conversion, pyruvamide-C^{14} was converted to pyruvic acid-C^{14} by the method of Thomas, *et al.*[9] The remaining steps in the conversion were carried out using the procedure of Calvin, *et al.*[10] The specific activities of toluene-1,3,5-C^{14} and toluene-2,4,6,7-C^{14} were 45.9 μc./mM. and 38.4 μ C./mM.

Unlabeled Pyruvamide.—It was necesary to prepare unlabeled pyruvamide in order to dilute the radioactive pyruvamide before further reaction. This was accomplished in three steps. Acetyl bromide was prepared by the reaction between phosphorus tribromide and acetic anhydride.[11] The acetyl bromide was converted to acetyl cyanide (pyruvonitrile) by reaction with cuprous cyanide.[12] The pyruvonitrile was carefully hydrolyzed to produce pyruvamide.

Preparation of Mononitrotoluene.—Toluene (130 g., 1.4 moles) was added dropwise to 475 g. of mixed acid (63.92% H_2SO_4 and 20.50% HNO_3) while the acid was stirred with a magnetic stirrer. The temperature was maintained at 25° during the first half of the addition and then raised to 34° during the second half. After the addition was completed, the temperature was raised to 55° over a 30-minute period. The reaction mixture then was separated by means of a separatory funnel. The top layer was mononitrotoluene (170 ml.).

Preparation of Dinitrotoluene.—The mononitrotoluene was added to 430 g. of mixed acid (63.77% H_2SO_4 and 23.44 % HNO_3). The acid was stirred with a magnetic stirrer, the temperature being maintained at 55°. Following the addition, the temperature was raised slowly to 75° and maintained at this level for 40 minutes. The mixture then was poured into a separatory funnel which was heated by means of an infrared lamp. The top layer was dinitrotoluene. The acid layer was isolated and added to ice-water to precipitate the dinitrotoluene which was dissolved in the acid. This dinitrotoluene was isolated by filtration and dried. All of the dinitrotoluene was combined (190 ml.).

Preparation of Trinitrotoluene, Isolation of Potassium Nitroform and Conversion to 1,1,1-Trinitroethane.—Oleum (100 g., 33–35% SO_3) was added to 65 g. of mixed acid (38.95% H_2SO_4 and 80.28% HNO_3) stirred at 70°. The dinitrotoluene was melted and kept in a liquid state in a dropping funnel by means of an infrared lamp and added dropwise to the acid mixture while the temperature was kept at 75°. After the addition, the temperature of the mixture was raised to 110° over a 30-minute period and kept at 110° for 45 minutes. The reaction mixture then was cooled to 75°, and 500 λ of unlabeled tetranitromethane was added. The reaction mixture was then sparged with nitrogen (600 ml./minute). A flow meter was inserted in the line to help maintain a constant flow of nitrogen. After passing through the reaction flask, the nitrogen was bubbled into 150 ml. of an ice-cold alcoholic potassium hydroxide solution (1 g./10 ml. of absolute alcohol). The yellow precipitate which appeared, potassium nitroform, was formed by the reaction of tetranitromethane from the reaction mixture with the potassium hydroxide. After the 30 minutes at 75°, the temperature was raised to 95° over the next 30 minutes while the sparging continued at the same rate. The trinitration mixture was poured into 2 liters of ice-water to precipitate the trinitrotoluene. The crude trinitrotoluene then was isolated by filtration. The crude potassium nitroform was isolated on a medium sintered glass filter and washed with anhydrous ethyl ether. The precipitate was then dissolved in acetone and transferred to a stoppered flask. The acetone was then evaporated. The precipitate was redissolved in 30 ml. of fresh acetone and 2 ml. of methyl iodide was added.[13] The stoppered flask was allowed to stand for 1 week. As the reaction proceeded, crystals of potassium iodide appeared on the walls of the flask. At the end of 1 week, the acetone was removed under reduced pressure. The precipitate was then dissolved in ether and transferred to a separatory funnel. The ethereal solution was washed with three 20 ml. aliquots of a sodium bisulfite solution (30 g./100 ml. of H_2O). The ethereal solution was dried over anhydrous $MgSO_4$, and then the ether was removed under reduced pressure. The crude 1,1,1-trinitroethane was purified by sublimation, m.p. 55.0–55.5° (uncor.).

