distances are approximately in the direction of hydrogen atoms attached to the carbon. The closest intermolecular selenium–selenium distance is 4.42 Å.—well beyond the predicted van der Waals separation of 4.0 Å.

Added in proof.—As a check on the unexpectedly long selenium–carbon distances, the observed and calculated structure factors of the type *hk*0, *h*0*l*, and 0*kl* were used in a least-squares refinement of parameters. The 135 observational equations, appropriately weighted, were reduced to 9 normal equations in the usual manner.[9] Since the normal equations were essentially diagonal, the solutions were straightforward. The resulting best parameters, together with the probable errors as evaluated from the residuals, were as follows

	Se	C_1	C_2
x	0.2234 ± 0.0004	0.986 ± 0.005	0.189 ± 0.004
y	.1675 ± .0009	.190 ± .009	.827 ± .010
z	.0383 ± .0003	.162 ± .004	.956 ± .003

The corresponding bond distances and angles are

Se–C_1	1.99 ± 0.04 Å.	C_1–Se–C_2	97.6 ± 3.5°
Se–C_2	2.04 ± .06 Å.	Se–C_1–C_2	108.5 ± 3.0°
C_1–C_2	1.54 ± .04 Å.	Se–C_2–C_1	107.8 ± 4.0°
Se–Se	3.66 ± .02 Å.		

Since in only one case (the *z* parameter of C_2) was the shift in atomic parameter as indicated by the least-squares treatment significantly greater than the probable error in that parameter, it is not felt that the parameters obtained from the Fourier analysis should be revised. However, the least-squares treatment has resulted in a confirmation of the various interatomic distances and angles in general, and in particular has lent further weight to the observation of the unpredictedly long selenium–carbon bond.

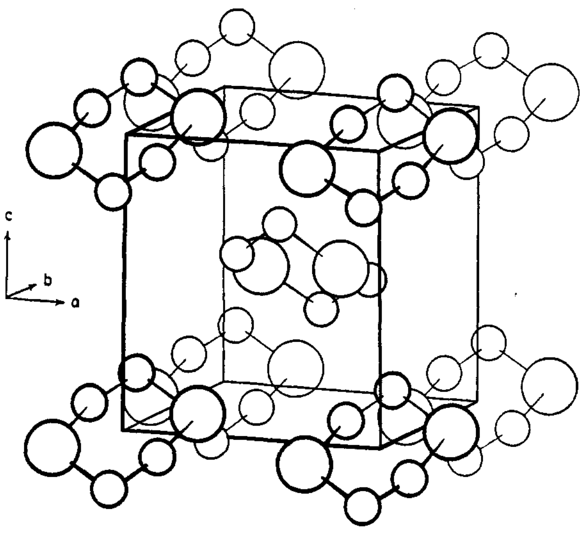

Fig. 5.—The structure of 1,4-diselenane.

Summary

The crystal structure of 1,4-diselenane ($C_4H_8Se_2$) has been determined by X-ray diffraction analysis. The crystals are monoclinic with space-group C_{2h}^5-$P2_1/n$ and with two molecules in the unit cell. The molecule is in the chair form, the only unanticipated feature being an unexpectedly long Se–C bonded separation of 2.01 ± 0.03 Å. which is 0.07 Å. longer than the sum of the single-bond covalent radii for selenium and carbon.

Los Angeles 24, Calif. Received July 10, 1950

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[9] For example, see E. T. Whittaker and G. Robinson, "The Calculus of Observation," Blackie and Son, Ltd., London and Glasgow, 2nd edition, p. 209 ff.

