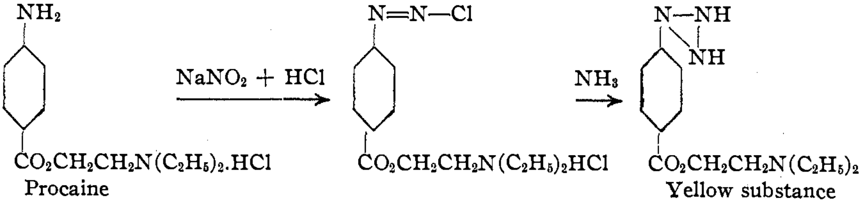
which on the addition of more water produces color, amyl alcohol is the most promising. Work in that direction will be continued. For the present, the yellow substance may be assigned the following formula.



Summary

1. A new color reaction is described for the local anesthetics procaine, tutocaine, butyn, butesin, propaesin, benzocaine and orthoform; no special reagents are necessary.

2. The reaction is extended to a quantitative method for procaine. The conditions which must be observed in order to obtain reliable results are detailed; they include temperature (20°), amounts, concentration, and order of addition of the reagents. The concentration of the procaine must lie between 10 mg. and 15 mg. in 10 cc. of solution.

3. The preparation of dichromate color standards is described.

4. The possible interference of admixed materials has been investigated.

5. The accuracy of the quantitative method is within 10%.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 11]

BIPHENYL DERIVATIVES OF AMMONIA, PARA-PHENYLENEDIAMINE AND BENZIDINE. MERIQUINONIC SALTS

BY JEAN PICCARD

RECEIVED MAY 13, 1926 PUBLISHED NOVEMBER 5, 1926

The first meriquinonic salt was described by C. Wurster,[1] and its constitution was established by Willstätter and Piccard.[2] Later, the present author described the preparation of the simplest of all the meriquinonic salts, that obtained by oxidation of *p*-phenylenediamine itself.[3] By adding two atoms of bromine for two molecules of the base we get the meriquinone di-imonium bromide.[4]

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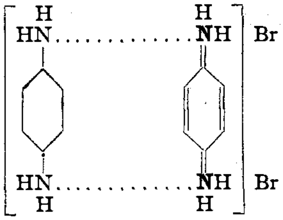
[1] Wurster, *Ber.*, **12**, 1803 (1879).

[2] Willstätter and Piccard, *Ber.*, **41**, 1458 (1908).

[3] Piccard, *Ann.*, **381**, 351 (1911).

[4] Coördination formula instead of quinquivalent nitrogen [see THIS JOURNAL, **48**, 2354 (1926)]. In dye chemistry we need the coördination formulas even if we keep the quinquivalent nitrogen, because most dyes are intramolecular or extramolecular addition compounds.



The other meriquinonic salts are derived from this one by substitution of the hydrogen atoms by alkyl, phenyl or biphenyl groups and replacement of phenylenediamine by benzidine. In the desire to establish as clearly as possible the relation between constitution and color of these meriquinonic salts, we prepared a certain number of new phenylenediamines and benzidines, from which we made the corresponding meriquinonic derivatives. In previous publications[5] we have already described some of these new bases, and technical details of their preparation can be found there as well as in the theses of my collaborators, so that we now may be relatively brief. Since the purification of compounds of this kind is a difficult problem, and since the elementary analysis does not of itself give a real proof of the identity of the new bases, we have never considered any

TABLE I

COLORS OF

MERIQUINONIC SALTS PRODUCED BY OXIDATION OF PHENYLENEDIAMINES AND BENZIDINES

p-Phenylenediamines	
Leuco base	Color of the meriquinonic salts
Phenylenediamine	yellow
Monomethyl-phenylenediamine	orange
Dimethyl-	red
Phenyl-	violet-red
Trimethyl-	violet
Tetramethyl-	violet-blue
Diphenyl-	blue
Dibiphenyl-	bluish-green
Tetraphenyl-	green
Diphenyl-dibiphenyl-	green
Tetrabiphenyl-	yellowish-green

Benzidines	
Leuco base	Color of the meriquinonic salts
Benzidine	blue
Diethyl-benzidine	green
Tetramethyl-	greenish-yellow
Diphenyl-	yellow
Dibiphenyl-	orange-yellow
Tetraphenyl-	orange
Diphenyl-dibiphenyl-	red
Tetrabiphenyl-	red (somewhat violet)

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[5] Piccard and others, (a) *Helv. Chim. Acta,* **6,** 1011 (1923); (b) **7,** 75 (1924); (c) **7,** 789 (1924).

of our syntheses as definite unless the compound had been made by at least two entirely different methods.

