TABLE II.

| Figure. | Substance. | Hydrogen number. | Per cent. of active constituent. | Theoretical per cent. of active constituent. |
|---|---|---|---|---|
| 3.......... | Safrol | 135.6 | 98.3 | 100.0 |
| 4.......... | Limonene | ... | .. | ... |
| 5.......... | Imitation sassafras oil | 111.9 | 81.1 | 80.0 |
| 6.......... | Authentic sassafras oil | 103.1 | 74.8 | ... |
| | | 102.0 | 74.0 | ... |
| 7.......... | Anethol | 150.5 | 99.6 | 100.0 |
| 8.......... | Imitation anise oil | 125.1 | 82.4 | 80.0 |
| | | 127.0 | 83.7 | 80.0 |
| 9.......... | Commercial anise oil | 125.8 | 82.9 | ... |
| | | 127.3 | 83.9 | ... |
| 10.......... | Commercial fennel oil | 101.3 | 66.8 | ... |
| | | 102.7 | 67.7 | ... |
| 11.......... | Eugenol | 134.4 | 98.3 | 100.0 |
| 12.......... | Imitation clove oil | 113.2 | 82.8 | 80.0 |
| | | 113.3 | 82.8 | 80.0 |
| 13.......... | Commercial clove oil | 114.6 | 83.8 | ... |
| | | 114.0 | 83.3 | ... |
| 14.......... | Commercial pimenta oil | 97.8 | 71.5 | ... |
| | | 97.8 | 71.5 | .. |

WASHINGTON, D. C.

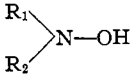
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

# THREE ISOMERIC ETHYL SECONDARYBUTYL HYDROXYLAMINES.

BY LAUDER WILLIAM JONES AND LEONORA NEUFFER.

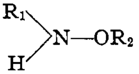
Received July 31, 1914.

By the substitution of two different groups for hydrogen in hydroxylamine, three isomeric compounds are possible and may be represented by the following general formulas:



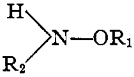
$$\genfrac{}{}{0pt}{}{R_1}{R_2}\!>N{-}OH$$

A.



$$\genfrac{}{}{0pt}{}{R_1}{H}\!>N{-}OR_2$$

B.



$$\genfrac{}{}{0pt}{}{H}{R_2}\!>N{-}OR_1$$

C.

Compounds of the type A, $\beta,\beta$-derivatives,[1] were first prepared by Bewad.[2] The first representative of types B and C, $\alpha,\beta$-derivatives, was the $\alpha$-benzyl-$\beta$-ethyl derivative prepared by Behrend and Leuchs[3] in 1890. Since then no compounds of the $\alpha,\beta$ type containing two different radicals were described until Jones,[4] in 1907, prepared two isomeric compounds, *viz.*, $\alpha$-ethyl $\beta$-methyl- and $\alpha$-methyl-$\beta$-ethyl hydroxylamines.

It is the purpose of the present paper to describe the preparation and properties of two new $\alpha,\beta$-dialkyl hydroxylamines, which are isomeric

---

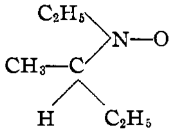
[1] In this paper $\alpha$ = attached to O; $\beta$ = attached to N.

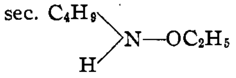
[2] Bewad, *Ber.*, [1] 479 (1888); *J. russ. phys. Chem. Soc.*, 32, 420 (1900).

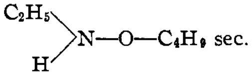
[3] Behrend and Leuchs, *Ann.*, 257, 237 (1890).

[4] Jones, *Am. Chem. J.*, 38, 253 (1907).

with the first dialkyl hydroxylamine prepared by Bewad, namely, β-ethyl-β-secondarybutyl hydroxylamine. The following formulas represent the three isomers:


I.


II.


III.

