TABLE III

Max.	Min.	I_n	C_n	s_0	s_J	s_J/s_0
	1	− 5	− 4	1.61		
1		6	4	2.49	2.45	(0.984)
	2	− 8	− 6	3.20	3.22	1.005
2		10	9	4.21	4.18	0.993
	3	− 7	− 8	5.14	5.28	1.027
3		5	7	6.23	6.47[a]	(0.972)
4		5	7	7.08		
	5	−11	−17	7.89	7.87	.997
5		10	16	9.03	9.07	1.003
	6	− 5	− 8	10.10	10.19	1.010
6		3	4	10.91	10.90	0.999
	7	− 7	−11	11.74	11.75	1.000
7		10	16	12.78	12.75	0.998
	8	−10	−16	13.74	13.84	1.008
8		6	9	14.90	14.86	0.999
	9	− 2	− 3	15.33	15.74	(1.027)
9		2	3	16.72	16.71	(1.000)
	10	− 6	− 8	17.12	17.27	(1.009)
10		10	12	18.18	18.13	0.997
	11	− 8	− 8	19.67	19.62	.997
11		8	7	21.25	21.24	1.000
	12	−10	− 7	22.71	22.61	0.996
12		10	6	23.96	23.61	(0.969)
				Average		1.002
				Av. dev.		0.003
				l_{Si-Br}		2.16

[a] See text for discussion.

for the Si–Cl distance, a value 2% higher than that (2.01 Å.) which has been reported for the Si–Cl bond in other molecules.[11]

Summary

The molecular structures of $SiBr_4$, $SiHBr_3$ and SiF_2Br_2 have been studied by the electron diffraction method. In all of these molecules the Si–Br distance is 2.16 ± 0.03 Å., and the valence angles are but little distorted from the tetrahedral value. The relative temperature factors have been estimated for $SiBr_4$ and $SiHBr_4$ from the appearance of the electron diffraction photographs.

(11) Lister and Sutton [*Trans. Faraday Soc.*, **37**, 393 (1941)] report from an electron diffraction study that the Si–Br distance in silicon tetrabromide is 2.14 ± 0.02 Å., in substantial agreement with our value.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 13, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE, ST. LOUIS, MISSOURI]

Preparation of Tetrahydroxyquinone and Rhodizonic Acid Salts from the Product of the Oxidation of Inositol with Nitric Acid*

BY PAUL W. PREISLER AND LOUIS BERGER

Some confusion exists in the literature concerning the identification of the salts of rhodizonic acid (dihydroxy-diquinone) and of tetrahydroxyquinone. The quantitative analytical procedures usually employed for this purpose do not distinguish with certainty between substances of such close elementary composition, especially when they are hydrated or cannot be properly dried.[1] These materials have now been conclusively identified by application of electrometric oxidation–reduction potential measurements.

Modification of the methods for the preparation of these substances from the products of the oxidation of inositol (cyclohexanehexol) by nitric acid have been devised and crystalline materials of high purity have been prepared. The quantities of rhodizonate or of tetrahydroxyquinone salt have been found to be affected by the rate of the addition and the basic properties of the salt added to the oxidized inositol, and by the degree of agitation with air or oxygen of the mixture so formed. When potassium acetate is used, pure potassium rhodizonate is obtained, whereas with potassium carbonate mixtures with tetrahydroxyquinone, salts usually result.

Salts of rhodizonic acid and of tetrahydroxyquinone are utilized as indicators in the volumetric determination of sulfates with barium salt solution.[2] A comparison of the properties of the pure substances indicates that the color changes when used as indicators are probably due to salts of rhodizonic acid rather than of tetrahydroxyquinone.

Preparation of Oxidation Products of Inositol.—To ensure uniform reproducible results the procedure is given in

* Presented before the American Chemical Society at St. Louis, Mo., April, 1941.

