pared by the decomposition of cyclobutyldimethylamine oxide[1] is shown in Fig. 1.

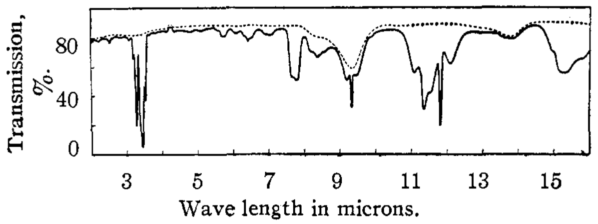

Fig. 1.—Infrared spectrum of cyclobutene at about 100 mm. pressure in 5-cm. cell with NaCl windows determined with Baird Spectrograph with NaCl prism. The solid line is the sample curve and the dashed line is the curve for the empty cell. The reference cell compartment contained a NaCl slab.

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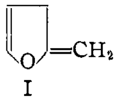
The Structure of Methylenedihydrofuran

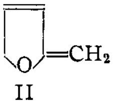
BY HAROLD L. RICE[1]

RECEIVED JANUARY 24, 1952

In the course of studies on the decomposition of hydrazones Kishner found[2] that furfural hydrazone half hydrate, when decomposed with heat in small portions over platinized clay plate and potassium hydroxide, gave, in addition to 2-methylfuran, a product which boiled at 78–80°. Two possible structures, I and II, were proposed for this material



I



II

on the basis of its conversion by a trace of acid into methylfuran and by analogy to the isomerization of methylenecyclohexane to methylcyclohexene.[3] Structure I, in which the exo- and endocyclic double bonds are not conjugated, was preferred by Kishner because the molecular refraction was in better agreement, and because a normal condensation product with maleic anhydride was not formed.[4] Levulinic anhydride and pentene-2-ol-1-one-4 were formed when the methylenedihydrofuran was hydrated, and this suggested that the material could be a mixture of I and II.

The present spectral investigation has, on the other hand, led to the conclusion that structure II is more likely. Non-aromatic conjugation is indicated by the strength and position of the absorption maximum; λ_{max}, 239 mμ; ϵ_{max}, 6300 mμ.

Comparison of the position of this maximum with those of β-phellandrene (232 mμ), 7-methylenecholesterol (236 mμ), $\Delta^{4,6}$-cholestadienol (238 mμ), and 9-oxycholestadienol (248 mμ) would indicate that there is conjugation.[5] That this conjugation is not aromatic can be seen from Fig. 1 wherein the maximum for methylfuran is at about 217 mμ The strength of the maximum in B is of the expected order of magnitude[6] when compared to those of vinylcyclohexene (8500) and cyclopentadiene (2,500).

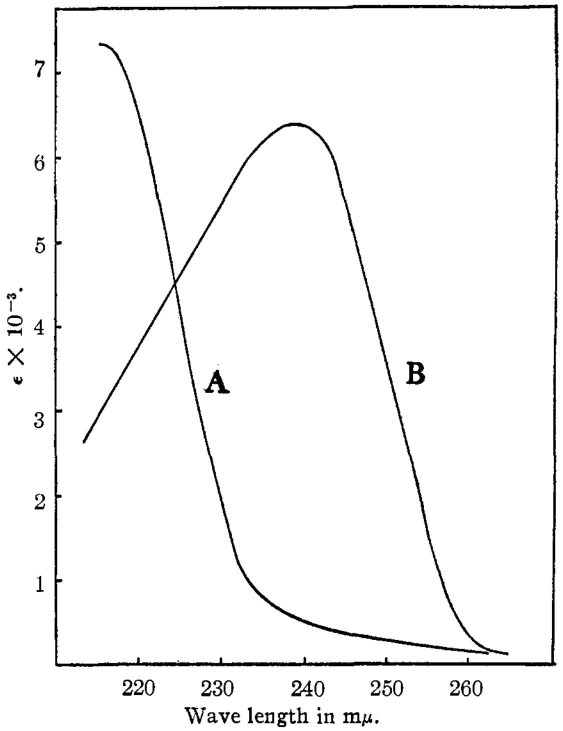


Fig. 1.—Absorption spectrum of 2-methylfuran (A) and 2-methylene-2,5-dihydrofuran (B) in absolute methanol.

The procedure which was reported by Kishner for the preparation of methylenedihydrofuran was followed closely here, but with somewhat variable results. The ratio of methylenedihydrofuran to methylfuran varied from 1.7 down to 0.43 in different preparations; ratios of about 1.0 were the most common. In order to improve the yield of methylenedihydrofuran and to decrease variability in the ratio of the isomers obtained, several different procedures were tried. The amount of hydrazone, of potassium hydroxide, and of platinized clay plate was changed independently with either no improvement in the constancy of the ratio of isomers or adverse effect on the yield. The time for each decomposition also was varied, again with no constant effect. The best yield of the unstable isomer was 29%, which was comparable to that reported by Kishner[2] (32%).

Experimental

Furfural Hydrazone Half Hydrate.—This compound was prepared in 89% yield by the method of Kishner.[2]

2-Methylene-2,5-dihydrofuran.—Furfural hydrazone half hydrate (530 g.) was added in 10–15-ml. portions to a mixture of 1.5 g. of potassium hydroxide pellets and 1.5 g. of platinized clay chips.[7] After each portion was added, the mixture was heated gently until the decomposition became self-sustaining. Because reaction was vigorous, a long and

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[2] N. Kishner, *J. Gen. Chem.* (*U.S.S.R.*), **1**, 1212 (1931).

[3] A. Favorskii and I. Borgmann, *Ber.*, **40**, 4871 (1907).

[4] N. Kishner, *J. Gen. Chem.* (*U.S.S.R.*), **3**, 198 (1933).

[5] R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

[6] E. A. Braude, *Ann. Reports, Chem. Soc.*, **111** (1946).

[7] In the preparation of the catalyst 15 g. of clay chips was soaked in 15 ml. of 5% chloroplatinic acid, the water evaporated on a steam-bath and the material was reduced in a stream of hydrogen. The temperature was raised to 150° over a two-hour period. After cooling the system, the hydrogen was displaced by carbon dioxide and the chips were stored, for later use, under an atmosphere of carbon dioxide.

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

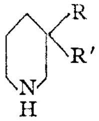
BY R. C. SCHREYER

RECEIVED DECEMBER 17, 1951

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).