[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

REACTIONS OF *p*-CHLOROBENZENESULFONIC ACID AND DERIVATIVES. THE $\sigma_p{}^*$ CONSTANT OF THE N,N-DIMETHYLSULFONAMIDO GROUP

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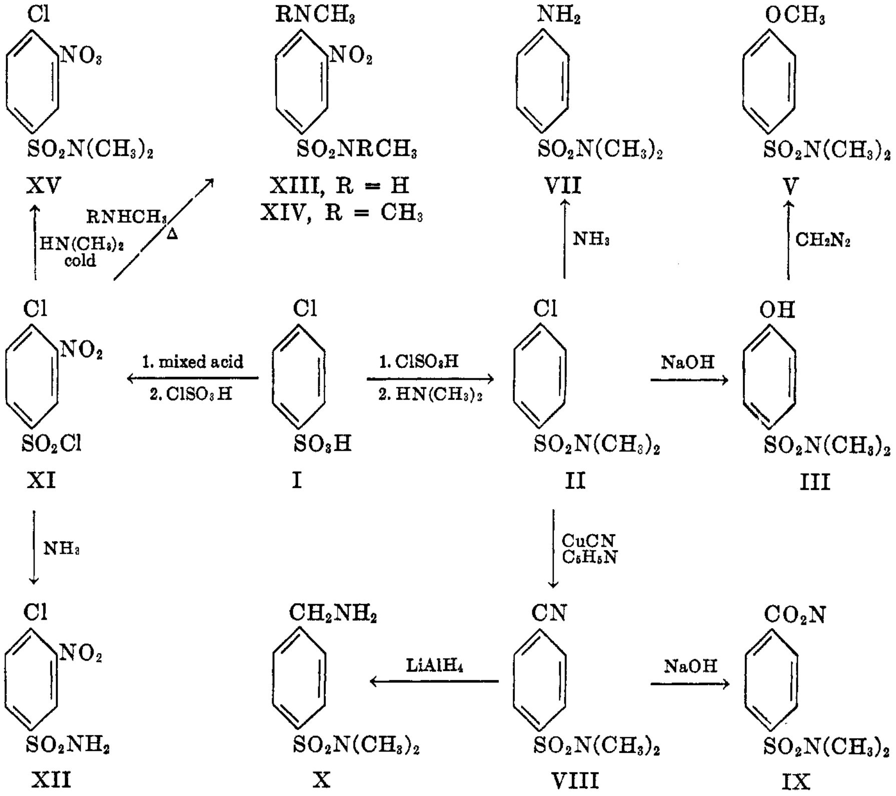
p-Chlorobenzenesulfonic acid (I) is the principal by-product in the manufacture of DDT from chlorobenzene and chloral in the presence of sulfuric acid. According to a recent patent (1), the acid accounts for 25–35% of the chlorobenzene put into DDT process. Most of the *p*-chlorobenzenesulfonic acid so produced is reconverted to chlorobenzene by desulfonation (2), and it would evidently be desirable to find economically more attractive uses for this major by-product. It was with this thought in mind that an investigation of some reactions of *p*-chlorobenzenesulfonic acid was undertaken.

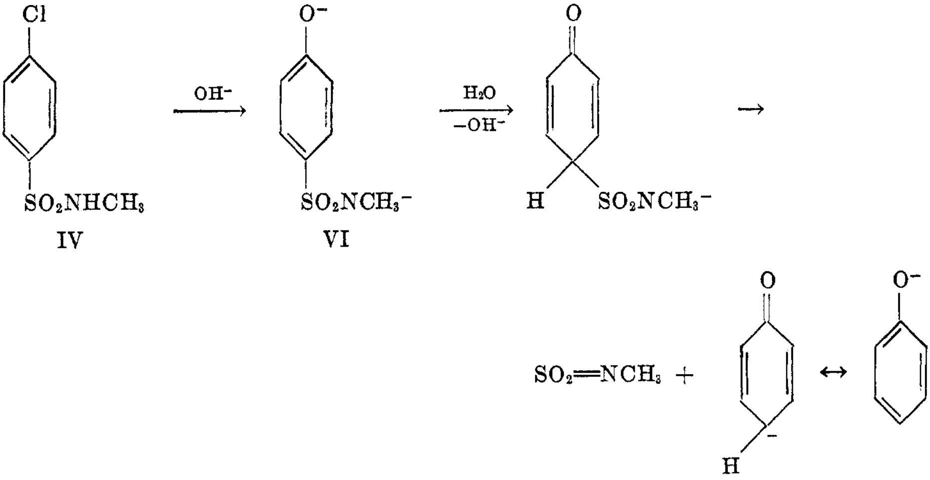
Replacement of the chlorine atom in I by hydroxyl requires rather stringent conditions (3–5), one reference (4) specifying the use of aqueous sodium hydroxide at 300°. It appeared that part of the difficulty was due to the fact that



