of 1.4 c./m./mg. corrected for background and self absorption. The activity decreased to 0.7 c./m./mg. after leaching with water and recrystallizing. We did not obtain a completely inactive sample of phenyl glyoxal monohydrate but the rapid decrease in activity led us to believe the activity found was due to occluded formaldehyde. The formaldehyde counted as the dimedon derivative showed a specific activity of 3 c./m./mg.

The results of the experiment indicate that there is no transposition of the carbon atoms during the formation of the Mannich base. Work is underway with a higher activity formaldehyde to determine if the unreacted formaldehyde is held in a complex with the acetophenone.

Experimental

The reaction conditions for the preparation of β-C^{14}-β-dimethylaminopropiophenone were changed somewhat from those normally used.[5] On the basis of work done by Plati and Wenner,[6] it was believed to be possible to improve the yield of the base by changing the solvent conditions. A 50–50 mixture of acetophenone and 95% ethanol was finally adopted.

The Mannich base was prepared by heating, under reflux, 1.84 g. (0.06 mole) of radioactive paraformaldehyde and 9.70 g. (0.12 mole) of dimethylamine hydrochloride in a solution of 10 ml. of acetophenone and 10 ml. of 95% ethanol. After heating for two hours, the solution was seeded and chilled overnight. The product, recrystallized from acetone, weighed 6.62 g. (0.031 mole). The yield was 51% based upon the radioactive paraformaldehyde; uncorrected m.p. 155–157° (reported 157–158°).

The Mannich base was subjected to steam distillation and the resulting vinyl phenyl ketone was extracted from the distillate with chloroform. The chloroform was removed by distillation and the unsaturated ketone was dissolved in 100 ml. of glacial acetic acid. The solution was heated to 80° and treated with ozone for a period of four hours. The material was poured into 100 ml. of water with 2 g. of zinc added to prevent oxidation. The precipitate of phenyl glyoxal monohydrate was removed by filtration. A saturated ethanol solution of 5 g. of dimedon was added to the filtrate. The mixture was seeded and chilled to recover the methylene-bis-dimedon (320 mg. m.p. 182–185°).

---

[5] C. Mannich and G. Heilner, *Ber.*, **55**, 356 (1922).

[6] J. T. Plati and W. Wenner, *J. Org. Chem.*, **14**, 543 (1949).

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

RECEIVED MAY 29, 1950

Absorption Spectra of Some Substituted Benzoquinones

BY CATHERINE M. MARTINI AND FREDERICK C. NACHOD

The ultraviolet absorption spectra[1] of a series of substituted benzoquinones were determined in solutions at various *p*H levels (Sørensen buffer, *p*H 7, 0.01 *N* NaOH solution, and 0.01 *N* HCl solution).

The spectra of the 2- and the 2,5-bis-alkylaminobenzoquinones in *p*H 7 buffer showed marked similarities, as illustrated by (1) 2,5-bis-(methylamino)-benzoquinone; (2) 2,5-bis-(*n*-butylamino)-benzoquinone; (3) 2,5-bis-[3-(1-piperidyl)-propylamino]benzoquinone; (4) 2-[3-(1-piperidyl)-propylamino]-benzoquinone methyl bromide and (5) 2-[3-(1-piperidyl)-propylamino]-benzoquinone in Fig. 1.[2]

