the boiling point of oxygen at this pressure one obtains 90.029°K. based on 273.16°K. for the ice point. This, corrected to the pressure coefficient used by Cath,[8] is 90.006°K. as compared with our value, on the same basis, of 90.02$_9$°K.

Acknowledgments.—The authors wish to thank the National Research Council for Grants-in-Aid, without which this investigation would have been impossible. They are indebted to Mr. M. G. Mayberry and Dr. P. A. Lasselle, who kindly helped with the measurements. The Linde Company lightened our task considerably by supplying us willingly with pure hydrogen suitable for liquefaction purposes. The help and advice of Mr. J. E. Key of the Industrial Engineering Department and of Mr. G. F. Nelson of the University of California in connection with the mechanical construction of the apparatus has been invaluable. Especially we wish to thank Professor W. F. Giauque of the University of California for encouragement and advice which have contributed much to the success of the work.

Summary

1. The establishment of a temperature scale from 12–273°K. in terms of the copper–constantan thermocouple, using a helium thermometer, is described.
2. An e. m. f. temperature reference table is given from 12–90°K.
3. The scale is compared with the Leiden scale, using hydrogen and oxygen vapor pressure thermometers.

STATE COLLEGE, PA. RECEIVED MAY 3, 1935

[CONTRIBUTION FROM THE NICHOLS LABORATORY OF NEW YORK UNIVERSITY]

Condensations of Benzoylformanilide with Cyano-activated Methylene Compounds[1]

BY JOHN V. SCUDI[2] AND H. G. LINDWALL

This paper is a further report on a series of studies of condensation reactions of alpha-ketoamides as exemplified by isatin and benzoylformanilide. The reactions of the latter with acetophenone give rise to the formation of pyrrolone structures.[3]

Benzoylformanilide reacts with malonitrile (Chart A) to yield an orange-red compound (1-phenyl - 1 - formanilido - 2,2 - dicyanoethylene) (I), which on treatment with hydrochloric acid is hydrolyzed to the corresponding di-amide (II). Reduction products III and IV, obtained from I and II, respectively, give phenylsuccinic acid (V) upon hydrolysis, identified by melting point methods and by conversion to phenylsuccinanil.

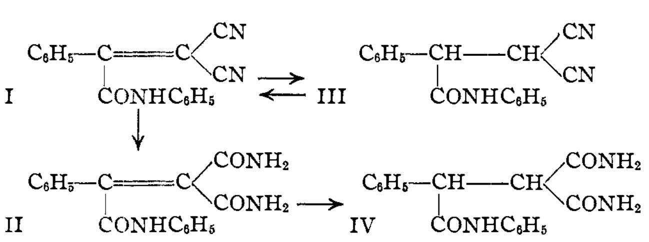

CHART A

Compound III gives positive Tollens' and Fehling's tests. Heating III in alcohol causes solution with an accompanying production of color and an 80% yield of I is obtained.

Cyanacetamide condenses with benzoylformanilide (Chart B) to yield VI which exhibits typical imide properties, liberating ammonia upon treatment with alkali, and giving VII under the influence of hydrochloric acid. The amide (VII) forms the corresponding nitrile (VIII) upon distillation from phosphorus pentoxide. Both VII and VIII undergo interesting addition reactions; VIII reacts with ammonia at zero degrees in moist ether giving VI, and VII reacts with diethylamine under the same conditions to yield an addition product (VII-A) for which no structure is postulated at present. Compound VII is regenerated from VII-A by heating with concentrated hydrochloric acid.

Further, the amide (VII) yields upon reduction the formamido substituted phenylsuccinanil (IX), which is hydrolyzed and subsequently decarboxylated by hot mineral acid to give phenylsuccinic acid. Compound IX gives a dibasic acid (X), as a result of careful alkaline hydrolysis, which is converted to phenylsuccinanil by

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(1) Presented in part at the New York Meeting of the American Chemical Society, April, 1935.

(2) From a dissertation presented by John V. Scudi in partial satisfaction of the requirements for the Ph.D. degree at New York University.

(3) Bashour and Lindwall, THIS JOURNAL, **57**, 178 (1935).

heating in mineral acid or by heating to its melting point.