Counting Instrument.—A Tricarb liquid scintillation counter equipped with two photomultiplier tubes in a coincidence circuit (Packard Instrument Co., LaGrange, Ill.) was used to radioassay all samples. The lower and upper discriminators were set at 10 volts and infinity, respectively. The high voltage was set at 1200 volts.

Counting System.—All samples were assayed using 5-dram screw-cap crystal-lite vials (Wheaton Manufacturing Co., Millville, N. J.). The counting system consisted of 50 mg. of either trinitrotoluene or 1,1,1-trinitroethane, and 20 ml. of toluene which contained 4 g. of 2,5-diphenyloxazole and 100 mg. of 1,4-bis-[2-(5-phenyloxazolyl)]-benzene per liter.

Acknowledgment.—The authors wish to express their gratitude to J. V. R. Kaufman, L. H. Eriksen and R. Frye for their encouragement and interest during this investigation, and are indebted to the Army Ordnance Corps for granting the release of this article for publication.

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[13] This reaction is similar to that reported by Hantzsch and Rinckenberger[2] who prepared the same compound by treating silver nitroform with methyl iodide in an ethereal solution.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, OHIO]

Aromatic Amination with Hydroxylammonium Salts. Reactivity and Directive Effects[1]

BY PETER KOVACIC, ROBERT P. BENNETT AND J. LINDSLEY FOOTE[2]

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A variety of hydroxylamine salts was found to aminate aromatic compounds in the presence of Friedel–Crafts catalysts. Toluene and the halobenzenes gave predominant *ortho–para* orientation with a comparatively high percentage of *m*- isomer. The amount of catalyst required varied with the nature of the salt. On the basis of the selectivity factors for the amination of toluene in the presence of aluminum chloride, an activity series may be formulated: $H_2NOH\cdot HBr \geqslant (H_2NOH)_2\cdot H_2SO_4 > H_2NOH\cdot C_2H_5OSO_3H > H_2NOH\cdot CH_3CO_2H > H_2NOH\cdot HCl > (H_2NOH)_3\cdot H_3PO_4 = H_2NOH$. From competitive amination with hydroxylammonium chloride, the relative rate, $k_{\text{toluene}}/k_{\text{benzene}}$, was found to be 2.9. Factors affecting orientation in the amination reactions are discussed.

The direct amination of aromatic compounds with hydroxylammonium chloride in the presence of Friedel–Crafts catalysts was reported independently by Graebe[3] and Jaubert[4] in 1901. The use of hydroxylammonium sulfate is described[5]

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[1] Part IV of a series on "Direct Aromatic Amination"; from the Ph.D. theses of R. P. Bennett and J. L. Foote, Case Institute of Technology, 1960; presented at the 140th Meeting of the American Chemical Society, September, 1961.

[2] National Science Foundation Fellow, 1958–1960.

[3] C. Graebe, *Ber.*, **34**, 1778 (1901).

[4] G. F. Jaubert, *Compt. rend.*, **132**, 841 (1901).

[5] J. Turski, (a) German Patent 287,756 (1914); *C. A.*, **10**, 2128 (1916); (b) British Patent 626,661 (1949); *C. A.*, **44**, 2761 (1950); (c) U. S. Patent 2,585,355 (1952); *C. A.*, **47**, 875 (1953).

