beryllium iodide and phenylberyllium iodide have been prepared and their reactions investigated.

Ames, Iowa

[Contribution from the Chemical Laboratories of Harvard University and the University of Illinois]

THE PREPARATION AND BASE STRENGTHS OF SOME AMINES

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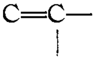
The measurements here recorded were made for the purpose of supplementing existing data on the base strengths of amines. The data obtained are summarized in the following table.

Table I

Data on Base Strengths of Amines

Formula	Neutral. equiv., calcd.	Neutral. equiv. found	$K_{\text{hydr.}} \times 10^{10}$ $t = 25°$	$K_B \times 10^5$
($C_6H_5NH_2$)	...	...	(2.17×10^5)[1]	(4.6×10^{-5})[1]
$C_6H_5CH_2NH_2$	107.1	107.3	4.26	2.35
$C_6H_5(CH_2)_2NH_2$	121.1	...	1.48	6.78
$C_6H_5(CH_2)_3NH_2$	135.1	135.1	0.63	15.9
$C_6H_5(CH_2)_4NH_2$	149.2	149.4	.40	24.8
$C_6H_5(CH_2)_5NH_2$	163.2	163.1	.33	30.6
o-$CH_3C_6H_4CH_2NH_2$	121.1	121.5	5.89	1.70
m-$CH_3C_6H_4CH_2NH_2$	121.1	121.8	4.24	2.40
p-$CH_3C_6H_4CH_2NH_2$	121.1	121.1	3.98	2.55
o-$CH_3OC_6H_4CH_2NH_2$	137.1	137.9	1.81	5.56
m-$CH_3OC_6H_4CH_2NH_2$	137.1	137.5	6.46	1.56
p-$CH_3OC_6H_4CH_2NH_2$	137.1	137.2	3.10	3.22
$C_6H_5CH_2NHCH_3$	121.1	121.3	2.63	3.80
$C_6H_5CH_2NHCH_2CH_3$	135.1	134.8	2.10	4.75
$C_6H_5CH_2NHCH_2CH_2CH_3$	149.1	149.1	2.40	4.18
$C_6H_5CH_2CH_2NHCH_3$	135.1	135.6	0.75	13.9

The first five amines constitute a series of the type $R(CH_2)_xNH_2$ where R is the negative phenyl group. The data are of some interest in connection with the transmission of polar effects through a chain of atoms. Data are available on several similar series of acids and it is well known that the effect of the substituent R on the dissociation of the acid diminishes continuously with the increasing values of x. Where R is $-CH{=}CH$, however, the dissociation constants appear to alternate with increasing values of x. Data on the acids $C_6H_5(CH_2)_xCOOH$ are not available, but since phenyl contains the group  $C{=}\underset{|}{C}{-}$, there was some possibility that alternation might be observed in the series of amines here under discussion.

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[1] Lunden, *Z. physik. Chem.*, **54**, 532 (1906).

The hydrolysis of an amine salt may be represented by the equation

$$RNH_3^+ \rightleftarrows RNH_2 + H^+$$

and the hydrolytic constant is defined by the expression

$$\frac{[RNH_2]\,[H^+]}{[RNH_3^+]} = K_{\text{hydr.}}{}^{2}$$

The hydrolytic constant of an amine then furnishes a measure of the tendency of a hydrogen ion to leave the nitrogen atom, and there should be a parallelism between the dissociation constants of acids and the hydrolytic constants of the corresponding bases.[3] The amines, however, seem to present a simpler picture than the acids, for apart from the fact that there is in these a greater distance between R group and the proton which dissociates, the relatively greater complexity of the carboxyl group may permit a more complex behavior. Hantzsch[4] has in fact advanced definite experimental evidence for concluding that two distinct types of carboxyl groups exist.

In regard to the amines $C_6H_5(CH_2)_xNH_2$, the data summarized above show that the values of $K_{\text{hydr.}}$ diminish continuously as the values of x increase. This decrease though continuous is not quite regular, and the data do not fit well the $^1/_3$ rule of Derick[5] or an equation of the type suggested by Simms.[6]

It is interesting to compare the data on these amines with those on the reactivities of the corresponding chlorides as measured by Conant and Kirner.[7] The effect of the phenyl group does not here diminish continuously as the distance from the halogen atom increases, but in the first members of the series there is evidence of alternation. It is evident

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[2] It is of course implied in this that the conditions are such that the concentrations are equal to the activities.

