

tions, maxima were observed at 377 and 227 $m\mu$ and minima at 297 $m\mu$. When the spectrum was determined in 0.01 *N* HCl solution, the expected hypsochromic shift was obtained producing a maximum at 288 $m\mu$, inflection point at 312 $m\mu$ and a minimum at 249 $m\mu$. In attempting to produce the same reversibility (see Fig. 2) which was observed with 2-hydroxy-5-dimethylamino-benzoquinone, the shift from 380 to 286 $m\mu$ 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 $m\mu$. It might be well to note that this value, 344 $m\mu$, is very close to the 343 $m\mu$ value obtained for the 2- and 2,5-bis-(monoalkylamino)-benzoquinones.

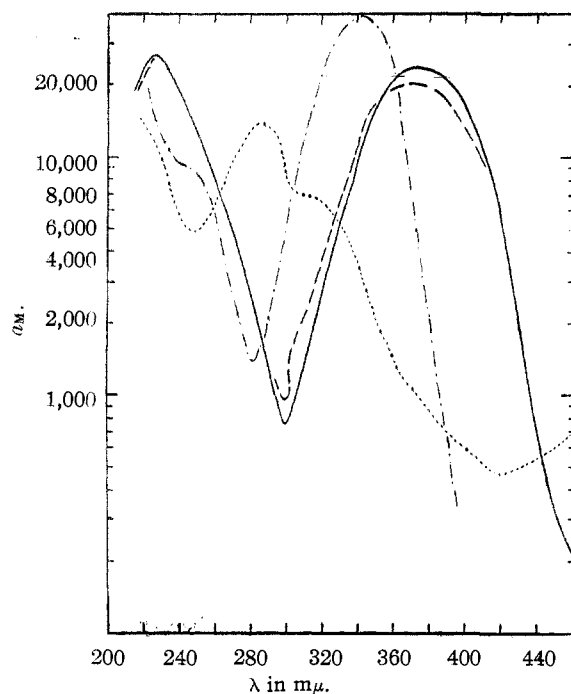


Fig. 2.—2,5-Bis-(dimethylamino)-benzoquinone: ———, *pH* 7; - - - - - , 0.01 *N* NaOH; - · - · - · , 0.01 *N* HCl; 2,5-bis-(methylamino)-benzoquinone: ·····, *pH* 7 and 0.01 *N* HCl.

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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 spectro-

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

photometrically 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 Hammett² 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

$\lambda(m\mu)$	<i>p</i> -Cl	<i>p</i> -CH ₃	<i>p</i> -CH ₃ O
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
<i>p</i> -CH ₃ O	0.019
<i>p</i> -CH ₃	.025
None (H)	.036
<i>p</i> -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

(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).

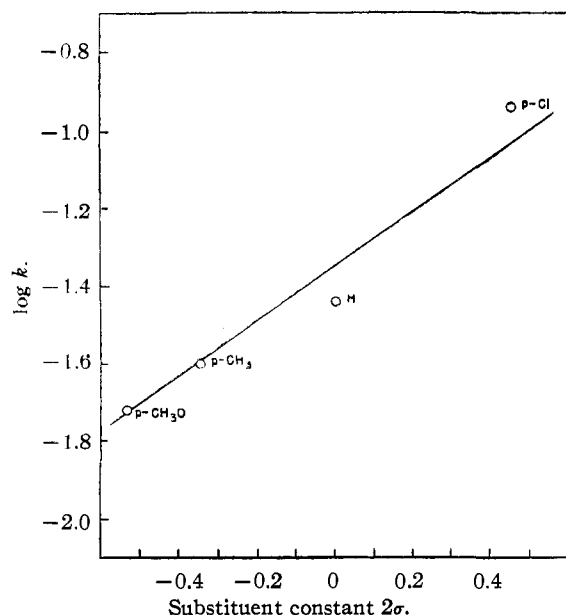


Fig. 1.—Plot of $\log k$ against the Hammett substituent constant.

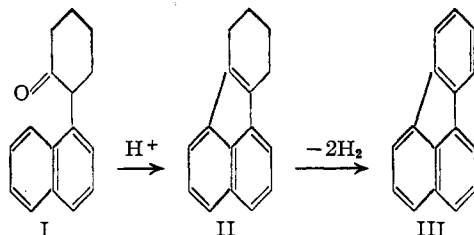
of the selenium-iodine bond by lowering the electron density on the selenium atom.