(1) E. Bartow and W. W. Walker, *Ind. Eng. Chem.*, **30**, 300 (1938); O. Gelormini and N. E. Artz, THIS JOURNAL, **52**, 2483 (1930); F. A. Hoglan and E. Bartow, *ibid.*, **62**, 2397 (1940); B. Homolka, *Ber.*, **54**, 1393 (1921); M. Maquenne, *Compt. rend.*, **104**, 297 (1887); R. Nietzki and T. Benckiser, *Ber.*, **18**, 499 (1885).

(2) G. Gutzeit, *Helv. Chim. Acta*, **12**, 725 (1929); W. A. Peabody and R. S. Fisher, *Ind. Eng. Chem., Anal. Ed.*, **10**, 651 (1938); W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **5**, 403 (1933); **8**, 127 (1936); **9**, 69 (1937); **10**, 206 (1938); R. Strebinger and L. Zombory, *Z. anal. Chem.*, **79**, 1 (1929).

detail: 10 g. of anhydrous inositol was added to 25 ml. of concentrated nitric acid contained in a Pyrex glass cylinder (35 × 120 mm.). The solution was mechanically stirred in a stirred water-bath maintained at 60°. After about fifteen minutes, evolution of brown fumes began, continuing for about thirty minutes. After three hours, the solution was diluted with water to 100 ml., filtered clear and divided into two portions.

The di-potassium salt of rhodizonic acid was prepared from this solution in the following manner. While rapidly bubbling air through one 50-ml. portion of this solution contained in a 250-ml. graduate, a clear filtered 50% potassium acetate solution (100 g. per 100 ml. H_2O) (free from alkaline earth salts) was added dropwise until one drop produced a permanent yellow color (about 20 ml.), and then 50 ml. more of the potassium acetate solution was quickly added. Aeration was continued for thirty minutes, after which the purple crystals formed were filtered from the dark red solution by suction on a hardened paper, washed once with potassium acetate and repeatedly with 95% alcohol to remove potassium acetate; 1.2 g. of purple prisms of di-potassium rhodizonate was obtained. Further aeration of the filtrate produced an additional 1.2 to 1.3 g. in seventeen hours; total yield 2.5 g. (from 5 g. of inositol).

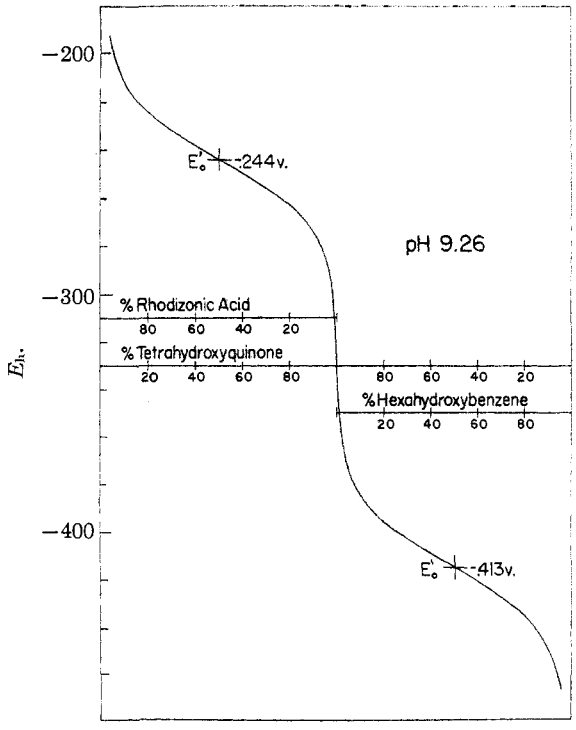

Fig. 1.

The color of the product varied with changes in the procedure, being dark purple, blue or green prisms or lustrous green octahedra by reflected light, but all were red in transmitted light; all were transformed into a purple-red powder on grinding. Analyses for potassium by ignition and conversion into potassium sulfate gave, within allowable experimental error, the correct value for potassium. Potentiometric titrations showed all were identical.

