one might reasonably expect a third power, or even higher, dependence. The importance of bisulfate ion in the hydration of acetylene is shown by the work of Vogt and Nieuwland,[5] whose best catalytic mixtures were saturated solutions of potassium (or similar) bisulfate in contact with mercuric sulfate.

One could propose a plausible mechanism for the hydration reaction, based upon the above equation, but the information at present available is still insufficient to permit of a definite decision.

Summary

Acetylene undergoes homogeneous hydration to acetaldehyde in aqueous solutions in the presence of mercuric sulfate and sulfuric acid. The initial rate of hydration is first order with respect to the acetylene concentration and second order with respect to the mercuric sulfate concentation, while the rate at time t has an apparent four-thirds power dependence upon the acetylene. This last is believed to result from the formation of a complex between mercuric sulfate and acetaldehyde.

A probable mechanism of the hydration involves the formation of an intermediate complex between one molecule of acetylene and two molecules of mercuric bisulfate, and the reaction of this complex with water, in the presence of an acid, to form vinyl alcohol, which rearranges to acetaldehyde.

The bromate–bromide method of determining unsaturation is applicable to aqueous solutions of acetylene, provided there is present a soluble mercuric salt whose molal ratio to total halide is greater than unity.

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[CONTRIBUTION FROM THE BURROUGHS WELLCOME AND CO., U. S. A., EXPERIMENTAL RESEARCH LABORATORIES]

Pharmacologically Active Compounds from Alkoxy-β-phenylethylamines

BY WALTER S. IDE AND JOHANNES S. BUCK

Considerable pharmacological data have been accumulated on compounds connected with or prepared from methoxy-β-phenylethylamines. It is therefore of great interest to examine the corresponding ethoxy compounds, for this would allow an exact comparison of the pharmacological effects of the ethoxy and methoxy groups to be made. The authors have therefore prepared seven such β-phenylethylamines and from them several series of compounds (N-methylamines, ureas, *unsym*-methylureas, barbituric acids, isoquinolines, N-methylisoquinolines, benzyl-β-phenylethylamines, and characterizing compounds).

Experimental

The amines were prepared by the series of reactions used by Buck.[1,2] As starting materials aldehydes with the following substituents were used (hereafter these letters refer to the same substituents):

A	2-Ethoxy-	D	2-Ethoxy-3-methoxy-
B	3-Ethoxy-	E	3-Methoxy-4-ethoxy-
C	4-Ethoxy-	F	3-Ethoxy-4-methoxy-
		G	3,4-Diethoxy-

The aldehydes A, B, C, D and E were prepared by ethylating (ethyl sulfate and sodium hydroxide) the corresponding phenolic aldehydes. Aldehyde F was prepared by methylating 3-ethoxy-4-hydroxybenzaldehyde and aldehyde G by ethylating the same phenolic aldehyde.

The aldehydes, together with a number of intermediates, have been described previously (see references, where *Cf.* indicates a different method of preparation or an indirect reference). New intermediates are given in the table.

(1) Buck, THIS JOURNAL, **54**, 3661 (1932).
(2) Buck, *ibid.*, **52**, 4119 (1930).

References on Intermediates

Aldehydes

A *Cf.* Perkin, *Ann.*, **145**, 306 (1868); Löw, *Monatsh.*, **12**, 396 (1892).
B *Cf.* Werner, *Ber.*, **28**, 2001 (1895); Subak, *Monatsh.*, **24**, 169 Note (1904).
C *Cf.* Kostanecki and Schneider, *Ber.*, **29**, 1892 Note (1896); Hildesheimer, *Monatsh.*, **22**, 499 Note (1902); Gattermann, *Ber.*, **31** 1151 (1898); *Ann.*, **357**, 347 (1907).
D *Cf.* Davies and Rubenstein, *J. Chem. Soc.*, **123**, 2846 (1923).
E, F, G. Buck and Ide, THIS JOURNAL, **54**, 3302 (1932).

