

identify by its reaction with  $H_2NOH \cdot HCl$ . The conversion to aldehyde is 43%.<sup>9</sup>

### Summary

All the nitroparaffins available from the nitration of propane, butane, and isobutane have been reduced to the corresponding amines by the use of iron and hydrochloric acid and catalytic hydrogenation. These processes produce good

(9) Pemberton, Card and Craven, *J. Soc. Chem. Ind.*, **54**, 163T (1935).

yields of easily purified products and require only simple technique. The results indicate that primary, secondary, and tertiary nitroparaffins can be reduced to give almost quantitative yields of the corresponding amines.

The conversion of nitroparaffins to oximes gives, in general, rather low yields because of the simultaneous formation of the amines.

LAFAYETTE, INDIANA

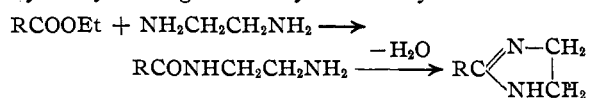
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE]

## Preparation and Cyclization of Monoacylethylenediamines. II

BY SAMUEL R. ASPINALL

It has been shown<sup>1</sup> that the best method of preparing 2-substituted-4,5-dihydroimidazoles is by dehydrating monoacylated ethylenediamines.



The investigation herein reported was undertaken to determine the extent of the applicability of this method. As a result of this and previous work<sup>1</sup> it is shown that an ester may be converted to the corresponding 4,5-dihydroimidazole in an over-all yield of about 75% when R is any one of such divergent groups as:  $CH_3-$ ,  $C_2H_5-$ ,  $n-C_5H_{11}-$ ,  $(C_2H_5)_2CH-$ ,  $(iso-C_5H_{11})_2CH-$ ,  $C_6H_5-$ ,  $p-CH_3C_6H_4-$ , or  $C_6H_5CH_2-$ . The yield of 2-diphenylmethyl-4,5-dihydroimidazole from ethyl diphenylacetate was considerably lower. Because reaction conditions for this series of experiments were more or less arbitrarily fixed in order to give comparable data, the yield reported for any given experiment is not necessarily the best obtainable.

Two slight changes in the procedure heretofore employed<sup>1</sup> have resulted in simplification and generally higher yields. (a) The reaction of ethylenediamine and esters of six or more carbon atoms which are branched in the alpha position requires higher temperatures than heretofore used. This effect is presumably due to the condition usually described as steric hindrance. (b) If the mixture of monoamide and diamide resulting from the reaction of ethylenediamine and an ester is treated in the usual way with lime, the yields are somewhat higher than those obtained by dehydrating the isolated monoamide with

lime. This fact is in accord with earlier observations<sup>2</sup> that ethylenediamides yield some 4,5-dihydroimidazole when heated at a high temperature with acid binding materials.

A typical experiment is now carried out as follows: 2-diethylmethyl-4,5-dihydroimidazole. Forty-eight grams ( $1/3$  mole) of ethyl diethylacetate and 60 g. (1 mole) of ethylenediamine are heated at 215° for twenty-four hours, and the low boiling material consisting of ethyl alcohol and excess ethylenediamine removed at diminished pressure. The remaining 39 g. of monoamide and diamide is heated with 94 g. ( $2/3$  mole) of calcium oxide at 225° for fifteen hours in an atmosphere of nitrogen. The organic products are extracted from the lime with alcohol, the solvent removed, and the product distilled at low pressure. 2-Diethylmethyl-4,5-dihydroimidazole, which distills as a pure white oil, solidifies immediately on cooling and is obtained as glistening white needles from petroleum ether.

It was earlier<sup>1</sup> pointed out that although the lower aliphatic monoacylethylenediamines are distillable under ordinary laboratory vacuum conditions, the corresponding aromatic derivatives are not, because the latter dehydrate to the 4,5-dihydroimidazole configuration at a temperature below that required for their distillation. It has now been found the behavior of the higher and phenylated aliphatic derivatives upon distillation is somewhat variable and depends upon structural features. (a) A higher aliphatic monoacylethylenediamine containing an alkyl group branched in the alpha position may be smoothly distilled at constant temperature to yield a distillate whose purity and homogeneity were demonstrated by quantitative conversion to simple derivatives. Presumably the steric factors which inhibit the initial reaction between the ester and

(1) Hill and Aspinall, *THIS JOURNAL*, **61**, 822 (1939).

