2-Chloro-6-methyl-6,6a-dihydro-11H-isoindolo[1,2-c][1,2,4]-benzothiadiazin-11-one 5,5-Dioxide (35).—A mixture of **33a** (3.97 g, 0.01 mol), 50% sodium hydride–mineral oil dispersion (0.72 g, 0.015 mol as NaH), anhydrous dimethylformamide (100 ml), and methyl iodide (2.85 g, 0.02 mol) was allowed to react as in the preparation of **18a**. There was obtained 3.8 g of solid, mp 246–247°. Comparison of the infrared and ultraviolet spectra of this compound with those of **35** showed them to be identical.

Registry No.—**1c**, 65-45-2; **10**, 118-92-3; **12a**, 16240-89-4; **12b**, 801-48-9; **14a**, 16240-91-8; **14b**, 16240-92-9; **17a**, 16240-93-0; **17b**, 16214-87-2; **18a**, 16240-77-0; **18b**, 16214-88-3; **22a**, 16240-78-1; **22b**, 16240-79-2; **24a**, 16240-80-5; **24b**, 16240-94-1; **26a**, 16240-95-2; **26b**, 16240-96-3; **29**, 16240-97-4; **31a**, 16240-98-5; **31b**, 16240-99-6; **33a**, 16214-90-7; **33b**, 16241-00-2; **35**, 16241-01-3.

Acknowledgments.—The authors wish to thank Mr. Urs Stoeckli and his associates for obtaining the analytical and instrumental data reported in this paper.

Oxidation with Metal Oxides. III. Oxidation of Diamines and Hydrazines with Manganese Dioxide

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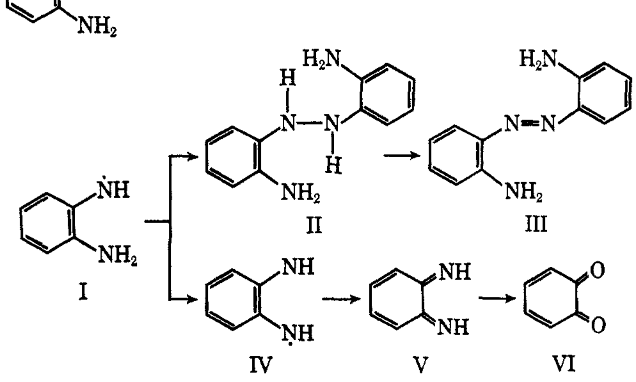
o-Phenylenediamine and *p*-phenylenediamine, on oxidation with manganese dioxide, gave the corresponding diaminoazo compounds. Under similar conditions, 2,2′-diaminobiphenyl gave dibenzopyridazine, whereas *o,o*′-diaminobiphenyl sulfide gave a linear azo compound. The oxidation of N-phenyl-*p*-phenylenediamine and N,N′-diphenyl-*p*-phenylenediamine gave N-phenyl-*p*-benzoquinone monoimine and N,N′-diphenyl-*p*-phenylenediimine, respectively. N,N′-Dibenzenesulfonyl-*p*-benzoquinone imine, benzenesulfonamide, and *p*-benzoquinone were formed from N,N′-dibenzenesulfonyl-*p*-phenylenediamine, whereas, both benzophenone and azobenzene were formed from the oxidation of benzophenone anil. Manganese dioxide oxidation of phenylhydrazine gave biphenyl and azobenzene. *p*-Nitrophenylhydrazine and 2,4,6-trichlorophenylhydrazine gave the corresponding substituted biphenyls, under similar conditions. Oxidation of N-aminopiperidine, N-aminohomopiperidine, N-aminomorpholine, and N,N-diphenylhydrazine gave the corresponding tetrazenes, whereas N,N-dibenzylhydrazine gave mainly bibenzyl.

In previous communications[2,3] we have reported the oxidation of several aldehyde and ketone phenylhydrazones, chalcone phenylhydrazones, pyrazolines, *o*-aminobenzylidine anils, and *o*-hydroxybenzylidine anils, with manganese dioxide. Chalcone phenylhydrazones, for example, give rise to pyrazoles, when oxidized with manganese dioxide in a neutral solvent like benzene. Under similar conditions, *o*-aminobenzylidine anils and *o*-hydroxybenzylidene anils give the corresponding benzimidazoles and benzoxazoles, respectively. The oxidation of aldehyde phenylhydrazones, on the other hand, give a mixture of several oxidative dimers, triazoles and biphenyl, depending on the reaction conditions. During the course of the present investigation, we have examined the oxidation of several aromatic diamines and hydrazines, employing active manganese dioxide.