Cinnamic Acids

A *Cf.* Perkin, *J. Chem. Soc.*, **39**, 413 (1881); Fittig and Ebert, *Ann.*, **216**, 146 (1883); Stoermer, *Ber.*, **44**, 645 (1911).
B *Cf.* Werner, *loc. cit.*
C *Cf.* Stoermer and Wodarg, *Ber.*, **44**, 637 (1911).
D Rubenstein, *J. Chem. Soc.*, 652 (1926).
E Schlittler, *Ber.*, **66**, 988 (1933); Slotta and Heller, *ibid.*, **63**, 3029 (1930).

TABLE I

NEW INTERMEDIATES

Substituent	Compound	Appearance	M. p., °C.	Formula	N Analyses, % Calcd. C	Calcd. H	Found C	Found H
G	3,4-Diethoxycinnamic acid[a]	Glitt. flakes	156	$C_{13}H_{16}O_4$	66.07	6.83	66.07	7.05
D	2-Ethoxy-3-methoxyphenylpropionic acid[b]	Large hard prisms	65	$C_{12}H_{16}O_4$	64.25	7.20	64.07	7.50
A	2-Ethoxyphenylpropionamide[c]	Felted needles	106	$C_{11}H_{15}O_2N$	68.35	7.83	68.15	8.10
B	3-Ethoxyphenylpropionamide[c]	Felted needles	80	$C_{11}H_{15}O_2N$	68.35	7.83	68.52	8.19
C	4-Ethoxyphenylpropionamide[c]	Felted needles	137	$C_{11}H_{15}O_2N$	68.35	7.83	68.66	8.15
D	2-Ethoxy-3-methoxyphenylpropionamide[c]	Large hard prisms	85	$C_{12}H_{17}O_3N$	64.53	7.68	64.38	7.86

[a] Moderately soluble in alcohol and benzene; sparingly soluble in ether and petroleum ether; insoluble in water. Recrystallized from alcohol–ether.

[b] Soluble in alcohol, benzene and ether; insoluble in petroleum ether and water; melts in hot water. Final solvent aqueous alcohol.

[c] Moderately to sparingly soluble in benzene, ethyl acetate, alcohol and water; insoluble in ether and petroleum ether. Final solvent benzene, washing with petroleum ether.

TABLE II

ALKOXY-β-PHENYLETHYLAMINES

Substituent	B. p. °C.	Mm.	$n^{25}D$	d^{25}_4	MD	Formula	N Analyses, % Calcd.	Found
A	128–130	13	1.5278	1.0091	50.37[a]	$C_{10}H_{15}ON$	8.48	8.36
B	135–138	13	1.5281	1.0082	50.44[a]	$C_{10}H_{15}ON$	8.48	8.44
C	138–140	13	1.5325	1.0084	50.78[a]	$C_{10}H_{15}ON$	8.48	8.65
D	148–150	13	1.5286	1.0519	57.18[b]	$C_{11}H_{17}O_2N$	7.17	7.13
E[3]	160	13	1.5393	1.0661	57.37[b]	$C_{11}H_{17}O_2N$	7.17	7.41
F[3]	168	15	1.5376	1.0646	57.29[b]	$C_{11}H_{17}O_2N$	7.17	7.08
G[4]	158	13	1.5270	1.0366	61.89[c]	$C_{12}H_{19}O_2N$	6.69	6.83
				ALKOXY-β-PHENYLETHYLMETHYLAMINES				
A	97	2	1.5142	0.9773	55.20[d]	$C_{11}H_{17}ON$	7.82	8.06
B	106	2	1.5157	.9791	55.24[d]	$C_{11}H_{17}ON$	7.82	7.66
C	107	2	1.5154	.9792	55.21[d]	$C_{11}H_{17}ON$	7.82	7.68
D	119	1.5	1.5146	1.0225	61.64[e]	$C_{12}H_{19}O_2N$	6.69	6.90
E	128	1.5	1.5275	1.0420	61.75[e]	$C_{12}H_{19}O_2N$	6.69	6.91
F	129	1.5	1.5234	1.0319	61.95[e]	$C_{12}H_{19}O_2N$	6.69	6.77
G	129	2	1.5146	1.0081	66.71[f]	$C_{13}H_{21}O_2N$	6.27	6.41

[a] Calcd. (Brühl) = 50.03
[b] Calcd. (Brühl) = 56.31
[c] Calcd. (Brühl) = 60.92
[d] Calcd. (Brühl) = 54.83
[e] Calcd. (Brühl) = 61.12
[f] Calcd. (Brühl) = 65.72

F Schlittler, *loc. cit.*
G See table.

