124 g. of guaiacol, 108 g. of large crystals of potassium 3-methoxy-4-hydroxybenzenesulfonate were obtained. The product gave a blue color reaction with ferric chloride.

Potassium 3-Methoxy-4-acetoxybenzenesulfonate (XXIII).—A mixture of 100 g. of the foregoing potassium salt with 200 cc. of acetic anhydride was heated to boiling with stirring for ten minutes. The reaction mixture was cooled and washed with ethyl acetate. Colorless needles, containing one mole of water, crystallized from ethanol.

3-Methoxy-4-acetoxybenzenesulfonyl Chloride (XXIV).—A mixture of equal weights of XXIII and of phosphorus pentachloride was gently warmed and poured into ice-water. The white, powdery sulfonyl chloride was crystallized from ligroin.

3-Methoxy-4-acetoxybenzenesulfinic acid (XXV) was prepared by the reduction of XXIV with sodium sulfite.

3-Methoxy-4-hydroxybenzene Thiol and Bis-(3-methoxy-4-hydroxyphenyl) Disulfide (XXVI).—The thiol was prepared using the procedure described for the preparation of thiophenol.[20] Compound XXIV (82 g.) was added to a stirred mixture of 173 cc. of concentrated sulfuric acid and 970 g. of ice at a temperature of −5°. Then 162 g. of zinc dust was added within ten minutes. The temperature was kept below 0° for two hours, then the reaction mixture was slowly heated until a reaction with evolution of heat took place. The mixture was cooled and the temperature kept at about 60° until the reaction subsided. The temperature was raised to 110° with constant stirring until the zinc dust had dissolved. The oily reaction product was separated from the mother liquor, dissolved in ether and dried with calcium chloride. The ether was distilled off; the remaining crude thiophenol (57 g.) was slightly yellow colored and was used for the following condensation with nitrobromobenzene. A sample of the crude thiophenol was distilled under diminished pressure; the boiling point was 150–152° at 20 mm. From the crude thiophenol, the corresponding disulfide (XXVI) could be isolated by dissolving a sample of 5 g. in little benzene and adding petroleum ether until the mixture became turbid. Crystals separated (1.9 g.) which were recrystallized from 36% acetic acid (charcoal). Colorless needles (1.2 g.) of m.p. 123–125° were obtained. Analysis agreed with the formula of XXVI.

3-Methoxy-4-hydroxy-4′-nitrodiphenyl Sulfide (XXXI).—The foregoing crude thiol (20 g.) was dissolved in a solution of 20 g. of potassium hydroxide in 200 cc. of methanol. To the mixture, 25 g. of *p*-bromonitrobenzene was added; a violent reaction occurred. The mixture was refluxed for six hours, then poured into water. The sticky mass was converted to the orange sodium salt by the addition of an excess of aqueous sodium hydroxide. The free acid, crystallized from 36% acetic acid, formed light yellow needles.

3-Methoxy-4-hydroxy-4′-nitrodiphenyl Sulfone (XXXV).—Compound XXXI (11.2 g.) was added to a mixture of 110 cc. of acetic anhydride and 55 cc. of 30% hydrogen peroxide. The temperature was kept at about 60° by cooling with water. The sulfide went rapidly into solution; from the reaction mixture pale yellow crystals separated. Water was added to complete precipitation. The crystals were collected, washed with water and dried in the desiccator (11.7 g.). From 36% acetic acid, pale yellow needles were obtained. A crystalline orange sodium salt was obtained by dissolving XXXV in dilute sodium hydroxide solution and adding an excess of 5 *N* sodium hydroxide.

3-Methoxy-4-hydroxy-4′-aminodiphenyl Sulfone (XXXVI).—Reduction of XXXV was performed with stannous chloride in glacial acetic acid, the tin being removed by hydrogen sulfide. From hot water, feathery needles were obtained.

Appendix

Sodium Estimation in the Presence of Phosphorus.—If sodium and phosphorus are present in the molecular ratio of 1:1, the estimation can be carried out by destroying the organic compound in a crucible with sulfuric and nitric acids and igniting. The residue then consists of sodium metaphosphate. In this way, sodium and phosphorus can be determined in one procedure.

