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Mechanism of the Benzidine Rearrangement. V.[1] Acid-Catalyzed Decomposition of Tetraphenyltetrazene and Related Compounds

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Decomposition of either tetraphenyltetrazene or tetraphenylhydrazine in the presence of strong acid leads to formation of N,N'-diphenylbenzidine, diphenylamine, and an amorphous material believed to be polymeric. The latter is believed to come from oxidation products of diphenylbenzidine. The oxidant must be a transient produced in the decomposition reactions. The most likely candidate for this role is the cation radical, $(C_6H_5)_2\dot{N}^+H$.

The decomposition of 1,1,4,4-tetraphenyltetrazene[2] in anhydrous chloroform containing hydrogen chloride has been reported by Wieland[3] to yield a dichloro-9,10-diphenyl-9,10-dihydrophenazine. He also commented on the similarity of the chemical behavior of the tetrazene to that of tetraphenylhydrazine. Thermal decomposition of tetraphenylhydrazine in nonacidic solutions was also studied by Wieland[4] who concluded that decomposition produced diphenylimino radicals as the primary dissociation products. His further observation that 9,10-diphenyl-9,10-dihydrophenazine (m.p. 172–175°) is one of the major reaction products was recently shown to be in error by Musso.[5] On repeating Wieland's experiments Musso demonstrated that no 9,10-diphenyl-9,10-dihydrophenazine (m.p. 283–285°)[6] is formed whatsoever. Therefore, it appears at least doubtful if a dichlorodiphenyldihydrophenazine was ever obtained by Wieland in the hydrogen chloride-catalyzed decomposition of tetraphenyltetrazene, especially since it also is reported that tetraphenylhydrazine under similar conditions (anhydrous benzene, hydrogen chloride in ether)[7] gives rise to *p*-chloro-*p*'-diphenylaminodiphenylamine. Wieland and Gambarjan[8] also reported that N,N'-diphenylbenzidine and a blue dye were formed when tetraphenylhydrazine was treated with sulfuric acid. Kehrmann[9] concluded that the blue compound was an oxidation product of diphenylbenzidine, a conclusion with which Wieland concurred.[10] A salt, having the composition of a monochloroplatinate of N,N'-diphenyl-*p*,*p*'-diphenoquinonimine, was isolated by Kehrmann.[9] Green solids, which were also produced, were believed by Kehrmann[9] to be "mero-quinones" but were considered to have a polymeric structure by Wieland since he could not convert them to diphenylbenzidine by reduction with zinc and acetic acid.

Similar products were formed by oxidation of diphenylamine in acidic solutions.[8] Subsequently, Kolthoff and Sarver[11] reported that diphenylamine can be oxidized to diphenylbenzidine without concomitant production of the quinonimine. They also reported that further oxidation of diphenylbenzidine in 0.1–1.0 *N* sulfuric acid produced a green material, referred to as "meroquinoid," without formation of detectable amounts of the quinonimine. They believed that this material was a sparingly soluble molecular compound formed from the benzidine and the quinonimine. From measurements of electrode potentials in solutions of diphenylbenzidinesulfonic acid to which potassium bichromate has been added, the same authors[12] concluded later that, in accordance with the theory of Michaelis,[13] a "semiquinone" instead of a "meriquinone" must be involved in the first oxidation step, and that the color sequence during the oxidation is yellow → green → violet. They attributed the green color to the semiquinone. An earlier report by Piccard,[14] that he had prepared the "meriquinone" and found it to be yellow, cast some doubt on this conclusion. Sarver and Kolthoff[12] also observed that the electrode potentials of oxidized solutions of diphenylbenzidine drifted rapidly,

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[1] Part IV: G. S. Hammond and J. S. Clovis, *Tetrahedron Letters*, 945 (1962).

[2] E. Fischer, *Ann.*, **190**, 182 (1878).

[3] H. Wieland, *Ber.*, **41**, 3498 (1908).

[4] H. Wieland, *Ann.*, **381**, 206, 214 (1911).

[5] H. Musso, *Ber.*, **92**, 2881 (1959).

[6] H. Gilman and J. J. Dietrich, *J. Am. Chem. Soc.*, **79**, 6178 (1957).

[7] St. Gambarjan, *Ber.*, **41**, 3507 (1908).

