hydrochloric acid, was accomplished by adding a solution of 0.70 g. of sodium nitrite in 20 ml. of water, and allowing the reaction mixture to stand for 2 hr. at room temperature. Filtration and drying gave a 95% yield of VIa, m.p. 169–170° dec. Recrystallization from ethanol gave straw-colored needles of the same melting point $[\alpha]_D$ −81.4° (*c* 1.72 in pyridine).

Anal. Calcd. for $C_{18}H_{20}N_2O_8$: C, 54.92; H, 7.09; N, 9.85. Found: C, 54.89; H, 6.98; N, 9.95.

That nitrosation had occurred on nitrogen rather than carbon was indicated by the following reductive cleavage reaction: About 100 mg. of the nitroso compound VIa was suspended in 10 ml. of dry ethanol containing a few granules of tin. The suspension was saturated with anhydrous hydrogen chloride, a few drops of water were added and the mixture was heated on the steam bath for 0.5 hr. On cooling, shiny white platelets of a tin salt crystallized. These were collected at the filter, unchanged tin granules were separated mechanically, and the salt was dissolved in water. Neutralization with a saturated sodium bicarbonate solution gave a white precipitate which was removed by filtration and dried. It proved, by m.p. and mixed m.p. (138–139°) to be the starting 1-deoxy-1-(3′,4′-xylidino)-D-arabitol.

1-Deoxy-1-(N-nitroso-3′,4′-xylidino)-D-arabitol tetraacetate (VIIa). A mixture of 2.6 g. of VIa and 8 ml. of dry pyridine was treated with 5.8 ml. of acetic anhydride, and warmed on the steam bath for 0.25 hr. after homogeneity occurred. After standing at room temperature for 2 hr., the solution was poured into 100 ml. of ice water containing 4 ml. of concd. hydrochloric acid. After standing at room temperature for several hours with occasional trituration, the yellow oil solidified and was collected at the filter. Drying gave 4.00 g. (97%) of VIIa, m.p. 70–72.° For analysis, a sample was recrystallized from 95% ethanol to give elongated prisms, m.p. 73–74°, $[\alpha]_D$ + 67.2° (*c* 1.80 in pyridine).

Anal. Calcd. for $C_{21}H_{28}N_2O_{12}$: C, 55.74; H, 6.24; N, 6.19. Found: C, 55.80; H, 6.53; N, 6.03.

As with Va the absence of prominent absorption bands in the 1600–1500 cm.$^{-1}$ region of the infrared absorption spectrum of VIIa (7% solution in chloroform) provides further support for the assigned *N*-nitroso structure.

The absence of a replaceable hydrogen on the nitrogen atom of VIa (and VIIa) was further demonstrated by dissolving a sample of VIIa in methanol, which had previously been saturated with potassium carbonate. Even without heating the solution, solvolysis of the acetate groups occurred rapidly to give a good yield of nitroso-compound VIa, m.p. and mixed m.p. 169–170° dec. It is extremely unlikely than an aniline *N*-acetyl group would solvolyze this readily. Hence, all four acetyl groups must be on oxygen, and the nitrogen atom in VIa must carry the nitroso group; otherwise it would have been acetylated under the above conditions.

1-Deoxy-1-(N-nitroso-3′,4′-xylidino)-D-ribitol (VIb). Nitrosation of 2 g. of 1-deoxy-1-(3′,4′-xylidino)-D-ribitol dissolved in 10 ml. of water containing 2 ml. of concd. hydrochloric acid in the above manner gave 1.82 g. (82%) of VIb, m.p. 133–135. Two recrystallizations from ethanol raised the m.p. to 138–139°, $[\alpha]_D$ +44.6 (*c* 1.68 in pyridine).

Anal. Calcd. for $C_{13}H_{20}N_2O_5$: C, 54.92; H, 7.09; N, 9.85. Found: C, 54.77; H, 7.25; N, 9.73. The infrared spectrum (potassium bromide) is consistent with the assigned nitrosamine structure.

Acknowledgment. The author is indebted to Mr. Frank Chadde for the ultraviolet spectra, to Mr. William Washburn for the infrared spectra, and to Mr. E. F. Shelberg for the microanalyses.

NORTH CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HAVERFORD COLLEGE, AND THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Preparation of Substituted 1-Picryl-2,2-diphenylhydrazyl Free Radicals[1]

MABEL M. CHEN, AMEDEO F. D'ADAMO, JR.,[2] AND ROBERT I. WALTER[3]

Received January 9, 1961

The preparation of a series of 1-picryl-2,2-diphenylhydrazyl free radicals substituted in the *para-* positions of the two benzene rings by —OCH_3, —CH_3, —F, —Cl, —Br, —$COOCH_3$, —NO_2, or —C_6H_5 groups is described. Some limitations in the conventional preparative sequence used for 1-picryl-2,2-diphenylhydrazyl (DPPH) are revealed in this series of compounds. Two new reagents, nitrosyl chloride for *N*-nitrosation of diarylamines, and *N*-picrylpyridinium chloride for picrylation of 1,1-diarylhydrazines, offer advantages at these stages of the preparative sequence. Some alternative methods which involve substitution reactions with various compounds of that sequence have also been developed.

