N-[2-(N-methyl-N-2-chlorobenzylamino)ethylidenyl]-aminomorpholine. b.p. 161°/0.06 mm., n_D^{20} 1.5547.

Anal. Calcd. for $C_{14}H_{20}ClN_3O$: N, 14.91; Cl, 12.58. Found: N, 14.89; Cl, 12.67.

N-Dimethyl-N'-2-(N-methyl-N-2-chlorobenzylamino)-ethylidenylhydrazine, b.p. 115°/0.4 mm., n_D^{20} 1.5435.

Anal. Calcd.for $C_{12}H_{18}ClN_3$: N, 11.68. Found: N, 11.66.

N-[2-(N-methyl-N-2-chlorobenzylamino)ethyl]aminopyrrolidine. A solution of 50.5 g. (0.189 mole) of *N*[2-(*N*-methyl-*N*-2-chlorobenzylamino)ethylidenyl]aminopyrrolidine in 500 cc. of ethyl ether was added dropwise to a slurry of 6.4 g. (0.168 mole) of lithium aluminum hydride in 500 cc. of dry ether. After the addition was completed, the solution was refluxed for an additional 4 hr., after which was added dropwise a 40% aqueous potassium hydroxide solution. The ethereal solution was decanted, dried over potassium carbonate, and subjected to distillation; yield 39.3 g. (77.8%), b.p. 135°/0.45 mm., n_D^{20} 1.5389.

Anal. Calcd. for $C_{14}H_{22}ClN_3$: N, 15.69; Cl, 13.24. Found: N, 15.66; Cl, 13.27.

Dimaleate salt. m.p. 129–131°.

Anal. Calcd. for $C_{22}H_{30}ClN_3O_8$: N, 8.40; Cl, 7.09. Found: N, 8.46; Cl, 7.24.

The following hydrazines were prepared by the same method:

N-[2-(N-methyl-N-2-chlorobenzylamino)ethyl]aminomorpholine, b.p. 158°/0.065 mm., n_D^{20} 1.5368.

Anal. Calcd. for $C_{14}H_{22}N_3O$: N, 14.80; Cl, 12.49. Found: N, 14.85; Cl, 12.77.

Dimaleate salt, m.p. 124°.

Anal. Calcd. for $C_{22}H_{30}ClN_3O_9$: N, 8.15; Cl, 6.87. Found: N, 8.18; Cl, 7.12.

N-Dimethyl-N'-2-(N-methyl-N-2-chlorobenzylamino) ethylhydrazine, b.p. 111°/0.7 mm., n_D^{20} 1.5215.

Anal. Calcd. for $C_{12}H_{20}ClN_3$: N, 17.39. Found: N, 17.37.

2-(N-methyl-N-substituted benzyl)aminoethylhydrazines—General method. To a stirred refluxing solution of 6 equivalents of 85% hydrazine hydrate in 500 cc. of alcohol was added dropwise in 3 hr. a solution of 1 equivalent of 2-(*N*-methyl-*N*-substituted benzyl)aminoethylchloride hydrochloride in 500 cc. of ethanol. After another hour of reflux, the ethanol and excess hydrazine hydrate were removed by distillation and the residue was poured into 500 cc. of water. The aqueous solution was saturated with potassium hydroxide and next extracted with ether. After the etheral solution had been dried over potassium carbonate, the solvent was removed by distillation and the product isolated by fractional distillation. The results are tabulated in Table III.

2-(N-Methyl-N-phenyl)aminoethylhydrazine. To a refluxing solution of 77.8 g. (1.32 moles) of 85% hydrazine hydrate in 150 cc. of ethanol was added dropwise in 3 hr. a solution of 44 g. (0.26 mole) of 2-(*N*-methyl-*N*-phenyl)aminoethylchloride[23] in 200 cc. of ethanol. After the addition was completed the solution was refluxed for another 3 hr. The alcohol was removed by distillation, 100 cc. water was added and the aqueous solution was saturated with potassium hydroxide. The base was extracted with ether, dried over potassium carbonate, filtered, and the ether was removed by distillation. Fractionation of the residue yielded 40.3 g. (98%) b.p. 105°/0.2 mm., n_D^{20} 1.5827.