aqueous base converts the sulfonic acid (I) to its anion, and that displacement of chlorine in the anion of I by hydroxide ion then is impeded by electrostatic repulsion of the negative charges. Accordingly, it was expected that *p*-chlorobenzene-N,N-dimethylsulfonamide (II) which does not form an anion in base should undergo substitution by hydroxide ion more readily than I. This expectation was borne out when it was found that II was converted to the corresponding hydroxy compound (III) in four hours by means of 10% aqueous sodium hydroxide at 200°. Under the same conditions, the N-methylamino compound (IV) was inert, presumably because IV, like the parent compound I but unlike II, forms an anion in aqueous base.

The structure of compound III was proved by methylation to the corresponding methyl ether V which was also obtained by treatment of anisole with chlorosulfonic acid followed by reaction of the resulting sulfonyl chloride with dimethylamine.

A surprising result was obtained when the temperature was raised to 250° for the reaction of *p*-chlorobenzene-N-methylsulfonamide (IV) with sodium hydroxide. Under these conditions, the principal product was phenol, identified by the infrared spectrum and the tribromo derivative. While desulfonations of sulfonic acids in acid medium are common, the desulfonation of a derivative of the acid in basic medium seems to be without precedent, even though a reasonable mechanism for the transformation can be written:



It is assumed here that the first step in the reaction of IV with sodium hydroxide is displacement of chlorine by hydroxyl, followed by electrophilic attack of water on the resulting dianion VI and expulsion of N-methylsulfimide with concomitant formation of the phenoxide ion. Although the electrophilic character of a 10% aqueous solution of sodium hydroxide might be expected to be low, electrophilic attack on VI is greatly facilitated by its high negative charge. It is of interest that a mechanism similar to the above, but involving elimination of sulfur trioxide instead of N-methylsulfimide can be written for the reaction of the free *p*-chlorobenzenesulfonic acid (I) with sodium hydroxide; and in fact it has been reported (4) that although the principal product of this reaction is *p*-hydroxybenzenesulfonic acid, phenol is obtained as a side-product.

Conversion of the dimethylamide II to the dimethylamide of sulfanilic acid (VII) by ammonolysis was effected in 63% yield at a temperature of 250°. Similarly, II could be converted to *p*-cyanobenzene-N,N-dimethylsulfonamide (VIII) in 62% yield by the Rosenmund-Von Braun (cuprous cyanide-pyridine) procedure. The structure of VIII was established by hydrolysis to the known acid IX. VIII could also be reduced to the corresponding amino compound X (isolated as the sulfate) by means of lithium aluminum hydride in tetrahydrofuran as a solvent. It is of some interest that the N,N-dimethlysulfonamide function is not affected under these conditions.

A qualitative comparison of the behavior of the N,N-dimethlysulfonamide II with the N-methylsulfonamide IV and the free acid I in nucleophilic displacement reactions suggested that II was more reactive under these circumstances than IV or I. It seemed advisable to put this conclusion on a more quantitative basis and, at the same time, to measure the as yet unknown $\sigma_p{}^*$ constant (6) for the dimethylsulfamyl group. To this end, 4-chloro-3-nitrobenzenesulfonic acid, its N,N-dimethylamide and its amide (chosen in preference to the less easily accessible N-methylamide) were synthesized and the rates of reaction of the latter two compounds with sodium methoxide were measured (7). Nitration of *p*-chlorobenzenesulfonic acid followed by treatment with chlorosulfonic acid (8) gave 3-nitro-4-chlorobenzenesulfonyl chloride (XI) which could be converted readily to the corresponding amide (XII) by treatment with aqueous ammonia. Conversion of the chloride XI to the corresponding N-methyl- and N,N-dimethyl-amide was less facile, since treatment of XI with methylamine and dimethylamine at steam-bath temperature led to the replacement of *both* chlorine atoms in XI to give the N-methylamide of *p*-methylaminobenzenesulfonic acid (XIII) and the N,N-dimethylamide of *p*-dimethylaminobenzenesulfonic acid (XIV) respectively. However, the N,N-dimethylamide of 3-nitro-4-chlorobenzenesulfonic acid (XV) could be obtained by treatment of the chloride XI with aqueous dimethylamine under controlled conditions.

