derivatives have been prepared and characterized. Bromination of the acid or its chloride yielded the corresponding α-bromo compounds. Several derivatives of α-bromo-*tert*-butylacetic acid have been prepared. No rearranged products were observed.

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The Chloro Derivatives of *m*-Cresol

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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 contradictory.

2-Chloro-*m*-cresol.—Gibson[2] describes 2-chloro-*m*-cresol, prepared from its methyl ether, as massive, ill-defined, transparent crystals melting at 55–56°. When prepared from 2-nitro-*m*-cresol or from *m*-cresol by chlorination of the disulfonic acid, it formed clusters of fragile tetragonal crystals which melted at 49–50°.

The 2-nitro-*m*-cresol was prepared from *m*-cresol by nitration in fuming sulfuric acid[3] and reduced to the corresponding amino compound by means of sodium hydrosulfite. Forty-four grams of 2-amino-*m*-cresol yielded, upon diazotization and treatment with cuprous chloride (using the technique developed by Marvel and McElvain for the preparation of *o*- and *p*-chlorotoluene[4]), 32 g. of 2-chloro-*m*-cresol boiling at 198–199°.

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

The clorination of *m*-cresol in fuming sulfuric acid was effected by a method similar to the one used for the preparation of 2-nitro-*m*-cresol[3] except that, in the place of nitric acid, one mole equivalent of chlorine[5] was passed into the acid solution. Chlorine was not readily absorbed. After hydrolysis at 200°, the resulting oil which 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.

Chlorination of the disulfonic acid of *m*-cresol (prepared by sulfonation with concd. sulfuric acid) in the presence of five moles of sodium hydroxide and subsequent hydrolysis in acid solution at 200° gave 2-chloro-*m*-cresol and a fraction boiling at 235–245° which consisted of 2,6-dichloro-*m*-cresol to be described later.

4-Chloro-*m*-cresol.—The preparation of 4-chloro-*m*-cresol from *m*-cresol by direct chlorination in the vapor state,[6] or in solution,[2,7] or by

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree.

[2] Gibson, *J. Chem. Soc.*, 1424–1428 (1926).

[3] Hodgson and Beard, *J. Chem. Soc.*, **127**, 498 (1925).

[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 33.

[5] Houben, "Die Methoden der organischen Chemie," Vol. III, p. 799.

[6] Biedermann, *Ber.*, **6**, 325 (1873).

[7] Kalle and Co., German Patents 90,847, 93,694.

treatment of the cresol with sulfuryl chlorine[8,9,10] or a mixture[11] of sulfuryl chloride and chlorine is described in the literature. The melting point is given as 56, 66, 52 and 57°; the boiling point as 240, 231 and 234°. The proof of structure was effected by Gibson[2] by oxidation of the methyl ether prepared from 4-chloro-*m*-cresol which he obtained by fractioning a mixture of the three monochloro-*m*-cresols obtained by chlorination in carbon tetrachloride.

We have prepared pure 4-chloro-*m*-cresol by the following sequence.

Carefully purified *o*-chlorotoluene was nitrated according to Goldschmidt and Hönig[12] and the 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°.[13] Eleven grams of the 3-amino-6-chlorotoluene 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 231–233°. It crystallized in clusters of very fine needles melting at 55.5°.

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

6-Chloro-*m*-cresol.—Raschig[9] obtained this compound together with 4-chloro-*m*-cresol by chlorination of *m*-cresol with sulfuryl chloride. He was unable to isolate it in solid form and described it as colorless liquid with a camphor-like odor which boiled at 197°. It was prepared by Hodgson and Moore[14] from 4-chloro-*m*-nitrotoluene by reduction, diazotization and hydrolysis. They give the melting point of 45°. Its formation by the diazotization and hydrolysis of 3-amino-4-chlorotoluene is also described by Kraay[15] as a check on its preparation from 3,4-dichlorotoluene by treatment with sodium methoxide (m. p. 46°). Gibson[2] who isolated 6-chloro-*m*-cresol from the products of direct chlorination of *m*-cresol gave 46° as the melting point.

We have repeated the preparation of 6-chloro-*m*-cresol from 4-chloro-*m*-nitrotoluene[14] after preparing the latter from both *p*-toluidine[16] and from *p*-chlorotoluene.[12] As a further check it was prepared from 6-nitro-*m*-cresol[17] by reduction according to the method of Raiford,[18] diazotization and treatment with cuprous chloride[4] (31 g. of 6-nitro-*m*-cresol gave 10.5 of 6-chloro-*m*-cresol). In all cases the product boiled at 197–198° and crystallized in rhombohedra melting at 46°.

