The preparation of the phosphonic and phosphinic acids has been reported recently.[2]

(2) G. O. Doak and L. D. Freedman, THIS JOURNAL, **74**, 753 (1952); L. D. Freedman and G. O. Doak, *ibid.*, **74**, 2884 (1952).

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Effect of N-Monosubstitution on the Basic Properties of Ethylenediamine[1]

BY R. N. KELLER[2] AND L. J. EDWARDS

RECEIVED FEBRUARY 6, 1952

Introduction

In connection with the determination of formation constants of complex ions containing various diamine ligands, it became necessary to know the consecutive dissociation constants for the two acid ions of the diamines. The results are reported here since the majority of these constants have not previously been determined. Furthermore, in view of the fact that most of the diamines are derivatives of ethylenediamine by N-monosubstitution, these dissociation constants reflect qualitatively the effect of substitution on the basic character of the nitrogen atoms.

Experimental

Aqueous solutions of the purified diamines[3] were standardized against hydrochloric acid. Precautions were taken to eliminate absorption of carbon dioxide during the titrations.

The consecutive dissociation constants of the acid ions of the diamines were determined by the method suggested by Bjerrum.[4] The titrations of standard solutions (*ca.* 0.15 *M*) of hydrochloric acid 1.0 molar in potassium chloride and 0.1 molar in barium chloride[5] by known quantities of the diamines were followed by means of *p*H measurements at 25° with a hydrogen electrode. Two platinized platinum electrodes were employed as a means of checking the potential. In general these electrodes were in good agreement; when the readings began to diverge, new electrodes were substituted. The calomel electrode was connected to the titration flask through a saturated potassium chloride–agar salt bridge. Immediately before and after each titration, the potential attributed to the calomel electrode was determined by measuring a standard acid solution of defined hydrogen ion concentration (0.005 *N*) and the same chloride concentration as the metal salt solutions titrated. The *p*H values from the above measurements were then used in computing the pK values for the dissociation constants of the acid ions of the diamines.

Results

Table I contains a summary of the values for the pK's and the corresponding equilibrium constants for the two acid ions of the eight diamines investigated.. From the data of this table it appears that N-monoalkyl substitution in the ethylenediamine molecule has only a slight influence on the values of the dissociation constants of the acid ions. N-Monoalkylol substitution, on the other hand, increases the acid strengths of both these ions. It is well established that monoalkyl substitution in the ammonia molecule results in an increase in basicity of the nitrogen. Reasoning by analogy, then, the constant K_{AH_2} presumably refers to the ionization of the proton which is on the primary amino group in an N-monoalkyl substituted ethylenediamine. On the contrary, replacing one hydrogen in ammonia with an OH group (*i.e.*, hydroxylamine) brings about a marked lowering of the basicity of the nitrogen.[6] Therefore, in the case of the hydroxyethylenediamines the dissociation constants can be identified with a particular amino group with much less certainty. In fact, the nitrogen on which substitution has taken place may now be the one of lesser basicity. However, an unqualified conclusion seems unwarranted from these data alone.

TABLE I

pK AND K VALUES FOR THE DISSOCIATION OF THE ACID IONS OF DIAMINES IN SOLUTIONS 1 MOLAR IN KCl AND 0.1 MOLAR IN $BaCl_2$

Diamine	pK_{AH_2}	pK_{AH}	$K_{AH_2} \times 10^8$	$K_{AH} \times 10^{10}$
$NH_2CH_2CH_2NH_2$[a]	7.44	10.17	3.63	0.676
$NH_2CH_2CH_2NHCH_3$	7.42	10.32	3.80	0.48
$NH_2CH_2CH_2NHCH_2CH_3$	7.42	10.36	3.80	0.437
$NH_2CH_2CH_2NHCH_2CH_2OH$	6.83	9.82	14.8	1.52
$NH_2CH_2CH_2NHCH_2CH(OH)CH_3$	6.94	9.86	11.5	1.38
$NH_2CH_2CH_2NHCH_2CH_2CH_2OH$	6.78	9.67	16.6	2.14
$NH_2CH_2CH(NH_2)CH_3$[b]	7.10	9.97	7.95	1.07
$NH_2CH_2CH(OH)CH_2NH_2$	7.94	9.57	1.15	2.70

[a] The following values were obtained for ethylenediamine by Bjerrum (ref. 4, p. 207) in 1 *M* KCl and 0.1 *M* $BaCl_2$ at 30° by means of the hydrogen electrode: $pK_{AH_2} = 7.34$ and $pK_{AH} = 10.08$. G. A. Carlson, J. P. McReynolds and F. H. Verhoek (THIS JOURNAL, **67**, 1334 (1945)) using the glass electrode and in the presence of 1 *M* KCl and 0.05 *M* $BaCl_2$ at 30° obtained the values 7.19 and 9.92. [b] Carlson, *et al.* (footnote *a*), in the presence of 0.5 *M* KCl and 0.05 *M* $BaCl_2$ at 30° and using the glass electrode obtained values for propylenediamine of 7.07 and 9.83 for pK_{AH_2} and pK_{AH}, respectively.

