in order to avoid partial saponification). As a result of combined distillation of products of two such runs there was obtained a 46.3% yield of the unsaturated ester, which boiled at 99–100° at 1 mm.; $n^{29.6}_D$ 1.4376, $d^{29.6}_4$ 1.0112; *MR* found: 50.3; *MR* calcd., 49.53. The discrepancy of 0.8 unit is undoubtedly the conjugation exaltation effect.

n-**Butanephosphonic Acid.**—The above ester (0.5 g.) in 25 ml. of ethanol was added to 0.3 g. of 5% palladium-on-charcoal catalyst and the mixture was subjected to the flow of hydrogen through a gas disperser placed at the bottom of the vessel. The reaction was complete within 30 minutes at room temperature. After filtration, the solution was treated with 100 ml. of concentrated hydrochloric acid and the whole was refluxed overnight. The alcohol was then largely distilled from the mixture and the residual liquid was refluxed for an additional 6 hours with a further addition of hydrochloric acid (50 ml.). Evaporation of the solution by means of an infrared lamp to near dryness, final drying by a similar evaporation with two small portions of benzene, and crystallization from benzene with a little charcoal, readily yielded substantially the theoretical yield of *n*-butanephosphonic acid, which melted at 105.5–106.0° whether alone or when mixed with an authentic specimen.

2-Chlorobutanephosphonic Acid.—The phosphonyl dichloride (17.8 g.) was added to 50 ml. of water and was permitted to hydrolyze with stirring and gentle warming. Removal of volatiles under reduced pressure yielded 14.7 g. of crude solid acid. Recrystallization from benzene gave the pure compound in the form of colorless plates which melted at 88–90° with slight decomposition. Titration of the substance with a *p*H meter was impossible as each addition of the standard alkali gave unstable voltage, indicating a rapid cleavage of hydrogen halide. A rapid addition of 0.1 *N* sodium hydroxide to methyl orange end-point, followed by acidification with nitric acid and addition of silver nitrate gave 18.6% chlorine content, against the theoretical value of 20.5%. The compound was not investigated further, but it was evident that its link to the chlorine atom was decidedly weak.

ROSS CHEMICAL LABORATORY
ALABAMA POLYTECHNIC INSTITUTE
AUBURN, ALABAMA

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The Dielectric Constant of Formamide[1]

BY GORDON R. LEADER

Formamide has long been known to have a high dielectric constant, but until recently, there have been no accurate values available for this property, the only reported determination being that of Walden[2] who gave its dielectric constant as >84. In 1947, Burdun and Kantor[3] reported measurements made by the Drude–Coolidge method with wave lengths in the range 1–5 meters. They found $\epsilon = 109 \pm 1.5$ at $20 \pm 1°$ and conclude from the absence of dispersion in this region that this is equivalent to the static value. An earlier reference to values for the dielectric constant of formamide determined by Burdun was made by Vasenko[4] who reported that $\epsilon = 126.07 - 0.7206\ t$ between 18 and 25°. Recently measurements of greater precision have been made in this Laboratory in the temperature range 15 to 35° which confirm in a general way the results of Burdun and Kantor, but indicate a smaller variation of dielectric constant with temperature than has previously been reported.

Capacitance measurements were made using a General Radio Type 821-A Twin-T Impedance Measuring Circuit.[5] Radio frequency current was supplied to the Bridge from a General Radio Type 1001-A Standard Signal Generator. A Hallicrafters Model S-40A multi-band receiver was used as null detector. Because of the relatively high conductivity of even carefully purified formamide, capacitance measurements were made at a frequency of 10 mc. The cell used was very similar in design to that described by Connor, Clarke and Smyth,[6] and was plugged directly into the unknown terminals of the bridge in order to minimize the effect of lead inductance. The cell construction was modified from the design of Connor, Clarke and Smyth chiefly in that the insulating plug was made of Teflon, and the lower portion of the central electrode which passed through the plastic was made of smaller diameter than the body of the electrode in order to reduce the invariant capacity of the cell and to permit a more rigid fit of this tapered stem in the similarly tapered hole in the plastic. The plug was held securely in place with the aid of small washers placed under the General Radio plugs and overlapping slightly on the plastic. The cell was made of brass, and all parts coming into contact with the liquids measured were first silver plated and then gold plated.

