# Alkaline Degradation of 1,1-Disubstituted 2-Arenesulfonhydrazides. Synthesis and Reactivity of 1-Amino-2,5-diphenyl- and -2,3,4,5-tetraphenylpyrrole[1]

LOUIS A. CARPINO

*Department of Chemistry, University of Massachusetts, Amherst, Massachusetts*

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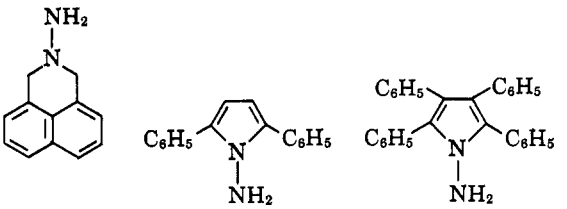
1-Amino-2,5-diphenylpyrrole (II) was prepared by treatment of 1,4-diphenyl-1,4-butanedione with *t*-butyl carbazate in ethanol–acetic acid followed by hydrogen chloride cleavage of the resulting carbo-*t*-butoxy derivative (VII). Oxidation of II did not lead to hydrocarbon coupling products. With N-bromosuccinimide as oxidant the tetrazene X was obtained. Compound X exhibited reversible phototropy, the initially bright lemon yellow needles becoming deep scarlet in color on irradiation with direct sunlight or even on standing in diffuse daylight for several hours. The benzenesulfonyl derivative IX was unreactive toward alkaline degradation, being recovered unchanged after refluxing in an ethylene glycol solution of sodium hydroxide. Similar results were obtained in the case of 1-amino-2,3,4,5-tetraphenylpyrrole (III). Neither oxidation nor sulfonhydrazide degradation of III gave any hydrocarbon products.

An apparently general reaction of 1,1-disubstituted hydrazines of the benzylic type involves the alkaline degradation of the corresponding arenesulfonyl derivative which yields hydrocarbon products formed by coupling of the benzyl groups originally attached to the disubstituted nitrogen atom.[2] Previously only one such 1,1-disubstituted benzylic hydrazine had been encountered which did not react normally, namely the cyclic hydrazine I.[3] In the present paper we report two examples of $\alpha$-phenylated hydrazines of a different type, namely the N-aminopyrrole derivatives II and III,



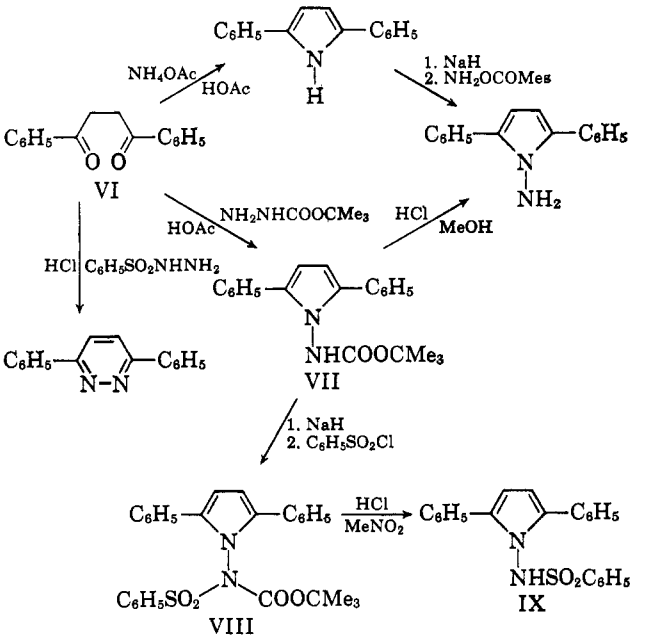
I II III

which fail to yield hydrocarbon products on sulfonhydrazide degradation or oxidation of the free hydrazines. While this work was in progress Lemal and co-workers[4] described a study of the decomposition of the sodium salt IV of the *p*-toluenesulfonyl derivative of the parent compound, N-aminopyrrole. In contrast to the ready fragmentation of the saturated analog V, the pyrrole derivative IV proved to be quite stable