[Contribution from the Department of Chemistry, University of California, Los Angeles]

The Dissociation Constants of Some Monosubstituted Benzeneseleninic Acids. II. A New Synthesis of Diaryl Diselenides[1]

By Edwin S. Gould and James D. McCullough

In work described in an earlier communication,[2] thirteen benzeneseleninic acids were prepared and the logarithms of their ionization constants were found to be a linear function of Hammett's σ values.[3] In a continuation of this work, five additional seleninic acids have been synthesized and their dissociation constants measured. This extension is of interest chiefly because the preparation of certain of these acids involved two reactions which, to our knowledge, have not been described in the literature. We have found that treatment of an aryllithium compound with elementary selenium, followed by hydrolysis of the product, yields appreciable amounts of the corresponding selenophenol which may be easily oxidized by air to a symmetrically substituted diaryl diselenide

$$\mathrm{ArLi + Se = ArSeLi}$$
$$\mathrm{ArSeLi + H_2O = ArSeH + Li^+OH^-}$$
$$\mathrm{2ArSeH + (O) = ArSeSeAr + H_2O}$$

The diaryl diselenides may be further oxidized, with or without purification, to the desired seleninic acids, using concentrated hydrogen peroxide. This series of steps was carried out using *p*-bromobiphenyl, *p*-bromodiphenyl ether and *m*-bromobiphenyl as starting materials for preparation of the corresponding aryllithium derivatives. The overall yields of the seleninic acids (based on the original aryl bromides) were, respectively, 24, 2 and 5%. Although these yields are poor, the method may possibly prove to be an improvement over that of Taboury[4] which would ordinarily be the method of choice in syntheses of this kind. In the latter reaction a selenophenol is prepared by treatment of an aryl Grignard reagent with selenium. For purposes of comparison, we attempted to apply Taboury's method to the synthesis of *p*-biphenylseleninic acid and to *p*-phenoxybenzeneseleninic acid. The yield of the biphenyl acid was 15%, while Taboury's method proved inapplicable to the synthesis of the phenoxy acid since *p*-bromodiphenyl ether would not form a Grignard reagent under the conditions used.

Although our synthesis has been applied to only

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[1] Based on research carried out under Task Order I of Contract N6onr-275, between the Office of Naval Research and the University of California, Los Angeles.

[2] J. D. McCullough and E. S. Gould, This Journal, **71**, 674 (1949).

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

[4] M. F. Taboury, *Bull. soc. chim.*, **35**, 668 (1906).

three aryl bromides, there seems no reason why it should not be generally applicable.

It is of interest that some months after these syntheses were carried out, an analogous reaction between sulfur and some aryllithium derivatives was reported by Gilman and Fullhart.[5]

A second new reaction was observed during attempts to prepare *p*-nitrobenzeneseleninic acid. Ordinarily, the acid would be approached through *p,p'*-dinitrodiphenyl diselenide; but the latter could not be prepared by adaptations of methods in the literature. Treatment of *p*-selenocyanonitrobenzene with methanolic potassium hydroxide in analogy to the method of Campbell and McCullough[6] produced none of the diselenide, but yielded elementary selenium and products which contained no selenium. (The course of this anomalous reaction is not yet clear.) A second attempt to prepare the diselenide was made by treating a mixture of selenium and sodium ethoxide in alcohol with *p*-chloronitrobenzene, a method based on that of Bogert and Stull[7] for preparing 2,2'-dinitrodiphenyl diselenide. From this reaction, a great deal of unreacted selenium was recovered. In addition, a compound having no selenium was isolated, this compound almost certainly being 4,4'-dichloroazoxybenzene, which may be prepared merely by heating a solution of sodium ethoxide in ethanol with *p*-chloronitrobenzene.[8] The melting point of our compound (151–152°) corresponded to that recorded for the azoxybenzene (151°). The compound obtained by treatment of our product with hot nitric acid melted at 135°; while 2(or 3)-nitro-4,4'-dichloroazoxybenzene, obtained by treating authentic 4,4'-dichloroazoxybenzene under the same conditions, melts at 134°.[9] Since these products had no bearing on our main objective, attempts at unequivocal identifications were not carried out.