Phenylpropionic (Hydrocinnamic) Acids

A *Cf.* Fittig and Ebert, *loc. cit.*, p. 153; Fittig and Claus, *Ann.*, **269**, 12 (1892).
B Bayer and Company, German Patent 234,852.
C *Cf.* Bougault, *Ann. chim. phys.*, [7] **25**, 505 (1902).
D See table.
E Schlittler, *loc. cit.*; Slotta and Heller, *loc. cit.*
F *Cf.* Schlittler, *loc. cit.*
G *Cf.* Kindler and Peschke, *Arch. Pharm.*, **272**, 60 (1934).

Amides

A, B, C, D. See table.
E Schlittler, *loc. cit.*, Slotta and Heller, *loc. cit.*
F Schlittler, *loc. cit.*
G Kindler and Peschke, *loc. cit.*

(3) Slotta and Heller, *loc. cit.*, Schlittler, *loc. cit.*, *cf.* Späth and Dobrowsky, *Ber.*, **58**, 1274 (1925).

(4) *Cf.* Slotta and Haberland, *Z. angew. Chem.*, **46**, 766 (1933); Kindler and Peschke, *loc. cit.*

Alkoxy-β-phenylethylamines.—These were prepared from the corresponding amide by a Hofmann reaction, using sodium hypochlorite. They are colorless liquids, insoluble in water, and having a faint musty odor when freshly distilled. After standing they smell of ammonia. They form solid carbonates very readily in the air.

Alkoxy-β-phenylethylmethylamines are prepared from the above amines by the Decker method, through the Schiff base and methyl iodide, as described by Buck.[1,2] The amines are colorless liquids, sparingly soluble in water and having a faint musty odor. They do not form solid carbonates as readily as the primary amines. The Schiff bases were not isolated at this point. The hydriodides are soluble in water and alcohol. They were recrystallized from alcohol–ether mixture.

Alkoxy-β-phenylethylamine hydrochlorides were prepared either from the amines by dissolving them in absolute alcohol and passing in dry hydrogen chloride, after which they were recrystallized from alcohol–ether mixture, or by the use of silver chloride on the hydriodides. They are very soluble in cold water, soluble in cold alcohol, spar-

TABLE III

ALKOXY-β-PHENYLETHYLMETHYLAMINE HYDRIODIDES

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	Faint yellow felted needles	118	$C_{11}H_{18}ONI$	4.56	4.44
B	Glittering flakes	74	$C_{11}H_{18}ONI$	4.56	4.51
C	Faint yellow tiny flakes	129	$C_{11}H_{18}ONI$	4.56	4.65
D	Faint yellow rosets of prisms	122	$C_{12}H_{20}O_2NI$	4.15	4.07
E	Faint yellow tiny flakes	228	$C_{12}H_{20}O_2NI$	4.15	4.04
F	Yellow tiny flakes	154	$C_{12}H_{20}O_2NI$	4.15	4.05
G	Faint yellow tiny flakes	100	$C_{13}H_{22}O_2NI$	3.99	3.93