The preceding table shows the colors of the meriquinonic salts produced by oxidation of these phenylenediamines and benzidines.

The regular succession of colors from the yellow of the first order to the red of the second order can clearly be seen in these tables. From these data one can also deduce easily some laws about the relative values of methyl, phenyl and biphenyl groups which are interesting, because the same laws hold good in the ordinary technical dyes.

I. Derivatives of Ammonia

The following bases were needed for the syntheses of the new phenylenediamines and benzidines. All of the nine possible derivatives which can be made by replacing the hydrogen atoms of ammonia either by phenyl or biphenyl groups are now known; (1) aniline, (2) diphenylamine, (3) triphenylamine (all well known), (4) aminobiphenyl, $C_6H_5C_6H_4NH_2$ (prepared by Schlenk),[6] (5) dibiphenylamine, $(C_6H_5C_6H_4)_2NH$ (prepared by Wieland).[7] The four others were prepared by the author.

(6) Phenylbiphenylamine, $C_6H_5—NH—C_6H_4—C_6H_5$

First Synthesis, $C_6H_5—C_6H_4N(COCH_3)\boxed{H + I}C_6H_5$.—A mixture of 1.3 g. of acetoaminobiphenyl, 4.1 g. of iodobenzene and 6 g. of potassium carbonate with 3 cc. of nitrobenzene and a trace of catalytic copper was heated[8] for 12 hours at 230° to 250° and then steam was passed through it to remove nitrobenzene and unchanged iodobenzene. The acetylphenylbiphenylamine was extracted with benzene[9] and recrystallized from alcohol. It is a colorless compound melting at 110°. It is hydrolyzed by being heated for two hours with a 20% potassium hydroxide solution in alcohol. The free base was washed with boiling water and recrystallized from alcohol, forming colorless, brilliant crystals; m. p., 112°.

Anal. Subs., 0.2604: 13.55 cc. of N_2 [18°, 718 mm. (corr., 711)]. Calcd. for $C_{18}H_{15}N_2$: N, 5.72. Found: 5.71.

Second Synthesis, $C_6H_5—N(COCH_3)\boxed{H + I}C_6H_4C_6H_5$.—This operation was a similar one; the identity of the product was established by comparison of the melting points of the acetyl derivatives and the melting point of the mixture of them.

(7) Diphenylbiphenylamine, $(C_6H_5)_2N—C_6H_4—C_6H_5$

First Synthesis, $C_6H_5—C_6H_4—\boxed{I + H}—N(C_6H_5)_2$.—We have already described this synthesis and given an analysis of the compound. To prove the identity of the base we made now a second synthesis.

Second Synthesis, $C_6H_5C_6H_4N\boxed{\begin{matrix}H & & I\\ H & + & I\end{matrix}}\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}$.—The operations were carried out in the usual way and the same compound was obtained.

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[6] Schlenk, *Ann.*, **368**, 303 (1909).

[7] Wieland, *Ann.*, **381**, 217 (1911).

[8] See Ref. 7, THIS JOURNAL, **48**, 2356 (1926).

[9] In the water solution we always make an iodine determination by titration with silver nitrate solution to find what yield we may expect. Only by this method was it possible always to find the exact conditions under which the condensation should be run.

(8) Phenyldibiphenylamine, $C_6H_5—N(C_6H_4—C_6H_5)_2$

First Synthesis, $(C_6H_5.C_6H_4)_2N\boxed{H + I}C_6H_5$.—One and five-tenths g. of dibiphenylamine was heated for eight hours with 1 g. of iodobenzene, 2 g. of potassium carbonate, 7 g. of nitrobenzene and a trace of catalytic copper. The yield was very good, but the purification was very difficult and cost us most of the substance. We recrystallized the base first from acetic acid and then from amyl alcohol. It is colorless and melts at 160°.

