all except one[6] agreed with the values recorded in the literature. A melting point of 42–43° was found for *n*-butyrohydroxamic acid.

In general hydroxamic acids are such weak acids in water that when they are titrated with sodium hydroxide potentiometric titration curves with satisfactory inflection points cannot be obtained. Therefore, the ionization constant of each hydroxamic acid given in Table I was determined by employing the following procedure. After the *p*H of a solution of the free acid and its sodium salt was measured, the K_a was found by solving the usual ionization constant expression, where $[A^-]$ the conjugate base of the hydroxamic acid was obtained from

$$[\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{OH}^-] + [\mathrm{A}^-]$$

TABLE I

THE IONIZATION CONSTANTS OF SOME HYDROXAMIC ACIDS

In these experiments no diverse salt was used to adjust the ionic strengths of the solutions to a given value.

	At Equilibrium			
Hydroxamic acid	Molarity of $(A^- + HA) \times 10^2$	Molarity of $Na^+ \times 10^3$	*p*H of soln.[a]	$K_a \times 10^9$
Aceto	1.00	4.98	9.39	0.40
Benzo	1.00	4.98	8.88	1.3
n-Butyro	1.00	4.98	9.47	0.33
p-Chlorobenzo	0.500	2.47	8.58	2.6
p-Methoxybenzo	0.500	2.47	8.99	1.0
α-Naphtho[b]	0.100	1.00	9.40	2×10^1
Phenylaceto	1.00	4.98	9.18	0.65
Propiono	1.00	4.98	9.45	0.35
Salicylo	0.500	2.13	7.25	42

[a] Average value of two runs. [b] The sodium salt was used, for the free acid is very insoluble in water.

The effects of ionic strength and concentration of the buffer mixture on the ionization constant of benzohydroxamic acid were investigated. The results showed that the effects of these two variables are very small. As the ionic strength is varied from 0.5 to 1.00, the K_a changes from 1.3×10^{-9} to 2.1×10^{-9}. If the ionic strength is held constant, the K_a varies from 1.6×10^{-9} to 3.0×10^{-9} as the volume is increased from 100 to 1000 ml.

The values given for the ionization constants of the hydroxamic acids listed in Table I do not agree with those reported in the literature.[3,4] In each case the literature value is about 100 times larger than the one that was obtained by the previously mentioned procedure. Since the values given in the literature were calculated from electrical conductance data, the K_a of the benzohydroxamic acid was evaluated by this method.

The equivalent conductances of the solute (Table II) were plotted against the square roots of the corresponding ionic strengths; and upon extrapolating the latter to zero, the equivalent conductance of potassium benzohydroxamate at infinite dilution was found to be 82. The equivalent conductance of the free benzohydroxamic acid was then calculated to be 358 by applying Kohlrausch's law.

The equivalent conductances of 1.000×10^{-3} and 1.000×10^{-2} *M* benzohydroxamic acid solutions were found by employing the previously mentioned procedure. The ionization constant was calculated at the two concentrations, and the values are given in Table III.

TABLE II

CONDUCTANCE DATA FOR POTASSIUM BENZOHYDROXAMATE AT VARIOUS CONCENTRATIONS

Potassium benzohydroxamate, *M*	Specific conductance of soln.	Specific conductance of solute	Equiv. conductance of solute
1.000×10^{-1}	4.78×10^{-3}	4.78×10^{-3}	47.8
1.000×10^{-2}	5.52×10^{-4}	5.50×10^{-4}	55.0
1.000×10^{-3}	5.94×10^{-5}	5.78×10^{-5}	57.8
1.000×10^{-4}	8.58×10^{-6}	7.00×10^{-6}	70.0

TABLE III

CONDUCTANCE DATA FOR CALCULATING THE IONIZATION CONSTANT OF BENZOHYDROXAMIC ACID

Benzohydroxamic acid, *M*	1.000×10^{-3}	1.000×10^{-2}
Specific conductance of soln.	3.64×10^{-6}	1.00×10^{-5}
Specific conductance of solute	2.06×10^{-6}	8.4×10^{-6}
Equiv. conductance of solute	2.06	0.84
Degree of ionization	0.0058	0.0023
K_a = ionization constant	3.4×10^{-8}	5.3×10^{-8}

