Our work, together with that of Newman and Smith, suggests the following order of reactivity of groups toward phenylmagnesium bromide at $-70°$: $-CH{=}O > -NO_2 > -COOCH_3$

Experimental[3]

Phenylmagnesium bromide prepared from 35.3 g. (0.195 mole) of redistilled bromobenzene and 6.5 g. of magnesium turnings in 100 ml. of dry ether was added dropwise over a period of 5 hours to 12.5 g. (0.069 mole) of methyl *p*-nitrobenzoate, m.p. 95–96°, in 175 ml. of dry toluene and 40 ml. of dry ether. The reaction mixture was continuously agitated and maintained at −70° under a nitrogen atmosphere. The product was hydrolyzed at −70° by addition of 30 ml. of saturated aqueous ammonium chloride. After removal of the solvent the product was dissolved in 200 ml. of ether, washed with 10% sulfuric acid, 10% sodium carbonate and water. It was then dried over calcium chloride and passed through a separatory funnel containing 300 g. of activated alumina (Harshaw A1-0109P) with 500 ml. of ether. Evaporation of the solvent followed by recrystallization from hexane produced 5 g. (45%) of brown crystals, m.p. 106–112°. Recrystallization from 95% methanol raised the m.p. to 114–116°. Purification by chromatography on an alumina column (with benzene as the eluant) gave white crystals of *p*-carbomethoxydiphenylamine, m.p. 115.8–116.5° (lit.[4] 115°). The structure was confirmed by infrared analysis (ester carbonyl at 1720 cm.$^{-1}$) and by hydrolysis with 2% sodium hydroxide in quantitative yield to *p*-carboxydiphenylamine which had m.p. 159.3–159.8° (lit.[4] 156°) after recrystallization from a benzene–hexane mixture.

---

[3] Melting points are corrected. We are indebted to Miss Helen Miklas for the infrared spectrum.

[4] H. Gilman and G. E. Brown, THIS JOURNAL, **62**, 3208 (1940).

NOYES CHEMICAL LABORATORY
THE UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

The Half-Wave Potential of Lithium

BY WALTER E. CLARK

RECEIVED JULY 27, 1953

An accurate determination of the half-wave potential of aqueous lithium ion recently has been made in this Laboratory. When the dropping electrode assembly is carefully damped to eliminate all vibration, it is possible to obtain a regular, well-defined lithium wave having the theoretical slope for a one-electron reversible reduction. The point of inflection corresponding to $E_{1/2}$ is not sharply defined, however, since $E_{1/2}$ could not be accurately determined by means of Muller's oscillographic technique.[1] As expected, the half-wave potential was found to be independent of concentration, of mercury height, and of the capillary employed. The average experimental value of the half-wave potential, corrected for cell resistance, was found to be −2.331 ± 0.003 v. *vs.* the S.C.E.

$E_{1/2}$ for the anodic wave obtained by using dilute (approx. 1×10^{-3} *M*) lithium amalgam as the dropping electrode agreed approximately with the value obtained by conventional electrolysis. Very accurate data could not be obtained from the dropping amalgam electrode due to frequent plugging of the capillary.

Even with the utmost precautions it was not possible to obtain a constant value for $i_d/Cm^{2/3}t^{1/6}$ at any concentration. The polarographic waves were well-defined except that when the concentration of lithium was greater than about 2×10^{-3} *M* the diffusion current became increasingly ill-defined; below about 1×10^{-4} *M* the residual current of the supporting electrolyte became inconveniently large compared to the height of the lithium wave.

Experimental

The polarograph employed was the high sensitivity visual recording instrument described by Kelley and Miller.[2] The supporting electrolyte was 0.1 *M* tetra-*n*-butylammonium hydroxide obtained by diluting the 1 *M* product supplied commercially by Southwestern Analytical Chemicals, Austin, Texas. The discharge potential of this electrolyte is about −2.8 v. *vs.* the S.C.E. which makes it preferable to the corresponding tetraethyl or tetramethyl compound. Occasionally a wave was observed in the supporting electrolyte which appeared to be due to some impurity as reported by Zlotowski and Kolthoff.[3] In 0.1 *M* solution this wave was usually negligible and in any event its effect was eliminated by determining the residual current before adding the lithium compound. The latter was hydroxide from a specially purified stock solution.

