impedances in the Bridge cause a considerable error in the observed readings. Correction for these errors was made empirically by measuring various liquids and liquid mixtures of low conductivity at 25° at both 1 mc. and 10 mc. using 650 $\mu\mu$f as the initial setting of the precision condenser in all cases. Assuming the 1 mc. measurements to be negligibly affected by the error sources mentioned, the difference between the 1 mc. and 10 mc. values for a given cell filling was plotted as a function of the 10 mc. value to give a smooth curve from which the correction to be applied to a given 10 mc. reading could be determined to within ± 0.1 $\mu\mu$f. Sufficient points were determined to accurately define the curve. In order to extend the curve to capacities as high as those involved in the working cell when filled with formamide, it was necessary to use a second cell (Cell No. 2), identical with Cell No. 1 except for the fact that the central electrode was $^1/_4$ in. longer, making its constants $C_0 = 2.0$ $\mu\mu$f and $C_v = 7.6$. It was assumed that the inductance of this second cell was essentially the same as that of Cell No. 1 and that the corrections determined with it were applicable to Cell No. 1. This appeared to be justified by the fact that the corrections determined with Cell No. 2 agreed closely with those from Cell No. 1 in the region of lower capacities where either cell could be used.

Water, methanol, benzene and chlorobenzene were purified by standard methods. The latter three were tested for purity either by density or melting point determination. Commercial formamide, supplied by the du Pont Co., was treated with calcium oxide (5 g./liter and distilled under a pressure of 1 mm. or less in a still affording essentially no fractionation. Two successive distillations of the middle fractions, treated each time with calcium oxide gave a colorless product having a m.p. of 2.3 to 2.4°. This material was subjected to three static crystallization steps in a container well protected from carbon dioxide and water. The final purified formamide had freezing points in the range 2.45 to 2.51° (lit. 2.55°)[10] and a specific conductivity of 4 × 10^{-6} ohm^{-1} cm.$^{-1}$ at 25°. The conductivity increased within 5 or 6 hours to about 1 × 10^{-5}. Its conductivity during measurements was less than 0.8 × 10^{-5} in all cases.

The observed values for the dielectric constant of formamide at 10 mc. are shown in Table I.

TABLE I

THE DIELECTRIC CONSTANT OF FORMAMIDE

Temp., °C.	ϵ
15.0	113.5
20.0	111.5
25.0	109.5
30.0	107.5
35.0	105.6

The above data, because of the short temperature range involved show a linear variation with temperature and can be represented by the equation: $\epsilon = 113.5 - 0.40\ (t - 15)$. It is estimated that the probable error of each of the reported values is ±0.2. As shown by Burdun and Kantor,[3] dielectric constants of formamide determined at 10 mc. can be regarded as equivalent to the limiting low frequency values.

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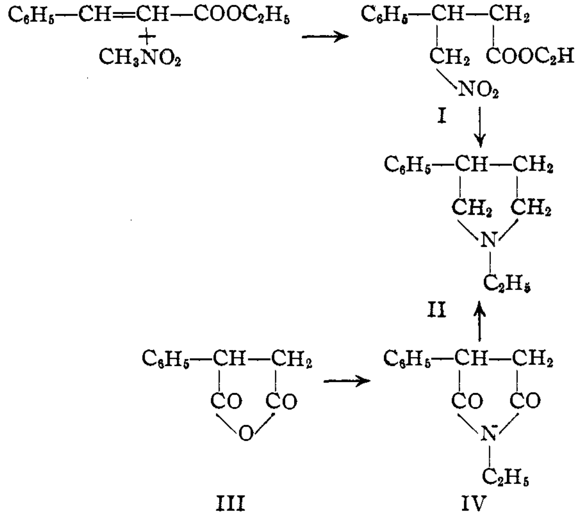
Reductive Cyclization. Synthesis of 1-Ethyl-3-phenylpyrrolidine

BY NELSON J. LEONARD, ALLEN B. SIMON AND DONALD L. FELLEY

Past experience in this Laboratory has shown that the reductive cyclization of γ-nitroaliphatic esters to dialkylpyrrolidines can be accomplished by hydrogenation over copper chromite catalyst at high temperature and pressure.[1] It was of interest to learn whether the reaction could be extended to aryl-substituted γ-nitro esters for the preparation of aryl-substituted pyrrolidines. A representative ester of this type, namely, ethyl β-phenyl-γ-nitrobutyrate (I), accordingly has been made and has been found to yield 1-ethyl-3-phenylpyrrolidine (II) when subjected to the reductive cyclization process.