The comparison of properties of structurally similar molecules which differ only by the substitution of groups with known effects on electron distribution has been a powerful tool in the investigation of organic compounds. This technique has seen very little application to the "stable" free radicals because of difficulties in the preparation and handling of the necessary compounds. These difficulties are well known in the case of the triarylmethyl radicals, which react with oxygen, disproportionate, and dimerize extensively. Members of the series of *para-* substituted 2,6-di-*t*-butylphenoxy[4] radicals also are unstable in air, and dimerize at the *para* carbon atoms. A reasonably complete series of stable substituted triarylaminium salt[5]

(1) This work was supported by U. S. Army Signal Research and Development Laboratory contract DA-36-039-SC-74917, administered by the University of Pennsylvania, and by Office of Naval Research contract N7-ONR-45403 with Rutgers University. Royalty-free reproduction for purposes of the United States Government is permitted.

(2) A portion of this material was abstracted from a thesis submitted by A. F. D'Adamo, Jr., to the Graduate School of Rutgers University in partial fulfillment of the requirements for the Ph.D. degree, September 1954.

(3) Inquiries should be addressed to this author at Haverford College.

(4) See the series of papers by E. Müller and co-workers. Paper XII; E. Müller, A. Rieker, K. Ley, R. Mayer, and K. Scheffler, *Ber.*, 92, 2278 (1959).

(5) R. I. Walter, *J. Am. Chem. Soc.*, 77, 5999 (1955).

radicals is known, but the unsubstituted parent compound, triphenylaminium perchlorate, is unstable in air.

The classic work of Goldschmidt and his students[6] introduced the group of free radicals derived formally by hydrogen abstraction from trisubstituted hydrazines, and outlined the structural features which determine the stability of these hydrazyl radicals with respect to dimerization to the corresponding tetrazanes. The most stable free radical which they prepared was 1-picryl-2,2-diphenylhydrazyl,[6c] (DPPH), which is completely monomeric and stable in air for an indefinite period.

In his survey of the effect of structure on the stability of these radicals, Goldschmidt showed that the 1,1,4,4-tetraaryl-2,3-diacyltetrazanes are more highly dissociated than the 1,2,3,4-tetraaryl-1,4-diacyl isomers.[6b,d] Acyl groups are effective in stabilizing the monomer in the order acetyl < benzoyl < picryl.[6d] Finally, he showed that in a series of substituted 1-benzoyl-2,2-diphenylhydrazyl radicals, substituents in the *para* positions of the two benzene rings contribute increasingly to the stability of the monomers as their electron-donating character increases.[6c] These results led us to expect that most members of a series of substituted 1-picryl-2,2-diarylhydrazyls would be stable monomeric substances which would be suitable for studies relating substituent effects and physical properties of the free radicals. Our synthesis of many of these compounds was based (with some alterations) upon that developed by Goldschmidt and Renn[6c] for the unsubstituted radical:

$$Ar_2NH \longrightarrow Ar_2N{-}NO \longrightarrow Ar_2N{-}NH_2 \longrightarrow Ar_2N{-}NH{-}Pic \longrightarrow Ar_2N{-}N{-}Pic$$

Most of the necessary secondary amines are available in fair yields by hydrolysis of the *N*,*N*-diarylacetamides formed by reaction of a *para*-substituted acetanilide and aryl iodide catalyzed by copper powder.[7] This reaction cannot be used when the *para*- substituents can themselves be displaced by nitrogen. For this reason, bis(*p*-bromophenyl)amine was prepared by bromination of *N*-benzoyldiphenylamine, followed by hydrolysis in alcoholic potassium hydroxide. It proved more convenient to prepare bis(*p*-nitrophenyl)amine in the same way, since the *N*-acetyl group in this case is so readily hydrolyzed that formation of tertiary amine cannot be avoided when the Ullmann synthesis is used.

Nitrosation of most of the amines was carried out in ethanol–hydrochloric acid with the temperature maintained below 5°, but when the electron-attracting groups $-NO_2$, $-COOCH_3$, and $-C_6H_5$ were present, this reaction failed because of the decreased basicity of the amines.[8] Nitrosation with solutions of nitrosyl chloride also was attempted. This reagent evidently has been used previously with aliphatic secondary amines,[9] but gave a maximum yield of 50% due to amine hydrochloride formation. Pyridine solutions of of the diarylamines reacted with nitrosyl chloride to give the nitrosoamines in up to 95% yield. The reaction evidently is quite general, for it was used successfully for the nitrosation of the amines substituted by $-OCH_3$, —H, $-COOCH_3$, and $-NO_2$ groups. It gave only partial nitrosation of bis(*p*-biphenylyl)amine.

The nitroso compounds were reduced to 1,1-diarylhydrazines with lithium aluminum hydride, using the inverse addition of reagent to *N*-nitroso compound reported by Poirier and Benington.[10] This is an important improvement over alternative methods using zinc and acetic acid or catalytic hydrogenation; these reagents gave large amounts of diarylamines, as has been reported by Paal and Yao.[11] It suffers from two disadvantages: Decomposition of the reaction mixture gives emulsions which are difficult to handle, and it cannot be used with nitroso compounds containing unsaturated substituents which can also be reduced. A survey of other reducing agents (using the inverse addition of reductant to *N*-nitrosodiphenylamine solution) did not reveal one which would preferentially reduce the nitroso group. Sodium borohydride and lithium-*t*-butoxyaluminohydride[12] failed to react. Sodium borohydride with aluminum chloride[13] or with lithium bromide,[14] thiourea dioxide,[15] and diphenylhydrazine with palladium catalyst all gave the secondary amine.

