Preparation of α-Phenyl-N-xenylnitrone.—The nitrone was prepared in three ways: first, benzaldehyde was added to the precipitated hydroxylamine prior to filtration and in the absence of acetic acid; second, the reduction of *p*-nitrodiphenyl was carried out in the presence of benzaldehyde; third, the benzaldehyde was condensed with the hydroxylamine after filtration of the dil. acetic acid solution. It is obtained pure as a yellow compound melting at 174–175° when recrystallized from alcohol.

Anal. Calcd. for $C_{19}H_{15}ON$: C, 83.5; H, 5.5; N, 5.1. Found: C, 83.1; H, 5.5; N, 5.5.

The nitrone is readily hydrolyzed to benzaldehyde by means of dil. hydrochloric and sulfuric acids. When hydrolyzed with dil. mineral acids in a current of steam to remove benzaldehyde, and then treated with slightly stronger mineral acids in order to effect the hydroxylamine rearrangement, no 4-amino-4′-hydroxydiphenyl was obtained. Under these conditions *p*-aminophenol is formed from the corresponding α-phenyl-N-phenylnitrone.[5,6]

Preparation of β-Xenylhydroxylamine.—The reduction mixture of *p*-nitrodiphenyl, alcohol, water, ammonium chloride and zinc dust was filtered into 15 cc. of glacial acetic acid. This solution, not entirely clear, was filtered into a volume of water equal to that of the reduction mixture and acetic acid. A pale yellow precipitate of the β-xenylhydroxylamine formed. It melts with preliminary softening and decomposition at 158° and is readily soluble in ether, acetone, alcohol and glacial acetic acid, and somewhat less soluble in benzene.

Anal. Calcd. for $C_{12}H_{11}ON$: N, 7.57. Found: 7.59, 7.84.

Like the hydroxylamine that is precipitated by water containing no acetic acid it gives the characteristic tests of hydroxylamine with Fehling's solution and ammoniacal silver nitrate, and forms the α-phenyl-N-xenylnitrone with benzaldehyde.

The authors wish to acknowledge help from Professor W. H. Perkin and Mr. L. C. Heckert.

Summary

β-Xenylhydroxylamine has been prepared by the reduction of *p*-nitrodiphenyl. It does not rearrange to 4-amino-4′-hydroxydiphenyl.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTICALLY ACTIVE DYES. III. PHYSICAL PROPERTIES, DYEING REACTIONS AND MECHANISM OF DYEING

BY WALLACE R. BRODE[1] WITH ROGER ADAMS

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In the previous papers[2] of this series a method was described for the preparation of optically active dyes and the physical properties of the basic dyes of this type were studied as to their suitability for use in the experiments on the absorption of dyes by fibers. This paper describes the re-

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[1] This communication is an abstract of a portion of a thesis submitted by Wallace R. Brode in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

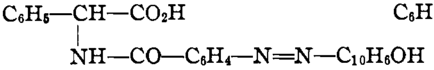
[2] (a) Ingersoll with Adams, THIS JOURNAL, **44**, 2930 (1922). (b) Brode with Adams, *ibid.*, **46**, 2032 (1924).

sults of careful dyeing experiments on wool and silk with the active and racemic modifications of certain dyes in the hope of determining whether chemical action takes place in the dyeing process.

It has been shown by analysis[3] that fibers such as wool and silk contain asymmetric compounds in their active forms and since the rates of reaction of enantiomorphic substances combining with the same active constituent are in general known to be different, it was considered probable that the combination of active dyes with fibers would have a different rate if the action were chemical; or rather it may be stated that if the absorption rates of the active forms of a dye were different or if a selective absorption occurred with a racemic modification, then this effect might be attributed to a chemical action between the dyes and the active part of the fiber. The results showed no difference in rates of the *d*- and *l*-forms and no selectivity with racemic modifications, and consequently no proof that chemical action takes place has been demonstrated.

