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CONVERSION OF METHYLCYCLOHEXANE TO 1-AMINO-1-METHYLCYCLOHEXANE BY TRICHLORAMINE–ALUMINUM CHLORIDE[1,2]

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Abstract—Methylcyclohexane underwent amination to 1-amino-1-methylcyclohexane on treatment with trichloramine and aluminum chloride. The simple procedure resulted in yields as high as 82% based on trichloramine Several reaction variables were studied: solvent, temperature, catalyst, and reagent concentration. A practical system entails C_7H_{14}–$AlCl_3$–NCl_3 (2:2:1) in methylene chloride at $0 \pm 5°$. Investigation of the neutral fraction revealed the presence of 1-chloro-1-methylcyclohexane, in addition to oligomers and polymer. Mechanistically, the reaction is believed to proceed *via* hydride abstraction with subsequent interaction of the methylcyclohexyl cation with the nitrogen-containing nucleophile. This direct amination of a t-alkane constitutes a useful, new synthesis for t-carbinamines.

THE trichloramine–aluminum chloride combination represents a versatile system for the amination of organic compounds. Most of our prior efforts in this area have been concerned with aromatic substrates. The unusual specificity of the reagent is indicated by the intriguing orientation which results, e.g. *ortho-para* directive groups gave rise to *meta* amination.[4–10] This paper reports a novel method for preparation of the t-alkyl amine functionality by use of a t-alkane in this system. The principal emphasis of the present study, which employs methylcyclohexane as the model alkane, is on the synthetic and mechanistic aspects.

RESULTS AND DISCUSSION

Amination of methylcyclohexane with trichloramine was carried out at low temperatures in the presence of aluminum chloride catalyst. After a solution of the halamine in methylene chloride was added to a suspension of the alkane and catalyst, a simple work-up procedure provided 1-amino-1-methylcyclohexane in good purity. With appropriate control of reaction variables, yields as high as 82% were realized, based on trichloramine. Characterization was accomplished by comparison with

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[1] Paper X, Chemistry of N-Halamines.

[2] For a preliminary report, see P. Kovacic, R. J. Hopper, S. S. Chaudhary, J. A. Levisky and V. A. Liepkalns, *Chem. Commun.* 232 (1966).

[3] Postdoctoral Research Associate, 1965–1966.

[4] P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky and R. M. Lange, *J. Am. Chem. Soc.* **87**, 1262 (1965).

[5] P. Kovacic, J. A. Levisky and C. T. Goralski, *J. Am. Chem. Soc.* **88**, 100 (1966).

[6] P. Kovacic and J. A. Levisky, *J. Am. Chem. Soc.* **88**, 1000 (1966).

[7] P. Kovacic and J. F. Gormish, *J. Am. Chem. Soc.* **88**, 3819 (1966).

[8] V. L. Heasley, P. Kovacic and R. M. Lange, *J. Org. Chem.* **31**, 3050 (1966).

[9] P. Kovacic and A. K. Harrison, *J. Org. Chem.*, **32**, 207 (1967).

[10] P. Kovacic, K. W. Field, P. D. Roskos and F. V. Scalzi, *J. Org. Chem.*, in press.

literature data and with authentic material prepared from 1-methylcyclohexene by the Ritter method.

Certain reaction variables were explored with the aim of ascertaining the optimum conditions and obtaining information as to the nature of the reaction (Table 1). Some attention was devoted to an investigation of the potency of various metal halides as catalysts. It is evident that a powerful Friedel–Crafts catalyst is required. Studies of the effect of variation in the $AlCl_3$–NCl_3 molar ratio were carried out in ethylene dichloride solvent. The yield of desired base attained a maximum at a ratio of two and then remained constant with further increase in the amount of catalyst. The question of the large catalyst requirement has been treated elsewhere.[4,7]

TABLE 1. REACTION VARIABLES

	Basic product	
	1-Amino-1-methylcyclohexane, yield, %	Distillation residue, % of crude base
	Catalyst studies[a]	
Catalyst		
$AlCl_3$	66	19
$AlCl_3$[b]	61	36
$AlBr_3$	42	32
$SbCl_5$[c]	9	50
$TiCl_4$[c]	trace	trace
none	0	0
	Variation in $AlCl_3$–NCl_3 *Ratio*[a,d]	
$AlCl_3$–NCl_3, *molar*		
1	25	15
2	54	19
4	53	23
	Temp effect[a]	
Temp, °C		
−25 to −20	66	18
0	66	19
25	52	22
	Solvent effect[e]	
Solvent		
CH_2Cl_2	66	19
$ClCH_2CH_2Cl$	54	21
o-$C_6H_4Cl_2$[f]	39	35
	Variation in C_7H_{14}–NCl_3[a]	
C_7H_{14}–NCl_3, *molar*[g]		
10	66	18
7	67	21
5	68	22
3	66	24
2	69	22
1	26	11

Table 1—cont.

