efficient condenser was required to condense the vapors; those vapors which were not trapped in an ice-cooled collection flask were caught in a Dry Ice trap at the end of the system.

The products of decomposition were washed with three 50-ml. portions of water and then steam distilled. The distillate was washed with three 50-ml. portions of water and the distillate dried with anhydrous potassium carbonate. The yield was 207 g. (56.6%). The mixture was subjected to fractional distillation at 690 mm.; results are noted below:

Fraction	Boiling range, °C.	Weight, g.	$n^{25}D$
1	57 -63	13.1	1.4328
2	63 -65.5	47.9	1.4342
3	65.5-68.5	25.2	1.4369
4	68.5-71.5	10.4	1.4415
5	71.5-75	17.0	1.4468
6	75 -77	81.4	1.4526

Redistillation of 35 g. of fraction six from barium oxide yielded 16.2 g. (46%) of material; b.p. 76.5-77°; $n^{24}D$ 1.4538; d^{25}_4 0.9316. Kishner[2] reported: b.p. 78.5-79°; $n^{18}D$ 1.457; d^{18}_4 0.9406.

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3,3-Dialkylpiperidines

BY R. C. SCHREYER

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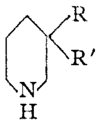
Several methods[1] for the synthesis of piperidines by ring closure at the nitrogen atom have been described. However, preparation by reductive amination of 4-cyanobutyraldehydes has not been previously reported. It has now been found in this Laboratory that 3,3-dialkylpiperidines can be synthesized from 2,2-dialkyl-4-cyanobutyraldehydes *via* the two-step process

$$RR'CHCHO + CH_2 = CHCN \longrightarrow RR'C(CHO)CH_2CH_2CN \quad (1)$$

$$RR'C(CHO)CH_2CH_2CN + H_2 + NH_3 \longrightarrow$$



(2)

Isobutyraldehyde, 2-methylbutyraldehyde and cyclohexanecarboxaldehyde were employed as the aldehydic components. Cyanoethylation of isobutyraldehyde[2,3,4] has been disclosed in the patent literature. The reaction of acrylonitrile with cyclohexanecarboxaldehyde was not exothermic in contrast to the other aldehydes used.

A novel spirane derivative, 2-azaspiro(5.5)hendecane, was obtained from 1-(2'-cyanoethyl)-cyclohexanecarboxaldehyde.

Experimental

2-Ethyl-2-methyl-4-cyanobutyraldehyde.—A charge of 86 g. of 2-methylbutyraldehyde and 159 g. of acrylonitrile was added slowly to 5 g. of a 50% sodium hydroxide solution over a one-hour period. The mixture was stirred throughout the addition and the temperature was maintained at 35-50° by external cooling. The solution was neutralized with 25% sulfuric acid and the oil layer distilled under vacuum to give 43 g., b.p. 66-70° (0.3-0.35 mm.), $n^{25}D$ 1.4441. *Anal.* Calcd. for $C_8H_{13}NO$: C, 69.06; H, 9.35; N, 10.07. Found: C, 68.78; H, 9.52; N, 9.99.

1-(2'-Cyanoethyl)-cyclohexanecarboxaldehyde.—A mixture of 106 g. of acrylonitrile, 102 g. of cyclohexanecarboxaldehyde and 2 g. of 50% sodium hydroxide solution was refluxed 30 minutes. The solution was cooled and 250 cc. of ether added. The ether solution was washed with 50 cc. of 10% hydrochloric acid, 50 cc. of 5% sodium bicarbonate solution and 50 cc. of water, and then distilled directly under vacuum to give 51 g., b.p. 103-105° (1 mm.), $n^{26}D$ 1.4750. *Anal.* Calcd. for $C_{10}H_{15}NO$: C, 72.72; H, 9.09; N, 8.48. Found: C, 72.56; H, 9.13; N, 8.54.

3,3-Dimethylpiperidine.[5]—A mixture of 55 g. of 2,2-dimethyl-4-cyanobutyraldehyde (b.p. 59-60° (0.6 mm.), $n^{23}D$ 1.4355) 119 g. of ammonia and 15 g. of Raney nickel was hydrogenated at 100-110° and 700 atmospheres pressure for one hour in a stainless steel shaker tube. The product was filtered to remove the catalyst and distilled under vacuum to give 12.5 g., b.p. 45-46° (33 mm.), $n^{25}D$ 1.4470. *Anal.* Calcd. for $C_7H_{15}N$: C, 74.34; H, 13.27; N, 12.39; neut. equiv., 113. Found: C, 74.58; H, 13.11; N, 11.91; neut. equiv., 115.

3-Ethyl-3-methylpiperidine.—A mixture of 50 g. of 2-ethyl-2-methyl-4-cyanobutyraldehyde, 102 g. of ammonia and 15 g. of Raney nickel was hydrogenated at 100-110° and 700 atmospheres for one hour in a silver shaker tube. The product was filtered to remove the catalyst and vacuum distilled to give 9 g., b.p. 67-69° (25 mm.), $n^{25}D$ 1.4565. *Anal.* Calcd. for $C_8H_{17}N$: neut. equiv., 127; N, 11.02. Found: neut. equiv., 126; N, 11.13.

2-Azaspiro(5.5)hendecane.—A charge of 50 g. of 1-(2'-cyanoethyl)-cyclohexanecarboxaldehyde, 119 g. of ammonia and 15 g. of Raney nickel was hydrogenated at 120-129° and 700 atmospheres pressure for one hour in a stainless steel shaker tube. The product was filtered to remove the catalyst and distilled under vacuum to give 17 g., b.p. 91-93° (10 mm.), $n^{25}D$ 1.4891. *Anal.* Calcd. for $C_{10}H_{19}N$: C, 78.43; H, 12.42; N, 9.15; neut. equiv., 153. Found: C, 78.15; H, 12.46; N, 9.21; neut. equiv., 149.

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[1] R. C. Elderfield, Editor, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 642-655.

[2] H. A. Bruson and T. W. Reiner, U. S. Patent 2,353,687.

[3] J. F. Walker, U. S. Patent 2,409,086.

[4] I. G. Farbenindustrie A. G., French Patent 886,846.

[5] Dunlop, *J. Chem. Soc.*, **107**, 1112 (1915), has prepared 3,3-dimethylpiperidine by the reduction of 2,2-dimethylglutarimide with sodium and amyl alcohol.

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Carbon Dioxide Production in the Browning Reaction[1]

BY F. H. STADTMAN, C. O. CHICHESTER AND G. MACKINNEY

RECEIVED NOVEMBER 26, 1952

Non-enzymatic browning reactions in certain natural systems and interactions of sugars and nitrogenous compounds have been thoroughly reviewed, the former by Stadtman in 1948,[2a] the latter by Danehy and Pigman[2b] in 1950. Many types of compounds can be involved. Haas and Stadtman[3] for example showed that brown pigments could be formed by combining and heating any two of the three fractions (anion, cation and neutral) that were obtained from apricot sirups by ion-exchange treatment. It is frequently assumed, however, in natural systems where both amino acids and carbohydrates are present, that

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[1] Presented at the XII International Chemical Congress, New York, 1951.

[2] (a) E. R. Stadtman, *Advances in Food Research*, 1, 325 (1948), (b) J. P. Danehy and W. W. Pigman, *ibid.*, 3, 241 (1951).

[3] V. A. Haas and E. R. Stadtman, *Ind. Eng. Chem.*, **41**, 983 (1949).