207° dec.; λ_{max} 261 mμ (sh., ε 5,480), 268 (sh. 4,560), 295 (2,470), 342–345 (2,420), 450–459 (1,520); λ_{min} 288 mμ (ε 2,360), 302–308 (2,230), 412 (1,290). The infrared spectrum showed absorption typical of ionic *p*-toluenesulfonate.

Anal. Calcd. for $C_{25}H_{20}O_3N_2Cl_4S$ (570.35): C, 52.65; H, 3.53; N, 4.91; Cl, 24.87. Found: C, 52.37; H, 3.70; N, 5.33; Cl, 25.31.

A small sample was crystallized from dimethylformamide and washed well with acetone. After the orange crystals had dried over Drierite *in vacuo* at 75° for 6 hr., they were further dried at 75° under a stream of dry nitrogen for 6 hrs.

Anal. Found: C, 52.42, H, 3.99; N, 5.01; Cl, 24.23.

Preparation of 7,8,9,10-tetrachloro-6,11-dihydrobenzo[b]-quinolizinium betaine (V) *from* IIc. A solution of 0.50 g. (0.89 millimole) of 3,4,5,6-tetrachloro-*o*-xylylene dipyridinium dibromide (IIc) in 30 ml. of methanol was added dropwise over 25 min. to a stirred solution of 0.50 g. (9.2 mmoles) of sodium methoxide in 40 ml. of methanol. The first drop turned the sodium methoxide solution pale yellow, and further addition caused color intensification from yellow to orange to red-orange. After 5 min. more stirring, the solution was stripped to dryness, and the red solid was slurry-washed with 25 ml. of water and dried. The 0.23 g. (79.3%) of red solid darkened above 200° but did not melt to 300°; λ_{max} 236 mμ (sh., ε 15,000), 267 (sh., 5,300), 354–360 (2,850), 378 (sh., 2,480), 447 (1,670), 472–474 (sh., 1,340); λ_{min} 308–312 mμ (ε 2,070), 437 (1,660); λ_{max}^{base} 360 mμ (ε 3,320), 378 (sh., 2,970), 410–412 (sh., 2,100), 446–450 (sh., 1,920), 472 (sh., 1,570); λ_{min}^{base} 300–303 mμ(ε 2,380); λ_{max}^{acid} 256 mμ (sh., ε 9,490), 267 (9,630), 297 (sh., 3,820), 375 (1,570), 399 (1,400), 420 (1,180); λ_{min}^{acid} 251 mμ (ε 9,230), 342–344 (1,340), 387 (1,330), 411 (1,120).

Anal. Calcd. for $C_{13}H_7NCl_4$ (319.04): C, 48.94; H, 2.21; N, 4.39. Found: C, 48.63; H, 2.41; N, 4.57.

The brick red solid was soluble in 48% hydrobromic acid, and in 36% or 3.6% hydrochloric acid.

A solution of 0.13 g. of V in 2.0 ml. of 48% hydrobromic acid was filtered and stripped to dryness. The residue was thoroughly dried, giving a brown solid which darkened but did not melt to 320°. The neutral ultraviolet absorption curve was the same as that of V in acid solution; λ_{max} 235 mμ (sh., ε 14,000), 256–257 (8,250), 266–268 (8,250), 296 (sh., 3,500), 312 (sh., 2,420), 376 (1,930), 399 (1,620), 423 (1,320).

Anal. Calcd. for $C_{13}H_8BrCl_4N \cdot H_2O$ (417.98): C, 37.36; H, 2.41. Found: C, 37.14; H, 2.83.

Probable preparation of o-xylylene-α-pyridinium-ylide-α'-pyridinium bromide (IVa) *and o-xylylene dipyridinium diylide from strong base treatment of* IIa. A solution of 3.00 g. (7.1 mmoles) of *o*-xylylene dipyridinium dibromide (IIa) in 20 ml. of methanol was added to a stirred solution of 3.84 g. (71 mmoles) of sodium methoxide in 30 ml. of methanol. The dark red solution was further stirred for 2 hr., and the dark purple-brown solution was stripped to dryness at reduced pressure. The residue was slurried with water, collected, and dried, giving 2.00 g. of brown solid decomposing 130–135°. The brown solid was swirled with 30 ml. of hot methanol and filtered. The insoluble material was washed again with hot methanol, leaving a small amount of brown solid (IVa) which darkened but did not melt to 300°. The material was too insoluble in alcohol to give a distinct ultraviolet absorption curve, but addition of hydrogen chloride caused a general hypsochromic shift.

Anal. Calcd. for $C_{18}H_{17}BrN_2$ (341.27): C, 63.35; H, 5.02; N, 8.21. Found: C, 63.81; H, 5.12; N, 8.47.

