

tions of these mixtures agreed to within 2% of the compositions of the original mixtures.

B. Sodium Acetate Solution.—A description of a typical experiment follows. A mixture of 20.1 g. of *p*-chlorotoluene and 250 ml. of 4 *M* sodium acetate solution was shaken for 2 hours at 340°. The reaction mixture remaining in the liner (233 ml.) was extracted three times with 50-ml. portions of ether. The combined extracts were extracted three times with 30-ml. portions of 1 *N* sodium bicarbonate solution, washed with 30 ml. of water and extracted three times with 30-ml. portions of 1 *M* sodium hydroxide solution. The sodium hydroxide solution was acidified with 6 *M* hydrochloric acid and extracted three times with 30-ml. portions of ether. The combined extracts were dried, the ether was removed and the residual cresol mixture was distilled through a semimicro column.²⁰ The distillate, b.p. 56–62° (2 mm.), weighed 0.98 g. (6.1%) and was found to consist of 5% *m*-cresol and 95% *p*-cresol. A mixture of 15.7% *m*-cresol and 84.3% *p*-cresol was carried through the reaction conditions and isolated as above. The infrared spectrum of the product indicated it to contain 11.8% *m*-cresol.

Attempted Hydrolysis of *p*-Iodotoluene with 4 *M* Sodium Iodide and 4 *M* Sodium Chloride Solutions.—A mixture of 20.0 g. of *p*-iodotoluene and 250 ml. of 4 *M* sodium iodide solution was shaken at 340° for 10 hours. A tarry acidic fraction of 45 mg. was obtained. The infrared spectrum of this fraction in carbon disulfide solution failed to indicate the presence of cresols. Similar treatment of 20.1 g. of iodotoluene with 4 *M* sodium chloride solution for 2 hours also yielded no cresols. The infrared spectrum of the crude recovered neutral material showed all the bands with the same relative intensities possessed by *p*-chlorotoluene but no band at 12.57 μ as is characteristic of *p*-iodotoluene. Considerable decomposition occurred during both attempted hydrolyses.

Hydrolysis of Chlorobenzene-1-¹⁴C.—The labeled chlorobenzene¹² (19.7 g.) was hydrolyzed with 250 ml. of 4 *M* sodium hydroxide solution at 340°. The reaction mixture remaining in the liner (233 ml.) was treated in the usual manner. The neutral fraction consisted of 0.15 g. of starting material, 0.30 g. of diphenyl ether, b.p. 74–95° (0.7 mm.), and about 10 mg. of a dark residue. The crude acidic fraction amounted to 13.0 g. (79%), 0.2 g. of which was probably a mixture of hydroxybiphenyls.⁹ The crude phenol-*X*-¹⁴C was hydrogenated in absolute alcohol over platinum oxide and yielded 8.9 g. (66%) of cyclohexanol-*X*-¹⁴C;

b.p. 159.0–159.4° (741 mm.), n_D^{25} 1.4629. The cyclohexanol was degraded^{5b} to 1,5-diaminopentane which was isolated as the dibenzenesulfonamide, m.p. 118.2–118.7 (lit.²¹ m.p. 119°) after 5 recrystallizations from ethanol, and carbon dioxide (collected as barium carbonate). The specific activity of the phenol-*X*-¹⁴C was taken as equal to the activity of the 2,4-dinitrophenylhydrazones of cyclohexanone-*X*-¹⁴C, m.p. 160.6–161.1° (lit.²² m.p. 162°) after 4 recrystallizations from ethanol. The ¹⁴C results are summarized in Table II.

1,5-Diaminopentane (0.28 g.) was oxidized^{5b} in 19% yield to glutaric acid with potassium permanganate; unlabeled glutaric acid was added to the reaction mixture as a carrier. The glutaric acid-*X*-¹⁴C was assayed as the di-*p*-bromophenacyl ester, m.p. 136.7–137.4° (lit.²³ m.p. 136.8°) after 3 recrystallizations from ethanol. The glutaric acid was degraded^{5b} to 1,3-diaminopropane, isolated as the dibenzamide, m.p. 147.6–149.0° (lit.^{5b} m.p. 150.0–150.5°) after one recrystallization from cyclohexane.

