

Radical Coupling Products from the Permanganate Oxidation of N-Phenyl-2-naphthylamine

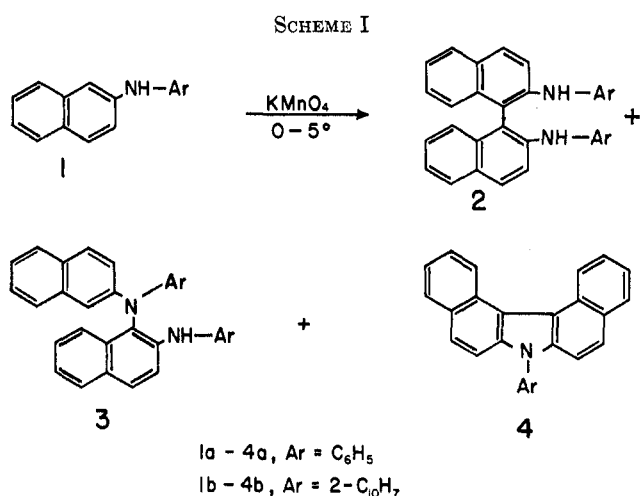
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The oxidative dimerization of N-phenyl-2-naphthylamine by neutral potassium permanganate results in the formation of coupling products **2** and **3**, with the dibenzocarbazole **4** as a minor product. The structures of **2** and **4** were reported earlier. The structure of **3** has now been confirmed by the synthesis of the N-phenyl derivative from a known 1,2-disubstituted naphthalene compound. The product distribution from the permanganate oxidation is the same as that from the coupling of amino radicals generated from the appropriate tetrazene. The effects of substituents on the permanganate oxidation of N-aryl-2-naphthylamines are correlated by σ^+ to give a ρ of -0.68 . These results are consistent with a mechanism involving hydrogen transfer to permanganate followed by product formation *via* carbon-carbon and carbon-nitrogen coupling of the resulting amino radicals.

Recently we reported¹ the products arising from the oxidation of N-phenyl-2-naphthylamine by neutral potassium permanganate in acetone (Scheme I).



In contrast to the oxidation of diphenylamine,² no tetrasubstituted hydrazine was detected. In the present paper we wish to confirm the tentative structural assignment of **3a** made earlier, and present additional results bearing on the mechanism of the reaction.

Results

The structures of **2a** and **4a** have been definitely assigned.¹ The carbon-nitrogen coupled product, **3a**, was tentatively assigned the semidine structure on the basis of elemental analysis, molecular weight, and the determination of one N-H bond per molecule. The chemical shift of the amino hydrogen of **3a** was 0.74 ppm downfield from that of **1a**, suggesting an *ortho* diamine structure.

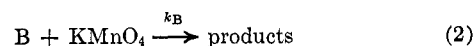
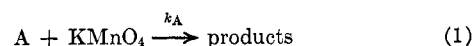
As mentioned earlier,¹ the most direct synthesis of **3a** should be afforded by the Ullmann reaction between **1a** and 1-iodo-N-phenyl-2-naphthylamine. The iodo compound could not be prepared, however. Attempts to treat iodine or iodine monochloride with **1a** under a

variety of conditions led to intractable tars. The reaction of iodine monochloride with the N-acetyl derivative of **1a** in acetic acid³ resulted in an addition compound.

Since the iodo compound was unavailable, the N-phenyl derivative of **3a** was prepared from a known *ortho*-substituted naphthalene compound (**5**) as shown in Scheme II. The reaction of **3a** with iodobenzene and copper gave N-(2-naphthyl)-N,N',N'-triphenyl-1,2-naphthylenediamine (**9**), which was identical with that prepared from 2-amino-1-nitronaphthalene *via* the route shown in Scheme II. These results confirm the earlier assignment of the semidine structure to N-(2-naphthyl)-N,N'-diphenyl-1,2-naphthylenediamine (**3a**).⁴