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

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(8) Peratoner and Condorelli, *Gazz. chim. ital.*, **28**, I, 213 (1898).

(9) Raschig, German Patent 232,071.

(10) Liebrecht, German Patent 233,118.

(11) Laschinger, U. S. Patent 1,847,566.

(12) Goldschmidt and Hönig, *Ber.*, **19**, 2440 (1886).

(13) Bamberger, *ibid.*, **35**, 3701 (1902).

(14) Hodgson and Moore, *J. Chem. Soc.*, 2036 (1926).

(15) Kraay, *Rec. trav. chim.*, **49**, 1082–1092 (1930).

(16) Gattermann and Kaizer, *Ber.*, **18**, 2600 (1885).

(17) Staedel and Kolb, *Ann.*, **259**, 210 (1890).

(18) Raiford, *Am. Chem. J.*, **46**, 419 (1911).

Monochloro-*m*-cresols by Direct Chlorination.—One mole of *m*-cresol chlorinated in 400 cc. of chloroform at 0° with one mole of chlorine[5] 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 consisted mostly of the unreacted *m*-cresol. The 230–238° fraction gave upon purification 32 g. of 4-chloro-*m*-cresol. 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 6-nitro-*m*-cresol, 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 yielded 2-chloro-*m*-cresol when chilled and seeded.

4,6-Dichloro-*m*-cresol.—The melting point of 4,6-dichloro-*m*-cresol is given by v. Walther and Zipper[19] as 45–46° and by Tanaka and Morikawa[20] as 58°. We obtained by the following sequences fine flat needles melting at 71.5–72.5° and boiling at 235–236°.

(*a*) Chlorination of 6-nitro-*m*-cresol in cold chloroform or acetic acid solution with two moles of chlorine gave only the 4-chloro-6-nitro-*m*-cresol (m. p. 131–133°).[21] This was reduced with stannous chloride and hydrochloric acid.[18] The resulting hydrochloride was diazotized and treated with a cold solution of cuprous chloride.[4] Upon steam distillation, 4,6-dichloro-*m*-cresol separated out from the distillate as an oil.

Anal. Calcd. for C_7H_7OCl: Cl, 40.11. Found: Cl, 40.39.

(*b*) Pure 4,6-dinitro-*m*-cresol was obtained from 4-nitro-*m*-cresol[17] by nitration in acetic acid solution according to Gibbs and Robertson.[22] 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 acetic acid gave a product melting at 71°.[23] After reduction with stannous chloride and hydrochloric acid,[18] both amino groups were diazotized and replaced with chlorine by the Sandmeyer method.[4] This method gave a smaller yield of 4,6-dichloro-*m*-cresol than the preceding.

The direct chlorination of either 4-chloro-*m*-cresol or 6-chloro-*m*-cresol gave as one of the products 4,6-dichloro-*m*-cresol (see below).

It may be significant that the 4,6-dichloro-*m*-cresol described by v. Walther and Zipper[19] has a melting point identical with 2,4,6-trichloro-*m*-cresol,[19,26,27] while that described by Tanaka and Morikawa melted at the same temperature as 2,4-dichloro-*m*-cresol.

2,4-Dichloro-*m*-cresol.—Tanaka and Morikawa[20] and Datta and Mitter[24] report the melting point of 2,4-dichloro-*m*-cresol as 44 and 45°. The latter workers state that their compound is identical with the dichloro-*m*-cresol prepared by Claus and Schweitzer[25] who gave its melting point as 46°. As was pointed out by Crowther and McCombie[26] and also supported by the work of Raiford,[27] Claus and Schweitzer's dichloro compound was

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(19) V. Walther and Zipper, *J. prakt. Chem.*, [2] **91**, 374 (1864).

(20) Tanaka and Morikawa, *J. Chem. Soc. Japan*, **51**, 275–277 (1930).

(21) Kenner, Tod and Withan, *J. Chem. Soc.*, **127**, 2349 (1925); v. Walther and Zipper, *J. prakt. Chem.*, [2] **91**, 411 (1864).

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

(23) Will, *Ber.*, **47**, 712 (1914); Sane and Joshi, *J. Indian Chem. Soc.*, **5**, 299–301 (1928).

(24) Datta and Mitter, THIS JOURNAL, **41**, 2033 (1919).

(25) Claus and Schweitzer, *Ber.*, **19**, 930 (1886).

(26) Crowther and McCombie, *J. Chem. Soc.*, **103**, 545 (1913).