	Basic product	
	1-Amino-1-methyl-cyclohexane, yield, %	Distillation residue, % of crude base
	Miscellaneous variables	
Procedure[a, e]		
A	66	18
A[h]	69	18
A[i]	74	16
A[i–k]	81	14
A[l]	72	22
B	80	18
B[m]	76	22
B[k]	82	12
B[n]	29	41

[a] See general procedure, method A.

[b] Isopropyl bromide (0·2 mole) was added to the mixture before the introduction of trichloramine.

[c] An insoluble precipitate formed on basification.

[d] Ethylene dichloride was used as the solvent for trichloramine.

[e] See general procedure, method B.

[f] 195 ml, 7–11°.

[g] The volume was made equal to that for the 10:1 experiment in all other cases by the addition of methylene chloride to the methylcyclohexane in the beginning.

[h] The crude base was steam distilled as part of the work-up.

[i] Nitrogen purge during reaction.

[j] Methylcyclohexane, 0·5 mole; purified ether was used; product distillation was carried out at 20 mm.

[k] 4 × scale.

[l] Methylcyclohexane, 0·2 mole.

[m] The mixture was worked up soon after reaction.

[n] Reverse addition; methylcyclohexane was added to a mixture of trichloramine and aluminum chloride in methylene chloride.

Amination was found to proceed within the 50° range, −25 to 25°, although the yield of purified amine was greatest at 0° and −25°.

In relation to the effect of solvent, we observed that halogenated alkanes and *o*-dichlorobenzene could be used, with methylene chloride being preferred. Peak yields were obtained at a methylcyclohexane–trichloramine molar ratio of two with no further improvement even with a large excess of the hydrocarbon. It is clear from analysis of the neutral fraction that substrate is also being consumed in side-reactions leading to oligomers and polymer.

In a study of miscellaneous variables, a beneficial effect on yield was noted when a nitrogen purge was maintained during reaction. The reason may be the removal of hydrogen chloride which is known to decompose trichloramine.[11] Gross destruction of the halamine reactant can also be used as an interpretation of the poor results

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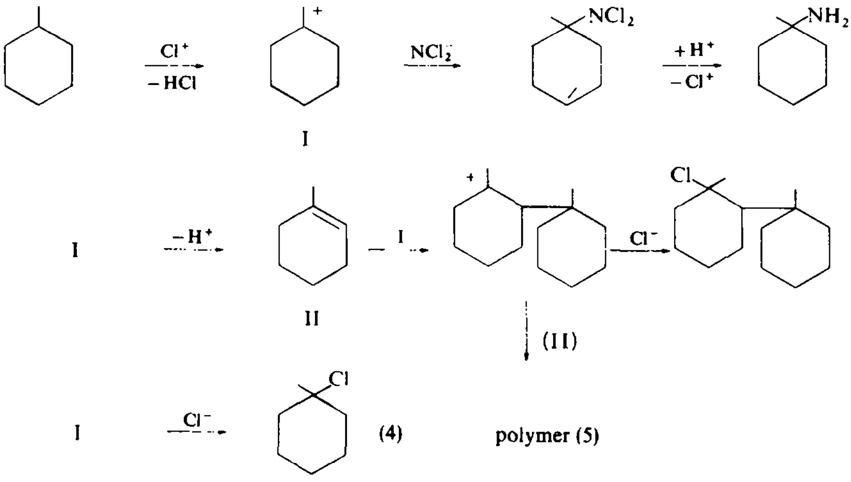
[11] W. A. Noyes, *J. Am. Chem. Soc.* **42**, 2173 (1920).

obtained from the method of inverse addition. The work-up procedure was also subjected to scrutiny. In a summation of the experimental data, considering the practical aspects we would recommend the conditions, C_7H_{14}–$AlCl_3$–NCl_3 = 2:2:1 (molar), 0 ± 5° (72% yield, 36% based on alkane). The results from investigation of reaction variables parallel in many cases those previously observed with aromatic substrates.[4, 7, 9]