As Brönsted has pointed out (Brönsted, *Rec. trav. chim.*, [4] **42,** 718 (1923)) the use of the equation $NH_4^+ + HOH \longrightarrow NH_4OH + H^+$ to represent the hydrolysis of an ammonium salt rests on an unnecessarily complicated conception. According to Brönsted's idea ammonium chloride reacts acid because the ammonium ion is an acid. The question of the extent to which the base strength of ammonia is determined by each of the reactions $NH_3 + HOH \rightleftarrows NH_4OH$ and $NH_4OH \rightleftarrows NH_4^+ + OH^-$ becomes immaterial when Brönsted's more general definition of a base is used. Incidentally the octet theory leads to a similar conclusion, since the most obvious manner of representing ammonium hydroxide is $\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{..}{\underset{..}{\mathrm{N}}}}}:\mathrm{H}^{+}\ \mathrm{OH}^{-}$ and the weakness of ammonia as a base is accounted for by supposing that the equilibrium lies in favor of $NH_3 + H_2O$, the formation of these involving merely the transfer of a hydrogen ion from the ammonium ion to the hydroxyl ion.

[3] See in this connection Hixon and Johns, This Journal, **49,** 1786 (1927).

[4] Hantzsch, *Ber.*, **50,** 1422 (1917).

[5] Derick, This Journal, **33,** 1181 (1911).

[6] Simms, *ibid.*, **48,** 1251 (1926).

[7] Conant and Kirner, *ibid.*, **46,** 232 (1924).

that those qualities of structure which govern the base strength of amines are not the same as those which govern the tendencies of the chlorides to undergo metathesis. Of the two reactions the hydrolysis of the amine salt is evidently the simpler, since it involves merely the reversible separation of a proton. Concerning the mechanism of the reaction of an alkyl halide nothing whatever is known. If the term polarity is to be used, it seems much more appropriate to use it in connection with the hydrolysis of the amine salt, a reaction involving the loss of an elementary positive charge, than in connection with the reactions of an alkyl chloride which proceed in a fashion at present wholly obscure.

The reasons which Conant, Kirner and Hussey[8] found for concluding that variations in the reactivities of chlorides could not be accounted for solely in terms of polarity find additional support in the above argument.

The data on the *o*-, *m*- and *p*-methyl- and methoxylbenzylamines indicate that the effects of these substituents are slight and vary in an irregular fashion with changes of position.

Of the secondary amines two have previously been measured by Bourgeaud and Dondelinger.[9] For methylbenzylamine these writers give $K_B = 7.95 \times 10^{-8}$, and for ethylbenzylamine 5.04×10^{-8}. The values indicated in the above table are in one case 500 and in the other 1000 times as great as these. Although some difficulty was experienced in getting sharply consistent readings on these amines, the writers are inclined to suppose that the values given by Bourgeaud and Dondelinger must be seriously in error. These values are of an entirely different order of magnitude from those of the corresponding primary and the analogous tertiary amines, and imply an effect due to the introduction of a simple alkyl group quite unprecedented. The measurements of these investigators were evidently carried out with great care but their method appears to be fundamentally untrustworthy. They measured, with the aid of the hydrogen or quinhydrone electrode, the P_H of solutions of the pure hydrochlorides of the amines. Their solutions were therefore very inadequately buffered; and slight traces of impurities or quite possible variations in the compositions of the purified hydrochlorides would suffice to render their results meaningless.

As the table shows, the amines $C_6H_5CH_2NHR$ where R is methyl, ethyl and *n*-propyl are just about twice as strong bases as benzylamine, and a similar relationship holds between methylphenethyl- and phenethylamine.

Benzylamine has been measured by Bredig by the conductivity method[10] and the value which he assigns to it ($K_B = 2.4 \times 10^{-5}$) agrees with that found in the present investigation.

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[8] Conant, Kirner and Hussey, THIS JOURNAL, **47**, 492 (1925).

[9] Bourgeaud and Dondelinger, *Bull. soc. chim.*, **37**, 282 (1925).

