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 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′-methylnaphthylthiourea. 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. C	H	Found C	H
β-N-Morpholinoethylguanidine sulfate	197	$C_7H_{16}ON_4(H_2SO_4)_{1/2}$	37.99	7.75	38.33	7.52
β,β-Diethoxyethylguanidine sulfate	154	$C_7H_{17}O_2N_3(H_2SO_4)_{1/2}$	37.47	8.09	37.38	7.99
N,N-Dicyclohexylguanidine sulfate	195	$C_{13}H_{25}N_3(H_2SO_4)_{1/2}$	57.28	9.62	57.05	9.28
N-Benzyl-N-methylguanidine sulfate	252 dec.	$C_9H_{13}N_3(H_2SO_4)_{1/2}$	50.90	6.65	50.87	6.59
δ-Phenoxybutylguanidine sulfate	199–199.5	$C_{11}H_{17}ON_3(H_2SO_4)_{1/2}$	51.53	7.08	51.32	7.33
N-Benzyl-N-α-naphthylguanidine hydrochloride	223–224	$C_{18}H_{17}N_3\cdot HCl$	69.33	5.82	69.19	5.80
N,N′-Dihomoanisylguanidine hydrochloride	125.5–126.5	$C_{19}H_{25}O_2N_3\cdot HCl$	62.69	7.21	62.63	7.05
N-α-Naphthyl-N′-methylguanidine hydrochloride	220–220.5 dec.	$C_{12}H_{13}N_3\cdot HCl$	61.12	5.99	61.06	5.99

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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.

$[p\text{-}XC_{10}H_{12}OCH_2CH_2OCH_2CH_2N^+(CH_3)_2R]Y^-$

R	X	Y	M. p., °C.	Formula	Analyses, % Calcd. C	H	Found C	H
CH_3	Cl	I	152	$C_{17}H_{29}O_2NClI$	46.19	6.62	46.20	6.42
$C_6H_5CH_2$	H	Cl	122–123	$C_{23}H_{34}O_2NCl$	3.58[a]	9.05[b]	3.91[a]	9.21[b]
p-$ClC_6H_4CH_2$	H	Cl	166–166.5	$C_{23}H_{33}O_2NCl_2$	64.76	7.80	64.85	7.80
p-$ClC_6H_4CH_2$	Cl	Cl	160	$C_{23}H_{32}O_2NCl_3$	59.92	7.00	60.12	7.01
p-$BrC_6H_4CH_2$	Cl	Cl	156.5–157	$C_{23}H_{32}O_2NCl_2Br$	54.64	6.38	54.95	6.35

[a] N. [b] Cl.

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N,N-Dimethylethylenediamine and Some Derivatives

The readily available dimethyl glycine nitrile[1] 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-

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

benzoylamidoethyl]-trimethylammonium chloride, hydrochloride (III).

The diamine reacted with *p*-nitrophenyl isocyanate to give β-[*p*-nitrophenylureidoethyl]-dimethylamine; m. p. of the hydrochloride, 247–248.5°. From this were obtained β-[*p*-aminophenylureidoethyl]-dimethylamine dihydrochloride (IV) and the corresponding trimethylammonium chloride, hydrochloride (V). The diamine with *p*-nitrophenylacetyl chloride gave the *p*-nitrophenylacetamide, m. p. of the hydrochloride, 190–192.5°, and reduction of this yielded β-[*p*-aminophenylacetamidoethyl]-dimethylamine dihydrochloride (VI). Reduction of the methochloride of the nitro compound gave β-[*p*-aminophenylacetamidoethyl]-trimethylammonium chloride hydrochloride (VII).

With phenyl isothiocyanate the diamine formed N-phenyl-N′-β-dimethylaminoethyl thiourea (VIII) and with *p*-acetamidobenzenesulfonyl chloride it formed the *p*-acetamidobenzenesulfonamide which was hydrolyzed with hydrochloric acid to β-[*p*-aminophenylsulfonamidoethyl]-dimethylamine dihydrochloride (IX). The thiourea was crystallized from benzene–hexane; the hydrochlorides from absolute alcohol.