Determination of Nitrogen Bound to Phosphorus (Amide Nitrogen).—About 1.5 g. of substance was boiled in a Kjeldahl flask with 5 cc. of hydrochloric acid of sp. gr. 1.12 for 30 minutes, in order to hydrolyze the amide. The flask was then connected with the distilling apparatus, the contents were alkalized with 22 cc. of 10 *N* sodium hydroxide solution, and distilled.

Acknowledgment.—I am indebted to Mr. E. A. Garlock, Mr. W. C. Alford, Mrs. M. M. Ledyard and Mrs. E. G. Peake for carrying out the microanalyses.

BETHESDA, MARYLAND RECEIVED AUGUST 10, 1950

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[20] R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 504.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CONNECTICUT]

The Action of Ammonia and Amines on 1,4-Dichloro-2-butene[1]

BY LAWRENCE H. AMUNDSEN, ROWLAND H. MAYER, LEONARD S. PITTS AND LENA A. MALENTACCHI

The vapor phase reaction between approximately equimolecular amounts of chlorine and butadiene is more satisfactory than liquid phase reactions for the preparation of 1,4-dichloro-2-butene. The product obtained from the vapor phase reaction appears to differ from *cis*-1,4-dichloro-2-butene prepared from *cis*-2-butene-1,4-diol, and is presumably *trans*.

Secondary amines react with 1,4-dichloro-2-butene to give fair yields of the corresponding diamine, whereas primary amines or ammonia under the conditions tried give largely polycondensation products. 1,4-Dichloro-2-butene has been converted to N,N,N′,N′-tetramethyl-, tetraethyl-, tetra-*n*-propyl- and tetra-*n*-butyl-2-butene-1,4-diamine and also to N,N-diethyl-2-butene-1,4-diamine, N,N′-dibutyl-2-butene-1,4-diamine and 2-butene-1,4-diamine.

Now that 1,3-butadiene is one of the cheap industrial chemicals there are many interesting possibilities for the synthesis of other compounds from it. It has been the purpose of this investigation to study the possibility of the synthesis of diamines by adding chlorine to 1,3-butadiene and treating the 1,4-dichloro-2-butene resulting therefrom with ammonia and with amines.

It was found that the addition of chlorine to butadiene was best accomplished by vapor phase reaction using equimolecular amounts of the gases. The reaction between the resulting 1,4-dichloro-2-butene and secondary amines gave fair yields of N,N,N′,N′-tetraalkyl diamines, but similar reactions with primary amines and with ammonia gave little diamine, the major products being condensation polymers.

After experimenting with certain modifications of the previously reported methods of carrying out the reaction between chlorine and butadiene,[2,3,4] we came to the conclusion that the reaction is best carried out between equal molecular quantities of the reactants in the vapor phase.

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[1] Reported in part at the 109th Meeting of the American Chemical Society, April 10, 1946.

[2] Muskat and Northrup, THIS JOURNAL, **53**, 4043 (1930).

[3] Schmidt, German Patent 709,942 (1941).

[4] Hearne and LaFrance, U. S. Patent 2,299,477 (1942).

After the original presentation of this portion of the work,[1] Taylor and Morey[5] reported excellent results with an essentially similar process. Since their procedure has been reported in considerable detail, it is not necessary to elaborate upon ours.

We had originally supposed that the 1,4-dichloro-2-butene contained both *cis* and *trans* isomers, but neither very careful rectification nor chromatographic adsorption showed that more than one isomer was present. A sample of the *cis* isomer was prepared by hydrogenation of 2-butyne-1,4-diol to the known 2-butene-1,4-diol, followed by treatment with thionyl chloride. The product differed slightly from that obtained by adding chlorine to butadiene, as shown in Table I, possibly indicating that the latter preparation yields at least predominantly the *trans* isomer. Failure to find evidence of a second isomer in this preparation suggests that only the *trans* isomer may have been formed.[5a]

TABLE I

	cis compound	Product from butadiene
Boiling point (22 mm.), °C.	59–62	60–63[a]
Density (25°)	1.191	1.189
$n^{25}\text{D}$	1.4891	1.4864
Reaction with NH_4OH	No solid	White solid polymer

[a] Calculated from boiling point at 6, 20 and 40 mm.

