Elmer model 12C infrared spectrometer with rock salt optics calibrated against water vapor and ammonia,[9] using the same fixed rock salt cell of thickness about 0.025 mm.

(NOTE: The complete spectrum will be available through the American Petroleum Institute.—Ed.)

[9] R. A. Oetjen, C. L. Kao and H. M. Randall, *Rev. Sci. Instruments*, **13**, 515 (1942).

JOINT CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE NEW SOUTH WALES UNIVERSITY OF TECHNOLOGY, SYDNEY, AND THE
CHEMISTRY DEPARTMENT, UNIVERSITY OF QUEENSLAND, BRISBANE, AUSTRALIA

Trinitrobenzene Complexes of Various Indole Compounds[1]

BY LOWELL E. WELLER, THEODORE L. REBSTOCK AND HAROLD M. SELL

RECEIVED DECEMBER 22, 1951

We have prepared a number of new 1,3,5-trinitrobenzene complexes of various indole derivatives for use in characterization of these substances.

The properties of these derivatives, prepared as previously described,[2,3] are summarized in Table I.

TABLE I

PROPERTIES OF 1,3,5-TRINITROBENZENE ADDUCTS OF INDOLE COMPOUNDS

Trinitrobenzene derivative of	M.p., °C.	Color	Formula	Dumas nitrogen, % Calcd.	Dumas nitrogen, % Found
Isatin (2,3-indolinedione)	116	Light brown	$C_{14}H_8O_8N_4$	15.6	15.7
Oxindole (2,3-dihydro-2-oxoindole)	123	Yellow	$C_{14}H_{10}O_7N_4$	16.2	16.3
Indole-3-aldehyde	144.5	Yellow	$C_{15}H_{10}O_7N_4$	15.6	15.8
Skatol (3-methylindole)[a]	184	Red	$C_{15}H_{12}O_6N_4$	16.3	16.4
Tryptophol (indole-3-ethanol)	109.5	Orange	$C_{16}H_{14}O_7N_4$	15.0	15.1
β-(Indole-3)-propionic acid	135	Orange	$C_{17}H_{14}O_8N_4$	13.9	14.1
2-Methylindole-3-acetic acid	208	Red	$C_{17}H_{14}O_8N_4$	13.9	13.8
β-(Indole-3)-*n*-butyric acid	152	Red	$C_{18}H_{15}O_8N_4$	13.5	13.4
2,3-Diphenylindole	160	Red	$C_{26}H_{18}O_6N_4$	11.6	11.6

[a] van Romburgh[4] reported the m.p. as 183°, but gave no analysis.

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[1] Journal Article No. 1307 from the Michigan Agricultural Experiment Station, East Lansing. This work was supported in part by the Horace H. Rackham Research Endowment of Michigan State College.

[2] C. T. Redemann, S. H. Wittwer and H. M. Sell, THIS JOURNAL, **73**, 2957 (1951).

[3] J. J. Sudborough, *J. Chem. Soc.*, **109**, 1339 (1916).

[4] M. P. van Romburgh, *Rec. trav. chim.*, **14**, 67 (1895).

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Synthesis of β-Acetamido-β,β-dicarbethoxypropionaldehyde and DL-Aspartic Acid[1]

BY OWEN A. MOE AND DONALD T. WARNER

RECEIVED DECEMBER 6, 1951

Previous publications[2-4] from this Laboratory have disclosed the syntheses of γ-acetamido-γ,γ-dicarbethoxybutyraldehyde and other closely related aldehydo compounds, and the utilization of these aldehyde intermediates in the production of diverse amino acids. This report concerns the synthesis of the lower aldehydo homolog, namely, β-acetamido-β,β-dicarbethoxypropionaldehyde.

Ethyl allylacetamidomalonate[5] was prepared by the allylation of the corresponding malonic ester with allyl bromide. The action of ozone on the allyl derivative yielded the ozonide which in turn was converted by reductive cleavage to the desired aldehydo compound, a crystalline product melting at 80–81°. The β-acetamido-β,β-dicarbethoxypropionaldehyde was further characterized as the 2,4-dinitrophenylhydrazone melting at 117–119°. Oxidation of the aldehyde by alkaline permanganate yielded the corresponding acid diester melting at 147–148°. Hydrolysis by refluxing in concentrated hydrochloric acid converted the acid diester to DL-aspartic acid.