The methanol solution of the original slurry was diluted with an equal volume of water, and the precipitated solid was collected and dried: dec. 262–270°.

Anal. Calcd. for $C_{18}H_{16}N_2 \cdot 2H_2O$ (296.37): C, 72.95; H, 6.80; N, 9.45. Found: C, 71.70; H, 6.14; N, 9.01.

Acknowledgment. The author thanks Mr. Louis Dorfman and his associates for the microanalytical determinations.

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Equilibrium Constants for the Hydrolysis of Some *N*-Aryl-D-glucosylamines

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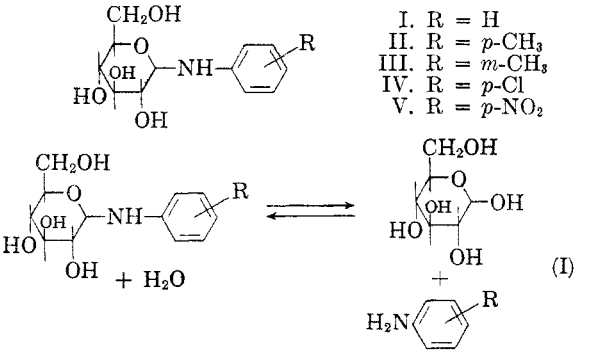
The relative stabilities of the *N*-aryl-D-glucosylamines in aqueous solutions have been studied by only a few workers.[1,2,3] Their results indicated that the extent of hydrolysis increased as the *p*H of the solution decreased and as the base strength of the parent aromatic amine increased.

The present work was concerned with the determination of the equilibrium constants for the hydrolysis of *N*-phenyl-(I), *N*-*p*-tolyl-(II), *N*-*m*-tolyl-(III), *N*-*p*-chlorophenyl-(IV), and *N*-*p*-nitrophenyl-D-glycosylamine (V). All of these compounds were prepared according to methods previously reported in the literature. The equilibrium constants for reaction I in aqueous ethanol were determined by polarimetric analysis of the solutions.



When dissolved in aqueous ethanol, *N*-phenyl-D-glucosylamine (I) underwent mutarotation and hydrolysis. The mutarotation caused a decrease while the slower hydrolysis reaction caused an increase in specific rotation. At a *p*H of 10.5 or greater, only the mutarotation reaction was observed and after fifty hours the specific rotation was constant at −71°. At a *p*H of 6.8, both reactions were noted and an extrapolation of the hydrolysis curve back to time zero indicated a specific rotation of −71°. In solutions of *p*H 5.4 or less, only the hydrolysis reaction was detected, apparently because mutaro-

(1) W. W. Pigman, E. A. Cleveland, D. H. Couch, and J. H. Cleveland, *J. Am. Chem. Soc.*, **73**, 1976 (1951).

(2) Eleanor Mitts and R. M. Hixon, *J. Am. Chem. Soc.*, **66**, 483 (1944).

(3) K. Hanaoka, *J. Biochem. (Japan)*, **28**, 109 (1938); **31**, 95 (1940).

tation had taken place before the first observation could be made. The hydrolysis curves in these more acidic solutions also extrapolated to a specific rotation of −71°. The curves of specific rotation against time are reproduced for these three cases in Fig. 1.

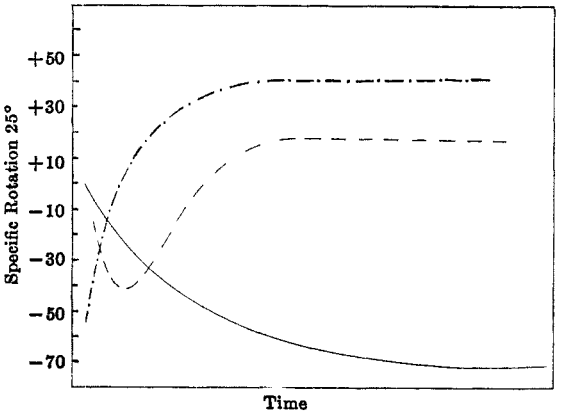


Fig. 1. Variation of specific rotation with time for *N*-phenyl-D-glucosylamine; ——— *p*H = 11, — — — *p*H = 7, — · — *p*H = 5

From these results we assumed that the constant specific rotation of *N*-phenyl-D-glucosylamine was −71° and that any positive deviation from this value was due to hydrolysis. The specific rotations of the remaining glycosylamines were determined in a similar manner and are listed in Table I.