It is evident that the formation of XIV and XIII from XI involves XV (or its monomethyl homolog) as an intermediate. The high susceptibility of these intermediates towards further attack by dimethyl- (or monomethyl-) amine as compared to the stability of the amide XII towards ammonia is not surprising in view of the established (9) fact that mono- and di-methylamine are more nucleophilic than ammonia.

The rate of displacement of chlorine in the N,N-dimethylamide of 3-nitro-4-chlorobenzenesulfonic acid (XV) by sodium methoxide in absolute methanol at 25.0° was found to be 0.0911–0.0920 lit. mole^{-1} min.^{-1} as compared to 1.54–1.57 lit. mole^{-1} min.^{-1} for 2,4-dinitrochlorobenzene. [The value recorded in the literature (10) for the latter compound is 1.50.] Using a value of 3.9 for ρ for the reaction of *p*-substituted *o*-nitrochlorobenzenes with sodium methoxide in methanol at 25° (10) one obtains a value of 0.99 for the $\sigma_p{}^*$ constant (6) of the dimethylsulfamyl group.

The reaction of 3-nitro-4-chlorobenzenesulfonamide (XII) with sodium

TABLE I

Group	$-NO_2$	$-SO_2CH_3$	$-SO_2N(CH_3)_2$	$-SO_2NH_2$	$-SO_2O^-$	$-SO_2NH^-$
σ_p^*	1.27 (6, 9)	1.13 (10)	0.99	(0.62)[a] (6)	(0.38)[a] (6)	*ca.* 0.3

[a] This is a σ_p value. The σ_p^* value should be larger by perhaps as much as 0.4–0.5.

methoxide in methanol was too slow to follow at 25°. At 60°, a rate constant of 0.0106 lit. mole^{-1} min.$^{-1}$ was obtained, on the assumption that the first mole of sodium methoxide added converted the sulfonamide to its sodium salt and that displacement of the *p*-chlorine atom was effected exclusively by sodium methoxide and not by the sodium salt of the sulfonamido function. In view of the uncertainty of this assumption we do not ascribe too much significance to this value, nor to the corresponding value of 0.3 for the σ_p^* constant of the $—SO_2NH^-$ group. [The value for ρ_{60} for the reaction of *p*-substituted *o*-nitrochlorobenzenes with sodium methoxide needed for computation of σ_p^* ($—SO_2NH^-$) was found to be 3.5 by calculating rate constants at 60° for various *p*-substituents from data in ref. (10) and plotting these k_{60} values *vs.* σ_p^* for the appropriate groups].

Table I gives a comparison of σ_p^* for $—SO_2N(CH_3)_2$ and $—SO_2NH^-$ with related σ_p^*-values from the literature.

EXPERIMENTAL

(All melting points are uncorrected. Microanalyses by Micro-Tech Laboratories, Skokie, Illinois.)

p-Chlorobenzenesulfonamides. To 100 g. (0.475 mole) of *p*-chlorobenzenesulfonic acid monohydrate, dried in a vacuum desiccator over phosphorus pentoxide, was added 200 g. (1.73 moles) of chlorosulfonic acid cooled to about 10° over a period of 10 minutes. The mixture was heated on a steam-bath in a hood until evolution of hydrogen chloride subsided. Then it was cooled and poured very slowly and with constant stirring into a 3-l. beaker three-quarters filled with crushed ice. The resulting chloride was collected and washed thoroughly with cold water; yield 70–85 g. (70–85%), m.p. 49–50°. A sample recrystallized from petroleum ether melted at 51°; lit. (11) 50.5–51.5°.