IV V

thermally. The stability of IV was ascribed to the low basicity of the ring nitrogen atom, with consequent lack of stabilization of the intermediate azamine. In the present study the 2,5-diphenylated derivatives II and III were examined in view of earlier results on benzylic hydrazines and since the products expected for the normal reaction would be derivatives of the elusive cyclobutadiene system.[5]

CHART I



1-Amino-2,5-diphenylpyrrole has been obtained previously[6] by reaction of 1,4-diphenyl-1,4-butanedione[7] (VI) with thiosemicarbazide followed by treatment of the thiocarbamoyl derivative with ethanolic sodium ethoxide in a sealed tube at 150°. This route can be improved considerably by substitution of *t*-butyl carbazate[8] for the thiosemicarbazide (see Chart I).

Cleavage of the resulting protected derivative VII by gaseous hydrogen chloride under mild conditions gave II in 82% yield. The structure of II was established by Beyer, Pyl, and Völcker,[6] and this assignment was confirmed in the present work by an alternate synthesis. Treatment of the sodium salt of 2,5-diphenylpyrrole with mesitoxyamine[9] in dimethylformamide yields a compound identical with that prepared by cleavage of VII. All direct attempts to convert the N-aminopyrrole II to the benzenesulfonyl or *p*-toluenesulfonyl derivatives by reaction with the corresponding sul-

(1) Supported by a grant from the National Science Foundation (G-19506).

(2) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 4427 (1957).

(3) L. A. Carpino, *ibid.*, **85**, 2144 (1963).

(4) D. M. Lemal, T. W. Rave, and S. D. McGregor, *ibid.*, **85**, 1944 (1963).

(5) For example, H. H. Freedman [*ibid.*, **83**, 2194 (1961)] has isolated a nickel bromide complex of tetraphenylcyclobutadiene, the product expected upon normal oxidation or sulfonhydrazide degradation of III.

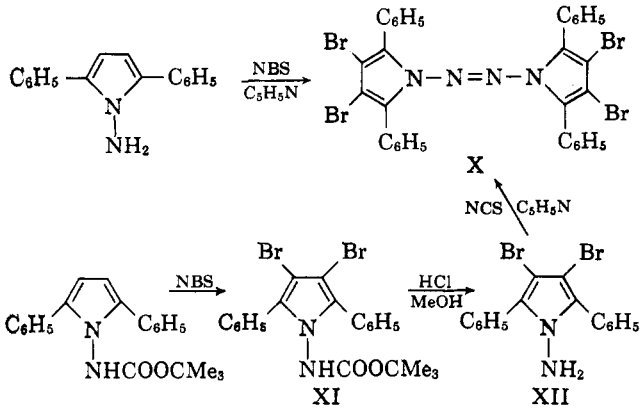
(6) H. Beyer, T. Pyl, and C.-E. Völcker, *Ann.*, **638**, 150 (1960).

(7) J. P. Schaefer, *J. Org. Chem.*, **25**, 2027 (1960).

(8) L. A. Carpino, *ibid.*, **28**, 1909 (1963).

(9) L. A. Carpino, *J. Am. Chem. Soc.*, **82**, 3133 (1960).

CHART II



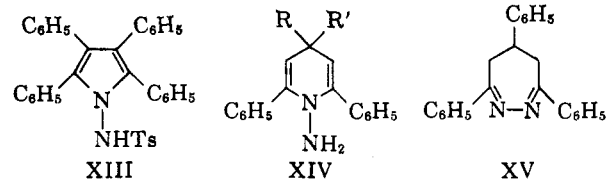
fonyl chlorides in the presence of a variety of bases and solvent systems were unsuccessful.