TABLE I

HYDROXYLAMMONIUM SALTS AND TOLUENE

Hydroxylammonium salt	Mole	Catalyst,[a] mole	Time, min.	Toluidine, %				S_f
				Yield	*o*	*m*	*p*	
$(H_2NOH)_2 \cdot H_2SO_4$	0.1	0.187	5	1[b]				
$(H_2NOH)_2 \cdot H_2SO_4$	.1	.187	10	2	38	20	42	0.62
$(H_2NOH)_2 \cdot H_2SO_4$	.1	.4	30	8	37	22	41	.57
$(H_2NOH)_2 \cdot H_2SO_4$	.3	1.12	120	65	37	23	40	.54
$(H_2NOH)_3 \cdot H_3PO_4$	.2	0.4	120	0				
$(H_2NOH)_3 \cdot H_3PO_4$	.2	1.2	120	41	30	14	56	.90
$H_2NOH \cdot CH_3COOH$	.2	0.4	15	1				
$H_2NOH \cdot CH_3COOH$	.2	.6	120	32	33	19	48	.70
$H_2NOH \cdot C_2H_5OSO_3H$	.1	.2	120	10[b]	29	23	48	.62
$H_2NOH \cdot HCl$	.2	.4	120	36	30	18	52	.76
$H_2NOH \cdot HBr$	.219	.438	120	60	38	23	39	.53
$(H_2NOH)_3 \cdot HI$	.012	.035	120	14[b]				
$H_2NOH \cdot HCl$	.2	..[c]	90	0				
$H_2NOH \cdot HCl$	.188	.375[d]	120	19[e]	30	14	56	.90
$H_2NOH \cdot HBr$	.188	.375[d]	120	19[e]	30	14	56	.90
(H_2NOH)[f]	.3	1	20	37	31	14	55	.90

[a] $AlCl_3$, unless otherwise indicated. [b] Crude. [c] BF_3. [d] $AlBr_3$. [e] Bromotoluene was also obtained. [f] Ref. 6.

in the patent literature. Other derivatives of hydroxylamine, such as alkylhydroxylamines[6] and hydroxylamine-O-sulfonic acid,[7,8] have also proved effective.

The purpose of this investigation was to examine a variety of hydroxylamine salts as aminating agents for aromatic compounds in the presence of Friedel–Crafts catalysts. More specifically, it was desired to ascertain the influence of the anion of the salt on orientation, particularly in relation to the activity of the aminating species.

Results and Discussion

Part of the study was concerned with determination of suitable reaction times and effective catalyst/salt ratios. When the amination of toluene was carried out with a 2/1 molar ratio of aluminum chloride to hydroxylammonium sulfate, the reaction mixture formed a solid mass after a short period of heating. Toluidine, having an isomer distribution of 38% *ortho*, 20% *meta* and 42% *para*, was obtained in 1–2% yield. The reaction was repeated with a 4/1 molar ratio of catalyst to salt so that there would be a 2/1 ratio of aluminum chloride to each hydroxylamine of the salt. When the reaction mixture was heated for thirty minutes, an 8% yield of toluidine was obtained with a distribution of 37% *ortho*, 22% *meta* and 41% *para*. Increasing the reaction time to two hours resulted in a 65% yield of toluidine possessing essentially the same isomer distribution. In view of the pronounced dependence of yield on reaction time, it was decided to standardize the time at two hours.

The ethylsulfuric acid salt of hydroxylamine, $H_2NOH \cdot C_2H_5OSO_3H$, gave a 10% crude yield of toluidine (29% *ortho*, 23% *meta* and 48% *para*) in addition to ethyltoluene. The ethylsulfuric acid in the presence of aluminum chloride presumably was responsible for the alkylation reaction.

The reaction with the phosphate salt, $(H_2NOH)_3 \cdot H_3PO_4$, also demonstrated the importance of the appropriate catalyst/salt ratio. When the reaction was carried out at a 2/1 molar ratio, no toluidine was obtained. However, with a 6/1 ratio (a 2/1 ratio of catalyst to each hydroxylamine) a vigorous reaction occurred producing a 41% yield of toluidine, 30% *ortho*, 14% *meta* and 56% *para*. Distillation of the neutral fraction gave large amounts of xylene and higher disproportionation products along with much tar. The hydrocarbon products most likely are formed from exposure of toluene at 100° to large amounts of aluminum chloride and phosphoric acid.

In the investigation of hydroxylammonium acetate, another factor was discovered which must be considered in determining the proper amount of catalyst. At a 2/1 ratio of catalyst to salt, a solid mass soon formed and toluidine was isolated in only 1% yield. It was suspected that the liberated acetic acid was complexing with the aluminum chloride and thereby interfering with the amination reaction. When the reaction was repeated with a 3/1 ratio of aluminum chloride to salt, a 32% yield of toluidine was obtained (33% *ortho*, 19% *meta*, 48% *para*). Additional evidence for the presence of an aluminum chloride–acetic acid complex was provided by the identification of *p*-methylacetophenone (14% yield) as a reaction product.