The crude chloride (75 g.) was added to 200 ml. of an ice-cold aqueous solution of the appropriate ammonia derivative (28% ammonia, 40% methylamine, or 40% dimethylamine) at such a rate that the temperature did not exceed 40°. The reaction mixture then was boiled in a hood to expel excess amine. On chilling and stirring the product solidified and was collected and washed with cold water. Recrystallization from aqueous methanol gave the pure sulfonamides in 70–80% yield. The amide melted at 143–144°; lit. (12) 143–144°; the N-methylamide at 62–64°; lit. (13) 59°; and the N,N-dimethylamide at 78–79°; lit. (14) 79–80°.

p-Hydroxybenzene-N,N-dimethylsulfonamide (III). A mixture of 5 g. (0.025 mole) of *p*-chlorobenzene-N,N-dimethylsulfonamide (II) and 100 ml. of 10% aqueous sodium hydroxide was heated to 200° in a 300-ml. stainless steel bomb. After being shaken for four hours the bomb was cooled and the contents were transferred to a flask and acidified cautiously with concentrated hydrochloric acid. Crystallization was allowed to proceed in the refrigerator. The material was collected and recrystallized from water; yield 4.2 g. (91%); m.p. 94°; lit. (15) 95–96°.

Anal. Calc'd for $C_8H_{11}NO_3S$: C, 47.74; H, 5.51.

Found: C, 47.34; H, 5.89.

p-Methoxybenzene-N,N-dimethylsulfonamide (V). This compound was obtained from the corresponding hydroxy compound (III) by treatment with diazomethane; it melted at 71–72°.

Anal. Calc'd for $C_9H_{13}NO_3S$: C, 50.21; H, 6.09.
Found: C, 50.46; H, 6.12.

The same compound was obtained by treating anisole with chlorosulfonic acid, precipitation of the resulting sulfonyl chloride by water, and conversion to the N,N-dimethylamide by means of 40% aqueous dimethylamine. The two samples did not depress each other's melting point and had identical infrared spectra.

Reaction of p-chlorobenzene-N-methylsulfonamide (IV) *with alkali.* In a 300-ml. stainless steel bomb were placed 100 ml. of 10% aqueous sodium hydroxide and 5 g. (0.025 mole) of *p*-chlorobenzene-N-methylsulfonamide (IV). Heating at 200° for four hours led only to the recovery of unchanged starting material (83%). When the reaction temperature was raised to 250°, phenol was isolated from the reaction mixture. It was identified by its infrared spectrum and its tribromo derivative, m.p. 92° (lit. 95°) not depressed by admixture of an authentic specimen of 2,4,6-tribromophenol.

N^1-Dimethylsulfanilamide from II. To 7 g. of *p*-chlorobenzene-N,N-dimethylsulfonamide (II) was added 130 ml. of cold 36% aqueous ammonia (prepared by adding the required amount of liquid ammonia to an ice-cold 28% aqueous ammonia solution) in a 300-ml. stainless steel bomb, cooled to 0°. The bomb was sealed, the temperature raised to 250° (pressure *ca.* 2700 p.s.i.), and the bomb was shaken at this temperature for four hours. Then it was cooled, vented, opened and the contents were filtered with suction. The product so obtained was recrystallized from aqueous alcohol to yield 4.6 g. (63%) of N^1-dimethylsulfanilamide melting at 164–165°. The material contained a small amount of a non-basic impurity and could be further purified by extraction with concentrated hydrochloric acid, filtration, precipitation with aqueous sodium bicarbonate and recrystallization from aqueous alcohol. Material so purified melted at 170.5–171°; lit. (16) 172°.

p-Cyanobenzene-N,N-dimethylsulfonamide (VIII). A mixture of 20 g. (0.091 mole) of *p*-chlorobenzene-N,N-dimethylsulfonamide (II), dried in a vacuum desiccator over phosphorus pentoxide, 10 g. (0.11 mole) of oven-dried cuprous cyanide, and 12 ml. of pyridine was heated at 240–250° for four hours. A small amount of the pyridine was allowed to boil off at the beginning; when escape of pyridine ceased, the reaction mixture was protected by means of a drying tube. At the end of the reaction time the mixture was allowed to cool to 100° and was poured on to 100 ml. of concentrated hydrochloric acid. The resultant suspension was allowed to cool to room temperature and then was stirred for 30 minutes with 200 ml. of benzene to insure complete extraction of organic material. The benzene layer was separated, washed with dilute ammonia until the ammonia wash no longer became blue, then washed with water, dried over sodium sulfate, and concentrated. The residue after crystallization from alcohol weighed 12 g. (62%) and melted at 124–127°.

