

sodium sulfate and fractionated to give 24.9 g. (97%) of tetra-*n*-butylsilane: b. p. 156–157° (22 mm.); d^{20}_4 0.8008 and d^{22}_4 0.8002; n^{20}_D 1.4465 and n^{22}_D 1.4460; M_R 85.47 (calcd. M_R 85.49).

*Anal.*¹¹ Calcd. for $C_{18}H_{38}Si$: Si, 10.93. Found: Si, 11.12.

From a similar preparation using 20.8 g. (0.1 mole) of ethyl silicate and 0.41 mole of *n*-butyllithium there was obtained 22.4 g. (95%) of tetra-*n*-butylsilane: b. p. 156–157° (22 mm.); d^{20}_4 0.8010; n^{20}_D 1.4463.

(11) It should be mentioned here that the method of analysis now being used by us for relatively non-volatile organosilicon compounds involves oxidation by means of conc. sulfuric acid, the platinum crucible being heated in a Rogers ring burner. This procedure is better than the one described recently [Gilman, Clark, Wiley and Diehl, *THIS JOURNAL*, **68**, 2728 (1946)] in which perchloric acid is used.

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(chloramine-T) was prepared in 100 cc. of water and 0.04–0.10 mole of the sulfide, which had previously been dissolved in 75 to 100 cc. of acetone, was added dropwise with continuous stirring. In some cases the reaction was complete in thirty minutes while in others several days were required for a complete condensation. When the reaction was complete the product, which sometimes came down as an oil, was washed several times with water to dissolve any excess of chloramine-T and finally with ether which removed any unreacted sulfide. It was then crystallized several times from an appropriate solvent until a constant melting point was obtained. The compounds prepared were all white crystalline solids of definite melting point. They are recorded in the following table together with some of their physical and chemical properties.

The author is grateful to Dr. Walter E. Lawson who offered assistance during the course of this work.

The experimental work reported in this paper was completed in November, 1938.

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Preparation of a Series of *p*-Toluenesulfilimines¹

By THOMAS P. DAWSON²

The condensation of chlorosulfides with sodium toluene-*p*-sulfonchloroamide to form compounds containing quadrivalent sulfur was first discovered by Raper,³ and later investigated by Mann and Pope.⁴ Recently, Fuson,⁵ *et al.*, have reported the *p*-toluenesulfilimine of several additional chlorosulfides.

Coumarins from 2-Hydroxy-3-methoxybenzaldehyde

By E. C. HORNING AND M. G. HORNING

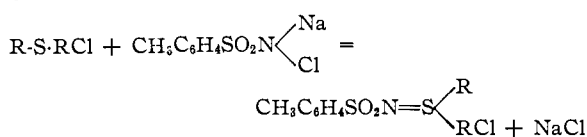
In studying condensations of derivatives of 2,3-dihydroxybenzaldehyde with active methylene compounds, we have had occasion to prepare a number of coumarins from 2-hydroxy-3-methoxybenzaldehyde and esters, $RCH_2COOC_2H_5$. The condensation was carried out by the Knoevenagel¹

TABLE I
ANALYSES AND PROPERTIES OF SUBSTITUTED SULFINE-*p*-TOLUENE SULFILIMINES

Substituent	Form	M. p., °C.	Formula	Chlorine		Sulfur	
				Calcd. %	Found %	Calcd. %	Found %
2-Chloroethyl <i>n</i> -propyl	Needles	118–119	$C_{12}H_{18}O_2ClNS_2$	11.52	11.37	20.83	20.72
2-Chloroethyl <i>n</i> -butyl	Rect. or sq. plates	117–118	$C_{13}H_{20}O_2ClNS_2$	11.02	10.77	19.92	19.59
2-Chloroethyl <i>i</i> -amyl	Tri. or hex. rods	91–92	$C_{14}H_{22}O_2ClNS_2$	10.56	10.85	19.08	18.82
2-Chloroethyl benzyl	Rect. pl. in clusters	133–134	$C_{16}H_{18}O_2ClNS_2$	9.97	10.18	18.02	18.36
2-Chloropropyl ethyl ^a	Square plates	119–120	$C_{12}H_{18}O_2ClNS_2$	11.52	11.52	20.83	19.42
3-Chloropropyl ethyl	Plates	86–87	$C_{12}H_{18}O_2ClNS_2$	11.52	11.59	20.83	20.77
bis-(2-Chloropropyl)	Cl. of short rods	169–170	$C_{13}H_{19}O_2Cl_2NS_2$	19.90	20.00	18.00	17.90
bis-(Chloromethyl) ^b	Needles	101–102	$C_9H_{11}O_2Cl_2NS_2$
2-Bromoethyl ethyl	Rectangular	146	$C_{11}H_{16}O_2BrNS_2$	23.63	23.43	18.96	19.06