From an investigation of the halogen acid salts, it is evident that the activity,[9] as measured by the selectivity factor,[10,11] $S_f = \log [(2 \times \%p)/\%m]$, decreases in the order, $H_2NOH \cdot HBr > H_2NOH \cdot HCl > H_2NOH$. Graebe, who used the oxalate method[7] of analysis, reported[3] a *para*/*ortho* ratio of 90/10 for toluidine obtained from hydroxylammonium chloride–toluene–aluminum chloride. The fluoride salt was omitted of necessity from the series since attempted preparations were unsuccessful. The iodide salt yielded a basic product whose infrared spectrum indicated the presence of an unknown amine in addition to toluidine.

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(6) P. Kovacic and J. L. Foote, *J. Am. Chem. Soc.*, **83**, 743 (1961).

(7) R. N. Keller and P. A. S. Smith, *ibid.*, **66**, 1122 (1944); **68**, 899 (1946).

(8) P. Kovacic and R. P. Bennett, *ibid.*, **83**, 221 (1961).

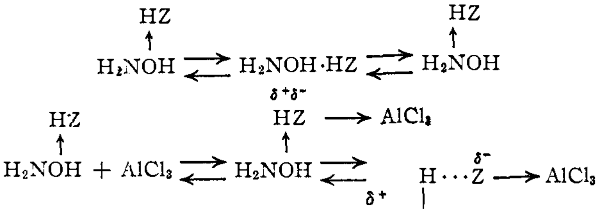
(9) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

(10) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(11) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959); H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955).

Furthermore, free iodine was obtained as a reaction product. The iodide salts of hydroxylamine are known[12-14] to be extremely unstable. Apparently, the hydrogen iodide acts as a reducing agent on hydroxylamine forming ammonia, nitrogen, iodine and water.

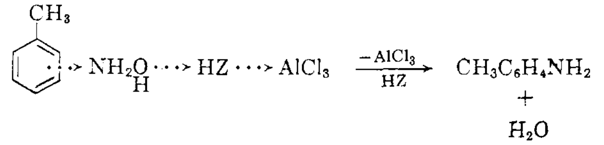
In a consideration of all the salts investigated, they can be arranged in this order of activity based on the selectivity factor: $H_2NOH \cdot HBr \geqslant (H_2NOH)_2 \cdot H_2SO_4 > H_2NOH \cdot C_2H_5OSO_3H > H_2NOH \cdot CH_3COOH > H_2NOH \cdot HCl > (H_2NOH)_3 \cdot H_3PO_4 = H_2NOH$. It is proposed that the activity of the salts is related to the extent of polarization of the H–Z bond by the catalyst (Z = anion of the acid). The extent of ionization of the H–Z bond in the complex $H_2NOH \cdot HZ \cdot AlCl_3$ will depend upon a number of factors—inherent ionization of the H–Z bond, stability of $AlCl_3Z^-$, ability of the catalyst to coördinate with Z. An increase in the polarization of the H–Z bond would be expected to produce a corresponding increase in the cationic character of nitrogen.



$$\overset{\overset{HZ}{\uparrow}}{H_2NOH} \rightleftharpoons H_2NOH \cdot HZ \rightleftharpoons \overset{\overset{HZ}{\uparrow}}{H_2NOH}$$

$$\overset{\overset{HZ}{\uparrow}}{H_2NOH} + AlCl_3 \rightleftharpoons \overset{\overset{\overset{\delta+\delta-}{HZ} \longrightarrow AlCl_3}{\uparrow}}{H_2NOH} \rightleftharpoons \underset{\overset{\delta+}{H_2N\cdots OH}}{\underset{|}{H\cdots\overset{\delta-}{Z}}} \longrightarrow AlCl_3$$

The predominant *ortho–para* orientation accompanied by a relatively high *meta* content suggests electrophilic substitution by an attacking species of high activity. As discussed in the case of hydroxylamine-O-sulfonic acid,[8] it is likely that amination proceeds *via* a concerted displacement reaction.