TABLE II

RADIOACTIVITY DETERMINATIONS OF DEGRADATION PRODUCTS OF PHENOL-*X*-¹⁴C FROM HYDROLYSIS OF CHLOROBENZENE-1-¹⁴C

| Compound | Activity ^a | % Total act. |
|------------------------------------|---------------------------|-------------------------|
| Phenol- <i>X</i> - ¹⁴ C | 0.2908 ± 1.1% | (100) |
| 1,5-Diaminopentane | .1207 ± 1.5% | 41.5 ± 0.8 |
| Carbon dioxide | .1644 ± 0.9% | 56.5 ± 0.8 ^b |
| Glutaric acid | .0227 ± 1.3% ^c | (41.5) ^d |
| 1,3-Diaminopropane | .00028 ± 100% | 0.6 ± 0.6 |

^a μ c./mmole. ^b Possibly low by 0.4–2.0%.^{5b} ^c The 1,5-diaminopentane was substantially diluted during the oxidation. ^d Assumed to be the same as the 1,5-diaminopentane.

(21) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd Ed., 1948, p. 234.

(22) Reference 21, p. 262.

(23) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 98.

PASADENA, CALIFORNIA

[CONTRIBUTION NO. 2130 FROM THE GATES OF CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Products from the Reaction of N-(2-Bromoallyl)-ethylamine with Sodium Amide¹

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RECEIVED SEPTEMBER 4, 1956

The principal product obtained from N-(2-bromoallyl)-ethylamine and sodium amide in liquid ammonia has been shown to be N-ethylallenimine (I) as proposed by Ettlinger and Kennedy rather than N-ethylallylideneamine (II). N-Ethylpropargylamine (III) was also isolated in small yield from this reaction. III was obtained in 71% yield by treatment of N-(2-chloroallyl)-ethylamine with potassium amide in liquid ammonia.

Pollard and Parcell,³ in an attempt to extend their synthesis of N,N-dialkylpropargylamines⁴ to N-alkylpropargylamines, treated N-(2-bromoallyl)-ethylamine with sodium amide in liquid ammonia. The main product was shown by its infrared spectrum not to be the expected N-ethylpropargylamine (III), and the isomeric N-ethylallylideneamine structure (II) was assigned.⁵ This

(1) Supported in part by a grant from the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow, 1954–1957.

(3) C. B. Pollard and R. F. Parcell, *THIS JOURNAL*, **73**, 2925 (1951).

(4) R. F. Parcell and C. B. Pollard, *ibid.*, **72**, 2385, 3312 (1950).

(5) The absence of N-ethylaminoallene was indicated by the lack of nitrogen-hydrogen stretching absorption at about 3230 cm^{-1} . V. A. Engelhardt, *ibid.*, **78**, 107 (1956), has recently observed rapid base-

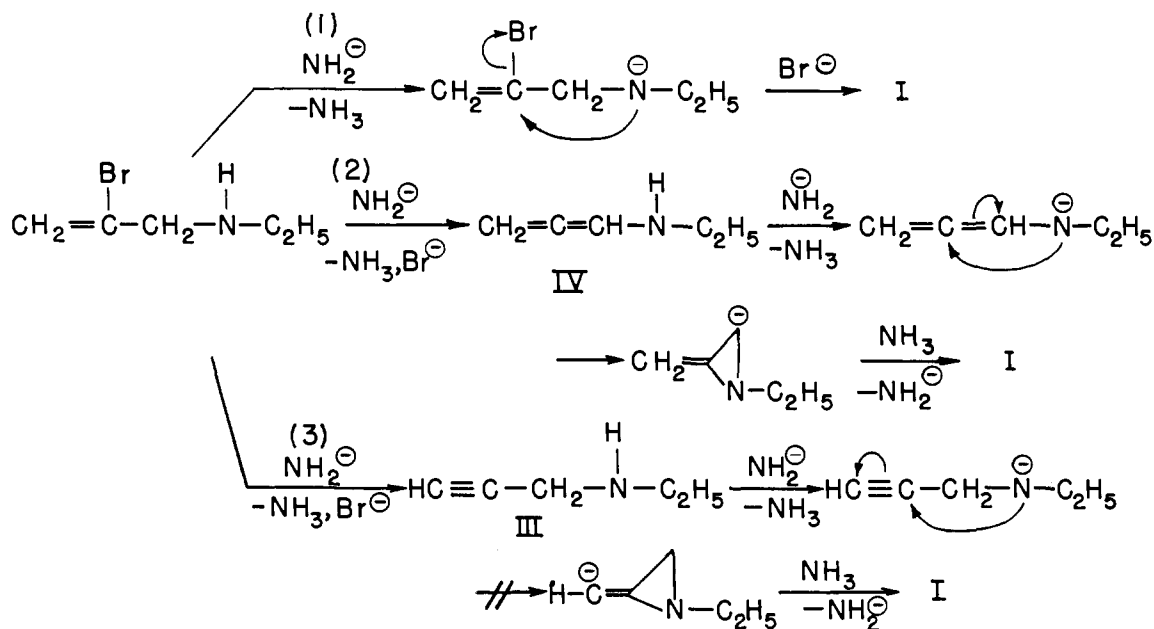
compound rapidly took up two moles of hydrogen to yield N-ethyl-*n*-propylamine. With hydrochloric acid, the compound was hydrolyzed to ethylamine and a chlorine-containing "aldehyde" which reduced Fehling solution, formed a silver mirror with Tollens reagent but could not be isolated in pure form. When hydrolyzed with dilute hydrochloric acid in the presence of 2,4-dinitrophenylhydrazine, the compound yielded a derivative which melted at 124–125° and was reported to contain 50.89% C, 3.85% H and 12.03% Cl.