Anal. Subs., 0.0936: CO_2, 0.3126; H_2O, 0.0506.

Subs., 0.2087: 6.8 cc. of N_2 [18°, 703 mm. (corr., 696)]. Calcd. for $C_{30}H_{23}N$: C, 90.64; H, 5.84; N, 3.53. Found: C, 90.89; H, 6.04; N, 3.47.

By oxidation in glacial acetic acid a compound was obtained which seemed to be tetrabiphenyldiphenoquinonedi-imonium acetate. The oxidation reaction is, however, not a simple one and we gave up our plan of preparing tetrabiphenylbenzidine by reduction of this quinonic salt. (See the preparation of tetraphenylbenzidine by this method.)[10] It will be seen below that we prepared the desired tetrabiphenylbenzidine in another way.

Second Synthesis, $C_6H_5N\boxed{\begin{matrix}H & + & I\\ H & + & I\end{matrix}}\begin{matrix}C_6H_4C_6H_5\\ C_6H_4C_6H_5\end{matrix}$.—The yield was very poor, but sufficient to allow an identification of the compound.

(9) Tribiphenylamine, $(C_6H_5—C_6H_4—)_3N$

Synthesis, $(C_6H_5—C_6H_4)_2N—\boxed{H + I}—C_6H_4—C_6H_5$.—A mixture of 0.64 g. of dibiphenylamine, 0.56 g. of *p*-iodobiphenyl and 3 g. of potassium carbonate was heated for 12 hours at 200° to 230° with 2 cc. of nitrobenzene and a trace of catalytic copper. After the usual steam distillation and extraction with benzene the new base was obtained as a white powder which was recrystallized from benzene; m. p., 257–259° (corr.).

Anal. Subs., 0.0866: 2.4 cc. of N_2, [16°, 117 mm. (corr., 711)]. Calcd. for $C_{36}H_{27}N$: N, 2.96. Found: 3.05.

This base is very soluble in benzene, acetone, nitrobenzene and in hot acetic acid. The solutions have a strong violet fluorescence.

In one of the publications already mentioned we gave a provisional description of this compound which must be revised, because we did not have in hand the compound we believed we had. The original compound was prepared by only one synthesis. Very shortly after our publication and independently from it, W. Bülow[11] published a description of tribiphenylamine which he had prepared by heating iodobiphenyl with aminobiphenyl. Although the melting point given by him is correct, his description shows that his compound was not pure, because he says that it is soluble with an intense green color in concd. sulfuric acid, which would be very surprising. A careful examination of our pure substance shows, indeed, that in the absence of any oxidizing agent its solution in sulfuric acid is colorless, but in the presence of air this solution turns green remarkably fast.

An absolute certainty of the identity of tribiphenylamine—here as in the other cases—can be obtained only by a second independent synthesis.

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[10] Wieland, *Ber.*, **46**, 3301 (1913).

[11] Bülow, *Ber.*, **57**, 1434 (1924).

The two syntheses made by Bülow and by us are not independent syntheses, because in Bülow's synthesis dibiphenylamine, even though not isolated, is an intermediate compound, so that the second step of his reaction is the same as our synthesis. As a rule it is safer to make such condensations in two distinct operations. Unfortunately we do not see any convenient way to obtain tribiphenylamine by another synthesis, but we do not doubt that such a synthesis would produce the same compound.

II. Derivatives of *p*-Phenylenediamine

The five possible symmetrical derivatives which can be made by replacing the amino-hydrogen atoms of *p*-phenylenediamine by phenyl or biphenyl groups are now known. The three biphenylated compounds have been prepared by the author: (1) dibiphenyl-*p*-phenylenediamine, $C_6H_5—C_6H_4—NH—C_6H_4—NH—C_6H_4—C_6H_5$; (2) diphenyldibiphenyl-*p*-phenylenediamine, $(C_6H_5)(C_6H_5C_6H_4)N.C_6H_4.N(C_6H_5C_6H_4)(C_6H_5)$; (3) tetrabiphenyl-*p*-phenylenediamine, $(C_6H_5—C_6H_4)_2N.C_6H_4.N(C_6H_4—C_6H_5)_2$. The second and the third of these bases have been prepared by two different syntheses. The first one has been prepared by only one method; its identity was proved, nevertheless, by the fact that we could use it for one of the two syntheses of the second base and for one of the two syntheses of the third base.