LOS ANGELES 24, CALIF. RECEIVED FEBRUARY 20, 1951

A Synthesis of Fluoranthene by Cyclodehydration

BY MILTON ORCHIN AND LESLIE REGGEL

The cyclodehydration¹ of 2-(1-naphthyl)-cyclohexanone (I) followed by dehydrogenation of the intermediate tetrahydrofluoranthene (II) would provide a three-step synthesis of fluoranthene (III). The starting ketone, I, is prepared by condensation of the available^{2a,b} *o*-chlorocyclohex-



anone with 1-naphthylmagnesium bromide.³ The preparation of fluoranthene (III) by this synthesis was accomplished, but the cyclization of I proceeded so poorly that the method cannot be recommended as a route to this interesting tetracyclic hydrocarbon.

The cyclized hydrocarbon from I, isolated as the complex with *s*-trinitrobenzene, was at first assumed to have the structure II. However, the ultraviolet spectrum (Fig. 1) showed that it possessed the structure of a substituted acenaphthene rather than that of an acenaphthylene or a vinylnaph-

thalene. It is possible that the compound originally thought to be II was actually a hexahydrofluoranthene, formed by disproportionation during cyclization. (The amount of material available was too small to permit ready measurement of the hydrogen evolved during the dehydrogenation.) Its analysis, however, is more consistent with a tetrahydro structure; furthermore, fluoranthene should be a product of a disproportionation, but it was absent from the cyclization mixture. It is likely, therefore, that the double bond in the cyclized compound has migrated into a non-conjugated position, possibly because of steric factors.

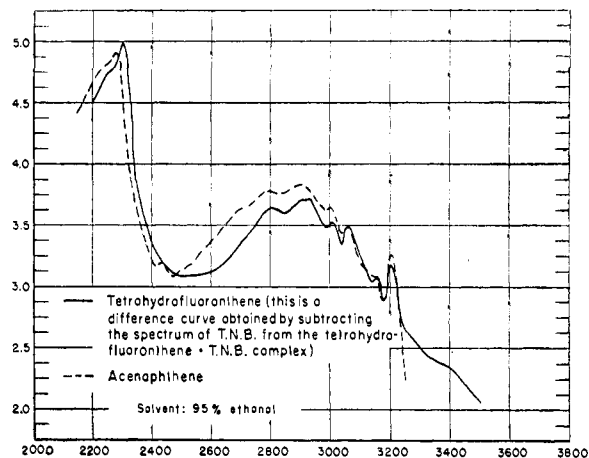


Fig. 1.—Ultraviolet absorption spectra.

Although the fluoranthene nucleus has previously been formed by cyclodehydration,⁴ the present synthesis is believed to be the first example in which cyclodehydration has closed the five-membered ring in this system.

Experimental⁵

2-(1-Naphthyl)-cyclohexanone (I).—The following is an improvement of the previously described procedure.³ To a cooled, vigorously stirred solution of 98.3 g. of *o*-chlorocyclohexanone in 150 ml. of benzene there was added during 35 minutes a solution of 1-naphthylmagnesium bromide (prepared from 155 g. of 1-bromonaphthalene, 20.0 g. of magnesium, 375 ml. of ether and 150 ml. of benzene; titration indicated a yield of 95%). After the reaction had subsided, stirring was continued at room temperature for 17 hours. The mixture was decomposed with dilute hydrochloric acid and then steam distilled. The residual red oil was taken up in benzene, washed, dried, and distilled, giving 90.6 g. of reddish material, b.p. 145–205° (1–3 mm.). Crystallization from benzene-petroleum ether and then from absolute ethanol gave 15.8 g. of I, m.p. 81.5–85.0°. The combined mother liquors in pyridine-ethanol were converted to the semicarbazones; the alcohol-soluble fractions gave 23.8 g. of crude semicarbazone, m.p. 211–216°, which on hydrolysis gave 8.83 g. of I. The total yield was 14.8%.

Cyclodehydration of I.—A mixture of 2.00 g. of I, 15 ml. of 48% hydrobromic acid, and 15 ml. of glacial acetic acid was refluxed for 24 hours. The dark-green product was taken up in benzene, washed with water, sodium bicarbonate solution and saturated sodium chloride solution and dried over sodium sulfate. The resulting oil (2.25 g.) was chromatographed on alumina. The more strongly adsorbed fraction (1.50 g. of orange gum) did not give a Beilstein test for halogen; it was not further investigated but may have consisted of condensation products of I. The less strongly

(1) C. K. Bradsher, *Chem. Revs.*, **38**, 447 (1946).

(2) (a) M. S. Newman, M. D. Farbman and H. Hipsher, "Organic Syntheses," Vol. 25, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 22. (b) From the Farchan Research Laboratories, 609 East 127 Street, Cleveland 8, Ohio.

(3) M. Orchin, *This Journal*, **70**, 495 (1948).

(4) H. France, S. H. Tucker and J. Forrest, *J. Chem. Soc.*, 7 (1945).

(5) All melting points corrected. Microanalyses by G. L. Stragand University of Pittsburgh. We wish to thank R. A. Friedel and Marion Springer for the spectral measurements.