[8] H. Wieland and St. Gambarjan, *ibid.*, **39**, 1499 (1906).

[9] F. Kehrmann and St. Micewicz, *ibid.*, **45**, 264 (1912).

[10] H. Wieland, *ibid.*, **46**, 3296 (1913).

[11] I. M. Kolthoff and L. A. Sarver, *J. Am. Chem. Soc.*, **52**, 4179 (1930).

[12] L. A. Sarver and I. M. Kolthoff, *ibid.*, **59**, 23 (1937); *Ind. Eng. Chem.*; *Anal. Ed.*, **7**, 271 (1935).

[13] L. A. Michaelis, *Chem. Rev.*, **16**, 243 (1935).

[14] J. Piccard, *J. Am. Chem. Soc.*, **48**, 2882 (1926).

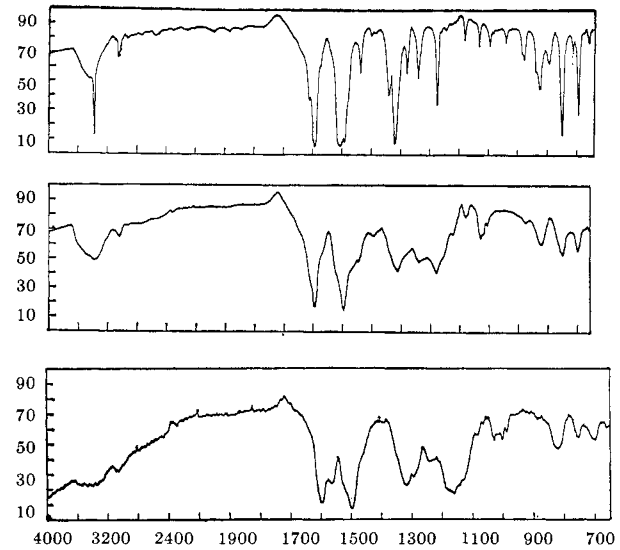

Fig. 1.—Infrared spectra of N,N′-diphenylbenzidine and "polymers": upper curve, diphenylbenzidine; center curve, polymer from oxidation of diphenylamine; lower curve, polymer from decomposition of tetraphenyltetrazine.

and Oldfield and Bockris[15] reported similar behavior for the oxidation of benzidine.

Largely because of the possible pertinence of these results to the problem of the mechanism of the benzidine rearrangement, we have reinvestigated the chemistry of tetraphenyltetrazene, tetraphenylhydrazine, and materials derived from them. Properties and spectra of the semiquinone obtained from the oxidation of diphenylbenzidine is reported in a subsequent paper.[16]

Results

Decomposition of tetraphenyltetrazene in concentrated sulfuric acid at −15° yields diphenylbenzidine, diphenylamine, and an olive green material which appears to be polymeric in nature. The material is insoluble in most organic solvents but dissolves in concentrated sulfuric acid to give a blue solution and partly dissolves in dimethylformamide to give solutions which show a strong blue fluorescence; the polymer is infusible at 360° and can be burned only with great difficulty. The material gives strong electron paramagnetic resonance absorption and has an infrared spectrum very similar to that of diphenylbenzidine. Materials essentially indistinguishable from that produced from tetraphenyltetrazene have also been produced by (1) decomposition of tetraphenylhydrazine in sulfuric acid or in ether containing hydrogen chloride at −78°, (2) by oxidation of diphenylamine with chromic acid in acetic acid–sulfuric acid solution or with hot concentrated sulfuric acid, and (3) by acid-catalyzed transformation of N,N′-diphenyl-*p,p*′-diphenoquinonimine.[16]

Figure 1 shows traces of infrared spectra of representative "polymeric" products and of diphenylbenzidine. All bands in the spectra of the polymers show the broadening which is usually characteristic of the spectra of polymers. The electronic spectra of the polymers all show maxima at 250 and at 610–650 mμ (in concentrated sulfuric acid). The former have apparent molar extinction coefficients of 15,000–24,300 (calculated, using the molecular weight of the monomer), and the long wave-length maxima have molar extinction coefficients ranging from 2700 to 10,000. The short wave-length maximum matches that of the second conjugate acid of diphenylbenzidine very closely[16] and the long wave-length absorption corresponds fairly well to the long wave-length absorption of N,N′-diphenyl-*p,p*′-diphenoquinonimine.[16] Addition of potassium dichromate to all "polymers" results in an increase in the long wave-length absorption and a decrease in the absorption at 250 mμ.