TABLE IV

ALKOXY-β-PHENYLETHYLAMINE HYDROCHLORIDES

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A[5]	Felted needles	218	$C_{10}H_{16}ONCl$	6.95	7.18
B[5]	Glitt. leaves	Jells at 146, flows at 168	$C_{10}H_{16}ONCl$	6.95	7.26
C[5]	Glitt. plates	206	$C_{10}H_{16}ONCl$	6.95	7.13
D	Glitt. plates	162	$C_{11}H_{18}O_2NCl$	6.04	6.18
E[6]	Tiny needles	168	$C_{11}H_{18}O_2NCl$	6.04	5.98
F[6]	Fine needles	168	$C_{11}H_{18}O_2NCl$	6.04	6.10
G[7]	Fine needles	Jells at 144, flows at 198	$C_{12}H_{20}O_2NCl$	5.70	5.80
	ALKOXY-β-PHENYLETHYLMETHYLAMINE HYDROCHLORIDES				
A	Felted needles	133	$C_{11}H_{18}ONCl$	6.49	6.80
B	Glitt. flakes	144	$C_{11}H_{18}ONCl$	6.49	6.59
C	Glitt. flakes	206	$C_{11}H_{18}ONCl$	6.49	6.61
D	Glitt. flakes	147	$C_{12}O_{20}O_2NCl$	5.70	5.89
E	Glitt. flakes	131	$C_{12}H_{20}O_2NCl$	5.70	5.90
F	Felted needles	159	$C_{12}H_{20}O_2NCl$	5.70	5.96
G	Felted needles	157	$C_{13}H_{22}O_2NCl$	5.39	5.58

ingly soluble in ether and ethyl acetate and readily soluble in cold concentrated hydrochloric acid.

Alkoxy-β-phenylethylmethylamine hydrochlorides were prepared as above. Their solubilities are practically the same.

TABLE V

ALKOXY-β-PHENYLETHYLUREAS

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	White powder	112	$C_{11}H_{16}O_2N_2$	13.45	13.49
B	Glitt. leaves	104	$C_{11}H_{16}O_2N_2$	13.45	13.46
C	Glitt. leaves	134	$C_{11}H_{16}O_2N_2$	13.45	13.46
D	Felted needles	120	$C_{12}H_{18}O_2N_2$	11.76	11.80
E	Felted needles	126	$C_{12}H_{18}O_3N_2$	11.76	11.67
F	Felted needles	145	$C_{12}H_{18}O_3N_2$	11.76	11.69
G	Felted needles	108	$C_{13}H_{20}O_3N_2$	11.10	11.18
	ALKOXY-β-PHENYLETHYLMETHYLUREAS				
A	White powder	84	$C_{12}H_{18}O_2N_2$	12.60	12.82
B	Glitt. prisms	118	$C_{12}H_{18}O_2N_2$	12.60	12.86
C	Glitt. leaves	149	$C_{12}H_{18}O_2N_2$	12.60	12.80
D	White powder	76	$C_{13}H_{20}O_3N_2$	11.10	11.12
E	Tiny flakes	112	$C_{13}H_{20}O_3N_2$	11.10	11.02
F	White powder	96	$C_{13}H_{20}O_3N_2$	11.10	11.07
G	Tiny flakes	97	$C_{14}H_{22}O_3N_2$	10.52	10.70

(5) Bayer and Company, German Patent, 233,551, 233,069.

(6) Sawai, *J. Pharm. Soc. Japan*, **49**, 48 (1929); *cf.* Kondo, *et al.*, *ibid.*, **48**, 169 (1928).

(7) Slotta and Haberland, *loc. cit.*; Kindler and Peschke, *loc. cit.*, give m. p. 195°, sintering above 130°.

Alkoxy-β-phenylethylureas and *unsym*-methylureas were prepared by using the nitrourea method as described earlier.[8-11] They are moderately soluble in benzene and alcohol, sparingly soluble in petroleum ether. Urea D was also prepared by the potassium cyanate method but the product requires more treatment.

1-(Alkoxy-β-phenylethyl)-5,5-diethyl Barbituric Acids.—The barbituric acids were prepared from the corresponding ureas by a method described by Buck.[8,12,13] B and C reaction mixtures were diluted and made acid to Congo red. The product separated as an oil and soon solidified. In the case of A, D, E, F, G, the reaction mix-

TABLE VI

1-(ALKOXY-β-PHENYLETHYL)-5,5-DIETHYLBARBITURIC ACIDS

Alkoxy substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	White powder	66	$C_{18}H_{24}O_4N_2$	8.43	8.53
B	Tiny flakes	86	$C_{18}H_{24}O_4N_2$	8.43	8.49
C	Large prisms	134	$C_{18}H_{24}O_4N_2$	8.43	8.69
D	Small prisms	68	$C_{19}H_{26}O_5N_2$	7.73	7.75
E	Tiny needles	120	$C_{19}H_{26}O_5N_2$	7.73	7.78
F	White powder	99	$C_{19}H_{26}O_5N_2$	7.73	7.97
G	Large prisms	88	$C_{20}H_{28}O_5N_2$	7.44	7.54

(8) Buck, THIS JOURNAL, **56**, 1607 (1934).

