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.

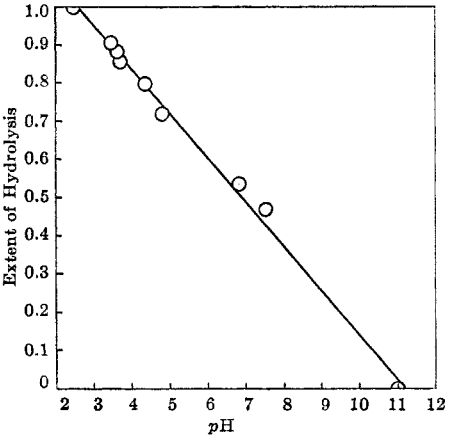

Fig. 2. Variation of extent of hydrolysis of *N*-phenyl-D-glucosylamine with *p*H. Glucosylamine concentration was $3.9 \times 10^{-2}M$

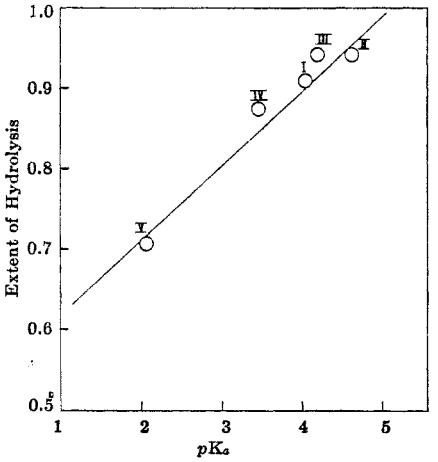

Fig. 3. Variation of extent of hydrolysis of glucosylamine with K_a of parent aniline. Numerals refer to compounds in Table I. The *p*H of all solutions was 3.5

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).

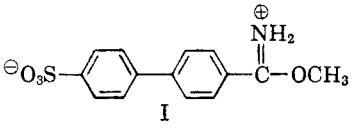
(4) C. R. McCullough, U. S. Patent 1,865,776.

(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.

Substituted biphenyls could be sulfonated in a similar manner, the procedure differing mainly in the quantity of chloroform solvent employed. It is expected that in the bromo-, nitro-, and cyanobiphenyls, sulfonation would occur only in the more active, unsubstituted ring in the 4′-position. In 4-methyl- and 4-*t*-butylbiphenyl structural assignments are less certain but on the basis of infrared spectra and from steric considerations 4′-substitution also might well be favored.

In the sulfonation of 4-biphenylcarbonitrile it was found that the first mole of chlorosulfonic acid was consumed in complex formation with the nitrile group and only on addition of a second mole of chlorosulfonic acid did sulfonation occur. In order to destroy the excess chlorosulfonic acid present after the completion of this reaction, methanol was added, which resulted in the formation of the zwitterion form of methyl 4′-biphenylimidoate-4-sulfonic acid (I).



I

EXPERIMENTAL[7]

4-Biphenylsulfonic acid. To a stirred solution of 154 g. (1 mole) of biphenyl in 850 ml. of chloroform was slowly added 144 g. (1.237 mole) of chlorosulfonic acid in 125 ml. of chloroform. (The excess chlorosulfonic acid was used to react with the ethanol present as a stabilizer in the chloroform.) During the course of the addition, a temperature increase of 15° was noted. After addition of about 75% of the chlorosulfonic acid, precipitation of 4-biphenylsulfonic acid began. The suspension was stirred for 30 min. after the completion of addition of the chlorosulfonic acid. The precipitate was filtered (sintered glass funnel), washed with 500 ml. of chloroform, and dried, yielding 187 g. (80%) of 4-biphenylsulfonic acid, m.p. 138–140° (lit.[1] m.p. 138°).

Anal. Calcd. for $C_{12}H_{10}SO_3$: S, 13.68. Found: S, 13.91, 13.91.

A second crop (about 15%) of less pure 4-biphenylsulfonic acid could be obtained from the mother liquor.

4′-Bromobiphenyl-4-sulfonic acid was prepared as described for 4-biphenylsulfonic acid except that 2 l. of chloroform was used per mole of 4-bromobiphenyl; yield 97%, m.p. 157–158°.

Anal. Calcd. for $C_{12}H_9BrO_3S$: C, 46.02; H, 2.89; Br, 25.53. Found: C, 45.30, 45.46; H, 3.04, 3.34; Br, 25.33, 25.41.

A copper salt was prepared in 75% yield.

Anal. Calcd. for $[C_{12}H_8BrO_3S]_2Cu\cdot{}^1/_2\ H_2O$: C, 41.36; H, 2.46; Br, 22.93; S, 9.20; Cu, 9.12. Found: C, 41.30, 41.56; H, 2.55, 2.76; Br, 22.93, 22.83; S, 9.42; Cu, 9.20.