Decompositions of tetraphenyltetrazene and tetraphenylhydrazine also were carried out in various other acidic solutions. The results are presented in the form of a balance sheet in Table I.

Diphenylbenzidine and "polymer" are formed only if the decompositions are carried out in very strongly acidic solutions. A modest increase in the initial temperature increases the yield of diphenylbenzidine with a concomitant decrease in the yields of both the amorphous material and diphenylamine. All solutions in which diphenylbenzidine was formed developed the deep blue color characteristic of N,N′-diphenyl-*p,p*′-diphenoquinonimine.[8,16] In comparable experiments slightly more noncrystalline oils and tars were produced from tetraphenylhydrazine than from tetraphenyltetrazene.

N,N-Diphenylhydroxylamine also was treated with hydrogen chloride in ether solution at −78°. The only product isolated from the reaction mixture, which stayed colorless at all times, was *p*-chlorodiphenylamine, a product not formed from tetraphenyltetrazene or tetraphenylhydrazine under the same reaction conditions. Furthermore, treatment of diphenylhydroxylamine with hydrogen chloride in the presence of either diphenylbenzidine or diphenylamine led to the formation of *no crossed* products and no colors were produced.

We do not know at what stage in the acid-catalyzed decomposition of tetraphenyltetrazene or tetraphenylhydrazine the "polymer" is formed. It is possible that at the end of the reaction in concentrated acid the solution contains only N,N′-diphenyl-*p,p*′-diphenoquinonimine. Since "polymerization" of the quinonimine becomes very rapid in dilute acid,[12,16] this compound would be expected to be destroyed rapidly when the concentrated acid is diluted with water in the course of isolation.

Discussion

The results reported here and others available from the literature can be accounted for if we assume that free radicals are produced in the decomposition of tetraphenyltetrazene and tetraphenylhydrazine in strongly acidic solutions. Evidently the same or similar intermediates are involved in the oxidation of diphenylamine in strong acid. The following equations present a speculative mechanism to account for the results. Formulation of the mechanism as involving decomposition of second conjugate acids of tetraphenyltetrazene and tetraphenylhydrazine is arbitrary as far as direct experimental evidence is concerned. Unfortunately, definitive kinetic evidence will be difficult

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[15] L. F. Oldfield and J. O. M. Bockris, *J. Phys. Colloid Chem.*, **55**, 1255 (1951).

[16] B. Seidel and G. S. Hammond, *J. Org. Chem.*, **28**, 3280 (1963).