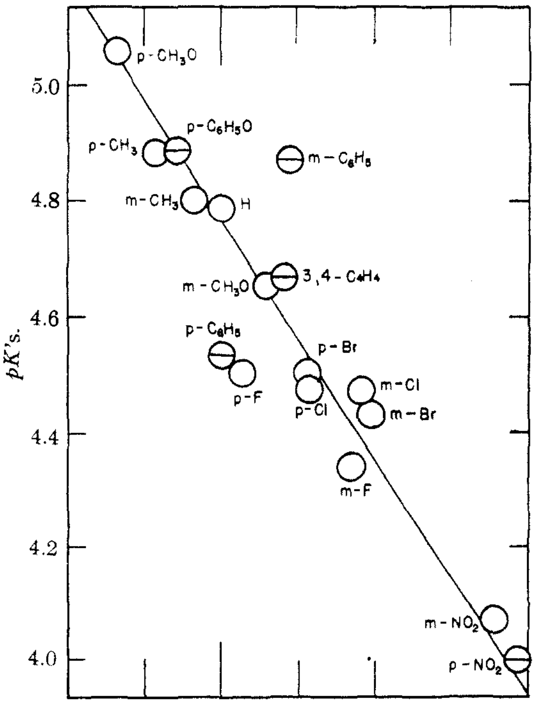
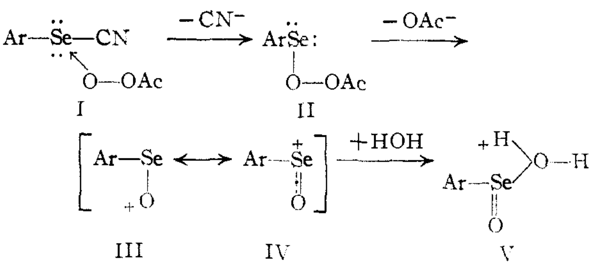


Fig. 1.—Plot of *pK* values *vs.* Hammett's substituent constants.

Being unable to make *p,p'*-dinitrodiphenyl diselenide, we felt that oxidative cleavage of the selenium–cyano linkage in *p*-nitroselenocyanobenzene might yield the desired *p*-nitrobenzeneseleninic acid. Although the selenocyanate was inert toward concentrated hydrogen peroxide, treatment with a 40% solution of peracetic acid in glacial acetic acid resulted in a smooth reaction, attended by the evolution of hydrogen cyanide gas. The seleninic acid was isolated in 45% yield following hydrolysis of the reaction mixture.

A possible mechanism for this unusual reaction is shown below, with the initial mode of attack by the peracetic acid patterned roughly after that suggested by Criegee[10] and, subsequently, by Friess[11]



The initial step is postulated as being a nucleophilic attack on the selenium atom by the peroxy-acid, followed by loss of a proton to yield the intermediate, I, having selenium with an expanded electron octet. The loss of cyanide ion, facilitated by the high electron density around the selenium atom, gives the peroxide, II. The latter yields the hybrid (III⟷IV) upon departure of acetate ion; and treatment of (III⟷IV) with water should yield V, the conjugate acid of the arylseleninic acid.

Analysis.—Tests of the purity of all seleninic acids were made by determining their neutralization equivalents. The three new acids were further characterized by iodometric titration and by combustion, both methods having been described by McCullough, *et al.*[12]

Discussion.—Figure 1 shows the *pK* values determined in previous experiments, plotted against Hammett's substituent constants (σ values). To the plot have been added our new values, indicated by the bisected circles. The σ value for the phenoxy substituent (−0.114), is not the one given by Hammett but stems from the work of McCullough and Eckerson[13] on the dissociation constants of substituted diaryl selenium dibromides.

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[5] H. Gilman and L. Fullhart, THIS JOURNAL, **71**, 1478 (1949).

[6] T. W. Campbell and J. D. McCullough, *ibid.*, **67**, 1965 (1945).

[7] M. T. Bogert and A. Stull, *ibid.*, **49**, 398 (1927).

[8] A. Laubenheimer, *Ber.*, **8**, 1626 (1875).