Anal. Calcd. for $C_9H_{15}N_3$: N, 25.43. Found: N, 25.70.

The *maleate salt* was prepared in ethanol, m.p. 90–91°.

Anal. Calcd. for $C_{13}H_{19}N_3O_4$: N, 14.94. Found: N, 15.08.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Sterically Hindered Amines. II. α-Amino Ketones and Alcohols[1]

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Received February 8, 1961

Twelve acetylenic amines, $R^1R^2C(NHR^3)—C{\equiv}CH$, were converted in good yields to the α-amino ketones, $R^1R^2C(NHR^3)—COCH_3$, and thence, by reduction with lithium aluminum hydride or sodium borohydride, to the α-amino alcohols, $R^1R^2C(NHR^3)—CH(OH)CH_3$.

The facile synthesis of sterically hindered acetylenic amines $R^1R^2C(NR^3R^4)—C{\equiv}CH$ described earlier[3,4] and the subsequent finding[5] that many of these and their hydrogenation products have notable hypotensive properties, prompted a study of the preparation of methyl ketones (B) and the corresponding alcohols (C) from the acetylenic compounds (A).

$$R^1R^2C(NHR^3)—C{\equiv}CH \xrightarrow[Hg^{++};\ H^+]{H_2O} R^1R^2C(NHR^3)—COCH_3 \xrightarrow{LiAlH_4} R^1R^2C(NHR^3)—CH(OH)CH_3$$

(A) (B) (C)

The hydration reaction,[6] catalyzed by mercuric ion, consistently gave good yields of the ketones when carried out with purified amine along with three equivalents of sulfuric acid in aqueous methanol. The ketones proved to be stable to distillation and yielded nicely crystalline nonhygroscopic hydrochloride salts.

(1) Paper No. 76 on substituted acetylenes; previous paper G. F. Hennion and A. P. Boisselle, *J. Org. Chem.*, **26,** 2677 (1961).

(2) Eli Lilly Co. Fellow, 1959–61. Abstracted from a portion of the Ph.D. Dissertation of P. E. B.

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TABLE I

AMINO KETONES
$R^1R^2C(NHR^3)—CO—CH_3$

Cmpd.	R^1	R^2	R^3	Molecular Formula	B.P.	Mm.	n_D^{25}	Yield,[a] %	Carbon Calcd.	Carbon Found
I	CH_3—	CH_3—	C_2H_5—	$C_7H_{15}NO$	52–55	14	1.4252	82	65.07	65.01
II	CH_3—	CH_3—	*i*-C_3H_7—	$C_8H_{17}NO$	62–63	17	1.4282	95	67.08	67.32
III	CH_3—	CH_3—	*t*-C_4H_9—	$C_9H_{19}NO$	78–79	19	1.4342	55	68.74	68.53
IV	CH_3—	C_2H_5—	C_2H_5—	$C_8H_{17}NO$	66–68	13	1.4329	57	67.08	66.98
V	CH_3—	C_2H_5—	*i*-C_3H_7—	$C_9H_{19}NO$	78	18	1.4341	87	68.74	68.62
VI	CH_3—	C_2H_5—	*t*-C_4H_9—	$C_{10}H_{21}NO$	80–83	14	1.4402	63	70.12	69.79
VII	C_2H_5—	C_2H_5—	C_2H_5—	$C_9H_{19}NO$	82–83	18	1.4371	80	68.74	68.51
VIII	C_2H_5—	C_2H_5—	*i*-C_3H_7—	$C_{10}H_{21}NO$	90–92	18	1.4408	70	70.12	70.61
IX	C_2H_5—	C_2H_5—	*t*-C_4H_9—	$C_{11}H_{23}NO$	51–52	0.4	1.4476	60	71.30	71.38
X	—$CH_2(CH_2)_3CH_2$—		C_2H_5—	$C_{10}H_{19}NO$	78–80	1.4	1.4670	88	70.96	71.03
XI	—$CH_2(CH_2)_3CH_2$—		*i*-C_3H_7—	$C_{11}H_{21}NO$	82–84	1.9	1.4662	85	72.08	72.19
XII	—$CH_2(CH_2)_3CH_2$—		*t*-C_4H_9—	$C_{12}H_{21}NO$	77–80	0.4	1.4710	69	73.04	73.23

[a] Yield corresponds to once or twice distilled material of 3° boiling range or less. [b] Melts with decomposition.