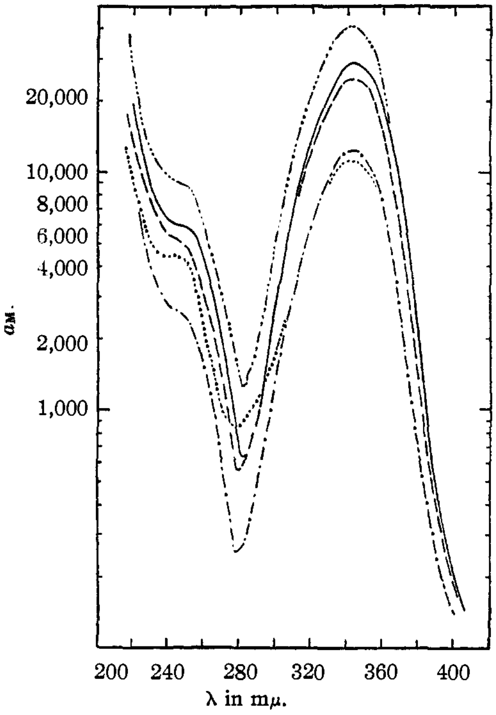

Fig. 1.—(1) —··—···—, 2,5-bis-(methylamino)-benzoquinone; (2) ———, 2,5-bis-(*n*-butylamino)-benzoquinone; (3) — - —, 2,5-bis-[3-(1-piperidyl)-propylamino]benzoquinone; *(4)—— — - —, 2-[3-(1-piperidyl)-propylamino]*-benzoquinone methyl bromide; (5) - - - - - - - - - - -, 2-[3-(1-piperidyl)-propylamino]-benzoquinone.

All the spectra have maxima at 343 mμ, minima at 280 mμ and inflection points at 244 mμ, and differ only in the hyperchromic molar absorbency (a_M) produced by the bis compounds. Contrary to what might be expected there were no changes produced in the spectra when determined in basic or acidic solutions.

The situation, however, was found to be quite different with 2- and 2,5-bis-dialkylaminobenzoquinones. When the spectrum of 2-hydroxy-5-dimethylaminobenzoquinone[3] was determined in water solution, *p*H 6; or in 0.01 *N* NaOH solution, *p*H 13, a maximum was observed at 318 mμ. In 0.01 *N* HCl solution, *p*H 2, the expected hypsochromic shift due to prototropic changes was observed producing a maximum at 282 mμ. In order to demonstrate, qualitatively, the equilibrium involved above, the spectrum was determined in water and the maximum at 318 mμ was obtained. When the *p*H of this solution was adjusted to 2.0 with concentrated HCl, the hypsochromic shift to 282 mμ was obtained.

When the *p*H was once again adjusted to 7 with alkali, the expected bathochromic shift took place and the compound once again exhibited a maximum at 318 mμ. The same experiment was attempted with 2,5-bis-(dimethylamino)-benzoquinone.[2] In *p*H 7 buffer and 0.01 *N* NaOH solu-

---

[1] The spectra were determined with a Beckman quartz spectrophotometer, Model DU, Serial No. D-337, using a minimal slit width and 10 mm. quartz cells.

[2] C. J. Cavallito, A. E. Soria and J. O. Hoppe, THIS JOURNAL, **72**, 2661 (1950).

[3] F. Kehrmann, *Ber.*, **23**, 897 (1890).

tions, maxima were observed at 377 and 227 mμ and minima at 297 mμ. When the spectrum was determined in 0.01 N HCl solution, the expected hypsochromic shift was obtained producing a maximum at 288 mμ, inflection point at 312 mμ and a minimum at 249 mμ. In attempting to produce the same reversibility (see Fig. 2) which was observed with 2-hydroxy-5-dimethylaminobenzoquinone, the shift from 380 to 286 mμ was obtained as the pH was changed from 6.8 to 2. However, after adding alkali to bring the pH back to 7, the maximum did not completely recover but instead appeared at 344 mμ. It might be well to note that this value, 344 mμ, is very close to the 343 mμ value obtained for the 2- and 2,5-bis-(monoalkylamino)-benzoquinones.