[9] K. Heumann, *ibid.*, **5**, 912 (1872).

[10] R. Criegee, *Ann.*, **560**, 127 (1948).

[11] S. L. Friess, THIS JOURNAL, **71**, 2574 (1949).

[12] J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Anal. Chem.*, **18**, 638 (1946).

[13] J. D. McCullough and B. A. Eckerson, THIS JOURNAL, **67**, 707 (1945).

It is seen that although our values for the *p*-nitro and *p*-phenoxy substituted acids and for 2-naphthaleneseleninic acid fall very close to the line, the values for the *m*- and *p*-biphenyl acids are rather far removed. The divergence of the latter two acids is, however, of doubtful significance. Hammett's σ value for the *m*-phenyl substituent was determined from consideration of only one reaction series, the rates of hydrolysis of arylsulfuric acids, studied by Burkhardt and coworkers.[14] These workers point out that the rate constant for hydrolysis of *m*-biphenylyl sulfuric acid may be in considerable error, presumably because the low water solubility of the reactants and products made it necessary to carry out the reaction with small quantities of material at high dilutions. Hammett selected his σ value for the *p*-phenyl substituent from the work of Kindler,[15] involving rates of saponification of substituted ethyl benzoates but indicated that considerations of two additional reaction series involving *p*-biphenyl derivatives give substituent constants at considerable variance with the one chosen. In fact, the mean deviation of the three possible values from the chosen value is 0.22 σ unit, much larger than the deviation associated with any of the other substituents. It may be seen from the plot that an increase of the σ value of the *p*-phenyl substituent by 0.22 unit would put the point for this group almost exactly on the line drawn.

Experimental

2-Naphthaleneseleninic Acid.—This acid, prepared as described by Loevenich and co-workers,[16] melted at 155.5° (Loevenich reports 156°).

Anal. Calcd. for $C_{10}H_8SeO_2$: neut. equiv., 239.2. Found: neut. equiv., 239.0; *pK*, 4.67 (σ = 0.170).

Dixenyl Diselenide from Xenylmagnesium Bromide.—To 4.9 g. of magnesium turnings was added a solution of 46.8 g. of Eastman Kodak Co. white label *p*-bromobiphenyl in 150 ml. of dry ether. The mixture was refluxed on a warm water-bath for 6 hours while vigorous stirring was maintained. The Grignard reagent was converted to the corresponding selenophenol by treatment with 16 g. of dry elementary selenium as described by Foster.[17] The selenophenol was not isolated but was oxidized to dixenyl diselenide by passage of air through the reaction mixture. The diselenide was extracted from the mixture with hot benzene, the benzene removed by evaporation and the residue recrystallized twice from boiling benzene; yield 14 g. (31%), m.p. 177–179° (dec.).

Anal. Calcd. for $C_{24}H_{16}Se_2$: Se, 34.1. Found: Se, 34.0.

Dixenyl Diselenide from Xenyllithium.—To 40 ml. of anhydrous ether in a 500-ml. 3-neck flask, equipped with a mechanical liquid-sealed stirrer, reflux condenser, dropping funnel and nitrogen gas supply, was added 1.39 g. of lithium metal, cut into small pieces. One gram of redistilled *n*-butyl bromide was added, the stirring initiated and, when refluxing had ceased, a solution of 23.3 g. of *p*-bromobiphenyl in 100 ml. of dry ether was added dropwise. The mixture was cooled externally with a cold water-bath if refluxing became too vigorous. The entire addition required 1 hour, after which the mixture was allowed to reflux an additional hour while stirring was continued. Elementary selenium (7.9 g.) was added in small portions and the refluxing was continued for 30 minutes more, adding additional dry ether if the volume became inconveniently small. The mixture was taken into an efficient hood and transferred to a large beaker. After the unreacted lithium metal had been removed with tongs, 40 ml. of saturated ammonium chloride solution was added to effect hydrolysis. Much less hydrogen selenide gas was released than was observed during the corresponding Grignard synthesis. The air oxidation, extraction and isolation of the diselenide was carried out as described in the previous synthesis. Ten grams (45%), of the diselenide, m.p. 177–178.5°, was recovered after two recrystallizations from boiling benzene.