Salts of rhodizonic acid cannot be purified by recrystallization without great loss, due to conversion into croconate, so that the original material must be prepared pure. The conditions for the above preparations were carefully regulated because a comparative study was being conducted; however, for ordinary preparation of potassium rhodizonate the temperature of the oxidation need not be so carefully regulated, but must be above 60°. The important factor is the proper regulation of the acidity by the addition of the acetate before aeration. The maximum yield is produced by aeration in twelve to eighteen hours.

Solutions of potassium rhodizonate are rapidly oxidized by atmospheric oxygen to potassium croconate taking up approximately one atom of oxygen per mole. For analytical reagent indicator purposes, the dry potassium rhodizonate may be diluted by adding it to the proper amount of some material which will not affect the titrations and powdering the mixture, a measured quantity of the dry mixture then being added before the titration.

The di-potassium salt of tetrahydroxyquinone (containing some di-potassium rhodizonate) was prepared in a manner similar to the foregoing by adding a potassium carbonate solution instead of potassium acetate to the other 50 ml. portion of oxidized inositol. 50% potassium carbonate (100 g. per 100 ml. H_2O) was added dropwise to the first permanent yellow color (about 10 ml.) and then 60 ml. more of potassium carbonate was added quickly. The solution became dark red, and was soon transformed to a dark yellow-green color with the precipitation of dark purple crystals principally of the di-potassium salt of tetrahydroxyquinone; 1.5 to 1.7 g. of di-potassium tetrahydroxyquinone contaminated with a little potassium rhodizonate was obtained (from 5 g. of inositol). Further aeration produced little additional substance.

Tetrahydroxyquinone was prepared from this product in very good yields (85 to 90%) by dissolving 1 g. in 20 ml. of boiling normal hydrochloric acid and cooling. The bluish-black plates which formed were filtered and washed with slightly acidified cold water. Reduction of the hot filtrate with a piece of metallic zinc and subsequent cooling produced a small additional amount of tetrahydroxyquinone. The sum of the two quantities was practically the theoretical yield. The reduction of di-potassium rhodizonate by this method produced almost the theoretical yields of tetrahydroxyquinone.

Di-potassium tetrahydroxyquinone (free of rhodizonate) was prepared in an atmosphere of deoxygenated commercial nitrogen by the addition of potassium acetate solution to a hot acid solution of tetrahydroxyquinone, prepared as above.

The di-potassium salts of rhodizonic acid and of tetrahydroxyquinone are easily distinguishable by their respective solubilities in water and in cold normal hydrochloric acid. In water the salt of rhodizonic acid was much more easily soluble and gave a deep yellow solution while the salt of tetrahydroxyquinone was relatively insoluble, imparting a very pale purple tint to the solution. The rhodizonate dissolved readily in cold hydrochloric acid producing a colorless solution, whereas the tetrahydroxyquinone remained insoluble being slowly converted into insoluble tetrahydroxyquinone and coloring the solution pale purple.

Potentiometric titrations of rhodizonate and tetrahydroxyquinone were used for identification and quantitative estimation of these substances or their mixtures. The usual potentiometric oxidation–reduction potential apparatus and procedure for conducting titrations in the absence of oxygen was employed, details of which have been described previously.[3] The titrations were carried out in buffer of *p*H 9.26 where the components of the two systems, rhodizonic acid-tetrahydroxyquinone, and tetrahydroxyquinone-hexahydroxybenzene were stable and yet sufficiently separated to make interpretation of the results easy.[4]

The sample of potassium rhodizonate (3 to 4 mg. weighed to 0.1 mg.) was added as solid to 55 ml. of buffer, deoxygenated by passage of purified nitrogen, and titrated with deoxygenated sodium hydrosulfite ($Na_2S_2O_4$) in the same buffer, resulting in a curve as illustrated in the figure. A sample was reduced with hydrogen gas in the presence of colloidal palladium and, after hydrogen gas removal by purified nitrogen, was reoxidized by titration with standard potassium ferricyanide contained in the same buffer. A curve similar in form to that obtained in the hydrosulfite reduction was obtained. Slightly less than four equivalents of ferricyanide were used in the reoxidation.

