol prepared by the method of Staedal and Kobb[23] was chlorinated with two mols of chlorine in glacial acetic acid. The crystals that separated out were filtered off and the filtrate poured into a large quantity of water from which another crop of crystals was obtained. Recrystallized from benzene both crops melted at 143° with decomposition[28]. The 2,6-dichloro-4-nitro-m-cresol was reduced with stannous chloride in the usual manner. An attempt to liberate the amine from the hydrochloride by means of ammonium carbonate was not successful.

Eight grams of the hydrochloride was diazotized and the amino group replaced with hydrogen by means of an alkaline solution of stannous chloride[29]. The resulting 2,6-dichloro-m-cresol boiled at 240.5-242.5° and melted at 27°. Yield 6 g.

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(27) Will, Ber., 47, 712 (1914); Sane and Joshi, J. Indian Chem. Soc., 5, 299-301 (1928).
(28) Raiford, This Journal, 36, 675 (1914). (J.A.C.S.)
(29) Houben, "Die Methoden der organischen Chemie", Leipzig, 1924, Vol. IV, 612.

Anal. Calcd. for $C_7H_6OCl_2$: Cl, 40.11. Found: Cl, 40.04.

By Chlorination of the sodium sulfonate: The fraction boiling at 235-245° obtained in the preparation of 2-chloro-m-cresol (page 10) was repeatedly fractionated. Most of it came over at 240.5-242.5°. This was shown by analysis, ester formation, and chlorination to 2,4,6-trichloro-m-cresol to be identical with the 2,6-dichloro-m-cresol prepared from 4-nitro-m-cresol.

2,4-Dichloro-M-Cresol

This compound as prepared by the chlorination of either 2-chloro-m-cresol or 4-chloro-m-cresol (see below) came down in prismatic plates, melting at 58° and boiling at 234°.

Anal. Calcd. for $C_7H_6OCl_2$: Cl, 40.11. Found: Cl, 40.20.

Dichloro-M-Cresols by Direct Chlorination

Chlorination of one mol of m-cresol in chloroform solution at 0° with two mols of chlorine gave a mixture which was separated by five distillations into the following fractions:

233-235°	20 g.
235-237°	82 g.
237-240°	27 g.
240-250°	13 g.

The crystals that separated out from the first three fractions upon standing were filtered at the pump and purified. A yield of 60° g . of pure 4,6-dichloro-m-cresol was obtained.

Crystals obtained from the mother liquor consisted of a mixture of both the 4,6- and the 2,4-dichloro-m-cresols, the separation of which could be effected by dissolving in excess of petroleum ether and allowing to crystallize slowly in the ice box. Under these conditions the less soluble 2,4-dichloro-m-cresol was deposited around the edge while the 4,6- isomer was deposited at the bottom.

More of the 2,4-dichloro compound was separated from the residual oil from which the crude 4,6-dichloro-m-cresol had been filtered, when this was allowed to stand several days at -10°. The total yield of 2,4-dichloro-m-cresol was about 20 g.

After all possible 2,4-dichloro-m-cresol had been chilled out, the residual oil from the first three fractions was combined with the fourth fraction, which gave nocrystals, and fractionated. A portion was collected at 240.5-242.5° which corresponds to the boiling point of 2,6-dichloro-m-cresol. While we were unable to isolate any of this compound (the 2,6-dichloro-m-cresol melts at 27°) or to prepare a sharp melting ester from it, it did show two atoms of chlorine upon analysis and was changed to 2,4,6-trichloro-m-cresol when further chlorinated.

Chlorination of Mono Chloro-M-Cresols

Chlorination of each of the mono chloro-m-cresols in cold chloroform with one mol of chlorine gave two dichloro-m-cresols as follows:

2-Chloro-m-cresol gave 2,4-dichloro-m-cresol and 2,6-dichloro-m-cresol.
4-Chloro-m-cresol gave 2,4-dichloro-m-cresol and 4,6-dichloro-m-cresol.
6-Chloro-m-cresol gave 4,6-dichloro-m-cresol and a small amount of oil which was doubtless the 2,6- isomer.

The 2,4- and 4,6-dichloro-m-cresols were isolated in the pure state. The 2,6- isomer was checked by formation of the p-toluene sulfonic ester and further chlorination to 2,4,6-trichloro-m-cresol.

Chlorination of the Dichloro-M-Cresols

All three dichloro-m-cresols gave almost theoretical yield of 2,4,6-trichloro-m-cresol (m. p. 46°)[14] when chlorinated in chloroform with one mol of chlorine. This complete chlorination may be effected by chlorination of m-cresol itself in chloroform with three mols of chlorine.

Esterification

The following esters of the various chloro-m-cresols were prepared according to the method of Einhorn and Holland[30].

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(30) Einhorn and Holland, Ann., 301, 95 (1898).

Table 1

Benzoyl Esters

Compound, Benzoyl ester of m-cresol	Crystalline form	M. p. °C	Chlorine	
			Calcd.	Found
2-chloro	clusters of prisms	55-56	14.38	13.47
4-chloro	needle-like plates	86[1]	14.38	14.39
6-chloro	prisms	38[1]	14.38	14.39
2,4-dichloro	fine plates	78-78.5	25.24	24.74
2,6-dichloro	clusters of small prismatic plates	90.5	25.24	25.57
4,6-dichloro	mats of very fine needles	57.5	25.24	25.27
2,4,6-trichloro	very fine prismatic plates	53	33.73	34.00

Table 2

Benzene Sulfunyl Esters

Compound, benzene sulfonyl ester of m-cresol	Crystalline form	M. p. °C	Chlorine	
			Calcd.	Found
2-chloro	prismatic plates	58-58.5	12.74	12.11
4-chloro	clusters of large needle-like plates	66	12.74	12.50
6-chloro	fine prisms	99	12.74	12.53
2,4-dichloro	fine needle-like plates	69.5	22.38	22.73
2,6-dichloro	thin lustrous plates	70	22.38	22.82
4,6-dichloro	clusters of elongated prisms	86	22.38	22.01
2,4,6-trichloro	prismatic plates	121	30.28	30.21

Table 3

P-toluene Sulfonyl Esters

Compound, p-toluene sulfonylester of m-cresol	Crystalline form	M. p. °C	Chlorine	
			Calcd.	Found
2-chloro	fine lustrous prisms	96	12.13	11.75
4-chloro	clusters of needle-like plates	98[1]	12.13	12.69
6-chloro	prismatic plates	93-94[1]	12.13	11.92
2,4-dichloro	very shiny plates	100-101	21.43	21.72
2,6-dichloro	small prisms	92-92.5	21.43	21.21
4,6-dichloro	very fine needles	104-105	21.43	20.69
2,4,6-trichloro	prismatic plates	92-93	29.12	29.24

Summary

1. Chlorination of m-cresol in chloroform with one mol of chlorine gave rise to 2-, 4-, and 6-chloro-m-cresols.

2. Chlorination of m-cresol in chloroform with two mols of chlorine gave rise to 2,4-, 2,6-, and 4,6-dichloro-m-cresols.

3. The structures of the chloro-m-cresols were proven by a number of methods.

4. The benzoyl, benzene sulfonyl, and p-toluene sulfonyl esters of all chloro-m-cresols were prepared.