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(1) From the Ph.D. Thesis of L. J. Edwards, University of Michigan, June, 1950.

(2) Department of Chemistry, University of Colorado, Boulder, Colorado.

(3) R. N. Keller and L. J. Edwards, THIS JOURNAL, **74**, 215 (1952).

(4) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

(5) For subsequent titrations in which the values for the constants determined here were made use of, complex-forming metal ions replaced the barium ions.

(6) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 98.

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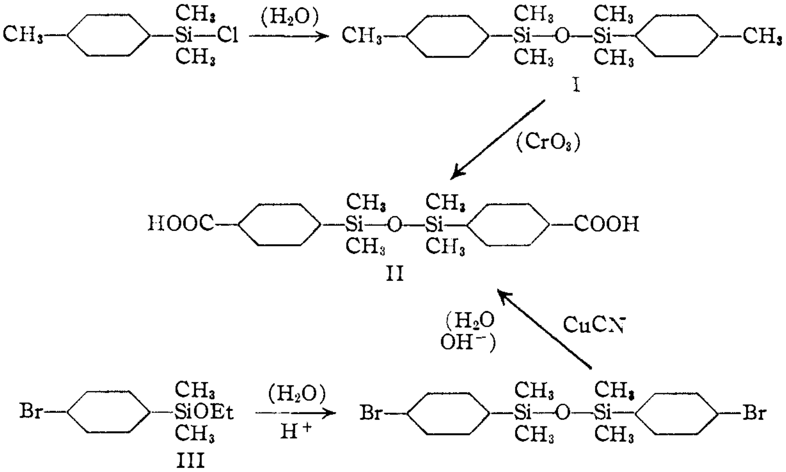
The Oxidation of Tetramethyl-1,3-bis-(*p*-tolyl)-disiloxane to 1,3-Bis-(*p*-carboxyphenyl)-tetramethyldisiloxane

BY DANIEL W. LEWIS AND GORDON C. GAINER

RECEIVED NOVEMBER 29, 1951

In connection with certain studies on substituted arylsilicon compounds, it seemed of interest to prepare some carboxyphenyl-substituted siloxanes. Several orienting experiments involving application of the usual oxidizing procedures to *p*-tolyl-containing organosilicon compounds indicated that a mild oxidation was required, lest the carbon–silicon bond be also attacked. During the course of these investigations, there was reported the oxidation of 2-acetyl-5-trimethylsilylthiophene to (5-trimethylsilyl-2-thienyl)-glyoxal monohydrate,[1] using selenium dioxide. We have found that tetramethyl-1,3-bis-(*p*-tolyl)-disiloxane (I) may be oxidized directly to 1,3-bis-(*p*-carboxyphenyl)-tetramethyldisiloxane (II) by use of chromic acid in acetic acid–acetic anhydride medium at low temperature. Normally, this procedure yields the aldehyde diacetate when applied, for example, to *p*-nitrotoluene.[2]

As a proof of structure, the silicon-containing acid (II) was prepared by an alternate synthesis. The following equations illustrate the reactions involved.



The *p*-bromophenyldimethylethoxysilane (III) required for the structure proof was synthesized in poor yield by the reaction of *p*-dibromobenzene with dimethyldiethoxysilane in the presence of magnesium. The other products formed in the reaction are being studied and will be reported in another paper.

Experimental

Dimethyl-*p*-tolylchlorosilane.—One liter of an ethereal solution containing one mole of *p*-tolylmagnesium bromide was added dropwise with stirring to 210 g. (1.63 moles) of dimethyldichlorosilane. The supernatant liquid was then poured from the salts which had formed and the latter were washed with several portions of dry ether. After distillation of solvent and unreacted dimethyldichlorosilane, vacuum was applied and 122.2 g. (66%) of product boiling at 90° (10 mm.) was obtained. The latter was fractionally distilled on a laboratory column and had the constants: b.p. 130–131° (40 mm.), n^{25}_D 1.5055, d^{25}_4 1.0071.[3]

Anal. Calcd. for $C_9H_{13}ClSi$: Cl, 19.24. Found: Cl, 19.15.