Experimental

β-Acetamido-β,β-dicarbethoxypropionaldehyde.—Ethyl allylacetamidomalonate[5] (30 g.) was dissolved in 50 cc. of absolute ethanol. The resulting alcoholic solution was treated with ozone at 0–5° for a period of 5 hours. The water-clear alcoholic solution of the ozonide was diluted with absolute ethanol to a total volume of 200 cc. Five per cent. palladium-on-charcoal (2 g.) was added and the reductive cleavage[6] of the ozonide was accomplished at an initial pressure of 30 p.s.i. After 90 minutes the reduction was complete. The reaction mixture was refrigerated overnight and then the catalyst was removed by filtration. The water-clear filtrate gave no test for ozonide and it was concentrated *in vacuo*. A solid crystalline cake resulted which possessed a pungent odor of formaldehyde. The yield of crude aldehydo compound melting at 65–67° was 29.3 g. Purification by crystallization from ethanol increased the melting point to 80–81°.

Anal. Calcd. for $C_{11}H_{17}O_6N$: C, 50.93; H, 6.61; N, 5.40. Found: C, 50.58; H, 6.39; N, 5.87.

The 2,4-dinitrophenylhydrazone of β-acetamido-β,β-dicarbethoxypropionaldehyde was prepared following the conventional procedure and after purification by crystallization from ethanol melted at 117–119°.

Anal. Calcd. for $C_{17}H_{21}O_9N_5$: C, 46.44; H, 4.82; N, 15.94. Found: C, 46.33; H, 4.41; N, 15.85.

The Diester Acid.—A water solution containing 3.3 g. of the aldehydo compound was mixed with 5–10 drops of 10% aqueous sodium hydroxide. The resulting clear solution was treated with portions of a saturated aqueous solution of potassium permanganate until a slight excess was indicated. The oxidation of the aldehydo compound was very rapid and it was necessary to cool the reaction mixture in a cold water-bath in order to avoid an increase in the reaction temperature. After the oxidation was complete, the manganese dioxide was removed by filtration and the mixture acidified to *p*H 3. The excess permanganate was

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[1] Paper 126, Journal Series, General Mills, Inc., Research Department.

[2] O. A. Moe and D. T. Warner, THIS JOURNAL, **70**, 2763 (1948).

[3] D. T. Warner and O. A. Moe, *ibid.*, **70**, 2765 (1948).

[4] D. T. Warner and O. A. Moe, *ibid.*, **70**, 3918 (1948).

[5] N. F. Albertson, *ibid.*, **68**, 450 (1946).

[6] H. S. Mason, *ibid.*, **67**, 420 (1945).

decomposed by the addition of sodium bisulfite. The resulting solution was concentrated *in vacuo* to a volume of 13 cc. The oxidation product appeared to be very soluble in the aqueous medium. However, extraction with three 30-cc. portions of chloroform yielded a white crystalline product melting at 137–141°. Recrystallization from benzene yielded the pure diester acid melting at 147–148°.

Anal. Calcd. for $C_{11}H_{17}O_7N$: C, 47.99; H, 6.23; N, 5.09; neut. equiv., 275. Found: C, 47.96; H, 6.21; N, 4.73; neut. equiv., 277.

DL-Aspartic Acid.—The acid diester was hydrolyzed by refluxing with concentrated hydrochloric acid for a period of four hours. After the removal of the excess hydrochloric acid *in vacuo* and neutralization until just acid to methyl red, the aspartic acid was isolated as blue copper salt. The DL-aspartic acid was recovered as described by Dunn and Fox[7] and melted with decomposition at 300°.

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(7) M. S. Dunn and S. W. Fox, *J. Biol. Chem.*, **101**, 493 (1933).

CHEMICAL LABORATORIES
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Complexing of Pyridine with Phenol and Other Acids in Benzene Solution[1]

BY C. GARDNER SWAIN AND JOHN F. BROWN, JR.

The complexing of pyridine with phenol, *p*-nitrophenol, 2,4-dinitrophenol, benzoic acid and 2-hydroxypyridine has been studied in benzene solution at 25° by a dynamic vapor pressure method. This supplements cryoscopic and kinetic data previously reported.[2] In solutions of pyridine and phenol, the data indicate the presence of 1:1 and 1:2 pyridine–phenol complexes, in agreement with the results of a freezing-point study on the pyridine–phenol system.[3] The following equilibria appear to be present.

$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$

(from the literature[4]) $K_x = 0.57\ M^{-1}$

$$C_5H_5N + C_6H_5OH \rightleftharpoons C_5H_5N{\cdot}C_6H_5OH \qquad K_y = 18.4\ M^{-1}$$

$$C_5H_5N + 2C_6H_5OH \leftrightarrows C_5H_5N{\cdot}2C_6H_5OH \qquad K_z = 109\ M^{-2}$$

The complexing of pyridine with several other acidic species was examined briefly, and the equilibrium constants for the formation of 1:1 pyridine–acid complexes are estimated in Table I.