N-Aryl-2-naphthylamines with substituents in the benzene ring were oxidized by permanganate in the same manner as **1a**. The carbon-carbon coupling products (**2c-2g**) were isolated in the crystalline state and each was characterized by molecular weight, analysis, and the presence of two secondary N-H bonds per molecule. Results are summarized in Table I. The predominant fragmentation in the mass spectrum of each oxidative dimer was the extrusion of an arylamino moiety, analogous to the chemical degradation reported for **2a**.¹ Although the thin layer chromatograms of reaction mixtures indicated that semidines **3c-3g** were formed, none was isolated in crystalline form. The amorphous semidine fraction, **3d**, from the oxidation of **1d** was isolated by column chromatography. Its infrared spectrum was consistent with the assigned structure and showed one N-H bond per molecule. Attempts to induce crystallization have been unsuccessful. The difficulty of obtaining crystalline forms of **3a** and **3b** has been discussed.¹

Competitive oxidations of N-aryl-2-naphthylamines were conducted by allowing mixtures of two amines to



compete for a deficient quantity of potassium permanganate in acetone at 0° (eq 1, 2).

(1) R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, **33**, 4329 (1968).

(2) (a) H. Wieland and S. Gambarjan, *Chem. Ber.*, **39**, 1499 (1906); (b) H. Wieland, *Justus Liebig's Ann. Chem.*, **381**, 200 (1911).

(3) This procedure has been reported successful in the preparation of 1-iodo-2-acetamidonaphthalene: H. Willstaedt and G. Scheiber, *Chem. Ber.*, **67**, 466 (1934).

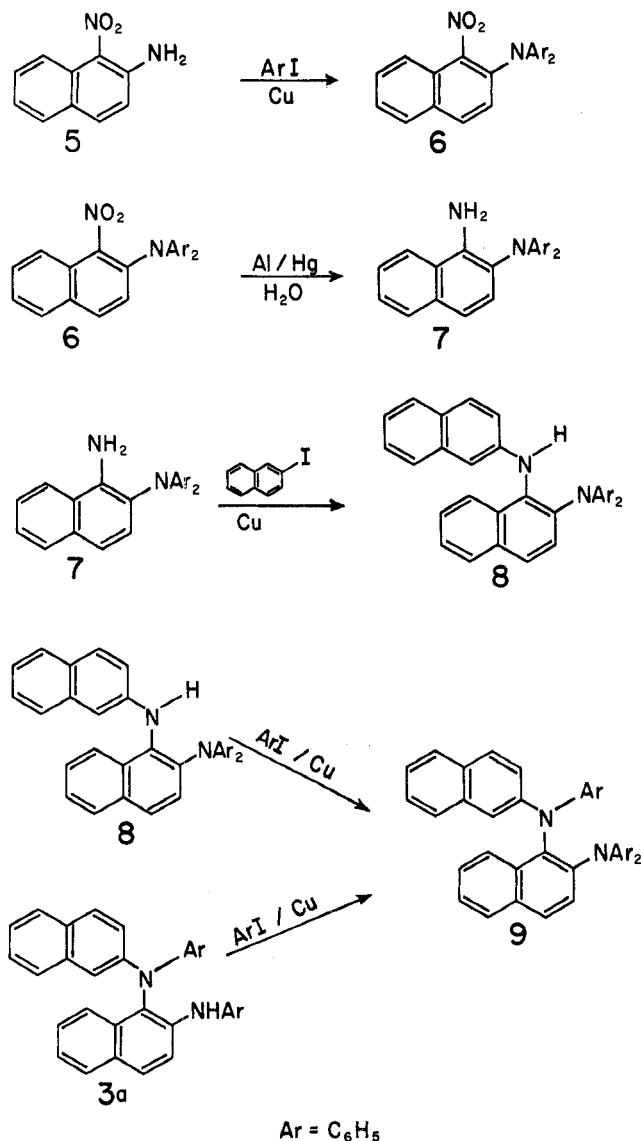
(4) See ref 1 for a discussion of the incorrect assignments of structure **3** to **2a** and **2b** by previous workers.