With this experimental background, it is now appropriate to consider the mechanistic aspects of the amination reaction. Our working hypothesis is illustrated for the pathways leading to 1-amino-1-methylcyclohexane and the neutral products.

$$NCl_3 + AlCl_3 \rightleftharpoons Cl_3N \cdots > AlCl_3 \rightleftharpoons Cl\delta^+(Cl_2NAlCl_3\delta^-) \qquad (1)$$



(2)

(3)

This postulate receives support from a variety of sources. A control experiment demonstrated that amination does not proceed when the catalyst is omitted. In the absence of alkane, a mixture of aluminum chloride and trichloramine in methylene chloride reacted with evolution of chlorine. Presumably chloronium ion interacts with chloride ion. When methylcyclohexane is present the chloronium moiety apparently effects hydride abstraction. Effluent gas was found to contain hydrogen chloride, but no chlorine. The ensuant tertiary carbonium ion is then attacked by a nitrogen-containing nucleophile. Currently the NCl_2^- ion is tentatively designated as the active species.[5, 12] Since there was no evidence at the conclusion of reaction for the presence of the N-chloro derivative of 1-amino-1-methylcyclohexane, this intermediate, if it is formed, must then undergo subsequent, rapid transformation. Analogy for the step involving carbonium ion formation may be found in the bromination of adamantane.[13] This result from the literature has been ascribed to initial abstraction of hydride by bromonium ion. Additional support for an ionic pathway in the present work is provided by the observation that reaction proceeds nicely at quite low temperatures.

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[12] P. Kovacic and M. K. Lowery, *Chem. Commun.* 651 (1966).

[13] R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.* **64**, 287 (1964).

An attempt was made to promote the conversion of methylcyclohexane to the corresponding tertiary carbonium ion by inclusion of isopropyl bromide[14] in the reaction mixture. However, the experiment failed to increase the yield of the t-alkyl amine.

The reaction mixtures also afforded various amounts of by-product amine mostly in the form of distillation residue. It is reasonable to surmise that these materials arise from interaction of the nitrogen-containing nucleophile with carbonium ion species formed during the propagation phase of the polymerization side-reaction (Eqs. 3 and 5). We also obtained evidence that chloride to a minor extent was a constituent of the basic fraction since a small amount of 1-amino-1-methylcyclohexane hydrochloride was isolated from the distillation residue. Apparently the halogen-containing amine product generates hydrogen chloride on standing and during fractionation. Even after steam distillation the volatile base was found to contain chlorine. Various hypotheses can serve to account for the presence of halogen. As an example, Coleman and co-workers demonstrated that trichloramine adds to olefins with formation of β-chloroalkylamines.[15] Application to our system would involve a hypothetical methylcyclohexene as the precursor. GLC analysis of the distilled, main product revealed a few per cent of unidentified contaminants. The impurities may be isomeric methylcyclohexylamines, ethylcyclopentylamine, or dimethylcyclopentylamines. It is relevant that the 6-membered ring is markedly favored in the acid-catalyzed equilibration of cyclohexane-methylcyclopentane.[16]

Investigation of the neutral products aided in illuminating the theoretical aspects. The presence of 1-chloro-1-methylcyclohexane can be attributed to intermediacy of the methylcyclohexyl cation. Cationic polymerization of 1-methyl-cyclohexene, a postulated labile intermediate, would account for the formation of oligomers and polymers.[17] This scheme is in accord with analytical data which reveal a decrease in chlorine content with increase in molecular weight.

Other studies in this laboratory involving various classes of organic compounds with this same system reveal striking similarities to the present work. Closest resemblance is found in the side-chain amination of *p*-cymene leading to 8-amino-*p*-cymene.[14] t-Alkyl chlorides are smoothly transformed to the corresponding t-alkyl amines.[12] In addition, nuclear amination of aromatic substrates gave rise to unusual orientation.[4, 5, 7, 9, 10] The results from these diverse systems have been rationalized by a common mechanistic feature—combination of an intermediate carbonium ion with a nitrogen-containing nucleophile.

Let us next focus the discussion on the significance of our findings in relation to the synthetic aspects. The literature contains few reports dealing with the direct amination of alkanes. Mention will be made of several which have come to our attention. Recently Ogata *et al.* disclosed that photochemical amination of cyclohexane with hydrazine gave rise to cyclohexylamine in 45% yield.[18] Isopropylamine was one of

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[14] P. Kovacic and R. J. Hopper, *Tetrahedron* **23**, 3965 (1967).

