uncertainty of the conversion factor is fully as large. Therefore it is doubtful whether the atomic weight of arsenic could at present be determined with the mass spectrograph within 0.01 unit aside from the possibility that arsenic may contain small amounts of undiscovered isotopes.

## Summary

1. The preparation of pure arsenic trichloride and tribromide is described.

2. By analysis of the trihalides the atomic weight of arsenic is found to be 74.91.

CAMBRIDGE, MASSACHUSETTS

RECEIVED OCTOBER 31, 1932
PUBLISHED MARCH 7, 1933

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY. DIVISION OF INDUSTRIAL SCIENCES, WEST VIRGINIA UNIVERSITY]

# Reactions of Ethylene Oxide. I. The Action of Ethylene Oxide on Diethylamine

BY A. J. W. HEADLEE, A. R. COLLETT AND C. L. LAZZELL

## Introduction

Previous to the recent paper of Horne and Shriner[1] the literature contained no satisfactory directions for the preparation of diethylaminoethanols from ethylene oxide and diethylamine. Simultaneously with Horne and Shriner, the present authors, using a different method of preparation, obtained products whose physical properties do not agree with those obtained by the above workers. The authors do not agree with Horne and Shriner's statement that ethylene oxide does not react with their solvent, methyl alcohol, an appreciable reaction being easily obtained at 55°. By successive additions of ethylene oxide to diethylamine and the resulting products the following compounds were prepared and will be referred to hereafter by the Roman numeral assigned to each.

I $(C_2H_5)_2NCH_2CH_2OH$
II $(C_2H_5)_2NCH_2CH_2OCH_2CH_2OH$
III $(C_2H_5)_2N(CH_2CH_2O)_2CH_2CH_2OH$
IV $(C_2H_5)_2N(CH_2CH_2O)_3CH_2CH_2OH$
V $(C_2H_5)_2N(CH_2CH_2O)_4CH_2CH_2OH$
VI $(C_2H_5)_2N(CH_2CH_2O)_5CH_2CH_2OH$
VII $(C_2H_5)_2N(CH_2CH_2O)_6CH_2CH_2OH$

## Experimental

**Preparation of Diethylaminoethanol.**—38.3 grams of diethylamine (b. p. 55–57°) and 23.5 g. of ethylene oxide were caused to react in a copper autoclave of 500-ml. capacity at 100°. The reaction was complete within one hour; 49.6 g. of (I) was obtained, a yield of 81%. The reaction could be completed in two to ten minutes in the presence of small quantities of water, but this greatly increased the difficulties of separating the products. The reaction was also carried out in the presence of ether and alcohol as solvents but with a decrease in the rate of the reaction. Diethylaminoethanol

---

(1) Horne and Shriner, THIS JOURNAL, **54**, 2925 (1932).

and ethylene oxide were autoclaved yielding (II). (II) was then autoclaved with ethylene oxide to produce (III). This process was continued until sufficient quantities of each compound were obtained for purification. On careful fractional vacuum distillation, colorless products were obtained for compounds I–VII.

**Preparation of the *p*-Nitrobenzoate of (II).**—4.2 grams of (II) in benzene was added to 4.6 g. of *p*-nitrobenzoyl chloride. The crystals (m. p. 128.5°) obtained were soluble in water, alcohol, chloroform, and only slightly soluble in acetone.

*Anal.* Calcd. for $(C_2H_5)_2NHCl(C_2H_4O)_2COC_6H_4NO_2$: Cl, 10.2; mol. wt. 347. Found: Cl, 10.06; mol. wt., 344.

In Table I are collected the pertinent data relating to the compounds prepared. The data of Horne and Shriner are also presented here in order to form a basis of comparison.