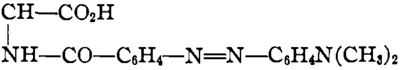
In addition to the work on the selective absorption by fibers to which references were given in the first articles in this series there should be mentioned the work of Euler and Bucht[4] who showed that casein (whose constitution as a protein is similar to that of fibers) shows no selective absorption of α-bromopropionic acid under the most favorable conditions where approximately half the acid in solution was absorbed. Similar data have been obtained upon the absorption of stereoisomeric compounds by active and inactive absorption agents and in no case has any evidence of selective absorption of active isomers been obtained.[5]

In this investigation the β-naphthol (I) and dimethylaniline (II) coupling products of diazotized *d*-, *l*- and *dl*-phenyl (*p*-aminobenzoylamino)acetic acid, the dyes prepared first by Ingersoll and Adams,[2a] were made again, carefully purified and studied. In order to have the results in the dyeing experiments of value, the determination of the exact amount of dye absorbed must be accurate and the dyes must be pure.



$$\begin{array}{l} C_6H_5—CH—CO_2H \\ \qquad\quad | \\ \qquad\quad NH—CO—C_6H_4—N{=}N—C_{10}H_6OH \end{array}$$

I



$$\begin{array}{l} C_6H_5—CH—CO_2H \\ \qquad\quad | \\ \qquad\quad NH—CO—C_6H_4—N{=}N—C_6H_4N(CH_3)_2 \end{array}$$

II

The best methods for the determination of the strength of dye solutions have been studied recently.[6] The three methods generally used are those

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[3] Matthews, "Textile Fibres," John Wiley and Sons, New York, **1913**. Abderhalden, *Z. physiol. Chem.*, **46**, 31 (1905). Georgievics, "Chemical Technology of Textile Fibres," Scott, Greenwood and Sons, New York, **1920**. Bowman, "Structure of Wool Fibres," Macmillian and Co., Ltd. London, **1908**.

[4] Euler and Bucht, *Z. anorg. Chem.*, **126**, 267 (1922).

[5] Hermans, *Z. physik. Chem.*, **113**, 385 (1924), Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, **1923**, **268**, 1189.

[6] (a) Appel, Brode and Welch, *Ind. Eng. Chem.*, **18**, 627 (1926). (b) Calcott and English, *ibid.*, **15**, 1042 (1923).

of titration by titanous chloride in case the dye is reducible, determination by spectrophotometric measurements and by comparative dyeing tests. Under usual conditions the error in the amount of dye determined by the first two methods is about ±0.5% though in many cases the determination may be more accurate. The dyeing method is accurate to about 2% in the blue and green, and the error is probably much larger in the red and yellow. The titanous chloride method was used in this work for determining the strength of the exhausted solutions and the dye samples were studied photometrically. In no case was one dye absorbed more rapidly than its mirror image, nor was an active solution ever produced by treatment of a racemic dye solution with wool or silk.

The results of the dyeing experiments just mentioned are at variance with those obtained by Porter and Hirst[7] and particularly with those by Porter and Ihrig[8] who presented data that certain azo dyes obtained from *m*-aminomandelic acid showed a selective absorption toward fibers for one of the enantiomorphic forms. The dyes described by Porter and Ihrig were made again and their dyeing experiments were repeated. The results of these authors could not be checked. No selectivity could be found, a fact which confirms the results with the dyes from phenylamino-acetic acid. More details of work on Porter and Ihrig's dyes are described in the following paper.

Since the completion of this investigation there has been published by Morgan and Skinner[9] a paper on stereoisomeric azo dyes. These were prepared by coupling various diazonium salts with diphenyl-β,γ-diamino-*n*-butane. The resolutions into the active forms were then carried out on the racemic dye, thereby presenting an entirely different method for the preparation of optically active dyes from that used by Porter and Ihrig and by Ingersoll and Adams. Morgan and Skinner claim to have observed a slight selectivity for the *l*- form of *dl*-di-4′-sulfobenzene-di-4-azodiphenyl-β,γ-diamino-*n*-butane, as compared with the *d*- form, using the titanous chloride method to determine the strength of the exhausted dye bath. Their conclusions were based on a difference of dye content of 0.0003 g. of dye as detected by titration of 5 cc. of the solution. With very dilute solutions of dyes such as were used, the accuracy cannot possibly be so great as that established for the titration of more concentrated solutions, and consequently a difference so slight as that found can hardly be considered within the experimental error of the analytical method. Moreover, the experimental evidence of these authors is that the observed difference in absorption is only slightly greater than the actual error in titration of the solutions. The amount of *l*-dye by weight per 100 cc. of solution was