(2) Chitwood and Reid, *THIS JOURNAL*, **57**, 2424 (1935).

TABLE I

REACTION OF ESTERS WITH ETHYLENEDIAMINE, CYCLIZATION TO 4,5-DIHYDROIMIDAZOLES AND PROPERTIES OF THEIR DERIVATIVES

| Reacting ethyl ester | Product  | M. p.,<br>°C. corr. | B. p.,<br>°C. Mm. | Yield,<br>%     | % N    |                     | Picrate <sup>b</sup> |                  |                            | Hydrochloride <sup>c</sup> |        |                            | Phenylureido derivative <sup>d</sup> |                  |                            |       |
|----------------------|--|---------------------|-------------------|-----------------|--------|---------------------|----------------------|------------------|----------------------------|----------------------------|--------|----------------------------|--------------------------------------|------------------|----------------------------|-------|
|                      |  |                     |                   |                 | Calcd. | Kjeld. <sup>e</sup> | M. p.,<br>°C. corr.  | Calcd.           | % N<br>Kjeld. <sup>e</sup> | M. p.,<br>°C. corr.        | Calcd. | % N<br>Kjeld. <sup>e</sup> | M. p.,<br>°C. corr.                  | Calcd.           | % N<br>Kjeld. <sup>e</sup> |       |
| Caproate             | C <sub>6</sub> H <sub>11</sub> —C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sup>g</sup>                | ...                 | ...               | 80 <sup>f</sup> | ...    | ...                 | 93                   | 18.09            | 18.16                      | 141                        | 14.40  | 14.47                      | 171                                  | 15.16            | 15.22                      |       |
| Caproate             | C <sub>6</sub> H <sub>11</sub> —C <sub>3</sub> H <sub>5</sub> N <sub>2</sub>                               | 54 <sup>g</sup>     | 108               | 7               | 75     | 20.00               | 19.98                | 127 <sup>h</sup> | 18.97                      | 18.89                      | ...    | ...                        | ...                                  | ...              | ...                        |       |
| Diethylacetate       | (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CH—C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O            | ...                 | 113               | 7               | 60     | ...                 | ...                  | 123              | 18.09                      | 18.09                      | 133    | 14.40                      | 14.44                                | 179 <sup>h</sup> | 15.16                      | 15.26 |
| Diethylacetate       | (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CH—C <sub>3</sub> H <sub>5</sub> N <sub>2</sub>              | 86                  | 97                | 9               | 70     | 20.00               | 19.98                | 106              | 18.97                      | 19.02                      | 245    | 15.86                      | 15.90                                | 133              | 16.22                      | 16.20 |
| Diisoamylacetate     | (C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> CH—C <sub>3</sub> H <sub>5</sub> N <sub>2</sub>              | 103                 | 123               | 6               | 75     | 12.50               | 12.48                | 125              | 15.45                      | 15.44                      | ...    | ...                        | ...                                  | 82 <sup>f</sup>  | 12.24                      | 12.22 |
| Phenylacetate        | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sup>g</sup> | ...                 | ...               | 80 <sup>f</sup> | ...    | ...                 | ...                  | 133              | 17.20                      | 17.21                      | 142    | 13.05                      | 13.16                                | 191              | 14.14                      | 14.09 |
| Phenylacetate        | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —C <sub>3</sub> H <sub>5</sub> N <sub>2</sub>                | 68                  | 134               | 6               | 75     | 17.50               | 17.45                | 149              | 18.00                      | 17.94                      | 174    | 17.94                      | 17.96                                | ...              | ...                        | ...   |
| Diphenylacetate      | (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH—C <sub>2</sub> H <sub>4</sub> N <sub>2</sub>              | 137                 | ...               | ...             | 35     | 11.86               | 11.90                | 185              | 15.05                      | 15.00                      | ...    | ...                        | ...                                  | ...              | ...                        | ...   |