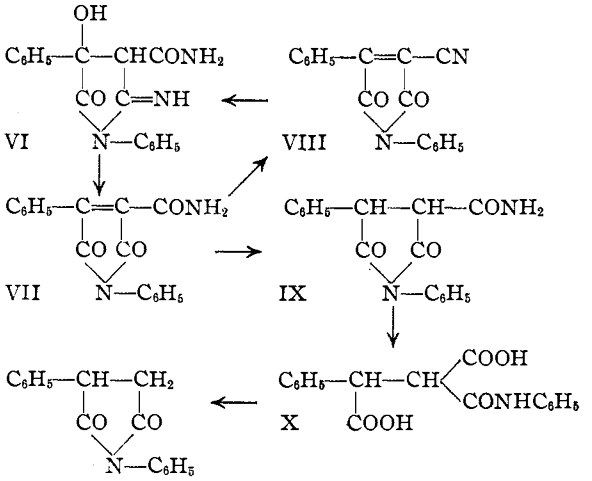

CHART B

Ethyl cyanoacetate and benzoylformanilide condense in the presence of diethylamine giving a product (XI) which evidently involves one mole of the catalyst. Piperidine and sodium hydroxide when used as condensation catalysts form similar complexes. Compound XI is evidently an intermediate in the course of the condensation for if it is not isolated from the reaction mixture it is converted over a long period of time into α-cyano-β-phenylmaleinanil (VIII). The piperidine (XII) and sodium hydroxide (XIII) compounds, as well as XI, produce VIII upon acid treatment. No structures are postulated now for these intermediates, but it is significant that VIII gives XI when treated with diethylamine in moist ether at low temperatures. Compound VIII, thus obtained from XI, is identical with the VIII obtained above in the cyanoacetamide series of reactions. Reduction of VIII gives α-cyano-β-phenylsuccinanil (XIV) which, as expected, is hydrolyzed to the dibasic acid (X).

The maleinanil derivatives, VII and VIII, dissolve in hot sodium bisulfite solution with loss of color. Acidification regenerates the original compounds. Compound I behaves similarly, but gives II upon acidification of the colorless solution.

Experimental Part

1-Phenyl-1-formanilido-2,2-dicyanoethylene (I).—Five grams of benzoylformanilide, 1.5 g. of malonitrile and 6 drops of ethylamine in 8 cc. of 95% alcohol were allowed to stand at room temperature for three hours. Orange-red needles separated; yield, 90% after crystallization from alcohol; m. p. 206–207°.

Anal. Calcd. for $C_{17}H_{11}ON_3$: C, 74.73; H, 4.03; mol. wt., 273. Found: C, 74.59; H, 3.91; mol. wt., 265.

1-Phenyl-1-formanilido-2,2-diformamidoethylene (II).—To 1 g. of I in 30 cc. of boiling alcohol was added 20 cc. of concd. hydrochloric acid. Cooling caused the crystallization of yellow needles in almost quantitative yield, and in a good state of purity, m. p. 216°.

Anal. Calcd. for $C_{17}H_{15}O_3N_3$: N, 13.59. Found: N, 13.58, 13.79.

1-Phenyl-1-formanilido-2,2-diformamidoethane (IV).—One gram of II and 1 g. of sodium hyposulfite ($Na_2S_2O_4$) in 10 cc. of water shaken at 50° for five minutes produced a quantitative yield of IV as glassy needles, m. p. 164–165°, after crystallization from water, soluble in alcohol and ether.

Anal. Calcd. for $C_{17}H_{17}O_3N_3$: N, 13.50. Found: N, 13.43, 13.35.

1-Phenyl-1-formanilido-2,2-dicyanoethane (III).—A hot solution of 1 g. of sodium hyposulfite in 5 cc. of water was added to 1 g. of I in 15 cc. of boiling alcohol. After shaking, 15 cc. of cold water was added to crystallize the product which was then triturated successively with water, alcohol and ether; yield, almost quantitative; m. p. 215° with decomp.; gives positive Tollens' and Fehling's tests. When III is refluxed for one week in alcohol an 80% yield of I is obtained.

