

## Preparation of [2-D], [2,2'-D<sub>2</sub>], [1-<sup>15</sup>N], and [2-<sup>13</sup>C] Enriched Ethylenimines.

Børge BAK and Steen SKAARUP

Chemical Laboratory V, The H. C. Ørsted Institute  
University of Copenhagen, DK - 2100 Copenhagen, Denmark

Received March 8 1971

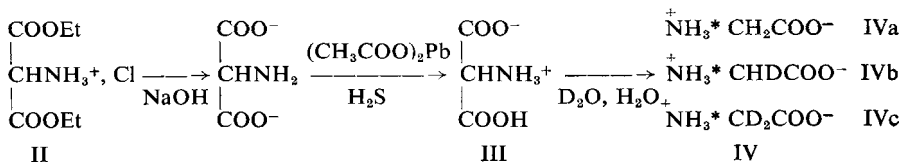
### SUMMARY

Three isotopically enriched samples of ethylenimine [aziridine] have been prepared, namely, mixtures containing ca. 50 % [2-D]ethylenimine, 25 % [2,2'-D<sub>2</sub>]ethylenimine, and 25 % parent molecule; 97 % [<sup>15</sup>N]ethylenimine and 3 % parent molecule; 64 % [<sup>13</sup>C]ethylenimine and 36 % parent molecule. Infrared gas spectra showed the samples (ca. 90 mg) to be of high chemical purity (>98 %). The preparations have been used successfully for high-resolution microwave studies.

### INTRODUCTION.

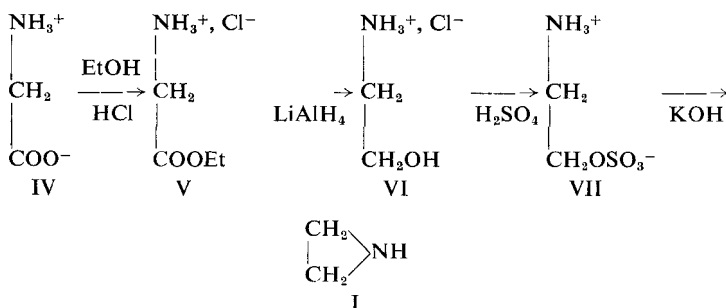
The purpose of this investigation was to prepare the 'family' of mono-isotopically substituted ethylenimines in high yields and chemical purity in order to establish the 'substitution' ( $r_s$ ) structure of ethylenimine (I) by microwave technique. Up till now only naturally occurring (I) and the [1-D] species have been examined (1, 2, 3, 4, 5, 6, 7), yielding incomplete structural information so that assumptions as to, for example, the spatial orientation of the methylene groups are necessary.

We have found isotopically enriched glycine a convenient starting material except for the deuterated species for which the ethyl ester hydrochloride of aminomalonic acid was applied, leading to deuterated glycines :



in which H\* is H or D.

For the remaining isotopic species commercially available enriched samples of  $^{15}\text{NH}_3^+\text{CH}_2\text{COO}^-$  (IV d) and  $\text{NH}_3^+ ^{13}\text{COO}^-$  (IV e) were used :



#### EXPERIMENTAL.

The reactions  $\text{II} \rightarrow \text{IV a, b, c}$  were carried out by saponification of 6 g (29 mmoles) of commercial **II** (100 ml in NaOH at 60° in 45 h), neutralizing by  $\text{CH}_3\text{COOH}$  and precipitating by 30 ml 0.5 m  $(\text{CH}_3\text{COO})_3\text{Pb}$  (15 mmoles). The yield of lead salt was 5.6 g (13 mequiv. Pb or 26 mmoles of 'acid'). Decomposition of the lead salt by  $\text{H}_2\text{S}$  in water, evaporation of water and drying of the crystalline residue in a high vacuum produced 17.9 mmoles of anhydrous <sup>(8)</sup> **III** as seen by its <sup>1</sup>HMR spectrum in  $\text{CF}_3\text{COOH}$  (TFA) and by analysis of the elements (found : C 30.13% (theory 30.25); H 4.20% (4.20); N 11.62% (11.76) of a sample dried to constant weight over  $\text{P}_2\text{O}_5$ ). In preliminary experiments it was established that the instantaneous exchange  $\text{H} \rightarrow \text{D}$  between the  $-\text{NH}_3^+$  and  $-\text{COOH}$  protons of (**III**) in  $\text{D}_2\text{O}$  solutions at 95° C (where the necessary decarboxylation takes place at a convenient rate) is accompanied by a substantial  $\text{H} \rightarrow \text{D}$  exchange involving the tertiary H of **III**. For this reason 4.6 mmoles of **III** was dissolved in an excess of a 1 : 1 mixture of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The solution was heated for 2 h at 95° C under evolution of  $\text{CO}_2$  and the solvent removed in a vacuum, leaving a mixture of **IV a**, **IV b**, and **IV c** in almost quantitative yield. Infrared and <sup>1</sup>HMR spectra of the product were not inconsistent with an approximate composition of 25% **IV a**, 50% **IV b**, and 25% **IV c**.