TABLE II

N,N,N',N'-TETRAALKYL-2-BUTENE-1,4-DIAMINES[a]

	Diamines				Picrates									
	Yield,	B.p.				Carbon, %			Hydrogen, %			Nitrogen, %		
Alkyl	%	°C.	Mm.	$n^{21}\text{D}$	M.p.,[b] °C.	Calcd.	Found		Calcd.	Found		Calcd.	Found	
C_2H_5	66	115–116	20	1.4532	154–155.5	43.90	43.84	43.60	4.91	5.02	4.78	17.08	17.30	17.16
C_3H_7[c]	51	150–154	15	1.4538	173–174	47.18	47.52	47.70	5.65	6.31	6.06	15.72	15.93	15.71
C_4H_9[c]	57	165–170	3	1.4572	183–184	49.99	49.78	49.55	6.29	6.55	6.31	14.57	14.47	14.41

[a] Prepared from 1,4-dichloro-2-butene by a procedure essentially the same as that used by Willstatter and Wirth (*Ber.*, **46**, 537 (1913)) for preparing the tetramethyl compound from 1,4-dibromo-2-butene. They reported the tetramethylamine to boil at 65–65.5° (17 mm.) and its picrate to melt at 222–223°. We obtained it in 53% yield, b.p. 70–71° (17 mm.). [b] Corrected. [c] Prepared by Morey (U. S. Patent 2,440,724 (1948)) by a similar procedure. The products, however, were not described, or characterized, or was an analysis given.

TABLE III

N,N,N',N'-TETRAALKYLPUTRESCINES[a]

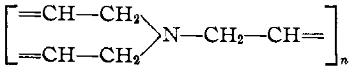
	Putrescines				Picrates									
	Yield,[b]	B.p.				Carbon, %			Hydrogen, %			Nitrogen, %		
Alkyl	%	°C.	Mm.	$n^{20}\text{D}$	M.p.,[c] °C.	Calcd.	Found		Calcd.	Found		Calcd.	Found	
C_2H_5	61	70–73.7	3–4	1.4421	172.0–172.9	43.77	43.64	43.72	5.21	4.89	5.00	17.02	17.38	17.56
C_3H_7	43	129–130	4	1.4443	194.0–195.5	47.05	46.89	47.01	5.92	5.70	5.59	15.67	16.43	16.50
C_4H_9	38	157.5–160	4	1.4505	170.2–171.2	49.86	49.56	49.68	6.53	6.26	6.43	14.53	15.23	15.08

[a] These compounds were prepared by hydrogenation of 0.1 mole of the corresponding N,N,N',N'-tetraalkyl-2-butene-1,4-diamines in absolute ethanol with Raney nickel at room temperature and 3 atmospheres. Willstätter and Heubner (*Ber.*, **40**, 3869 (1907)) and Clarke (*J. Chem. Soc.*, **103**, 1700 (1913)), reported the boiling point of the methyl derivative as 169° and 168°; of its picrate 198° and 197°, respectively. Von Braun and Lemke (*Ber.*, **55**, 3555 (1922)) found the picrate to melt at 199–200°. We prepared the methyl derivative in 52% yield, b.p. 164–166°, and obtained a picrate m.p. 202.8–203.3°. [b] After distillation. [c] Corrected.

Muskat[6] states that both 1,4-dichloro-2-butene and 3,4-dichloro-1-butene polymerize under the catalytic action of bases, including ammonia and amines. We have carried out numerous experiments with 1,4-dichloro-2-butene and ammonia or amines, and have found invariably that they react readily with the liberation of something approaching the theoretical quantity of chloride ion, although it has often not been possible to isolate more than a small fraction of the possible yield of diamine. Since the quantities of chloride liberated have never quite reached the theoretical, it might be argued that there is *some* polymerization of the dichloride taking place simultaneously with the condensation reaction. It seems improbable, however, that there is *any* polymerization because no insoluble material separated when the reactions were carried out in aqueous ethanol. It appears likely that a polymerization product of 1,4-dichloro-2-butene would be insoluble in such a solution.