(9) Davis and Blanchard, *ibid.*, **51**, 1790 (1929).

(10) Buck and Ferry, *ibid.*, **58**, 854 (1936).

(11) Buck, Hjort and deBeer, *J. Pharmacol.*, **54**, 188 (1935).

(12) Buck, THIS JOURNAL, **58**, 1284 (1936).

(13) Buck, *ibid.*, **58**, 2059 (1936).

ture was treated as described in the above references. A and D were especially difficult to obtain crystalline. Both were distilled at 1 mm. (*ca.* 212 and 225°). Many months at 0° in hexane were necessary to obtain seeding crystals. The barbituric acids are moderately soluble in hexane, soluble in alcohol and ether. They are best re-

TABLE VII

BENZYL-(ALKOXY-β-PHENYLETHYL)-AMINE HYDROCHLORIDES

Phenylethyl substituent	Benzyl substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	Unsubst.	White powder	122	$C_{17}H_{22}ONCl$	4.80	4.77
A	A	Hard prisms	153	$C_{19}H_{26}O_2NCl$	4.17	4.14
A	B	Crusts of prisms	113	$C_{19}H_{26}O_2NCl$	4.17	4.46
A	C	White powder	134	$C_{19}H_{26}O_2NCl$	4.17	4.24
A	G	Tiny flakes	148	$C_{21}H_{30}O_3NCl$	3.69	3.91
B	Unsubst.	Short prisms	194	$C_{17}H_{22}ONCl$	4.80	4.91
B	A	Needles	135	$C_{19}H_{26}O_2NCl$	4.17	4.44
B	B	Glitt. flakes	146	$C_{19}H_{26}O_2NCl$	4.17	4.30
B	C	Glitt. tiny flakes	195	$C_{19}H_{26}O_2NCl$	4.17	4.27
B	G	Glitt. white powder	114	$C_{21}H_{30}O_3NCl$	3.69	3.73
C	Unsubst.	Large silvery flakes	240	$C_{17}H_{22}ONCl$	4.80	5.02
C	A	Crusts of prisms	143	$C_{19}H_{26}O_2NCl$	4.17	4.37
C	B	Glitt. flakes	167	$C_{19}H_{26}O_2NCl$	4.17	4.36
C	C	Needles	280	$C_{19}H_{26}O_2NCl$	4.17	4.26
C	G	White powder	186	$C_{21}H_{30}O_3NCl$	3.69	3.68
D	Unsubst.	Hard gray rhombs	162	$C_{18}H_{24}O_2NCl$	4.35	4.39
D	A	Small prisms	168	$C_{20}H_{28}O_3NCl$	3.83	4.05
D	B	Needles	124	$C_{20}H_{28}O_3NCl$	3.83	3.93
D	C	White powder	120	$C_{20}H_{28}O_3NCl$	3.83	3.96
D	G	White powder	113	$C_{22}H_{32}O_4NCl$	3.42	3.56
E	Unsubst.	Felted needles	200	$C_{18}H_{24}O_2NCl$	4.35	4.30
E	A	White powder	128	$C_{20}H_{28}O_3NCl$	3.83	4.02
E	B	White powder	106	$C_{20}H_{28}O_3NCl$	3.83	4.08
E	C	Needles	239	$C_{20}H_{28}O_3NCl$	3.83	3.96
E	G	White powder	154	$C_{22}H_{32}O_4NCl$	3.42	3.49
F	Unsubst.	Tiny needles	195	$C_{18}H_{24}O_2NCl$	4.35	4.48
F	A	Glitt. leaves	174	$C_{20}H_{28}O_3NCl$	3.83	4.06
F	B	Fine cryst.	103	$C_{20}H_{28}O_3NCl$	3.83	4.10
F	C	Tiny needles	218	$C_{20}H_{28}O_3NCl$	3.83	4.13
F	G	White cryst. powder	122	$C_{22}H_{32}O_4NCl$	3.42	3.62
G	Unsubst.	Felted needles	190	$C_{19}H_{26}O_2NCl$	4.17	4.23
G	A	Cryst. powder	168	$C_{21}H_{30}O_3NCl$	3.69	3.95
G	B	Felted needles	104	$C_{21}H_{30}O_3NCl$	3.69	3.81
G	C	Glitt. leaves	208	$C_{21}H_{30}O_3NCl$	3.69	3.92
G	G	Silvery flakes	112	$C_{23}H_{34}O_4NCl$	3.30	3.35
		BENZYL-(ALKOXY-β-PHENYLETHYL)-AMINES				
A	A	Felted needles	133	$C_{19}H_{25}O_2N$	4.69	4.73
E	C	Tiny plates	78	$C_{20}H_{27}O_3N$	4.25	4.25
E	G	Tiny plates	92	$C_{22}H_{31}O_4N$	3.75	3.78
G	C	Prisms	105	$C_{21}H_{29}O_3N$	4.08	4.16
G	G	Tiny glitt. plates	98	$C_{23}H_{33}O_4N$	3.62	3.63
		BENZYLIDENE-(ALKOXY-β-PHENYLETHYL)-AMINES				
C	C	Large rhombs	90	$C_{19}H_{23}O_2N$	4.71	4.68
C	G	Platelets	86	$C_{21}H_{27}O_3N$	4.10	4.15
F	A	Rhombs	66	$C_{20}H_{25}O_3N$	4.28	4.26
E	Unsubst.	Faint yellow needles	67	$C_{18}H_{21}O_2N$	4.94	5.23
E	C	Glitt. leaves	107	$C_{20}H_{25}O_3N$	4.28	4.33
E	G	Glitt. leaves	115	$C_{22}H_{29}O_4N$	3.76	3.89
F	G	Tiny needles	96	$C_{22}H_{29}O_4N$	3.76	3.89
G	C	Glitt. small prisms	96	$C_{21}H_{27}O_3N$	4.10	4.19
G	G	Glitt. plates	122	$C_{23}H_{31}O_4N$	3.63	3.70
F	C	Faint yellow flakes	60	$C_{20}H_{25}O_3N$	4.28	4.37
G	A	Hard cream prisms	52	$C_{21}H_{27}O_3N$	4.10	4.09