TABLE I
 PROPERTIES OF 1,1'-BIS(N-ARYL-2-NAPHTHYLAMINES)

Compd ^a	Ar	Mp, °C	Calcd, %			Found, %			Infrared spectra ^b			Yield, %
			C	H	N	C	H	N	NH (2), cm ⁻¹	NH (1), cm ⁻¹	$\frac{\epsilon_{\text{NH}}(2)}{\epsilon_{\text{NH}}(1)}$ ^b	
2c	<i>m</i> -CH ₃ OC ₆ H ₄	182-183	82.23	5.68	5.64	82.53	5.75	5.57	3405	3440	2.0	23
2d	<i>p</i> -CH ₃ OC ₆ H ₄	240-241	82.23	5.68	5.64	82.31	5.74	5.62	3405	3420	1.9	44
2e	<i>m</i> -CH ₃ C ₆ H ₄	167-168	87.89	6.07	6.03	87.89	6.07	6.08	3410	3435	2.1	22
2f	<i>p</i> -CH ₃ C ₆ H ₄	229-230 ^c	87.89	6.07	6.03	87.82	6.11	5.98	3405	3435	2.1	24
2g	<i>m</i> -ClC ₆ H ₄ ^d	177-178	76.04	4.39	5.54	76.08	4.47	5.49	3405	3435	1.9	31

^a Mass spectra of all compounds gave correct molecular weights. ^b 1.4% (w/v) in CDCl₃. See ref. 1. ^c Another form with mp 208-210° was observed when first isolated. ^d Calcd: Cl, 14.03. Found: Cl, 14.10.

SCHEME II



When the ratio of the rates of disappearance of a pair of competing amines, A and B, was taken, the permanganate concentrations cancel and the relative reactivity is given by eq 3.

$$\frac{k_B}{k_A} = \frac{\log[B]_0/[B]}{\log[A]_0/[A]} \quad (3)$$

The validity of eq 3 was tested by changing amine concentration and extent of oxidation and by comparing relative reactivities cross-calculated from different

pairs of reactants. Results are summarized in Table II.

 TABLE II
 COMPETITIVE OXIDATIONS OF N-ARYL-2-NAPHTHYLAMINES BY POTASSIUM PERMANGANATE AT 0°

Amine ^a (concn, M)		Conversion, %	<i>k_B/k_A</i>
A	B		
1a (0.3)	1c (0.3)	38	0.90
1a (0.4)	1d (0.2)	41	3.15
1a (0.3)	1e (0.3)	17	1.23
1a (0.3)	1e (0.3)	32	1.19
1a (0.4)	1e (0.2)	39	1.24
1a (0.4)	1f (0.2)	48	1.58
1a (0.3)	1g (0.3)	39	0.53
1e (0.3)	1c (0.3)	43	0.72 (vs. 0.73) ^b
1f (0.4)	1d (0.2)	45	2.24 (vs. 2.0) ^b

^a Substituents on C₆H₄X: a, H; c, *m*-OCH₃; d, *p*-OCH₃; e, *m*-CH₃; f, *p*-CH₃; g, *m*-Cl. ^b Calculated from reactivities of each component relative to 1a.

Discussion

There are several reasons for considering the mechanism of the permanganate oxidation of 1. General knowledge of diarylamino radicals is surprisingly meager. Recent investigations reveal that these radicals are not particularly stable toward coupling and disproportionation reactions.⁵⁻⁷ The few examples of stable diarylamino radicals which have been unambiguously identified by esr show that electron-donating *para* substituents are necessary.⁵ Since the classic work of Wieland and coworkers, there has been little activity in the oxidation of secondary aromatic amines by permanganate in neutral solution. Most of the quantitative information available deals with other substrates in acidic or basic media.⁸ The formation of tetraphenyl hydrazine from the oxidation of diphenylamine seems best explained by the coupling of neutral radicals (eq 4), though the dimer-monomer equilibrium



suggested by Wieland² is not detectable except in the special cases mentioned above.⁵ In the naphthyl series, however, the hydrazine is not a product.¹ While the products are those expected of radical cou-

(5) F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, **98**, 844 (1965).

(6) H. Musso, *ibid.*, **92**, 2881 (1959).