catalyzed isomerizations of allenic amines to acetylenic amines and concluded that these reactions probably proceed by way of carbanion intermediates as postulated by T. L. Jacobs, R. I. Akawie and R. G. Cooper, *ibid.*, **73**, 1273 (1951).

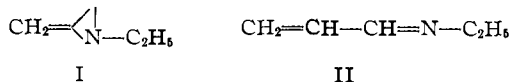
Treatment of other N-(2-bromoallyl)-alkylamines in the same manner yielded related compounds as shown by similarities in their ultraviolet and infrared absorption spectra as well as formation of the same hydrazone derivative and the respective alkylamine when hydrolyzed with dilute hydrochloric acid in the presence of 2,4-dinitrophenylhydrazine. Pollard and Parcell⁸ pointed out that the strong band near 1770 cm.^{-1} in the infrared spectra of these compounds was of too high frequency to be considered as a fundamental stretching vibration of either the carbon-carbon or carbon-

to expected resonances of vinylic hydrogens⁸ and the cyclic methylene hydrogens of ethylenimine.⁹ II would be expected to possess an n-m-r spectrum having, together with the absorptions of the N-ethyl group, three or four principal bands split into extensive fine structure characteristic of the grouping $\text{CH}_2=\text{CH}-\text{CHR}_2$. These resonances would appear at lower field strengths than that of the methylene-hydrogens of the N-ethyl group.

Although the n-m-r spectrum of I leaves little doubt as to the correctness of the structure, some of the results of Pollard and Parcell might appear



nitrogen double bond of II and was "therefore probably a harmonic or combination frequency." Ettlinger and Kennedy⁶ have noted that this unusual band corresponds to the double bond stretching frequency of methylenecyclopropane⁷ and have assigned these compounds the N-alkylallenimine structure.



At the suggestion of Dr. Ettlinger, we have repeated the preparation of the reported N-ethylallylideneamine and have examined its nuclear magnetic resonance (n-m-r) spectrum (Fig. 1). The spectrum is in complete agreement with the N-ethylallenimine structure (I) proposed by Ettlinger and Kennedy. Besides the characteristic and *undistorted* bands of the methylene- and methyl-hydrogens of the N-ethyl group (B and D, respectively) the n-m-r spectrum possesses two other unsplit bands of equal intensity at lower (A) and higher (C) field strengths than resonance B. The positions of A and C correspond, respectively,

to contradict this assignment. On hydrolysis with dilute hydrochloric acid, compound I would be expected to yield chloroacetone rather than an aldehyde.

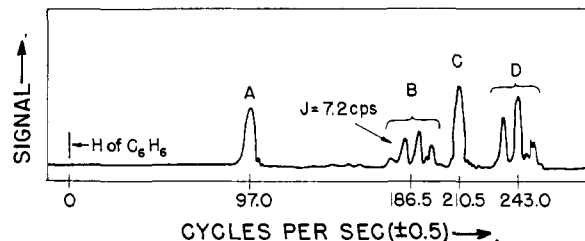


Fig. 1.—Nuclear magnetic resonance spectrum for protons of N-ethylallenimine taken with Varian Associates high resolution nuclear magnetic resonance spectrometer (V-4300) with 12-in. magnet equipped with a flux stabilizing unit (super stabilizer) at 40 mc. using a spinning 5-mm. sample: A, the protons of the double-bond methylene group; B, the methylene protons of the N-ethyl group; C, the ring methylene protons; D, the methyl protons of the N-ethyl group.

hyde. The tests employed on the hydrolysis product,³ however, failed to distinguish between chloroacetone and an aldehyde since chloroacetone is

(6) M. G. Ettlinger and F. Kennedy, *Chemistry & Industry*, 166 (1956).