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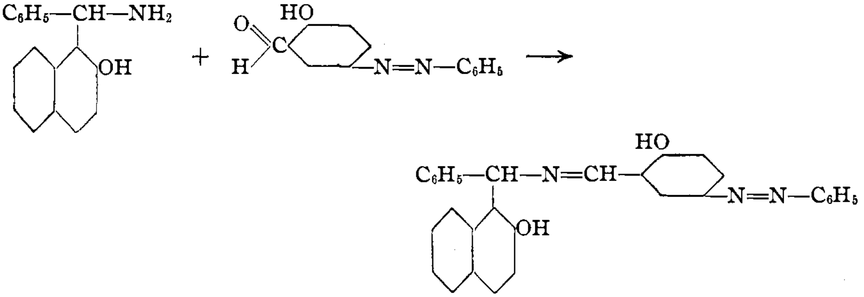
[7] Porter and Hirst, THIS JOURNAL, **41**, 1264 (1919).

[8] Porter and Ihrig, *ibid.*, **45**, 1990 (1923).

[9] Morgan and Skinner, *J. Chem. Soc.*, **127**, 1731 (1925).

0.4545, and the amount of *d*-dye by weight per 100 cc. was 0.4575 but the titrations on these two solutions were both given as exactly the same. It must also be considered that the *l*-dye varied widely in rotation depending upon the alkaloid used for resolution, and that the rotation of the *d*- and *l*-forms studied differed by more than 5%. With all these facts considered and the numerous possible and probable ways of explaining the experimental results besides that by selective absorption, the conclusion that selective absorption has been demonstrated seems entirely unwarranted.

Another type of dye (III) which it has been hoped could be used for tests similar to those just described was that obtained by the condensation of benzene-azosalicylaldehyde and the various stereoisomeric forms of α(β-naphthol)benzylamine. No difficulty was found in preparing the active and racemic dyes, but unfortunately they were so insoluble as to give unsatisfactory results in dyeing experiments.



III

Experimental Part

Preparation of Dyes.—The method used for preparing the dimethylaniline and β-naphthol coupling products of phenyl(*p*-aminobenzoylamino) acetic acid was essentially that described by Ingersoll and Adams except that the resolution of the *d*-form of phenylamino-acetic acid was carried out according to the more recent directions of Ingersoll.[10] The purification of the dimethylaniline dyes was more satisfactorily accomplished by crystallization from ethyl acetate than from 50% alcohol as was previously done by Ingersoll.[10]

Physical Properties.—The physical properties of the β-naphthol dyes were discussed in detail in a previous paper.[2a] The determinations of the physical properties of the dimethylaniline dyes were not carried out so completely as with the β-naphthol dyes, observations being made on only the more important physical constants. The absorption spectra were determined throughout the visible and ultraviolet to a frequency of 1360. These data which are given in Fig. 1 confirm the fact that the absorption

[10] Ingersoll, This Journal, **47**, 1168 (1925).

spectra of optical enantiomorphs are the same, a point which previous to the work on the β-naphthol dyes of this series had not been definitely confirmed for both of the enantiomorphic forms. The curve obtained from the absorption-spectra observations did not follow so closely the curve of dimethylaniline-azobenzene as the β-naphthol dye did that of the absorption spectra of benzene-azo-β-naphthol. This might have been expected, as the naphthol group is acidic and the addition of an extra acidic group in the form of phenylamino-acetic acid would cause less change than the addition of the acidic group to the basic dye derived from dimethylaniline.