[15] G. H. Coleman, G. M. Mullins and E. Pickering, *J. Am. Chem. Soc.* **50**, 2739 (1928).

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

[17] [a] W. J. Roberts and A. R. Day, *J. Am. Chem. Soc.* **72**, 1226 (1950); [b] D. N. Kursanov, V. N. Setkina, S. V. Vitt and Z. N. Parnes, *Problemy Kinetiki i Kataliza, Akad. Nauk S.S.S.R.* **9**, 242 (1956); [c] P. Kovacic, S. T. Morneweck and H. C. Volz, *J. Org. Chem.* **28**, 2551 (1963).

[18] Y. Ogata, Y. Izawa and H. Tomioka, *Tetrahedron* **22**, 483 (1966).

the products formed from photolysis of ammonia in the presence of propane and oxygen.[19]

In terms of preparative utility, the present method displays marked promise. Only a very limited number of convenient procedures are available for preparation of t-carbinamines.[20] Of these the Ritter reaction, which commonly utilizes an olefin or carbinol in a two-stage sequence, appears to have received the most attention. As applied to 1-amino-1-methylcyclohexane various substrates have been used as part of the Ritter technique with the indicated results, 1-methylcyclohexene[21,22] (35%) (58% in present work), 1-methylcyclohexanol[22-25] (60–76%), 1-chloro-1-methylcyclohexane[22] (12%), and related cyclohexane and cyclopentane derivatives.[22,24,25] Other methods which are known to provide this amine include: the Schmidt reaction with 1-methylcyclohexanecarboxylic acid[26] (42–45%), the Hofmann reaction with 1-methylcyclohexanecarboxamide[27] (60%), and nitration of methylcyclohexane followed by reduction[23,27,28] (14–19%).

Thus, it is evident that amination of a t-alkane with trichloramine-aluminum chloride provides a simple procedure for the synthesis of the corresponding t-carbinamine in reasonable yield.[29] A type of organic substrate not previously used is now available as the immediate precursor for t-alkyl amines.

EXPERIMENTAL[30]

Materials. Ethylene dichloride and *o*-dichlorobenzene were distilled from calcium hydride. Triethylenetetramine (Eastman) was fractionated, b.p. 175–178°/50 mm. Methylcyclohexane (Eastman pure grade) was used without further purification. The other materials were high purity grades which were used as obtained.

Analytical procedures. The IR spectra were taken with a Beckman IR-8 spectrophotometer, and the NMR spectra with a Varian A-60 or A-60A instrument. Neat samples were used. GLC studies were carried out on a home-made unit with the indicated columns: (A) 10 ft by ¼ in., Carbowax 6000 (15%) on Chromosorb W (40–60 mesh) (10% NaOH); (B) 10 ft by ¼ in., Apiezon L (10%) on acid-washed firebrick (60–80 mesh).

Preparation of trichloramine. Trichloramine solns were prepared according to a published method (B).[4] The soln can be stored in a colored bottle at 0° for several days without any appreciable change in strength. Caution: exercise the necessary precautions when working with N-halamines.

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[19] H. Gesser. *J. Am. Chem. Soc.* **77**, 2626 (1955).

[20] P. A. S. Smith, *The Chemistry of Open-Chain Organic Nitrogen Compounds* Vol. I. Chap. 2, Benjamin, New York, N.Y. (1965); R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry* Chap. 24. Wiley, New York, N.Y. (1953).

[21] A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *J. Am. Chem. Soc.* **79**, 4729 (1957).

[22] W. Haaf, *Chem. Ber.* **96**, 3359 (1963).

[23] H. J. Barber and E. Lunt, *J. Chem. Soc.* 1187 (1960).

[24] R. Jacquier and H. Christol, *Bull. Soc. Chim. Fr.* 556 (1954).

[25] M. Mousseron, R. Jacquier and H. Christol, *C.R. Acad. Sci., Paris* **235**, 57 (1952); R. Jacquier and H. Christol, *Bull. Soc. Chim. Fr.* 600 (1957).

[26] [a] C. Schuerch, Jr., and E. H. Huntress, *J. Am. Chem. Soc.* **71**, 2233 (1949); [b] H. E. Baumgarten, F. A. Bower and T. T. Okamoto, *Ibid.* **79**, 3145 (1957).

[27] K. E. Hamlin and M. Freifelder, *J. Am. Chem. Soc.* **75**, 369 (1953).