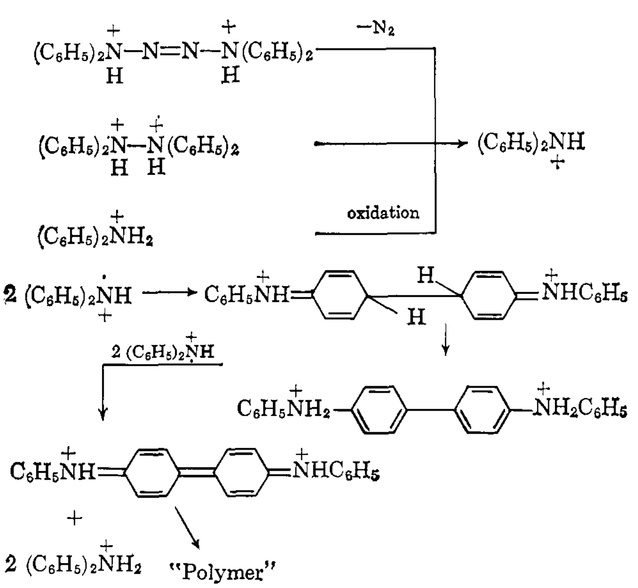
TABLE I

DECOMPOSITION OF TETRAPHENYLTETRAZENE (TPT) AND TETRAPHENYLHYDRAZINE (TPH) IN VARIOUS ACIDIC MEDIA

Starting material	TPT	TPT	TPT	TPT	TPT	TPT	TPT	TPT	TPT	TPT	TPT	TPH	TPH	TPH	TPH
Medium	H_2SO_4	H_2SO_4[b]	H_2SO_4[d]	H_2SO_4[f]	H_2SO_4[g]	HOAc,[b] H_2SO_4 (1:1)	HOAc,[b] H_2SO_4 (1:2)	HOAc	HCO_2H	H_2SO_4,[b] H_2O (1:4)	H_2SO_4[j]	H_2SO_4	HCl, ether	HCl, ether	HCl, ether
Temp., °C.	−15	−15	0	5	5	−15	−15	60, 1 hr.	0	0	0	−10 to −20	−60	0	20
Recovery in mg. per gram of starting material [as $(C_6H_5)_4N_2$]															
Initial precipitate	925	853	5300[e]		853	808	955		821	966		705	678		
Diphenylamine	230	161	79	*c*	283	*c*	296	+	+	359	+	197	338	+	+
Diphenylbenzidine	352	335	396	454	448[h]	*c*	324	−	+	222	+	181	101	−	−
Polymer	228	172	91	*c*	118	155	135	−	14	319	121	157	25	−	−
o-Diphenylamino-biphenyl (?)[k]	8	*c*	*c*	*c*	*c*	*c*	5		*c*	*c*		15–20	*c*	*c*	*c*
Others[a]	<1	*c*	*c*	*c*	*c*	*c*	*c*	Oils, dyes, pastes	*c*	*c*		40[i]	*c*	*c*	*c*

[a] Unidentified materials. [b] Exceptionally clean product practically free of dyestuffs and tars. [c] No attempt to isolate. [d] Three grams of benzidine present in the reaction medium. [e] Mostly benzidine sulfate. [f] TPT diluted with about 25 g. of finely divided Celite. [g] One gram of TPT dissolved in 1 ml. of acetic acid; 4 ml. of H_2SO_4 added as rapidly as possible. [h] Crude, m.p. 240–248°. [i] Paste, twelve fractions of dyes and oils. [j] Seven grams of acrylonitrile added, which does not appear in any product. [k] See ref. 4.

to obtain because diphenylbenzidine is formed *only in very strongly acidic solutions* in which reactions are immeasureably rapid.



Since the amorphous material is essentially indistinguishable from that formed from an oxidation product from diphenylbenzidine[16] the latter may well be a precursor to the formation of "polymer" from tetraphenyltetrazene and tetraphenylhydrazine. In any event it is fairly evident that oxidation–reductions occur producing diphenylamine, the reduction product, and "polymer," the oxidation product. We have chosen to formulate the oxidation–reduction step as involving the cation radical, $(C_6H_5)_2\dot{N}^+H$, and diphenylbenzidine. Another likely oxidant, $(C_6H_5)_2N^+$, is tentatively rejected because N,N-diphenylhydroxylamine reacts with acid in the presence of diphenylbenzidine without effecting oxidation of the latter.

In one experiment tetraphenyltetrazene was decomposed in sulfuric acid to which a large amount of benzidine had been added. It was anticipated that oxidation of benzidine might occur. There was no significant change in the yields of any of the products (see Table I). While the result leaves us with reservations concerning our general conclusions, it can be accounted for without abandoning the scheme. Benzidine is a much stronger base than diphenylbenzidine and would be less likely to undergo oxidation if either the free base or its first conjugate acid is actually involved in the oxidative step. It is also possible that the reaction, which is very rapid, occurred within very narrow zones around the initially solid particles of the tetrazene.

The mechanism accommodates very nicely the fact that careful oxidation of dilute solutions of diphenylamine gives an almost quantitative yield of diphenylbenzidine,[12] whereas oxidation of more concentrated solutions results in the formation of polymer. We have repeated the oxidation in dilute solution and confirmed the earlier report completely by isolation of diphenylbenzidine in high yield. Only a trace of polymer was produced. The result is also consistent with the fact that benzidines are produced in high yield in the oxidation of tertiary amines such as triphenylamine[17] and N,N-dimethylaniline.[18] The production of N,N,N′,N′-tetramethylbenzidine by one-electron, electrolytic oxidation of dimethylaniline recently has been confirmed in an elegant fashion by Adams.[19]

It is reasonably certain that neutral diphenylimino radicals, $(C_6H_5)_2N\cdot$, couple primarily to give tetraphenylhydrazine. We find, in agreement with Schlenk and Bergmann,[20] and in analogy to the work of Wieland[3] (formation of tetra-*p*-tolylhydrazine from thermal decomposition of tetra-*p*-tolyltetrazene) that decomposition of tetraphenyltetrazene in neutral media gives tetraphenylhydrazine as a principal primary product. Many years ago Wieland suggested,[10] in essence, that protonation of diphenylimino radicals prevents them from undergoing N–N coupling. That C–C coupling at *para* positions should be a preferred alternative is reasonable since separation of the two positive charges is maximized.