TABLE II

AMINO ALCOHOLS $R^1R^2C(NHR^3)—CHOH—CH_3$

Cmpd.	R^1	R^2	R^3	Molecular Formula	B.P.	Mm.	n_D^{25}	Yield,[a] %	Carbon Calcd.	Carbon Found
XIII	CH_3—	CH_3—	C_2H_5—	$C_7H_{17}NO$	68–69	14	1.4422	91	64.07	64.23
XIV	CH_3—	CH_3—	*i*-C_3H_7—	$C_8H_{19}NO$	74–76	17	1.4360	90	66.15	66.09
XV	CH_3—	CH_3—	*t*-C_4H_9—	$C_9H_{21}NO$	79–82	14	1.4403	90	67.87	67.49
XVI	CH_3—	C_2H_5—	C_2H_5—	$C_8H_{19}NO$	86–89	21	1.4441	90	66.15	66.28
XVII	CH_3—	C_2H_5—	*i*-C_3H_7—	$C_9H_{21}NO$	87–89	17	1.4412	95	67.87	67.77
XVIII	CH_3—	C_2H_5—	*t*-C_4H_9—	$C_{10}H_{23}NO$	94–96	16	1.4459	84	69.31	69.22
XIX	C_2H_5—	C_2H_5—	C_2H_5—	$C_9H_{21}NO$	96–97	15	1.4498	88	67.87	67.75
XX	C_2H_5—	C_2H_5—	*i*-C_3H_7—	$C_{10}H_{23}NO$	98–101	14	1.4502	89	69.31	69.23
XXI	C_2H_5—	C_2H_5—	*t*-C_4H_9—	$C_{11}H_{25}NO$	109–111	16	1.4553	96	70.53	70.66
XXII	—$CH_2(CH_2)_3CH_2$—		C_2H_5—	$C_{10}H_{21}NO$	74–76	0.6	1.4738	88	70.12	70.19
XXIII	—$CH_2(CH_2)_3CH_2$—		*i*-C_3H_7—	$C_{11}H_{23}NO$	83–85	0.4	1.4720	99	71.30	71.68
XXIV	—$CH_2(CH_2)_3CH_2$—		*t*-C_4H_9—	$C_{12}H_{25}NO$	89–90	0.4	1.4760	97	72.30	72.13

[a] Yield corresponds to once or twice distilled material of 3° boiling range or less. [b] Melts with decomposition.

Treatment of the ketones (B) with either lithium aluminum hydride or sodium borohydride in the usual manner gave the corresponding amino alcohols (C) in excellent yields (85% or better). The alcohols also were stable to distillation and gave crystalline nonhygroscopic hydrochloride salts.

The new amino ketones and alcohols are described in Tables I and II. Many of these compounds have been evaluated as hypotensive agents in the Lilly Research Laboratories, Indianapolis, Ind., and the results will be described elsewhere.

In this work particular attention was given to products having a secondary amine group since we are interested in converting the alcohols to aziridines. Preliminary experiments have shown that the cyclization proceeds well by treatment of the aminoalcohols (C) with thionyl chloride and subsequent reaction of the α-chloroamines with base. These studies will be described in a subsequent paper.

EXPERIMENTAL

The acetylenic amines were prepared as described previously[4] and were purified immediately before use as follows. The amine was dissolved in a slight excess of 10–15% hydrochloric acid, the aqueous solution was extracted twice with ether (ether extracts discarded) and the amine was then released from the aqueous solution with cold 40% sodium hydroxide. The amine was taken up in ether and the ethereal solution was dried with anhydrous potassium carbonate, then with potassium hydroxide pellets, and recovered by distillation.