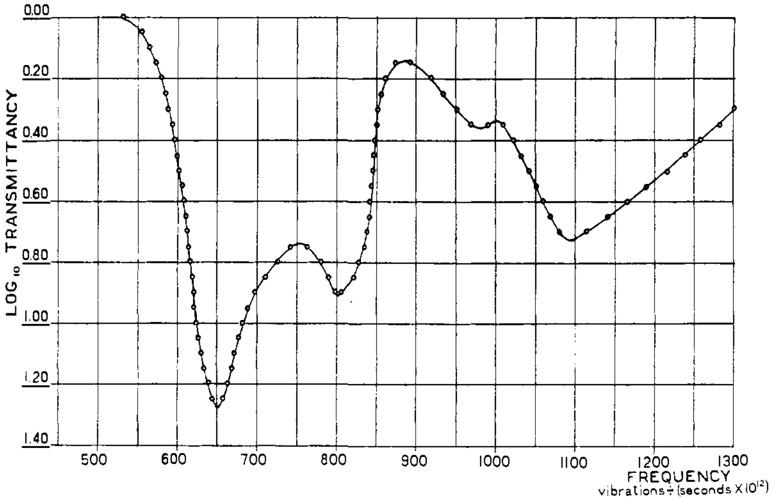


Fig. 1.—The absorption spectrum of *dl*-phenyl(*p*-dimethyl-aminobenzene-azobenzoylamino) acetic acid in alcohol. Concn., 0.01 × 25 g. per liter; cell thickness, 1 cm. The absorption-spectra curves of the *l* and *d* forms were also determined and found to be identical within the allowable experimental deviations.

The rotation of the dimethylaniline dyes, while normal, was different from the β-naphthol rotation in that the rotatory-dispersion curve crossed the 0° axis and hence changed in sign. This is a common occurrence in rotatory-dispersion curves, but gave considerable difficulty and trouble at first due to the fact that the original rotation measurements were made by using sunlight as a light source and this heterogeneous light source gave a 0° rotation for both forms. The dyes in all other respects behaved as optical pairs should. By the use of monochromatic light, however, it was possible to observe rotations on these dyes, which in the case of the *d*-dye was positive on the longer wave-length side and negative on the shorter wave-length side, and *vice versa* for the *l*-dye (Fig. 3).

The rotatory-dispersion curves of a number of the active intermediates used in this work have been determined and are given in Fig. 2. The concentrations of the solutions used in these curves are the same as those used by Ingersoll and Adams.[2a] The observations on the absorption spectra in the visible were made on Koenig, Martens, and Keuffel and Esser spectrophotometers and in the ultraviolet on a Hilger sector photometer. The rotational measurements were made on a Franz Schmidt and Haensch polarimeter.