(27) Raiford, *Am. Chem. J.*, **46**, 424 (1911).

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 co-workers.

Attention might 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 was not analyzed. Furthermore, they state that 2,4-dichloro-*m*-cresol was 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.

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°.

Anal. Calcd. for C_7H_6OCl: Cl, 40.11. Found: Cl, 40.20.

2,6-Dichloro-*m*-cresol.—The literature gives no description of 2,6-dichloro-*m*-cresol.[25] When prepared by the following sequences it boiled at 240.5–242.5° and crystallized in prisms melting at 27°.

(*a*) Crude 4-nitro-*m*-cresol prepared by the method of Staedel and Kolb[17] was chlorinated with two moles 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.) Eighty grams of hydrochloride was diazotized and the amino group replaced with hydrogen by means of an alkaline solution of stannous chloride;[29] yield 6 g.

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

(*b*) The fraction boiling at 235–245° obtained in the preparation of 2-chloro-*m*-cresol (p. 4214) was repeatedly fractionated. Most of it came over at 240–242.5°. This was shown by analysis, ester formation and chlorination to 2,4,6-trichloro-*m*-cresol to be 2,6-dichloro-*m*-cresol.

Dichloro-*m*-cresols by Direct Chlorination.—Chlorination of one mole of *m*-cresol in chloroform solution at 0° with two moles of chlorine gave a mixture which after five distillations gave 20 g. boiling at 233–235°; 82 g., at 235–237°; 27 g., at 237–240°; 13 g., at 240–250°. 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 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 of the beaker 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 for 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

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(28) Raiford, THIS JOURNAL, **36**, 675 (1914).

(29) Houben, "Die Methoden der organischen Chemie," Leipzig, 1924, Vol. 4, p. 612.

fractions was combined with the fourth, which gave no crystals, and fractionated. A portion was collected at 240.5–242.5° which corresponds to the boiling point of 2,6-dichloro-*m*-cresol.

Chlorination of Monochloro-*m*-cresols.—Upon chlorination in cold chloroform with one mole of chlorine: 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 the theoretical yields of 2,4,6-trichloro-*m*-cresol (m. p. 46°)[25] when chlorinated in chloroform with one mole of chlorine. This complete chlorination may be effected by chlorination of *m*-cresol itself in chloroform with three moles of chlorine.

MELTING POINTS, ANALYSES AND CRYSTALLINE FORMS

	Benzoyl ester of *m*-cresol[30,31]	Benzene sulfonyl esters of *m*-cresol[30,31]	*p*-Toluene sulfonyl esters of *m*-cresol[30,31]
2-Chloro-*m*-cresol	Clusters of prisms	Prismatic plates	Fine lustrous prisms
4-Chloro-	Needle-like plates	Clusters of large needle-like plates	Clusters of needle-like plates
6-Chloro-	Prisms	Fine prisms	Prismatic plates
2,4-Dichloro-	Fine plates	Fine needle-like plates	Very shiny plates
2,6-Dichloro-	Clusters of small prismatic plates	Thin lustrous plates	Small prisms
4,6-Dichloro-	Mats of very fine needles	Clusters of elongated prisms	Very fine needles
2,4,6-Trichloro-	Very fine prismatic plates	Prismatic plates	Prismatic plates

		Chlorine, %			Chlorine, %			Chlorine, %	
	M. p., °C.	Calcd.	Found	M. p., °C.	Calcd.	Found	M. p., °C.	Calcd.	Found
2-Chloro-	55–56	14.38	14.47	58–58.5	12.74	12.11	96	12.13	11.75
4-Chloro-	86[2]	14.38	14.39	66	12.74	12.50	98	12.13[2]	12.69
6-Chloro-	38[2]	14.38	14.39	99	12.74	12.53	93–94[2]	12.13	11.92
2,4-Dichloro-	78–78.5	25.24	24.74	69.5	22.38	22.73	100–101	21.43	21.72
2,6-Dichloro-	90.5	25.24	25.57	70	22.38	22.82	92–92.5	21.43	21.21
4,6-Dichloro-	57.5	25.24	25.27	86	22.38	22.01	104–105	21.43	20.69
2,4,6-Trichloro-	53	33.73	34.00	121	30.28	30.21	92-93	29.12	29.24

The chloro-*m*-cresols described 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.

Summary

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

2. Chlorination of *m*-cresol in chloroform with two moles of chlorine gave 2,4-, 2,6- and 4,6-dichloro-*m*-cresols.

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

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

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

[31] Reverdin applied this method to sulfone chlorides (*Ber.* **35**, 1443 (1902).