Half-wave values were determined from the plot of *E vs.* log $i/i_d - i$, which allows the $E_{1/2}$ value to be read to a precision greater than the accuracy of the experimental data. The limiting factor in the accuracy of the method appears to be the determination of the diffusion current. It was found advantageous to employ an undamped circuit in this determination.

The values of *E* used in the log plots were determined in the conventional way by interpolation on the polarogram between points the potentials of which were accurately determined with a potentiometer. In the course of the investigation several different calomel electrodes were employed. These were checked against each other prior to making a run and the maximum variation observed was 0.2 millivolt.

The polarographic cell employed was of the "H" type described by Lingane and Laitinen.[4] Instead of housing the reference anode in the second arm of the cell, this arm was filled with a solution of the supporting electrolyte and used as a salt bridge to make connection with a separate calomel electrode. As further insurance against diffusion of potassium ion into the polarographic cell, an agar plug containing 0.1 *M* tetra-*n*-butylammonium chloride was inserted next to the fritted disc in the salt bridge arm of the cell. The cell was immersed in a water-bath thermostatically controlled to a temperature of 25 ± 0.1°.

The author wishes to acknowledge his indebtedness to Dr. W. B. Schaap and to Dr. D. J. Fisher for helpful suggestions on experimental technique and on instrumentation, respectively.

---

[1] R. H. Muller, R. L. Garman, M. E. Droz and J. Petras, *Ind. Eng. Chem., Anal. Ed.*, **10**, 339 (1938).

[2] M. T. Kelley and H. H. Miller, *Anal. Chem.*, **24**, 1895 (1952).

[3] I. Zlotowski and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 473 (1942).

[4] J. J. Lingane and H. A. Laitinen, *ibid.*, **11**, 504 (1939).

MATERIALS CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

The Leuckart Reaction of Some 1,5-Diketones

BY FRANCIS CHUBB, ALLAN S. HAY AND REUBEN B. SANDIN

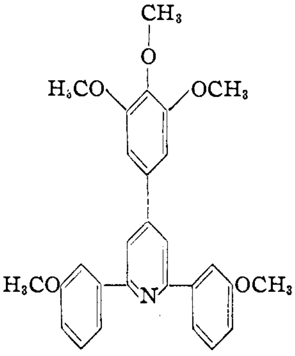
RECEIVED JULY 20, 1953

In an attempt to prepare some 1,5-diamines it was decided to examine the behavior of some 1,5-diketones toward the ammonium formate–formamide reagent, described by Ingersoll and co-workers in their investigation of the Leuckart reaction.[1]

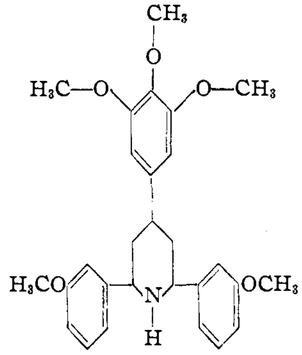
---

[1] A. W. Ingersoll, J. H. Brown, C. K. Kim, W. D. Beauchamp and G. Jennings, THIS JOURNAL, **58**, 1808 (1936).

We have found that when a mixture of benzaldiacetophenone and an excess of the formate–formamide reagent is heated for 5 hours at 180–185°, 2,4,6-triphenylpyridine (31%) and 2,4,6-triphenylpiperidine (47%) are formed. Similarly, 3,4,5-trimethoxybenzal-di-(3-methoxyacetophenone) affords 2,6-di-(3-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-pyridine (I) (35%) and the corresponding piperidine derivative (II) (45%).



I



II

Apparently under the conditions of the Leuckart reaction[2] the 1,5-diketones are converted into 1,5-diamines which then cyclize to form piperidine derivatives.[3] Also under the same conditions the pyridine compounds can be accounted for on the basis of a reaction between ammonia and the 1,5-diketones. Dihydropyridines are formed and these compounds are known to disproportionate to form pyridine and piperidine derivatives.[4] In our work the yield of piperidines is too high to account for their formation solely on the basis of the disproportionation of the corresponding dihydropyridines. It seems likely that the direct cyclization of the 1,5-diamines is also an important reaction.[5]

Experimental

3,4,5-Trimethoxybenzaldi-(3-methoxyacetophenone) (III).—A mixture of 3-methoxyacetophenone (4.5 g.), 3,4,5-trimethoxybenzaldehyde (1.96 g.), alcohol (10 ml.) and 40% sodium hydroxide solution (2.0 ml.) was heated on a steam-bath for 15 minutes and then poured into cold water. The mixture was extracted with ether, the ether solution was washed with dilute hydrochloric acid and water and then dried over sodium sulfate. Evaporation of the ether gave 3.0 g. (62.7%) of 3,4,5-trimethoxybenzaldi-(3-methoxyacetophenone), colorless needles, m.p. 97–99°. An analytical sample, recrystallized from alcohol, melted at 100–101°.