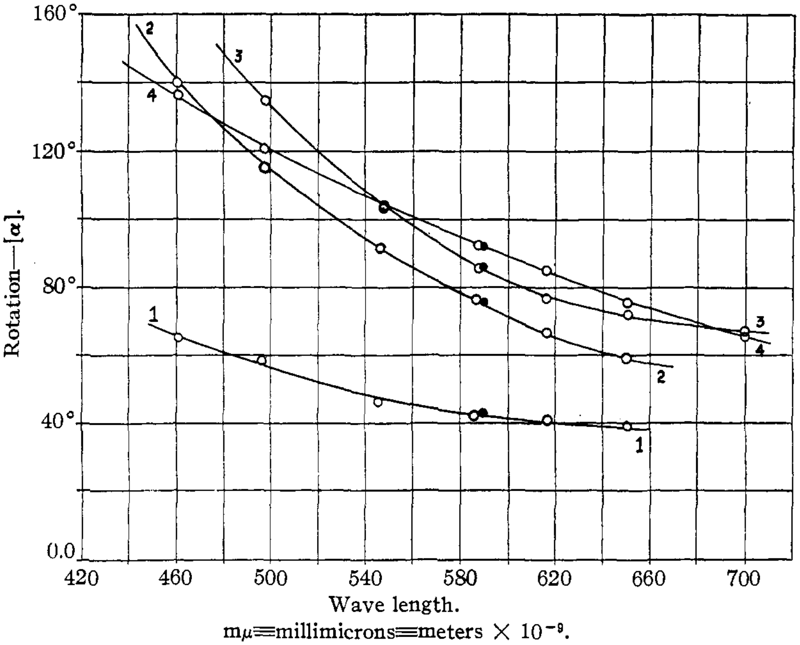


Fig. 2.—The rotatory-dispersion curves of the intermediate active products used in the preparation of these dyes. These observations were taken on the *l* compounds as follows; (1) *d*-camphor-sulfonate salt of *l*-phenylamino-acetic acid (3.8364 g. made up to 50 cc. with 34.54 cc. of *N* hydrochloric acid and the remainder water; 0.4177 g. in 20 cc. of water at 20°); (2) *l*-phenylamino-acetic acid, values given are $\alpha/2$; (3) *l*-phenyl(*p*-nitrobenzoylamino)acetic acid (2.000 g. in 25 cc. of absolute alcohol at 20°); (4) *l*-phenyl(*p*-aminobenzoylamino)acetic acid (2.000 g. in 25 cc. of *N* hydrochloric acid at 20°). The black dots represent the values for these same compounds as prepared and observed by Ingersoll.[2]

Dyeing Experiments.—The wool cloth used in the dyeings was material from the Bureau of Standards dye laboratory employed particularly for standard dyeings. It was of very high purity. The silk was unweighted material from the same source. The dyeings were made in a standard dye vat consisting of porcelain cups all immersed in the same heating bath. Dyeings were made for the same length of time, allowed to drain for the same time and then carefully washed. The remaining solution was titrated with titanous chloride according to the method of Calcott and English.[6b]

The dyeing experiments were made at high temperatures (95°) rather than at the low temperatures (20°) used in other similar experiments by other observers,[8,9] because it was felt that if a chemical action did take place it would be accelerated at higher temperatures. Observations of other investigators have definitely shown that for most dyes there is a physical adsorption of dyes by fibers at low temperatures which is more or less reversible and that at higher temperatures the amount of dye adsorbed is increased. There appears to be a different relation existing between the dye and the fiber at the higher temperature which is not so reversible as that found in dyeings at lower temperatures.

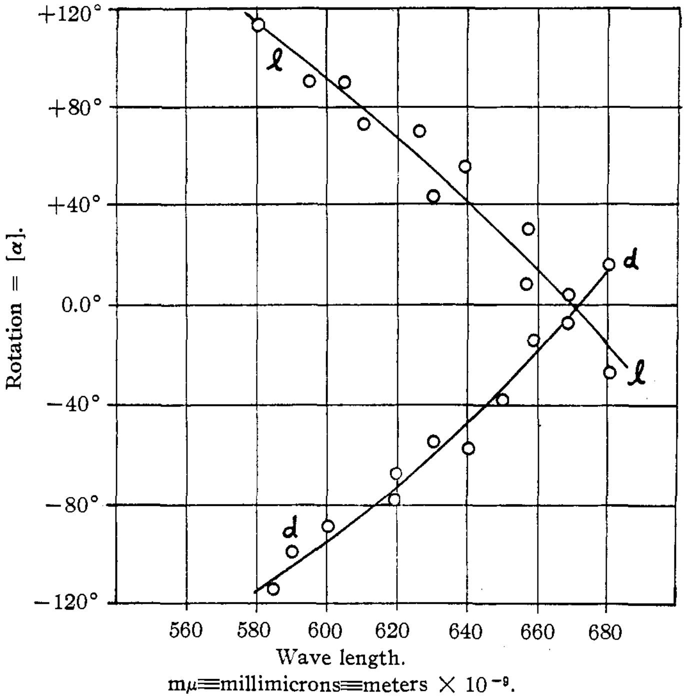


Fig. 3.—The rotatory-dispersion curves of *d*- and *l*-phenyl(*p*-dimethylaminobenzene-azobenzoylamino)acetic acid in ethyl acetate; concn., 1.000 g. per liter.

The dye solutions used in these dyeing experiments were prepared as follows.

For the β-naphthol dyes, 0.4000 g. of the dye was dissolved in a solvent consisting of 40 cc. of 95% alcohol and 160 cc. of water to which had been added 0.100 g. of anhydrous sodium sulfate and 0.075 g. of anhydrous sodium carbonate. For the dimethylaniline dyes, 0.4000 g. of the dye was dissolved in 100 cc. of 95% alcohol and 100 cc. of water to which had been added 0.100 g. of anhydrous sodium sulfate and 0.100 g. of sodium acid sulfate. The time and temperature for all the dyeing experiments were, respectively, 30 minutes and 95° (Table I).

