Aromatic Amination with Hydroxylamine-O-sulfonic Acid[1]

BY PETER KOVACIC AND ROBERT P. BENNETT

Hydroxylamine-O-sulfonic acid aminates toluene in the presence of aluminum chloride to yield toluidines (51% *ortho*, 13% *meta* and 36% *para*). From competitive amination, the relative rate $k_{toluene}/k_{benzene}$ was found to be 3.7. A number of reaction variables were investigated—age of the aminating agent, effect of atmosphere, time, catalysts and solvents. The evidence indicates that amination proceeds by electrophilic substitution involving an attacking species of high activity.

Direct aromatic amination has received relatively little attention. In 1901, Graebe[2] and Jaubert[3] independently reported the amination of aromatic compounds with hydroxylammonium chloride in the presence of Friedel–Crafts catalysts. The use of hydroxylammonium sulfate is described in the patent literature.[4] More recently Keller and Smith[5-7] investigated hydroxylamine-O-sulfonic acid (HSA) and some of its derivatives. Compounds other than those in the hydroxylamine class have also been used to effect amination. For example, primary aromatic amines were formed[8] from hydrazoic acid and aromatic compounds in the presence of strong Lewis acids. Benzene has been aminated by ammonia in a silent discharge tube.[9,10]

The present study was undertaken to investigate more thoroughly the mechanism of aromatic amination with hydroxylamine-O-sulfonic acid.

Results and Discussion

The aminating ability of HSA was fairly extensively investigated by Keller and Smith.[5-7] They found that a variety of aromatic compounds, including benzene, chlorobenzene, toluene and the xylenes, was aminated by this reagent in the presence of aluminum chloride. In addition, these authors studied the effectiveness of a large number of catalysts, the variation of yield with time of reaction, and the optimum ratio of catalyst to HSA.

$$\text{ArH} + \text{H}_2\text{NOSO}_3\text{H} \xrightarrow{\text{AlCl}_3} \text{ArNH}_2 + \text{H}_2\text{SO}_4$$
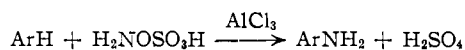
The reaction of HSA with toluene (Table I) in the presence of aluminum chloride was carried out according to the procedure of Keller and Smith,[5] except for isolation of the product which involved distillation in our case. Toluidines were obtained in 50% yield, in good agreement with the earlier report. Quantitative infrared analysis showed the product to consist of 51% *o*-, 13% *m*- and 36% *p*-toluidine. This isomer distribution is in marked

(1) Part I of a series on "Direct Aromatic Amination"; from the Ph.D. thesis of R. P. Bennett, Case Institute of Technology, 1960; presented at the 138th Meeting of the American Chemical Society in New York, N. Y., Sept., 1960.

(2) C. Graebe, *Ber.*, **34**, 1778 (1901).

(3) G. F. Jaubert, *Comp. rend.*, **132**, 841 (1901).

(4) J. F. de Turski, German Patent 287,756 (1914); *C. A.*, **10**, 2128 (1916); British Patent 626,661 (1949); *C. A.*, **44**, 2761 (1950); U. S. Patent 2,585,355 (1952); *C. A.*, **47**, 875 (1953).

(5) R. N. Keller and P. A. S. Smith, THIS JOURNAL, **66**, 1122 (1944).

(6) R. N. Keller and P. A. S. Smith, *ibid.*, **68**, 899 (1946).

(7) P. A. S. Smith, Ph.D. thesis, University of Michigan, 1944.

(8) K. F. Schmidt, *Ber.*, **57**, 704 (1924); **58**, 2413 (1925); K. F. Schmidt and P. Zutavern, U. S. Patent 1,637,661 (1927); *C. A.*, **21**, 3057 (1927).

(9) K. Sugino and E. Inoue. *J. Soc. Org. Synthetic Chem. (Japan)*, **7**, 198 (1949); *C. A.*, **47**, 6884 (1953).