***p*-Biphenylseleninic Acid.**—An ether suspension of 14 g. of dixenyl diselenide was heated gently on a warm waterbath until refluxing began. Refluxing was maintained while 20 ml. of 30% hydrogen peroxide was added through the top of the reflux condenser. After all of the peroxide had been added, the preparation was allowed to reflux an additional 15 minutes. At the end of this time, the ether was removed by blowing air through the mixture. The solid was filtered off and 30 ml. of warm methanol added, dissolving the acid and leaving the unreacted diselenide as a residue. The methanolic solution was filtered, decolorized twice and the acid reprecipitated by addition of distilled water. The acid was then filtered off and recrystallized from 80% ethanol; yield 8.8 g. (55%), m.p. 166–167°.

Anal. Calcd. for $C_{12}H_{10}SeO_2$: Se, 29.8; neut. equiv., 265; equiv. wt., 88.2. Found: Se, 29.9; neut. equiv., 267; iodometric equiv. wt., 88.6; *pK*, 4.53 (σ = 0.01).

A small portion of this acid was converted into its methyl ester. To a mixture of 0.66 g. of *p*-biphenylseleninic acid and 0.21 g. of sodium carbonate was added 10 ml. of water. The entire mixture was gently warmed on a steam-bath until evolution of carbon dioxide ceased. The solution was filtered and 150 ml. of acetone was added to the filtrate, precipitating the sodium salt which was filtered off, washed with acetone and dried in the air for one hour. The salt was then added to 3.0 ml. of absolute methanol, the solution cooled to 0° and 0.5 g. of methyl chlorocarbonate was added dropwise. After the evolution of carbon dioxide had ceased, the solution was allowed to remain at 0° for 20 minutes. The solid sodium chloride formed from the reaction was filtered off, yielding a clear, yellow solution. The solvent was removed *in vacuo* at 0°. The residue so remaining was dissolved in a minimum volume of benzene, an excess of dry petroleum ether was added, and the mixture allowed to remain in the ice-box overnight. The white precipitate was filtered off and dried in a vacuum desiccator for two days, at the end of which time it had discolored slightly. Only 60 mg. of ester (8%) was obtained, m.p. 141° (dec.).

Anal. Calcd. for $C_{13}H_{12}SeO_2$: Se, 28.3. Found: Se, 28.4.

***m*-Biphenylseleninic Acid.**—*m*-Bromobiphenyl was prepared from *m*-bromoaniline by the method of Gomberg and Bachmann.[18] A 13.6-g. portion of the bromide was converted to the aryllithium compound and thence to the corresponding diselenide as described for the para isomer. The diselenide, an oil, was not purified but was oxidized with 30% hydrogen peroxide, using oxidation procedure 2 described in our previous paper.[2] The acid was purified by purification method 1 of the same paper. Four-fifths gram (5%) of white solid, m.p. 119–120° was isolated.

Anal. Calcd. for $C_{12}H_{10}SeO_2$: Se, 29.8; neut. equiv., 265; equiv. wt., 88.2. Found: Se, 29.7; neut. equiv., 266; equiv. wt. (iodometric), 89.1; *pK*, 4.87 (σ = 0.218).

***p*-Phenoxybenzeneseleninic Acid.**—Although a Grignard reagent could not be prepared from *p*-bromodiphenyl ether, the aryllithium compound could be made by treating the ether with an equimolar quantity of *n*-butyllithium. The aryllithium derivative was converted to the corresponding diselenide by the procedure described above. The diselenide (apparently an oil) was oxidized and the resulting *p*-phenoxybenzeneseleninic acid purified as indicated for the *m*-biphenyl acid. The phenoxy acid was stable at room temperature, but considerable decomposition resulted when attempts were made to recrystallize it from hot water. Recrystallization was carried out by dissolving the acid in warm alcohol, then adding warm water until cloudiness appeared. Cooling for two days at −5° deposited white

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[14] G. N. Burkhardt, C. Horrex and D. I. Jenkins, *J. Chem. Soc.*, 1654 (1936).