TABLE I

PROPERTIES OF THE ETHANOL AMINES

| | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| B. p., °C. | 160[a] | 135 | 163–165 | 185–188 | 182–184 | 254–259 | 205–209 |
| Mm. | 741 | 46 | 30 | 53 | 9 | 36 | 4 |
| B. p., °C., H. & S.[b] | 163 | 92–95 | 123–128 | 164–172 | 190–200 | | |
| Mm. | 760 | 7 | 7 | 7 | 7 | | |
| $n_D^{25}$ | 1.4389 | 1.4464 | 1.4501 | 1.4529 | 1.4566 | 1.4592 | 1.4620 |
| H. & S.[b] | 1.4400 | 1.4457 | 1.4534 | 1.4570 | 1.4622 | | |
| $M_D^{25}$ Calcd. | 34.94 | 45.82 | 56.70 | 67.58 | 78.46 | 89.63 | 100.51 |
| Found | 34.94 | 45.61 | 56.61 | 67.85 | 78.70 | 89.25 | 99.95 |
| Found, H. & S.[b] | 35.81 | 45.65 | 56.80 | 66.31 | 74.92 | | |
| $d^{25}_{\text{Abs.}}$ | 0.8800 | 0.9421 | 0.9753 | 0.9905 | 1.0128 | 1.0325 | 1.0474 |
| H. & S.[b] | 0.8575 | 0.9371 | 0.9734 | 1.0206 | 1.048 | | |
| $\eta^{25}_{\text{Abs.}}$ | 0.0405 | 0.0856 | 0.1284 | 0.1596 | | | |
| $\gamma$ 26.5° | 27.50 | 30.05 | 31.26 | 32.05 | 33.47 | 34.65 | 35.51 |
| Mol. wt. Calcd. | 117 | 161 | 205 | 249 | 293 | 337 | 381 |
| Found | 116 | 171 | 223 | 245 | 281 | 321 | 367 |
| $N_2$, %, Calcd. | 11.95 | 8.69 | 6.83 | 5.62 | 4.77 | 4.15 | 3.67 |
| Found | 11.88 | 8.40 | 6.51 | 5.74 | 4.82 | 3.96 | 3.80 |

[a] The following boiling points were obtained for (I): 55° (10 mm.); 100° (80 mm.); 96° (73 mm.). [b] (H. & S.) Data of Horne and Shriner.[1] For comparison their specific gravities were converted to absolute densities.

All thermometers were checked against certified thermometers and were corrected for emergent stem. The refractive indices were determined with an Abbé refractometer; the density with an 8-cc. pycnometer; the viscosity with an Ostwald viscometer; the surface tension by the Du Noüy method (corrected by the formula of Harkins and Jordan);[2] the molecular weights by the freezing point method using benzene as a solvent; the nitrogen content by the Kjeldahl method, and by titration with sulfuric acid.

## Discussion of Results

In Fig. 1 are plotted curves showing the change in density and refractive index with increase in molecular weight. The continuous addition of ethylene oxide to the aminoethanols suggests the possibility of preparing

---

(2) Harkins and Jordan, THIS JOURNAL, **52**, 1751 (1930).

a series of ethoxyethanols of indeterminate length. No indication of a decrease in activity of the hydroxyl group with increasing length of the chain was noted. Thus the number of additions seems to be limited only by the stability of the chain. This offers a possible explanation of the so-called polymers[3] of ethylene oxide described in the recent literature. The continuous addition of ethylene oxide to a very limited number of hydroxyl groups might produce a compound whose empirical formula would be very near that of ethylene oxide. In fact when the authors autoclaved 1.5 g. of diethylaminoethanol with 28 g. of ethylene oxide, no uncombined ethylene oxide was detected. The resulting product was a very highly viscous liquid. The proportions of the reactants used would indicate that as an average the molecules of this product contain approximately fifty $—CH_2CH_2O—$ groups, provided the ethylene oxide continued to add on to each newly formed hydroxyl group. This phase of the work is now being investigated.

