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Preparation of [2-D], [2,2'-D_2], [1-^{15}N], and [2-^{13}C] Enriched Ethylenimines.

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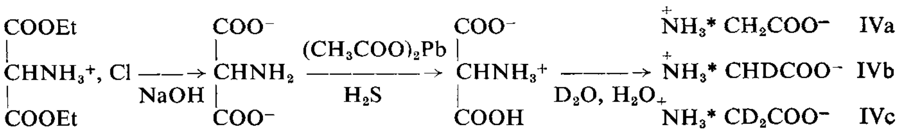
SUMMARY

Three isotopically enriched samples of ethylenimine [aziridine] have been prepared, namely, mixtures containing ca. *50 % [2-D]ethylenimine, 25 % [2,2'-D_2]ethylenimine, and 25 % parent molecule; 97 % [^{15}N]ethylenimine and 3 % parent molecule; 64 % [^{13}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 monoisotopically 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.

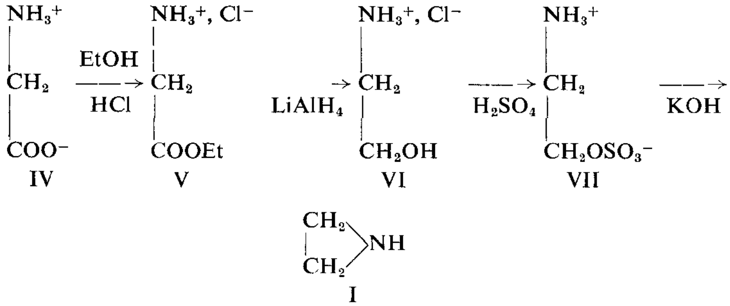
We have found isotopically enriched glycine a convenient starting material except for the deuterated species for which the ethyl ester hydrochloride of aminomalonic acid was applied, leading to deuterated glycines :



$$\begin{array}{llll}
\text{COOEt} & \text{COO}^- & \text{COO}^- & \overset{+}{\text{N}}\text{H}_3{}^*\ \text{CH}_2\text{COO}^- \quad \text{IVa}\\
| & | & | & \\
\text{CHNH}_3{}^+,\ \text{Cl} \xrightarrow[\text{NaOH}]{} & \text{CHNH}_2 \xrightarrow[\text{H}_2\text{S}]{(\text{CH}_3\text{COO})_2\text{Pb}} & \text{CHNH}_3{}^+ \xrightarrow[\text{D}_2\text{O},\ \text{H}_2\text{O}_+]{} & \overset{+}{\text{N}}\text{H}_3{}^*\ \text{CHDCOO}^- \quad \text{IVb}\\
| & | & | & \\
\text{COOEt} & \text{COO}^- & \text{COOH} & \text{NH}_3{}^*\ \text{CD}_2\text{COO}^- \quad \text{IVc}\\
\text{II} & & \text{III} & \text{IV}
\end{array}$$

in which H* is H or D.

For the remaining isotopic species commercially available enriched samples of $^{15}NH_3^+CH_2COO^-$ (IV d) and $NH_3^+\,^{13}COO^-$ (IV e) were used :



EXPERIMENTAL.

The reactions II $\rightarrow$ IV a, b, c were carried out by saponification of 6 g (29 mmoles) of commercial II (100 ml 1n NaOH at 60° in 45 h), neutralizing by CH_3COOH and precipitating by 30 ml 0.5 m $(CH_3COO)_2Pb$ (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 H_2S in water, evaporation of water and drying of the crystalline residue in a high vacuum produced 17.9 mmoles of anhydrous (8) III as seen by its ^{1}HMR spectrum in CF_3COOH(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 P_2O_5). In preliminary experiments it was established that the instantaneous exchange H $\rightarrow$ D between the $-NH_3^+$ and $-COOH$ protons of (III) in D_2O solutions at 95° C (where the necessary decarboxylation takes place at a convenient rate) is accompanied by a substantial H $\rightarrow$ 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 H_2O and D_2O. The solution was heated for 2 h at 95° C under evolution of 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 ^{1}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 IV $\rightarrow$ V $\rightarrow$ VI $\rightarrow$ VII $\rightarrow$ I were carried out (quantities in Table 1) by using V directly instead of removing HCl as suggested in reference (9). 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 (10). 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_2O, NH_3, 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, $t = 20^\circ$ C, path length 10 cm) showed no evidence of impurities, but at our subsequent microwave investigation traces of NH_3 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 1. Quantities and yields of reactions IV → V → VI → VII → I.

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

[b] b (i + 1) produced from b (i).

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