An alternate route to 1,1-bis(*p*-carbomethoxyphenyl)hydrazine avoided this reduction step. 1,1-Bis(*p*-bromophenyl)hydrazine was metallated with butyllithium, carbonated, and esterified with diazomethane to give the carbomethoxy compound in low yield.

An effort to carry out substitution in 1,1-di-

(6) (a) S. Goldschmidt, *Ber.*, **53B**, 44 (1920). (b) S. Goldschmidt and K. Euler, *Ber.*, **55B**, 616 (1922). (c) S. Goldschmidt and K. Renn, *Ber.*, **55B**, 628 (1922). (d) S. Goldschmidt, A. Wolf, E. Wolffhardt, I. Drimmer, and S. Nathan, *Ann.*, **437**, 194 (1924). (e) S. Goldschmidt and J. Bader, *Ann.*, **473**, 137 (1929).

(7) F. Ullmann, *Ber.*, **36**, 2382 (1903); I. Goldberg, *Ber.*, **39B**, 1691 (1906).

(8) H. Wieland and H. Lecher, *Ann.*, **392**, 167 (1912), reported the incomplete nitrosation of bis(*p*-nitrophenyl)-amine with nitrous acid in warm acetic acid. We made no effort to vary conditions to get this compound since a method was lacking for reducing the nitroso group without affecting the nitro groups.

(9) W. Solonina, *J. Russ. Phys. Chem. Soc.*, **30**, 449 (1898); *Chem. Zentr.*, **1898** II, 888.

(10) R. H. Poirier and F. Benington, *J. Am. Chem. Soc.*, **74**, 3192 (1952).

(11) C. Paal and W. N. Yao, *Ber.*, **63B**, 57 (1930).

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(13) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956).

(14) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

(15) P. H. Gore, *Chem. & Ind.*, 1355 (1954).

phenylhydrazine was less successful.[16] Friedel-Crafts acetylation of the hydrochloride gave a triacetyl compound which we assume is 1,1-bis-(*p*-acetylphenyl)-2-acetylhydrazine, but it proved impossible to hydrolyze an acetyl group to get 1,1-bis(*p*-acetylphenyl)hydrazine.

Picrylation of the 1,1-diarylhydrazines with picryl chloride gives a maximum yield of 50%, because half of the hydrazine is converted to the hydrochloride by the acid formed. Poirier, Kahler, and Benington[17] avoided this loss by heating the reagents in ethanol with sodium bicarbonate. At this temperature, however, there occurred appreciable decomposition of a number of our compounds. These difficulties were avoided by picrylation at or below room temperature with *N*-picrylpyridinium chloride[18] suspended in chloroform. The products were normally stable except for the dianisyl compound. This was quite unstable, and required special care in its preparation and isolation to avoid extensive formation of green decomposition products. Since the green diarylnitrogen free radicals are stabilized by electron-donor substituents,[19] we believe that the decomposition occurred by homolysis of the nitrogen-nitrogen bond to give the dianisylnitrogen radical. If this postulate is correct, it would be very difficult to prepare 1,1-bis(*p*-dimethylaminophenyl)-2-picrylhydrazine, which would undergo homolysis to form a still more stable diarylnitrogen free radical. No attempt was made to do so in our work.

Our efforts to carry out substitution reactions on 1,1-diphenyl-2-picrylhydrazine were unsuccessful: no product was isolated from Friedel-Crafts acetylation with a variety of catalysts and solvents or from nitration in nitric acid-sulfuric acid at −10°. However, this compound has been shown to react in benzene solution with nitrogen dioxide to give successively the mono and the di-*p*-nitro derivatives.[20] This procedure was used to prepare the latter compound.

The Tafel-Gattermann reaction[6c,21] offers a possible alternate route to the substitution 1,1-diaryl-2-acylhydrazines which avoids the reduction step. 1-*p*-Nitrophenyl-2-benzoylhydrazine heated in alcohol solution with cupric acetate gave 1,1-bis(*p*-nitrophenyl)-2-benzoylhydrazine, but it was impossible to hydrolyze the benzoyl group in order to prepare the picryl compound. When 1-picryl-2-*p*-nitrophenylhydrazine in ethanol was heated with cupric acetate, the product was 2,4,6,4′-tetranitroazobenzene. This substance is the second stage in the mechanistic sequence proposed by Goldschmidt and Bader[6e] for the Tafel-Gattermann reaction. Evidently it is too stable to undergo the succeeding steps.