The precursor ester I was obtained by the addition of nitromethane to ethyl cinnamate in the presence of benzyltrimethylammonium butoxide in butanol solution, and was hydrogenated over copper chromite catalyst at 265° and 250 atm. in dioxane solution. The attendant N-alkylation, with the production of 1-ethyl-3-phenylpyrrolidine (II), has been observed previously in similar reductive cyclizations.[1] The identity of the product (II), obtained in 40% yield, was established by an alternative synthesis which actually proved to be the preferable method of preparation. In the second synthesis, phenylsuccinic anhydride (III) was converted to 1-ethyl-3-phenylsuccinimide (IV) by treatment with ethylamine, and the imide (IV) was reduced to 1-ethyl-3-phenylpyrrolidine (II) in 71% yield by the action of lithium aluminum hydride. The properties of the bases obtained by the two methods of synthesis were in every way identical, as were those of their corresponding derivatives.

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[10] Smith, *J. Chem. Soc.*, 3257 (1981).

[1] N. J. Leonard and K. M. Beck, THIS JOURNAL, **70**, 2504 (1948); N. J. Leonard and W. V. Ruyle, *ibid.*, **71**, 3094 (1949); N. J. Leonard and E. Barthel, Jr., *ibid.*, **72**, 3632 (1950).

Experimental

Ethyl β-Phenyl-γ-nitrobutyrate.—To a stirred solution of 48.8 g. (0.8 mole) of nitromethane and 15 g. of benzyltrimethylammonium butoxide solution in butanol (Rohm and Haas Company) was added 35.2 g. (0.2 mole) of ethyl cinnamate. While the reaction mixture was stirred for 68 hours at 65–70°, additional 5-g. portions of catalyst were added at 24-hour intervals. The mixture was acidified with 1 *N* hydrochloric acid, an equal volume of ethylene dichloride was added, and the ethylene dichloride layer was washed with water. The solvent was removed and the residual oil was fractionally distilled in vacuum. Unchanged ethyl cinnamate (18.0 g.) was recovered at 100–110° (1 mm.), and the ethyl β-phenyl-γ-nitrobutyrate was collected as a light yellow oil; b.p. 156–158° (1 mm.); n^{20}_{D} 1.5085; d^{20}_{4} 1.162; yield 17.6 g. (76% based on unrecovered ethyl cinnamate).

Anal. Calcd. for $C_{12}H_{15}NO_4$: N, 5.90; MR_{D}, 61.40. Found: N, 5.90; MR_{D}, 60.91.

1-Ethyl-3-phenylpyrrolidine by **Reductive Cyclization.**—A solution of 3.2 g. (0.014 mole) of ethyl β-phenyl-γ-nitrobutyrate in 34 ml. of dioxane was hydrogenated in the presence of 3 g. of copper chromite catalyst at 265° and 250 atm. during 3 hours. After removal of the catalyst and solvent in the usual manner,[1] the residue was fractionally distilled, and the product boiling at 64.5° (0.12 mm.) was collected; n^{19}_{D} 1.5238; yield 0.8 g. (40%).

Anal. Calcd. for $C_{12}H_{17}N$: N, 7.99. Found: N, 8.13.

1-Ethyl-3-phenylpyrrolidine Picrate (Picrate 1).—Prepared in ether and recrystallized from methanol, the picrate formed yellow elongated prisms, m.p. 153–155°.

Anal. Calcd. for $C_{18}H_{20}N_4O_7$: C, 53.46; H, 4.99; N, 13.86. Found: C, 53.41; H, 5.23; N, 14.00.

1-Ethyl-3-phenylpyrrolidine Picrolonate (Picrolonate 1).—Prepared in ethanol and recrystallized from methanol, the picrolonate formed yellow microcrystals, m.p. 149.5–151.5°.

Anal. Calcd. for $C_{22}H_{25}N_5O_5$: C, 60.13; H, 5.73; N, 15.94. Found: C, 59.90; H, 5.82; N, 16.20.

1-Ethyl-3-phenylsuccinimide.—A mixture of 35.0 g. (0.20 mole) of phenylsuccinic anhydride[2] and 25.6 g. (0.40 mole) of 70% aqueous ethylamine was heated gradually under a reflux air condenser to 280°. When the temperature had reached 280°, the reaction mixture was maintained there for 1 hour, then cooled and distilled twice *in vacuo* using a short-path apparatus; b.p. 140–146° (1.5–2.5 mm.); n^{20}_{D} 1.5501; d^{20}_{4} 1.1574; yield 25.9 g. (65%).

Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.95; H, 7.17; N, 6.95.

The infrared spectrum indicated the absence of any absorption due to N–H, and the presence of carbonyl absorption similar to that exhibited by succinimide.[3]

1-Ethyl-3-phenylpyrrolidine by **Lithium Aluminum Hydride Reduction.**—The procedure which was followed was identical with that described by Nystrom and Brown[4] for the reduction of amides by their lithium aluminum hydride reagent. The product was a colorless liquid, b.p. 77–78° (1.4–1.5 mm.); n^{20}_{D} 1.5240; d^{20}_{4} 0.9608; yield 71%.

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99; MR_{D}, 55.97. Found: C, 82.11; H, 9.82; N, 8.13; MR_{D}, 55.82.

The picrate (Picrate 2), m.p. 153–155°, was undepressed on mixing with the picrate of 1-ethyl-3-phenylpyrrolidine obtained by reductive cyclization (Picrate 1).

Anal. Calcd. for $C_{18}H_{20}N_4O_7$: C, 53.46; H, 4.99; N, 13.86. Found: C, 53.50; H, 5.28; N, 13.91.

The picrolonate (Picrolonate 2), m.p. 149.5–151°, was undepressed on mixing with Picrolonate 1.

Anal. Calcd. for $C_{22}H_{25}N_5O_5$: C, 60.13; H, 5.73; N, 15.94. Found: C, 60.19; H, 5.92; N, 16.10.

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(2) P. E. Verkade and H. Hartman, *Rec. trav. chim.*, **52**, 945 (1933).

(3) Infrared analysis by Miss Elizabeth M. Petersen.

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The Molar Absorbancy Indices of Some 2,4-Dinitrophenylhydrazones

BY E. E. LOCKHART, M. C. MERRITT AND C. D. MEAD[1]

The molar absorbancy indices of several 2,4-dinitrophenylhydrazones of saturated aliphatic aldehydes have already been published.[2,3] However, for a continuing investigation of the carbonyl fraction of food products, it became necessary to prepare and study the spectral characteristics of hydrazones of other members of the aliphatic series. The results of this study are reported here (Table I), to provide a more complete picture of this group of compounds.

TABLE I

MOLAR ABSORBENCY INDICES OF SOME 2,4-DINITROPHENYLHYDRAZONES

Aldehyde	Maximum Primary $a_M \times 10^{-2}$	 Secondary $a_M \times 10^{-2}$	Minimum $a_M \times 10^{-2}$
Isobutyr-	230	156	22
n-Valer-	231	157	22
Isovaler-	232	160	21
n-Capro-	238	161	21
n-Capryl-	218	149	21
n-Nonyl-	217	146	21
n-Decyl-	216	146	19
n-Dodecyl-	216	148	20

Our results agree essentially with those previously reported, with respect to wave lengths of maximum and minimum absorption. We were unable, however, to obtain any indication that a third or fourth absorption band might be present in the spectra studied, as suggested by Braude and Jones.[2] The resolution possible with their equipment may account for this discrepancy. With the exception of the formaldehyde hydrazone, all maxima occur at 224–226 mμ (secondary) and 357–358 mμ (primary). The minima are located at 282–283 mμ.

A portion of this study included a repetition of the earlier work. The results obtained, together with those reported here, seemed to indicate that the length of the alkyl chain has some small effect on the intensity of resonance. There is a relatively regular increase in the molar absorbancy indices with increase in chain length, until a maximum is reached at $C_5 \cdot CH=$. Chain lengths greater than this seem to have a damping effect on resonance. The significance of this effect is being tested by a study of other carbonyl series.

Experimental.—The 2,4-dinitrophenylhydrazones were prepared according to the method of Allen.[4] They were recrystallized from 95% ethyl alcohol until a constant melting point was obtained. A Beckman model DU ultraviolet spectrophotometer and 1.000-cm. silica cells were used throughout this work. The absorption data were obtained from solutions containing uniformly 0.0125 mg. of hydrazone per ml. The solvent was 95% U.S.P. ethyl alcohol (U.S.I. synthetic). Preliminary work indicated that heating solid–liquid mixtures to facilitate dissolution of the hydrazones caused decomposition. It was necessary, therefore, to dissolve the compounds at room temperature. The time required varied from several hours to several days.

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