Anal. Calc'd for $C_9H_{10}N_2O_2S$: C, 51.41; H, 4.79.
Found: C, 51.72; H, 4.84.

p-Carboxybenzene-N,N-dimethylsulfonamide (IX). A suspension of 2 g. (0.0095 mole) of the cyano compound VIII (purified by sublimation) in 20 ml. of 10% aqueous sodium hydroxide was boiled under reflux until it became homogeneous. Then it was treated with Norit, filtered, acidified, and chilled. The acid IX so precipitated weighed 2.28 g. (97%) and melted at 251–253°; lit. (17) 255–256°; lit. (18) 247–248°.

p-Aminomethylbenzene-N,N-dimethylsulfonamide (X). Preliminary experiments indicated that the N,N-dimethylsulfonamide function is not extensively affected by lithium aluminum hydride. N,N-dimethylbenzenesulfonamide was recovered in 81% yield after four hours' refluxing with an ethereal solution of the hydride.

A solution of 20 g. (0.095 mole) of VIII in 100 ml. of dry tetrahydrofuran was added, over a period of one hour, to a slurry of 8 g. (0.21 mole) of lithium aluminum hydride in 50 ml. of the same solvent. The mixture was boiled under reflux for one hour after which time water was added slowly with cooling to decompose the excess hydride. Addition of dilute sulfuric acid to the reaction mixture led to the precipitation of a solid which, after recrystallization from water, did not melt below 250°. Analysis indicated this compound to be the neutral sulfate of X:

Anal. Calc'd for $C_{18}H_{30}N_4O_8S_3$: C, 41.05; H, 5.74.
Found: C, 40.71; H, 5.98.

Difficulties were encountered in the purification of the free amine which melted in the vicinity of 100° and the compound was not analyzed.

4-Chloro-3-nitrobenzenesulfonic acid. *p*-Chlorobenzenesulfonic acid (I) monohydrate, dried over phosphorus pentoxide, (20 g., 0.096 mole) was added to a mixture of 15 ml. of 18% fuming sulfuric acid, 35 ml. of concentrated sulfuric acid, and 30 ml. of yellow fuming nitric acid. After one hour's standing at room temperature, 100 ml. of water was added cautiously to the mixture. The water and nitric acid then were boiled off by heating the mixture until the temperature reached 220°. Upon chilling, the product separated and was collected on a sintered glass funnel and was purified by recrystallization from concentrated hydrochloric acid; yield 11 g.

4-Chloro-3-nitrobenzenesulfonyl chloride (XI). The recrystallized acid (10 g., 0.042 mole) was added to 20 g. (0.17 mole) of chlorosulfonic acid at room temperature. The mixture then was heated at 100° for one hour, following which it was cooled and poured on to crushed ice. The resulting sulfonyl chloride (4 g., 18% from I) was not purified but was used immediately in the preparation of the amides.

4-Chloro-3-nitrobenzenesulfonamide (XII). A mixture of 50 ml. of 28% aqueous ammonia and 3 g. (0.012 mole) of the above chloride XI was slowly raised to the boiling point and then was cooled. The resulting solid was collected and recrystallized from ethanol; yield 2.0 g. (79%), m.p. 175–177°; lit. (8) 175–176°.

4-Chloro-3-nitrobenzene-N,N-dimethylsulfonamide (XV). To 25 ml. of 40% aqueous dimethylamine was added 5 g. (0.02 mole) of the chloride XI at such a rate that the temperature did not exceed 40°. After 15 minutes, the solid was collected on a sintered glass funnel and washed with water.Then it was slurried with 25 ml. of concentrated hydrochloric acid in a small beaker to remove any basic material (XIV). It was again collected and the hydrochloric acid treatment was repeated. The material then was crystallized from ethanol to give 2.9 g. (56%) of the amide XV melting at 100–102°.

Anal. Calc'd for $C_8H_9ClN_2O_4S$: C, 36.30; H, 3.43; Cl, 13.40.
Found: C, 36.62; H, 3.37; Cl, 13.76.