(10) C. L. Thomas, U. S. Patents 2,749,297 and 2,749,298 (1956).

disagreement with that determined by Keller and Smith who reported that the product consisted of approximately 96% *p*-toluidine. In their work, the orientation was ascertained by separation of the isomers by crystallization of their oxalates. It would appear that the oxalate method, possessing the inherent weaknesses of an analytical procedure based upon chemical reaction and crystallization, is less accurate than infrared analysis. We are unable, however, to reconcile with our results the finding by Keller and Smith that the crude toluidine is converted in 96% yield to an N-acetyl derivative which, on the basis of melting point, appears to be the *p*-isomer of rather good purity.

TABLE I
HYDROXYLAMINE-O-SULFONIC ACID AND TOLUENE[a]

Cata-lyst	Mole	Time, hr.	Solvent or conditions	Toluidine, % Yield	o	m	p	S_t
AlCl₃	0.187	0.5	....	50	51	13	36	0.74
AlCl₃	.187	.5	Fresh HSA	40	46	11	43	.89
AlCl₃	.187	.5	Under N₂	52	53	12	35	.77
AlCl₃	.187	.5	DMF[b]	<1	..	..	..	..
AlCl₃	.187	.5	TiCl₄[c]	36	51	13	36	0.74
AlCl₃	.187	1	....	47	51	13	36	0.74
H₂SO₄	.20	2	....	0	..	..	..	..

[a] Unless otherwise specified, all runs were made according to the general procedure with HSA (0.1 mole, 6 days old) and toluene (1.09 moles). [b] 0.776 mole. [c] 0.455 mole.

A number of reaction variables were investigated—age of HSA, effect of atmosphere, time, catalysts and solvents. It was found that freshly prepared HSA gave toluidine in lower yield (40%) than material six days old and with a somewhat changed isomer distribution (46% *ortho*, 11% *meta* and 43% *para*). Another difference was that the fresh HSA yielded a solid mass in the reaction mixture during the heating which made stirring difficult, whereas the older HSA gave two fluid layers. For these reasons, all subsequent experiments were performed with six-day-old aminating agent. It is interesting that there is little difference in melting point between the fresh (m.p. 207–209° dec.) and aged (m.p. 205–208°, dec.) samples. On long standing, however, decomposition becomes more evident. The reactions were carried out under an ordinary atmosphere since no alteration in yield or orientation was observed when the reaction was performed under nitrogen. Lengthening the reaction time to one hour from the usual period of thirty minutes also produced no noticeable change. Of a number of catalysts studied, aluminum chloride was shown by Keller and Smith[6] to be the only effective one. Sulfuric acid was found to be inactive in accord with the previous report. Two solvents of different polarity were investigated. With titanium

tetrachloride the yield of toluidine was lowered to 36%, but the isomer distribution remained unchanged, 51% *ortho*, 13% *meta* and 36% *para*. In contrast, dimethylformamide decreased the yield to less than 1%—too small to permit accurate analysis. It is believed that the ability of these solvents to complex with and deactivate aluminum chloride is responsible for the decreased yields. Of the two, dimethylformamide would be expected to coördinate more effectively with the catalyst.

As a check on the validity of the observed isomer distributions, isomerization studies were conducted on the three pure toluidine isomers by approximating the HSA amination reaction conditions as closely as possible. In no case was any isomerization indicated by infrared analysis, and the recovery of toluidine was greater than 85% for all isomers.

In brief, the HSA–toluene reaction displays the following characteristics: predominant *ortho–para* orientation, relatively high *ortho/para* ratio, relatively high *m*-isomer content, large requirement and high specificity for the catalyst, adverse effect by polar solvents. A mechanism involving electrophilic aromatic substitution by a species of high activity would be consistent with these observations.