TABLE I

SPECIFIC ROTATIONS OF GLUCOSYLAMINES (25°)[a]

Glucosylamine	$[\alpha]_D^{25}$
N-Phenyl (I)	−71°
N-*p*-Tolyl (II)	−60°
N-*m*-Tolyl (III)	−75°
N-*p*-Chlorophenyl (IV)	−66°
N-*p*-Nitrophenyl (V)	−60°

[a] All rotations were taken in 2-D tubes with concentrations from 2×10^{-2} to $8 \times 10^{-2} M$. The solvent was 41% ethanol in water.

The acid dissociation constants of the anilinium ions necessary for the calculation of the equilibrium values were those determined by Gutbezahl and Grunwald[4] except for *p*-chloro- and *p*-nitroaniline, and the constants for these were estimated from a log K_a −σ-plot of the values obtained by those workers.

Calculations and results. In all of the calculations activity coefficients were assumed to be unity; solutions used were from 2 to $8 \times 10^{-2} M$ in glucosylamine, and the ionic strength of the buffer was $0.05M$. Hydrogen ion activities were determined by a glass electrode.

The optical rotation of a glucosylamine solution at equilibrium is given by the equation:

$$\alpha_{equil} = l\left[\frac{(180.2)(\alpha_g^{25})(g) - (n)(\alpha_{ga}^{25})(GA_0 - g)}{1000}\right] \quad (1)$$

where l is the tube length in decimeters, GA_0 the initial concentration of glucosylamine, α_{ga}^{25} the specific rotation of glucosylamine at 25°, α_g^{25} the specific rotation of glucose at 25°, n the molecular weight of glucosylamine, and g the concentration of glucose.

At equilibrium, the concentration of glucose is equal to the sum of the concentrations of the aniline (a) and its ion, or in terms of the dissociation constant of the ion (K_a),

$$g = a\left[\frac{H^{\oplus} + K_a}{K_a}\right] \quad (2)$$

which substituted into the equation for the hydrolysis equilibrium yields:

$$K_{eq} = \frac{(g)^2(K_a)}{(GA_0 - g)(H^{\oplus} + K_a)} \quad (3)$$

The equilibrium constants calculated from Equations 3 and 1 for the compounds studied appear in Table II.

TABLE II

EQUILIBRIUM CONSTANTS: HYDROLYSIS OF ARYL-D-GLUCOSYLAMINES IN AQUEOUS ETHANOL (25°)[a]

Glucosylamine	*p*H Range		$K_a \times 10^2$
N-Phenyl (I)	4–5		10.1 ± 1.6 (12)
	5–6		8.5 ± 1.2 (5)
	6–7		8.3 ± 1.0 (2)
		Av.	9.5 ± 1.6 (19)
N-*p*-Tolyl (II)	4–5		9.8 ± 2.0 (2)
	5–6		8.4 ± 0.9 (5)
	6–7		7.4 ± 0.3 (3)
	7–8		7.8 ± 0.1 (3)
		Av.	8.2 ± 1.0 (13)
N-*m*-Tolyl (III)	5–6		8.7 ± 1.0 (5)
	6–7		11.4 ± 2.5 (2)
	7–8		8.5 ± 2.5 (3)
		Av.	9.2 ± 1.8 (10)
N-*p*-Chlorophenyl (IV)	3–4		10.1 ± 2.0 (2)
	5–6		8.3 ± 0.2 (2)
		Av.	9.2 ± 1.4 (4)
N-*p*-Nitrophenyl (V)	5–6		8.0 ± 0.2 (2)
	6–7		8.1 ± 0.2 (7)
	7–8		9.0 ± 0.5 (3)
		Av.	8.3 ± 0.5 (12)

[a] The numbers in parentheses indicate the number of determinations used for average given.

While the equilibrium constants in Table II are not sufficiently accurate to detect small trends due to *p*H of the solution or *pK* of the amine, they do demonstrate that there are no large variations due to these factors.

Both Pigman and co-workers[1] and Mitts and Hixon[2] demonstrated that the extent of hydrolysis (defined as the final divided by the initial glucosylamine concentration) was a function of the *p*H and basicity of the anilines formed. Our work is consistent with this observation. It may be seen from Equation 3 that an increase in hydrogen ion will

(4) Boris Gutbezahl and Ernest Grunwald, *J. Am. Chem. Soc.*, 75, 559 (1953).

cause an increase in the concentration of glucose at the expense of the glucosylamine and, at any *p*H, a decrease in K_a (increase in base strength of amine) will cause a corresponding increase in the concentration of glucose, again at the expense of the glucosylamine. Thus, we found that the position of the equilibrium (extent of hydrolysis)was a function of *p*H (Fig. 2) and the base strength of the amine (Fig. 3), but that the equilibrium constant was essentially unaffected by these factors.