No product was isolated from an attempted reaction of paranitrochlorobenzene with 1-picryl-2-*p*-nitrophenylhydrazine under Ullmann conditions. This reaction has been applied successfully to the preparation of 1,1-diaryl-2-benzoylhydrazines.[22]

The diarylpicrylhydrazines have been oxidized to the free radicals in the usual manner with lead dioxide.[6c,17] All of the products have been shown to be paramagnetic by observation of their electron spin resonance (ESR) absorptions. (Only the data on the earlier preparations have been published.[23]) With the exception of the compound substituted by methyl groups, they showed no absorption above background noise in the infrared region around three microns, where the parent hydrazines have their N—H band. Melting points (except those for the compounds substituted by methyl carbomethoxy, or phenyl groups) are within a 3° range or better. In spite of these indications of a reasonable degree of purity, only those radicals substituted by methoxy or chloro groups gave satisfactory analytical data. After the preparations were dried *in vacuo* at 100° for two hours, the analyses were excellent, but melting points had been seriously lowered and broadened. The literature contains a number of reports of tenacious retention of solvents by 1-picryl-2,2-diphenylhydrazyl.[24] The same behavior might be expected from the substituted compounds. Rather surprisingly, two recent papers on the preparation of monosubstituted 1-aryl-1-phenyl-2-picrylhydrazyls which were crystallized from chloroform-ether report excellent analytical data with no mention of any difficulty in drying the radicals.[25]

1-Picryl-2,2-diphenylhydrazyl and the intermediates in its synthesis are of course well known compounds. Since our earliest work[2] on these radicals, the preparation by the same reaction sequence of one of them—that substituted by

(16) Very recently a procedure has appeared for the sulfonation of diphenylhydrazine with chlorosulfonic acid in nitrobenzene. The resulting *p,p′*-disulfonic acid of 1,1-diphenylhydrazine has been picrylated and oxidized to a water-soluble free radical. G. V. Putyrskaya, *J. Research Inst. (Chem.) Hung. Acad. Sci.*, **3**, 143 (1959).

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(20) J. A. Wiel, K. V. Sane, and J. M. Kinkade, *J. Phys. Chem.*, in press. We are indebted to Dr. Weil for a copy of his procedure in advance of publication.

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(23) R. I. Walter, R. S. Codrington, A. F. D'Adamo, and H. C. Torrey, *J. Chem. Phys.*, **25**, 319 (1956).

(24) (a) E. Müller, I. Muller-Rodloff, and W. Bunge, *Ann.*, **520**, 244 (1935). (b) A. Lyons and W. F. Watkins, *J. Polymer Sci.*, **18**, 141 (1955). (c) J. J. Lothe and G. Eia, *Acta Chem. Scand.*, 12, 1535 (1958).

(25) R. O. Matevosyan, I. Ya. Pastovskii, and A. K. Chirkov, *J. Gen. Chem. (U.S.S.R.)*, (English Translation), 29, 843, 3071 (1959).

methyl groups—has been published.[26] The compounds from these two series have been omitted from the Experimental section except in those cases where they were prepared with the use of a new reagent.

EXPERIMENTAL

Impure compounds were chromatographed on Merck alumina. Melting points were determined on a Kofler hot-stage microscope. Most of the analyses were run by Galbraith Laboratories.

Diarylamines by the Ullmann reaction.[7] Most of the necessary *para*-substituted anilines are commercially available. *p*-Fluoroaniline was prepared from fluorobenzene by nitration followed by reduction in ethanol solution with a palladium catalyst.[27] Biphenyl was nitrated in acetic acid solution,[28] reduced with iron and hydrochloric acid,[29] and acetylated by refluxing with acetic anhydride. The other amines were acetylated in aqueous solution by Fieser's method.[30] The necessary *para*-substituted iodobenzenes were prepared from the anilines by diazotization and reaction with iodide ion.

A number of changes in the reaction conditions have approximately doubled the yields obtained in the Ullmann reaction at the beginning of this work.[5] For the copper bronze catalyst formerly used, we have substituted Fernlock brand copper powder.[31] The reaction of the aryl iodide and acetylamine has been carried out in the presence of a small amount of xylene; this solvent lowers the viscosity of the mixture of molten organic reagents, and it serves as a temperature control: the stirred mixture is heated in an oil bath maintained at 200°, but reflux of the xylene maintains the temperature of the reaction mixture at about 180°. Purification of large batches by chromatography[6] is inconvenient; it has proved more satisfactory in many cases to extract the crude products with a suitable solvent in a Soxhlet extractor. Tars are retained in the solvent when the solution is concentrated to precipitate the extracted product. A general procedure for preparation of the secondary amines follows.

A 0.5-mole sample of *N*-acetylarylamine, 0.5 mole of aryl iodide, 50 ml. of xylene, 0.5 formula weight of potassium carbonate (previously powdered and dried at 180°), 10 g. of Fernlock copper powder, and a few crystals of iodine are placed in a three-neck 1000-ml. round-bottom flask. The flask is equipped with a stirrer and an air condenser which terminates in a 180° bend, so that the less volatile of the distilled liquids which condense in the vertical portion will be returned to the reaction mixture, while water, which condenses near the top, will run out of the system. The flask is heated with vigorous stirring in an oil bath held at 200° for 48 hr. or more. At the end of this period, the mixture is allowed to cool, 1500 ml. of 10% alcoholic potassium hydroxide is added, and the suspension stirred slowly under reflux for 8–15 hr. to hydrolyze the amide. Solvents are removed by vacuum distillation, and the solid residue is dried and transferred to the thimble of a Soxhlet extractor, where it is extracted with petroleum ether (b.p. 60–70°) until removal of organic matter is complete. The extract is concentrated under vacuum, cooled, and the crystalline solids are collected; if they are still tarry, the extraction step is repeated. In some cases additional purification steps are required. The product is finally recrystallized from a suitable solvent to constant melting point. Details for the individual preparations are given in Table I.