(7) J. T. Gragson, K. W. Greenlee, J. M. Derfer and C. E. Boord, *THIS JOURNAL*, **75**, 3344 (1953).

(8) L. H. Meyer, A. Saika and H. S. Gutowsky, *ibid.*, **75**, 4567 (1953).

(9) H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, *ibid.*, **76**, 4242 (1954).

oxidized by silver oxide¹⁰ and is capable of reducing Fehling solution through preliminary formation of acetol with excess alkali.¹¹ The melting point (124–125°) of the 2,4-dinitrophenylhydrazone obtained from the hydrolysis products of I is the same as that reported for chloroacetone 2,4-dinitrophenylhydrazone¹² and the identity of these compounds has now been established by comparison of their infrared spectra. Hydrolysis of I with sulfuric acid in the presence of 2,4-dinitrophenylhydrazine was reported to yield a derivative which contained organic sulfur and melted above 200°. We found this reaction to yield two substances, separable by solubility differences, which melted at 134–135° and 302–304°. The higher melting compound was shown to be methylglyoxal bis-(2,4-dinitrophenyl)-osazone by its melting point and infrared spectrum. The lower melting compound has not been identified.

In two separate preparations of I from N-(2-bromoallyl)-ethylamine, a small amount of material boiling at about 100° was obtained. The infrared spectrum of this fraction, which contained some I, had a weak band at 2100 cm.⁻¹, the characteristic stretching frequency of monosubstituted carbon-carbon triple bonds.¹³ The main constituent was shown to be N-ethylpropargylamine (III) by comparison of its infrared and n-m-r spectra with those of authentic III prepared in 71% yield by treatment of N-(2-chloroallyl)-ethylamine with potassium amide in liquid ammonia. III slowly took up 98% of the theoretical amount of hydrogen over platinum oxide in ethanol at atmospheric pressure to yield N-ethyl-n-propylamine which was identified as its hydrochloride.

The formation of I from N-(2-bromoallyl)-ethylamine and sodium amide can occur by either an internal displacement of bromide ion (1) or by an elimination-addition mechanism (2) involving an allenic amine intermediate (IV). The possibility of an analogous elimination-addition mechanism (3) involving N-ethylpropargylamine (III) is precluded by the high yield of III from the reaction of N-(2-chloroallyl)-ethylamine with potassium amide. A choice between paths 1 and 2 might be made by employing N-(2-bromoallyl-1,1-d₂)-ethylamine and determining the amount of deuterium in the resulting I.

Acknowledgment.—We are indebted to Dr. Martin Ettlinger for drawing this problem to our attention in advance of publication⁶ and suggesting the use of n-m-r spectra in its solution.

Experimental¹⁴

N-Ethylallenimine, b.p. 77.0–78.2° (745 mm.), *n*_D²⁰ 1.4283, was prepared by the method of Pollard and Parcell.³ A fraction collected at 95–101° (745 mm.) representing 6% of the theoretical yield was shown by its infrared spectrum to be mainly N-ethylpropargylamine.

Hydrolysis of N-Ethylallenimine in the Presence of 2,4-Dinitrophenylhydrazine.—To a warm solution prepared from

(10) E. Linnemann, *Ann.*, **134**, 170 (1865).

(11) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 683.

(12) C. Bulow and F. Seidel, *Ann.*, **439**, 48 (1924).

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 49.

(14) Boiling points are uncorrected. Infrared spectra were obtained with a model 21 Perkin-Elmer spectrophotometer. Microanalyses were performed by Dr. A. Elek.

0.25 g. of 2,4-dinitrophenylhydrazine, concentrated hydrochloric acid and ethanol¹⁵ was added 0.1 g. of N-ethylallenimine. The mixture was allowed to stand overnight at room temperature and the yellow-brown needles were collected. After two recrystallizations from ethanol, the product had m.p. 123.6–124.6° (lit.³ m.p. 124–125°).