Samples of tetrahydroxyquinone oxidized to rhodizonic acid with ferricyanide at *p*H 9.26 used essentially the two required equivalents; however, when first reduced to hexahydroxybenzene (hydrogen gas with palladium as catalyst) and reoxidized to rhodizonic acid with ferricyanide, somewhat less than four equivalents were required. The above observations indicate that during the reduction with hydrogen a portion of the hexahydroxybenzene was converted into an electromotively inactive substance, possibly to inositol.[5]

For the quantitative determination of a mixture, the ratio of tetrahydroxyquinone to rhodizonic acid was determined from the oxidation–reduction potential of the buffered solution containing the sample. Titration of a weighed sample with standard ferricyanide determined the amount of tetrahydroxyquinone present. From these data the amount of each could be calculated.

Potentiometric observations of solutions of the original oxidized product give an indication of its structure. The colorless, water-soluble material obtained by oxidation of inositol with nitric acid, when added (about 6 mg. to 55 ml.) to deoxygenated buffer of *p*H 9.87 yielded a yellow solution. The oxidation–reduction potential of this solution, as determined by the usual procedure,[4] at first was such as to indicate the presence of rhodizonic acid salts with a little tetrahydroxyquinone salt. The yellow color then slowly faded to a very pale purple, and the potential after about twenty-five minutes indicated the presence of virtually only tetrahydroxyquinone salt. During the next twenty-five minutes the potential became progressively more negative, and finally indicated a ratio of about 25% tetrahydroxyquinone salt to 75% hexahydroxybenzene salt. This phenomenon together with the slowness of formation of potassium rhodizonate during its preparation even in the presence of excess oxygen as described above, indicates that the original oxidized inositol product was principally a substance, probably triketo-trihydroxycyclohexane, which slowly liberated hexahydroxybenzene at low acidities or alkalinities.

(3) P. W. Preisler and L. H. Hempelmann, THIS JOURNAL, **58**, 2305 (1936).

(4) P. W. Preisler, E. S. Hill, E. Ronzoni and L. Young, *J. Biol. Chem.*, **123**, XCV (1938); complete report in publication.

(5) H. Wieland and R. S. Wishart, *Ber.*, **47**, 2082 (1914).

Summary

Methods for the preparation of pure salts of rhodizonic acid and tetrahydroxyquinone are described.

The color changes obtained when using these substances as an indicator for sulfate titrations with barium salts are probably due to salts of rhodizonic acid.

ST. LOUIS, MISSOURI RECEIVED JULY 15, 1941

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

9-Vinylphenanthrenes. III. α-(9-Phenanthryl)-stilbene

BY FELIX BERGMANN

In a recent paper[1] we described the synthesis of α-(9-phenanthryl)-stilbene (II) by dehydration of the carbinol I. From the mother liquors of II there was obtained an isomeric hydrocarbon (IIa) the structure and reactions of which are discussed in this paper.

By addition of lithium the isomers II and IIa could both be converted into α-(9-phenanthryl)-dibenzyl (III). They therefore represent a pair of geometric isomers although the simultaneous formation of *cis–trans* isomeric ethylenes on dehydration of an alcohol has rarely[2] been observed. The relationship between the two "stilbenylphenanthrenes" is further proved by conversion of IIa into II by heating with iodine in nitrobenzene solution. The behavior of II and IIa toward alkali metal might be expected to resemble the analogous behavior of stilbene and isostilbene, each of which gives[3,4] the same mix-

(1) F. Bergmann and E. Bergmann, THIS JOURNAL, **62**, 1699 (1940).

(2) See E. Bergmann and Weiss, *Ber.*, **64**, 1485 (1931); E. Bergmann, *et al.*, *Ann.*, **500**, 122 (1933).

(3) Schlenk and E. Bergmann, *ibid.*, **463**, 106 (1928).

(4) Wright, THIS JOURNAL, **61**, 2106 (1939).