In general the highest yields of diamines have been obtained when secondary amines were allowed to react with the dichloride in benzene (Table II). Insoluble hydrochlorides precipitated from which the N,N,N',N'-tetraalkyl-2-butene-1,4-diamines were obtained by treatment with sodium hydroxide. All of these products were converted by catalytic hydrogenation to N,N,N',N'-tetraalkylputrescines (Table III).

Ammonia and 1,4-dichloro-2-butene reacted in water (2 phases) or in aqueous alcohol to produce 2-butene-1,4-diamine, but the yields were very low. This could have been caused by losses during isolation, by polymerization of the dichloride as reported by Muskat,[6] or by polymerization of the diamine. Analysis of the solid insoluble product, however, showed a ratio of six carbon atoms to every nitrogen atom, thus indicating that polyalkylation of ammonia actually is the primary cause for the low yield. Such polyalkylation would produce a structure that would be in agreement with the analysis.



The action of primary amines with dichlorobutene also was investigated, using butylamine in

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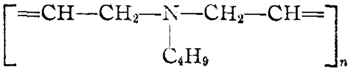
[5] Taylor and Morey, *Ind. Eng. Chem.*, **40**, 432 (1948), and U. S. Patent 2,453,089 (1948).

[5a] Since this was written, this supposition has been substantiated by Mislow and Hellman, THIS JOURNAL, **73**, 244 (1951).

[6] Muskat, U. S. Patent 2,038,593 (1936).

benzene. Here, again, the yield was low, and much tarry by-product was obtained. Undoubtedly the tar was also the result of polyalkylation which produced in this case long-chain tertiary polyamines.



$$\left[=CH-CH_2-\underset{C_4H_9}{\underset{|}{N}}-CH_2-CH=\right]_n$$

The reaction of 1,4-dichloro-2-butene successively with a secondary amine and ammonia should yield among other things unsymmetrical disubstituted diamines. N,N-Diethyl-2-butene-1,4-diamine was prepared by this method, but the yield was low, as would be expected from the above.

Since it appeared to be impossible to control the reaction of ammonia and dichlorobutene so that a satisfactory yield of the simple monomeric diamine, $NH_2-CH_2-CH=CH-CH_2-NH_2$, could be obtained, a number of indirect methods of amination were investigated. Of these, only the Gabriel phthalimide synthesis showed potentialities of being a satisfactory method. The other methods attempted involved the intermediate preparation of isocyanate, isothiocyanate, acetamide and benzenesulfonamide derivatives from 1,4-dichloro-2-butene.

Experimental

Addition of Chlorine to 1,3-Butadiene.—After considerable experimentation with variations of the procedure of Muskat and Northrup,[4] it was found that comparable yields could be obtained by the more convenient process of passing chlorine and butadiene simultaneously at a rate of 0.6 mole per hour into the top of a Liebig condenser cooled by tap water (about 10°) in much the same way as has subsequently been described in detail by Taylor and Morey[5]; yield 30–32% (and 19–30% of 3,4-dichloro-1-butene). Somewhat lower yields (16–19% and 5–8%, respectively) were obtained when chlorine was passed into liquid butadiene without a solvent.[7]

Attempts were made to separate the product into *cis* and *trans* isomers. Careful rectification with a 120-cm. column packed with glass helices gave no evidence of separation, the product boiling quite constantly at 75–76° at 40 mm. (3,4-dichloro-1-butene boils at 45–45.5° at this pressure) with the refractive index measured at 25° increasing only from 1.4861 for the first portion of the distillate to 1.4864 for the last portion. Chromatographic separation also was attempted, using a 250 × 14 mm. column of activated alumina and "Supercel." A solution of 15 ml. of 1,4-dichloro-2-butene in 35 ml. of pentane was passed through the column, followed by an additional 100 ml. of pentane. The filtrate was collected in nine 10-ml. fractions. The solute was frozen out of each fraction with Dry Ice and its refractive index was taken. The quantity of solute in the several fractions followed a normal distribution curve, but the refractive index of the 1,4-dichloro-2-butene from all fractions was the same to within ±0.0001.

Rearrangement of 3,4-Dichloro-1-butene.—The 3,4-dichloro-1-butene accumulated during chlorination studies was converted to the 1,4-isomer by refluxing with a trace of cuprous chloride, following the procedure described by Otto.[8] The method yielded 42% unchanged 3,4-dichloro-1-butene and 51% 1,4-dichloro-2-butene.