[28] S. Nametkin, *J. Russ. Phys. Chem. Soc.* **42**, 691 (1909); *Chem. Abstr.* **5**, 3246 (1911).

[29] Current investigation of the scope indicates that other t-alkanes undergo amination by this procedure.

[30] M.ps and b.ps are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee; we are grateful to Mr. V. A. Liepkalns and Dr. F. V. Scalzi for assistance during the preliminary stages.

Amination of methylcyclohexane

General procedure. A. The apparatus consisted of a 1 l., 3-neck flask fitted with a paddle stirrer, condenser, thermometer, and an addition funnel having an extension for below-surface addition. A cold soln of trichloramine (0·1 mole in about 160 ml CH_2Cl_2) was added during 40–50 min to a suspension of $AlCl_3$ (26·6 g, 0·2 mole) in methylcyclohexane (98 g, 1 mole) at 0 ± 5°. Stirring was continued for another 20 min at the same temp. The dark brown reaction mixture was poured with stirring into 500 g ice containing 30 ml conc HCl. After standing, usually overnight, the layers were separated, and the organic portion was washed with dil HCl. The combined aqueous phase was thoroughly washed with ether,[31] made strongly basic with 50% NaOH aq, and then extracted several times with ether. Removal of solvent on a steam cone from the dried ethereal soln provided the crude basic product. The last portion of solvent was removed under reduced press.

Distillation was accomplished with a Minilab Vigreaux column, b.p. 62–63°/50 mm. The principal peak in gas chromatography (column A) comprised >95% of the total area. Further purification can be effected with good recovery by drying over caustic pellets and then distilling through an helices-packed or spinning-band column. In most cases duplicate runs were made, which were in satisfactory agreement.

B. In some cases a nitrogen purge was maintained at a moderate rate[32] throughout the reaction. Addition of triethylenetetramine[33] (20% by weight of crude base) prior to distillation alleviated bumping and exerted some favorable influence on yield.

In one case (5 × standard scale) the crude amine deposited 0·4 g solid, m.p. 278°, dec, when allowed to stand overnight. After fractionation of the liquid portion, the residue was diluted with ether and filtered. After thorough washing with ether, the solid weighed 1·3 g, m.p. 278°, dec, was soluble in water, and gave a positive test with $AgNO_3$. The total yield of salt was about 2%. The IR spectrum was identical to that of authentic 1-amino-1-methylcyclohexane hydrochloride, and the mixture m.p. showed no depression. Treatment of the salt with caustic liberated a base which was shown to be 1-amino-1-methylcyclohexane.

The base obtained from steam distillation of the crude amine was also analyzed for halogen. Following fractionation of the steam-distilled product, the residue gave a positive test for Cl (sodium fusion).

In another experiment a test for positive Cl was carried out at the end of reaction. After the mixture was stirred with aqueous acid, 1 ml of the organic layer was diluted to 50 ml with CH_2Cl_2. Titration for positive Cl gave a negative result. High dilution of the aliquot was necessary because of the dark color of the original soln. In a control, analysis for positive halogen proceeded satisfactorily with 1 ml trichloramine soln diluted to 100 ml. Similarly, the reaction mixture produced a negative test before addition to aqueous acid.

1-Amino-1-methylcyclohexane was characterized by comparison with authentic material and literature data (present work, Ritter product, literature values): b.p. 139–141°, 140–141°, 143°[28], $n_{\mathrm{D}}^{21\cdot5}$ 1·4541, $n_{\mathrm{D}}^{21\cdot5}$ 1·4542, n_{D}^{20} 1·4539;[34] hydrochloride m.p. (dec) 278°, 278°, 285°[27]; picrate m.p. 151°, 151°, 150–151°[23]; benzamide m.p. 101–102°, 101–102°, 97–99°.[26a]

Authentic 1-*amino*-1-*methylcyclohexane*[22, 23]

A soln of conc H_2SO_4 (50 ml) in glacial AcOH (50 ml) was added with stirring during 3 hr at room temp to a mixture of 1-methylcyclohexene (19·2 g, 0·2 mole), glacial AcOH (20 ml), and powdered NaCN (13·7 g, 0·3 mole). Following the introduction of additional conc H_2SO_4 (50 ml), the temp was raised gradually to 60° over a period of 3 hr. After standing overnight at room temp, the reaction mixture was mixed with 400 g of ice and then heated at reflux for 6 hr. Treatment with 50% NaOH (600 ml) was followed by refluxing for 5–6 hr and then steam distilling. About 1200 ml distillate was collected in dil HCl. The non-basic impurities were taken up in ether, the base was liberated with excess NaOH, and then extraction was accomplished with ether. Removal of solvent from the dried soln provided a residue which was distilled, b.p. 63–64°/49–50 mm., 58% yield.