4-(N,N-Dimethylamino)-3-nitrobenzene-N,N-dimethylsulfonamide (XIV). When 3 g. (0.012 mole) of the chloride XI was treated with 25 ml. of 40% aqueous dimethylamine and the temperature of the reaction mixture was raised to 90°, the principal product was the amine XIV. Collection of the material obtained on cooling the reaction mixture followed by recrystallization from ethanol gave 2.7 g. (84%) of a product readily soluble in concentrated hydrochloric acid; m.p. 182–183°.

Anal. Calc'd for $C_{12}H_{15}N_3O_4S$: C, 39.18; H, 4.52.
Found: C, 39.07; H, 4.58.

4-(N-Methylamino)-3-nitrobenzene-N-methylsulfonamide (XIII). This was obtained as described above for the homolog XIV when 3 g. (0.012 mole) of the chloride XI was heated with 20 ml. of 40% aqueous methylamine at 90° for ten minutes. Yield 2.5 g. (88%), m.p. 183°.

Anal. Calc'd for $C_8H_{11}N_3O_4S$: C, 43.95; H, 5.53.
Found: C, 43.90; H, 5.33.

Kinetic studies. Standard methanolic sodium methoxide was prepared by dissolving sodium in absolute methanol. Titration showed this solution to be 0.2372 *N*. For a kinetic run, the chloride sample was weighed, dissolved in absolute methanol, made up to volume in a measuring flask, thermostatted and then mixed with the requisite amount of the thermostatted methoxide solution and placed in the thermostat again. Aliquots were withdrawn at intervals, quenched by running them into an excess of standard hydrochloric acid, and backtitrated with standard base using phenolphthalein as indicator. Rate constants were determined from the second-order equation $k = \frac{1}{at}\frac{x}{a - x}$ both graphically and by calcula-

TABLE II

REACTION OF 2,4-DICHLORONITROBENZENE WITH SODIUM METHOXIDE

50 ml. of methanol containing 2.4028 g. (0.01186 mole) of 2,4-dinitrochlorobenzene, 50 ml. of 0.2372 *N* methanolic sodium methoxide (0.01186 mole), and 100 ml. of absolute methanol thermostatted at 25.0°. Concentration of reactants at time first aliquot was taken: $a = 0.0506\ M$.

Time (min.)	Titer	% Completion	$x/a - x)$	at (min. mole. lit.$^{-1}$)	k (lit. mole^{-1} min.$^{-1}$)
0	7.47	0	0	0	
1	7.61	6.4	0.068	0.0506	(1.35)[a]
3	7.95	21.9	.219	.152	(1.84)[a]
5	8.12	29.6	.421	.253	1.66
8	8.30	38.4	.623	.404	1.54
11	8.47	45.7	.842	.557	1.51
18	8.71	56.7	1.29	.911	1.43
28	8.95	67.7	2.09	1.420	1.47
43	9.15	76.8	3.31	2.108	1.52
∞	9.66[b]	100.0			——
					Average Value: 1.54 ± 0.09

[a] Disregarded in computing average.

[b] Calculated.

Value determined graphically: 1.57. Literature values (Ref. 9, p. 357) range from 1.49 to 1.51; our value is probably somewhat less accurate and is included mainly for purposes of calibration.

TABLE III

REACTION OF 3-NITRO-4-CHLOROBENZENE-N,N-DIMETHYLSULFONAMIDE (XV) WITH SODIUM METHOXIDE

50 ml. of methanol containing 1.5720 g. (0.00594 mole) of XV, 25 ml. of 0.2372 *N* methanolic sodium methoxide (0.00593 mole), and 25 ml. of absolute methanol thermostatted at 25.0°. $a = 0.0588\ M$.

Time (min.)	Titer	% Completion	$x/(a - x)$	at (min. mole. lit.$^{-1}$)	k (lit. mole^{-1} min.$^{-1}$)
0	7.10	0	0	0	
5	7.17	2.74	0.0282	0.294	0.0966
15	7.30	7.83	.0850	.880	.0966
30	7.45	13.7	.159	1.76	.0905
60	7.71	23.8	.312	3.53	.0885
120	8.08	38.3	.620	7.05	.0880
180	8.32	47.7	.910	10.58	.0860
280	8.60	58.7	1.42	16.45	.0865
360	8.80	66.4	1.98	21.15	.0935
450	8.90	70.4	2.38	26.50	.0933
	9.66[a]	100			——
					Average Value: 0.0911 ± 0.0037

[a] Calculated.