Other characteristics of the reaction provide information concerning the mechanistic aspects. First, it should be pointed out that there is not complete agreement on the structure of HSA.[11,12] A zwitterion[5,13] is one form which has been proposed. In keeping with the earlier report,[5] it was noticed during the aminations with HSA that acid gas began to evolve at 60–80°. Since hydrogen chloride was not a product expected from the amination reaction, it appeared that the observed gas might arise from initial interaction of HSA with aluminum chloride.

$$H_2NOSO_3H + AlCl_3 \longrightarrow H_2NOSO_2OAlCl_2 + HCl$$
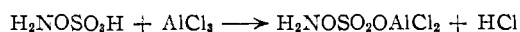
If this is the case, then the aluminum salt of HSA might well be the actual participant in the amination reaction, as originally suggested by Keller and Smith.[6] Additional evidence is available to support this concept. If one mole of aluminum chloride is needed as the catalyst, then the report[7] that two moles produces the best results with HSA is nicely explained. Keller and Smith also prepared[6,7] a crude aluminum derivative by grinding together HSA and aluminum chloride in different proportions. By testing the resulting powders as aminating agents for toluene they determined that a 2:1 ratio of catalyst to salt again gave the optimum yield. Similarly, in the present investigation equimolar amounts of HSA and aluminum chloride were heated in an inert solvent at 100° until hydrogen chloride was no longer evolved. The product, used as an aminating agent in the presence of an additional mole of aluminum chloride, gave a 22% yield of toluidine, 60% *ortho*, 8% *meta* and 37% *para* (Table II). These values are of the same relative order as those obtained with HSA by the

(11) A. Y. Berlin, *J. Gen. Chem. (U.S.S.R.)*, **17**, 95 (1947); *C. A.*, **42**, 51 (1948).

(12) R. F. Belt, *Dissertation Abstr.*, **16**, 1592 (1956).

(13) U. Wannagat and R. Pfeiffenschneider, *Naturwissenschaften*, **43**, 178 (1956); *C. A.*, **53**, 12908 (1959).

TABLE II

TOLUENE AND METAL DERIVATIVES OF HYDROXYLAMINE-*O*-SULFONIC ACID[a]

| Aminating agent, mole	Catalyst, mole	Time, hr.	Toluidine, % Yield	o	m	p	S_t
HSA–AlCl₃	AlCl₃, 0.1	0.5	22	60	8	32	0.90
Product,[b] 0.1 H₂NOSO₂ONa, 0.1	AlCl₃, 0.2	0.5	42	52	9	39	0.94

[a] Both runs were made according to the general procedure with toluene (1.087 moles); only toluene was recovered from the neutral fraction. [b] From HSA (0.1 mole) and AlCl₃ (0.1 mole) in *n*-heptane.

general method, with *ortho* being somewhat higher and *meta–para* correspondingly lower.

The sodium salt of HSA was also used as an aminating agent in the presence of aluminum chloride (two moles). An extremely vigorous exothermic reaction took place producing a 42% yield of toluidine, 52% *ortho*, 9% *meta* and 39% *para* (Table II)—values close to those obtained with HSA itself. Keller and Smith reported[6] that the sodium derivative alone was inactive and that with one mole of aluminum chloride only a 2% yield of toluidine resulted. The advantage gained from the use of two moles of catalyst in this case suggests a preliminary double decomposition reaction involving one mole of aluminum chloride.

$$H_2NOSO_2ONa + AlCl_3 \longrightarrow H_2NOSO_2OAlCl_2 + NaCl$$
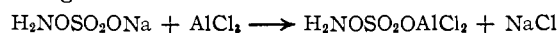
As compared with Friedel–Crafts alkylations with alcohols or alkyl halides, theoretical considerations are complicated, in the case of amination, by the possibility for coördination by the catalyst on either oxygen or nitrogen.
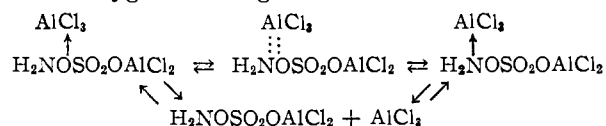
The other oxygen atoms present could also participate in complex formation. It is believed that the complex with oxygen is the form involved in amination, since an increase in the cationic character of nitrogen would then be expected.
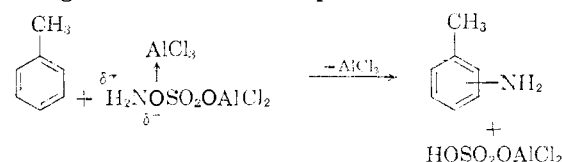
Alternatively, the catalytic agent might be a proton derived from aluminum chloride and a co-catalyst. A co-catalyst (water, alcohol or other polar compound) is necessary for alkylation of benzene with an alkyl halide in the presence of boron trifluoride.[14]

