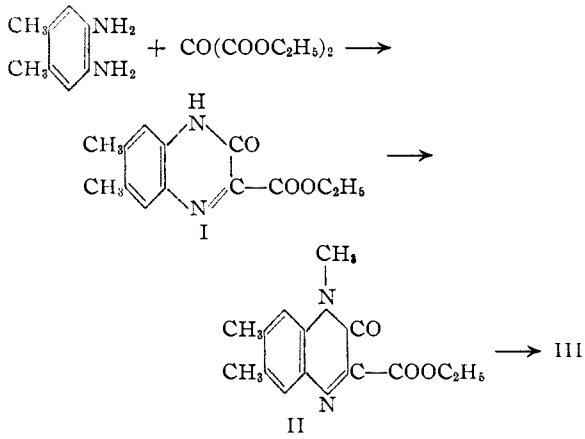

The keto ester, II, was also prepared from ethyl oxomalonate and 1-methylamino-2-amino-4,5-dimethylbenzene. Because of the difficulty in preparing the latter[4] the first synthesis is preferable.

### Experimental

**3,4-Dihydro-3-keto-6,7-dimethyl-2-quinoxalinecarboxylic Acid, Ethyl Ester.**—A solution of 6.5 g. of ethyl oxomalonate in 25 cc. of ethanol was added to a cooled solution of 5 g. of 4,5-dimethyl-*o*-phenylenediamine, and the mixture was refluxed for fifteen minutes. After storage at 5° for three hours, the product (8 g., 88% yield) was separated and recrystallized from ethanol. The product was obtained as matted needles; m. p. 199°.

*Anal.* Calcd. for $C_{13}H_{14}O_3N_2$: C, 63.41; H, 5.69. Found: C, 63.30; H, 5.81.

**3,4-Dihydro-3-keto-4,6,7-trimethyl-2-quinoxalinecarboxylic Acid, Ethyl Ester.**—Five grams of the above keto ester was added to a solution of sodium ethoxide in 25 cc. of ethanol prepared from 0.46 g. of sodium. The mixture was stirred fifteen minutes, 7 g. of methyl iodide was added and the mixture was refluxed. The reaction was completed in about fifteen minutes as evidenced by the disappearance of the insoluble sodio-derivative. The mixture was diluted with two volumes of ice water, and the precipitated product was recrystallized by dissolving in hot ethanol and adding water to slight turbidity; wt. 4.1 g., 94% yield, m. p. 125–126°.

*Anal.* Calcd. for $C_{14}H_{16}O_3N_2$: C, 64.62; H, 6.15. Found: C, 64.71; H, 6.40.

The same N-methyl keto ester was prepared by heating a mixture of 3.0 g. of 1-methylamino-2-amino-4,5-dimethylbenzene[4] and 4.0 g. of ethyl oxomalonate in 50 cc. of ethanol for one hour. After adding an equal volume of water, the product (wt. 4.5 g.) separated completely. After recrystallization from ethanol–water, the product melted at 124–126°.

**3,4-Dihydro-3-keto-4,6,7-trimethyl-2-quinolxalinecarboxylic Acid.**—To a solution of 0.5 g. of the above ester in 5 cc. of ethanol was added one equivalent of sodium ethoxide dissolved in 2 cc. of ethanol. One drop of water was added to the solution, whereupon a crystalline sodium salt separated within a few minutes. After chilling to 0° the product was separated, dissolved in ice water, and carefully acidified. The mixture was extracted with ether, and the ether extract, after drying with anhydrous magnesium sulfate, was concentrated to a small volume whereupon the acid crystallized. The product (0.25 g.) melted at 212–214° with carbon dioxide-liberation as previously recorded.[2] The identity of the acid was confirmed by decarboxylation to the known 3,4-dihydro-3-keto-4,6,7-trimethylquinoxaline; m. p. 174–175°.[2]

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(4) Kuhn and Reinemund, *Ber.*, **67**, 1932 (1934).

## Isolation of *l*-Arabinose

BY E. V. WHITE

Methods for the isolation of *l*-arabinose from natural sources have been described by several authors.[1] The procedure usually involves partial hydrolysis of a complex polysaccharide followed by fractional precipitation of portions more resistant to hydrolysis with alcohol and finally crystallization of the sugar from ethyl alcohol–water solution. The yield of arabinose is often low and the method is both tedious and expensive. A substantial improvement[2] is made when the hydrolyzate is dialyzed in an equal volume of distilled water. Residual polysaccharide and most hydrolytic decomposition products are thus separated from arabinose which collects in the dialyzate. Upon evaporation of the latter and addition of ethyl alcohol, *l*-arabinose crystallizes in good yield.