There are many complicating factors—the various sites available in the salt for coördination with the catalyst, the large amount of aluminum chloride required, the possibility of reaction of the salt with aluminum chloride to give $H_2NOAlCl_2$, dissociation of the salt to its component parts, anion interchange, cocatalytic effects and variation in the polarity of the medium with the type of salt used. The large requirement for aluminum chloride may be rationalized on the basis of conversion to $H_2NOAlCl_2$, or reaction with the products formed, namely, aromatic amines and water. The observed evolution of acid gas may result from one or more of these reactions. Since there is evidence for the intermediate involvement of $H_2NOSO_2OAlCl_2$ in the hydroxylamine-O-sulfonic acid reaction,[7,8] similar considerations may be applied to the present case with respect to $H_2NOAlCl_2$. Although the amount of dissociation of the various salts to free hydroxylamine under the reaction conditions is not known, some of the salts used, *e.g.*, iodide and phosphate,[15] are reported to dissociate quite readily on heating.

Additional evidence relative to the activity of the attacking species was obtained from the competitive amination of toluene and benzene with hydroxylammonium chloride. From the amounts of toluidine and aniline formed, the relative rate, $k_{toluene}/k_{benzene}$, was calculated[16] to be 2.9. This value, which indicates a highly reactive aminating species, agrees very well with the figure (3.2) obtained from calculations[10] involving the selectivity factor, and also is in the same range as the relative rate (3.7)[8] for hydroxylamine-O-sulfonic acid. A plot of log p_f (0.95), calculated[10] from the relative rate, *versus* S_f yields a good fit to the linear relationship shown[11] to exist between these quantities for electrophilic substitution in toluene. Similarly, the plot for amination with hydroxylamine-O-sulfonic acid[8] (log p_f = 0.90) is in accord with the linear relationship.

Aminations with hydroxylammonium chloride and bromide were also carried out with aluminum bromide as the catalyst. It was found that toluidine was produced in low yields (19%) and that, surprisingly, both salts gave the same isomer distribution: 30% *ortho*, 14% *meta* and 56% *para*. Several factors should be considered in an interpretation of the data: the relative donor properties[17] of the salt anions, the relative ionization of HCl and HBr, and the possibility of exchange reactions involving the salt anion and the catalyst. Although aluminum chloride gave a lower S_f value than aluminum bromide in the hydroxylammonium chloride reaction, the evidence in other cases[18-21] indicates that aluminum bromide is the stronger of the two catalysts. Bromotoluene, which was also formed in the reactions involving aluminum bromide, might arise according to the sequence

$$AlBr_3 + H_2O \longrightarrow HOAlBr_2 + HBr$$

$$H_2NOH \cdot HBr \longrightarrow H_2NOH + HBr$$

$$H_2NOH + 2HBr \longrightarrow NH_3 + Br_2 + H_2O$$

$$C_6H_5CH_3 + Br_2 \xrightarrow{AlBr_3} CH_3C_6H_4Br + HBr$$

The amination of toluene by hydroxylammonium chloride was attempted with boron trifluoride as the catalyst. When boron trifluoride was bubbled continuously through the hot reaction mixture, the hydroxylammonium chloride under-

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[12] M. Adams, *Am. Chem. J.*, **28**, 198 (1902).

[13] W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **69**, 839 (1896).

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[17] H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **77**, 5584 (1955).

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[21] (a) R. E. Burk, "Twelfth Report of the Committee on Catalysis," National Research Council, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 251; (b) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 875.