Details of preparation and analysis may be found in a previous publication. Also will be found there a description of dibiphenylquinone-di-imine,[5b] $C_6H_5—C_6H_4—N{=}C_6H_4{=}N—C_6H_4—C_6H_5$, which is brick red and is one of the few stable quinone di-imino bases; m. p., 266°. We analyzed it by titration with titanium trichloride.

The three bases are soluble in glacial acetic acid and these solutions give upon oxidation the meriquinonic salts. The colors of these are, respectively, bluish-green, green and yellowish-green. By further oxidation we obtain the holoquinonic salts.

III. Derivatives of Benzidine

In the preceding section the described meriquinonic salts derived from *p*-phenylenediamine reached to the very end of the colors of the first order (yellowish-green). In this section, where we begin only with blue, we shall reach far into the colors of the second order.

Here, again, the five possible symmetrical derivatives which can be made by replacing the amino hydrogen atoms of benzidine by phenyl[12] or bi-

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[12] Tetraphenylbenzidine had been prepared by only one method, the oxidation of triphenylamine.[10] We made two new syntheses of this compound. First synthesis: *p,p'*-di-iodobiphenyl was treated with diphenylamine in the usual way and tetraphenylbenzidine was obtained, which was identified with a preparation made by Wieland's method. Second synthesis: benzidine itself was phenylated by treatment with iodobenzene in the same way and tetraphenylbenzidine was again obtained.

phenyl groups are now known. The three biphenylated derivatives have been prepared by the author.

(1) Dibiphenylbenzidine, $C_6H_5.C_6H_4\text{—}NH\text{—}C_6H_4.C_6H_4\text{—}NH\text{—}C_6H_4.C_6H_5$

First Synthesis, $C_6H_5C_6H_4.N(COCH_3)\boxed{H+I}C_6H_4C_6H_4\boxed{I+H}(COCH_3)N.C_6H_4C_6H_5$. —A mixture of 0.84 g. of aceto-aminobiphenyl, 0.81 g. of *p,p'*di-iodobiphenyl, 1 g. of potassium carbonate and 3 cc. of nitrobenzene was heated 12 hours at 200° to 230° with a trace of catalytic copper. After the usual steam distillation, the substance was extracted with boiling toluene and the solution filtered while still hot. The toluene was evaporated in a vacuum and the dibiphenyldiacetyl-benzidine was hydrolyzed by being heated during two hours with 1 g. of potassium hydroxide in 15 cc. of alcohol. The remaining mixture was thoroughly washed with boiling water. The unchanged organic compounds were extracted with a small amount of boiling toluene and the dibiphenylbenzidine was recrystallized from boiling nitrobenzene, in which it is relatively quite soluble (0.27 g. in 7 cc.). It is slightly soluble in acetic acid. The solutions have a strong violet fluorescence; the base itself is nearly colorless; m. p., 300° (corr.). By oxidation in glacial acetic acid the meriquinonic salt, which is yellow of the second order, is obtained first. Thick layers are orange.[18] By further oxidation the meriquinonic salt can be transformed into the holoquinonic derivative, which is green (monosalt). By adding fuming sulfuric acid the blue color of the disalt can be observed.

Anal. Subs., 0.1002: 5.05 cc. of N_2 [13°, 724 mm. (corr., 719)]. Calcd. for $C_{36}H_{28}N_2$: N, 5.73. Found: 5.69.

Second Synthesis, $C_6H_5C_6H_4\boxed{I+H}N(COCH_3)C_6H_4C_6H_4N(COCH_3)\boxed{H+I}C_6H_4C_6H_5$. —The reaction proceeded very slowly. Even after 25 hours' heating, only 56% of the iodine was found in the form of potassium iodide by the silver nitrate titration. The final yield was, of course, very low, but we could identify the two acetyl derivatives.

Diacetyldibiphenylbenzidine.—This compound may be purified by crystallization from boiling glacial acetic acid, in which it is soluble with a green fluorescence. It is then washed by being boiled for one hour with alcohol and recrystallized from benzene, to which also it gives a green fluorescence. The compound is colorless; m. p., 245–249° (corr.). In contrast with the free base, the acetyl derivative is not colored by oxidation in acetic acid solution.