TABLE I

PREPARATION OF SECONDARY AROMATIC AMINES

para-Group	Extraction Solvent	Recryst. Solvent	M.P.	Yield, %
—OCH_3	Hexane	Benzene-hexane	100–102	46
—CH_3	Hexane	Hexane	82–83	60
—F	None	None	[a]	71
—Cl	Hexane	Hexane	77–78	51
—$COOCH_3$[b]	Chloroform	Benzene	178–180	42
—C_6H_5	Benzene	Benzene	209–210	32

[a] Boiled 123–125° at 0.5 mm. [b] Amide hydrolyzed with 20% sulfuric acid in methanol, to avoid splitting the ester groups.

Bis(p-bromophenyl)amine.[32] Bromination at 40° of a chloroform solution of *N*-benzoyldiphenylamine gave this compound; yield after recrystallization from hexane, 69%, m.p., 105.5–107°.

Bis(p-nitrophenyl)amine.[33] This compound was prepared by nitration of *N*-benzoyldiphenylamine (0.1 formula wt.) in acetic acid (150 ml.) by dropwise addition of fuming nitric acid (27 ml., sp. gr. 1.52) at 90–95°. The reaction mixture was poured on ice, the precipitated amide refluxed in 500 ml. ethanol containing 10 g. of potassium hydroxide, and the amine recovered by again pouring on ice. It was extracted into benzene and this solution concentrated to recover the product. The yield was 38%, m.p. 217–218°.

Nitrosation with nitrous acid. This reaction was carried out by adding sodium nitrite solution (1.2 formula wt. in 250 ml. water) to a stirred solution of the secondary amine (1 formula wt. in 500 ml. of ethanol and 100 ml. of hydrochloric acid) which was maintained at 0°. The mixture was stirred an additional 30 min., diluted with water, and the product recovered and recrystallized from hexane. This procedure gave *N*-nitrosodi-*p*-anisylamine[34] m.p. 79–80°, in 90% yield. The new compounds prepared in this manner are listed in Table II.

Nitrosation with nitrosyl chloride. The reagent was made up as a 10% solution in pyridine by condensing the gas from a cylinder. This solution was added in about 50% excess to a solution of the amine (0.1 formula wt.) in 50 ml. pyridine at 0°, and the mixture was stirred for 30 min. at this temperature. It was then allowed to warm to room temperature over night. Soda-lime was added to destroy the excess reagent, solids were removed by filtration, and the filtrate evaporated to dryness under vacuum. Reaction with diphenylamine gave the nitroso compound, after recrystallization from ethanol, in 95% yield; m.p. 65–66°. It gave *N*-nitrosodi-*p*-anisylamine, m.p. 78–80°, in 60% yield. It was also used to nitrosate the amines substituted by carbomethoxy, nitro, and phenyl groups. Data for these compounds are given in Table II. (It is less convenient to use nitrosyl chloride than the conventional method with nitrous acid in those cases where the acid is effective, because the product is more easily recovered and purified in the latter case.)

Those nitrosamines which are substituted by electron-withdrawing groups are appreciably less stable than *N*-nitroso-diphenylamine.[8] *N*-Nitrosobis(*p*-carbomethoxyphenyl)amine is converted to the free amine by sublimation

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(30) L. F. Fieser, *Experimenta in Organic Chemistry*, 3rd ed., Heath and Co., Boston, Mass., 1955, page 151.

(31) Available from the United States Bronze Powder Works, 220 West 42nd St., New York, N. Y.

(32) E. Lellmann, *Ber.*, 15, 830 (1882).

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(34) H. Wieland, *Ber.*, 41, 3503 (1908).

TABLE II

PREPARATION OF SUBSTITUTED SECONDARY *N*-NITROSOAMINES

para-Groups	Nitrosation Reagent	Recryst. Solvent	M.P.	Yield, %	Calcd. % C	Calcd. % H	Calcd. % N	Calcd. % X	Found % C	Found % H	Found % N	Found % X
—F	HNO_2	Hexane	45–46.5	90	—	—	11.97	—	—	—	12.15	—
—Cl	HNO_2	Hexane	81–82.5	81	56.94	3.98	11.07	28.01	56.94	3.99	11.19	28.22
—Br	HNO_2	Hexane	104–106	80	40.48	2.27	7.87	44.89	40.48	2.33	7.62	44.83
—$COOCH_3$	NOCl	Methanol	105–107	80	—	—	8.92	—	—	—	8.75	—
—NO_2	NOCl	Nitromethane	145–148	[a]	—	—	—	—	—	—	—	—
—C_6H_5	NOCl	Ethanol	155–180	[b]	—	—	—	—	—	—	—	—

[a] The major part of the product decomposed during attempted recrystallization from nitromethane. [b] This reaction produced a mixture which could not be separated. The crude material was used for reduction to the hydrazine.