## Historical.

*I. β-Ethyl β-Secondarybutyl Hydroxylamine.*—In an article on the action of zinc ethyl on nitro compounds of the fatty series and on their bromo derivatives published in 1888,[1] Bewad described, what he believed to be, triethyl hydroxylamine obtained by the action of zinc ethyl on nitroethane. In this first stage of the reaction he obtained a crystalline compound which he assumed to have the formula $2C_2H_5NO_2 + Zn(C_2H_5)_2$. The subsequent disappearance of these crystals was explained by the formation of $(C_2H_5)_3N(OZnC_2H_5)_2$ which interacted with water to give the hydrate of triethyl hydroxylamine,

$$(C_2H_5)_3N(OZnC_2H_5)_2 + 4H_2O = (C_2H_5)_3N(OH)_2 + 2C_2H_6 + 2Zn(OH)_2.$$

He assumed that the hydrate lost water, leaving triethyl hydroxylamine, $(C_2H_5)_3N = O$. Upon reducing the supposed triethyl hydroxylamine, Bewad believed he obtained triethyl amine, and, therefore, arrived at the conclusion that the action of zinc alkyls on nitroparaffins was a means of preparing trialkyl hydroxylamines.

In 1899, Dunstan and Goulding[2] showed that by the action of ethyl iodide upon diethyl hydroxylamine, triethyl oxamine was produced. They gave an account of its reactions and showed it to be a true oxamine, $(C_2H_5)_3N = O$, and not the isomeric triethyl hydroxylamine $(C_2H_5)_2NOC_2H_5$. They later obtained the same compound by the direct oxidation of triethylamine with hydrogen peroxide. Bewad had given his compound the formula $(C_2H_5)_3N = O$, on account of its having furnished, as he believed, triethylamine upon reduction. But the properties of Bewad's compound differed so markedly from those of the compound described by Dunstan and Goulding, it was considered possible that Bewad had obtained the isomeric triethyl hydroxylamine, $(C_2H_5)_2N—OC_2H_5$, and not the oxamine. But the properties of the compound described by Bewad were not such as would be expected from a substituted hydroxylamine of the formula $(C_2H_5)_2NOC_2H_5$.

In 1900, Lachman[3] prepared β-diethyl hydroxylamine by the action

---

[1] Bewad, *J. Russ. Phys. Chem. Soc.*, 1, 125 (1888).

[2] Dunstan and Goulding, *Trans. J. Chem. Soc.*, 75, 792 (1899).

[3] Lachman, *Ber.*, 33, 1022 (1900).

of zinc ethyl on diphenyl nitrosamine, and found the product to be identical with the one obtained by Dunstan and Goulding from ethyl iodide and hydroxylamine. The identity of these two compounds, and the isomerism existing between the triethyl oxamine of Bewad and of Dunstan and Goulding led Lachman to compare the properties of the two triethyl oxamines obtained by the two methods. He, too, concluded that Bewad's compound had not the same properties as Dunstan's and Goulding's triethyl hydroxylamine. Lachman, to investigate the problem further, prepared a compound by the action of methyl iodide upon Bewad's so-called triethyl oxamine and assigned to it the formula $(C_2H_5)_3NOCH_3I$, having concluded that it underwent decomposition into formaldehyde and triethyl amine. This, however, did not agree with the conclusion he had previously reached, that Bewad's compound was not identical with Dunstan's and Goulding's.

It was soon shown that the properties Lachman had assigned to his methyl iodide derivative were not correct. Almost simultaneously, Bewad[1] and Dunstan and Goulding[2] arrived at the conclusion that Bewad's supposed triethyl hydroxylamine was $\beta$-ethyl-$\beta$-secondary butyl hydroxylamine, and the formula $C_2H_5(CH_3)CHN(C_2H_5)OH$ satisfactorily accounted for its properties. Bewad described a general method for the preparation of $\beta$-dialkyl hydroxylamines by the action of zinc alkyls on primary or secondary nitroparaffins. The $\beta$-dialkyl hydroxylamines obtained in this way were identical with the ones prepared by Dunstan and Goulding by the action of alkyl iodides upon hydroxylamine.