Upon comparing the data in Tables I and III, it can be seen that the two methods which were used for determining the ionization constant of benzohydroxamic acid give different results. Several reasons for this discrepancy may be postulated. In order to determine the equivalent conductance of the potassium salt at infinite dilution a fairly long extrapolation is required. In solution it is questionable whether large organic ions adhere to Kohlrausch's law. If the sample of benzohydroxamic acid contained a fraction of 1% of a highly ionizable impurity or if a small amount of carbon dioxide were present in the solution, serious errors would have been introduced. For these reasons the authors consider that in the case of a hydroxamic acid, data obtained from the measurement of the *p*H of a buffer solution yield a more correct value for the ionization constant than conductance data.

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[6] L. Francesconi and A. Bastianini, *Gazz. chim. ital.*, **34I**, 432 (1904).

The Effect of Anion Exchange Resins on Reducing Sugars

BY C. N. TURTON AND EUGENE PACSU

RECEIVED SEPTEMBER 23, 1954

In a recent joint communication from this Laboratory and the Textile Research Institute, Princeton, N. J.,[1] the interconversion and degradation of sugars on anion exchange resins were described. Subsequent work has revealed facts which necessitate the correction and amplification of this report.

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[1] E. Pacsu and L. Rebenfeld, THIS JOURNAL, **75**, 4370 (1953).

It was originally stated that D-mannose could not be detected in the sugar mixtures resulting from the treatment of D-glucose or D-fructose with Amberlite IRA-400 (OH-form).[2] The use of improved paper chromatographic techniques has shown D-mannose to be present in low concentration.[3] Complementarily, D-mannose has been found to give D-glucose and D-fructose on treatment with the same resin. The interconversion therefore appears to conform to the accepted enediol mechanism.

Further support for this mechanism is derived from the fact that in addition to D-fructose a second ketose was found in the sugar mixtures produced from either D-glucose, D-fructose or D-mannose on treatment with Amberlite IRA-400 (OH-form). On paper chromatograms where butanol–ethanol–water–ammonia mixture was used, this ketose had R_g 0.29 when D-glucose and D-fructose had R_g 0.18 and 0.23, respectively. This ketose appeared to be D-psicose (D-*ribo*-hexulose)[4,5] By yeast fermentation[6] the ketose was largely freed from D-glucose, D-fructose and D-mannose and it was possible to prepare a phenylosazone which corresponded to D-psicose phenylosazone.

The loss of sugar reported in the previous communication, and attributed to conversion to acidic products on the evidence of Hulme[7] and Phillips and Pollard,[8] initially appears to be due solely to adsorption of the sugar on the resin. This adsorption of the sugar on the hydroxide form of the resin was rapid and reached equilibrium in periods of 30 min. to 1 hr. (see Fig. 1), when in the cases of D-glucose, D-fructose and D-mannose similar amounts of sugar had been adsorbed. When the Amberlite IRA-400 was in the carbonate form a negligible amount of adsorption occurred. Hence the conversion of the resin to the carbonate form was a convenient method of removing adsorbed sugar from the hydroxide form. If this procedure was carried out shortly after D-glucose had been adsorbed onto the resin (up to 40 min. after), all the sugar was recovered though a little of the sugar which had been eluted from the resin had already been converted to D-fructose, as found by paper chromatography. It is interesting to note that although D-sucrose was not chemically changed by the resin in the hydroxide form, it was quite strongly adsorbed.