TABLE II

HYDROXYLAMMONIUM CHLORIDE–ALUMINUM CHLORIDE WITH HALOBENZENES AND PHENOL[a]

$H_2NOH \cdot HCl$, mole	C_6H_5Z, Z =	Moles	Temp., °C.	Time, min.	$H_2NC_6H_4Z$ Yield,[b] %	B.p., °C. (mm.)	$n^{25}D$	% *o*	*m*	*p*	S_f
0.2	F	2	83–84	120	61[c]	83–94 (33)		36	26	38	0.47
.8	Cl	8	95–124	100	61[d,e]	96–120 (20)	1.5886	47	17	36	.63
.16	Br	1.6	115–125	105	62[f,g]	105–130 (18–20)	1.6179	45	16	39	.69
.3[h]	OH[i]	0.3	68–92	120	7[j,k]						

[a] Toluene–aluminum chloride–hydroxylammonium chloride = 10/2/1 molar ratio. [b] Based on the aminating agent. [c] Plus 3.5 g. of amorphous solid (does not contain nitrogen). [d] *Anal.* Calcd. for C_6H_6NCl: N, 10.98; Cl, 27.79. Found: N, 10.71; Cl, 27.63. [e] Plus 3.1 g. of amorphous solid. [f] Including 4.2 g. of aniline. [g] Plus 2.6 g. of amorphous solid. [h] 0.9 mole of aluminum chloride was used. [i] *n*-Heptane, 300 ml., was added to keep the mixture fluid. [j] Sodium bicarbonate was used in place of sodium hydroxide to render the solution basic. [k] Apparently crude aminophenol (based on the infrared spectrum).

went a change in appearance, but there was no evidence for formation of aminated product. Muetterties reported[22] that hydroxylammonium chloride and boron trifluoride–etherate form a complex in which coördination is believed to involve the nitrogen. If the same complex is the preferred form under the amination conditions, this could explain the lack of reaction, on the assumption that association of the catalyst with the oxygen is a prerequisite for amination. Keller and Smith found[7] that with this same catalyst only a trace of aminated product resulted from toluene and hydroxylamine-O-sulfonic acid. A recent report[23] concerning the catalytic effectiveness of various Lewis acids showed boron trifluoride to be relatively ineffective.

Hydroxylammonium chloride was also used for the amination of halobenzenes (Table II). In comparison with the toluene procedure the conditions were somewhat more drastic. Of the aromatic compounds studied, the halobenzenes produced the highest yields (61–62%) of aminated product.

Various aspects of the orientation resulting from amination in the halobenzene series are worthy of discussion. The high *meta* content is similar to that obtained with hydroxylamine-O-sulfonic acid.[8] Amination resembles other processes of electrophilic substitution in the halobenzene series in that fluorobenzene yields the lowest *ortho/para* ratio[24] (Table III). The increasing amount of *ortho* substitution as the atomic number of the halogen increases has been encountered with other electrophilic reagents,[26,27] and is explained on the basis of the inductive effect of the substituent. Of particular interest is the relatively high degree of *ortho* orientation in the aminations of halobenzenes—significantly higher than for the other reactions listed.

TABLE III

Ortho/Para RATIOS

Reaction	Agent	*o/p* from C_6H_5X, X = F	Cl	Br	I	CH_3	Ref.
Amin.	$H_2NOH \cdot HCl$	0.94	1.30	1.15		0.58	
Nitrn.	HNO_3	.14	0.43	0.61	0.69	1.14	25
Chlorn.	$FeCl_3$	<.05	.12	.15	1.00	0.15	26
Chlorn.	$SbCl_5$	.04	.18	.34	1.00	0.92	27
Chlorn.	Cl_2		.52			2.77	27
Bromn.	Br_2		.13			0.66	25
Sulfon.	H_2SO_4		0			0.52	25

It is instructive to compare toluene and chlorobenzene in relation to the *ortho/para* ratios arising from electrophilic substitution (Table III). The evidence shows that the *ortho/para* ratio for a given reaction is lower for chlorobenzene, except in the case of amination. These observations suggest that an *ortho* coördination effect, involving the nuclear chlorine and a positive site in the attacking reagent, *e.g.*, $H_2NOAlCl_2 \cdot HCl \cdot AlCl_3$, might play a role in the *ortho* amination of chlorobenzene.