In the preparation of the $\alpha,\beta$-compounds containing the same two alkyl groups as Bewad's $\beta,\beta$ compound, the method described by Jones in the preparation of two isomeric $\alpha,\beta$-methyl ethyl hydroxylamines was followed.[3] Two different alkyl groups were introduced successively into hydroxyurethane, and the resulting product hydrolyzed. To prepare the mono-substituted hydroxyurethane, an alcoholic solution of hydroxyurethane was mixed with a theoretical quantity of alkyl halide, and treated with the calculated amount of potassium hydroxide dissolved in alcohol. The potassium iodide which separated was filtered off, and the solution extracted with ether. In the work of Jones, and in the later work of Hecker[4] the ether solution was found to contain a mixture of the mono- and dialkyl esters of hydroxyurethane. These two products were separated by shaking the ether solution with dilute alkalies, whereby the salt of the mono-alkyl compound dissolved in water, and the di-compound remained in the ether solution. But in the preparation of the second-

---

[1] Bewad, *J. Russ. Chem. Soc.*, **32**, 420 (1900).

[2] Dunstan and Goulding, *J. Chem. Soc.*, **79**, 641 (1901).

[3] Jones, *Am. Chem. J.*, 38, 253 (1907).

[4] Hecker, *Ibid.*, 50, 444 (1913).

arybutyl hydroxyurethane no di-derivative was formed. This was shown by extracting with dilute alkali, and fractionating the ether solution which was left. Only a few drops of an oil were obtained and these gave an analysis agreeing with that for the mono-compound.

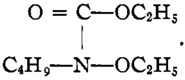
To prepare the α,β-dialkyl derivatives, equivalent quantities of the monoalkyl hydroxyurethane and of alkyliodide were treated with the theoretical amount of sodium ethylate in alcohol. The α,β-dialkyl derivatives of hydroxyurethane were converted into their corresponding hydroxylamines by heating them with an excess of potassium hydroxide solution in sealed tubes, at a temperature below 100°. The product was distilled into dilute hydrochloric acid, and the resulting chloride decomposed with solid potassium hydroxide.

The hydroxyurethane used in the following work was prepared according to the method described by Jones.[1]

## Experimental Part.

### II. *The Preparation of α-Ethyl β-Secondarybutyl Hydroxylamine.*

The α-ethyl hydroxyurethane used was prepared according to the method described by Jones.[2]

(*a*) *α-Ethyl β-Secondarybutyl Hydroxyurethane*, 

$$\begin{array}{c} O = C—OC_2H_5 \\ | \\ C_4H_9—N—OC_2H_5 \end{array}$$

.—Thirty grams of secondarybutyl iodide and 23 g. of α-ethyl hydroxyurethane were mixed with a quantitative amount of sodium ethylate and enough absolute alcohol to make a homogeneous mixture. When the mixture was allowed to stand at room temperature for five days, a slight precipitate formed. The contents of the flask were then heated on a water bath for 3 hrs. A heavy precipitate of sodium iodide was formed and was filtered off. After most of the alcohol was removed by distillation, the solution was diluted with water and extracted repeatedly with ether. Traces of iodine were removed with sodium thiosulfate and the ether solution was dried with sodium sulfate. The ether was removed by distillation and the residue fractionated under diminished pressure. Upon analysis, the colorless oil which was obtained was found to contain more nitrogen than was required by theory. The oil was found to contain a small amount of unconverted hydroxyurethane which was readily removed by shaking it with sodium hydroxide solution. After drying the oil and fractionating it again, 10.2 g. of a colorless liquid with a peculiar, rather pleasant odor were obtained. It boiled at 105–106.4° under 55 mm. pressure, was only slightly soluble in water, but readily soluble in alcohol and in ether.

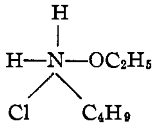
Calc. for $C_9H_{19}O_3N$: N, 7.41; found: 7.9.

---

[1] Jones, *Am. Chem. J.*, 20, 41 (1898).

[2] Jones, *Loc. cit.*

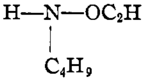
(*b*) *α-Ethyl β-Secondarybutyl Hydroxylammonium Chloride,*



—Five grams of α-ethyl β-secondarybutyl hydroxyurethane were mixed with a water solution containing 7 g. of potassium hydroxide and heated in a sealed tube from 95–100°, for 36 hrs. The contents of the tube were distilled into a dilute solution of hydrochloric acid. The acid solution was evaporated to the consistency of a thick oil and was then transferred to a vacuum desiccator. When the last traces of liquid were removed, a colorless crystalline solid, somewhat deliquescent, remained. This was purified by dissolving in absolute alcohol and reprecipitating it with dry ether. Its melting point was 94°. 1.9 g. were obtained. The chloroplatinate was precipitated as a yellow well defined crystalline solid, by mixing an alcoholic solution of the hydrochloride with an alcoholic solution of platinic chloride, and adding an excess of dry ether.