The predominant *ortho–para* orientation is characteristic of electrophilic aromatic substitution.[15] The relatively high *meta* content suggests an attacking species of considerable activity. Brown and Nelson related[16] the degree of *meta* orientation in

(14) G. F. Hennion and R. A. Kurtz, THIS JOURNAL, **65**, 1001 (1943).

(15) K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publishing Corp., New York, N. Y., 1955, pp. 465–578.

(16) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

electrophilic substitution to the "activity" of the attacking species, i.e., meta content increases with increase in electrophilic character of the reagent. Recently, Brown and co-workers calculated[17,18] for various electrophilic substitutions in toluene the Selectivity Factor, S_f, defined as $S_f = \log (p_f/m_f)$, where p_f and m_f are the partial rate factors. The S_f value may also be obtained[17] from the expression, $S_f = \log (2 \times \%p)/\%m$, the method used in the present work. Amination is compared with related processes as shown in Table III.

TABLE III

SELECTIVITY FACTORS

Reaction	Reagent	Conditions	S_f	Ref.
Amination	HSA	AlCl₃, 100°	0.74	
Methylation	CH₃Br	GaBr₃, 25°	.84	17
Isopropylation	i-PrBr	GaBr₃, 25°	.55	17

Evidence indicates that there is a change in the mechanism of alkylation in proceeding from methylation to t-butylation.[17] In the latter case, there is initial carbonium ion formation whereas methylation apparently takes place by a concerted process.[19,20] It is significant that the S_f factors for amination and methylation are very similar. If a free amino cation were involved in amination, as suggested by Keller and Smith,[5,6] a much lower S_f value would be expected. By analogy with methylation, the amination process can reasonably be considered to proceed by a concerted displacement mechanism.
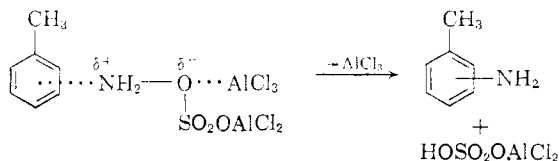
In order to obtain additional evidence concerning the "activity" of the attacking species, a competitive amination of benzene and toluene was performed with HSA in the presence of aluminum chloride. From the amounts of aniline and toluidine formed, the relative rate, $k_{toluene}/k_{benzene}$, was calculated[21] to be 3.7. This value, which indicates a very reactive species,[15] agrees favorably with the figure (4.3) obtained from calculations involving the Selectivity Factor.[17] For some unknown reason, the amount of high-boiling basic by-product (10%) was higher than usual. Comparison with reactivity ratios reported in the literature (Table IV) illustrates the high "activity" of the aminating agent.

The amination of chlorobenzene[5] by HSA in the presence of aluminum chloride was also examined and found to produce chloroanilines, 31% ortho, 20% meta and 49% para, in 11% yield. Isomerization studies of the pure chloroaniline isomers under simulated reaction conditions demonstrated that no isomerization occurred, but surprisingly showed that the o-isomer was selectively lost during the re-

TABLE IV

REACTIVITY RATIOS

Process	$k_{toluene}/k_{benzene}$	Ref.[15]
Isopropylation	2	22
Amination	4	
Sulfonation	5	23
Mercuration	8	24
Chlorination	353	25
Bromination	467	26

action. On the assumption that the same loss occurred during the amination, the isomer distribution would then become 40% ortho, 17% meta and 43% para. The similarity in S_f values for HSA (0.69–0.70) and hydroxylammonium chloride (0.63)[27] in this reaction lends support to these data. Two factors are apparent, however, despite some uncertainty concerning the isomer distribution. First, the o-isomer is not predominant in this amination as it is in the toluene reaction. Second, the amount of m-isomer formed is quite high in comparison with other electrophilic substitutions in chlorobenzene for which accurate isomer distributions are available. For example, nitration of chlorobenzene results[28] in the orientation: 30% ortho, 1% meta, 69% para.

