

and mixed m. p. with diosgenin acetate, 198–200°; yield, 1 g. from 15 lb. of dry root.

Anal. Calcd. for $C_{29}H_{44}O_4$: C, 76.3; H, 9.7. Found: C, 76.1; H, 10.0.

Hydrolysis of the acetate gave a product which was crystallized from acetone; m. p. and mixed m. p. with diosgenin, 208–210°.

Anal. Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 78.0; H, 10.0.

(h) *Chamaelirium carolinianum*.—Five pounds of the dried roots were pulverized in a mill to a fine powder and the sapogenin was isolated as in (g). The unacetylated product was crystallized from acetone; m. p. and mixed m. p. with diosgenin, 203–205°; yield, 0.4 g.

Anal. Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 78.0; H, 10.1.

When refluxed with acetic anhydride it gave an acetate which melted at 196–198° and gave no depression in melting point when mixed with an authentic sample of diosgenin acetate.

Anal. Calcd. for $C_{29}H_{44}O_4$: C, 76.3; H, 9.7. Found: C, 76.5; H, 9.9.

Summary

Eight new sources for diosgenin have been reported.

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Intermediates of Pentryl Analogs. Chloronitroanilino Alkanols¹

BY CHESTER B. KREMER AND M. MELTSNER

In the course of a study of the condensation of substituted nitrobenzenes with amino alcohols to produce intermediates from which analogs of pentryl can be obtained, the alcohols described below have been prepared and characterized. In these reactions, condensation occurs mainly through the amino group. Condensation through the alcohol group, to produce substituted amino ethers, is found to occur in some cases,

3-Amino-propanol-1 and 5-amino-propanol-1 were prepared from the appropriate bromoalkylphthalimide through Gabriel syntheses.

2,5- and 3,4-dichloronitrobenzenes were commercial products which were further purified by recrystallization from dilute ethanol.

2,3-Dichloronitrobenzene was prepared either by the chlorination of *o*-chloronitrobenzene in the presence of antimony chloride,² or from 2,3-di-

TABLE I

Compound (R = nitroanilino)	NITRO ANILINO ALKANOLS		Molecular formula	Nitrogen, %	
	Cryst. from	M. p., °C.		Calcd.	Found
2-(4-Chloro-2-R)-ethanol	<i>n</i> -BuOH	107.5	$C_8H_9O_3N_2Cl$	12.93	13.04
3-(4-Chloro-2-R)-propanol-1	C_6H_6 -pet. ether	60	$C_9H_{11}O_3N_2Cl$	12.14	12.20
3-(4-Chloro-2-R)-propanol-2	C_6H_6	116.5	$C_9H_{11}O_3N_2Cl$	12.14	12.33
3-(4-Chloro-2-R)-2-methylpropanol-2	C_6H_6	121.5	$C_{10}H_{13}O_3N_2Cl$	11.55	11.32
2-(4-Chloro-2-R)-2,2-dimethylethanol	C_6H_6 -pet. ether	122	$C_{10}H_{13}O_3N_2Cl$	11.55	11.44
2-(6-Chloro-4-R)-ethanol	$C_6H_5CH_3$	120	$C_8H_9O_3N_2Cl$	12.93	13.05
3-(6-Chloro-4-R)-propanol-1	C_6H_6 -pet. ether	73	$C_9H_{11}O_3N_2Cl$	12.14	12.01
3-(6-Chloro-4-R)-propanol-2	EtOH	144	$C_9H_{11}O_3N_2Cl$	12.14	12.31
3-(6-Chloro-4-R)-2-methylpropanol-2	C_6H_6 -pet. ether	71.5	$C_{10}H_{13}O_3N_2Cl$	11.55	11.01
2-(5-Chloro-2-R)-ethanol	Dil. EtOH	116	$C_8H_9O_3N_2Cl$	12.93	13.07
3-(5-Chloro-2-R)-propanol-1	Dil. EtOH	78.5	$C_9H_{11}O_3N_2Cl$	12.14	11.99
3-(5-Chloro-2-R)-propanol-2	Dil. EtOH	109	$C_9H_{11}O_3N_2Cl$	12.14	12.10
3-(5-Chloro-2-R)-2-methylpropanol-2	C_6H_6 -pet. ether	127	$C_{10}H_{13}O_3N_2Cl$	11.55	11.54
2-(3-Chloro-2-R)-ethanol	Dil. EtOH	78.5	$C_8H_9O_3N_2Cl$	12.93	13.15
3-(3-Chloro-2-R)-propanol-2	C_6H_6 -pet. ether	83.5	$C_9H_{11}O_3N_2Cl$	12.14	12.04
3-(3-Chloro-2-R)-2-methylpropanol-2	Dil. EtOH	98.5	$C_{10}H_{13}O_3N_2Cl$	11.55	11.23
2-(6-Chloro-2-R)-ethanol	Oil	155–157 (2 mm.)(b. p.)	$C_8H_9O_3N_2Cl$	12.93	12.87

Materials.—1-Amino-propanol-2, 1-amino-2-methyl-propanol-2 and 2-amino-2-methyl-propanol-1 were commercial products which were purified by redistillation.

(1) The tenth paper in a series dealing with amino alcohols.

nitroaniline by the usual Sandmeyer reaction. The product, purified by vacuum distillation, melted at 61°.

2,4- and 2,6-dichloronitrobenzenes were pre-

(2) Holleman and Reiding, *Rec. trav. chim.*, **23**, 357–359 (1904).