Calc. for $C_{12}H_{12}O_2NPtCl_6$: Pt, 30.30; found: 30.07.

(*c*) *α-Ethyl β-Secondarybutyl Hydroxylamine,*



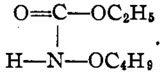
$$\begin{array}{l} H\text{—}N\text{—}OC_2H_5 \\ \quad\;\; | \\ \quad C_4H_9 \end{array}$$

.—One and five-tenths grams of the chloride were placed in a distilling flask and covered with an excess of powdered potassium hydroxide. Action began at once, and, upon application of gentle heat, a colorless liquid with a faint but distinct ammoniacal odor and boiling at 88.4–89° was obtained.

Calculated for $C_6H_{15}ON$: N, 11.96; found: 11.76.

### *III. The Preparation of α-Secondarybutyl β-Ethyl Hydroxylamine.*

(*a*) *α-Secondarybutyl Hydroxyurethane,*



$$\begin{array}{l} O{=}C\text{—}OC_2H_5 \\ \quad\;\; | \\ H\text{—}N\text{—}OC_4H_9 \end{array}$$

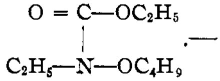
.—An alcoholic solution containing 100 g. of secondarybutyl iodide, 57 g. of hydroxyurethane and 30.4 g. of potassium hydroxide were allowed to stand for several days and then was heated for two hours on a water bath. The precipitate of potassium iodide which separated was filtered off and the excess of alcohol removed by distillation. Water was added and the solution extracted repeatedly with ether. The ether solution was extracted with a calculated amount of potassium hydroxide solution, a solution of the potassium salt of α-secondarybutyl hydroxyurethane being thereby obtained.

The free ester was obtained by acidifying the solution with 10% sulfuric acid, extracting it with ether, after removing traces of iodine, drying, and fractionating. The fractionation was carried out under diminished pressure, as the ester decomposed at atmospheric pressure. Before a satisfactory analysis could be made, it was necessary to remove traces of oxyurethane by shaking the oil with sodium hydroxide solution.

Thirty-four grams of a colorless oil, with a peculiar, rather unpleasant odor, slightly soluble in water, and boiling at 116–116.6° at 27 mm., were obtained.

Calculated for $C_7H_{15}O_3N$: N, 8.69; found: 8.88.

(*b*) *α-Secondarybutyl β-Ethyl Hydroxyurethane,*

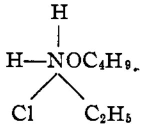


$$\begin{array}{c} O = C\text{—}OC_2H_5 \\ | \\ C_2H_5\text{—}N\text{—}OC_4H_9 \end{array}$$

.—A mixture of 10 g. of α-secondarybutyl hydroxyurethane, 9.6 g. of ethyl iodide and the calculated amount of sodium ethylate in absolute alcohol was treated as described under α-ethyl β-secondarybutyl hydroxyurethane. 6.8 g. of a colorless oil, very slightly soluble in water and boiling at 86.5–87° under 30 mm. pressure were obtained.

Calculated for $C_9H_{15}O_3N$: N, 7.41; found: 7.72.

(*c*) *α-Secondarybutyl β-Ethyl Hydroxylammonium Chloride,*

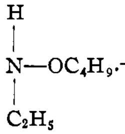


$$\begin{array}{c} H \\ | \\ H\text{—}NOC_4H_9. \\ / \quad \backslash \\ Cl \qquad C_2H_5 \end{array}$$

—Five grams of α-secondarybutyl β-ethyl hydroxyurethane were sealed in a tube with a water solution containing 20 g. (large excess) of potassium hydroxide. The tube was heated for 40 hrs. at 98–103°. The contents of the tube were treated as described under α-ethyl β-secondarybutyl hydroxylammonium chloride. 1.8 g. of an oily white solid, too deliquescent to make a melting point determination, were obtained. The chloroplatinate was prepared and precipitated by dry ether as a deep yellow, crystalline solid.