Acknowledgment.—We gratefully acknowledge support from Research Corporation during part of this investigation.

Experimental[29]

Materials.—Unless otherwise indicated, commercially available materials were used. Toluene, chlorobenzene and dimethylformamide were dried and distilled before use.

Hydroxylamine-O-sulfonic acid (HSA) was prepared in greater than 95% yield by the method of Sommer, Schulz and Nassau,[30] m.p. 207–209° dec., lit.[5] m.p. 210° dec. The HSA was stored over phosphorus pentoxide in a vacuum desiccator for 6 days before use; HSA which had decomposed somewhat from standing (39 days), as evidenced by its turning brown at 150–180° and decomposing at 202–205°, could be readily purified by trituration with ice-cold anhydrous ether. As evidence that HSA is relatively stable when kept over phosphorus pentoxide in a vacuum desiccator, the melting point of one sample was unchanged after 13 days. When this sample was 49 days old, it was triturated with ice-cold anhydrous ether and the melting point (205–208° dec.) was unchanged after an additional 68 days. The analysis indicates a purity of 98.6%.

Anal.[31] Calcd. for H_2NOSO_3H: equiv. wt., 56.55. Found: equiv. wt., 57.73.

HSA–Aluminum Chloride Product.[6,7]—A mixture of HSA (0.1 mole), aluminum chloride (0.1 mole) and n-heptane (150 ml.) was heated under nitrogen at 95–100° for 30 min. Evolution of hydrogen chloride began at 55° and became vigorous at about 65°. After dilution with dry ether the mixture was filtered and the solid washed with ether.

(17) H. C. Brown and C. R. Smoot, THIS JOURNAL, 78, 6255 (1956).

(18) L. M. Stock and H. C. Brown, ibid., 81, 3323 (1959).

(19) H. C. Brown and H. Jungk, ibid., 77, 5584 (1955).

(20) H. Jungk, C. R. Smoot and H. C. Brown, ibid., 78, 2185 (1956).

(21) S. U. Choi and H. C. Brown, ibid., 81, 3315 (1959).

(22) F. E. Condon, ibid., 70, 2265 (1948).

(23) F. J. Stubbs, C. D. Williams and C. N. Hinshelwood, J. Chem. Soc., 1065 (1948).

(24) H. C. Brown and C. W. McGary, Jr., THIS JOURNAL, 77, 2300 (1955).

(25) P. B. D. de la Mare and P. W. Robertson, J. Chem. Soc., 279 (1943).

(26) E. Berliner and F. Berliner. THIS JOURNAL, 71, 1195 (1949).

(27) P. Kovacic, R. P. Bennett and J. L. Foote, unpublished work.

(28) J. D. Roberts, J. K. Sanford, F. L. G. Sixma, H. Cerfontain and R. Zagt, THIS JOURNAL, 76, 4525 (1954).

(29) Melting points and boiling points are uncorrected. Microanalyses were performed by Drs. Weiler and Strauss, Oxford, England.

(30) F. Sommer, O. F. Schulz and M. Nassau, Z. anorg. allgem. Chem., 147, 142 (1925).

(31) H. J. Matsuguma and L. F. Audrieth, Inorg. Syntheses, 5, 122 (1957).

The brown, powdery product did not melt at temperatures up to 230° and had no oxidizing power toward an acidic potassium iodide solution.

Sodium Salt of HSA.—The product was prepared as previously described[6,7] in 66% yield, m.p. 147–150° dec., lit.[6] m.p. ca. 150° (sinters). The analysis indicates a purity of 91.5%.

Anal.[31] Calcd. for H_2NOSO_3Na: equiv. wt., 67.54. Found: equiv. wt., 73.81.