Anal. Calcd. for $C_{28}H_{30}O_7$: C, 70.28; H, 6.32; mol. wt., 478. Found: C, 69.81; H, 6.39; mol. wt., 492.

Leuckart Reaction of 3,4,5-Trimethoxybenzaldi-(3-methoxyacetophenone).—A mixture of 12 g. of III and 24 g. of ammonium formate–formamide reagent was heated in an oil-bath for 5 hours at 180–185°. After cooling and the addition of alcohol (80 ml.) and concentrated hydrochloric acid (80 ml.), the mixture was refluxed for 1 hour. The solution was cooled and made basic by the addition of excess sodium hydroxide solution. The reaction mixture was extracted with ether and the ether solution was dried over sodium sulfate. After evaporation of the solvent, the residue was dissolved in boiling alcohol and on cooling afforded 4.1 g. of I (35%), colorless crystals, m.p. 102–105°. An analytical sample crystallized from alcohol melted at 105–106°.

Anal. Calcd. for $C_{28}H_{27}NO_5$: C, 73.50; H, 5.95. Found: C, 73.38; H, 6.26.

The picrate was prepared from a solution of the amine in alcohol and picric acid. It was crystallized from alcohol, m.p. 166–168°.

Anal. Calcd. for $C_{34}H_{30}N_4O_{12}$: C, 59.47; H, 4.40. Found: C, 59.75; H, 4.42.

The filtrate from the separation of I was diluted with water and treated with concentrated hydrochloric acid. On standing, the solution deposited 5.2 g. (45%) of the colorless hydrochloride of II, m.p. 140–143° dec. The salt was crystallized from dilute alcohol and it then melted at 150° with considerable preliminary decomposition.

Anal. Calcd. for $C_{28}H_{34}NO_5Cl$: Cl, 7.10. Found: Cl, 6.89.

The hydrochloride was decomposed with dilute sodium hydroxide, and extracted with ether. The ether solution was dried over sodium sulfate. Evaporation of the solvent afforded the amine (II), colorless needles from alcohol, m.p. 107–108°.

Anal. Calcd. for $C_{28}H_{33}NO_5$: C, 72.54; H, 7.17; mole of active H, 1.00. Found: C, 72.76; H, 7.48; moles of active H, 1.04.[6]

The picrate was prepared by treating a solution of the amine in alcohol, with excess picric acid. It was crystallized from alcohol, m.p. 215–216°.

Anal. Calcd. for $C_{34}H_{36}N_4O_{12}$: C, 58.95; H, 5.24. Found: C, 59.32; H, 5.19.

The melting point of a mixture of I and II showed a depression. Moreover, a solution of I in hydrochloric acid was colored yellow, whereas II in hydrochloric acid showed no coloration.

Leuckart Reaction of Benzaldiacetophenone.—Thirty grams of benzaldiacetophenone was treated with the ammonium formate–formamide reagent (80 g.) as previously described. The amine reaction mixture was dissolved in alcohol and afforded 15 g. (31%) of the picrate of triphenylpyridine, m.p. 189–192°. According to Pictet and Stehelin[7] the m.p. is 192°. The picrate was decomposed with 2% ethanolamine and there was obtained 6.5 g. of 2,4,6-triphenylpyridine, m.p. 137–138°. The m.p. of this compound[5] has been given as 137°. The filtrate from the above picrate was evaporated and the residue was treated with excess of ethanolamine solution and extracted with ether. The ether solution was dried over sodium sulfate. Removal of the solvent left an oily residue which was dissolved in absolute alcohol and treated with dry hydrogen chloride. This afforded 15 g. (47%) of 2,4,6-triphenylpiperidine hydrochloride, colorless needles, m.p. 292–300° dec.