TABLE VIII

ALKOXYTETRAHYDROISOQUINOLINE HYDROCHLORIDES

Amine substituent	Compound	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	5-Ethoxy					
B	6-Ethoxy	White cryst. powder	251	$C_{11}H_{16}ONCl$	6.55	6.74
C	7-Ethoxy					
D	5-Ethoxy-6-methoxy	Glitt. small leaves	184	$C_{12}H_{18}O_2NCl$	5.74	5.84
E	6-Methoxy-7-ethoxy[15]	Tiny needles	284	$C_{12}H_{18}O_2NCl$	5.74	5.74
F	6-Ethoxy-7-methoxy	Tiny needles	282	$C_{12}H_{18}O_2NCl$	5.74	5.71
G	6,7-Diethoxy	Tinted flakes	268	$C_{13}H_{20}O_2NCl$	5.43	5.57
	ALKOXY-N-METHYLTETRAHYDROISOQUINOLINE HYDROCHLORIDES					
A	5-Ethoxy					
B	6-Ethoxy	White powder	froth at 144, dec. at 220	$C_{12}H_{18}ONCl$	7.03	7.14
C	7-Ethoxy					
D	5-Ethoxy-6-methoxy	White powder	220	$C_{13}H_{20}O_2NCl$	5.43	5.33
E	6-Methoxy-7-ethoxy	Tinted flakes	270	$C_{13}H_{20}O_2NCl$	5.43	5.71
F	6-Ethoxy-7-methoxy	White powder	208	$C_{13}H_{20}O_2NCl$	5.43	5.59
G	6,7-Diethoxy	White powder	198	$C_{14}H_{22}O_2NCl$	5.15	5.28