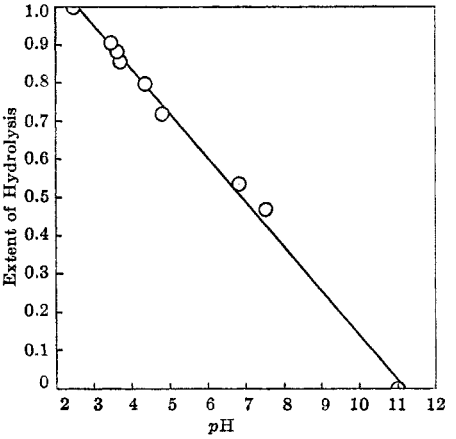


Fig. 2. Variation of extent of hydrolysis of *N*-phenyl-D-glucosylamine with *p*H. Glucosylamine concentration was $3.9 \times 10^{-2}M$

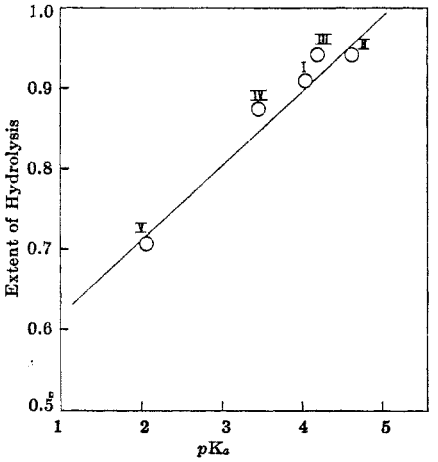


Fig. 3. Variation of extent of hydrolysis of glucosylamine with K_a of parent aniline. Numerals refer to compounds in Table I. The *p*H of all solutions was 3.5

EXPERIMENTAL

Preparation of glucosylamines. *N*-Phenyl-D-glucosylamine (I) was prepared by the method of Irvine and Gilmour,[5] *N*-*p*-tolyl-(II) and *N*-*m*-tolyl-(III) according to Ellis and Honeyman,[6] and *N*-*p*-chlorophenyl-(IV) and *N*-*p*-nitrophenyl-(V) by the method of Ellis and Honeyman[6] with the reflux time increased to 6 hr. All glucosylamines were recrystallized from ethanol or ethanol-ether and dried in vacuum.

(5) J. C. Irvine and R. Gilmour, *J. Chem. Soc.*, **93**, 1545 (1909).

(6) G. P. Ellis and J. Honeyman, *J. Chem. Soc.*, 1490 (1952).

Solvent. The solvent was prepared by mixing equal volumes of redistilled 95% ethanol and water. Portions of solvent were buffered to the desired *p*H with the systems hydrochloric acid–potassium acid phthalate, sodium hydroxide–potassium acid phthalate, sodium hydroxide–monopotassium phosphate, or acetic acid–sodium acetate. In all cases the ionic strength of the buffer solutions was $0.05M$.

Procedure. Samples of glucosylamine (approximately 3.0×10^{-3} to 8.0×10^{-3} moles) were weighed into flasks and diluted to exactly 100 ml. with the appropriate solvent. The solutions were brought to 25°, and their rotations determined with a Schmidt and Haensch Model 14174 polarimeter in 2-decimeter tubes maintained at 25°. The solutions were stored at 25.0° ± 0.5° and their rotations determined periodically until the observed rotation changed less than 0.01° in 48 hr.[7] The *p*H of the equilibrated solutions were determined on a Beckman Model G *p*H meter standardized against Coleman standards of *p*H 4 and 7.

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Preparation of Some Substituted Biphenylsulfonic Acids

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While there is extensive literature on the sulfonation of biphenyl,[1-6] no information is to be found on the direct monosulfonation of the substituted biphenyls reported herein. The present work stems from the development of a convenient procedure for the specific monosulfonation of biphenyl. It was found that 4-biphenylsulfonic acid is much less soluble in chloroform than is biphenyl, so that by taking advantage of this solubility difference, it was possible to preclude any further reaction by precipitation of the monosulfonic acid.

(7) Difficulty was encountered in determining rotations of some acidic solutions because of discoloration with time.

(1) J. Pollak, M. Heimberg-Krauss, E. Katscher, and O. Lustig, *Monatsh.*, **55**, 358 (1930); *Chem. Abstr.*, **24**, 4004 (1930).

(2) R. Fusco and L. Renieri, *Gazz. chim. ital.*, **78**, 435 (1948); *Chem. Abstr.*, **43**, 1033f (1949).

(3) J. Rahm and F. Juračka, *Chem. listy*, **50**, 837 (1956); *Chem. Abstr.*, **50**, 15475f (1956).

(4) C. R. McCullough, U. S. Patent 1,865,776.

(5) W. C. Stoessner and R. F. Marschner, U. S. Patents 1,942,386; 1,981,337.

(6) R. L. Jenkins, U. S. Patent 2,368,361.