In pyridine or quinoline the weakly basic N-amino compound was recovered unchanged after such treatment. Undesirable competing reactions occurred in dimethylformamide–triethylamine. Furthermore reaction of the diketone VI with benzene or *p*-toluenesulfonhydrazide in the presence of hydrochloric acid gave only 3,6-diphenylpyridazine in each case. Finally, a convenient indirect route to the benzenesulfonyl derivative IX was developed by treatment of the carbo-*t*-butoxy derivative VII with sodium hydride or sodium methoxide in dimethylformamide, acylation by means of benzenesulfonyl chloride, and removal of the protecting group by means of hydrogen chloride in nitromethane. Such an indirect technique should also be of value in the synthesis of the arenesulfonyl derivatives of 1,1-disubstituted hydrazines which are prone to yield the disulfonyl derivatives under the normal conditions.

The sulfonyl derivative IX proved to be exceedingly stable toward aqueous sodium hydroxide under conditions which cause rapid decomposition of benzylic sulfonhydrazides. For example, it was recovered unchanged after refluxing for 8 hr. in ethylene glycol in the presence of sodium hydroxide.[10] In line with the stability of IX toward alkali, the free hydrazine II was not affected by continued refluxing in carbon tetrachloride solution in the presence of mercuric oxide (insoluble) or mercury diacetamide[11] (soluble). At least partial oxidation occurred with manganese dioxide suspended in methylene dichloride, but the only product which was isolated from the reaction mixture was a trace of 2,5-diphenylpyrrole. When N-bromosuccinimide was used, oxidation was accompanied by bromination of the two available positions on the pyrrole nucleus (Chart II). The resulting tetrabromotetrazene X was found to exhibit reversible phototropy. Crystallization of the tetrazene from nitromethane in the dark gave bright lemon yellow needles which on exposure to diffuse daylight became scarlet red in a few minutes. The change was immediate upon exposure to direct sunlight or a sun lamp. The yellow color reappeared on storage of the exposed material in the dark for several hours. The n.m.r. spectrum of X in trichloroacetonitrile showed only two complex multiplets centered at about $\delta$ 7.0 and 7.4 due to the aromatic protons of the phenyl substituents, thus excluding an alternate structure with the bromine atoms substituted on the phenyl rings. In such a case, additional resonances would be expected at higher fields due to the 3,4-protons of the pyrrole system.[12] In addition, oxidative degradation of X by means of aqueous alkaline permanganate gave only benzoic acid. Furthermore, compound X could be obtained by oxidation of 1-amino-2,5-diphenyl-3,4-dibromopyrrole (XII) by means of either N-bromo- or N-chlorosuccinimide. The required 3,4-dibromo derivative XII was obtained by bromination of the protected amino compound VII and subsequent cleavage of the protective group. Compound X represents the first example of a phototropic tetrazene. A study of related tetrazenes is in progress.

Although compound II was most conveniently prepared by cyclization through the diketone VI, the analogous tetraphenyl derivative III was best obtained from the readily available 2,3,4,5-tetraphenylpyrrole[13] by direct amination of the sodium salt by means of mesitoxyamine[9] in dimethylformamide. As in the case of the 2,5-diphenyl analog it was not possible to prepare the benzene or *p*-toluenesulfonyl derivatives of III by direct reaction with the sulfonyl chloride in dimethylformamide–triethylamine or pyridine. A technique[14] recommended for the acylation of weakly basic amino compounds involving acetic acid as solvent in the presence of sodium acetate gave only the monoacetyl derivative of III. Fortunately the monoacetyl derivative, which could be obtained more easily by acetylation of III by means of acetic anhydride in pyridine, could be converted to the *p*-toluenesulfonyl derivative of III by a method analogous to, but in practice much less convenient than that involving the carbo-*t*-butoxy derivative of the 2,5-diphenyl analog. Attempts to obtain the carbo-*t*-butoxy derivative by direct acylation of III were abortive.