Temperature control was secured by circulating water through the cell jacket from a thermostat whose temperature was regulated to ±0.05°. Temperatures were measured using a 0.1° thermometer calibrated by the National Bureau of Standards. It was established by measurements on water and methanol whose dielectric constants are accurately known at these temperatures that within the temperature range 15 to 35° the cell contents were held at the indicated bath temperatures.

The procedure in making measurements was essentially that described by Connor, Clarke and Smyth.[6] The constants in the equation: $C = C_0 + C_v\epsilon$ were determined by measurements of the capacity of the cell when filled with purified benzene and chlorobenzene as reference substances.[7] To secure greater accuracy in measurement of the small capacities involved with these liquids, a heterodyne beat apparatus of the type described by Chien[8] was used, together with a calibrated General Radio Type 722N Precision Condenser. It was found that $C_0 = 1.80 \pm 0.01\ \mu\mu f$ and $C_v = 3.800 \pm 0.005$ at all temperatures from 15 to 35°. Determination of C_v was also carried out at each of the temperatures studied by measurements at 1 mc. with the Twin-T Bridge of the capacity of the cell when filled with purified methanol and water. The values of Albright and Gosting[9] for the dielectric constants of these substances were used. In this manner also a value of $C_v = 3.800 \pm 0.005$ was obtained, independent of temperature in the 15 to 35° range.

At 10 mc. the inductance of the cell and residual

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[1] Based on research performed for the U. S. Army Signal Corps, Fort Monmouth, N. J. under contracts W36-039-sc-32265 and W36-039-sc-38184.

[2] Walden, *Z. physik. Chem.*, **46**, 175 (1903).

[3] Burdun and Kantor, *Doklady Akad. Nauk. S. S. S. R.*, **67**, 985 (1949).

[4] Vasenko, *J. Phys. Chem.* (*U. S. S. R.*), **21**, 361 (1947).

[5] Sinclair, *Proc. Inst. Radio Eng.*, **28**, 310 (1940).

[6] Conner, Clarke and Smyth, THIS JOURNAL, **64**, 1379 (1942).

[7] Davies, *Phil. Mag.*, **21**, 1, 1008 (1936).

[8] Chien, *J. Chem. Ed.*, **24**, 494 (1947).

[9] Albright and Gosting, THIS JOURNAL, **68**, 1062 (1946).

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.

UNIVERSITY OF KENTUCKY
LEXINGTON, KENTUCKY

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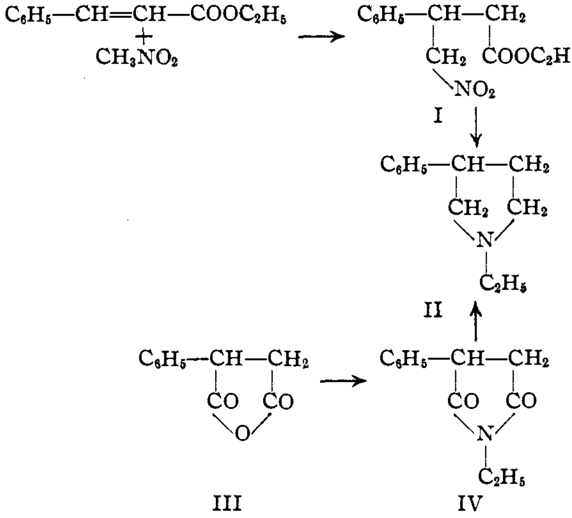
[10] Smith, *J. Chem. Soc.*, 3257 (1981).

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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[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).