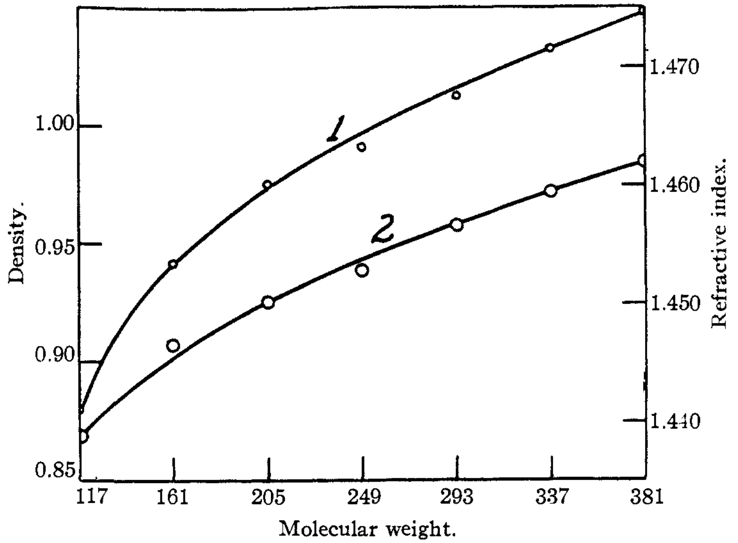


Fig. 1.—Physical properties of the amines: curve 1, density; curve 2, refractive index.

The authors wish to acknowledge their indebtedness to the Carbide and Carbon Chemicals Corporation, Charleston, West Virginia, for the supply of ethylene oxide used in this investigation.

## Summary

1. Methods for the preparation of diethylaminoethanol giving yields of 80–87% are described. Some physical properties of this compound have been determined.

---

[3] Staudinger and Schweitzer, *Ber.*, **62**, 2395 (1929).

2. A series of diethylaminoethoxyethanols have been prepared and some of their physical properties determined. Two members of this series have not been reported previously.

MORGANTOWN, WEST VIRGINIA

RECEIVED JUNE 27, 1932
PUBLISHED MARCH 7, 1933

---

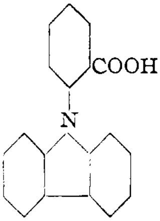
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# Stereochemistry of N-Phenylpyrroles. XXIX.[1] Preparation and Properties of *o*-N-Carbazyl- and *o*-N-(3-Nitrocarbazyl)-benzoic acid

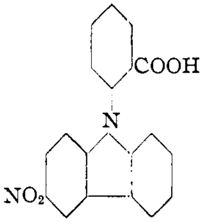
BY W. I. PATTERSON[2] AND ROGER ADAMS

A discussion of the optical isomerism of substituted phenylpyrroles and dipyrryls[3] has been given in previous papers and representative compounds of both classes have been prepared and resolved (III and IV). The experimental evidence all pointed to the conclusion that the isomerism is essentially of the same type and due to essentially the same causes as are found in substituted diphenyls.

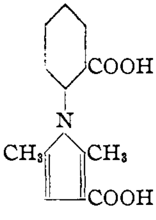
The present investigation has involved the extension of this work to certain substituted N-phenylcarbazoles. In *o*-N-carbazylbenzoic acid (I) there is a symmetrical substitution of the pyrrole ring and, therefore, the compound should be resolvable only if the nitrogen atom retains a more or less fixed tetrahedral structure. No resolution was accomplished. On the other hand, if a substituting group is introduced into the carbazole nucleus, unsymmetrical substitution of the pyrrole is present and substitution conditions resembling those necessary for resolution in the diphenyl series obtain. The *o*-(3-nitrocarbazyl)-benzoic acid (II) was resolved into enantiomorphic forms. The fact that the introduction of a substituting group so far removed from the carbazole nitrogen atom is all that is necessary to render the molecule capable of being resolved, is a potent argument against the probability that optical activity is due to the nitrogen atom.



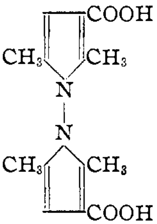
I



II



III



IV

---

[1] For the last paper, XXVIII, see Kleiderer and Adams, THIS JOURNAL, **55**, 716 (1933).

[2] The experimental work was done by W. I. Patterson and is part of his thesis for the Degree of Doctor of Philosophy at the University of Illinois.

[3] Bock and Adams, THIS JOURNAL, **53**, 374, 3519 (1931); Chang and Adams, *ibid.*, **53**, 2353 (1931).