[10] Bredig, *Z. physik. Chem.*, **13**, 191 (1894).

Method Used in Measuring the Base Strengths.—The method used was to determine the P_H of solutions of the base in water to which a definite fraction of an equivalent amount of hydrochloric acid had been added. This fraction was usually $^1/_2$ but sometimes $^2/_3$ or $^3/_4$. This method is satisfactory only if the amine is appreciably soluble in water and quite pure, and if the composition of the solution is definitely known. The purified amine was distilled in a vacuum in a small Claisen flask with a sealed-in thermometer, etc., and was collected with the aid of a bifurcated adaptor in two test-tubes. One of these contained a number of small bulbs weighed and marked standing on their capillary tips. The middle fraction of the amine was collected in this tube and when air was admitted to the receiver the bulbs were automatically filled. The amine was thus preserved from contact with moisture and carbon dioxide. The bulbs were immediately sealed off and weighed. To control the purity some of the tubes were broken under water and the solutions titrated using a suitable indicator (usually methyl red). To prepare a solution for measurement the bulb containing a known amount of the amine was placed in a glass-stoppered bottle, $^1/_2$ an equivalent of 0.01 N hydrochloric acid added and the stoppered flask shaken vigorously to break the thin bulb. This method of operation protected the amine against exposure to the air.

The electrodes were usually palladized platinum foils, though platinized platinum foils were also tried and in some cases wires were used. The hydrogen electrode was connected to 0.1 N and saturated calomel electrodes through a saturated potassium chloride salt bridge. Boundary potentials were disregarded. The two calomel electrodes were frequently compared with each other and with a hydrogen electrode in a standard 0.05 M potassium hydrogen phthalate buffer. The cells were immersed in a water-bath, the temperature of which was regulated by hand to $25 \pm 0.2°$. For measurement of potentials a Leeds and Northrup Student Potentiometer was used. Measurements were made on three or more samples of each amine, with at least two fresh electrodes on each solution and usually at two different dilutions. In each case a series of readings was made against the 0.1 N calomel ($E = 0.3370$) and the saturated calomel ($E = 0.2458$) electrode. The agreement of the various series of readings was usually quite good, although some difficulty was experienced in getting sharply consistent results with the secondary amines. With a similar series of tertiary amines no consistent readings could be obtained.

Preparation of the Amines.—All of the amines measured in this work with the exception of one have been previously described. The following notes may, however, be of interest to those who have to prepare similar compounds.

The amines of the series $C_6H_5(CH_2)_xNH_2$ with the exception of benzylamine were prepared by the reduction of the corresponding nitriles. As von Braun has shown[11] this method, which gives poor yields in the preparation of phenethylamine, works very well for the higher members of the series. Commercial phenethyl alcohol was the starting point in the preparation of phenethyl cyanide. γ-Phenyl-*n*-propyl alcohol was prepared by the catalytic reduction of cinnamic aldehyde. This provided the starting point for the synthesis of phenylpropyl cyanide.

δ-Phenyl-*n*-butyl alcohol was prepared from β-phenethyl magnesium bromide by the action of ethylene oxide. This method has been used with satisfactory results in passing from RBr to RCH_2CH_2OH in a number of cases. In a small run this method gave a yield of 50% of the phenylbutyl alcohol, but in larger runs the yields were still poorer and the product required repeated careful fractionation. Although further study might increase the yields, this method cannot at present be recommended for obtaining compounds of the series $C_6H_5(CH_2)_4$—.

The substituted benzylamines were all prepared by the catalytic reduction of the appropriate nitriles or oximes, using acetic anhydride as the solvent. This method yields the acetyl derivative of the primary amine and avoids the formation of any secondary amine.[12] Hydrolysis of the amide then yields pure primary amine. The details of the preparation of *o*- and *p*-methylbenzylamines have already been described. The preparation of *m*-methylbenzylamine proceeds smoothly in the same fashion.

***p*-Anisylamine.**—The reduction of 0.1 mole of anisaldoxime in 40 cc. of acetic anhydride was complete in four hours using 0.1 g. of catalyst. The yield of the crude amide was quantitative. On crystallization from alcohol, it melted at 95.5–97°. The amide was hydrolyzed by boiling with 6 *N* hydrochloric acid for 24 hours. Some of the amide was transformed into a gum in this process and the yield of *p*-anisylamine (b. p. 132.8 to 134° at 33 mm.) was rather poor.