TABLE IX

4-NITROBENZOYL-(ALKOXY-β-PHENYLETHYL)-AMINES

Substituent	Appearance	M. p., °C.	Formula	N Analyses, % Calcd.	Found
A	Tiny white prisms	120	$C_{17}H_{18}O_4N_2$	8.91	8.89
B	Tiny white prisms	113	$C_{17}H_{18}O_4N_2$	8.91	9.03
C	Tiny white prisms	154	$C_{17}H_{18}O_4N_2$	8.91	8.97
D	Felted white needles	102	$C_{18}H_{20}O_5N_2$	8.13	8.20
E	Bright yellow needles	157	$C_{18}H_{20}O_5N_2$	8.13	8.28
F	Bright yellow needles	156	$C_{18}H_{20}O_5N_2$	8.13	8.35
G	Yellow felted needles	138	$C_{19}H_{22}O_5N_2$	7.82	7.98
	4-NITROBENZOYL-(ALKOXY-β-PHENYLETHYL)-METHYLAMINES				
A	Faint yellow felted needles	235	$C_{18}H_{20}O_4N_2$	8.53	8.45
B	Faint yellow felted needles	222	$C_{18}H_{20}O_4N_2$	8.53	8.73
C	White felted needles	118	$C_{18}H_{20}O_4N_2$	8.53	8.49
D	Faint yellow fine prisms	78	$C_{19}H_{22}O_5N_2$	7.82	7.97
E	Bright yellow needles	155	$C_{19}H_{22}O_5N_2$	7.82	7.99
F	Faint yellow glitt. leaves	102	$C_{19}H_{22}O_5N_2$	7.82	7.96
G	Large clear prisms	58	$C_{20}H_{24}O_5N_2$	7.52	7.41

crystallized by taking up in a little absolute alcohol–ether mixture from which the crystals separate on evaporation of the solvent.

Benzyl-(alkoxy-β-phenylethyl)-amine Hydrochlorides.—These were prepared by condensing the amine with the appropriate aldehyde to form the Schiff bases and reducing these by the Adams method.[14] While no attempt was made to isolate the Schiff bases, a number of these separated on removing water from the reaction mixture and are recorded. A few amines were obtained solid and are recorded but the majority were converted directly into the hydrochloride by the addition of concentrated hydrochloric acid. The amines are rather soluble in the ordinary solvents. A small amount of absolute alcohol–ether mixture was found best for recrystallization. The hydrochlorides are in general moderately soluble in alcohol and benzene, sparingly soluble in hot water, ether and petroleum ether.

Alkoxytetrahydroisoquinoline and N-Methyltetrahydroisoquinoline Hydrochlorides.—The hydrochlorides were prepared by treating the corresponding amines with 40% formalin and then cyclizing the product with hydrochloric acid, as described elsewhere.[15] In line with previous experience it was found that, unless a substituent (alkoxy) was present meta to the side-chain of the amine, cyclization did not proceed normally under the conditions used.[16] The two series of hydrochlorides show little difference. They are readily soluble in cold water, moderately soluble in cold absolute alcohol, sparingly soluble in ether and ethyl acetate, and readily soluble in cold concd. hydrochloric acid.

4 - Nitrobenzoyl - (alkoxy - β - phenylethyl) - amines and N-Methylamines.—The 4-nitrobenzoyl compounds were prepared by treating the amine hydrochloride in benzene with 4-nitrobenzoyl chloride.[17] After heating for a short time the benzene was evaporated and the solid residue further heated on the steam-bath. The compound was taken up in a little benzene, shaken with dilute potas-

(14) Buck, THIS JOURNAL, **53**, 2192 (1931).

(15) Buck, *ibid.*, **56**, 1769 (1934).

(16) Kondo and Tanaka, *J. Pharm. Soc. Japan*, **49**, 4 (1929).