The general method used for hydration of the triple bond is illustrated by the following example.

3-Isopropylamino-3-methyl-2-pentanone (V). To a cold solution of 95 ml. of methanol, 95 ml. of distilled water, and 143 g. of 95% sulfuric acid contained in a 1-l. three-neck flask provided with reflux condenser and mechanical stirrer was added 128.5 g. (0.93 mole) of 3-isopropylamino-3-methyl-1-pentyne. Two grams of red mercuric oxide was added to the hot solution and the mixture was boiled gently with stirring for 2.5 hr. Additional mercuric oxide was added periodically in 2-g. portions until a total of 10 g. had been added. The hot solution was treated with 2–3 g. of decolorizing charcoal, cooled with stirring, and filtered

TABLE I (*Continued*)

Hydrogen		Nitrogen		Molecular		Hydrochlorides					
						Carbon		Hydrogen		Nitrogen	
Calcd.	Found	Calcd.	Found	Formula	M.P.	Calcd.	Found	Calcd.	Found	Calcd.	Found
11.70	11.30	10.84	10.75	$C_7H_{16}ClNO$	215–217	50.75	50.75	9.74	9.52	8.46	8.23
11.97	12.05	9.78	9.61	$C_8H_{18}ClNO$	152–154	53.47	53.35	10.10	9.85	7.79	7.94
12.18	12.34	8.91	9.01	$C_9H_{20}ClNO$	201	55.80	55.97	10.41	10.52	7.23	6.94
11.97	11.87	9.78	9.59	$C_8H_{18}ClNO$	138–141	53.47	53.67	10.10	10.08	7.79	7.82
12.18	11.99	8.91	8.80	$C_9H_{20}ClNO$	120–121	55.80	56.03	10.41	10.60	7.23	7.18
12.36	12.06	8.19	8.25	$C_{10}H_{22}ClNO$	157–159[b]	57.81	58.04	10.68	10.78	6.74	6.46
12.18	11.96	8.91	8.96	$C_9H_{20}ClNO$	140–142	55.80	56.06	10.41	10.40	7.23	7.05
12.36	12.33	8.19	8.27	$C_{10}H_{22}ClNO$	159–160	57.81	57.99	10.68	10.41	6.74	6.53
12.51	12.31	7.56	7.54	$C_{11}H_{24}ClNO$	172–174[b]	59.57	59.87	10.91	10.72	6.32	6.09
11.31	11.20	8.28	8.28	$C_{10}H_{20}ClNO$	218–219	58.38	58.63	9.80	9.92	6.81	6.62
11.55	11.31	7.64	7.65	$C_{11}H_{22}ClNO$	211–213	60.12	60.12	10.09	9.96	6.37	6.20
11.75	11.86	7.10	7.19	$C_{12}H_{24}ClNO$	218–220[b]	61.65	61.68	10.35	10.45	5.99	5.75

[a] Yield corresponds to once or twice distilled material of 3° boiling range or less. [b] Melts with decomposition.

TABLE II (*Continued*)