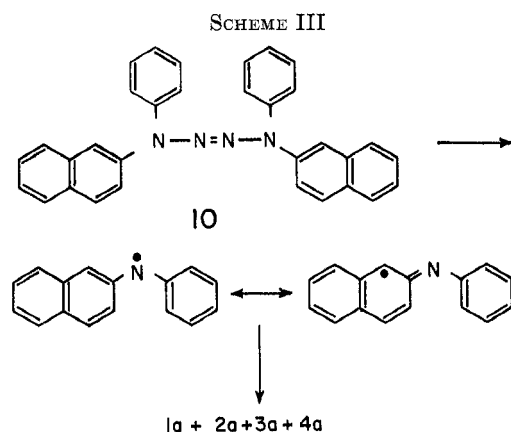
(7) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc., B*, 1114 (1966).

(8) R. Stewart in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 1.

pling reactions, both carbon-carbon⁹⁻¹² and carbon-nitrogen¹³ coupled products have been isolated from oxidations of other amines proceeding *via* radical cation intermediates which were identified by esr.

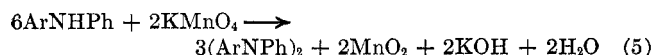
A detailed kinetic study of the permanganate oxidation in acetone is impracticable because the medium is constantly changing during the course of the reaction. It is possible, however, to probe the initial reaction by measuring the effects of substituents from competitive experiments. The nature of the intermediates involved in product formation can be defined by comparing the products of permanganate oxidation with those from an independent source of amino radicals. The oxidation of **1** is well suited for this approach, as the products¹ are well defined and stable toward oxidation, and no significant quantities of disproportionation⁶ products or oligomers are formed.

N-Phenyl-2-naphthylamino radicals were generated by the photolysis and thermolysis of 1,4-diphenyl-1,4-di(2-naphthyl)-2-tetrazene (**10**), as shown in Scheme III. Photolysis and thermolysis of the tetrazene gave



essentially the same results. Products from the decomposition of **10** are compared with those of the permanganate oxidation of **1a** in Table III. The relative amounts of **2a** and **3a** from the two reactions are the same within experimental error, and only minor variations were observed in the yields of **4a**. While this work was in progress, Waters and White¹⁴ reported a similar study of the oxidation of carbazole. Although the complexity of the reaction mixture precluded quantitative comparison, their qualitative results agree with the present findings.

The formation of substantial quantities of **1a** from the decomposition of **10** was not expected. This is of interest in connection with the stoichiometry of permanganate oxidation of amines. Experimentally the stoichiometry of eq 5 is usually not observed and con-



siderable amounts of starting material are recovered, even though all of the permanganate is consumed.

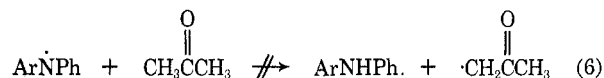
- (9) R. F. Nelson and R. N. Adams, *J. Amer. Chem. Soc.*, **90**, 3925 (1968).
 (10) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. M. Adams, *ibid.*, **88**, 3498 (1966).
 (11) D. H. Iles and A. Ledwith, *Chem. Commun.*, 498 (1968).
 (12) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *ibid.*, 319 (1965).
 (13) Y. Tsujino, *Tetrahedron Lett.*, 763 (1969).
 (14) W. A. Waters and J. E. White, *J. Chem. Soc.*, C, 740 (1968).

TABLE III
COMPARISON OF PRODUCTS FROM PERMANGANATE OXIDATION AND TETRAZENE DECOMPOSITION

Compd	Yield, %		
	Permanganate reaction ^a	Tetrazene photolysis ^b	Tetrazene thermolysis ^c
1a	25 ± 1 ^d	16 ± 1 ^e	15 ± 1 ^e
2a	36 ± 2 ^f	35 ± 2	33 ± 2
3a	24 ± 1 ^f	25 ± 1	25 ± 1
4a	0.4 ^f	1.0	2.8
Ratio, 2a to 3a	1.5 ± 0.2	1.4 ± 0.2	1.3 ± 0.2

^a In acetone at 0–5°, initially 0.5 M **1a**. ^b In acetone at 5°, 0.02 M **10**. ^c In acetone at 40°, 0.02 M **10**. ^d Error limits represent range of duplicate experiments. ^e Mol/200 mol of **10**. ^f Mol/50 mol of **1a**.