Bromoaniline isolated from the bromobenzene reaction possessed an isomer distribution similar to that of the chloroaniline product. However, the presence of aniline in the reaction mixture clouds the significance of the analytical data. Since bromobenzene probably underwent a disproportionation reaction[28,29] yielding benzene and dibromobenzene, the aniline might arise from benzene, and the bromoaniline to some extent from aniline. In addition, aniline may have been formed from bromoaniline. A side-reaction occurred with all of the halobenzenes leading to amorphous solid insoluble in acid or organic solvents.

Hydroxylammonium chloride was investigated as an aminating agent for phenol. Although attempts to purify the crude product were not successful, it did appear to contain aminophenol isomers on the basis of the isolation procedure and comparison of the infrared spectrum with the spectra of authentic aminophenols. The large amount of tar isolated from the reaction mixture and the low recovery of phenol point to the occurrence of side reactions.

The individual toluidine[6] and chloroaniline isomers were stable to rearrangement by aluminum chloride under simulated reaction conditions.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation for support of part of this work.

Experimental[30]

Materials.—Commercially available materials were used where possible. Toluene, chlorobenzene and bromobenzene were distilled and dried before use.

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[22] E. L. Muetterties, *Z. Naturforsch.*, **12b**, 265 (1957).

[23] G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4834 (1959).

[24] Although the fluorobenzene amination was carried out at somewhat lower temperatures than for chlorobenzene, the lower *ortho* orientation for fluoroaniline is probably not a temperature effect entirely.

[25] A. F. Holleman, *Chem. Revs.*, **1**, 187 (1924).

[26] P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

[27] P. Kovacic and A. K. Sparks, *ibid.*, **82**, 5740 (1960).

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[29] F. Fairbrother and N. Scott, *Chemistry & Industry*, 998 (1953).

[30] Melting and boiling points are uncorrected; microanalyses were performed by Drs. Weiler and Strauss, Oxford, England.

Hydroxylammonium Bromide.—The procedure[12] of Adams was used for preparation of the salt, 60% yield, m.p. 137.5–138.5° dec.

Anal.[12] Calcd. for $H_2NOH \cdot HBr$: equiv. wt., 56.98. Found: equiv. wt., 56.70.

Hydrogen Iodide Salt of Hydroxylamine.—The procedure[12] of Adams was used for preparation of the salt, m.p. 97–99° dec.; lit.[14] for $H_2NOH \cdot HI$, m.p. 83–84° (dec.); lit. for $(H_2NOH)_3 \cdot HI$, m.p. *ca.* 100° dec.[13] and 103–104°.[31]

Hydroxylammonium Phosphate.—The method[15] of Uhlenhuth gave the salt in 91% yield, m.p. 157.5–158.5° dec.

Anal. Calcd. for $(H_2NOH)_3 \cdot H_3PO_4$: N, 21.33; P, 15.72. Found: N, 21.22; P, 15.31.

Hydroxylammonium ethyl sulfate was obtained in 76% yield according to the reported procedure,[32] m.p. 101–103° dec., lit.[32] m.p. 102.5° dec.

General Procedure for Amination.—The general procedure and identification of products are basically the same as previously reported.[8] The data are outlined in Tables I and II. In the reaction of hydroxylammonium chloride with chlorobenzene the cooled reaction mixture was poured onto ice and sufficient concentrated sodium hydroxide solution was added to dissolve the aluminum hydroxide. The separated aqueous layer was extracted with ether which was then combined with the organic layer. The organic layer was extracted with hydrochloric acid and the usual procedure was then followed.

Distillation of the dried neutral fraction usually yielded only recovered toluene and slight traces of xylene disproportionation product. The reaction with hydroxylammonium phosphate also produced 17.6 g. of xylene, b.p. 134–145°, identified by infrared analysis, and 22.1 g. of viscous brown tar which would not distil at 135° (13 mm.). The reactions with hydroxylammonium chloride or bromide in the presence of aluminum bromide produced 19.76 g. and 18.05 g., respectively, of bromotoluene, b.p. 62–71° (14 mm.), n^{20}_D 1.5506, identified by comparison of the spectrum with those of the authentic bromotoluene isomers.