Treatment of the potassium salt of the monoacetyl derivative with *p*-toluenesulfonyl chloride in xylene gave an oil which upon refluxing in aqueous–ethanolic sodium hydroxide solution for 24 hr. gave the *p*-toluenesulfonyl derivative XIII. As indicated by the method of formation, the tosyl derivative XIII is stable toward alkaline degradation. Similarly the free hydrazine III was not attacked by mercuric oxide upon refluxing for 24 hr. in chloroform solution.



The reason for the lack of conversion of II and III and the corresponding sulfonyl derivatives to hydrocarbon products has not been established. The question as to whether the low basicity of the pyrrole ring nitrogen atom, the nature of the expected products, and/or the fact that the normally activating phenyl groups are in these cases attached at sp²-hybridized

(10) Decomposition of the salts in nonhydroxylic solvents at high temperatures as reported by Lemal and co-workers[4] for the parent compound has not been investigated.

(11) W. Schöller and W. Schrauth, *Ber.*, **42**, 777 (1909).

(12) For a discussion of the n.m.r. spectra of pyrrole derivatives, see R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).

(13) D. Davidson, *J. Org. Chem.*, **3**, 361 (1938).

(14) R. G. Shepherd, *ibid.*, **12**, 275 (1947).

centers are important factors in determining the present results remains for further study. In order to examine the influence of the phenyl substituents at $sp^2$-hybridized centers separate from the greatly reduced basicity of the pyrrole ring nitrogen atom, it would be of interest to examine an N-amino-1,4-dihydropyridine derivative such as XIV. Indeed Merz and Richter[15] have described a compound claimed to have structure XIV (R = H, R′ = $C_6H_5$) which was obtained by reaction of 1,3,5-triphenyl-1,5-pentanedione with hydrazine hydrate in a sealed tube at 130°. Spectral examination of the product of this reaction showed, however, that structure XIV (R = H, R′ = $C_6H_5$) is untenable. The infrared spectrum shows no N–H band and the n.m.r. spectrum establishes the absence of any vinyl hydrogens. The data support the alternate structure XV. Experiments to obtain an appropriate derivative of XIV for further study such as the 4,4-dimethyl compound (XIV, R = R′ = $CH_3$) are continuing.

## Experimental[16]

**1-*t*-Butyloxycarbonylamino-2,5-diphenylpyrrole (VII).**—A solution of 50 g. of 1,4-diphenylbutane-1,4-dione[7] and 39.8 g. of *t*-butyl carbazate[8] in 1700 ml. of ethanol and 210 ml. of acetic acid was refluxed for 4 hr. and then diluted with water to a total volume of 6 l. The mixture was stirred well, allowed to stand overnight at room temperature, and filtered to remove the precipitated white solid. After drying in air the crude solid was recrystallized from 150–200 ml. of nitromethane which deposited 41.5–50 g. (59–71%) of tiny white crystals, m.p. 182–185°. An analytical sample was obtained by recrystallization from nitromethane and 88–98° ligroin–benzene (1:1), m.p. 183–184.5°. The n.m.r. spectrum showed a sharp singlet at δ 6.31 due to the 3,4-protons of the pyrrole system in addition to a singlet at δ 1.27 due to the carbo-*t*-butoxy group and a multiplet for the aromatic protons centered at δ 7.4. The N–H absorption was not located.

*Anal.* Calcd. for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.50; H, 6.66; N, 8.32.

**1-Amino-2,5-diphenylpyrrole (II) from 1-*t*-Butyloxycarbonylamino-2,5-diphenylpyrrole (VII).**—There was dissolved 22 g. of VII in 150 ml. of boiling methanol and hydrogen chloride gas was passed through the solution for about 20 min. A pink solid separated. The mixture was allowed to stand at room temperature for 2 hr. and the solid was filtered and washed with methanol. The crude solid, 15 g. (97%), m.p. 219.5–222°, was recrystallized from dimethylformamide which gave 10.5 g. of cream white flakes, m.p. 219–221°. The filtrate was diluted with water, and the precipitated solid recrystallized from dimethylformamide to give an additional 1.8 g. of the pure hydrazine, m.p. 218–220° (lit.[6] m.p. 214°). The total yield was 12.3 g. (80%). The same compound (melting point and mixture melting point) was obtained by amination of the sodium salt of 2,5-diphenylpyrrole[17] by means of mesitoxyamine[9] according to the procedure described below for the 2,3,4,5-tetraphenyl compound.

