

cator over sulfuric acid the compound melted at 276–278° (uncor.).

Anal. Calcd. for $C_{22}H_{18}S_3O_8N_4$: N, 9.96; S, 17.09. Found: N, 9.54; S, 16.85.

CHEMO-MEDICAL RESEARCH INSTITUTE
GEORGETOWN UNIVERSITY FILADELFO IRREVERRE
WASHINGTON, D. C. M. X. SULLIVAN

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Some Diamino Peptides

Dimethylamine reacted with *p*-nitro- β -bromopropionanilide to form *p*-nitro- β -dimethylaminopropionanilide, m. p. of the hydrochloride, 200–201°. A portion of this was transformed into the methochloride and both substances were reduced catalytically in alcohol containing hydrogen chloride to give, respectively, *p*-amino- β -dimethylaminopropionanilide dihydrochloride (I), colorless felted needles, m. p. 218–219°, and *p*-amino- β -dimethylaminopropionanilide methochloride hydrochloride (II), hygroscopic crystals, m. p. 211–212°.

N,N-Diethylethylenediamine,¹ prepared by the reduction (sodium and alcohol) of diethylglycine nitrile, reacted with *p*-nitrobenzoyl chloride, forming β -[*p*-nitrobenzoylamidoethyl]-diethylamine hydrochloride, colorless needles melting at 164–5°. This substance and its ethochloride were reduced catalytically in alcoholic hydrogen chloride to β -[*p*-aminobenzoylamidoethyl]-diethylamine dihydrochloride (III), m. p. 176.5–178°, and to β -[*p*-aminobenzoylamidoethyl]-triethylammonium chloride, hydrochloride (IV), which forms stubby prisms melting at 228°.

Reduction of β -dimethylaminopropionitrile gave γ -dimethylaminopropylamine, m. p. of the dihydrochloride, 182–184°. The base reacted with *p*-nitrobenzoyl chloride

Formula	M. p., °C.	Composition
$(n-C_{18}H_{37})C_6H_5NMe_2I$	93–94	$C_{26}H_{46}NI$
$(C_6H_{11}CH_2CH_2)(C_6H_5CH_2)NMe_2Cl$	206 dec.	$C_{17}H_{28}NCl$
$(C_6H_5CH_2)(BrCH_2CH_2)NMe_2Br$	174	$C_{11}H_{17}NBr_2$
$(\alpha-C_{10}H_7CH_2)NEt_3Cl$	197 dec.	$C_{17}H_{24}NCl$

to form γ -[*p*-nitrobenzoylamidopropyl]-dimethylamine hydrochloride, m. p. 190–192°. This was reduced catalytically in alcoholic hydrogen chloride solution to γ -[*p*-aminobenzoylamidopropyl]-dimethylamine dihydrochloride (V), m. p. 184–185°.

Reduction of the *p*-nitrophenylurethan of β -hydroxyethyltriethylammonium chloride yielded β -[*p*-aminophenylcarbamatoethyl]-triethylammonium chloride, hydrochloride (VI), which forms irregular prisms melting at 138–139°.

By the reduction of β -[*p*-nitrobenzoyloxyethyl]-triethylammonium chloride, there was obtained β -[*p*-aminobenzoyloxyethyl]-triethylammonium chloride, hydrochloride (VII), m. p. 214–215°. This has been reported² previously, but the synthesis used was not free from ambiguity.

The salts described here were crystallized from absolute alcohol or from alcohol-ethyl acetate mixtures. The analytical data are in the table.

(1) Ristenpart, *Ber.*, **29**, 2526 (1896).

(2) Einhorn and Uhlfelder, *Ann.*, **371**, 138 (1909).

No.	Formula	Analyses, %			
		Calcd. C	Calcd. H	Found C	Found H
I	$C_{11}H_{19}ON_3Cl_2$	47.12	6.84	47.38	6.61
II	$C_{12}H_{21}ON_3Cl_2$	48.96	7.20	48.67	7.27
III	$C_{13}H_{23}ON_3Cl_2$	50.63	7.52	50.67	7.80
IV	$C_{16}H_{27}ON_3Cl_2$	53.56	8.13	53.45	8.04
V	$C_{12}H_{21}ON_3Cl_2$	48.96	7.20	49.05	7.51
VI	$C_{16}H_{27}O_2N_3Cl_2$	51.12	7.73	51.27	7.75
VII	$C_{16}H_{26}O_2N_3Cl_2$	53.39	7.77	53.02	7.62

BURROUGHS WELLCOME & CO., U. S. A. RICHARD BALTZLY
EXPERIMENTAL RESEARCH LABORATORIES WALTER S. IDE
TUCKAHOE, NEW YORK JOHANNES S. BUCK

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Some New Quaternary Salts

Methylaniline and octadecyl iodide reacted to yield methyloctadecylaniline, a yellow oil, b. p. (3 mm.), 234°. This was treated in benzene solution with methyl iodide forming octadecylphenyldimethylammonium iodide which crystallized in leaflets from ethyl acetate.