The obvious explanation that compound **1a** is formed by a hydrogen-transfer reaction (eq 6) must be



rejected because the formation of **1a** from **10** is independent of temperature (*i.e.*, no apparent activation energy) and fails to exhibit a primary deuterium isotope effect, as shown in Table IV. Since **1a** is formed in

TABLE IV
DECOMPOSITION OF TETRAZENE **10** IN ACETONE AND ACETONE-*d*₆

Solvent	Conditions (temp, °C)	Yield ^a of 1a
Acetone	Thermolysis (25)	19
Acetone- <i>d</i> ₆	Thermolysis (25)	19
Acetone	Thermolysis (56)	16
Acetone- <i>d</i> ₆	Thermolysis (56)	15
Acetone	Photolysis (5)	16
Acetone- <i>d</i> ₆	Photolysis (5)	17

^a Mol/200 mol of **10**.

5–10% yields from the decomposition of **10** in solvents which are poor hydrogen donors,¹⁵ we must conclude that its formation is a property of N-aryl-2-naphthyl-amino radicals or of the tetrazene. Deviations from the stoichiometry of eq 5 most likely occur by oxidation of acetone, especially in the later stages of the reaction as base accumulates. Drummond and Waters¹⁶ have reported that the consumption of permanganate by acetone under basic conditions can be quite high. The well-known precautions² of purifying the acetone and adding permanganate slowly do not always ensure good conversion of amine. We have observed that the amine concentration is an important variable also. At low concentrations (0.15 M) of **1**, very little amine is converted in spite of fairly rapid consumption of permanganate. At amine concentrations of 0.5 M or higher, the reaction proceeds normally, indicating competition between amine and solvent for the permanganate.

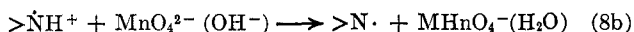
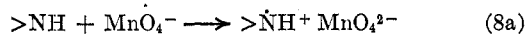
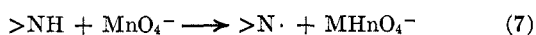
The quantitative agreement between the products of the tetrazene decomposition and those of the permanganate oxidation (Table III) establishes that the oxidation products of **1a** are formed by coupling of amino radicals, as shown in Scheme III. The competitive oxidations of Table II show that the rates of disappear-

(15) Unpublished results from this laboratory; a detailed investigation of the decomposition of tetrazene **10** is in progress and will be reported soon.

(16) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 435 (1953).

ance of amine are not strongly influenced by substituents. These data follow a Hammett relationship, correlating well with σ^+ . The plot in Figure 1 has a slope of -0.68 . While the magnitude of ρ may be attenuated somewhat by the naphthyl group, it indicates that reaction is at the amino group. The observed value of ρ is in the range expected for a free-radical hydrogen-transfer reaction. Values of ρ for reactions of alkoxy and peroxy radicals with a variety of substrates fall in the range -0.4 to -1.5 .¹⁷ Brownlie and Ingold¹⁸ have reported substituent effects in the reaction of peroxy radicals with diphenylamines at 65° to give a ρ of -0.89 , correlated with σ^+ . The σ^+ correlation implies significant polar contributions to the transition state for hydrogen removal, as has been demonstrated for a variety of free-radical reactions.^{18,19} Since formation of the hydroxyl radical²⁰ is unlikely^{18,21} in weakly basic or neutral solution, the permanganate ion seems the most probable hydrogen abstraction reactant.

Experimentally, a rigorous distinction cannot be made between a hydrogen atom transfer and a two-step sequence involving electron transfer at nitrogen, followed by rapid loss of a proton to oxyanion or some other base²² (eq 7, 8). It is probable that reaction 8



would exhibit a substituent effect much larger than that observed experimentally. If a radical cation is involved, its lifetime is insufficient to have any effect on product formation.