[15] K. Kindler, *Ann.*, **452**, 90 (1927).

[16] J. Loevenich, H. Fremdling and M. Fohr, *Ber.*, **62**, 2861 (1929).

[17] D. G. Foster, *Org. Synth.*, **24**, John Wiley & Sons, Inc., New York, N. Y., 1944.

[18] M. Gomberg and W. E. Bachmann, THIS JOURNAL, **46**, 2339 (1926).

microcrystals, m.p. 102–103° (dec.). The yield was very small (2%).

Anal. Calcd. for $C_{12}H_{10}SeO_3$: Se, 28.1; neut. equiv., 281; equiv. wt., 93.8. Found: Se, 28.7; neut. equiv., 283; equiv. wt. (iod.), 94.0; pK, 4.88 ($\sigma = -0.114$).[13]

The Reaction between *p*-Nitrochlorobenzene and Selenium in Sodium Ethoxide.—Five 5-g. pieces of metallic sodium were dissolved in 250 ml. of 95% ethanol, and 16 g. of dried elementary selenium was added. The mixture was stirred for 30 minutes while refluxing was maintained. Thirty-two grams of *p*-nitrochlorobenzene was dissolved in 200 ml. of hot ethanol and the solution added slowly to the sodium ethoxide–selenium mixture. Refluxing and stirring were maintained for 3 hours, at the end of which time the preparation was cooled to 5°. The solid was filtered off and treated with boiling glacial acetic acid, leaving a residue of 12 g. of elementary selenium. Cooling the acetic acid solution yielded 40 g. of orange solid. Two additional recrystallizations from glacial acetic acid yielded a product melting at 151–152°, containing no selenium. This product, presumably *p,p'*-dichloroazoxybenzene, was not affected by concentrated hydrogen peroxide or peracetic acid, but was converted by refluxing 90 minutes with concentrated nitric acid to a bright yellow compound, m.p. 135° (from ethanol).

***p*-Nitrobenzeneseleninic Acid.**—*p*-Selenocyanonitrobenzene was prepared from *p*-nitroaniline by the procedure of Bauer.[19]

To 25 ml. of 40% solution of peracetic acid in glacial acetic acid[20] was added 2.5 g. of *p*-selenocyanonitrobenzene. The mixture was heated on a hot plate, gases being vigorously evolved when the temperature reached 60–70°. After gas evolution had ceased, the solution was slowly evaporated to 15 ml. and excess 15 *N* ammonium hydroxide was added. The solution was heated to 80° and filtered, and the filtrate cooled and treated with dilute sulfuric acid, yielding a cream-colored precipitate which was filtered off, washed with cold water, and dissolved in a minimum quantity of boiling methanol. The methanolic solution was added cautiously to 250 ml. of water at 90°. Upon cooling the solution, orange-yellow crystals appeared. These were dried for an hour, then dissolved in a minimum quantity of concentrated nitric acid. The resulting solution was added to 200 ml. of boiling water, and the mixture allowed to cool. The pale yellow crystals which formed were filtered off after two days standing and were dried 3 days in a vacuum desiccator over anhydrous calcium chloride. The yield was 1.2 g. (45%), m.p. 212–213° (Behagel and Seibert report 214–215°[21]).

Anal. Calcd. for $C_6H_5SeNO_4$: neut. equiv., 234; equiv. wt., 78.0. Found: neut. equiv., 235.5; equiv. wt. (iod.), 77.4; pK, 4.00 ($\sigma = 0.778$).