Anal. Calcd. for $C_{23}H_{24}NCl$: Cl, 10.15. Found: Cl, 10.36.

The free amine was obtained by decomposing the hydrochloride with sodium hydroxide and extracting with ether. The amine formed colorless needles from alcohol and melted at 83–85°. Active hydrogen was determined at 100° as

---

(2) For a review of the Leuckart reaction see M. L. Moore in R. Adams, "Organic Reactions," Vol. V, John Wiley and Sons, New York, N. Y., 1949, p. 301. For some recent work see J. F. Bunnett and J. L. Marks, THIS JOURNAL, **71**, 1587 (1949); P. A. S. Smith and A. J. Macdonald, *ibid.*, **72**, 1037 (1950); J. H. Burckhalter and S. H. Johnson, *ibid.*, **73**, 4830 (1951); D. S. Noyce and F. W. Bachelor, *ibid.*, **74**, 4577 (1952).

(3) H. S. Mosher in R. C. Elderfield's "Heterocyclic Compounds," Vol. I, John Wiley and Sons, New York, N. Y., 1950, p. 650.

(4) M. Scholtz, *Ber.*, **30**, 2295 (1897); E. Knoevenagel and J. Fuchs, *ibid.*, **35**, 1788 (1902); K. W. Merz and H. Richter, *Arch. Pharm.*, **275**, 294 (1937).

(5) M. Weiss, THIS JOURNAL, **74**, 200 (1952), in some careful studies on the Chichibabin pyridine synthesis has shown that when a mixture of benzaldehyde, acetophenone, ammonium acetate and acetic acid is refluxed, triphenylpyridine and benzylacetophenone are formed. In this case the sequence of reactions involves an aldol condensation, followed by the formation of the 1,5-diketone which then condenses with ammonia to form the dihydropyridine. The latter then undergoes dehydrogenation by transfer of hydrogen to benzalacetophenone. We have found that when a mixture of benzaldiacetophenone (9.8 g.), ammonium acetate (30 g.) and acetic acid (75 ml.) is refluxed under the above conditions, triphenylpyridine (6.1 g.) and triphenylpiperidine (2.7 g.) isolated as the hydrochloric acid salt, are formed.

(6) Active hydrogen was determined at 100° and in the apparatus described by P. M. Maginnity and J. B. Cloke, *Anal. Chem.*, **20**, 978 (1948). At 26° the amine showed 0.03 mole of active hydrogen.

(7) A. Pictet and P. Stehelin, *Compt. rend.*, **162**, 876 (1916).

previously described. At 28° there was no indication of active hydrogen.

Anal. Calcd. for $C_{23}H_{23}N$: C, 88.34; H, 7.40; mole of active H, 1.00. Found: C, 88.26; H, 7.45; moles of active H, 1.05.

Acknowledgment.—The authors wish to express their thanks to the Canadian Cancer Society for financial aid in support of this work.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA
EDMONTON, CANADA

Dielectric Constant and Refractive Index from 20 to 35° and Density at 25° for the System Tetrahydrofuran–Water[1]

BY FRANK E. CRITCHFIELD,[2] JOHN A. GIBSON, JR., AND JAMES L. HALL[3]

RECEIVED JUNE 15, 1953

For studies of conductance, activities and rates of reaction in solution it is desirable to have available solvent mixtures which may be made up to any specified dielectric constant within a wide range of dielectric constant values. To know to what extent the effects measured are functions of the dielectric constant only, and not of the specific solvent mixture used, it is necessary to use different mixtures to cover the same range of dielectric constant. Dioxane–water, methanol–water and other mixtures have been used for such studies. The system tetrahydrofuran–water is proposed as an alternate solvent system for these studies. The dielectric constant of tetrahydrofuran is relatively low and it is miscible with water in all proportions. Tetrahydrofuran of high purity is now available commercially. For the tetrahydrofuran–water system we report here the dielectric constants and refractive indices from 20 to 35° and the densities at 25°.