Dimethyl-*p*-tolylethoxysilane.—An ether solution containing 3 moles of *p*-tolylmagnesium bromide was added dropwise with stirring to 592 g. (4 moles) of dimethyldiethoxysilane. The ether solution was then decanted from the sirupy salts which had formed. After removal of ether and unreacted dimethyldiethoxysilane, vacuum was applied and there was obtained 307 g. (53%) of product boiling at 48–50° (1–2 mm.), n^{25}_D 1.4811, d^{26}_4 0.9134.

Anal. Calcd. for $C_{11}H_{18}OSi$: Si, 14.43. Found: Si, 14.22.

Tetramethyl-1,3-bis-(*p*-tolyl)-disiloxane (I).—One hundred and six grams (0.57 mole) of dimethyl-*p*-tolylchlorosilane (the corresponding ethoxysilane may be used) was hydrolyzed by rapid stirring for one hour with 120 ml. of 5% sulfuric acid. After separating the organic layer, complete condensation was effected by similar treatment with 120 ml. of 75% sulfuric acid. Ice was added and the organic layer was extracted with toluene and washed several times with distilled water. The extract was then dried and distilled. The product, obtained in quantitative yield, boiled at 143–144° (1 mm.), and had the following constants: n^{25}_D 1.5135, d^{25}_4 0.9651.

Anal. Calcd. for $C_{18}H_{22}OSi_2$: C, 68.79; H, 8.28; Si, 17.84. Found: C, 68.66; H, 8.36; Si, 17.57.

***p*-Bromophenyldimethylethoxysilane** (III).—A solution consisting of 6600 g. (28 moles) of *p*-dibromobenzene, 6216 g. (42 moles) of dimethyldiethoxysilane and 14 l. of anhydrous ether was added with stirring to an anhydrous ether slurry containing 973 g. (40 g. atoms) of magnesium turnings. The addition required several days and was run at the reflux temperature of the mixture (*ca.* 45°). At the end of each day, the slurry was stirred and refluxed overnight. Upon completion of the reaction, the granular salts which had formed were allowed to settle and the product was drawn off. The salts were washed with several portions of ether, and the latter added to the main product. After removal of solvent together with a small amount of dimethyldiethoxysilane, vacuum was applied. Approximately 4 l. of distillate was obtained which boiled over the range 76–98° (2 mm.). Fractional distillation on a Podbielniak column yielded 965 g. (13.3%) of product which boiled at 148° (34 mm.), n^{25}_D 1.5131, d^{25}_4 1.2212.

Anal. Calcd. for $C_{10}H_{15}OBrSi$: C, 46.33; H, 5.80; Br, 30.88. Found: C, 46.70; H, 5.91; Br, 30.68.

***p*-Bromophenyldimethylchlorosilane.**—Two liters of Grignard reagent prepared by the reaction of 472 g. (2 moles) of *p*-dibromobenzene with 55 g. (2.26 g. atoms) of magnesium shavings was added with stirring to 387 g. (3 moles) of dimethyldichlorosilane. The resulting slurry was filtered (sintered glass funnel) from the salts which had formed. Ether and unreacted dimethyldichlorosilane were removed by distillation. Further filtration was required to remove the salts which had precipitated. The filtrate was distilled to yield 324 g. (65%) of product which boiled over the range 60–110° (1–2 mm.). This liquid was fractionally distilled on a two-foot packed laboratory column and yielded 232 g. (46.5%) of product boiling at 135.5° (18 mm.), n^{25}_D 1.5438, d^{25}_4 1.3904.

Anal. Calcd. for $C_8H_{10}BrClSi$: Cl, 14.22. Found: Cl, 14.27.

1,3-Bis-(*p*-bromophenyl)-tetramethyldisiloxane.—One hundred and forty grams (0.54 mole) of *p*-bromophenyldimethylethoxysilane dissolved in 115 ml. of benzene was added to 200 ml. of 75% sulfuric acid. The mixture was stirred for 3 hours. Crushed ice was added and the organic layer was separated, washed several times with water, and dried over anhydrous sodium sulfate. After removal of solvent, 111 g. (92%) of product was distilled under vacuum, and boiled at 119–121° (0.07 mm.), n^{25}_D 1.5550, d^{25}_4 1.3641.

Anal. Calcd. for $C_{16}H_{20}OBr_2Si_2$: Br, 36.03; Si, 12.61. Found: Br, 35.68; Si, 12.49.