HSA–Toluene. General Procedure.[5]—A vigorously stirred mixture of HSA (11.3 g., 0.1 mole) and toluene (100 g., 1.09 moles) was cooled in an ice-bath to below 10° and anhydrous aluminum chloride (25 g., 0.187 mole) was added. The temperature was increased to 100° during 15 min. and kept at 100–105° for 30 min. Evolution of gas usually began at about 80°. The reaction mixture was cooled to room temperature and poured into a slush of 150 ml. of dilute hydrochloric acid and ice. The resulting two-phase mixture was filtered yielding a negligible amount of tar, and the two layers were separated. The non-aqueous layer was re-extracted with a slush of 50 ml. of dilute hydrochloric acid and ice, the mixture filtered and the layers separated. The combined acid portions were extracted repeatedly with ether and the combined ether extracts added to the non-aqueous portion. After removal of the ether from the dried (anhydrous sodium sulfate) non-aqueous fraction, only unreacted toluene and a very small amount of tarry residue were obtained on distillation.

The acidic portion was made basic with sufficient concentrated sodium hydroxide solution to dissolve the aluminum hydroxide formed. The red-brown oily product was separated from the aqueous phase by repeated extractions with ether. The combined ether extract was dried and, after removal of ether, the basic product was distilled *in vacuo* through an Ace Minilab distillation head. A single fraction was collected (Table I) and identified as toluidine by elemental and infrared analysis; wt. 5.31 g. (50%), b.p. 72–74° (11 mm.), $n^{23}D$ 1.5675.

Anal. Calcd. for C_7H_9N: C, 78.50; H, 8.41; N, 13.08. Found: C, 78.65; H, 8.46; N, 13.01.

The residue from distillation amounted to 0.22 g. of a dark brown tar.

HSA–Chlorobenzene.—The general procedure was followed with 56.5 g. (0.5 mole) of HSA, 562.8 g. (5 moles) of chlorobenzene and 133.3 g. (1 mole) of anhydrous aluminum chloride. The temperature was increased to 120° during 1.25 hr. and maintained at 120–125° for 2 hr. Upon distillation of the basic product, one fraction, wt. 7.02 g. (11%), b.p. 110–124° (27 mm.), was collected. The residue amounted to 0.62 g. of dark brown tar. Infrared analysis showed the product to consist of 31% *o*-, 20% *m*- and 49% *p*-chloroaniline.

Distillation of the neutral fraction yielded, in addition to unreacted chlorobenzene, a 6.39-g. fraction, b.p. 64° (13 mm.), which was identified by infrared analysis as dichlorobenzene, and tarry residue (3.9 g.).

Competitive Amination of Benzene–Toluene.—Addition of anhydrous aluminum chloride (0.6 mole) to a stirred mixture of HSA (0.3 mole), benzene (1.5 moles) and toluene (1.5 moles) below 20° resulted in a temperature rise to 68°. After the reaction mixture was heated at 75–80° for 30 min., it was worked up according to the usual procedure. The basic product consisted of 11.2 g. of aniline–toluidine, b.p. 91–105° (27 mm.), and 1.2 g. of distillation residue. The aniline–toluidine mixture was analyzed[32] by gas chromatography (165°, 6 ft. of fire brick with 20% LAC-446).[33] The weight ratio (toluidine/aniline = 4.12, average) was obtained from the ratio of peak heights in comparison with mixtures of known composition containing toluidine comprised of 51% *ortho*, 13% *meta* and 36% *para*. The relative rate, $k_{toluene}/k_{benzene}$, was calculated[21] to be 3.7.