Anal. Calcd. for $C_{17}H_{13}ON_3$: C, 74.18; H, 4.73. Found: C, 73.94; H, 4.75.

Phenylsuccinic Acid from III, IV or IX.—One gram of III (or of IV or of IX), in 10 cc. of 10% sodium hydroxide was refluxed until no more ammonia was evolved. After acidification, which liberated carbon dioxide, the solution was evaporated to dryness at steam-bath temperature; yield, after purification, 70%; m. p. 166–168°. Identified by melting point methods[4] and by conversion to phenylsuccinanil.

Anal. Calcd. for $C_{10}H_{10}O_4$: neutr. equiv., 97. Found: neutr. equiv., 97.

1,4 - Diphenyl - 2 - imido - 3 - formamido - 4 - hydroxypyrrolidone-5 (VI).—Five grams of benzoylformanilide, 3 g. of cyanoacetamide, and 5 drops of diethylamine in 10 cc. of alcohol and 5 cc. of water were allowed to stand at ice-box temperature for one week. The product was obtained as white needles from alcohol; yield, 85%; m. p. 209–210° with decomp.

Anal. Calcd. for $C_{17}H_{15}O_2N_3$: C, 66.02; H, 4.85; N, 13.59. Found: C, 66.31; H, 4.92; N, 13.55, 13.52.

α-Formamido-β-phenylmaleinanil (VII).—One gram of VI was dissolved in 10 cc. of cold 10% hydrochloric acid. Five minutes of standing at room temperature, or boiling, caused the quantitative precipitation of VII. Crystallization from alcohol, toluene or 50% acetic acid gave yellow needles, m. p. 207°.

Anal. Calcd. for $C_{17}H_{12}O_3N_2$: C, 69.86; H, 4.11; N, 9.59; mol. wt., 296. Found: C, 70.05; H, 4.14; N, 9.55, 9.37; mol. wt., 302.

Diethylamine Derivative of VII (VII-A).—A mixture of 1 g. of VII, an excess of diethylamine, and 10 cc. of moist

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(4) Lapworth and McRae, *J. Chem. Soc.*, **121**, 1699 (1922).

ether was allowed to stand at ice-box temperature for three days. A white crystalline product separated which was purified by trituration with ether and small amounts of alcohol· crystallization methods were impracticable because of ease of decomposition in hot solvents; soluble in water; decomposed with liberation of diethylamine by warm sodium hydroxide solutions; yield, 1 g.; m. p. 163–164°, with decomp.

Anal. Calcd. for $C_{21}H_{23}O_3N_3 \cdot H_2O$: C, 65.79; H, 6.53. Found: C, 65.73; H, 6.49.

α-Cyano-β-phenylmaleinanil (VIII) from VII.—One gram of VII was intimately mixed with 1 g. of phosphorus pentoxide and distilled. The product crystallized in yellow needles from alcohol; m. p. 118–119°; yield, 70%.

Anal. Calcd. for $C_{17}H_{10}O_2N_2$: C, 74.45; H, 3.65; N, 10.22. Found: C, 74.35; H, 3.81; N, 9.88.

VI from VIII.—A suspension of 1 g. of VIII in 8 cc. of ether and 2 cc. of 95% alcohol was saturated with dry ammonia and kept at ice-box temperature for three days. A 70% yield of VI separated; identified by melting point methods and chemical behavior.

α-Formamido-β-phenylsuccinanil (IX) from VII.—Compound VII (0.85 g.) was shaken with 1 g. of sodium hyposulfite in 40 cc. of 50% alcohol for a few minutes. White glassy needles separated; crystallized from alcohol; yield, 80%; m. p. 193–194°.

Anal. Calcd. for $C_{17}H_{14}O_3N_2$: C, 69.39; H, 4.77; N, 9.52. Found: C, 68.99; H, 4.77; N, 9.39.

α-Phenyl-β-formanilidosuccinic Acid (X) from IX or XIV.—One gram of IX, or of XIV, was warmed on the steam-bath in 10 cc. of 10% sodium hydroxide until the evolution of ammonia ceased. Acidification, cold, caused the formation of a solid which crystallized as white needles from water; m. p. 156–157°; yield 60%.