2′-Bromobiphenyl-4-sulfonic acid. To a solution of 11.6 g. (0.05 mole) of 2-bromobiphenyl in 25 ml. of chloroform was slowly added 6.6 g. (0.056 mole) of chlorosulfonic acid in 25 ml. of chloroform. After stirring at 25° for 1 hr., 25 ml. of hexane was added and the resulting precipitate was filtered, washed with hexane, and vacuum dried yielding 13.5 g. (86%) of 2′-bromobiphenyl-4-sulfonic acid, m.p. 58–62°, very hygroscopic. A sample was recrystallized from methylene chloride–hexane and then from carbon tetrachloride, m.p. 62–64°. A sample was dried (Abderhalden) at 25° and 0.5 mm. for 24 hr. and submitted for analysis.

Anal. Calcd. for $C_{12}H_9BrO_3S\cdot 2.5\ H_2O$: C, 40.23; H, 3.92. Found: C, 40.39; 39.91, 40.57; H, 4.35, 4.07, 3.96.

A copper salt was prepared in 86% yield.

Anal. Calcd. for $[C_{12}H_8BrO_3S]_2Cu\cdot 2H_2O$: C, 39.82; H, 2.78; Br, 22.08; S, 8.86; Cu, 8.77. Found: C, 40.06, 40.16; H, 2.84, 3.11; Br, 22.42, 22.09; S, 8.73, 8.73; Cu, 8.58, 8.57.

4′-Nitrobiphenyl-4-sulfonic acid was prepared as described for 4-biphenylsulfonic acid in 99% yield, m.p. 148–149.5° dec. A sample was purified for analysis by precipitation from aqueous solution by acidification with concentrated hydrochloric acid, m.p. 149–150°.

Anal. Calcd. for $C_{12}H_9NSO_5$: C, 51.60; H, 3.25; S, 11.47; N, 5.01. Found: C, 51.16; H, 3.87; S, 10.97; N, 4.60.

A silver salt was prepared in 38% yield.

Anal. Calcd. for $C_{12}H_8NSO_5Ag\cdot{}^1/_2\ H_2O$: Ag, 27.30. Found: Ag, 27.05; 27.25.

4′-Methylbiphenyl-4-sulfonic acid was prepared as described for 4-biphenylsulfonic acid in 82% yield, m.p. 166–168°, infrared band at 807 cm.$^{-1}$ in Nujol, characteristic of 1,4-aromatic substitution.[8]

Anal. Calcd. for $C_{13}H_{12}SO_3\cdot H_2O$: C, 58.62; H, 5.29; S, 12.04. Found: C, 58.28, 58.13; H, 5.36, 5.29; S, 12.15, 12.21.

A copper salt was prepared in 90% yield.

Anal. Calcd. for $[C_{13}H_{11}SO_3]_2Cu\cdot H_2O$: C, 54.20; H, 4.19; S, 11.13; Cu, 11.03. Found: C, 54.30, 54.43; H, 4.50, 4.60; S, 11.15, 11.17; Cu, 10.70, 10.81.

4′-t-Butylbiphenyl-4-sulfonic acid was prepared as described for 2′-bromobiphenyl-4-sulfonic acid in 91% yield, m.p. 127–129°, infrared band at 820 cm.$^{-1}$ in Nujol, characteristic of 1,4-aromatic substitution.[8]

Anal. Calcd. for $C_{16}H_{18}O_3S\cdot H_2O$: C, 62.31; H, 6.53; S, 10.40. Found: C, 62.02; H, 6.76; S, 10.68.

A copper salt was prepared in 95% yield.

Anal. Calcd. for $[C_{16}H_{17}O_3]_2Cu\cdot 3H_2O$: C, 55.17; H, 5.78; S, 9.21; Cu, 9.13; H_2O, 7.76. Found: C, 55.35, 55.23; H, 6.02, 6.05; S, 9.15, 8.97; Cu, 9.09, 9.05; H_2O, 7.25, 7.39.

Methyl-4′-biphenylimidoate-4-sulfonic acid (I). To a solution of 17.9 g. (0.1 mole) of 4-biphenylcarbonitrile in 60 ml. of chloroform was added 24.5 g. (0.21 mole) of chlorosulfonic acid in 15 ml. of chloroform. The mixture was stirrred at 25° for 2.5 hr. An oily solid separated from the chloroform solution. The chloroform was decanted and the residual solid dissolved in 25 ml. of methanol. Ether (75 ml.) was added and the resulting bright yellow solid was filtered, washed with ether, and dried, yielding 17.5 g. (68%) of methyl-4′-biphenylimidoate-4-sulfonic acid (I), m.p. 238–240°, infrared bands at 1670 cm.$^{-1}$, characteristic of the $\diagdown C{=}N- \diagup$ linkage,[9] and at 1165 and 1030 cm.$^{-1}$ in Nujol, characteristic of the $-SO_2-O-$ group.[10]

Anal. Calcd. for $C_{14}H_{13}NO_4S$: C, 57.71; H, 4.70; N, 4.81; S, 11.01. Found: C, 56.95; 57.10; H, 4.39, 4.68; N, 4.98, 4.96; S, 10.88, 10.74.

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(7) All melting points are corrected. Analyses are by Mr. E. M. Hubbard and associates or by Galbraith Laboratories, Knoxville, Tenn. Samples for analysis were dried in an Abderhalden apparatus at 80° and 0.5 mm. for 16 to 24 hr.

(8) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1954, p. 67.

(9) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1954, p. 227.

(10) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1954, pp. 300–1.