The benzal derivative had m.p. 157–158.5° (lit.[6] m.p. 157°); the acetyl derivative had m.p. 139.5–141° (lit.[6] m.p. 137°). The n.m.r. spectrum in dimethyl sulfoxide showed two singlets at δ 5.60 (2H, $NH_2$, broad) and 6.23 (2H, pyrrole protons), and a multiplet centered at 7.50 (10H, phenyl protons).

**1-(N-Benzenesulfonyl-N-*t*-butyloxycarbonylamino)-2,5-diphenylpyrrole (VIII).**—A suspension of 2.16 g. of powdered sodium hydride in 190 ml. of dimethylformamide (distilled from calcium hydride) was treated with 20 g. of the carbo-*t*-butoxy derivative VII. The mixture was stirred gently at room temperature for 3 hr., and 7.62 ml. (10.52 g.) of benzenesulfonyl chloride was dropped in over 5–10 min. and then stirred at room temperature for 8–10 hr. The mixture was allowed to settle, and the solution was decanted from a small amount of unchanged sodium hydride into 600 ml. of water. After it stood for 2 hr., filtration gave 25 g. (88%) of cream-colored solid, m.p. 140–146° dec. Recrystallization by solution in hot benzene, filtration, and addition of 1 vol. of 60–70° ligroin to the filtrate gave 18 g. (63%) of tiny white crystals, m.p. 146–149° dec.; a second recrystallization gave 16 g. (56%), m.p. 147–153° dec. The analytical sample had a decomposition point of 154.5–158°.

*Anal.* Calcd. for $C_{27}H_{26}N_2O_4S$: C, 68.34; H, 5.52; N, 5.90; S, 6.76. Found: C, 68.49; H, 5.41; N, 5.97; S, 6.65.

**1-(N-Benzenesulfonylamino)-2,5-diphenylpyrrole (IX).**—By warming slightly, 16 g. of VIII was dissolved in 100 ml. of nitromethane and hydrogen chloride gas was passed through the solution for 10–15 min. After the mixture was allowed to stand at room temperature for 20 min., it was evaporated by an air jet (5 hr.) and the pink residue was triturated with ethanol, filtered, and washed a second time with ethanol. There was obtained 11.8 g. (93%) of a light pink powder, m.p. 190–195°. Recrystallization from ethanol–nitromethane, benzene, and nitromethane gave 5.5 g. (43%) of snow-white well-formed crystals, m.p. 196–198°. The analytical sample (ethanol–nitromethane) had m.p. 197.5–199°. The n.m.r. spectrum exhibited a sharp peak at δ 6.26 (2H, pyrrole protons) and a multiplet at 7.2 (15H, aromatic protons). A broad absorption at about 8.1 (1H) was shown to be due to the NH proton by deuterium exchange.

*Anal.* Calcd. for $C_{22}H_{18}N_2O_2S$: C, 70.58; H, 4.85; N, 7.48; S, 8.56. Found: C, 70.20; H, 4.75; N, 7.51; S, 8.65.

**3,6-Diphenylpyridazine.**—A solution of 11.9 g. of 1,4-diphenylbutane-1,4-dione and 8.6 g. of benzenesulfonhydrazide in 400 ml. of ethanol and 40 ml. of concentrated hydrochloric acid was refluxed for 30 min., diluted to 1.7 l. with water, allowed to stand at room temperature for 2 hr., and filtered. The cream-colored powder was recrystallized twice from dimethylformamide which gave 6 g. (52%) of snow-white flakes, m.p. 225–227°. There was no depression on admixture with an authentic sample of 3,6-diphenylpyridazine (lit.[18] m.p. 221–222°).