A by-product from the amination by hydroxylammonium ethyl sulfate was a mixture of ethyltoluene isomers in 39% yield, b.p. 51–54° (17 mm.), n^{20}_D 1.4951. The infrared spectrum was consistent with those[33] of the authentic ethyltoluene isomers.[34]

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.51; H, 9.82.

The hydroxylammonium acetate reaction also produced methylacetophenone in 14% yield, b.p. 108.5–109° (21 mm.), n^{20}_D 1.5324; lit.[35] for *p*-methylacetophenone, b.p. 93.5° (7 mm.), n^{20}_D 1.5335.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.70; H, 7.96.

Infrared analysis showed the sample to be exclusively *p*-methylacetophenone. The 2,4-dinitrophenylhydrazone was prepared and crystallized from acetic acid, m.p. 250–252°, lit.[36] m.p. 252–253°.

The reaction of bromobenzene with hydroxylammonium chloride also yielded 10 g. of benzene, 59.8 g. of dibromobenzene and 5.4 g. of residue in addition to recovered bromobenzene.

The amination of phenol by hydroxylammonium chloride produced 19 g. of black viscous residue in addition to recovered phenol.

Competitive Amination of Benzene–Toluene with Hydroxylammonium Chloride.—A mixture of anhydrous aluminum chloride (294 g., 2.2 moles), benzene (429 g., 5.5 moles), toluene (506 g., 5.5 moles) and hydroxylammonium chloride (76.5 g., 1.1 moles) was heated at 75–78° for 2 hr. and then worked up in the usual manner. The basic product consisted of an aniline–toluidine mixture, 19.1 g., b.p. 89–103° (31 mm.), and distillation residue (0.7 g.). The aniline–toluidine mixture was analyzed by gas chromatography as previously described.[8] A weight ratio, toluidine/aniline, of 3.34 was obtained with the toluidine standard consisting of 30% *ortho*, 18% *meta* and 52% *para* isomer. The relative rate, $k_{toluene}/k_{benzene}$, was calculated[16] to be 2.9.

Isomerization Studies with Chloroanilines.—The procedure, previously described,[6] involved use of *o*-, *m*- or *p*-chloroaniline (0.1 mole), chlorobenzene (2 moles), aluminum chloride (0.4 mole), water (0.1 mole) and hydrogen chloride. On the basis of infrared analysis, no isomerization of the individual isomers occurred. The recoveries obtained were: *ortho* (84%), *meta* (96%), *para* (97%).

Isomer Distributions.—The procedure for the quantitative determination of isomer distributions has been reported previously.[8] The following peaks (μ) were taken as characteristic: bromoaniline (*ortho*, 14.0; *meta*, 13.1; *para*, 12.7); fluoroaniline (*ortho*, 13.45; *meta*, 13.1; *para*, 12.1). The data for the fluoroaniline standards were corrected for the *meta* contaminant (7.5%) present in *o*-fluoroaniline. The method was shown to be accurate within ±1.5% except for *m*-fluoroaniline (±4%).

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE 12, R. I.]

The Mechanism of the Oxidation of Some Aromatic Amines by Peroxyacetic Acid

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The rates of oxidation of phenylhydroxylamine, aniline and three ring-substituted anilines by peroxyacetic acid have been measured. The oxidations follow second-order kinetics, being first order in each reactant. The Hammett relationship is followed with a ρ value of -1.86 in solvent ethanol. The dependence of rates on temperature has been studied; the energies of activation are low (12 to 16 kcal. mole^{-1}) and the entropies of activation are highly negative (-23 to -26 cal. mole^{-1} deg.$^{-1}$). Methylmethacrylate, an effective radical trap, does not inhibit the rate of reaction. *p*-Nitroaniline reacts about 25 times faster in water than in ethanol. There is a slight decrease in rate when the solvent is changed from H_2O to D_2O. Phenylhydroxylamine reacts faster than would be expected on the basis of its basicity and polarizibility. These results are consistent with a bimolecular nucleophilic attack of the amine on the outer oxygen of peroxyacetic acid.

Introduction

The oxidation of aromatic amines to phenylhydroxylamines and nitroso-, nitro-, azo- and azoxy-compounds with organic peracids has been reported by several groups of workers.[1–8]

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