(17) Buck, THIS JOURNAL, **55**, 2593 (1933).

sium hydroxide, and washed with water, and further purified by recrystallizing from alcohol. They are insoluble in water and moderately soluble in alcohol.

The amines, N-methylamines, benzylphenylethylamines, isoquinolines and N-methylisoquinolines were not O-dealkylated as the corresponding hydroxy derivatives required for the pharmacological work have been prepared previously by demethylating the appropriate methoxy derivatives.[1,2,14,15]

The pharmacological work will be reported in another place. Some of that previously done is reported elsewhere.[11,18-21]

(18) Hjort, *J. Pharmacol.*, **50**, 131 (1934).
(19) Hjort, deBeer, Buck and Ide, *ibid.*, **55**, 152 (1935).
(20) Hjort, *ibid.*, **52**, 101 (1934).
(21) DeBeer and Hjort, *ibid.*, **52**, 211 (1934).

Nitrogen determinations were carried out by a micro-Dumas method. Melting points are corrected.

Summary

A series of seven alkoxy-β-phenylethylamines has been prepared, and from these amines the corresponding N-methylamines, ureas, *unsym*-methylureas, barbituric acids, isoquinolines, N-methylisoquinolines, benzyl-β-phenylethylamines and characterizing compounds have been made. Over one hundred and twenty of these compounds have not been described previously.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of the Conductance of Electrolytes.[1,2] VIII. A Redetermination of the Conductance of Kohlrausch's Standard Potassium Chloride Solutions in Absolute Units

BY GRINNELL JONES AND MAURICE JOSEPH PRENDERGAST

Most of the experimenters who have measured the electrical conductance of solutions have calibrated their cells by means of either a 1 or 0.1 or 0.01 *N* solution of potassium chloride whose absolute conductance was assumed to be known from the measurements of Kohlrausch, Holborn and Diesselhorst.[3] Unfortunately, Kohlrausch gives alternative definitions of these solutions. Kraus and Parker[4] have shown that although the alternative definitions of the 1 *N* solution are mutually consistent, the alternative definitions of the 0.1 *N* and of the 0.01 *N* solutions are not mutually consistent. Parker and Parker[5] have redetermined the absolute values of the conductance of the Kohlrausch solutions with substantially different results. They proposed new definitions of three different standard solutions, which they call 1, 0.1 and 0.01 demal and gave the results of measurements of the absolute conductance of these solutions. The experimental method used by Parker and Parker was in principle similar to that used by Kohlrausch although evidently improved in many details.

The Editors of the "International Critical Tables" accepted Parker and Parker's work as more reliable than that of Kohlrausch, Holborn and Diesselhorst and have applied corrections to the data in the literature based on the Kohlrausch standards to make them conform to the newer standards of Parker and Parker. As a result very few of the figures for the conductance of solutions found in the "International Critical Tables" agree with the original literature.

In the fifth paper of this series Jones and Bradshaw have described a new and more precise method of making absolute measurements and have redetermined the specific conductance of the three solutions defined by Parker and Parker at 0, 18 and 25°. These results indicate that on the whole the results obtained by Parker and Parker are not as accurate as the earlier work of Kohlrausch, Holborn and Diesselhorst, and that the corrections recommended by Parker and Parker and used by the "International Critical Tables" are unreliable. We have, therefore, undertaken to redetermine the absolute specific conductivity of three standard potassium chloride solutions used by Kohlrausch at 0, 18, 20 and 25° by the new method developed by Jones and Bradshaw. It is hoped that the re-

(1) Original manuscript received August 3, 1936.
(2) Earlier papers in this series: Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928); Grinnell Jones and G. M. Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411, 1207 (1931); Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933); Grinnell Jones and S. M. Christian, *ibid.*, **57**, 272 (1935); Grinnell Jones and D. M. Bollinger, *ibid.*, **57**, 280 (1935).
(3) F. Kohlrausch, L. Holborn and H. Diesselhorst, *Wied. Ann. Physik*, **64**, 417 (1898).
(4) C. A. Kraus and H. C. Parker, THIS JOURNAL, **44**, 2422 (1922).
(5) H. C. Parker and E. W. Parker, *ibid.*, **46**, 312 (1924).