Value determined graphically: 0.920.

TABLE IV

Reaction of 3-Nitro-4-chlorobenzenesulfonamide (XII) with Sodium Methoxide

50 ml. of methanol containing 1.9358 g. (0.00818 mole) of XII and 50 ml. of 0.2372 N methanolic sodium methoxide (0.01186 mole) thermostatted at 60.0°. a = 0.0818 M; b = 0.0368 M, assuming that one mole of sodium methoxide becomes unavailable for reaction by neutralizing the sulfonamide XII.

Time (min.)	Titer	$(a-x)$ (lit. mole^{-1})	$(b-x)$ (lit. mole^{-1})	Y^a	k(lit. mole^{-1} min.$^{-1}$)
0	4.52	0.0818	0.0368	0	
60	4.60	.0795	.0345	0.817	0.0136^b
160	4.74	.0764	.0314	1.99	.0124
280	4.83	.0726	.0202	2.45	.0088
548	5.10	.0682	.0232	6.50	.0118
1460	5.77	.0606	.0154	13.7	.0094
1860	6.00	.0551	.0101	19.9	.0107
					Average Value: 0.0106 ± 0.0012

[a] $Y = 2.303/(a-b) \log b(a-x)/a(b-x)$.

[b] Disregarded in computing average.

Value determined graphically: 0.0101.

TABLE V

Reaction of o-Chloronitrobenzene with Sodium Methoxide

50 ml. of methanol containing 1.8691 g. (0.01186 mole) of o-nitrochlorobenzene and 50 ml. of 0.2372 N methanolic sodium methoxide (0.01186 mole) thermostatted at 60°. a = 0.1186.

Time (min.)	Titer	% Completion	$x/(a-x)$	at (min. mole. lit.$^{-1}$)	k (lit. mole^{-1} min.$^{-1}$)
0	4.50	0	0	0	
280	4.55	0.97	0.0098	33.2	0.000295
548	4.60	1.94	.0198	65.0	.000305
1860	4.83	6.40	.0684	221	.000309
	9.66^a	100			
					Average Value: 0.000306

[a] Calculated.

Value determined graphically: 0.000328.

(The accuracy of this value is evidently not high, since the reaction was followed only to 6% completion.)

tion, except in the case of the amide XII where initial concentrations of XII and free sodium methoxide were unequal and the equation $k = \frac{2 \cdot 3}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$ was used. The data are summarized in Tables II–V.

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SUMMARY

p-Chlorobenzene-N,N-dimethylsulfonamide (II) with aqueous sodium hydroxide at 200° gave the *p*-hydroxy compound (III). The corresponding N-methylsulfonamide was inert under the same conditions, but at 250° yielded phenol as the only product isolated.

Reaction of *p*-chlorobenzene-N,N-dimethylsulfonamide (II) with aqueous ammonia at 250° yielded N^1-dimethylsulfanilamide (VII). Reaction of the chlorosulfonamide II with cuprous cyanide in pyridine gave *p*-cyanobenzene-N,N-dimethylsulfonamide (VIII) which was hydrolyzed to the corresponding acid IX and reduced with lithium aluminum hydride to *p*-aminomethylbenzene-N,N-dimethylsulfonamide (X), the sulfonamide function remaining unaffected in the reduction.

Nitration of *p*-chlorobenzenesulfonic acid (I) followed by treatment with chlorosulfonic acid gave 3-nitro-4-chlorobenzenesulfonyl chloride (XI) which was converted to the corresponding amide (XII) by hot aqueous ammonia. Treatment of the chloride XI with hot aqueous methylamine and dimethylamine gave the N-substituted 3-nitro-4-aminobenzenesulfonamides XIII and XIV respectively. Treatment of XI with dimethylamine in the cold gave the corresponding N,N-dimethylsulfonamide XV.

The rate of reaction of XV with sodium methoxide was measured to be 0.0911–0.0920 lit. mole^{-1} min.$^{-1}$ From this value, $\sigma_p{}^*$ for $SO_2N(CH_3)_2$ was calculated to be 0.99.

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