DERIVATIVES OF N,N-DIMETHYLETHYLENEDIAMINE

No.	Formula	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
I	$O_2NC_6H_4CONHCH_2CH_2NMe_2 \cdot HCl$	182.5–183.5	48.24	5.89	48.09	5.90
II	$H_2NC_6H_4CONHCH_2CH_2NMe_2 \cdot 2HCl$	190–191	47.12	6.84	47.23	6.89
III	$H_2NC_6H_4CONHCH_2CH_2NMe_3Cl \cdot HCl$	dec. > 230	48.96	7.20	49.37	7.39
IV	$H_2NC_6H_4NHCONHCH_2CH_2NMe_2 \cdot 2HCl$	182–184 dec.	44.73	6.83	44.88	6.87
V	$H_2NC_6H_4NHCONHCH_2CH_2NMe_3Cl \cdot HCl$	186	46.59	7.17	46.59	7.40
VI	$H_2NC_6H_4CH_2CONHCH_2CH_2NMe_2 \cdot 2HCl$	209.5–210.5	48.96	7.20	49.12	7.13
VII	$H_2NC_6H_4CH_2CONHCH_2CH_2NMe_3Cl \cdot HCl$	155–156 dec.	50.63	7.52	50.49	7.61
VIII	$C_6H_5NHCSNHCH_2CH_2NMe_2$	83–83.5	59.15	7.68	58.97	7.69
IX	$H_2NC_6H_4SO_2NHCH_2CH_2NMe_2 \cdot 2HCl$	211.5–213 dec.	37.96	6.06	37.86	6.02

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Some Unsymmetrical Disubstituted Ureas

The substances, data on which are presented in the subjoined table, were prepared by the action of nitrourea on the corresponding secondary amines.[1] They crystallize in colorless prisms from alcohol or benzene–petrol ether.

UNSYMMETRICAL DISUBSTITUTED UREAS
$R,R'NCONH_2$

Substituents R	Substituents R′	Formula	M. p., °C.	Analyses, % Calcd. N	Analyses, % Found N
CH_3	$(n)C_6H_{13}$	$C_8H_{18}ON_2$	75	17.72	17.92
$(4)CH_3OC_6H_4$	$C_2H_5(CH_3)CH$	$C_{12}H_{18}O_2N_2$	140	12.61	12.70
$(4)CH_3OC_6H_4$	$C_2H_5(CH_3)CHCH_2$	$C_{13}H_{20}O_2N_2$	130	11.86	12.17
$(4)CH_3OC_6H_4$	$(CH_3)_3CCH_2$	$C_{13}H_{20}O_2N_2$	155	11.86	12.13
$(4)CH_3OC_6H_4$	$(CH_3)_2CHCH_2(CH_3)CH$	$C_{14}H_{22}O_2N_2$	110	11.19	11.25

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(1) *Cf.* Buck and Ferry, THIS JOURNAL, **58**, 854 (1936).

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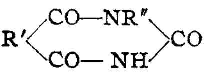
Some N-Substituted Barbituric Acids

The subjoined table contains data on five new compounds of this type. 1-*p*-Nitrophenyl-5-*i*-butyl-5-ethyl barbituric acid was obtained by nitration[1] of 1-phenyl-5-*i*-butyl-5-ethyl barbituric acid[2] and in turn was reduced catalytically[1] to the *p*-amino derivative. The other three substances were prepared by the conventional method from the corresponding ureas and malonic esters. All crystallized in colorless prisms, the 1-*n*-hexyl derivative from hexane, the others from alcohol.

DERIVATIVES OF BARBITURIC ACID R,R′



Substituents R	Substituents R′	Substituents R″	Formula	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
C_2H_5	C_2H_5	$(n)C_6H_{13}$	$C_{14}H_{24}O_3N_2$	41	62.64	9.02		62.79	9.09	
C_2H_5	$(n)C_4H_9$	$(4)C_2H_5C_6H_4$	$C_{18}H_{24}O_3N_2$	107	68.31	7.65		68.21	7.81	
C_2H_5	$(CH_3)_2CHCH_2$	$(4)H_2NC_6H_4$	$C_{16}H_{21}O_3N_3$	153	63.33	6.98		63.58	7.32	
H	H	$(2)C_2H_5OC_6H_4$	$C_{12}H_{12}O_4N_2$	193.5			11.29			11.47
C_2H_5	$(CH_3)_2CHCH_2$	$(4)O_2NC_6H_4$	$C_{16}H_{19}O_5N_3$	188			12.61			12.89

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(1) *Cf.* Buck, THIS JOURNAL, **59**, 1249 (1937).

(2) Hjort and Dox, *J. Pharmacol.*, **35**, 155 (1929).

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