TABLE III

PREPARATION OF SUBSTITUTED 1,1-DIARYLHYDRAZINES

para-Groups	Recryst. Solvent	M.P.	Yield, %	Calcd. % C	Calcd. % H	Calcd. % N	Calcd. % X	Found % C	Found % H	Found % N	Found % X
—F	Ethanol	185–186[a]		—	—	8.64	—	—	—	8.53	—
—Cl	Hexane	92.5–93.5	72	56.94	3.98	11.07	28.01	56.94	3.99	11.19	28.22
—Br	Ethanol	117–119	89	42.13	2.95	8.19	46.73	42.11	3.10	8.18	46.60
—$COOCH_3$	Methanol	169–172	17	63.99	5.37	9.33	—	64.08	5.28	9.24	—
—C_6H_5[b]	Ethanol	226–227.5	34	85.68	5.99	8.33	—	85.83	6.27	8.14	—

[a] These data were obtained on the benzhydrazide, rather than the unstable hydrazine. [b] Prepared from the crude nitrosation product. The yield given is for the two stages from the secondary amine.

at 100° or by heating the molten nitroso compound. *N*-Nitrosobis(*p*-nitrophenyl)amine was also formed by the nitrosyl chloride, and a small amount was isolated by extraction with hexane (which is very slow). When recrystallization of the remaining product from hot nitromethane was attempted, only secondary amine was recovered. Decomposition to the amine in boiling alcohol also has been reported.[35]

Reduction of N-nitrosamines. This reaction was carried out with lithium aluminum hydride by the procedure of Poirier and Benington,[10] using solutions of 0.1 formula wt. of the nitroso compounds in 300–400 ml. of anhydrous ether. Decomposition of the reduction intermediates always produced emulsions; there were least troublesome when ethyl acetate, wet ether, and 20% sodium potassium tartrate were used in that order. The reduction gave 1,1-di-*p*-anisylhydrazine,[31] recrystallized from methanol, in 90% yield; m.p. 110–111°. The new compounds so prepared are listed in Table III.

1,1-Bis(p-carbomethoxyphenyl)hydrazine. 1,1-Bis(*p*-bromophenyl)amine (0.022 formula wt.) in 200 ml. of anhydrous ether was added to 50% excess over the equivalent amount of butyllithium in pentane-heptane. After stirring 15 min., the mixture was poured over 100 g. of crushed Dry Ice and allowed to stand over night. The product was extracted into 10% sodium hydroxide solution, this was acidified, and the solid recovered and dried thoroughly. Yield of this crude product was 50 to 70%. The dry solid was suspended in ether, treated with excess diazomethane in ether, and the product recovered and recrystallized from methanol. Data are given in Table III.

Acetylation of 1,1-diphenylhydrazine hydrochloride. To a solution of 0.3 formula wt. of aluminum chloride in 150 ml. of dry 1,2-dichloroethane at 10° was added 26 ml. of acetyl chloride, followed by 0.03 mole of the solid diphenylhydrazine hydrochloride in small portions. The mixture was stirred over night at room temperature, poured on ice, and solvent removed by steam distillation. The crude residue (yield, 60%) was recrystallized from ethanol to give the product, m.p. 193–194°. We assume that this is 1,1-bis(*p*-acetylphenyl)-2-acetylhydrazine, but this structure has not been verified.

Anal. Calcd. for $C_{18}H_{18}O_3N_2$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.47; H, 5.60; N, 8.88.

Picrylation of 1,1-diarylhydrazines. The reagent forms as an amorphous orange precipitate on adding an equimolar amount of dry pyridine to a solution of picryl chloride in dry chloroform.[18] To carry out the reaction, a solution of the diarylhydrazine (0.05 formula wt.) in 100 ml. of dry chloroform was added to a suspension of an equivalent amount of the reagent in 250 ml. of dry chloroform. The mixture was stirred at room temperature until a color shift to deep red, accompanied by disappearance of the orange reagent and precipitation of colorless pyridinium chloride, indicated completion of the reaction. Reaction time was shortest for the most basic hydrazines; it was necessary to heat the solution containing the least basic compound which we attempted to picrylate, that containing carbomethoxy groups. This suggests that it would be difficult or impossible to picrylate the nitro-substituted compound, even if it were available. The suspended pyridinium chloride was filtered off, the filtrate washed with water, dried over sodium sulfate, and concentrated under vacuum to obtain the dark red product. Data on the individual compounds are given in Table IV.

1,1-Di-p-anisyl-2-picrylhydrazine. Attempts to prepare this compound under the conditions described above gave large amounts of a green decomposition product. Better results were obtained by starting the picrylation in a cold solution. Dianisylhydrazine (0.067 formula wt.) in 160 ml. of dry chloroform was cooled to 3° and added to a freshly prepared suspension of *N*-picrylpyridinium chloride (0.067 formula wt.) in 240 ml. of chloroform which was also at 3°. The mixture was stirred 10 min. with cooling in an ice bath, then removed from the bath and stirred an additional 40 min. The chloroform solution was filtered, washed with water, dried for 15 min. over magnesium sulfate, and evaporated to dryness on the aspirator at room temperature. The residue was immediately taken up in cold benzene and chromatographed on alumina. The initial reddish benzene eluate con-

(35) P. Juillard, *Bull. soc. chim. France*, **33**, 1177 (1905).