**Procedure.**—Two hundred grams of crude mesquite gum is dissolved in 1000 cc. of water, filtered to remove extraneous material and heated upon a boiling water-bath for thirty-six hours with 0.15 *N* sulfuric acid. The solution is then cooled, neutralized with barium carbonate, filtered and dialyzed against an equal volume of distilled water. The dialyzate is replaced by fresh water after twenty-four hours and the process repeated one or more times. The combined dialyzates are then evaporated under reduced pressure to a thin sirup and ethyl alcohol added slowly with stirring to 85% concentration. A small quantity of tarry material is separated in the centrifuge and the clear liquid re-evaporated to a sirup. The latter is thinned slightly with ethyl alcohol and *l*-arabinose crystallizes readily from the liquor. The over-all yield is about 75% of theoretical from three dialyzates.

(1) (a) Kiliani and Kohler, *Ber.*, **37**, 1210 (1904); (b) Tollens, *Hdb. biochem. Arbmeth.*, **2**, 64 (1909); (c) Anderson and Sands, "Organic Syntheses," **8**, 18 (1929); (d) Harding, *Sugar*, **24**, 656 (1922); *ibid.*, **25**, 124 (1923).

(2) White, THIS JOURNAL, **69**, 622 (1947).

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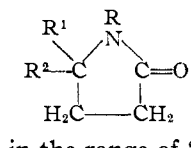
## N-Substituted 2-Pyrrolidones

BY F. B. ZIENTY AND G. W. STEAHLY

Since γ-valerolactone now has become commercially available, it was of interest to prepare a number of N-substituted 2-pyrrolidones by thermal liquid phase reaction of lactones with amines



at temperatures in the range of 250° according to a procedure similar to one previously applied to γ-butyrolactone.[1]

Several of the compounds described, when

(1) (a) Späth and Lintner, *Ber.*, **69**, 2727 (1936); (b) catalytic vapor phase reaction of γ-butyrolactone with primary amines has been the subject of a patent; Schuster and Seib, U. S. Patent 2,267,757 (December 30, 1941); *C. A.*, **36**, 2566 (1942).

TABLE I

| Substituted 2-pyrrolidone R | $R^1$ | $R^2$ | Yield, % | B. p., °C. | Mm. | Formula | Nitrogen, %[a] Calcd. | Found |
|---|---|---|---|---|---|---|---|---|
| Dodecyl[b] | H | H | 83 | 202–205 | 11 | $C_{16}H_{31}NO$ | 5.5 | 5.8 |
| Tridecyl[c] | H | H | 61 | 210–213 | 9.5 | $C_{17}H_{33}NO$ | 5.2 | 5.3 |
| Tetradecyl[d] | H | H | 72 | 201–201.5 | 2.5 | $C_{18}H_{35}NO$ | 5.0 | 5.0 |
| Hexadecyl[d] | H | H | 72 | 213–215 | 2.5 | $C_{20}H_{39}NO$ | 4.5 | 4.5 |
| Octadecyl[b,d] | H | H | 78 | 219–221 | 1.5 | $C_{22}H_{43}NO$ | 4.2 | 4.0 |
| Benzyl[b] | H | H | 33 | 168–170 | 14 | $C_{11}H_{13}NO$ | 8.0 | 7.9 |
| 4-Diethylamino-1-methylbutyl | H | H | 77 | 162–166 | 11 | $C_{13}H_{26}N_2O$ | 12.4 | 12.4 |
| Dodecyl | H | $CH_3$ | 56 | 185–187 | 3.5 | $C_{17}H_{33}NO$ | 5.2 | 5.1 |
| Tetradecyl | H | $CH_3$ | 45 | 189–190 | 1.5 | $C_{19}H_{37}NO$ | 4.7 | 4.8 |
| Hexadecyl[d] | H | $CH_3$ | 31 | 200–201 | 1 | $C_{21}H_{41}NO$ | 4.3 | 4.2 |
| Octadecyl[d] | H | $CH_3$ | 33 | 219–222 | 1.2 | $C_{23}H_{45}NO$ | 4.0 | 3.8 |
| Dodecyl | $CH_3$ | $C_2H_5$ | 48 | 162–172 | 4 | $C_{19}H_{37}NO$ | 4.7 | 4.9 |

[a] The analyses were performed by Mrs. J. D. Nevins and Mrs. R. C. Schropp of the Monsanto Analytical Laboratory. [b] Preparation mentioned, but compound not described, in ref. (1b). [c] Prepared by Mr. H. L. Morrill. [d] Waxy solid.

tested *in vitro*, were found to have no bacteriostatic activity. The 2-pyrrolidones with the dodecyl, tetradecyl, octadecyl and 4′-diethylamino-1′-methylbutyl groups in the 1-position were inactive against experimental tuberculosis in guinea pigs. These products were evaluated for chemotherapeutic and pharmacologic action in The Lilly Research Laboratories.