(2) Diphenyldibiphenylbenzidine,

$(C_6H_5)(C_6H_5C_6H_4)N\text{—}C_6H_4C_6H_4\text{—}N(C_6H_4C_6H_5)(C_6H_5)$

First Synthesis.—Oxidation of diphenylbiphenylamine to diphenyldibiphenyldiphenoquinone-di-immonium acetate and subsequent reduction to the benzidine: $(C_6H_5C_6H_4)(C_6H_5)NC_6H_4\boxed{H + O + H}C_6H_4N(C_6H_4C_6H_5)(C_6H_5)$.

Second Synthesis: $C_6H_5C_6H_4\boxed{I + H}N(C_6H_5)C_6H_4C_6H_4N(C_6H_5)\boxed{H + I}C_6H_4C_6H_5$. —The second synthesis is less convenient, but we could identify the preparations made

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[18] The phenomenon is the same as that with diphenylbenzidine. Kehrmann [*Ber.*, **45**, 2641 (1912)] described the meriquinonic salt derived from this base as being green. The solutions are, however, yellow but dissociation takes place very easily. This dissociation produces the blue holoquinonic salt which, when present only in very small percentage, makes the yellow color of the solution turn green. In order to see the real color of the meriquinonic salt, a large excess of diphenylbenzidine must be added, which by its mass action holds the dissociation back. Both meriquinonic salts, that derived from diphenylbenzidine as well as that derived from dibiphenylbenzidine, are yellow, the second being more orange-yellow.

by both methods. By oxidation the red meriquinonic salt is obtained first and then the blue-green holoquinonic salt. Details and analysis can be found in a previous publication.[5]

(3) Tetrabiphenylbenzidine, $(C_6H_5C_6H_4)_2N—C_6H_4C_6H_4—N(C_6H_4C_6H_5)_2$

First Synthesis, $(C_6H_5C_6H_4)_2N—\boxed{H + I}—C_6H_4C_6H_4—\boxed{I + H}—N(C_6H_4C_6H_5)_2$. A mixture of 0.8 g. of *p,p'*-di-iodobiphenyl, 1.3 g. of dibiphenylamine and 1 g. of potassium carbonate was heated during 14 hours at 190° to 220° with 4 cc. of nitro benzene and a trace of catalytic copper powder. After the usual separations the new base was recrystallized four or five times from toluene and dried in a vacuum at 200° to decompose the toluene addition compound. Tetrabiphenylbenzidine gives yellow, very brilliant crystals; m. p., 254–259°.

Anal. Subs., 0.1423, 0.1166, 0.1221, 0.1017: CO_2, 0.4694, 0.3852, 0.4053, 3372; H_2O, 0.0805, 0.0651, 0.0674, 0.0532.

Subs., 0.1248: 3.70 cc. of N_2, [15°, 712 mm. (corr., 706)]. Calcd. for $C_{60}H_{44}N_2$: C, 90.87; H, 5.59; N, 3.53. Found: C, 90.08, 90.10, 90.53, 90.43; H, 6.33, 6.24, 6.17, 5.85; N, 3.26.

Second Synthesis, $(C_6H_5.C_6H_4)_2\boxed{I_2 + H_2}N—C_6H_4.C_6H_4—N\boxed{H_2 + I_2}(C_6H_4.C_6H_5)_2$. This method gave very poor results. The base showed the color reactions of tetrabiphenylbenzidine, but we did not succeed in its purification. The reaction must be carried out in two steps as follows.

Third Synthesis.—Bidiphenylbenzidine is made first and is then treated with iodobiphenyl:

$$C_6H_5C_6H_4—\boxed{I + H}—N(C_6H_4C_6H_5)—C_6H_4C_6H_4—N(C_6H_4C_6H_5)—\boxed{H + I}—C_6H_4C_6H_5.$$

A mixture of 0.14 g. of *p*-iodobiphenyl, 0.12 g. of dibiphenylbenzidine and 1 g. of potassium carbonate was heated 20 hours at 200° to 230° with 1 cc. of nitrobenzene and a trace of catalytic copper. After the usual operations good crystals of tetrabiphenylbenzidine appeared as soon as the toluene solution was cooled.