TABLE IV

PREPARATION OF SUBSTITUTED 1,1-DIARYL-2-PICRYLHYDRAZINES

para-Groups	Reaction Time, Hr.	Recrystn. Solvent	M.P.	Yield, %	Calcd. % C	Calcd. % H	Calcd. % N	Calcd. % X	Found % C	Found % H	Found % N	Found % X
—OCH_3	0.8[a]	C_6H_6	92–95[b]	39	52.74	3.76	15.38	—	53.98	3.48	13.25	—
—CH_3	4	2:1 $CHCl_3$–C_2H_5OH	166–167	80	56.73	4.05	16.54	—	56.37	3.93	16.62	—
—H	20	3:2 $CHCl_3$–C_2H_5OH	174–176	95	—	—	—	—	—	—	—	—
—F	6	3:2 $CHCl_3$–C_2H_5OH	196–198	92	50.12	2.58	16.24	—	49.63	2.66	15.75	—
—Cl	20	CCl_4	165–166	73	46.57	2.39	15.09	15.28	46.41	2.43	14.96	15.52
—Br	24	CCl_4	107.5–109.5	90	39.08	2.00	12.66	28.89	39.28	2.26	12.30	—
—$COOCH_3$	46[c]	$CHCl_3$	184–188	45	51.67	3.35	13.70	—	51.82	3.55	13.63	—
—NO_2	0.5[d]	Dioxane	212–213.5	75	[d]	—	—	—	—	—	—	—
—C_6H_5	24	$CHCl_3$–CCl_4	121–123	38	65.81	3.86	12.78	—	65.83	3.91	12.89	—

[a] Used special conditions described in text. [b] Crystals from benzene had this m.p. Solid from a lyophilized benzene solution melted 64–67°. [c] Reaction was carried out at reflux temperature of the chloroform solution. [d] Prepared by reaction of 1,1-diphenyl-2-picrylhydrazine in benzene with nitrogen dioxide. See reference 20.

TABLE V

PREPARATION AND PROPERTIES OF 1-PICRYL-2,2-DIARYLHYDRAZYL FREE RADICALS

para-Group	Hydrazine, Mole	PbO_2, Mole	Na_2SO_4, G.	Solvent, Ml.	Reaction Time, Hr.	Solution Color	Purification	M.P.[a]
—OCH_3	0.0022	0.11	15	$CHCl_3$, 50	0.25	Blue	None	145–148
—CH_3	0.0024	0.11	20	$CHCl_3$, 50	0.33	Blue-purple	Lyophilized from benzene	108–118
—H	0.0051	0.051	0	CCl_4, 60	1.0	Purple	Recryst. from CCl_4	127–129
—Cl	0.0065	0.053	7.2	CCl_4, 180	1.0	Purple	Recryst. from CCl_4	154–156
—Br	0.011	0.22	15	CCl_4, 300	1.0	Purple	Recryst. from CCl_4	139–141
—$COOCH_3$	0.001	0.08	20	$CHCl_3$, 70	1.0	Dull purple	Lyophilized from benzene	90–100
—NO_2	0.0043	0.15	17	$CHCl_3$, 80	2.0	Brown-purple	Recryst. from ethyl acetate	204–207
—C_6H_5	0.0042	0.05	6	$CHCl_3$, 150	1.0	Blue-purple	Lyophilized from $CHCl_3$	140–150

[a] Melting points after drying at room temperature are listed.

tained the product; concentration of the solution gave dark red crystals, m.p. 92–95°. When the benzene was completely removed by lyophilization, the residue melted 64–67°. Later fractions from the column, or solutions which were allowed to stand or were heated above room temperature were green. We believe the green substance may be the dianisylnitrogen radical, on the basis of its color and reported stability.[19]

Because the analytical data on this compound are so poor, presumably because of rapid decomposition of the sample, its structure was confirmed by reduction in ether solution with stannous chloride-hydrochloric acid. The more basic product was precipitated as the hydrochloride, then condensed with benzil by adding this reagent to an ethanol solution of the free base. The melting point was 259–260°, identical to that reported for the benzil condensation product of 1,2,3,5-tetraaminobenzene from the reduction of picramide.[36] No effort was made to identify the dianisylamine also formed by the reduction.

Attempts to prepare 1,1-bis(p-nitrophenyl)-2-picrylhydrazine by the Tafel-Gattermann reaction. The procedure of Goldschmidt and Bader[6c] was used to prepare 1,1-bis(*p*-nitrophenyl)-2-benzoylhydrazine. Our melting point, 292–293°, was higher than that reported in the literature.[6c,21] Attempts to hydrolyze the benzoyl group in sulfuric acid of various concentrations, hydrochloric acid, or in phosphoric acid either gave no reaction or gave a tarry mixture of decomposed hydrolysis products from which only benzoic acid could be recovered by sublimation.

An attempt was also made to prepare the picrylhydrazine directly. 1-Picryl-2-*p*-nitrophenylhydrazine,[37] m.p. 214–215°, was prepared in 92% yield by reaction of *N*-picrylpyridinium chloride and *p*-nitrophenylhydrazine in dry chloroform. When this compound in boiling ethanol was treated with cupric acetate under Tafel-Gattermann conditions, the product recovered was 2,4,6,4′-tetranitroazobenzene, m.p. 171–173°. There was no depression of the melting point by an authentic sample prepared by oxidation of 1-picryl-2-*p*-nitrophenylhydrazine with nitric acid.[38]

Preparation of 1-picryl-2,2-diarylhydrazyl free radicals.