***cis*-1,4-Dichloro-2-butene.**—A solution of 10.8 g. of *cis*-2-butene-1,4-diol[9] in 20 ml. of dry pyridine was cooled in an ice-bath during the dropwise addition of 25 ml. of thionyl chloride. The mixture was allowed to stand in the ice-bath for one hour and at room temperature for four hours after which it was poured onto cracked ice. The oil layer was removed, the water layer was extracted with ether, and the combined oil and ether extracts were washed with sodium bicarbonate solution. Finally the ether solution was washed with water, dried over calcium chloride and distilled through a 35-cm. heated Vigreux column; yield 7.9 g. (51%), b.p. 59–62° (22 mm.), d^{25}_4 1.191, n^{25}_D 1.4891.

2-Butene-1,4-diamine. A.—Just enough 95% ethanol to produce one phase was added to a mixture of 2.5 l. (40 moles) of 28% ammonia and 250 g. (2 moles) of 1,4-dichloro-2-butene, about 3.5 l. being required. The mixture was left standing at room temperature. After ten hours the solution was evaporated to one-half of its volume, made slightly acid with concentrated hydrochloric acid, and evaporated to dryness. One liter of 50% sodium hydroxide solution was added to the residue, and the amine layer was separated, dried over sodium hydroxide, and distilled from a simple apparatus at reduced pressure to separate the diamine from high-boiling by-products; yield 35 ml., b.p. 60–70° (25–30 mm.). This distillate was rectified through a 15-cm. semi-micro column packed with a metal spiral; yield 19 g. (11%), b.p. 163–170° (mostly at 169°). The product was converted to the picrate, benzenesulfonamide and benzamide derivatives for analysis and characterization. The unusually insoluble picrate was recrystallized from 10% acetic acid. It melted with violent decomposition at 271° when dropped into a bath preheated to almost this temperature. When heated slowly, it decomposed over a wide and indefinite range. (Calcd. for $C_{16}H_{16}N_8O_{14}$: C, 35.17; H, 3.31; N, 20.51. Found: C, 35.50, 35.28; H, 3.28, 3.42; N, 20.65, 20.41). The benzenesulfonamide, which had been crystallized from 95% ethanol melted at 155°. (Calcd. for $C_{16}H_{18}N_2O_4S_2$: C, 52.44; H, 4.95; N, 7.65. Found: C, 51.45, 51.22; H, 4.91, 4.73; N, 8.21, 8.12. The benzamide, which had been crystallized from dilute alcohol, melted at 178.5–179.5°. (Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.44; H, 6.16; N, 9.51. Found: C, 72.75, 72.61; H, 6.83, 6.75; N, 9.45, 9.58).

B.—One mole of 1,4-dichloro-2-butene and five moles of 28% ammonia were placed in a two-liter bottle and shaken mechanically for three hours. The mixture became very warm after the first hour, and after two hours it began to cool and a white precipitate of polymer began to form. After standing for an additional hour, the mixture was filtered to remove the polymer and the filtrate was treated as in A. After being released by an excess of 50% sodium hydroxide solution, the amine layer was separated, dried and distilled in a simple apparatus at a pressure of less than 1 mm. Only 25 ml. of distillate could be driven from a considerable volume of tarry residue, and this, when saturated with sodium hydroxide, yielded 20 ml. of aqueous solution and only 5 ml. of diamine; yield 5 g. (4%). Picrate, benzenesulfonamide and benzamide derivatives showed this product to be the same as in A.

C.—A 0.05-mole sample of *cis*-1,4-dichloro-2-butene was treated with 40 ml. of 28% ammonia and shaken overnight. No white polymer formed. An identical experiment with the 1,4-dichloro-2-butene from butadiene and chlorine was run in parallel and yielded white solid polymer to the extent of 34% of the weight of the initial dichlorobutene. This pair of experiments was repeated and the same difference was again noted.

D.—In a series of experiments liquid ammonia and 1,4-dichloro-2-butene were allowed to react at low temperature and under pressure at room temperature, both with and without solvent, but only solid polymers and tars could be isolated.