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[31] In the latter stages of our work it was found that purification of the product is facilitated if use is made of purified ether (A. I. Vogel, *A Textbook of Practical Organic Chemistry* p. 163, Wiley, New York, N.Y.) The contaminant appears to be ethanol from the technical ether.

[32] If the flow of the gas stream is too rapid, appreciable amounts of alkane and trichloramine will be lost by volatilization.

[33] Subsequently we found that distillation proceeds more smoothly at 20 mm, thereby eliminating the need for the additive during distillation.

[34] N. Kornblum, R. J. Clutter and W. J. Jones, *J. Am. Chem. Soc.* **78**, 4003 (1956).

Neutral products

After separation of the basic components from the reaction mixture, the remaining organic portion was washed with water and 2% Na_2CO_3aq. Separation into steam volatile and steam nonvolatile fractions was accomplished.

A. *Steam volatile.* The organic layer was washed with water and 2% Na_2CO_3aq, dried, and then fractionated through a Vigreaux column. CH_2Cl_2 and methylcyclohexane were recovered. Data for the remaining product (6 g) are summarized in Table 2.

All cuts decomposed when distillation was attempted at atm press. Except for fraction 2, the material exhibited satisfactory stability under the conditions described in Table 2. Each sample gave a positive test for halogen with alcoholic $AgNO_3$, and was a mixture according to GLC analysis (column B).

1-Chloro-1-methylcyclohexane was identified as a component of cut 1; b.p. 150–154°/751 mm, 70–72°/48–49 mm, n_{D}^{22} 1·4569, lit[17c] b.p. 69–71°/54 mm, n_{D}^{20} 1·4570. The IR spectrum and GLC retention time were in agreement with those for the authentic material. (Found: Cl, 27·1. Calc. for $C_7H_{13}Cl$: Cl, 26·7%.)

B. *Steam nonvolatile.* The tar was dissolved in ether, washed with salt soln, and dried. Removal of ether yielded 8 g of black solid. (Found: C, 76·1; H, 8·1; Cl, 3·3%.)

Table 2. Neutral products

Fraction	B.p.,[a] °C	% of total	Elem. Anal., %[b] C	H	Cl
1	<50	12	—	—	—
2	50–110	8	57·6	8·2	34·2
3	110–118	9	—	—	—
4	118–122	23	66·1	9·8	24·2
5[c]	122–126	25	73·6	11·1	15·5
6	125–128[d]	4	—	—	—
7	residue	12	—	—	—

[a] 14–15 mm.

[b] Analytical samples were prepared by refractionation.

[c] Calcd. for $C_{14}H_{25}Cl$: C, 73·1; H, 10·9; Cl, 16·0%.

[d] 9–10 mm.

Analysis of effluent gas

A. *Hydrogen chloride.* The amination was conducted according to general procedure B. The effluent gas was passed through a condenser cooled with ice water and then into two traps containing standardized 0·1N NaOH. About 0·1 mole of acid was evolved during 10 hr.

B. *Chlorine.* The procedure described in the preceding section was followed with the exception that the gas was passed through cold glacial AcOH for 2 hr. On addition of NaI soln to the trap liquor, no I was liberated indicating the absence of Cl and trichloramine.

Trichloramine and aluminum chloride

A soln of trichloramine (0·0032 mole) in CH_2Cl_2 (5 ml) was added to a suspension of $AlCl_3$ (1 g, 0·0084 mole) in CH_2Cl_2 (60 ml) at room temp. The evolved gas was carried by a N stream into traps containing glacial AcOH. After 3 hr at 27° iodometric titration of the AcOH soln revealed the presence of ⅓ of the positive Cl originally bound in the trichloramine.

With hexane as the trap liquor, UV analysis gave λ_{max} 335 mμ. A soln of Cl in hexane gave essentially the same absorption spectrum.

In a control experiment carried out in the absence of $AlCl_3$ negligible amounts of positive Cl were found in the AcOH. Another experiment revealed that a CH_2Cl_2 soln which contained Cl (about 0·003 mole) gave up about 86% of the dissolved gas during 1·5 hr of purging with N.

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