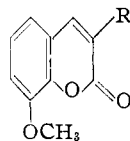
^a Fuson, *et al.*, *J. Org. Chem.*, **11**, 469 (1946). ^b Prepared by Mann and Pope⁴ and confirmed by us.

In connection with certain chemical warfare projects in 1928 this type of reaction was studied and eight new compounds of the sulfilimine type were isolated. The following equation represents the mechanism of the reaction.



Procedure.—All of the sulfilimines were prepared by the same general procedure as follows: An aqueous solution of 0.04–0.10 mole of sodium toluene-*p*-sulfonchloroamide

method, using piperidine as a catalyst. The reactions proceeded readily, but the yields of coumarins varied considerably with different esters. The following 8-methoxycoumarins were prepared.



- I R = $-COC_2H_5$
 II R = $-COCH_3$
 III R = $-CN$
 IV R = $-COOC_2H_5$
 V R = $-COCH_2COOC_2H_5$

Experimental

To a solution of 1.50 g. (0.01 mole) of 2-hydroxy-3-methoxybenzaldehyde in 20 ml. of warm absolute ethanol was added 0.011 mole of the ester and 3 drops of piperidine. The solution was heated under reflux for five minutes. After chilling, the crystalline product was removed by filtration and washed with absolute alcohol.

The yields, melting points and analytical data are given in Table I.

(1) Knoevenagel, *Ber.*, **31**, 2585 (1898).

(1) Published with the permission of the Chief, Chemical Corps.
 (2) Chemical Corps Technical Command, Edgewood Arsenal, Md.
 (3) Report to the British Chemical Warfare Service.
 (4) Mann and Pope, *J. Chem. Soc.*, **121**, 1052 (1922); *ibid.*, **123**, 1172 (1923).
 (5) Fuson, *et al.*, *J. Org. Chem.*, **11**, 469 (1946).

TABLE I

Cpd.	Formula	Yield, %	M. p., °C. ^a	Analysis, %			
				Calcd.		Found ^b	
			C	H	C	H	
I ^c	C ₁₇ H ₂₄ O ₄	94	145-146	72.85	4.32	72.81	4.58
II ^{d,e}	C ₁₂ H ₁₆ O ₄	94	173-174	66.05	4.62	65.91	4.67
III ^e	C ₁₁ H ₇ O ₂ N	35	224-226	65.67	3.50	65.46	3.47
IV ^f	C ₁₃ H ₁₂ O ₅	62	81-83 ^g	62.90	4.87	63.00	4.78
			88-90				
V ^e	C ₁₁ H ₁₄ O ₄	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.

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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 Hixon³ prepared a number of such substances. For their preparation of glucosyl-N-butylamine they report C₁₀H₂₃O₆N, although the glucoside formulation requires C₁₀H₂₁O₅N. Since it was of importance to determine whether the instability of this compound¹ 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 Wolfrom⁴ 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.

(1) H. S. Olcott and H. J. Dutton, *Ind. Eng. Chem.*, **37**, 1119 (1945).

(2) E. C. Bate-Smith and J. R. Hawthorne, *J. Soc. Chem. Ind.*, 297T (1945).

(3) E. Mitts and R. M. Hixon, *THIS JOURNAL*, **66**, 483 (1944).

(4) Cavalieri and Wolfrom, *ibid.*, **68**, 2023 (1946).

Experimental

D-Glucosyl-N-butylamine.—The compound, prepared according to Mitts and Hixon³ 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 C₁₀H₂₁O₅N: 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 C₁₀H₂₃O₆N: 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 pH 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 C₈H₁₉O₆N: 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.

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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 Curtin¹ reports that the metalation of trifluoromethylbenzene by

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