When the compound was prepared from *p*-bromophenyldimethylchlorosilane, the yield was 72%.

1,3-Bis-(*p*-cyanophenyl)-tetramethyldisiloxane.—A mixture of 73 g. (0.16 mole) of 1,3-bis-(*p*-bromophenyl)-tetramethyldisiloxane, 21.4 g. (0.33 mole) of potassium cyanide, 9.0 g. (0.10 mole) of cuprous cyanide and 9.0 g. (0.14 g. atoms) of copper powder was stirred and heated to 275–300° for 10 hours. The liquid was decanted, washed with water and extracted with ether. After drying and removing ether, 22 g. (24%) of product boiling at 190–200° (1–2 mm.) was

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(1) R. A. Benkeser and H. Landesman, THIS JOURNAL, **71**, 2493 (1949).

(2) S. V. Lieberman and R. Connor, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 441.

(3) These data are inconsistent with the constants reported by Barry and Gilkey, U. S. Patent, 2,500,652 (1950). They report the formation of the compound by the catalyzed reaction of toluene with trimethylchlorosilane at 400° and give a b.p. of 110–114° (30 mm.), sp. gr. 1.133 at 20.4°. No analyses are given.

obtained. The liquid had the following constants: $n^{25}\text{D}$ 1.5351, $d^{25}{}_4$ 1.0460.

Anal. Calcd. for $C_{18}H_{20}ON_2Si_2$: N, 8.33. Found: N, 8.07.

1,3-Bis-(*p*-carboxyphenyl)-tetramethyldisiloxane (II) A. From **Tetramethyl-1,3-bis-(*p*-tolyl)-disiloxane.**—Eleven grams (0.035 mole) of tetramethyl-1,3-bis-(*p*-tolyl)-disiloxane was dissolved in a mixture of 114 ml. of glacial acetic acid and 114 ml. of acetic anhydride. After cooling to −5° (ice–salt-bath) 17 ml. of concentrated sulfuric acid was added dropwise with stirring. The temperature was not permitted to exceed 5°. Then 20 g. (0.20 mole) of finely ground chromium trioxide was added with vigorous stirring. After stirring for 1 hour at 12°, the solution was poured onto excess chopped ice. A white precipitate separated. The latter was filtered off and washed several times with distilled water. The crude product weighed 10.5 g. (63%) and melted at 236–240°. After charcoal treatment and several crystallizations from dry acetone, the compound melted at 241–242°. The neutral equivalent was 193.

Anal. Calcd. for $C_{18}H_{22}O_5Si_2$: C, 57.80; H, 5.89; Si, 14.98. Found: C, 57.75; H, 5.83; Si, 15.22.

B. From **1,3-Bis-(*p*-cyanophenyl)-tetramethyldisiloxane.**—A mixture of 2 g. of 1,3-bis-(*p*-cyanophenyl)-tetramethyldisiloxane and 25 ml. of 2% sodium hydroxide was refluxed for 2 hours. On cooling and acidifying the solution, a white solid precipitated. The latter was repeatedly extracted with hot water to remove benzoic acid. The remaining solid was crystallized twice from acetone and melted at 239–241°.

A mixed melting point determination involving this material and the compound described under A showed no depression.

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A Possible Explanation of the Anomalous Substitution Behavior of Iodine Monobromide

BY D. E. PEARSON AND C. J. ROSS

RECEIVED DECEMBER 29, 1951

From a theoretical viewpoint, iodine monobromide ($\overrightarrow{\text{IBr}}$) should be an iodinating agent in organic nuclear substitution. Militzer[1] has found that it is actually a brominating agent for phenol, naphthalene and 1-naphthol. This apparent anomaly is now incorporated in recent text-books on mechanisms of organic reactions.[2,3] Bennett and Sharpe[4] believe that iodine monobromide dissociates to iodine and bromine and that iodine-catalyzed bromination is the fastest of the reactions possible. Lambourne and Robertson[5] believe that the reaction is an iodine monobromide-catalyzed bromination.

An interesting observation has been made in this Laboratory which provides an alternate and possibly more attractive explanation. It has been found that hydrogen bromide exchanges with *p*-iodophenol at a rate comparable to the substitution reactions of Militzer[1]

$$2p\text{-}IC_6H_4OH + HBr \longrightarrow p\text{-}BrC_6H_4OH + C_6H_5OH + I_2$$

The above over-all equation may proceed *via* two different routes

$$p\text{-}IC_6H_4OH + HI \longrightarrow C_6H_5OH + I_2$$

or

$$p\text{-}BrC_6H_4OH + 2\,HI \longrightarrow C_6H_5OH + I_2 + HBr$$

Though the first route seems more likely, both lead to the products of the over-all equation.