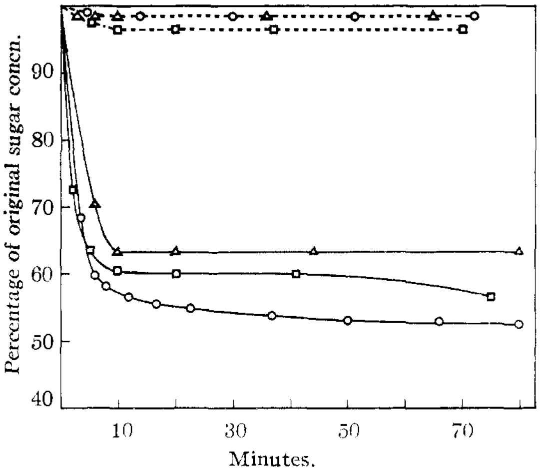

Fig. 1.—Adsorption of sugars on Amberlite IRA-400: □, D-glucose; O, D-fructose; △, D-mannose; —, hydroxide form of resin; ----, carbonate form of resin.

If the reducing sugars were allowed to remain adsorbed on the resin for long periods (10 to 400 hr.), the amount recoverable by carbon dioxide treatment progressively decreased. If, at this stage, the resin was eluted with formic acid and the eluant was concentrated and examined by paper chromatography, a number of non-volatile acids were found to have been produced. Two of these acids had R_f values corresponding to glycolic and lactic acids.

Experimental

Paper Chromatographic Methods.—For the separation of D-glucose, D-fructose and D-mannose the benzyl alcohol–acetic acid–water mixture of Jermyn and Isherwood[9] was used. Other paper chromatograms of sugars were irrigated with a butanol–ethanol–water–ammonia mixture.[10] Aldoses and ketoses were detected with aniline hydrogen phthalate[10a] and naphthoresorcinol–trichloroacetic acid,[9a] respectively. Chromatograms of acids were developed by the method of Buch, Montgomery and Porter.[11]

Measurement of Adsorption of Sugar on Resin.—A sample of resin (1 g.) was placed into a 2-dm. polarimeter tube and an aliquot portion of a 2% sugar solution (10 cc.) was introduced. The sugar solutions were allowed to mutarotate to a constant rotation before use. The fall in rotation due to sugar adsorption was followed on a polarimeter. The rotation was considered to be a reasonable measure of the sugar concentration since paper chromatography showed that changes in the nature of the sugar in solution during the time of the experiment were negligible.

Determination of Total Sugar in Solutions of Mixtures of D-Glucose, D-Fructose and D-Mannose.—The method of Somogyi[12] was used with the modification that the heating time was increased to 50 min. so that D-glucose, D-fructose and D-mannose gave similar calibration curves.

Isolation of Phenylosazone of Unknown Ketose.—A solution of D-fructose (25 g.) in water (500 cc.) was allowed to stand in contact with Amberlite IRA-400-OH (50 g.) for nine days. The mixture was saturated with carbon dioxide and filtered. D-Glucose, D-fructose and D-mannose in the filtrate were largely removed by the yeast fermentation method of Sattler and Zerban.[6] The solution was concentrated to a sirup (0.8 g.) under reduced pressure and paper chromatography showed that it consisted mainly of the ketose. The sirup was converted to a bright yellow phenylosazone which was washed with benzene and water. The osazone was in a finely divided state which made it difficult to filter and it darkened in color when drying was attempted. The material was purified by means of chromatography on calcium carbonate.[13] The column was eluted with methyl ethyl ketone and it was found that under such conditions D-glucose phenylosazone moved very slowly. The major portion of the osazone was eluted rapidly from the column

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(2) Rohm and Haas Co., Philadelphia, Penna.

(3) In a recent communication [THIS JOURNAL, **76**, 4487 (1954)] J. C. Sowden reported the isolation of crystalline D-mannose phenylhydrazone after treatment of D-glucose with this resin.

(4) *Cf.* F. W. Zerban, L. Sattler, G. Rosenthal and A. Glaubach, *Sugar*, **47**, 33 (1952).

(5) *Cf.* F. Schneider and G. A. Erlemann, *Naturwissenschaften*, **39**, 160 (1952).

(6) L. Sattler and F. W. Zerban, *Ind. Eng. Chem.*, **37**, 1133 (1945).

(7) A. C. Hulme, *Nature*, **171**, 610 (1953).

(8) J. D. Phillips and A. Pollard, *ibid.*, **171**, 41 (1953).