Calc. for $[C_2H_5NOC_4H_9H_2]PtCl_6$: Pt, 30.30; found: N, 30.11.

(*d*) *α-Secondarybutyl β-Ethyl Hydroxylamine,*



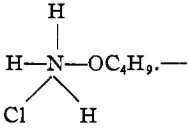
$$\begin{array}{l} H \\ | \\ N\text{—}OC_4H_9. \\ | \\ C_2H_5 \end{array}$$

—One and three-tenths grams of the hydrochloride were placed in a distilling flask with 3 g. of powdered potassium hydroxide. Action began at once. The flask was heated gently and a colorless liquid with a distinctly ammoniacal odor was collected in an ice-cooled receiver. Its boiling point was found to be 93.5–94°.

Calc. for $C_6H_{15}ON$: N, 11.96; found: N, 11.76.

### *IV. The Preparation of α-Secondarybutyl Hydroxylamine.*

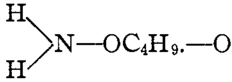
(*a*) *α-Secondarybutyl Hydroxylammonium Chloride,*



$$\begin{array}{c} H \\ | \\ H\text{—}N\text{—}OC_4H_9.\text{—} \\ / \quad \backslash \\ Cl \qquad H \end{array}$$

Ten grams of α-secondarybutyl hydroxyurethane were sealed in a tube with 20 g. of potassium hydroxide dissolved in water and heated at 90–100°, for 28 hrs. The contents of the tube were treated as described above and 2.4 g. of a white, crystalline solid, melting at 54.7–55° and not in the least deliquescent, were obtained. The chloroplatinate was precipitated as beautiful, well defined, deep yellow crystals.

Calc. for $[C_4H_9ONH_3]_2PtCl_6$: Pt, 33.19; found: Pt, 32.89.

(*b*) *α-Secondarybutyl Hydroxylamine,*  $\begin{matrix}H\\H\end{matrix}\!\!>N\text{—}OC_4H_9$.—One and eight-tenths grams of the chloride and 5 g. of potassium hydroxide were gently heated in a distilling flask. A clear, colorless liquid with a strongly ammoniacal odor, boiling at 85.5°, was obtained.

Calc. for $C_4H_{11}ON$: N, 15.72; found: N, 15.78.

The preparation of α-ethyl β-secondarybutyl and α-secondarybutyl β-ethyl hydroxylamines completes a set of three isomers of the type $R_1R_2HNO$.

The following table summarizes the properties of the compounds described:

| | Esters of hydroxyurethane. B. p. | Alkyl hydroxylamines. B. p. | Alkyl hydroxyl ammonium chloride. M. p. |
|---|---|---|---|
| β-Ethyl β-sec.-butyl... | .............. | 155–158° (Bewad) | 56–57° (Bewad) |
| α-Ethyl β-sec.-butyl... | 105–106.4° [55 mm.] | 88.4–89° | 94° |
| α-Sec.-butyl β-ethyl... | 86.5–87 [30 mm.] | 93.5–94° | [deliquescent] |
| α-Sec.-butyl.......... | 116–116.6° [27 mm.] | 85.5° | 54.7–55° |

## Summary.

(1) The preparation and properties of secondarybutyl, and mixed ethyl secondarybutyl hydroxyurethanes are described in this paper. These compounds are high boiling, oily liquids with a characteristic odor. They reduce neither ammoniacal silver nitrate nor Fehling's solution. They are readily hydrolyzed by potassium hydroxide solution below 100°.

(2) The preparation and the properties of secondarybutyl, and mixed ethyl secondarybutyl hydroxylamines, their chlorides and chloroplatinates are described. The free hydroxylamines are liquids which have a characteristic ammoniacal odor, all boil between 85 and 90° at ordinary pressure, and are reducing agents toward ammoniacal silver nitrate in the cold, and toward Fehling's solution when heated.

CINCINNATI, OHIO.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

# SOME NEW HYDROXYURETHANES AND CHROMOISOMERIC SILVER SALTS OF THEIR ACYL DERIVATIVES.

BY LAUDER WILLIAM JONES AND RALPH OESPER.

Received July 31, 1914.

In a recent article[1] we described some experiments which had in view

---

[1] THIS JOURNAL, 36, 726 (1914).