This observation of the halogen interchange suggests that iodine monobromide may be an iodinating agent, as it should be, but that stability relationships of the theoretical products, *p*-iodophenol and hydrogen bromide (or intermediates leading to these products), favor the formation of *p*-bromophenol.

It was also found that hydrogen chloride did not react appreciably with *p*-iodophenol under similar conditions.

Experimental[6]

p-Iodophenol[7] (8 g., 0.036 mole, m.p. 92–94°) was dissolved in 100 ml. of alcohol-free chloroform contained in a 200-ml. flask, equipped with gas-inlet tube, condenser and drying tubes. Hydrogen bromide (Matheson Co.) was passed through a U-tube containing phenol (to remove elemental bromine) and through a calcium chloride tube, and was then led directly into the chloroform solution, maintained at 45 ± 2°. The rate of flow was approximately one bubble per 15–30 sec., probably sufficient to maintain saturation (calculated as less than 0.05 mole HBr per 100 ml. of chloroform).[8] After 85 minutes, the time of maximum color development, the solution was cooled, washed with 25 ml. of water containing 4 g. of sodium bisulfite, with 20 ml. of water saturated with sodium bicarbonate, and was then dried with anhydrous sodium sulfate. After removing the chloroform, the mixed phenols were distilled at reduced pressure in a 15-ml. flask with a 2-in. Vigreux column. The yield of phenol was 1.52 g., 44% (b.p. 43–45° at 2 mm.; fern-like crystals; phenoxyacetic acid derivative, m.p. 96–99°). The yield of *p*-bromophenol was 2.53 g., 40% (b.p. 77–78° at 2 mm.; m.p. 61–65°; small prisms; after sublimation at room temperature and 2 mm. pressure, m.p. 65–66°; mixed m.p. with *p*-bromophenol 64–66°). No iodophenol could be detected.

Further runs and comments: Chloroform was used rather than carbon tetrachloride because of the poor solubility of *p*-iodophenol in the latter solvent. The reaction also proceeded at room temperature but did not reach its maximum color development until after 8–10 hours exposure to hydrogen bromide. In a second run which was maintained at 45° for 5 hours, the yield of phenol was 47% and of *p*-bromophenol was 32%. In a third run which was maintained at 45° for 10 minutes, the yield of phenol was 36%, of a mixture of *p*-bromo- and *p*-iodophenol (b.p. 75–80° at 2 mm., m.p. 62.5–67.5°) was approximately 35% and of a different composition mixture (b.p. 80–90° at 2 mm., m.p. 69–73°) was 3%. This reaction was therefore incomplete, and it was difficult to separate *p*-bromo- and *p*-iodophenol. In a control experiment in which an equimolecular mixture of phenol and *p*-bromophenol was subjected to the general purification and isolation procedure, the yield of phenol (b.p. 47–48° at 2 mm.) was 48% and *p*-bromophenol (b.p. 81–82° at 2 mm.) was 47%. In a final run, hydrogen chloride was used in place of hydrogen bromide. After 2 hours at 45° and the usual isolation procedure, the yield of unreacted *p*-iodophenol (b.p. 99° at 2 mm., m.p. 92–94°) was essentially quantitative except for a small fraction (0.06 g., b.p. 47–50° at 2 mm.) having the properties of phenol. A light wine color (from iodine liberation) developed in the original hydrogen chloride reaction mixture as contrasted to the dark, iodine colors of the mixtures exposed to hydrogen bromide.

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[1] W. Militzer, THIS JOURNAL, **60**, 256 (1938); for the reaction with methyl-1-naphthyl ether see E. C. Spaeth, T. A. Geissman and T. L. Jacobs, *J. Org. Chem.*, **11**, 399 (1946).

[2] E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 249.

[3] A. E. Remick, "Electronic Interpretations of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 354.

[4] F. W. Bennett and A. G. Sharpe, *J. Chem. Soc.*, 1383 (1950).

[5] L. J. Lambourne and P. W. Robertson, *ibid.*, 1167 (1947).

[6] All melting points are corrected; A.S.T.M. specification, partial immersion thermometer.

[7] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 355.

[8] J. J. Howland, Jr., D. R. Miller and J. E. Willard, THIS JOURNAL, **63**, 2807 (1941).