<sup>a</sup> Reported analytical results are the average of two determinations whose maximum absolute deviation from theoretical is less than 0.15%. <sup>b</sup> Picrates are made in the usual way in water, alcohol or dilute alcohol and recrystallized from alcohol or dilute alcohol. <sup>c</sup> All hydrochlorides are made by passing dry hydrogen chloride into an absolute alcohol-absolute ether solution of the base, and are recrystallized from absolute alcohol or absolute alcohol-absolute ether mixtures. All hydrochlorides are extremely soluble in water, warm alcohol and acetone. Insoluble in absolute ether. <sup>d</sup> Usually made in benzene and recrystallized from alcohol or acetone. <sup>e</sup> Reaction temperature, 100°. Isolated by solvent extraction. See Hill and Aspinall, *THIS JOURNAL*, **61**, 822 (1939). <sup>f</sup> Crude product. <sup>g</sup> Literature 38.8°, *ibid.*, **57**, 2424 (1935). <sup>h</sup> Literature 128°, *ibid.*, **57**, 2424 (1935). <sup>i</sup> The spaces so marked indicate that the hydrochloride is unsuitable for characterization because it is liquid or excessively hygroscopic. In these cases the hydrochlorides may be converted to well-defined chloroplatinates which may be accurately analyzed for platinum by ignition, provided extreme care is exercised to prevent spattering. The derivatives have no sharp melting points but char and melt with decomposition at a temperature dependent upon the rate of heating. A typical analysis: Calcd.

for (iso-C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>CHC $\begin{matrix} \text{N} \text{---} \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{NH} \text{---} \text{CH}_2 \end{matrix}$  · 1/2 H<sub>2</sub>PtCl<sub>6</sub>: Pt, 22.78; found 22.75. <sup>i</sup> Made in and recrystallized from petroleum

ether. <sup>k</sup> This derivative apparently exists in dimorphic forms. When a sample is slowly heated there is a definite slight shrinking at 150° (corr.) after which no further change occurs until the sample melts sharply at 179° (corr.). If, however, a sample is introduced into a melting point bath at any temperature between 150 and 179° there is an immediate and complete fusion followed in a few seconds by an equally rapid and complete solidification, after which no change is evident until the sample permanently remelts at 179°. A sample once melted always remelts at 179°. <sup>l</sup> Undistillable. After extraction with alcohol 2-diphenylmethyl-4,5-dihydroimidazole was isolated as follows: the alcohol was removed the solid residue dissolved in dilute hydrochloric acid, boiled with charcoal, filtered, and reprecipitated with sodium carbonate. The white product so obtained was recrystallized from acetone.

ethylenediamine likewise prevent cyclization to the 4,5-dihydroimidazole configuration. (b) On the other hand, a monoacylethylenediamine derived from an ester containing five or more carbon atoms and not branched in the alpha position does undergo a slow dehydration at the temperature required to distil it at ordinary laboratory vacuum or if too high reaction temperature is used. When monocaproylethylenediamine is distilled, the temperature is originally at 135° (7 mm.), but slowly falls during the course of the distillation to 108° (7 mm.). The lower temperature is the boiling point of 2-*n*-amyl-4,5-dihydroimidazole and the higher temperature is probably the boiling point of monocaproylethylenediamine.<sup>3</sup> That dehydration proceeds during distillation was definitely proved by the fact that derivatives

(3) The boiling point of any 2-alkyl-4,5-dihydroimidazole has been found to be invariably lower than the boiling point of the corresponding monoacylethylenediamine from which it is derived.

of both the cyclic and acyclic bases were isolated from the distillate.

The higher and phenylated aliphatic 4,5-dihydroimidazoles are well-defined white solids which may be recrystallized from petroleum ether, ethyl acetate or benzene. They react readily with picric acid, hydrogen chloride and phenyl isocyanate, although the derivatives formed are not suitable for characterization in all cases. The author is indebted to Miss Bettina Meyerhof for preparing some of the esters used in this work. Further investigations dealing with monoacylated aliphatic polyamines are in progress.

### Summary

1. The preparation of 2-substituted-4,5-dihydroimidazoles from monoacylethylenediamines has been shown to proceed in excellent yields for many types of hydrocarbon substituents.

2. Refinements in previous experimental procedure have been introduced.

3. A study of the ease of dehydration of mono-acylethylenediamines has been made.

4. The cyclic and acyclic bases prepared in this study have been fully characterized as picrates, hydrochlorides, chloroplatinates and phenyl ureas.