TABLE I

THE COMPLEXING OF PYRIDINE WITH ACIDS IN BENZENE AT 25°

Acid	Total acid, *M*	Total pyridine, *M*	Free pyridine, *M*	K_y, M^{-1}
p-Nitrophenol	0.0482	0.0396	0.0120	110
2,4-Dinitrophenol	.102	.00989	.00915	0.8
Benzoic acid[a]	.100	.0495	.0197	210
2-Hydroxypyridine	.100	.0099	.0104	0.0

[a] K_y based upon monomeric benzoic acid. The dimerization constant of the benzoic acid was calculated from literature data[5] to be 617 M^{-1}.

Experimental

The complexing between pyridine and various acidic species in benzene solution was studied by slowly passing a fixed volume (about 4 liters) of dry, benzene-saturated air through 25 ml. of a benzene solution of pyridine and the acid in question, and then through 10 ml. of 0.10 *M* hydrochloric acid. This resulted in the transfer of about 2% of the free pyridine in the benzene solution to the aqueous acid. The latter was then boiled to expel traces of benzene, cooled, diluted to 25 ml. with 0.10 *M* hydrochloric acid, and examined in a spectrophotometer in the region 250–275 mμ to determine the pyridine concentration.

In some of the determinations where phenol was the acid, appreciable amounts of it were also carried over, and the observed extinction had to be corrected for light absorption by phenol. To do this, the phenol concentrations were determined from the extinction at 275 mμ, where there was negligible absorption by pyridinium ion.

Similar runs on solutions of pyridine alone in benzene showed that the amount of pyridine vaporized by the air stream and transferred to the aqueous acid was directly proportional to the pyridine concentration of the benzene solution; hence, knowing the amount of pyridine transferred to the aqueous acid made it possible to calculate the pyridine concentration of the benzene solution.

In calculating the values of K_y and K_z from the association measurements, a graphical method was used. Taking the results of any one association measurement, various values of the concentration of the 1:1 complex were assumed, and for each assumed value a pair of values of K_y and K_z was determined. Plotting these one against the other gave a curve on a plot of K_y *vs.* K_z. From the other association measurements other curves were calculated, and their intersection gave the desired solution for K_y and K_z, with a precision of ± 2%.

From K_x, K_y and K_z, the amounts of free phenol and free pyridine in each solution in Table II were calculated by a method of successive approximations.

TABLE II

THE COMPLEXING OF PYRIDINE AND PHENOL IN BENZENE AT 25°

Total phenol, *M*	Total pyridine, *M*	Free phenol (calcd.)	Free pyridine (calcd.)	Free pyridine (found)
0.200	0.0099	0.159	0.00148	0.00150
.100	.0099	.083	.00302	.00303
.050	.0099	.042	.00502	.00500
.209	.103	.096	.0274	.0276
.104	.103	.042	.0526	.0528

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(1) For more complete experimental data see J. F. Brown, Jr., Ph.D. Thesis, M.I.T., July, 1950, pp. 178–183.

(2) C. G. Swain and R. W. Eddy, THIS JOURNAL, **70**, 2993 (1948).

(3) A. Bramley, *J. Chem. Soc.*, **109**, 469 (1916).

(4) E. N. Lassettre and R. G. Dickinson, THIS JOURNAL, **61**, 54 (1939).

(5) F. T. Wall and F. W. Banes, *ibid.*, **67**, 898 (1945).

NEW COMPOUNDS

Preparation of 5-Nitro-2-chlorothiophene

5-Nitro-2-chlorothiophene was prepared from 2-chlorothiophene by a modification of the method of Babasinian.[1]

An ice-cold mixture of 50 g. of fuming nitric acid (sp. gr. 1.51) and 100 ml. of acetic anhydride was added dropwise over a period of 2.5 hours to a vigorously-stirred mixture of 50 g. of 2-chlorothiophene and 100 ml. of acetic anhydride in a one-liter flask cooled by an ice–salt mixture so that the temperature did not rise above 0°. An orange-colored precipitate formed. Stirring was continued an additional hour. The flask was then packed in an ice–salt mixture and allowed to stand in an ice-box for 24 hours. The mixture was then poured with stirring onto 400 g. of crushed ice. The yellowish-red oil was separated, dissolved in 500 ml. of petroleum ether, washed several times with sodium bicarbonate solution and with water, and decolorized with

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(1) V. S. Babasinian, THIS JOURNAL, **57**, 1763 (1935).