Anal. Calcd. for $C_{17}H_{15}O_5N$: N, 4.47. Found: N, 4.42, 4.24. **Di-silver Salt:** Calcd. for $C_{17}H_{13}O_5NAg_2$: Ag, 40.83. Found: Ag, 40.81.

Phenylsuccinanil from X.—Heating X above its melting point produces the anil, m. p. 137–138°. Boiling hydrochloric acid gives the same result.

Condensation of Benzoylformanilide and Ethyl Cyanoacetate: XI, XII and XIII.—Equimolecular quantities of benzoylformanilide, ethyl cyanoacetate and catalyst allowed to stand at ice-box temperature in 95% alcohol produce colorless crystalline compounds in 75 to 80% yields as follows, depending upon the respective catalysts used: with diethylamine, compound XI in three hours; with piperidine, XII in two hours; with sodium hydroxide, XIII in three days. Compounds XI and XII are insoluble in common organic solvents in the cold, and decompose into VIII and catalyst upon being heated; they were purified by trituration with water, alcohol and ether. Compound XIII is a sodium salt, soluble in water, and was recrystallized from aqueous alcohol. Melting point data: XI, 156–158°, with decomp.; XII, turns red at 124°, decomp. at 125–126°; XIII, turns brown at 210°, decomp. at 225–226°.

Anal. **XI** Calcd. for $C_{21}H_{23}O_3N_3$: C, 69.04; H, 6.30; N, 11.51. Found: C, 67.88; H, 6.49; N, 11.53, 11.76. **XII** Calcd. for $C_{22}H_{23}O_3N_3$: C, 66.83; H, 6.33. Found: C, 67.66; H, 6.07. **XIII** Calcd. for $C_{17}H_{15}O_5N_2Na$: Na, 6.57. Found: Na, 6.36. **XIII, Silver Salt.** Calcd. for $C_{17}H_{15}O_5N_2Ag$: Ag, 24.83. Found: Ag, 24.81, 25.06.

Compound VIII from XI, XII and XIII. From XI.—(A) A solution of XI in 10% sodium hydroxide gives an odor of diethylamine upon being heated. Gentle acidification with cold dilute hydrochloric acid gives VIII (*vide supra*, VIII from VII). (B) Boiling a suspension of XI in alcohol, water or acetone converts it to VIII. (C) Saturation of a suspension of XI in absolute alcohol with dry hydrogen chloride gives VIII. Yields, in A, B and C, 75%. **From XII and XIII.**—VIII is obtained as above, upon acidification.

Compound XI from VIII.—VIII (0.5 g.) suspended in 10 cc. of ether and 1 cc. of 95% alcohol with 0.15 g. of diethylamine at ice-box temperature for three days, precipitated 0.5 g. (75%) of XI; m. p. 156–157°, with decomp.

Anal. Calcd. for $C_{21}H_{23}O_3N_3$: C, 69.04; H, 6.30. Found: C, 67.80; H, 6.09.

α-Cyano-β-phenylsuccinanil (XIV) from VIII.—To a boiling solution of 2 g. of VIII in 40 cc. of alcohol was added 10 cc. of hot water containing 2 g. of sodium hyposulfite. More water was added until precipitation of the white product (XIV) began. Slow cooling gave minute white crystals; yield, 75%; m. p. 135–136°, after recrystallization from 50% alcohol, or 50% acetic acid. The product gives positive Fehling's and Tollens' tests.

Anal. Calcd. for $C_{17}H_{12}O_2N_2$: C, 73.91; H, 4.35; N, 10.14; mol. wt., 276. Found: C, 73.83; H, 4.53; N, 10.09; mol. wt., 274.

Summary

Malonitrile condenses with benzoylformanilide to yield a product which upon reduction and hydrolysis gives phenylsuccinic acid. Cyanoacetamide and ethyl cyanoacetate also react with this alpha-keto-amide, but in these cases ring closure accompanies condensation and the products are derivatives of phenylmaleinanil, from which phenylsuccinanils may be prepared by reduction.

NEW YORK, N. Y. RECEIVED JUNE 26, 1935