Hydrogen		Nitrogen		Molecular		Hydrochlorides					
						Carbon		Hydrogen		Nitrogen	
Calcd.	Found	Calcd.	Found	Formula	M.P.	Calcd.	Found	Calcd.	Found	Calcd.	Found
13.06	12.81	10.68	10.53	$C_7H_{18}ClNO$	149–152	50.14	49.92	10.82	10.65	8.36	8.56
13.19	13.23	9.64	9.88	$C_8H_{20}ClNO$	125–127	52.88	52.84	11.09	10.97	7.71	7.90
13.29	13.26	8.80	8.74	$C_9H_{22}ClNO$	102–104	55.22	55.18	11.33	11.32	7.16	6.81
13.19	13.17	9.64	9.79	$C_8H_{20}ClNO$	173–174	52.88	52.94	11.09	10.93	7.71	7.59
13.29	13.29	8.80	9.16	$C_9H_{22}ClNO$	123–124	55.22	55.37	11.33	11.10	7.16	7.38
13.38	13.51	8.08	8.12	$C_{10}H_{24}ClNO$	131–132	57.26	57.40	11.48	11.60	6.68	6.40
13.29	13.03	8.80	8.78	$C_9H_{22}ClNO$	165–167	55.22	55.38	11.33	11.52	7.16	6.95
13.38	13.40	8.08	8.36	$C_{10}H_{24}ClNO$	128–131	57.26	57.29	11.48	11.36	6.68	6.55
13.45	13.39	7.48	7.43	$C_{11}H_{26}ClNO$	158–159	59.03	58.79	11.71	11.57	6.26	6.41
12.36	12.26	8.19	8.20	$C_{10}H_{22}ClNO$	163–164	57.81	58.05	10.68	10.51	6.74	6.48
12.51	12.55	7.56	7.46	$C_{11}H_{24}ClNO$	180–181	59.57	59.58	10.91	11.07	6.32	6.63
12.64	12.39	7.03	7.19	$C_{12}H_{26}ClNO$	177[b]	61.12	61.62	11.12	11.54	5.94	5.94

[a] Yield corresponds to once or twice distilled material of 3° boiling range or less. [b] Melts with decomposition.

with suction. The filtrate was transferred to a beaker, cooled with ice, and the product was released by slow addition of cold 40% sodium hydroxide in excess. The upper oily layer was taken up in ether and the aqueous layer was extracted three times with 100-ml. portions of ether. The combined ethereal solution was dried over anhydrous potassium carbonate. Distillation gave 126 g. of product (86% yield), b.p. 78° at 18 mm.; infrared bands (neat) at 3.0 (NH) and 5.9 μ (CO); —C≡CH bands absent.

3-Isopropylamino-3-methyl-2-pentanol (XVII), *lithium aluminum hydride reduction.* The ketone (V) described above (114.1 g., 0.81 mole) dissolved in 125 ml. of anhydrous ether was added dropwise with stirring to 33.2 g. (0.81 mole) of lithium aluminum hydride in 250 ml. of anhydrous ether. The mixture was boiled for 3 hr., cooled in ice, and excess hydride was destroyed by slow addition of cold water. The complex was then hydrolyzed with 40% sodium hydroxide solution (*ca.* 100 ml.) and the mixture was boiled for 4 hr., cooled, and the ether layer decanted. The pasty inorganic layer was extracted with four 100-ml. portions of ether. The combined ethereal solution was dried with anhydrous potassium carbonate. Distillation yielded 109 g. (95% yield), b.p. 87–89° at 17 mm.; infrared band (neat) at 2.95 μ (broad, NH and OH); CO band absent.

3-Isopropylamino-3-methyl-2-butanol (XIV), *sodium borohydride reduction.* A 37.1-g. portion (0.26 mole) of the ketone (II) dissolved in 50 ml. of absolute ethanol was added dropwise to 9.75 g. (0.25 mole) of sodium borohydride in 150 ml. of absolute ethanol. The mixture was boiled for 3 hr., cooled (solidification), and hydrolyzed with 15% hydrochloric acid. The solution was concentrated to near dryness and water and ice were then added to a total volume of about 200 ml. The solution was made strongly alkaline with solid potassium hydroxide added in small portions with cooling. The oil was taken up in 50 ml. of ether and the aqueous layer was extracted three times with 50-ml. portions of ether. The combined ethereal solution was dried over anhydrous potassium carbonate. Distilation gave 34.7 g. (92% yield), b.p. 77–78° at 19 mm.; infrared band (neat) at 2.95 μ (broad, NH and OH); CO band absent.

Hydrochlorides were precipitated in substantially quantitative yields by addition of cold, dry ethereal hydrogen chloride to solutions of the amino compounds in anhydrous ether and were purified by crystallization from a mixture of pure ethyl acetate and absolute ethanol. Melting points listed in Tables I and II were determined in sealed capillaries and are uncorrected.