An alternative mechanism would involve electron transfer from the aromatic nucleus, such as is operative in the cobalt(III) oxidation of aromatic hydrocarbons.²³ This type of reaction, however, is characterized by a much higher ρ value (-2.4 at 65°). The good fit observed with methoxy substituents discounts a change of mechanism with substituent. Nave and Trahanovsky²⁴ observed both *m*- and *p*-methoxy to be greatly enhanced in reactions of cerium(IV) which change to a π -electron-transfer mechanism in the presence of strongly electron-donating substituents.

In summary, the oxidation of **1** may be described as originating in a hydrogen transfer from the amino group to permanganate, followed by coupling of amino radicals to products. The initial oxidation of amine by permanganate produces manganate ion (or its con-

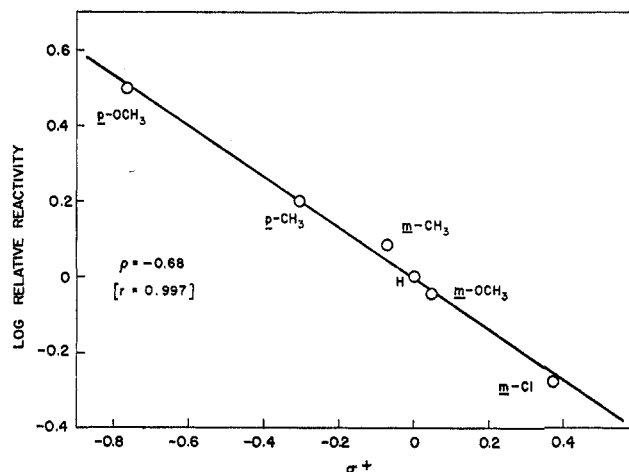
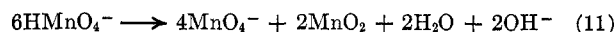
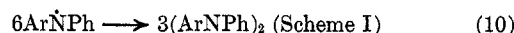
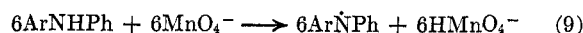


Figure 1.—Effects of substituents on the oxidation of N-phenyl-2-naphthylamine by potassium permanganate.

jugate acid), which is known to disproportionate²⁵ rapidly in neutral or weakly basic media to permanganate and manganese dioxide.



Experimental Section

Analytical Methods.—Compounds **1a**, **2a**, and (**3a** + **4a**) were separated on silica gel sheets of $100\text{-}\mu$ thickness (Eastman "Chromagram") by developing in carbon tetrachloride. Compound **4a** was completely resolved on a thicker ($250\text{-}\mu$) silica layer (Brinkmann). After visualization with ultraviolet light, spots or streaks were removed and treated twice (20 min) with boiling ethanol. Samples were diluted to a known volume, and concentrations were determined by ultraviolet absorption at 305 nm for compounds **1a**–**3a** and 365 nm for **4a**. Gas chromatography¹ was used as an independent method for **1a**, which was sometimes incompletely resolved from **2a**. Compounds **1a** and **1c**–**1g** were determined in reaction mixtures by glpc with a 10-ft silicone rubber column, using *m*-diphenoxybenzene as an internal standard.

The nmr method employed earlier¹ was found unreliable for quantitative purposes. Broadening of the N–H absorption of **3a** in some reaction mixtures made accurate integration difficult. This is believed to be due to impurities in the reaction mixture, possibly oxidation products of acetone.

Materials.—Preparations of **1a**–**4a** have been described.¹ N-Aryl-2-naphthylamines **1c**–**1g** were prepared by the iodine-catalyzed reactions of the appropriate anilines with 2-naphthol.²⁶ Melting points agreed with literature values, and ultraviolet and nmr spectra confirmed structures. Contrary to the original reference, extensive dehydrochlorination took place during the reaction of *p*-chloroaniline with 2-naphthol; the only product isolated was **1a**.

2-Amino-1-nitronaphthalene (**5**), mp $126\text{--}127^\circ$, was used as received from Aldrich Chemical Co., Inc. Other materials are described below. Conditions for the copper-catalyzed arylation of amino groups have been described.¹ Anhydrous potassium carbonate was employed as the base for these reactions. Changes in solvent or reaction time are noted where appropriate.