Experimental

Decomposition of Tetraphenyltetrazene.—1,1,4,4-Tetraphenyltetrazene was prepared from 43 g. of freshly recrystallized 1,1-diphenylhydrazine hydrochloride (Eastman) which was dissolved in 2400 ml. of distilled water (45°) and 25 ml. of concentrated hydrochloric acid. Nitrogen was bubbled through the solution which also was stirred and cooled to 0°. A solution of 11.5 g. of potassium permanganate in 1000 ml. of water was dropped in over a period of 1.5 hr., maintaining a temperature close to 0°.

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(17) H. Wieland, *Ber.*, **52B**, 886 (1919).

(18) W. Michler and S. Pattison, *Ber.*, **14**, 2163 (1881); **17**, 115 (1884); W. Loeb, *Z. Elektrochem.*, **7**, 603 (1901); R. Willstätter and L. Kalb, *Ber.*, **37**, 3765 (1904).

(19) Dr. R. Adams, private communication.

(20) W. Schlenk and E. Bergmann, *Ann.*, **463**, 281 (1927).

Stirring was continued for another 1.5 hr. and the temperature was allowed to rise to 5°. The dark precipitate was separated from the reaction mixture by filtration, washed three times with 50-ml. portions of cold methanol, and then dried *in vacuo* for 24 hr. The finely powdered product was extracted with 150 ml. of methanol, dissolved in 200 ml. of chloroform, and the solution was decolorized by heating it briefly with 2 g. of Norit A. The product was then precipitated with cold methanol. This operation was repeated rapidly using 100 ml. of hot carbon disulfide as the solvent. A second crop of crystals was obtained by addition of methanol to a concentrate of the mother liquor from which the first crop of crystals was obtained. The tetraphenyltetrazene was finally dried over calcium chloride *in vacuo* to give 9.6 g. of off-white crystals (27.6%), m.p. 124.5° dec., lit.[1] 123°. The tetrazene was stored under nitrogen in a dark bottle.

One gram of tetraphenyltetrazene was introduced in (about) 10-mg. portions into 10 ml. of concentrated sulfuric acid, kept at a temperature of −15°, and shaken after each addition. Immediate formation of a blue solution was accompanied by vigorous evolution of gas. On pouring the reaction mixture onto 100 g. of ice a green precipitate formed instantaneously. It was collected on a filter and washed to neutrality. The dried precipitate (839 mg., 90% yield) was extracted with three 20-ml. portions of hot benzene (15 min.) and with three successive 10-ml. portions of toluene. Two more extractions with xylene yielded less than 1 mg. of an unidentified material, m.p. 260–262°. The concentrated benzene and toluene extracts were cooled and colorless crystals of diphenylbenzidine formed, m.p. (after recrystallization) 249.5–250.5°, m.p. (with authentic diphenylbenzidine) 249–250.5°. The infrared spectrum of the product in potassium bromide pellets[21] was identical with that of authentic material. Fractional evaporation of the remaining benzene solution yielded more diphenylbenzidine of lower purity (total 324 mg.). The greenish residue was chromatographed on alumina using benzene–chloroform mixtures and chloroform as eluents. Eight milligrams of a clear colorless film, m.p. 78–80°,[22] was obtained along with a few milligrams of a bluish green oil (unidentified). One hundred ninety-five milligrams of an initially bluish paste (m.p. 44–48°) was shown to be slightly impure diphenylamine by mixture melting point determination and comparison of its infrared spectrum with a spectrum of authentic material. After the extractions an olive green solid remained (210 mg.) which was infusible up to 360° and did not burn easily. It dissolved in concentrated sulfuric acid to give a blue solution, and was partly soluble in dimethylformamide giving a solution with a strong blue fluorescence. The solid darkened slowly from the surface in air.