**Attempted Alkaline Degradation of 1-Benzenesulfonylamino-2,5-diphenylpyrrole.**—A solution of 0.37 g. of the benzenesulfonyl derivative in 25 ml. of water containing 0.2 g. of sodium hydroxide was refluxed for 8 hr., and the resulting clear solution was acidified with 1.7 ml. of concentrated hydrochloric acid. There was precipitated 0.35 g. (94%) of the unreacted benzenesulfonylhydrazide, m.p. 195–198°. Recrystallization from ethanol–nitromethane gave a sample, m.p. 197–198°. There was no depression on admixture with a sample of the starting material. The same lack of reaction was observed on substitution of 25 ml. of ethylene glycol for water as the solvent (again at the reflux temperature for 8 hr.).

**Oxidation of 1-Amino-2,5-diphenylpyrrole.**—A suspension of 2.35 g. of 1-amino-2,5-diphenylpyrrole in 20 ml. of nitromethane and 1.6 ml. of pyridine was treated in small portions over 5–8 min. with 5.4 g. of N-bromosuccinimide. The mixture became warm and a green-black color developed as the hydrazine dissolved and a new cream yellow solid precipitated. The mixture which became darker and darker was swirled for 5 min. after which time the solid was filtered and washed with nitromethane. Recrystallization from 125 ml. of nitromethane gave 0.75 g. (19%) of the tetrazene (X), m.p. 159–163° dec. If the recrystallization flask was covered with aluminum foil, the tetrazene separated in the form of bright lemon yellow needles. When allowed to stand in the light, even in diffuse daylight, the crystals became reddish in 2–3 min. and after 15–20 min. were bright scarlet in color. When the scarlet material was stored in the dark for several hours the yellow color returned. Development of the red color was immediate in direct sunlight or under a sun lamp. Storage in the dark maintained the bright yellow color indefinitely. The color disappeared on heating, as in determination of the melting point, at about 110°.

(15) K. W. Merz and H. Richter, *Arch. Pharm.*, **275**, 294 (1937). The Merz–Richter compound was obtained by the reported method except that a mixture of ethylene glycol and ethanol (3:2) was used as solvent, thus dispensing with the sealed tube of Merz and Richter.

(16) Melting points and boiling points are uncorrected. Except where specified otherwise, n.m.r. spectra were taken in deuteriochloroform solution using tetramethylsilane as internal standard on a Varian A-60 spectrometer. Where necessary in the case of compounds having hydrogen attached to nitrogen, assignment was verified by shaking the deuteriochloroform solution with a drop of $D_2O$ in the sample tube and recording the spectrum again. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Microanalyses were performed by Dr. A. Bernhardt, Mülheim (Ruhr), Germany.

(17) S. Kapf and C. Paal, *Ber.*, **21**, 3053 (1882).

(18) C. Paal and H. Schulze, *ibid.*, **33**, 3795 (1900).

*Anal.* Calcd. for $C_{32}H_{20}Br_4N_4$: C, 49.26; H, 2.58; N, 7.18; mol. wt., 780.2. Found: C, 48.98; H, 2.98; N, 7.31; mol. wt., 770.

Oxidation of the tetrazene by alkaline potassium permanganate in water suspension at the reflux temperature was very slow, but after 4 days of refluxing there was isolated a trace of benzoic acid, m.p. and m.m.p. 121–123°. No other organic acid was isolated from the reaction mixture.

By the same method but using only 1 equiv. of N-bromosuccinimide, 1-amino-2,5-diphenyl-3,4-dibromopyrrole was oxidized to the same phototropic tetrazene, m.p. and m.m.p. 159–160° dec., in 45% yield. The same product was obtained using 1 equiv. of N-chlorosuccinimide as the oxidizing agent.