1-Nitro-N,N-diphenyl-2-naphthylamine (6).—The copper-catalyzed reaction of **5** (10 g , 0.053 mol) with excess iodobenzene (110 ml) serving as solvent yielded 12 g of crude product. Chromatography over alumina and recrystallization from diethyl ether produced 8.69 g (48% yield) of red, crystalline **6**, mp $153.5\text{--}154.5^\circ$. The infrared spectrum showed no NH absorption. *Anal.* Calcd for $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$: C, 77.63 ; H, 4.74 ; N, 8.23 . Found: C, 77.69 ; H, 4.78 ; N, 8.03 .

(25) Reference 8, p 2.

(26) E. Knoevenagel, *J. Prakt. Chem.*, [2] **89**, 1 (1914).

(17) See G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964), and references cited therein.

(18) I. T. Brownlie and K. U. Ingold, *Can. J. Chem.*, **45**, 2419 (1967).

(19) (a) G. A. Russell, *J. Amer. Chem. Soc.*, **78**, 1047 (1956); (b) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); (c) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744, 2800 (1963).

(20) (a) M. C. R. Symons, *J. Chem. Soc.*, 3956 (1953); (b) J. Kenyon and M. C. R. Symons, *ibid.*, 3580 (1953); (c) A. Schlund and H. Wendt, *Ber. Bunsenges. Phys. Chem.*, **72**, 649 (1968).

(21) W. A. Waters, *Quart. Rev. (London)*, **12**, 277 (1958).

(22) The two-step sequence has been considered in the reactions of organic free radicals and atoms; grounds for its rejection are given by G. A. Russell, *Tetrahedron*, **5**, 101 (1959). The behavior of permanganate is too different from organic free radicals to include it categorically in these arguments.

(23) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), A-44 (1969).

(24) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **90**, 4755 (1968).

N',N'-Diphenyl-1,2-naphthylenediamine (7).—A solution of 6 (4 g, 11.8 mmol) in 200 ml of diethyl ether was added alternately with small portions of water (1 ml total) to 4 g of aluminum amalgam²⁷ during 1 hr at room temperature. The solution was stirred for an additional 1 hr, filtered, and dried over K₂CO₃. The product was eluted from alumina with diethyl ether and recrystallized from the same solvent to give 1.88 g (51% yield) of colorless 7, mp 171–172°. The infrared spectrum showed NH absorptions at 3405 and 3490 cm⁻¹.

Anal. Calcd for C₂₂H₁₈N₂: C, 85.13; H, 5.84; N, 9.03. Found: C, 85.29; H, 5.90; N, 9.04.

N-(2-Naphthyl)-N',N'-diphenyl-1,2-naphthylenediamine (8).—This compound was prepared by the copper-catalyzed reaction of 1 g (3.22 mmol) of 7 with 0.818 g (3.22 mmol) of 2-iodonaphthalene. *n*-Dodecane was used as solvent, and reaction time was 6 hr at 200°. After distillation of the solvent under a stream of nitrogen, the crude product was eluted from alumina with benzene to give 0.9 g of a pale yellow glassy solid. The thin layer chromatogram showed that only a small amount (*ca.* 5%) of diarylation had occurred. The product was reluctant to crystallize, and seed crystals were obtained by allowing the glassy solid to stand under absolute ethanol at room temperature for 6 weeks. Crystallization of the main lot from ether–alcohol yielded 0.477 (34% yield) of 8, mp 130–130.5°. The NH absorption at 3400 cm⁻¹ had the intensity required for one NH bond per molecule.¹

Anal. Calcd for C₃₂H₂₄N₂: C, 88.04; H, 5.54; N, 6.42. Found: C, 87.97; H, 5.60; N, 6.36.

N-(2-Naphthyl)-N,N',N'-triphenyl-1,2-naphthylenediamine (9).—The copper-catalyzed reaction of 8 (0.834 g, 1.91 mmol) with excess iodobenzene (10 ml) as solvent yielded after chromatography 0.824 g of pale yellow glassy solid, which crystallized within 1 hr upon addition of diethyl ether. Recrystallization from diethyl ether afforded 0.584 g (59% yield) of 9, mp 205–207°. No NH absorption was observed in the infrared spectrum.