As has been previously pointed out the hydrolysis of benzylacetamide and substituted benzylacetamides is a slow process, although the reaction is much more rapid with hydrochloric acid than with alkalies. The presence of the methoxyl groups, however, complicates the hydrolysis by hydrochloric acid, and with the corresponding *o*- and *m*-compounds, methyl alcoholic sodium hydroxide at high temperature was used with much more satisfactory results.

Acetyl-*m*-methoxybenzylamine.—*m*-Anisic nitrile was prepared in good yield from *m*-anisidine by the Sandmeyer reaction; a colorless liquid, b. p. 111–112° at 12–13 mm. It readily crystallizes in an ice-bath to a mass of long needles. Reduction of the nitrile in acetic anhydride solution by the method already described yielded acetyl-*m*-methoxybenzylamine; b. p. 191–198° at 11 mm.; m. p. 58.5–59° (from ether and petroleum ether).

Anal. Calcd. for $C_{10}H_{13}O_2N$: N, 7.82. Found: 7.62.

***m*-Methoxybenzylamine.**—The amide was hydrolyzed by heating for seven hours with methyl alcoholic sodium hydroxide in a sealed tube at 140–150°. The solution was steam distilled, the distillate neutralized with hydrochloric acid, evaporated to dryness, treated with sodium hydroxide, etc. The amine was obtained as a colorless liquid; b. p. 131° at 26 mm., 140° at 37 mm.

Neutral equivalent. Calcd. for $C_8H_{11}ON$: 137.1. Found: 137.5.

The hydrochloride of this amine has been described by Curtius.[13]

Acetyl-*o*-methoxybenzylamine.[14]—This was prepared in the same way as the *m*-

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[11] Von Braun, *Ber.*, **44**, 2869 (1911).

[12] Carothers and Jones, This Journal, **47**, 3051 (1925).

[13] Curtius, *J. prakt. Chem.*, [2] **85**, 406, 436 (1912).

[14] Previously prepared by Goldschmidt and Ernst, *Ber.*, **23**, 2740 (1890).

compound, b. p. 176–178 at 8 mm.; white needles from benzene and dry ether, m. p. 95–96°. It is practically insoluble in dry ether.

Anal. Calcd. for $C_{10}H_{13}O_2N$: C, 67.04; H, 7.32; N, 7.82. Found: C, 67.27; H, 7.59; N, 7.71.

o-**Methoxybenzylamine**[14] was prepared by hydrolysis of the amide; b. p. 127–28° at 30 mm.

Anal. Calcd. for $C_8H_{11}ON$: N, 10.22. Found: 10.07.

Neutral equivalent. Calcd.: 137.1. Found: 137.9.

The secondary amines were prepared from the corresponding primary amines by transformation into the *p*-toluenesulfonyl derivatives, alkylation and hydrolysis. Benzyl- and β-phenethylamines are much more readily acylated than aromatic amines. Hence, when the usual procedure of employing a 50% excess of the sulfonyl chloride is followed, considerable disulfonyl derivative is formed. The yields are therefore better if only 10–20% excess of the *p*-toluenesulfonyl chloride is used. The sulfonamides were prepared by adding a benzene solution of *p*-toluenesulfonyl chloride to an ice-cold solution of the amine in aqueous alkali. Afterward the mixture was heated on a steam-bath for two hours, the benzene distilled off and the residue acidified.

As the writer has previously stated, the benzenesulfonyl and *o*-toluenesulfonyl derivatives of benzylamine, β-phenethylamine, etc., are not soluble in aqueous alkali, statements in the literature to the contrary notwithstanding. It was found, however, that these amides are soluble in aqueous alcoholic sodium hydroxide (33% water, 66% alcohol). The use of this solvent made it possible to separate the *p*-toluenesulfonyl derivative from the di-*p*-toluenesulfonyl derivative and so to obtain the former in a state of purity.