TABLE II
 AMINO ANILINO ALKANOLS

Compound (R' = aminoanilino)	Cryst. from	M. p., °C.	Molecular formula	Nitrogen, %	
				Calcd.	Found
2-(4-Chloro-2-R')-ethanol	C ₆ H ₆	122.5	C ₈ H ₁₁ ON ₂ Cl	15.01	15.17
3-(4-Chloro-2-R')-propanol-2	C ₆ H ₆	130	C ₉ H ₁₃ ON ₂ Cl	13.96	13.99
3-(4-Chloro-2-R')-2-methylpropanol-2	C ₆ H ₆	121	C ₁₀ H ₁₅ ON ₂ Cl	13.06	13.01
2-(4-Chloro-2-R')-2,2-dimethyl ethanol	C ₆ H ₆ -pet. ether		C ₁₀ H ₁₄ ON ₂ Cl	13.06	12.94
2-(5-Chloro-2-R')-ethanol	C ₈ H ₅ CH ₃	104.5	C ₈ H ₁₁ ON ₂ Cl	15.01	15.00
3-(5-Chloro-2-R')-propanol-1	C ₆ H ₆ -pet. ether	73.5	C ₉ H ₁₃ ON ₂ Cl	13.96	13.87
3-(5-Chloro-2-R')-propanol-2	C ₆ H ₆ -pet. ether	101.5	C ₉ H ₁₃ ON ₂ Cl	13.96	14.00
2-(3-Chloro-2-R')-ethanol	C ₆ H ₅ CH ₃	74	C ₈ H ₁₁ ON ₂ Cl	15.01	14.88
2-(6-Chloro-2-R')-ethanol	Oil	135-137 (2 mm.)(b. p.)	C ₈ H ₁₁ ON ₂ Cl	15.01	15.06

pared from 3,5-dichloroacetanilide.³ The former boiled at 100-101° (4 mm.); the latter at 105-107° (3 mm.).

Condensations.—The appropriate dichloronitrobenzene was dissolved in butanol and twice the molar quantity of the desired amino alcohol added. The mixture was then refluxed for approximately four hours. Upon cooling the reaction mixture in ice, the condensation product frequently was found to separate as a highly colored solid. In some instances, steam distillation of the reaction mixture was resorted to whereupon the condensation product separated out in the steam distillation flask upon cooling.

(3) Holleman and De Mooy, *Rec. trav. chim.*, **35**, 1 (1916).

Reduction of the nitro compounds was effected with sodium hydrosulfite in a weakly alkaline medium.

In the case of the 2,4-dichloronitrobenzene condensation, the position of the hydroxy alkyl group was established by effecting the condensation using 3,4-dinitrochlorobenzene. Identical products were obtained. Hence the mobile chlorine atom in the 2,4-dichloronitrobenzene is that ortho to the nitro group.

Summary

A number of new chloronitroanilino and chloroaminoanilino alkanols, intermediates of pentryl analogs, are reported.

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Bis(Amino Acid) Derivatives. I. Diglycine¹ Halogen Acid Addition Products

BY WALTER S. FROST

Attempts to prepare crystalline glycine hydriodide from a glycine-water solution treated with excess hydriodic acid proved unsatisfactory. When, however, two molecules of glycine were used with one of hydriodic acid a white crystalline product with a sharp melting point and the theoretical iodine content for diglycine hydriodide was obtained. Further investigation showed that other diglycine acid addition products may be easily prepared.

The diglycine hydrochloride,² diglycine nitrate³ and diglycine picrate⁴ have been reported previously.

(1) Refers to two glycine molecules, not glycylglycine.

(2) K. Kraut and F. Hartmann, *Ann.*, **133**, 101 (1865).

(3) (a) M. V. Dessaignes, *Ann. chim. phys.*, III, **34**, 143 (1852); *Ann.*, **82**, 236 (1852); (b) J. V. Dubský and J. Maitner, *Práce Mor. Přírodověd. spol. v Brně*, **6**, No. 3; *Chem. Obzor*, **10**, Abstract sect., 45 (1935); see *C. A.*, **30**, 7478 (1936).

(4) P. A. Levene and D. D. Van Slyke, *J. Biol. Chem.*, **12**, 283 (1912).

Experimental

Diglycine Hydrochloride.—This compound can be made in several ways. When theoretical quantities of glycine and monoglycine hydrochloride or theoretical quantities of glycine and hydrochloric acid are brought together in water the diglycine compound can be recovered either by cooling the hot saturated solution or by evaporation. It may also be made by cooling a hot saturated solution of glycine with excess monoglycine hydrochloride or excess hydrochloric acid in water or by cooling a hot saturated solution of monoglycine hydrochloride or hydrochloric acid and excess glycine in glacial acetic acid.

For instance, using equivalent quantities in water, 22.3 g. of monoglycine hydrochloride (calcd. for C₂H₆ClNO₂: Cl, 31.79. Found: Cl, 31.78, m. p. 176-177°) and 15 g. of glycine were dissolved in 30 cc. of water on heating nearly to boiling. The colorless crystals formed on cooling, ground and dried, weighed 24 g. (64% yield); m. p. 186-187°.

Anal. Calcd. for C₄H₁₁ClN₂O₄: Cl, 19.00; N, 15.01. Found: Cl, 19.01; N, 14.91; mol. wt. (Rast), impossible because of insolubility.