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## Lactonization of Dihydro-*l*-abietic and Dihydro-*l*-pimaric Acids

BY ELMER E. FLECK AND S. PALKIN

As is well known in the pine resin acid series, isolation of the individual isomers, because of pronounced isomorphism, is attended with considerable difficulty. Similar difficulties are encountered in isolating the individual isomers from dihydro mixtures obtained on hydrogenating *l*-abietic or *l*-pimaric acid. Thus there are reported in the literature dihydroabietic acids ranging from  $[\alpha]_D -23$  to  $+108^\circ$ , and melting points of  $141$  to  $218^\circ$ , and dihydro-*l*-pimaric acids from  $[\alpha]_D +24$  to  $+35^\circ$ , and melting points of  $135$  to  $144^\circ$ .

Ruzicka and co-workers<sup>1</sup> first showed that dihydroabietic acid,  $[\alpha]_D -12^\circ$ , m. p.  $167-168^\circ$ , may be converted with strong mineral acids into a completely saturated lactone,  $C_{20}H_{32}O_2$ . It has now been found possible to prepare this same lactone from the high-rotating dihydro-*l*-abietic acid,  $[\alpha]_D +108^\circ$ ,<sup>2</sup> and from dihydro-*l*-pimaric acid,  $[\alpha]^{20}_D +35^\circ$ . This raises the question as to the identity of the dihydro acid shown to exist in pine oleoresin and in rosin,<sup>3</sup> since the dihydro acid was isolated as the lactone and therefore may be any one or a mixture of the three dihydro compounds shown to give this lactone.

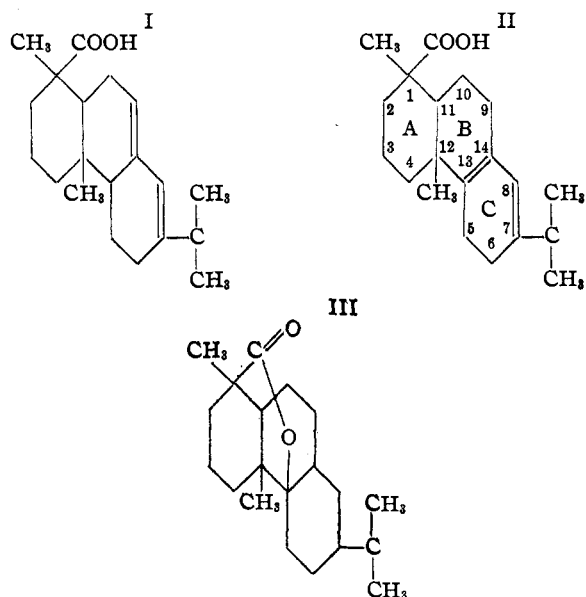
Up to the present time there has been little evidence as to the point of lactonization in lactonized dihydroabietic acid. The C-10 position has been suggested<sup>4</sup> and seemed possible on the basis that the positions of the double bonds in *l*-abietic acid I are such that, on hydrogenation to the dihydro compound, lactonization could occur on the residual double bond in ring B, with the postulation of a shift to the 9,10-position, thus forming a five-membered lactone. There are, however, other possibilities for this lactone that appear more plausible.

(1) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 333 (1922); Ruzicka, Waldmann, Meier and Hösli, *ibid.*, **16**, 178 (1933).

(2) Fleck and Palkin, *THIS JOURNAL*, **60**, 2821 (1938).

(3) Fleck and Palkin, *ibid.*, **61**, 1230 (1939).

(4) Hasselstrom and McPherson, *ibid.*, **60**, 2840 (1938).



*l*-Pimaric acid II<sup>5</sup> is now represented as containing a system of conjugated double bonds confined to ring C. *l*-Abietic acid I<sup>5</sup> is represented as having a conjugated system of double bonds distributed in rings B and C. An inspection of the structure of *l*-pimaric acid and *l*-abietic acid indicates the  $\Delta^{13,14}$  for dihydro-*l*-pimaric acid, and  $\Delta^{9,14}$  for dihydro-*l*-abietic acid, assuming hydrogenation to take place at the  $\Delta^{7,8}$  position in both cases, that is, under the simplest possible conditions. A 1:4 addition to the conjugated system of either *l*-pimaric or *l*-abietic acid would produce a  $\Delta^{14,8}$  dihydro derivative.

On saturation of one of the double bonds of either acid, formation of a series of isomeric dihydro-*l*-pimaric and dihydro-*l*-abietic acids which have the residual double bond in any one of the positions, 14,13, 14,9, 14,8 and 7,8 would seem quite possible.

It may be shown how the three possible positions of the double bond in dihydro derivatives

(5) Fieser and Campbell, *ibid.*, **60**, 159 (1938).