Cyclohexylethylenediamine (prepared from cyclohexylacetic acid by the sequence: acid \rightarrow acid chloride \rightarrow amide \rightarrow nitrile \rightarrow amine) was methylated by the Clarke-Eschweiler method. The resulting tertiary amine reacted with benzyl chloride in ether to give cyclohexylethylbenzyltrimethylammonium chloride.

Benzyl- β -bromoethyltrimethylammonium bromide was prepared from benzyltrimethylamine and ethylene bromide.

Triethylamine and α -menaphthyl chloride (α -naphthylmethyl chloride) yielded α -menaphthyltriethylammonium chloride. Data on these substances are presented in the subjoined table.

Formula	M. p., °C.	Composition	Analyses, %			
			Calcd. C	Calcd. H	Found C	Found H
$(n-C_{18}H_{37})C_6H_5NMe_2I$	93–94	$C_{26}H_{46}NI$	62.25	9.65	62.12	9.69
$(C_6H_{11}CH_2CH_2)(C_6H_5CH_2)NMe_2Cl$	206 dec.	$C_{17}H_{28}NCl$	72.44	10.02	72.15	10.16
$(C_6H_5CH_2)(BrCH_2CH_2)NMe_2Br$	174	$C_{11}H_{17}NBr_2$	40.87	5.31	40.91	5.61
$(\alpha-C_{10}H_7CH_2)NEt_3Cl$	197 dec.	$C_{17}H_{24}NCl$	73.49	8.71	73.41	8.62

BURROUGHS WELLCOME & CO., U. S. A.
EXPERIMENTAL RESEARCH LABORATORIES
TUCKAHOE, NEW YORK

RICHARD BALTZLY
CLAYTON W. FERRY
JOHANNES S. BUCK

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Some Mono- and Disubstituted Guanidines

The guanidines here described were all prepared by conventional methods. The *S*-methyl-isothiourea sulfate method (generally applicable with amines of moderate strength and water solubility) was used to prepare the five following: β -[*N*-morpholinoethyl]-guanidine sulfate (from aminoethylmorpholine), β,β -diethoxyethylguanidine sulfate (from amino acetal), *N,N*-dicyclohexylguanidine sulfate (from dicyclohexylamine), *N*-benzyl-*N*-methylguanidine sulfate (from benzylmethylamine) and δ -phenoxybutylguanidine sulfate (from δ -phenoxybutylamine prepared by reduction of γ -phenoxybutyronitrile). In all these cases the salt was isolated by evaporation of the reaction mixture

and crystallized from mixtures of polar and non-polar solvents. Diethoxyethylguanidine sulfate crystallized best from *n*-butanol-ethyl acetate. The others were crystallized from alcohol-ether.

N-Benzyl-N- α -naphthylguanidine Hydrochloride.—Benzyl- α -naphthylamine was refluxed in amyl alcohol with 1 mol of cyanamide and 1.2 mols of hydrogen chloride. On cooling, ether was added and the hydrochlorides separated as a purple sirup. Attempts to crystallize having failed, the mixture was dissolved in water and ammonia added. Some unreacted benzylnaphthylamine separated together with most of the color. The aqueous layer was then basified with sodium hydroxide and the precipitated guanidine taken into ether. After drying over potassium carbonate, alcoholic hydrogen chloride was added. The salt was recrystallized from alcohol-ether mixtures.

N,N'-Dihomoanisylguanidine Hydrochloride.—To a

$[p\text{-XC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}^+(\text{CH}_2)_2\text{R}]^+\text{Y}^-$						Analyses, %			
R	X	Y	M. p., °C.	Formula	Calcd.		Found		
					C	H	C	H	
CH ₃	Cl	I	152	C ₁₇ H ₂₉ O ₂ NCI	46.19	6.62	46.20	6.42	
C ₆ H ₅ CH ₂	H	Cl	122-123	C ₂₃ H ₃₄ O ₂ NCl	3.58 ^a	9.05 ^b	3.91 ^a	9.21 ^b	
<i>p</i> -ClC ₆ H ₄ CH ₂	H	Cl	166-166.5	C ₂₃ H ₃₀ O ₂ NCl ₂	64.76	7.80	64.85	7.80	
<i>p</i> -ClC ₆ H ₄ CH ₂	Cl	Cl	160	C ₂₃ H ₃₀ O ₂ NCl ₂	59.92	7.00	60.12	7.01	
<i>p</i> -BrC ₆ H ₄ CH ₂	Cl	Cl	156.5-157	C ₂₃ H ₃₂ O ₂ NCl ₂ Br	54.64	6.38	54.95	6.35	

^a N, ^b Cl.

solution of 2 mols of homoanisylamine in absolute ether was added, with shaking and ice-cooling, a solution of 1 mol of cyanogen bromide in ether. After standing one-half hour the ether was evaporated by a stream of dry air, a little absolute alcohol added to homogenize the mixture and the whole was heated three hours in an oil-bath at 150°. The material was then dissolved in water, the base liberated with alkali, and extracted with ether. On drying over potassium carbonate a crystalline solid appeared on the surface of the drying agent. The ether was decanted off, the solid dissolved in chloroform and transformed into the hydrochloride by alcoholic hydrogen chloride. It was recrystallized from alcohol-ether, forming lustrous plates.