Physical Measurements.—The dissociation constants of the acids were determined as described in our earlier communication, merely by measuring the *p*H of a half-neutralized solution of the acid and correcting for the activity coefficient of the acid anion.[2] However, these acids were difficultly soluble in warm water and were best dissolved by adding to the weighed sample 4.0 ml. of C.P. methanol, (in which they dissolve readily) diluting with 100 ml. of boiled distilled water, then titrating with standard sodium hydroxide. This procedure necessitated a correction for the effect of the added methanol on the *p*H at half-neutralization, determined by measuring the *p*H of half-neutralized solutions of benzeneseleninic acid and *p*-tolueneseleninic acid in water before and after successive known volumes of methanol were added to the solutions. In this way it was shown that the observed *p*H of these solutions containing 0.0025 mole/liter of both the arylseleninic acid and its salt rises 0.04 unit for each 5.0 ml. of methanol added to 100 ml. of solution; it was assumed that the effect of methanol on the observed *p*H of solutions of the heavier seleninic acids and their salts was roughly the same. In some determinations, the titration was omitted, and only the *p*H at half-neutralization was recorded. In the case of *p*-biphenylseleninic acid, its extremely low water solubility (2.7×10^{-4} fwt. per liter at 25°) made it more convenient to determine a pK value by the "partition method" described by Sherrill,[22] using the sodium salt of benzeneseleninic acid, the pK value for the latter acid having been previously determined.

Acknowledgments.—The authors wish to express thanks to Dr. J. Robert McCormick for valuable suggestions during the course of this work.

Summary

1. Treatment of aryllithium compounds with elementary selenium, followed by hydrolysis and air oxidation of the reaction mixture, has been found to yield symmetrically substituted diaryl diselenides.

2. Peracetic acid oxidation of *p*-selenocyanonitrobenzene yields *p*-nitrobenzeneseleninic acid.

3. The dissociation constants (as pK) for five additional substituted benzeneseleninic acids have been determined. Three of these fall on the ρ–σ curve constructed from previous experiments.

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[19] H. Bauer, *Ber.*, **46**, 92 (1913).

[20] Obtained as a sample from the Buffalo Electrochemical Company, Buffalo, N. Y.

[21] O. Behagel and H. Seibert, *Ber.*, **66B**, 708 (1933).

[22] M. S. Sherrill, "A Course of Laboratory Experiments in Physico-Chemical Principles," The Macmillan Co., New York, N. Y., 1924, p. 64.

LOS ANGELES, CALIFORNIA RECEIVED JULY 27, 1950

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids.[1] V. The Heat Capacity of Pure Elementary Boron in Both Amorphous and Crystalline Conditions between 13 and 305°K. Some Free Energies of Formation

BY HERRICK L. JOHNSTON, HERBERT N. HERSH AND EUGENE C. KERR

Introduction

Although boron was reported in 1808 by Gay Lussac and Thenard,[2] who obtained it by the action of potassium on boric acid, there have been very few preparations of the pure metal[3] up until now. Methods employed have been: (a) Reduction of the chloride or oxide by aluminum,[4] which invariably leads to heavy contamination with AlB_{12}. (b) Reduction of the oxide by magnesium, a method due to Moissan[5] who reported the preparation of small amounts of 98.3% pure boron in the amorphous condition. (c) Electrolytic reduction,[6] which has given no better than 92% boron.

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] Gay-Lussac and Thenard, *Ann. chim.*, **68**, 169 (1808).

[3] *Cf.* Laubengayer, *J. Chem. Ed.*, **19**, 382 (1942), for a review of the subject.

[4] (a) St. Clair Deville and Wohler, *Compt. rend.*, **43**, 1088 (1856); (b) Wohler, *Ann.*, **141**, 262 (1867).

[5] (a) Moissan, *Ann. chim. phys.*, **6**, 296 (1895); (b) Cueilleron, *Ann. chim.*, **19**, 459 (1944).

[6] Andireux, *Ann. chim. phys.*, **12**, 423 (1929).