3-Ethylamino-3-methyl-2-butyl acetate. A 17-g. portion (0.13 mole) of 3-ethylamino-3-methyl-2-butanol (XIII) was converted to the acetate ester by heating on the steam bath for 3 hr. with 18 g. (0.17 mole) of acetic anhydride. The ester (13.9 g., 61% yield) had b.p. 88–92° at 24 mm. n_D^{25}, 1.4268.

Anal. Calcd. for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09. Found: C, 62.21; H, 10.97; N, 8.10.

The hydrochloride had m.p. 157–160°.

Anal. Calcd. for $C_9H_{20}ClNO_2$: C, 51.54; H, 9.61; N, 6.68. Found: C, 51.94; H, 9.43; N, 6.75.

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NOTRE DAME, IND.

CONTRIBUTION FROM THE DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, SCHOOL OF PHARMACY, PURDUE UNIVERSITY]

Synthesis and Stability Studies of Certain Disubstituted Aminoacetoxybenzoic Acids

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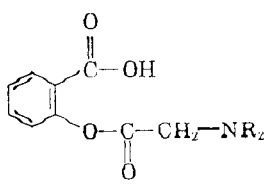
Five disubstituted aminoacetoxybenzoic acids were synthesized as their hydrochloride salts. Their hydrolysis rates were determined and compared with those of aspirin.

Aspirin is probably the most widely used chemical medicinal agent. Production in the United States alone was 18.0 million pounds in 1957.[2]

Despite its great utility and popularity, however, acetylsalicylic acid has two major drawbacks. It has poor solubility in aqueous media and, more important, it has a tendency to hydrolyze in the presence of only traces of moisture.

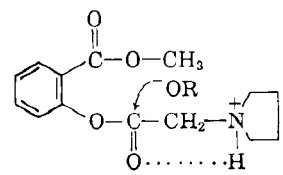
The purpose of this study is to synthesize compounds similar to aspirin which, it is hoped, might, due to steric and/or electronic factors be more stable to hydrolysis and water soluble.

The desired structure is:



A

Garrett[3] showed that a group of hindered acylsalicylic acids were more resistant to acid-catalyzed hydrolysis than aspirin. Garrett[4] also showed that B was resistant to hydrogen ion catalyzed hydrolysis, due to a "proton shield" effect. However, the compound was very susceptible to nucleophilic catalysis. He explains this as an electrophilic-nucleophilic catalysis whereby the hydrogen of the protonated amine hydrogen bonds with the carbonyl oxygen, thus facilitating attack on the carbonyl carbon.



B

Kagan and Birkenmeyer[5] have described reactions which support the hypothesis that the carboxylate anion of acylsalicyclic acid can participate in a neighboring group nucleophilic attack on the carbonyl carbon of the acyl moiety and on the carbon atom *alpha* to the carbonyl group.

EXPERIMENTAL

o-Disubstituted aminoacetoxybenzoic acid. a. tert-Butyl salicylate. Method A. Silver salicylate, 54 g. (0.22 mole), *tert*-butyl chloride, 61 g. (0.66 mole) and 150 ml. of dry thiophene-free benzene were agitated in a closed container, protected from light, during a 24-hr. period. The mixture was filtered and the filtrate concentrated under reduced pressure. The resulting oil was treated with 5% sodium bicarbonate solution, the aqueous layer extracted with ether and the combined oil and ethereal extracts dried over calcium chloride.

After removal of the ether the residue was fractionated at 16–18 mm. yielding 23.5 g. (48%) of a product distilling at 120–123°, n_D^{25} 1.5029, d^{27} 1.0579.

Method B: Salicyloyl chloride, obtained from 0.2 mole of salicyclic acid and prepared according to a modification of Wolffenstein's[6] method, was added dropwise to a well-

(1) Abstracted from a dissertation submitted to the Graduate School of Purdue University in partial fulfillment for the Ph.D. degree. Present address: Brooklyn College of Pharmacy, Long Island University.

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