(36) R. Nietzki and H. Hagenbach, *Ber.*, **30**, 541 (1897).

(37) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, 101, 2450 (1912).

(38) R. Ciusa, *Gazz. chim. ital.*, **41**, 694 (1911).

TABLE VI

ANALYSES OF 1-PICRYL-2,2-DIARYLHYDRAZYL FREE RADICALS

para-Group	Drying Temperature	Calcd. % C	Calcd. % H	Calcd. % N	Calcd. % X	Found % C	Found % H	Found % N	Found % X
—OCH_3	25	52.86	3.55	15.42	—	52.66	3.54	15.15	—
—CH_3	25	56.87	3.82	16.58	—	45.83	3.13	13.08	—
—H	100	54.82	3.07	17.76	—	55.05	3.13	17.67	—
—Cl	25	46.67	2.28	15.12	15.31	46.50	2.17	14.97	15.50
—Br	25	39.10	1.83	12.69	28.95	39.31	2.00	12.52	28.71
—$COOCH_3$	100	51.77	3.26	13.72	—	51.82	3.32	13.51	—
—NO_2	100	44.64	2.08	20.24	—	44.41	2.08	19.93	—
—C_6H_5	25	65.93	3.69	12.82	—	63.70	3.78	11.30	—

The diarylpicrylhydrazines were oxidized by stirring carbon tetrachloride or chloroform (if the compound was not sufficiently soluble in carbon tetrachloride) solutions of these compounds with excess lead dioxide in the presence of anhydrous sodium sulfate. The lead dioxide was more reactive, and could be used in smaller excess, when it was freshly prepared from the tetraacetate by the procedure reported by Wilmarth and Schwartz.[39] Reaction time varied from 0.25–2 hr. Inorganic compounds were then filtered off, washed, and the combined filtrates evaporated *in vacuo*. In most cases, crystallization began toward the end of the evaporation process. When it did, the solids had fairly sharp melting points. The data are given in Table V.

Of the set of hydrazyl free radicals described here, the unsubstituted member, 1-picryl-2,2-diphenylhydrazyl, appears to be the most stable. The radicals substituted by two methyl groups or by two fluorine atoms have not been prepared in a pure state, and neither of them has kept very well. Thus, the solid tolylpicrylhydrazyl has an N—H absorption in the infrared, gives poor analytical data, and slowly loses its ESR signal over a period of 2 months. This may in part be connected with the impurities in these preparations: It appears that any sample of the radicals keeps better if it is quite pure to begin with. The solid radicals containing two —OCH_3, —Cl, —Br, —$COOCH_3$, —NO_2, and —C_6H_5 groups have been stored for 3 months at −8° with no evidence of decomposition.

Solutions of the radicals decompose slowly, at rates which increase with substitution by stronger electron-accepting groups. Solutions in pure solvents are adequately stable for physical measurements. There is no evidence for dimerization in solution. The radical containing two nitro groups, for which the equilibrium should lie farthest toward the dimer,[6c] has been checked through the concentration range 1×10^{-3} to 1×10^{-6} *F* in purified benzonitrile. When corrected for the concentration differences, the optical densities at the position of the visible absorption band of the radical decrease uniformly over this concentration range. The total decrease is about 5%. This is in the wrong direction to indicate dimerization, and is evidently due to reaction with the solvent or with impurities in it. Drifts in the readings are greatest with the most dilute solutions.

We have been unable to work out a satisfactory method for recrystallization of the radicals. Solutions of the compounds substituted by —OCH_3, —CH_3, or —F groups undergo substantial decomposition if heated above room temperature. The other radicals are more stable, but we have so far not found solvents from which crystals can be recovered easily. The crystalline products of the oxidation reaction retain solvent in most cases. The exceptions are the radicals substituted by methoxy or chloro groups, which gave good analyses after drying at room temperature. Analytical data for 1-picryl-2,2-diphenylhydrazyl and 1,1-bis(*p*-carbomethoxyphenyl)-2-picrylhydrazyl were unsatisfactory when the samples were dried at room temperature or at 50°.[23a] 1-Picryl-2,2-diphenylhydrazyl has been reported not to contain solvent when recrystallized from carbon tetrachloride, but in our experience it retained about 8% of this solvent until it had been dried at 100°.

All of the reasonably stable radicals except that substituted by phenyl groups gave good analyses (Table VI) after drying *in vacuo* for two hours at 100°. Unfortunately, this process also broadened and lowered all of their melting points. We have no direct evidence as to the nature of the impurities which caused this. The hydrazine might be formed; this would not interfere with the analysis, because it differs from the corresponding radical by only one hydrogen atom. This impurity should be evident from its N—H band in the infrared near 3 μ. Except for the impure radical substituted by —CH_3 groups and that substituted by —$COOCH_3$ groups (after heating only), no N—H absorption above background noise was observed in either the unheated or the heated samples. We believe that we could detect hydrazine present as 5% of the sample by this method. The solid radicals have been characterized by their ESR absorptions,[22] which demonstrated that all of the samples are paramagnetic. Their blue to violet-brown colors are strikingly different from the reddish brown hydrazines, due to a single broad absorption in the visible region of the spectra of the radicals. Data on the spectra and the ESR of solutions of these preparations will be published separately.

(39) Reference (22), footnote (9).

HAVERFORD, PA.