**1-(*t*-Butyloxycarbonylamino)-2,5-diphenyl-3,4-dibromopyrrole (XI).**—To a solution of 26.7 g. of VII in 400 ml. of methylene dichloride there was added within 1–2 min. 28.5 g. of N-bromosuccinimide. Most of the N-bromosuccinimide dissolved in a few minutes, and the remainder was brought into solution by crushing the solid against the sides of the flask. Soon after the brominating agent had dissolved, a new yellow cream solid began to separate. The mixture was poured into a dish and allowed to evaporate spontaneously overnight. The residual solid was stirred well with 500 ml. of boiling water, filtered hot, washed with water, dried in the air, and recrystallized from nitromethane–dimethylformamide (1:1). There was obtained 26.5 g. (67%) of the dibromide, m.p. 218–220° dec. The analytical sample had m.p. 220–222° dec.

*Anal.* Calcd. for $C_{21}H_{20}Br_2N_2O_2$: C, 51.24; H, 4.10; Br, 32.47; N, 5.69. Found: C, 51.14; H, 4.17; Br, 32.48; N, 5.52.

**1-Amino-2,5-diphenyl-3,4-dibromopyrrole (XII).**—A suspension of 26.5 g. of the carbo-*t*-butoxy derivative (XI) in 600 ml. of methanol was heated to the boiling point, the source of heat was removed, and hydrogen chloride gas was passed into the mixture until the solid dissolved completely (35–40 min.). The solution was corked and allowed to stand at room temperature for 24 hr. and then diluted with water slowly with stirring to a total volume of 1 l. which caused the separation of a crystalline cream-colored solid. If the material separated as an oil it could be caused to solidify by heating the mixture to the boiling point. After 2 hr. at room temperature the solid was filtered and washed with ethanol–water (2:1) to give 17 g. (80%) of the crude hydrazine, m.p. 144–148°. Recrystallization once from ethanol–nitromethane (2:1) and twice from 60–70° ligroin–benzene (1:1) gave 7.5 g. (35%) of the hydrazine as small white plates, m.p. 150.5–155°. The analytical sample (benzene–ligroin) had m.p. 153–155°. The n.m.r. spectrum in carbon tetrachloride showed a singlet at $\delta$ 4.18 (2H, $NH_2$) and a multiplet at 7.37 (10H, aromatic protons).

*Anal.* Calcd. for $C_{16}H_{12}Br_2N_2$: C, 49.01; H, 3.09; Br, 40.76; N, 7.16. Found: C, 49.13; H, 3.19; Br, 40.78; N, 6.85.

**1-Amino-2,3,4,5-tetraphenylpyrrole (III).**—By stirring magnetically for several minutes at room temperature, 22 g. of 2,3,4,5-tetraphenylpyrrole was dissolved in a mixture of 3.2 g. of sodium methoxide suspended in 110 ml. of dimethylformamide (dried by distillation over calcium hydride). The solution was cooled in an ice bath and over a period of 2–3 min. 21 g. of mesitoxyamine[9] was added. The mixture was allowed to stir in the ice bath for 2 hr., at room temperature for 10 hr., and finally at 65–75° for 30 min. The resulting mixture was poured into a solution of 11 g. of sodium hydroxide in 500 ml. of water. Heating the mixture to the boiling point for 2–3 min. caused the initially precipitated oil to solidify. The yellow solid was filtered from the hot solution, washed with water, and recrystallized at once by solution in 60 ml. of hot dimethylformamide. Storage at room temperature for 10 hr. caused the separation of 5 g. of yellow-white solid, primarily the unchanged pyrrole. Dilution of the filtrate to 250 ml. with water, heating to the boiling point, and filtering gave the crude N-amino derivative. After air drying, recrystallization from nitromethane gave 11 g. (48%) of III as yellow cream crystals, m.p. 200–212°. A second recrystallization from the same solvent gave 8.5 g. (37%) of the pure N-amino compound as colorless crystals, m.p. 208–212.5°. The analytical sample (nitromethane) had m.p. 212–214.5°. The n.m.r. spectrum showed a singlet at $\delta$ 4.37 (2H, $NH_2$) and a multiplet centered at 7.10 (20H, phenyl protons).