Experimental

Materials.—The water used in these measurements was prepared as described previously.[4] The fraction retained had a specific conductance of 1×10^{-6} ohm^{-1} cm.$^{-1}$. The tetrahydrofuran, from the Electrochemicals Department of E. I. du Pont de Nemours and Co., contained hydroquinone as an inhibitor. The tetrahydrofuran was separated by distillation after being mixed with an equal volume of heavy mineral oil to prevent an accumulation of concentrated peroxides in the still. For the product thus obtained, time–temperature cooling curves were determined using an N.B.S. calibrated platinum resistance thermometer and a Leeds and Northrup Co. Mueller Bridge. The freezing point was found to be −109.238° and the purity, as determined from the shape of the curves by the method of Rossini,[5] was found to be not less than 99.87%. This purity was adequate for the present purpose and so no further purification was attempted.

Method.—The measurements of dielectric constant were made with the apparatus previously described[4] except that a larger inner electrode was used in the cell. The cell was calibrated at each temperature used, since the cell capacitance was relatively large and small changes in the dimensions of the cell with temperature variations caused slight variations in cell capacitance. For calibration of the cell, the dielectric constant of water at the various temperatures was assumed to be as reported by Wyman[6] and Albright.[7]

Table I lists for the various temperatures the capacitance of the cell containing water, the dielectric constant of water with the corresponding literature reference, the calculated cell capacitance, d*ε*/d*c*, and the lead capacitance.

TABLE I

CALIBRATION DATA FOR NON-INDUCTIVE TYPE CELL

Temp., °C.	Cell capacitance with water	Dielectric constant of water	Cell capacitance	Lead capacitance
20	390.13	80.38	4.836	1.41
25	381.66	78.48	4.846	1.35
30	372.76	76.75	4.839	1.37
35	363.05	74.95	4.825	1.42

In order to check this calibration, the dielectric constants of methanol and acetone were determined at 25°. The value, 20.74, which was obtained for acetone agrees exactly with the value given by Albright,[7] and the value, 32.66, which was obtained for methanol is in exact agreement with the value of Albright and Gosting.[8]

A Bausch and Lomb Abbé refractometer was used for the refractive index measurements. The density determinations were made by the usual method using a 50-ml. Leach specific gravity bottle, fitted with a thermometer by means of a ground glass joint. This pycnometer was filled and the liquid level was adjusted in a constant temperature-bath which was controlled within 0.01°. All density calculations were based upon the density of water at 25°.

Results

The dielectric constants for the system tetrahydrofuran–water from 20 to 35° are shown in Table II. These data are believed to be accurate to about one part in 1000 in the low range of dielectric constant and one part in 2000 at the higher range.

TABLE II

DIELECTRIC CONSTANT FOR THE TETRAHYDROFURAN–WATER SYSTEM

THF, wt. %	Temperature, °C.			
	20	25	30	35
0.00	80.37	78.48	76.75	74.95
10.00	73.73	71.76	70.15	68.68
20.00	66.46	64.60	63.02	61.64
30.00	58.42	56.59	55.24	53.88
40.00	49.77	48.22	46.91	45.65
50.00	41.21	39.96	38.77	37.75
60.00	33.04	31.97	31.04	30.24
70.00	25.45	24.62	24.08	23.39
80.00	18.75	18.25	17.77	17.38
90.00	12.90	12.59	12.36	12.05
95.00	10.24	9.97	9.74	9.58
100.00	7.58	7.39	7.25	7.16

Table III shows the refractive indices for the system tetrahydrofuran–water over the temperature range 20 to 35°.

The absolute densities of the tetrahydrofuran–water system were determined at 25°. The density of water was taken as 0.9970 and the density of the tetrahydrofuran was measured to be 0.8811 at this temperature. The intermediate densities may be calculated by the equation

$$d = 0.9970 - 2.582 \times 10^{-4}P - 1.074 \times 10^{-5}P^2 + 1.73 \times 10^{-8}P^3$$

---

(1) Presented before the Division of Physical and Inorganic Chemistry, 124th National Meeting of the American Chemical Society, Chicago, Ill., September 6–11, 1953.

(2) The data upon which this report is based are included in the Ph.D. Dissertation of Frank E. Critchfield, West Virginia University, 1953.

(3) Please address communications to James L. Hall.

(4) F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, THIS JOURNAL, **75**, 1991 (1953).

(5) B. J. Mair, A. R. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

(6) J. Wyman, Jr., *Phys. Rev.*, **35**, 623 (1930).

(7) P. S. Albright, THIS JOURNAL, **59**, 2098 (1937).

(8) P. S. Albright and L. J. Gosting, *ibid.*, **68**, 1061 (1946).