Isomerization Studies.—The following procedure was used for each of the toluidine isomers. A solution of toluene (92 g., 1 mole) and toluidine (10.7 g., 0.1 mole) was stirred

and cooled to below 20°. Concentrated sulfuric acid (9.8 g., 0.1 mole) was slowly added, forming the toluidine salt. Anhydrous aluminum chloride (25 g., 0.187 mole) was then added and the reaction mixture stirred for several minutes before removal of the ice-bath. The temperature was increased to 100° during 25 min. and kept at 100–105° for 30 min. During the heating period, anhydrous hydrogen chloride was passed into the reaction mixture periodically. The cooled reaction mixture was worked up according to the general procedure. An infrared spectrum of the basic product was taken both after removal of the ether and after distillation. No isomerization was indicated. The yields of pure recovered toluidine were 85% or greater, with no more than normal amounts of tarry residue. It was found that when the order of addition of sulfuric acid and aluminum chloride was reversed, a large amount of tar was obtained, but again no isomerization was indicated.

The same general procedure was followed for each of the chloroaniline isomers with the indicated amounts of reagents: chloroaniline, 12.76 g. (0.1 mole); chlorobenzene, 112.56 g. (1 mole); concentrated sulfuric acid, 9.8 g. (0.1 mole); anhydrous aluminum chloride, 26.67 g. (0.2 mole). The temperature of the reaction mixture was increased to 120° during 30 min. and then kept at 120–125° for 2 hr. Anhydrous hydrogen chloride was bubbled into the reaction mixture periodically. Ether was used during the work-up to facilitate the separation of the chlorobenzene and aqueous acid layers. Infrared analysis of the recovered chloroaniline indicated no isomerization had occurred in any case. Recovery of the crude chloroaniline was greater than 85% for the *m*- and *p*- isomers, but only 67% for the *o*-isomer. A repeat run with *o*-chloroaniline gave identical results.

o-Chloroaniline (12.76 g.) was dissolved in a solution consisting of 200 ml. of dilute hydrochloric acid and 9.8 g. of concentrated sulfuric acid. The resulting solution was made basic with a concentrated sodium hydroxide solution and the insoluble oil was extracted with ether. Removal of the ether from the dried extracts gave essentially a 100% recovery of crude *o*-chloroaniline indicating that the loss previously observed probably occurred during the heating of the reaction mixture, presumably due to a reaction peculiar to this isomer.

Toluidine Isomer Separation as Oxalate Salts.[2]—To 1 g. of oxalic acid was added enough anhydrous ether to completely dissolve the solid. This solution was then added to an ether solution of *o*-toluidine (0.5 g.), *m*- toluidine (0.15 g.) and *p*-toluidine (0.35 g.). The white precipitate which formed was filtered and washed with a small amount of anhydrous ether. The wash ether was added to the original filtrate.

The dried precipitate, wt. 1.49 g., was dissolved in 40 ml. of water and 12 ml. of acetic anhydride was added. Upon cooling and scratching, crystals formed which were filtered and dried; wt. 0.42 g., m.p. 137–147°. Infrared analysis of the crude product showed it to be essentially pure *p*-acetotoluide. The material was crystallized from aqueous ethanol; m.p. 146–150°. A mixture melting point with authentic *p*-acetotoluide was undepressed. The yield of product amounts to an 86% recovery of the *p*-toluidine originally present.

The original ethereal filtrate was evaporated to dryness yielding a yellow, semi-crystalline mass, wt. 0.38 g. Water (5 ml.) and acetic anhydride (3 ml.) were added forming a homogeneous solution from which no crystals could be obtained. No pure *o*- or *m*-acetotoluide was recovered.

Analytical Procedure.—The isomer distributions of toluidine and chloroaniline were determined by a modified baseline method.[34] Either a Perkin–Elmer model 21 or a Beckman IR-7 infrared spectrophotometer with sodium chloride optics was used. The absorbance was measured at the indicated wave length (μ):toluidine (*ortho*, 13.43; *meta*, 13.03; *para*, 12.35); chloroaniline (*ortho*, 13.52; *meta*, 13.08; *para*, 12.23). With either spectrophotometer, comparison of data from known and unknown mixtures showed the method to be accurate within ±1.5%.

(32) We are grateful to Dr. J. L. Foote for this analysis.
(33) Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

(34) R. L. Bohon, R. Isaac, H. Hoftiezer and R. J. Zellner, *Anal. Chem.*, **30**, 245 (1958).