*Anal.* Calcd. for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.73; H, 5.72; N, 7.58.

1-Amino-2,3,4,5-tetraphenylpyrrole remained colorless on storage in the dark, whereas on standing in the light a bright yellow color slowly developed on the surface.

The **benzal** derivative was obtained in 80% yield on refluxing with benzaldehyde in ethanol in the presence of a trace of acetic acid. Recrystallization from dimethylformamide–nitromethane (1:1) gave tiny yellow needles, m.p. 274–276°.

*Anal.* Calcd. for $C_{34}H_{26}N_2$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.14; H, 5.59; N, 6.21.

**1-Acetylamino-2,3,4,5-tetraphenylpyrrole.**—A solution of 0.772 g. of 1-amino-2,3,4,5-tetraphenylpyrrole and 0.204 g. of acetic anhydride in 5 ml. of pyridine was refluxed for 7 hr. Dilution with 50 ml. of water gave an oil which solidified on standing. Recrystallization of the air-dried solid from nitromethane gave 0.5 g. (58.4%) of white crystals, m.p. 272–276°. The analytical sample had m.p. 275–277°.

*Anal.* Calcd. for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 84.22; H, 6.06; N, 6.31.

Treatment of 1-amino-2,3,4,5-tetraphenylpyrrole in acetic acid containing 1 equiv. of sodium acetate with either benzenesulfonyl chloride or *p*-toluenesulfonyl chloride gave the same acetyl derivative, m.p. and m.m.p. 276–277.5°.

The corresponding **diacetyl** derivative was obtained by refluxing the N-amino compound or the monoacetyl derivative with an excess of acetic anhydride containing a few drops of pyridine. Recrystallization from nitromethane gave colorless crystals, m.p. 202–203.5°. The n.m.r. spectrum showed a singlet at $\delta$ 2.12 (6H, $CH_3$) and complex multiplets centered at 7.0 and 7.23 (20H, phenyl protons).

*Anal.* Calcd. for $C_{32}H_{26}N_2O_2$: C, 81.68; H, 5.57; N, 5.95. Found: C, 82.01; H, 5.50; N, 6.00.

**1-(N-*p*-Toluenesulfonylamino)-2,3,4,5-tetraphenylpyrrole.**—A mixture of 2.2 g. of the monoacetyl derivative of III and 0.22 g. of potassium metal was refluxed with stirring in 100 ml. of dry xylene for 2.5 hr. The resulting mixture was cooled in an ice bath, 1.05 g. of *p*-toluenesulfonyl chloride was added, and the mixture was stirred at room temperature for 8 hr., heated to the boiling point for 0.5 hr., filtered, and evaporated to a thick red-brown oil by means of a water aspirator. Since the oil could not be induced to crystallize, there was added 100 ml. of water, 50 ml. of ethanol, and 5 g. of sodium hydroxide, and the mixture refluxed for 24 hr. During this period most of the oil dissolved. Filtration, dilution with water to a volume of 500 ml., and storage at room temperature overnight gave 1.9 g. (68%) of crude hydrazide, which on crystallization from nitromethane gave 0.8 g. (29%) of cream white crystals, m.p. 248–256°. Several additional recrystallizations gave the pure hydrazide, m.p. 258–261.5°. The n.m.r. spectrum showed two singlets at $\delta$ 2.28 (3H, $CH_3$) and 7.52 (1H, NH) as well as a multiplet centered at about 7.1 (24H, aromatic protons).

The N–H band was recognized by its disappearance on exchange with deuterium oxide.

*Anal.* Calcd. for $C_{35}H_{28}N_2O_2S$: C, 77.76; H, 5.22; N, 5.18; S, 5.93. Found: C, 77.65; H, 5.45; N, 5.26; S, 6.05.