This solvent was also found to be the best medium for the alkylation of the amines. Methyl iodide was found to be a much better methylating agent for these compounds than dimethyl sulfate, and ethyl bromide was better than diethyl sulfate. The alkylated *p*-toluenesulfonamides were freed from any unalkylated material by crystallizing them first from the alcoholic sodium hydroxide, in which the unalkylated material is soluble. This precaution was necessary because the alkylation was never quite complete and the separation of unalkylated material by the usual solvents required repeated crystallization. The alkylated amides were crystallized to constant melting point and then hydrolyzed in the usual fashion by heating in sealed tubes to 180° with concd. hydrochloric acid.

Sulfonamides

N-Methyl-N-benzyl-*p*-toluenesulfonamide, *p*-$CH_3C_6H_4SO_2NCH_3CH_2C_6H_5$, hexagonal leaflets from alcohol, m. p. 94.4–94.8°.

Anal. Calcd. for $C_{15}H_{17}O_2NS$: S, 11.62. Found: 11.62, 11.40.

N-Ethyl-N-benzyl-*p*-toluenesulfonamide, *p*-$CH_3C_6H_4SO_2NC_2H_5CH_2C_6H_5$, needles from alcohol, m. p. 49–50°.

Anal. Calcd. for $C_{16}H_{19}O_2NS$: S, 11.08. Found: 11.11, 11.20.

N-Propyl-N-benzyl-*p*-toluenesulfonamide, *p*-$CH_3C_6H_4SO_2NC_3H_7CH_2C_6H_5$, m. p. 46–47°.

Anal. Calcd. for $C_{17}H_{21}O_2NS$: S, 10.57. Found: 10.60, 10.60, 10.73.

N-Methyl-N-β-phenethyl-*p*-toluenesulfonamide, $p\text{-}CH_3C_6H_4SO_2NCH_3CH_2CH_2\text{-}C_6H_5$, white crystals from ether-petroleum ether, m. p. 44–45°.

Anal. Calcd. for $C_{16}H_{19}O_2NS$: S, 11.08. Found: 11.04.

N-Di-*p*-toluenesulfonylbenzylamine, $(p\text{-}CH_3C_6H_4SO_2)_2NCH_2C_6H_5$, m. p. 161°.

Anal. Calcd. for $C_{21}H_{21}O_4NS_2$: S, 15.44. Found: 15.38.

N-Di-*p*-toluenesulfonyl-β-phenethylamine, $(CH_3C_6H_4SO_2)_2NCH_2CH_2C_6H_5$, m. p. 101°.

Anal. Calcd. for $C_{22}H_{23}O_4NS_2$: S, 14.94. Found: 14.93.

Summary

Data are presented on the preparation and on the base strengths of some amines.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE STRUCTURE OF THE HYDROCARBON $C_{17}H_{18}$ OBTAINED BY THE DEHYDRATION OF *TERT*.-BUTYLDIPHENYLCARBINOL

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Some time ago Schlenk and Racky[2] reported the preparation of tetraphenyldi-*tert.*-butylethane and asserted that this product was a stable hydrocarbon which did not show any of the characteristics of the hexaarylethanes. The recent work of Conant and his students[3] on derivatives of dixanthyl has shown that certain aliphatic groups substituted for the hydrogens of what might be considered the ethane carbons in dixanthyl have almost as great a tendency to cause dissociation into free radicals as do phenyl groups in these positions. It has been shown that di-*sec.*-butyldixanthyl is dissociated to about the same degree as diphenyldixanthyl. One might expect from analogy then that a *tert.*-butyl group would have a strong tendency to produce dissociation. It would appear that the compound described by Schlenk needs to be reinvestigated, especially since his conclusions rest on rather incomplete experimental results.

In reviewing the subject in the literature it was found that Schlenk prepared diphenyl-*tert.*-butylmethyl chloride from diphenyl-*tert.*-butyl carbinol and acetyl chloride and obtained a product which melted at

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[1] This communication is an abstract of a thesis submitted by Dorothy E. Bateman in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in Chemistry, at the University of Illinois.

[2] Schlenk and Racky, *Ann.*, **394**, 202, 211, 212 (1912).

[3] (a) Conant and Sloan, THIS JOURNAL, **47**, 572 (1925); (b) *ibid.*, **47**, 3068 (1925); (c) Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).