TABLE I

DYEING EXPERIMENTS

40 cc. of dye solution containing 0.0800 g. of dye was used in each experiment.

β-NAPHTHOL DYEINGS

Dye	TiCl$_3$ Titrations		Dye adsorbed, %
	Blank soln., g.	Part. exhausted soln., g	
	A. WOOL, 2.000 G.		
d	0.0799	0.0308	61.45
l	.0798	.0302	62.15
dl	.0795	.0266	66.55
	B. SILK, 1.000 G.		
d	0.0799	0.0315	60.58
l	.0798	.0310	61.13
dl	.0795	.0274	65.52
	DIMETHYLANILINE DYEINGS A. WOOL, 2.000 G.		
d	0.0809	0.0331	59.08
l	.0785[a]	.0318[a]	59.45
dl	.0801	.0298	62.83
	B. SILK, 1.000 G.		
d	0.0809	0.0364	55.00
l	.0785[a]	.0352[a]	55.15
dl	.0801	.0338	57.85

[a] The consistent difference in both the blank run and the partially exhausted dye solutions with the values for the *d*-dyeings indicates that the dye solution was slightly weak and a correction for this difference would make the exhausted wool value 0.0326 and the exhausted silk value 0.0359. Dyes of this type are known to adsorb moisture readily on long exposure to air; the sample used had been prepared for some time.

The partially exhausted liquors from the dyeings of the racemic dyes with wool and silk were examined with a polarimeter with monochromatic light of various wave lengths and no rotation could be detected in either the β-naphthol or dimethylaniline dye solutions. The polarimeter used in these observations was capable of being read to 0.0002° with accuracy and was of the best design and construction.

Samples of these dyeings were examined spectrophotometrically by studying their reflection spectra and, while the height of the curve is not directly proportional to the concentration of the dye in the sample, the results showed that the racemic form is slightly stronger than the active forms and that the two active dyeings are of the same intensity.

Tests were also made on the dyed samples as to their fastness to light. The dyes were very fast to light and required over 200 hours' exposure to a violet-carbon arc to cause noticeable fading, and then no difference could be detected in the rates of fading of the active or racemic dyeings.

Benzene-azosalicylaldehyde-α(β-naphthol)benzylamine, III.—A solution of 11.3 g. of benzene-azosalicylaldehyde[11] in 100 cc. of alcohol and a solution of 12.4 g. of

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[11] Tummeley, *Ann.*, **251**, 174 (1889).

α-(β-naphthol)benzylamine[12] in an equal amount of alcohol were mixed together while hot. On cooling, the brilliant yellow-orange dye separates; m. p., 210–212°. It is quite soluble in benzene, slightly soluble in alcohol, insoluble in water or alkaline solutions.

Anal. Subs., 0.1147, 0.1112. Calcd. for $C_{30}H_{23}O_2N_3$: C, 78.7; H, 5.03. Found: C, 78.3, 78.6; H, 5.64, 5.24.

The active modifications of this dye have been prepared and have a somewhat higher melting point than the racemic modification (220–225°) and at a wave length of 610 mμ gave a rotation of about 80° in a benzene solution. The work on these active dyes is not completed and the purity of the active modifications has not been definitely established. They are unsatisfactory for dyeing experiments due to their low solubility. It is hoped that some derivatives of this type may be obtained which will give solutions from which comparative dyeings may be made.

Summary

1. The active isomers of optically active dyes have the same physical properties, including adsorption by inert and active materials, adsorption, color, fastness to light, melting points and all other physical properties tested.
2. The rotatory-dispersion curves of these active dyes and of the intermediates used have been studied and found to be normal.
3. A new type of asymmetric dye has been prepared from an asymmetric derivative of benzylamine.
4. No apparent difference in adsorption of the two active forms could be detected in the dyeing experiments on these dyes.
5. The racemic dyes appear to be adsorbed to a greater extent than the active dyes, by both inactive and active adsorbing agents.

URBANA, ILLINOIS

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[12] Betti, *Gazz. chim. ital.*, [ii] **50**, 301, 310 (1900), and subsequent articles in the same journal.