E.—Two moles of liquid ammonia, 150 ml. of methanol and 42 g. (0.33 mole) of 1,4-dichloro-2-butene were mixed at −70° and allowed to warm slowly to room temperature over a period of 20 hours. After this time, the entire contents of the tube had become a rubbery solid. The solid was removed from the tube and extracted with water, yielding only ammonium chloride. The polymer was insoluble in all solvents tried. One sample of it was washed thoroughly with sodium hydroxide, water and acetone. Both samples were dried and analyzed, showing a ratio of approximately six carbon atoms to one nitrogen atom. Analysis of first sample: C, 66.58, 66.75; N, 12.45, 12.32; ratio of C to N atoms, 6.24, 6.32. Analysis of second sample: C,

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(7) Recently Pudovik, *Zhur. Obschchei Khim*, (*J. Gen. Chem.*), **19**, 1179 (1949); *C. A.*, **44**, 1005 (1950), has claimed that chlorine does not add to butadiene in the absence of a solvent but that butadiene is merely polymerized to a gelatinous mass. This is completely contrary to our experience.

(8) Otto, U. S. Patent 2,422,252 (1947).

(9) Prepared by the method of French Patent 49,861 (I. G. Farbenindustrie, 1939) and U. S. Patent 2,267,749 (Reppe and Schnabel, 1941) in 30% yield and by the method of Johnson (*J. Chem. Soc.*, 1014 (1946)) in 68% yield, b.p. 105–108° (7 mm.), 98–100° (4 mm.), d^{25}_4 1.071, n^{25}_D 1.4720.

45.45, 45.26; N, 9.01, 9.18; ratio of C to N atoms, 5.88, 5.75.

F. Gabriel Synthesis.—The following procedure was adapted from that of Langenbeck,[10] who used 1,4-dibromo-2-butene. A mixture of 60 g. of phthalimide, 30 g. of potassium carbonate and 25 g. of dichlorobutene was heated for 6.5 hours at 175° under reflux. After cooling, the mixture was washed with hot water and hot alcohol to remove the by-products of the reaction, and the residue was recrystallized from chloroform, yielding 25 g. (32%) of 2-butene-1,4-diphthalimide. Six grams of the product was hydrolyzed by heating to 150° for 16 hours with 60 ml. of concentrated hydrochloric acid in a sealed tube. The phthalic acid was filtered off and the solution was evaporated to dryness, giving 2.5 g. (90%) of 2-butene-1,4-diamine hydrochloride, which was characterized by treatment with benzoyl chloride and aqueous sodium hydroxide, giving N,N′-dibenzoyl-2-butene-1,4-diamine shown by mixed melting points to be identical with that obtained from the product of the direct amination of 1,4-dichloro-2-butene.

G.—A solution of 0.2 mole of potassium thiocyanate and 0.1 mole of 1,4-dichloro-2-butene in 80 ml. of 75% ethanol when left in a refrigerator at −7° for three days precipitated yellow crystals of 2-butene-1,4-dithiocyanate; yield 75%, m.p. 82°. Muller and Freytag[11] report a melting point of 83.5° for this compound as obtained from thiocyanogen and butadiene. Distillation of these crystals yielded a yellow oil, possibly the isothiocyanate, but hydrolysis of the oil with hydrochloric acid produced only hydrogen sulfide and a heavy oil.

N,N′-Dibutylputrescine.—A solution of 25 g. (0.2 mole) of 1,4-dichloro-2-butene and 73 g. (1 mole) of butylamine in 200 ml. of benzene was allowed to stand for several days. Precipitated butylammonium chloride was removed periodically. When precipitation had ceased, the solution was extracted with dilute hydrochloric acid, the extract was made alkaline with sodium hydroxide and the amine layer was removed, dried and distilled. After the butylamine had been removed at atmospheric pressure, the pressure was reduced to less than 1 mm., but only 8.5 ml. of distillate could be removed from the residual tar. This distillate was hydrogenated at 3 atmospheres pressure and room temperature in alcohol solution; yield 4 g. (10%), m.p. 62–67°. *Anal.* Calcd. for $C_{12}H_{28}N_2$: N, 13.99. Found: N, 13.61, 13.75. The picrate of this product melted at 108–109°.