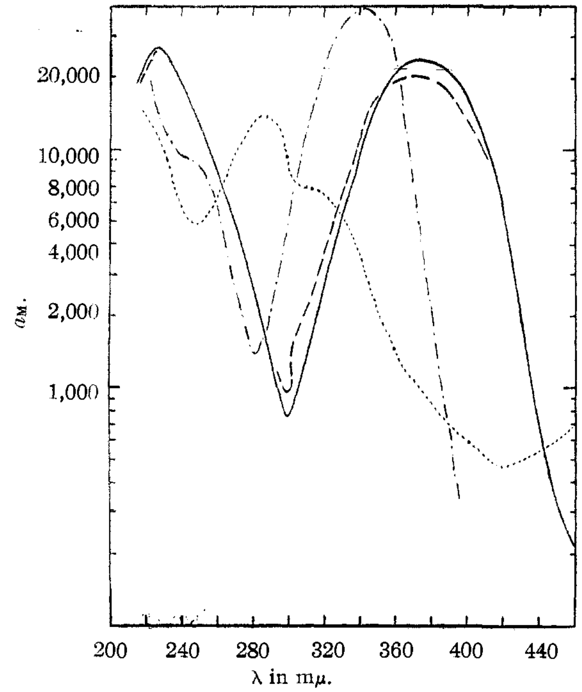

Fig. 2.—2,5-Bis-(dimethylamino)-benzoquinone: ———, pH 7; — — — — — —, 0.01 N NaOH; - - - - - - - - - -, 0.01 N HCl; 2,5-bis-(methylamino)-benzoquinone: —·—·—·— pH 7 and 0.01 N HCl.

Acknowledgment.—The authors would like to express their gratitude to Dr. C. J. Cavallito and Mr. A. E. Soria for preparing the compounds used in this work and to Mrs. Madelyn Becker for technical assistance.

STERLING-WINTHROP RESEARCH INSTITUTE
RENSSELAER, N. Y.
RECEIVED MARCH 5, 1951

The Dissociation Constants of Some Symmetrically Disubstituted Diphenylselenium Diiodides

BY JAMES D. MCCULLOUGH AND BRUCE A. ECKERSON

In a previous investigation,[1] diphenylselenium and iodine were found to form an unstable compound, $(C_6H_5)_2SeI_2$. The dissociation constant, K, for this compound was determined spectrophotometrically at 26° and found to have the value 0.036, where $K = ([(C_6H_5)_2Se][I_2])/([(C_6H_5)_2SeI_2])$. The purpose of the present investigation has been to study the effect of ring substituents on the dissociation constant and to correlate dissociation constants with the substituent constants of Hammett[2] as was done with the dibromides in previous investigations.[3,4]

Experimental

The preparation and purification of the substituted diphenylselenides was described in the previous publications.[3,4] Iodine and carbon tetrachloride were carefully purified by customary methods. The optical measurements were made on a Beckman model DU quartz spectrophotometer by use of procedures described earlier.

Results and Discussion

Molar extinction coefficients for the diiodides are given in Table I. Extinction coefficients of the selenides were published earlier.[3]

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF SYMMETRICALLY DISUBSTITUTED DIPHENYLSELENIUM DIIODIDES

λ(mμ)	p-Cl	p-CH_3	p-CH_3O
330	....	11,400	....
340	16,800	14,500	9,550
350	16,200	18,100	13,000
360	13,100	20,100	15,400
370	10,400	19,400	16,500
380	7,640	16,900	16,200
390	5,650	13,900	14,900
400	....	10,400	12,800
410	....	7,910	10,600
420	....	6,210	8,870

The calculated dissociation constants are shown in Table II.

TABLE II

DISSOCIATION CONSTANTS OF SOME SYMMETRICALLY DISUBSTITUTED DIPHENYLSELENIUM DIIODIDES IN CARBON TETRACHLORIDE AT 25°

Substituent	Dissociation constant
p-CH_3O	0.019
p-CH_3	.025
None (H)	.036
p-Cl	.116

The logarithms of the dissociation constants have been plotted against the substituent constants of Hammett in Fig. 1. Since the effects of substituent constants have been found to be additive,[4] the plot for the disubstituted compounds is shown as log k *vs.* 2σ. The best straight line through the points was drawn by the method of least squares. The slope of the line, the Hammett constant ρ, is 0.7. This value is only one-third that found for the analogous series of dibromides, indicating a much lower sensitivity of the selenium–iodine bond than the selenium–bromine bond to electron density. The positive value indicates a weakening

---

(1) J. D. McCullough, THIS JOURNAL, **64**, 2672 (1942).

(2) Louis P. Hammett, "Physical Organic Chemistry," Chapter VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

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

(4) J. D. McCullough and M. K. Barsh, *ibid.*, **71**, 3029 (1949).