Anal. Calcd. for C₉H₉N₃O₄Cl: C, 39.65; H, 3.32. Found: C, 39.58; H, 3.34.

The infrared spectrum of the compound was identical with that of chloroacetone 2,4-dinitrophenylhydrazone, m.p. 122–124° (lit.¹² m.p. 124–125.5°).

To a warm solution prepared from 0.25 g. of 2,4-dinitrophenylhydrazine, sulfuric acid, water and ethanol¹⁶ was added 0.1 g. of N-ethylallenimine. The mixture was allowed to stand overnight at room temperature and the orange platelets (52 mg.) were collected. The product was heated with 10 ml. of ethanol and 3 ml. of ethyl acetate on a steam-bath for 10 min. and filtered hot. The insoluble material (13 mg.) had m.p. 302–304° (uncor.) and an infrared spectrum identical with that of methylglyoxal bis-(2,4-dinitrophenyl)-osazone, m.p. 302–304° uncor. (lit.¹⁷ m.p. 300–302°). The filtrate was allowed to cool to room temperature and yielded 34 mg. of fine yellow needles which contained no sulfur and had m.p. 134–135°.

N-(2-Chloroallyl)-ethylamine.—To 88 ml. of a 70% aqueous solution of ethylamine was added 34 g. of 2,3-dichloropropene. The mixture was cautiously warmed on a steam-bath to start the reaction and then allowed to boil gently under reflux for 15 min. When the spontaneous ebullition ceased, the mixture was heated under reflux for an additional 35 min. The two-phase mixture was cooled in an ice-bath and 15 g. of solid sodium hydroxide was added cautiously. The upper layer (31.8 g.) was separated, dried over solid sodium hydroxide and distilled rapidly from a 50-ml. claisen flask. The colorless N-(2-chloroallyl)-ethylamine (18.9 g., 52%) had b.p. 127–131°, *n*_D²⁰ 1.4470.

Anal. Calcd. for C₃H₇NCl: C, 50.20; H, 8.43; N, 11.71. Found: C, 50.21; H, 8.54; N, 11.73.

N-Ethylpropargylamine.—To a stirred solution of potassium amide prepared from 6.9 g. of potassium and 350 ml. of anhydrous liquid ammonia in a three-necked flask equipped with a Dry Ice reflux condenser, stirrer and a dropping funnel was added 18.7 g. of N-(2-chloroallyl)-ethylamine over 10 min. Stirring was continued for eight hours, after which time the ammonia was allowed to evaporate until a volume of about 75 ml. remained in the flask. Water (100 ml.) was cautiously added while stirring was continued. The mixture was then extracted with ether and the ether extracts were combined, dried over solid sodium hydroxide and most of the ether was removed by flash distillation. The residual N-ethylpropargylamine (9.23 g., 71%) was distilled through a 60-cm. Podbielniak column, b.p. 100.2–101° (742 mm.), *n*_D²⁰ 1.4315.

Anal. Calcd. for C₅H₉N: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.01; H, 11.18; N, 16.82.

N-Ethylpropargylamine hydrochloride had m.p. 181.2–182.5° while the hydrobromide had m.p. 164.1–165.1° after crystallization from absolute ethanol-ether.

Anal. Calcd. for C₅H₁₀NBr: C, 36.61; H, 6.14; Br, 48.71. Found: C, 36.56; H, 6.24; Br, 48.87.

N-Ethylpropargylamine, when hydrogenated in absolute ethanol over platinum oxide at atmospheric pressure, took up 98% of the theoretical amount of hydrogen in 20 hours. The hydrochloride of the resulting N-ethyl-n-propylamine had m.p. 225.4–227.9° (lit.¹⁸ m.p. 225°).

The infrared spectrum of N-ethylpropargylamine had a strong, sharp band at 3300 cm.⁻¹, the characteristic stretching frequency of acetylenic carbon-hydrogen bonds,¹⁸ and a weak band at 2100 cm.⁻¹, the characteristic stretching frequency of carbon-carbon triple bonds.¹³ The n-m-r spectrum was in complete agreement with the assigned structure.

PASADENA, CALIFORNIA

(15) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1949, p. 199.

(16) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(17) W. Swoboda, *Monatsh.*, **82**, 388 (1951).

(18) K. N. Campbell, A. H. Sommers and B. K. Campbell, *THIS JOURNAL*, **66**, 82 (1944).