After partial neutralization of the mother liquors from filtration of the water-insoluble reaction products an additional 15 mg. of diphenylamine (total, 210 mg.), m.p. 49–50°, was isolated. Titration of the residual liquid with barium hydroxide until no more barium sulfate precipitated, followed by evaporation, yielded less than 1 mg. of organic material. A total of 88.3% of all solid material isolated initially was accounted for. Most reaction mixtures from decompositions in acidic solutions were worked up in the way described. An alternative procedure involved extraction of the initial precipitate with warm ligroin to dissolve all diphenylamine which was subsequently purified by chromatography of the resulting solution. Extraction with benzene could be omitted in this case and the solid residue was extracted directly with toluene or chloroform.

Decomposition of Tetraphenylhydrazine.—Tetraphenylhydrazine was prepared by the method of Gattermann and Wieland.[23] The crude product was repeatedly recrystallized in the dark by precipitation from warm benzene (50°) with cold methanol. The crystals were dried rapidly, m.p. 144–145° dec., lit.[8] 149°.

N,N-Diphenylbenzidine was prepared from diphenylamine (Eastman reagent grade) after the procedure given by Wieland and Wecker[24] and was purified by two recrystallizations from toluene and two from dioxane (precipitated slowly with methanol) using Norit for decolorization. The last recrystallization was done under a blanket of nitrogen; colorless crystals, m.p. 250–250.5°; lit.[25] 242°, 250.5–251.5°. The insoluble precipitate from the preparation of diphenylbenzidine was refluxed with glacial acetic acid and an excess of zinc was added during a period of more than one hr. It was then treated with warm 2 *N* HCl, until free of zinc, washed to neutrality, and dried. Extraction of 250 mg. of this material with toluene gave less than 2 mg. of unidentified organic compounds but no diphenylbenzidine was isolated.

N,N-Diphenylhydroxylamine was synthesized according to the method of Wieland and Roseeu.[26] The product was worked up and recrystallized in the dark, off-white crystals, m.p. 60.3–61.0°, lit.[31] 60°. Samples were stored at −78° in sealed ampoules under vacuum and in the dark. Infrared spectra in carbon tetrachloride and in carbon disulfide showed bands at 697 (vs), 718 (w), 755 (vs), 893 (m), 918 (w), 1030 (m), 1074 (m), 1175 (m), 1263 (m), 1341 (m), 1456 (m, 1493 (m), 1595 (s), 3040 (w), 3070 (w), 3550 (m) cm.$^{-1}$. The comparatively simple infrared spectrum is in accord with the assigned structure. The ultraviolet spectrum in methanol showed maxima at 284 (ϵ 6900) and at 238 mμ (7300).

Decomposition of Diphenylhydroxylamine in Ether–Hydrogen Chloride.—Dry nitrogen was passed through 20 ml. of anhydrous ether for 1 hr. at −78°. To this solution 1.40 g. of N,N-diphenylhydroxylamine was added, followed by 1 g. of phosphorus pentoxide which did not change the appearance of the yellowish tinted solution. The stream of nitrogen was replaced by dry hydrogen chloride gas and a nearly colorless precipitate formed which redissolved after introduction of more hydrogen chloride. The clear and practically colorless solution was poured on 100 g. of ice and 1275 mg. of colorless crystals, m.p. 68.5–69.5°, precipitated. The product was nearly completely soluble in pentane. Recrystallization or chromatography raised the melting point to 71–72°. The melting point, elementary analysis, and infrared spectrum identified the compound as *p*-chlorodiphenylamine (lit.[27] m.p. 66–67°, lit.[28] 74°). The infrared spectrum is very similar to that of diphenylamine above 1100 cm.$^{-1}$ but shows an additional band at 814 cm.$^{-1}$ (attributed to the C–Cl stretching frequency) and a group of bands near 1093 cm.$^{-1}$.[29]

Anal. Calcd. for $C_{12}H_{10}NCl$: Cl, 17.41%. Found: Cl, 17.45%.

Chromatography of the reaction product on alumina yielded only pure *p*-chlorodiphenylamine after a first fraction of yellowish oil (less than 5 mg., unidentified). Three milligrams of material which was insoluble in pentane dissolved in benzene producing a dark solution which gave none of the color tests for carbazole.