(9) M. A. Jermyn and F. A. Isherwood, *Biochem. J.*, **44**, 402 (1949).

(9a) F. A. Isherwood and M. A. Jermyn, *ibid.*, **48**, 515 (1951).

(10) S. M. Partridge, *Nature*, **158**, 270 (1946).

(10a) S. M. Partridge, *ibid.*, **164**, 443 (1949).

(11) M. L. Buch, R. Montgomery and W. L. Porter, *Anal. Chem.*, **24**, 489 (1952).

(12) M. Somogyi, *J. Biol. Chem.*, **160**, 61 (1945).

(13) P. Fischer-Jørgensen, *Dansk. Tids. Farm.*, **24**, 1 (1950).

leaving a yellow band behind and the solution obtained was evaporated to dryness under reduced pressure. The solid was twice recrystallized from methanol–water, using charcoal to remove tarry material. The product showed m.p. 175.5-177°, which was depressed to m.p. 155-170° by admixture with D-glucose phenylosazone, and $[\alpha]^{25}D$ −21.8° (0.25 hr.) and −19.8° (21 hr.) (*c* 0.253, pyridine). Melting points reported for D-psicose phenylosazone are 162-163°,[14] 165°,[15] 173-174°,[16] 178°,[17] and 183-185°.[18]

The material resembled D-psicose phenylosazone and differed from D-glucose phenylosazone in that it was readily soluble in hot water and acetone. In addition, its infrared absorption spectrum (Nujol mull) differed markedly from that of D-glucose phenylosazone. The following X-ray powder diffraction data[19] were obtained for the osazone: 3.21[20] (m),[21] 3.51 (vw), 3.74 (m), 4.34 (s), 4.72 (m), 5.56 (m), 6.82 (vw), 8.72 (m) and 10.27 (m). These values are in good agreement with those recorded by Clark, Gardner, Sattler and Zerban[22] for D-psicose phenylosazone but differ from the following values obtained[19] for D-glucose phenylosazone: 2.59 (vw), 3.14 (w), 3.40 (m), 4.14 (vw), 4.55 (m), 5.02 (s), 6.93 (vw) and 9.28 (m).

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[14] M. L. Wolfrom, A. Thompson and E. F. Evans, THIS JOURNAL, **67**, 1793 (1945).

[15] W. C. Austin and F. L. Humoller, *ibid.*, **56**, 1153 (1934).

[16] M. Steiger and T. Reichstein, *Helv. Chim. Acta*, **19**, 184 (1936).

[17] F. W. Zerban and L. Sattler, *Ind. Eng. Chem.*, **34**, 1180 (1942).

[18] P. A. Levene and W. A. Jacobs, *Ber.*, **43**, 3141 (1910).

[19] We are indebted to Dr. J. H. Dusenbury, Textile Research Institute, Princeton, N. J., for these measurements.

[20] Interplanar spacing, Å., CuKα radiation.

[21] Relative intensity: s strong, m medium, w weak and vw very weak.

[22] G. L. Clark, J. O. Gardner, L. Sattler and F. W. Zerban, *Sugar*, **47**, 40 (1952).

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Substitution Positions in the Nitration of Dibenzoselenophene