Anal. Calcd for C₃₈H₂₈N₂: C, 89.03; H, 5.50; N, 5.47. Found: C, 89.35; H, 5.44; N, 5.50.

Reaction of N-(2-Naphthyl)-N,N'-diphenyl-1,2-naphthylenediamine (3a) with Iodobenzene.—Under the conditions described above, 3a (1 g, 2.3 mmol) reacted with iodobenzene to give 0.627

g (53% yield) of recrystallized 9, mp 207–208.5°, mmp 205–208°. The infrared spectrum was identical with that of the authentic sample described above.

1,4-Diphenyl-1,4-di(2-naphthyl)-2-tetrazene (10).—A solution of potassium permanganate (2.69 g, 0.017 mol) in 500 ml of acetone was added dropwise during 3 hr to an acetone (100 ml) solution of 1-phenyl-1-(2-naphthyl)hydrazine²⁸ (6 g, 0.0256 mol) cooled in a Dry Ice–acetone bath under nitrogen. Stirring was continued at –78° for an additional 1 hr. The reaction was allowed to warm to 5° and filtered. The filtrate was evaporated to 60 ml at reduced pressure, stored at –18° for 16 hr, and filtered to give 3.72 g (62% yield) of tetrazene 10 as a rust-colored powder. The crude tetrazene was recrystallized with minimum decomposition by dissolving in boiling methylene chloride (30 ml), adding absolute ethanol (25 ml) gradually, and cooling. Recovery of the pale yellow product was 70–80%. Decomposition points at several heating rates were determined with a Du Pont 900 differential thermal analyzer (deg/min, decomposition point): 2, 101; 5, 107; 10, 111; 30, 114. The decompositions of solid samples were strongly exothermic and those at fast heating rates appeared to be explosive. Thermolysis in solution was controlled and yielded 99 ± 1% of the theoretical azo nitrogen. The infrared spectrum showed a complete absence of NH bonds in the recrystallized product; uv max (2% CH₂CN–98% C₂H₅OH)²⁹ 350 nm (ϵ 2.22 × 10⁴), 316 (1.9 × 10⁴), and 274 (2.36 × 10⁴).

Anal. Calcd for C₃₂H₂₄N₄: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.62; H, 5.24; N, 11.95.

Photolysis of 10 was conducted under nitrogen in a quartz reactor with 2537-Å light for 10 hr at 5°. Nitrogen evolution was 93% of theory.

Registry No.—1a, 135-88-6; 2c, 23854-07-1; 2d, 23854-08-2; 2e, 23854-09-3; 2f, 23854-10-6; 2g, 23854-11-7; 6, 23854-12-8; 7, 23854-13-9; 8, 23854-14-0; 9, 23890-44-0; 10, 23854-15-1.

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The Oxidative Coupling Reaction of Vinylidenebisdialkylamines¹

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A series of vinylidenebisdialkylamines, R₂C=C(NMe₂)₂, were oxidized by silver ion in acetonitrile solvent, yielding diamidinium salts *via* dimerization. Cyclization is also possible by this method, which is believed to involve radical cation intermediates.

While enamines and related compounds have been the focus of extensive research in recent years, rather limited attention has been paid to their oxidation.^{2–7} We felt that vinylidenebisdialkylamines (ketene-N,N-acetals), a somewhat less common class of enamines, would be ideally suited as substrates for oxidation. It is, of course, well known that olefinic systems having electron-withdrawing substituents will reductively accept electrons, giving rise to subsequent reactions.⁸

It seemed reasonable to assume that enamines would readily give up electrons to form reactive intermediates.

Results and Discussion

The observation that led to the present study was that 9-[bis(dimethylamino)methylene]fluorene (1) gradually turned blue on exposure to air and that the blue material was esr active. Bromine vapors caused the same transformation even more rapidly, and the oxidizing system settled on as the most convenient and free of side reactions was silver nitrate in acetonitrile.

Oxidation of 1 with silver nitrate produces a deep blue, esr active⁹ solution of radical cation, which can be isolated as a copper-colored crystalline hexafluorophosphate, 2. Although 1 and 2 can be reversibly interconverted electrochemically⁹ in what appears to

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