Decomposition of Tetraphenylhydrazine in 1,2-Dimethoxyethane–Hydrogen Chloride.—Twenty milliliters of anhydrous 1,2-dimethoxyethane was first saturated with nitrogen. Hydrogen chloride was then passed through the solution at −78° to −60°. One gram of tetraphenylhydrazine was added in small portions at −60°. The solution was initially purple but the color soon changed to blue. Thirty milliliters of a freshly prepared solution of ice and rock salt (cooled to −20°) was added at low temperature after 15 min. Then an additional 150 ml. of the saline solution was added and the temperature was allowed to rise. A green precipitate formed and was filtered off. Work-up of mother liquor and precipitate was performed as described previously. Isolated products were 25 mg. of green polymer, 223 mg. of diphenylamine, 101 mg. of diphenylbenzidine, and 124 mg. of unidentified oils and dyestuff materials in twelve different fractions.

Decomposition of tetraphenyltetrazene under the same conditions gave results similar to those obtained with tetraphenylhydrazine but neither polymer nor diphenylbenzidine was formed in solutions saturated with hydrogen chloride at either 0° or 25°. Rapid evolution of nitrogen took place in both cases but the reaction mixture turned green immediately and yielded only products soluble in benzene.

Production of Polymer from Diphenylbenzidine in Concentrated Sulfuric Acid.—Eight hundred milligrams of N,N′-

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(21) U. Schiedt and M. Reinwein, *Z. Naturforsch.*, **76**, 270 (1952).

(22) For the probable structure see ref. 4, footnote.

(23) L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry" (Trans. from the 24th Ger. Ed.), The MacMillan Co., New York, N. Y., 1937, p. 355.

(24) H. Wieland and A. Wecker, *Ber.*, **55**, 1808 (1922); *cf.* C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 2208 (1928).

(25) Beilstein, "Handbuch der organischem Chemie," Vol. XIII, 4th Ed., Springer-Verlag, Berlin, 1931, p. 323.

(26) H. Wieland and A. Roseeu, *Ber.*, **45**, 496 (1912).

(27) H. Burton and C. S. Gibson, *J. Chem. Soc.*, 2246 (1926).

(28) H. Wieland and A. Wecker, *Ber.*, **55**, 1804 (1922)

(29) L. N. Ferguson and A. J. Levant, *Anal. Chem.*, **23**, 1510 (1951), report that the spectrum of *p*-bromochlorobenzene shows ν_{C-Cl} at 806 cm.$^{-1}$ and has a band structure at 1080 cm.$^{-1}$ similar to that seen in the spectrum of *p*-chlorodiphenylamine at 1093 cm.$^{-1}$.

diphenylbenzidine was dissolved in 30 ml. of concentrated sulfuric acid under nitrogen and the solution was heated to 140° for 15 min. to give a dark blue solution. The mixture was poured onto 150 g. of ice and a yellowish precipitate formed immediately and was washed to neutrality. On drying in a desiccator overnight the product turned olive green. Extraction in the usual manner left 340 mg. of polymer with the same characteristics as the polymer from the decomposition of tetraphenyltetrazene in sulfuric acid. Heating another solution to 120° for 10 min. led to the formation of 160 mg. of yellowish, paramagnetic precipitate. A sample which was sealed *in vacuo* retained the yellow color for months.

Oxidation of Diphenylbenzidine at Controlled Potential.—A 155.4-mg. (4.6×10^{-4} mole) sample of diphenylbenzidine was weighed into the anode compartment of a vessel containing three cell compartments, one of which housed the reference electrode (silver wire in sulfuric acid). A platinum wire gauze served as the anode. Sulfuric acid was poured into the cell on both sides of the glass frit separating the anode and cathode rooms, and a stream of nitrogen was bubbled through the liquid. At a set control potential,[30] just above the threshold at which current began to flow, 1.70 microfarads of current (corresponding to abstraction of 3.70 electrons/molecule) were passed through the solution. The resulting blue solution showed absorption maxima at 615 (optical density, 1.03, arbitrary units) and at 250 mμ (optical density, 0.58) and a small maximum at 390 mμ. No extinction coefficients could be determined since some insoluble material was also formed. After precipitation of the products by addition of ice–water, a sample was extracted with benzene and found to still contain 30% of unoxidized diphenylbenzidine. The dark polymer could only be partially redissolved in concentrated sulfuric acid.