N,N-Diethyl-2-butene-1,4-diamine.—A mixture of 125 g. (1 mole) of 1,4-dichloro-2-butene, 146 g. (2 moles) of diethylamine and 1750 ml. of 95% ethanol was allowed to stand at room temperature. After 24 hours, 2.5 liters (40 moles) of 28% aqueous ammonia was added. When chloride ion determinations indicated that reaction was no longer proceeding at a significant rate, the solution was evaporated to half its volume, neutralized with concentrated hydrochloric acid, and evaporated to dryness. The residue was treated with 500 ml. of 50% sodium hydroxide solution, and the amine layer was separated, dried over sodium hydroxide, and rectified using a 120-cm. column packed with glass helices; yield 15.5 g. (11%), b.p. 89° (20 mm.) and 45 g. (23%), b.p. 113° (20 mm.). The second fraction was identified as N,N,N′,N′-tetraethyl-2-butene-1,4-diamine. The first fraction, N,N-diethyl-2-butene-1,4-diamine, was converted to the picrate for analysis. (Calcd. for $C_{20}H_{24}N_8O_{14}$: C, 40.01; H, 4.02; N, 18.67. Found: C, 40.01, 39.89; H, 3.90, 3.81; N, 19.18, 19.05). The picrate, after recrystallization from 95% ethanol to constant melting point, melted at 152–154.5°. The N,N-diethyl-2-butene-1,4-diamine was hydrogenated at 3 atmospheres pressure in absolute alcohol with Raney nickel as a catalyst. The resulting N,N-diethylputrescine was converted to the picrate, which melted at 155–156° as reported by Whitmore and coworkers.[12]

Acknowledgment.—The authors wish to acknowledge their indebtedness to the University of Connecticut Research Fund for financial support and to Professor Ernest R. Kline for many helpful suggestions and for much skillful assistance in the construction of glass apparatus. The elementary analyses were made by Dr. Carl Tiedcke's Laboratory of Microchemistry, Teaneck, New Jersey.

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[10] Langenbeck, Waltersdorf and Blachnetski, *Ber.*, **72B**, 671 (1939).

[11] Muller and Freytag, *J. prakt. Chem.*, **146**, 58 (1936).

[12] Whitmore, Mosher, Adams, Taylor, Chapin, Weisel and Yanko, THIS JOURNAL, **66**, 725 (1944).

STORRS, CONN. RECEIVED AUGUST 11, 1949

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Reactions of Ethylenimines. II. With Thiophenol. A Rate Study

BY GARBIS MEGUERIAN[1] AND LEALLYN B. CLAPP

The rates of the reaction of 2-ethyl- and 2,2-dimethylethylenimines with thiophenol in carbon tetrachloride solutions were studied. The infrared spectroscopic method was used to follow the change in thiophenol concentration. It is proposed that an unstable intermediate is first formed which then reacts bimolecularly to yield the product, an α-amino sulfide. The intermediate may be a mixture of a hydrogen bonded molecular compound and an ion-pair of thiophenol and the ethylenimine.

Although ethylenimines are stable in the absence of electrophilic reagents, catalytic amounts of acids such as hydrochloric or boron trifluoride and even carbon dioxide[2] induce their polymerization. The three-membered ring is not opened in the presence of anhydrous amines[3] but in the presence of water,[3,4] aluminum chloride[5] or ammonium chloride,[6] the ethylenimines react with amines to yield products mainly of type II. Acidic hydrolysis[7] and alcoholysis[8] yield products of type III only. Tarbell and Noble suggest that the best explanation of the appearance of a type III product in an acid-catalyzed reaction is by way of a carbonium ion, stabilized by solvation. The results of the rate study with two ethylenimines and thiophenol reported here are compatible with an S_N2 mechanism; the only product isolated (92% in the case of 2-ethylethylenimine) was proved by an independent synthesis to be of type II (see Experimental part).

Quantitative chemical determination of the starting imine in the presence of the product (an amino sulfide) or *vice versa* could not be performed because of their similar chemical properties while

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[1] Taken from the thesis of G. Meguerian submitted in partial fulfillment of the requirements for the Ph.D. degree at Brown University, June, 1950; Jesse Metcalf Fellow 1948–1950; present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts.

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