TABLE I

Cpd.	Formula	Yield, %	M. p., °C.[a]	Analysis, % Calcd. C	Analysis, % Calcd. H	Analysis, % Found[b] C	Analysis, % Found[b] H
I[c]	$C_{17}H_{12}O_4$	94	145–146	72.85	4.32	72.81	4.58
II[d,e]	$C_{12}H_{10}O_4$	94	173–174	66.05	4.62	65.91	4.67
III[c]	$C_{11}H_7O_3N$	35	224–226	65.67	3.50	65.46	3.47
IV[f]	$C_{13}H_{12}O_5$	62	81–83[g] 88–90	62.90	4.87	63.00	4.78
V[c]	$C_{15}H_{14}O_6$	33	155–156.5	62.06	4.86	62.12	4.83

[a] Corrected. [b] Analyses by Miss Sarah H. Miles. [c] Recrystallized from ethyl acetate–petroleum ether. [d] Condensation effected in ethyl acetate. [e] Recrystallized from methyl ethyl ketone. [f] Reported m. p. 96° (Perkin and Robinson, *J. Chem. Soc.*, **105**, 2382 (1914)). [g] Obtained by slow crystallization from benzene–petroleum ether; rapid crystallization gave the higher melting modification.

HARRISON LABORATORY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA 4, PENNA. RECEIVED DECEMBER 7, 1947

Relative Stabilities of D-Glucose-Amine Derivatives

BY ALI MOHAMMAD AND HAROLD S. OLCOTT

It has recently been shown that the development of a brown color in dried whole eggs containing more than 2% moisture is due in part to a reaction between the free glucose and the free amino groups of the egg proteins.[1,2] In attempts to determine the mechanism of this reaction, the behavior of the addition compounds of glucose with aliphatic amines has been studied.

Mitts and Hixon[3] prepared a number of such substances. For their preparation of glucosyl-N-butylamine they report $C_{10}H_{23}O_6N$, although the glucoside formulation requires $C_{10}H_{21}O_5N$. Since it was of importance to determine whether the instability of this compound[1] could be ascribed to the presence of water of crystallization, the anhydrous product was prepared. It was found to decompose at a readily measurable rate at 56.5° *in vacuo*. In contrast, D-glucosyl-N-ethanolamine appeared to be entirely stable under the same conditions. Glucamines, obtained by hydrogenation either of the glucosylamines or of mixtures of D-glucose with the amines, were found, as expected, to be stable products. D-Glucosyl-N-ethanolamine and the corresponding glucamine have not previously been described.

Cavalieri and Wolfrom[4] recently have demonstrated by ultraviolet absorption spectra measurements that the brown coloration which develops in aqueous solutions of D-glucosyl-N-butylamine on standing is caused by hydrolysis of the compound, followed by the action of the liberated hydroxyl ion upon the D-glucose. Such a simple explanation does not appear to be applicable to the decomposition of this compound in the pure, dry, and, presumably, neutral state.

Experimental

D-Glucosyl-N-butylamine.—The compound, prepared according to Mitts and Hixon[3] from D-glucose and *n*-butylamine, was recrystallized repeatedly from absolute alcohol. The final crystallizate was washed with petroleum ether and dried to constant weight over phosphorus pentoxide at 35° *in vacuo*, m. p., 96–97°.

Anal. Calcd. for $C_{10}H_{21}O_5N$: C, 51.06; H, 8.93; N, 5.95. Found: C, 51.1; H, 8.93; N, 5.87.

At 56.5° (Abderhalden drying tube heated with boiling acetone vapors) and at approximately 0.3 mm. pressure the compound lost weight, gradually turned brown, and finally (in three days) melted to a deep brown sirup. The loss of weight from a 100-mg. sample was, in one day, approximately 6%, in two days, approximately 12%.

N-Butylglucamine.—The product obtained by reduction with hydrogen and Raney nickel catalyst from D-glucosyl-N-butylamine melted, as reported by Mitts and Hixon,[3] at 127–128°.

Anal. Calcd. for $C_{10}H_{23}O_5N$: N, 5.9. Found: N, 5.9.

The same compound was prepared as follows: A mixture of 5 g. of D-glucose, 4.5 g. of butylamine, 1 ml. of 0.5 *N* hydrochloric acid, 130 mg. of platinum oxide and 50 ml. of absolute alcohol was hydrogenated for thirty hours at 40 lb./sq. in. hydrogen pressure (23°). The solution was filtered, evaporated to dryness at reduced pressure, and taken up in hot methanol, from which the D-glucamine crystallized.

After a second crystallization the dried product melted at 127–128°, yield, 5 g. An approximately 1% solution was at *p*H 10.2. There was no apparent decomposition in a sample held at 105° for eighteen hours.

D-Glucosyl-N-ethanolamine.—A mixture of 18 g. of D-glucose (0.1 mole), 6.1 g. of ethanolamine (0.1 mole), and 50 ml. of absolute alcohol was heated for one hour on a steam-bath. The brown solution was partially decolorized with carbon. Addition of ether caused an oil to separate. No crystals appeared in three weeks at 0°. The solvent was decanted, and the oil dissolved in absolute ethanol. Crystallization occurred at room temperature. After several crystallizations from methanol, the product contained 6.24% N (calcd., 6.26), m. p., 115–116°. A sample was heated *in vacuo* at 56.5° for forty-eight hours without change in weight or color.

N-Ethanol-D-glucamine.—A mixture of 18 g. of D-glucose, 6.1 g. of ethanolamine, 2 g. (approx.) of Raney nickel, and 50 ml. of absolute ethanol was shaken in a steel bomb for twenty-four hours under 1000 lb./sq. in. hydrogen pressure and at 77°. The contents were filtered and partially concentrated. Crystallization occurred at room temperature. After several recrystallizations from methanol, the compound decomposed at 96–103°.

Anal. Calcd. for $C_8H_{19}O_6N$: N, 6.22. Found: N, 6.18.

All the compounds described were difficult to obtain in analytically pure form. Whether the numerous crystallizations effected gradual removal of impurities or of water of crystallization is not known.

Elementary analyses were performed by L. M. White.

WESTERN REGIONAL RESEARCH LABORATORY
BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE
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Metalation of Compounds That Have Meta-directing Groups and the Electrophilic Character of Organoalkali Metal Reagents

BY AVERY A. MORTON

A recent paper by Roberts and Curtin[1] reports that the metalation of trifluoromethylbenzene by

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(1) Roberts and Curtin, THIS JOURNAL, **68**, 1658 (1946).