Tetrabiphenylbenzidine is very slightly soluble in organic solvents. The solutions have a very strong violet fluorescence. The meriquinonic salts are of a quite characteristic tint of red. It is at the same time somewhat orange and somewhat violet. The holoquinonic salts are yellowish-green.

Nitrobenzene Addition Compounds.—It is a well-known fact that nitrobenzene dissolves aniline with the development of a yellow color, and Ostromisslensky has given the colorimetric proof that in these solutions we have an addition compound of one molecule of aniline with one molecule of nitrobenzene.[14] All aniline derivatives, whether primary, secondary or tertiary, give this same reaction, but until now it had never been possible to isolate any of these addition compounds.[15] When the solutions are cooled each constituent crystallizes as such before the necessary concentration for the precipitation of the addition compound is reached. It was, therefore, a rather agreeable surprise when it was found that tetrabiphenylbenzidine crystallizes with two molecules of nitrobenzene. This compound is orange-red. It has no sharp melting point; in order to be decomposed it must be heated in a vacuum at 150°.

Anal. Subs., 0.2036, 0.1029: nitrobenzene (by loss of weight), 0.0443, 0.0236. Calcd. for $C_{60}H_{44}N_2.2C_6H_5NO_2$: $C_6H_5NO_2$, 23.7. Found: 21.8, 22.6.

Toluene Addition Compounds.—Tetrabiphenylbenzidine also crystallizes with one molecule of toluene. This yellow addition compound is very stable and had to be heated in a vacuum at 200° to be decomposed.

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[14] Ostromisslensky, *Ber.*, **44**, 268 (1911).

[15] Pfeiffer, "Organische Molekulverbindungen," Stuttgart, **1922**, p. 234.

Anal. Subs., 0.5470, 0.2182: toluene (by loss of weight), 0.0561, 0.0226. Calcd. for $C_{60}H_{44}N_2.C_6H_5CH_3$: $C_6H_5CH_3$, 10.40. Found: 10.25, 10.35.

For the numerous preparations described in this paper I have to express my thanks to my assiduous collaborators, Dr. F. de Montmollin, Dr. F. Abouchy, Dr. R. Bretagne, R. Mercanton, chim. dipl., Dr. E. Oppenheim and C. Pedrazzini, ing. chim. dipl., with whom I worked at the University of Lausanne.

Summary

A certain number of biphenyl derivatives of *p*-phenylenediamine and of benzidine have been prepared and described, as well as their meriquinonic salts. At the same time different biphenyl derivatives of ammonia have been prepared, which had not previously been made and which were necessary for the present work.[16]

CAMBRIDGE, MASSACHUSETTS

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

THE VAPOR PRESSURES, DENSITIES, AND SOME DERIVED QUANTITIES FOR ACETONE

BY W. A. FELSING AND S. A. DURBAN

RECEIVED JULY 2, 1926 PUBLISHED NOVEMBER 5, 1926

Introduction

In an investigation dealing with certain addition compounds of sodium iodide with acetone it became desirable to know accurately the vapor pressures of acetone at various temperatures, more especially at low temperatures. An examination of the literature pointed toward the necessity of checking the existing data from about —80° to +60°. Incidental to this investigation was a determination of the densities of liquid acetone over the same temperature range. An outside request was made for data on the solubility of carbon dioxide in acetone over the temperature range —75° to +25°. These data are also included.

Regnault[1] measured the vapor pressures of acetone from 20° to 140°. Taylor[2] covered practically the same range. Drucker, Jiméno and Kangro[3] investigated the range —94.8° to 10.7°. Sameshima[4] presents data, undoubtedly "smoothed out," from 5° to 50°. N. Jacob[5] bridges the gap

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[16] In another paper [*Ber.*, **59**, 1438 (1926)] will be found a discussion of the constitution formula of the meriquinonic salts. This has not been touched on in the present article.

[1] Regnault, *Mém. Paris*, **26**, 339 (1862).

[2] Taylor, *J. Phys. Chem.*, **4**, 366 (1900).

[3] Drucker, Jiméno and Kangro, *Z. physik. Chem.*, 90, 518 (1915).

[4] Sameshima, THIS JOURNAL, **40**, 1488 (1918).

[5] Jacob, *Recherches et Inventions*, N. S. [II] **12**, 460 (1924).