### Experimental

**Preparation of 2-Pyrrolidones.**—Equimolar quantities of the amine and the lactone were heated with agitation at 110–130° for about three hours and then at 250–270° for three to six hours while distilling off water. The excess reactants were distilled off under reduced pressure and the N-substituted pyrrolidone was distilled.

Long chain amines,[2] benzylamine and 1-diethylamino-4-aminopentane reacted satisfactorily, giving 35–85% yields of the corresponding pyrrolidones.

γ-Butyrolactone, γ-valerolactone and γ-ethyl-γ-valerolactone[3] reacted without difficulty with the amines used, although it is clearly seen that under the same conditions γ-valerolactone gives lower yields than does γ-butyrolactone.

The several pyrrolidones prepared were high-boiling liquids or waxy solids.

(2) Gift from Armour and Company. Tridecylamine was prepared in 55% yield by Dr. E. L. Hatlelid using the procedure of Ralston, Selby, Pool and Potts, *Ind. Eng. Chem.*, **32**, 1093 (1940); the ditridecylamine (35%) obtained as a by-product boiled at 240–242° (8 mm.), while Hoerr, Harwood and Ralston, *J. Org. Chem.*, **9**, 201 (1944), reported m. p. 56.5°. Didodecylamine, b. p. 263–265° (27 mm.), was obtained in a preparation of dodecylamine; Wibaut, Heierman and Wagtendonk, *Rec. trav. chim.*, **57**, 456 (1938), reported 195° (0.7 mm.).

(3) Grignard, *Compt. rend.*, **135**, 629 (1902). See Cason, Adams, Bennett and Register, THIS JOURNAL, **66**, 1764 (1944), for an improved method of making γ,γ-dialkyl-butyrolactones.

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# NEW COMPOUNDS

### Cadalene and Eudalene Trinitrotoluates

Cadalene (50 mg.) and trinitrotoluene (58 mg.) were heated in methanol solution on the water-bath for a few minutes. On cooling, long yellow glistening needles of cadalene trinitrotoluate crystallized out, m. p. 83°, not raised by further crystallization from methanol.

*Anal.* Calcd. for $C_{15}H_{18}\cdot C_7H_5N_3O_6$: C, 62.12; H, 5.45. Found: C, 62.04; H, 5.56.

Eudalene trinitrotoluate, similarly prepared from eudalene (87 mg.) and trinitrotoluene (103 mg.), formed short, dull yellow needles, m. p. 62–63°, not raised by further crystallization.

*Anal.* Calcd. for $C_{14}H_{16}\cdot C_7H_5N_3O_6$: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.02; H, 5.15; N, 10.4.

We are indebted to Mr. A. R. Penfold for a specimen of eudesmol from which the eudalene was prepared by dehydrogenation, to the Chemical Society and the Australian and New Zealand Association for the Advancement of Science for grants and one of us (W. I. T.) for a Duffus Lubecki Scholarship.

The analyses are by Drs. Weiler and Strauss.

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WILLIAM I. TAYLOR

RECEIVED NOVEMBER 5, 1946

### 2-Arylamino-4-chlorobenzoic Acids and 9-Chloroacridines[1]

**2-Anilino-4-chlorobenzoic Acid,** $C_6H_5NHC_6H_3ClCOOH$.—A mixture of 153 g. (0.8 mole) of 2,4-dichlorobenzoic acid, 93 g. (1 mole) of freshly distilled aniline, 111 g. (0.8 mole) of anhydrous potassium carbonate, 4 g. of copper bronze and 600 ml. of *n*-pentyl alcohol was heated under reflux with stirring for five hours. One hundred ml. of 35% potassium hydroxide solution was added, and the excess aniline and pentyl alcohol was removed by steam distillation. The residue was filtered and acidified (concentrated hydrochloric acid). The purple solid which separated was removed by filtration and washed with water. Crystallization of the moist product from alcohol gave purple needles, and a second recrystallization from benzene gave 105 g. (53% yield) of slightly grey needles melting at 201°, cor.

*Anal.* Calcd. for $C_{13}H_{10}ClNO_2$: Cl, 14.31; neut. equiv., 247.7. Found: Cl, 14.08; neut. equiv., 247.6, 248.5.

**2-*o*-Toluidino-4-chlorobenzoic Acid.**—Similar directions were followed. From 0.8 mole of 2,4-dichlorobenzoic acid and *o*-toluidine was obtained 75 g. (36%) of the desired acid, m. p. 208°, cor. after crystallization from alcohol.

*Anal.* Calcd. for $C_{14}H_{12}ClNO_2$: Cl, 13.54; neut. equiv., 261.7. Found: Cl, 13.40; neut. equiv., 262.1, 260.3.

(1) This report is based on work done under contracts, recommended by the National Defense Research Committee and the Committee on Medical Research, between the Office of Scientific Research and Development and Northwestern University.