N-Methyl-N'- α -naphthylguanidine.—Methylamine and α -naphthylisothiocyanate yielded N,N'-methyl-naphthylthiourea. Methylation with methyl sulfate gave the S-methyl derivative which was desulfurized in the usual manner with lead oxide and ammonia.

Data on these compounds are presented in the table.

Substance	M. p., °C.	Empirical formula	Analyses, %			
			Calcd.		Found	
			C	H	C	H
β -N-Morpholinoethylguanidine sulfate	197	C ₇ H ₁₆ ON ₄ (H ₂ SO ₄) _{1/2}	37.99	7.75	38.33	7.52
β,β -Diethoxyethylguanidine sulfate	154	C ₇ H ₁₇ O ₂ N ₃ (H ₂ SO ₄) _{1/2}	37.47	8.09	37.38	7.99
N,N-Dicyclohexylguanidine sulfate	195	C ₁₄ H ₂₈ N ₃ (H ₂ SO ₄) _{1/2}	57.28	9.62	57.05	9.28
N-Benzyl-N-methylguanidine sulfate	252 dec.	C ₉ H ₁₃ N ₃ (H ₂ SO ₄) _{1/2}	50.90	6.65	50.87	6.59
δ -Phenoxybutylguanidine sulfate	199-199.5	C ₁₁ H ₁₇ ON ₃ (H ₂ SO ₄) _{1/2}	51.53	7.08	51.32	7.33
N-Benzyl-N- α -naphthylguanidine hydrochloride	223-224	C ₁₈ H ₁₇ N ₃ ·HCl	69.33	5.82	69.19	5.80
N,N'-Dihomoanisylguanidine hydrochloride	125.5-126.5	C ₁₉ H ₂₆ O ₂ N ₃ ·HCl	62.69	7.21	62.63	7.05
N- α -Naphthyl-N'-methylguanidine hydrochloride	220-220.5 dec.	C ₁₂ H ₁₈ N ₃ ·HCl	61.12	5.99	61.06	5.99

BURROUGHS WELLCOME & Co., U. S. A. JOHANNES S. BUCK
EXPERIMENTAL RESEARCH LABORATORIES
TUCKAHOE, NEW YORK

RICHARD BALTZLY
CLAYTON W. FERRY

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Some Quaternary Salts from β -Dimethylamino- β' -cymoxydiethyl Ether

A concentrated aqueous solution of sodium thymolate or sodium *p*-chlorothymolate was heated under reflux with β,β' -dichlorodiethyl ether. After separation of the aqueous layer, unreacted dichlorodiethyl ether was removed *in vacuo*, and the residue was heated for seven hours at 145° (*p* = ca. 150 lb.) in a glass-lined bomb with 33% methanolic dimethylamine. After removal of volatile materials on the steam-bath under diminished pressure, the residual tertiary amines were partially purified by solution in acid and extraction with ether; on liberation with alkali, they were obtained as oils which could not be distilled *in vacuo*, but were converted directly into quaternary salts by warming on the steam-bath with the appropriate halides. The salts crystallized from acetone or alcohol on addition of ether.

BURROUGHS WELLCOME AND Co., U. S. A.
EXPERIMENTAL RESEARCH LABORATORIES
TUCKAHOE, NEW YORK

CLAYTON W. FERRY
ALAN E. ARDIS
JOHANNES S. BUCK

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N,N-Dimethylethylenediamine and Some Derivatives

The readily available dimethyl glycine nitrile¹ can be reduced by sodium and absolute alcohol to give N,N-dimethylethylenediamine. This is a colorless liquid boiling, when anhydrous, at 107°. As its dehydration is difficult and its dihydrochloride (melting around 160°) is also hygroscopic, it is better characterized through a derivative. The following compounds were prepared as outlined, nitro derivatives being reduced with Adams catalyst in alcoholic solution containing hydrogen chloride. β -[*p*-Nitrobenzoylamidoethyl] dimethylamine hydrochloride (I), formed from *p*-nitrobenzoyl chloride and the

diamine, was hydrogenated catalytically yielding β -[*p*-aminobenzoylamidoethyl]-dimethylamine dihydrochloride (II). The methochloride of I was reduced to β -[*p*-amino-

¹ J. v. Braun, *Ber.*, **40**, 3937 (1907).