Attempted Reaction between Diphenylhydroxylamine and Diphenylamine in 1,2-Dimethoxyethane.—To 38 mg. of N,N-diphenylhydroxylamine dissolved in 15 ml. of 1,2-dimethoxyethane containing phosphorus pentoxide and saturated with nitrogen was added 38 mg. of diphenylamine. No obvious reaction or coloration occurred when hydrogen chloride was introduced either at room temperature or at −78°. On work-up, 75 mg. of a colorless oil was isolated. The oil crystallized at 0° and gave the infrared spectrum expected of a mixture of diphenylamine and *p*-chlorodiphenylamine. An attempt to effect reaction of N,N-diphenylhydroxylamine with diphenylbenzidine under the same conditions failed likewise.

Infrared spectra were recorded on a Beckman Model IR-7 infrared spectrophotometer either in solution or as potassium bromide pellets[26] using about 1.5 mg. of substance.

Visible and ultraviolet spectra were obtained with a Cary Model 14 M spectrophotometer. Solvents were of commercial spectral grade or were purified specially.

E.p.r. spectra were observed with a Varian e.p.r. spectrometer with 100-kc. modulation or with an instrument built by Dr. Kivelson (UCLA) with a 4-in. Varian magnet.[31]

Oxidation of Diphenylbenzidine in 2% Concentrated Sulfuric Acid in Acetic Acid.—An 84.1-mg. (0.25 mmole) sample of diphenylbenzidine in a solvent composed of 2% sulfuric acid and 98% acetic acid (by volume) was oxidized with 52.5 mg. ("210% of theoretical for oxidation to quinonimine) of potassium dichromate in acetic acid at room temperature. After 3 days a dark precipitate had formed. Work-up by the standard procedure gave 52.1 mg. of polymer and 30.8 mg. of diphenylbenzidine. A similar experiment carried out in acetic acid alone gave rise to 30 mg. of a reddish crystalline material, m.p. 215–230°, from which no diphenylbenzidine could be isolated by chromatography. Possibly, diphenylbenzidine initially present reacted with other products or air.

Reduction of Oxidized Diphenylbenzidine.—A 112.1-mg. (0.33 mmole) sample of diphenylbenzidine was dissolved in 10 ml. of concentrated sulfuric acid at −5°; 68 mg. of potassium dichromate in 5 ml. of 85% sulfuric acid was added (200% oxidant theoretically required to oxidize diphenylbenzidine to the quinonimine). The solution was shaken briefly and a solution of 85 mg. of $SnCl_2 \cdot 2H_2O$ in two ml. of 35% sulfuric acid was added. In several hours the solution had turned a pale green color. Usual work-up gave a total of 109 mg. of precipitate from which 7 mg. of highly cross-linked (insoluble) polymer was extracted and 98 mg. of diphenylbenzidine (m.p. 238–241°, impure; recrystallized, m.p. 240–245°) was recovered.

Reduction of oxidized solutions of diphenylbenzidine in sulfuric acid after long standing gave larger amounts of polymer and only small amounts of diphenylbenzidine. Reduction of polymer from the decomposition of tetraphenyltetrazene in concentrated sulfuric acid gave a brownish polymer which formed an initially near colorless solution in concentrated sulfuric acid. No diphenylbenzidine was formed.

Analyses.—No satisfactory analyses have been obtained so far for any of the polymeric species. They are very hard to burn completely, possibly owing to fusion to a high molecular heterogenic system on heating. One analyst (Dr. Elek) invariably reported high per cent of ash, although in one case it was shown that the samples contained only 0.1 and 0.24% of material insoluble in dimethylformamide and no sulfate was found. Hydrogen analyses were satisfactory but carbon was reported low by 16–19% and nitrogen was low by 1.5–2.5%. In most cases the organic material did not come into contact with any reagent other than sulfuric acid, water, and pure organic solvents. Ash and low carbon (by about 2%) also were reported by the analyst for a sample of N,N′-diphenylbenzidine which had been sublimed *in vacuo*.

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