The conversions  $\text{IV} \rightarrow \text{V} \rightarrow \text{VI} \rightarrow \text{VII} \rightarrow \text{I}$  were carried out (quantities in Table 1) by using **V** directly instead of removing HCl as suggested in reference <sup>(9)</sup>. The presence of aqueous HCl in the receiver used at the continuous extraction is essential to obtaining a high yield of **VI**. Without purification **VI** was converted to **VII** <sup>(10)</sup>. Finally, **I** was successfully prepared from **VII** by placing a mixture of **VII** and a ten-fold excess of freshly ground KOH in a vessel, evacuating, immersing the vessel into a bath preheated to 130° C, and collecting the escaping gases in a trap cooled by liquid nitrogen (constant pumping). This procedure takes 5-6 minutes. The condensed product

(I, H<sub>2</sub>O, NH<sub>3</sub>, polymers of I (?)) was purified by five-fold distillation at room temperature in a vacuum over molecular sieve (3 Å pore size). The infrared gas spectrum (p = 57 mm Hg, t = 20° C, path length 10 cm) showed no evidence of impurities, but at our subsequent microwave investigation traces of NH<sub>3</sub> were easily observed. The ammonia lines did, however, not interfere with the lines from I. The pressure of the saturated vapors of the isotopic ethylenimines at 0° C was 57-58 mm Hg in accordance with the vapor pressure of authentic I.

The expected presence of pairs of lines in the microwave spectrum of [2-D]ethylenimine attributable to the 'inversion' isomers *syn* [2-D]- and *anti* -[2D] (in equal amounts) was established.

TABLE I. Quantities and yields of reactions IV → V → VI → VII → I.

Compounds		Deuterium enriched	<sup>15</sup> N enriched (97%)	<sup>13</sup> C enriched
IV	mg	340 <sup>b1</sup>	417 <sup>b1</sup>	367 <sup>b1</sup>
	mmoles	4.36	5.49	4.89
V	mg	567 <sup>b2</sup>	719 <sup>b2</sup>	664 <sup>b2</sup>
	mmoles	3.79	5.12	4.73
	yield %	88	94	97
VI	mg	318 <sup>b3</sup>	406 <sup>b3</sup>	396 <sup>b3</sup>
	mmoles	3.18	4.12	4.02
	yield %	84	81	85
VII	mg	410 <sup>b4</sup>	524 <sup>b4</sup>	537 <sup>b4</sup>
	mmoles	2.88	3.68	3.79
	yield %	91	90	94
I	mg	85 <sup>b5</sup>	85 <sup>b5</sup>	90 <sup>b5</sup>
	mmoles	1.9	1.9	2.1
	yield %	66	51	55
VI → I	Total yield %	43	35	43

<sup>b</sup> b (i + 1) produced from b (i).

#### REFERENCES

1. WILCOX, W. S., BRANNOCK, K. C., DEMORE, W. and GOLDSTEIN, J. H. — *J. Chem. Phys.*, **21** : 563 (1953).
2. TURNER, T. E., FIORA, V. C., KENDRICK, W. M. and HICKS, B. L. — *J. Chem. Phys.*, **21** : 564 (1953).

3. JOHNSON, R. D., MYERS, R. J. and GWINN, W. D. — *J. Chem. Phys.*, **21** : 1425 (1953).
4. TURNER, T. E., FIORA, V. C. and KENDRICK, W. M. — *J. Chem. Phys.*, **23** : 1966 (1955).
5. TOLLES, W. M. and GWINN, W. D. — *J. Chem. Phys.*, **42** : 2253 (1965).
6. KEMP, M. K. and FLYGARE, W. H. — *J. Am. Chem. Soc.*, **90** : 6267 (1968).
7. SUTTER, D. H. and FLYGARE, W. H. — *J. Am. Chem. Soc.*, **91** : 6895 (1969).
8. BAEYER, J. F. W. A. v. — *Annalen*, **131** : 295 (1964).
9. WEISSBACH, A. and SPRINSON, D. B. — *J. Biol. Chem.*, **203** : 1031 (1953).
10. LEIGHTON, P. A., PERKINS, W. A. and RENQUIST, M. L. — *J. Am. Chem. Soc.*, **69** : 1540 (1947).