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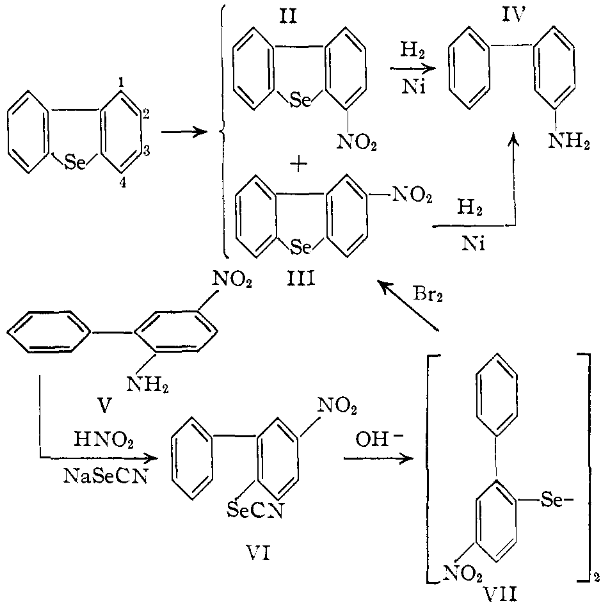
The nitration of dibenzoselenophene (I) in glacial acetic acid gives as the major product a mononitro derivative. Sawicki and Ray[1] compared the ultraviolet absorption spectrum of this compound with the spectra of known mononitrodibenzothiophenes, and on this basis assigned the nitro group to the 2-position (*i.e.*, *para* to the selenium atom). Subsequently, more detailed examination of the nitration products by Sawicki[2] indicated the presence of at least one additional mononitro derivative and at least one dinitro derivative.

Starting with 2-amino-5-nitrobiphenyl (V), and using a modification of a method for preparation of dibenzoselenophene,[3] we have synthesized 2-nitrodibenzoselenophene (III). This compound has been found to be identical to the major product formed from nitration of dibenzoselenophene, thus confirming the position assignment by Sawicki and Ray. It appears that our 2-nitro compound is the first dibenzoselenophene derivative made by methods other than substitution reactions on the parent heterocycle, and that this is the first chemical proof of the position of substitution on dibenzoselenophene.

Both the 2-nitro compound and a second mononitro compound (isolated in fair yield from the nitration mixture) yield 3-aminobiphenyl (IV) when subjected to simultaneous reduction and deselenization[4] with hydrogen and Raney nickel. The second mononitro derivative is thus 4-nitrodibenzoselenophene (II), for the 1-nitro compound would yield 2-aminobiphenyl and the 3-nitro compound would yield 4-aminobiphenyl.

We have found also that the deselenization procedure previously described[4] may be improved simply by carrying out the reaction in a Parr low-pressure hydrogenator. This modification permits the use of less active Raney nickel in a somewhat smaller quantity and lowers the necessary reaction time considerably. By careful control of conditions, the nitrodibenzoselenophenes may be reduced to the corresponding amines without removal of selenium from the molecules. The reactions reported here are summarized



Experimental[5]

2-Selenocyano-5-nitrobiphenyl (VI).—To 28 ml. of concentrated sulfuric acid in a 3-liter beaker cooled in an ice-bath, there was slowly added 4 g. of powdered sodium nitrite. The mixture was very carefully heated and agitated until all solid dissolved, then cooled to 0°. Nine grams of 2-amino-5-nitrobiphenyl[6] was dissolved in 90 ml. of glacial acetic acid. This solution was slowly added to the cold solution of sodium nitrite in sulfuric acid. The reaction was allowed to proceed for 20 minutes, after which was added 1 g. of urea (to destroy excess nitrous acid) and 800 ml. of ice-water. The mixture was made basic to congo red paper with sodium acetate, then 16 ml. of 3 *M* sodium selenocyanate added. The brown precipitate formed was allowed to stand overnight, then filtered off and recrystallized from carbon tetrachloride. By cooling the crystallizing solution to 0°, there was obtained 5.4 g. (43%) of pale brown crystals (m.p. 159-161°). Recrystallization from acetone-alcohol raised the melting point to 162-163°.

Anal. Calcd. for $C_{13}H_8N_2O_2Se$: Se, 26.0. Found: Se, 25.5.

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[1] E. Sawicki and F. E. Ray, THIS JOURNAL, **74**, 4120 (1952).

[2] E. Sawicki, *ibid.*, **77**, 957 (1955).

[3] J. D. McCullough, T. W. Campbell and E. S. Gould, *ibid.*, **72**, 5753 (1950).

[4] G. E. Wiseman and E. S. Gould, *ibid.*, **76**, 1706 (1954).

[5] All melting points are corrected.

[6] (a) F. Bell, *J. Chem. Soc.*, 2770 (1928); (b) F. H. Case, THIS JOURNAL, **65**, 2137 (1943).