The oxidation of *o*-phenylenediamine has been reported to give rise to different products, depending on the nature of the oxidizing agent and the reaction conditions. Thus, the oxidation of *o*-phenylenediamine with nickel peroxide[4] or lead tetraacetate[5] gives *cis,cis*-1,4-dicyano-1,3-butadiene, whereas the oxidation with lead peroxide[6] or silver oxide[6] gives a mixture of *o,o*′-diaminoazobenzene and 3,4-diaminophenazine. The formation of these products has been explained in terms of an *o*-quinone imine intermediate. We have examined the oxidation of *o*-phenylenediamine, employing manganese dioxide. When the reaction was carried out in benzene at room temperature, we were able to isolate a 13% yield of *o,o*′-diaminoazobenzene. No other product, including 1,4-dicyano-1,3-butadiene could be obtained from this run. The same reaction has been tried both in refluxing benzene, and also in the absence of any solvent by heating the mixture to around 110°, with a view to detecting the presence of other products which might be formed under these conditions. Considerable amount of ammonia was evolved during these reactions and, from both cases, only *o,o*′-diaminoazobenzene was isolated, but the yields were somewhat higher, compared with that of the room temperature reaction. In a typical run, involving the reaction of *o*-phenylenediamine with manganese dioxide in refluxing benzene, the amount of ammonia liberated was found to be around 21%. A probable mechanism for the formation of *o,o*′-diminoazobenzene is indicated in Scheme I. In this scheme, we assume that manganese dioxide effects the cleavage of one of the N–H bond of the amine

SCHEME I



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[1] To whom enquiries should be addressed.

[2] I. Bhatnagar and M. V. George, *J. Org. Chem.*, **32**, 2252 (1967).

[3] I. Bhatnagar and M. V. George, *Tetrahedron*, **24**, 1293 (1968).

[4] K. Nakagawa, H. Onoue, *Tetrahedron Lett.*, **20**, 1433 (1965).

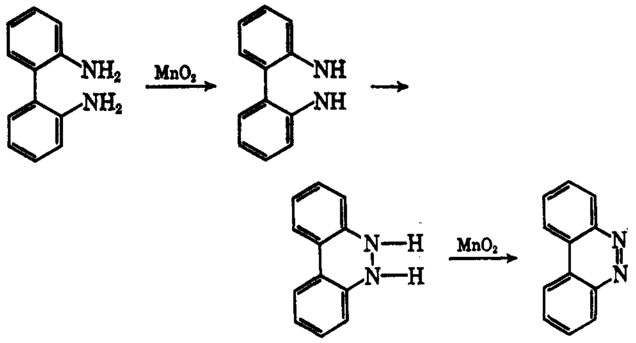
[5] K. Nakagawa and H. Onoue, *Chem. Commun.*, **16**, 396 (1965).

[6] R. Wilstätter and A. Pfannenstiel, *Ber.*, **38**, 2348 (1905).

to generate the radical I which dimerizes to the hydrazine II. Oxidation of II to *o,o'*-diaminoazobenzene (III) will be quite facile in presence of manganese dioxide. The formation of III from *o*-phenylenediamine is analogous to the formation of azobenzene from aniline.[7] However, the evolution of ammonia and the poor yield of III strongly suggests that other pathways are also important for this oxidation. One such possibility is the conversion of the intermediate radical I into the diradical IV which can isomerize to *o*-quinone diimine (V). The quinone diimine V will suffer ready hydrolysis under the experimental conditions, giving rise to *o*-quinone (VI) which is easily polymerized. The actual isolation of a small amount of *p*-benzoquinone in the oxidation of *p*-phenylenediamine supports the postulated mechanism. When *p*-phenylenediamine was oxidized with active manganese dioxide in benzene at room temperature, a 30% yield of *p,p'*-diaminoazobenzene was formed. In addition, a small quantity of benzoquinone (2%) and polymeric material could be isolated. It was not possible to detect the presence of any *p*-benzoquinone diimine; one would expect this compound to be easily hydrolyzed [8,9] during the reaction. With a view to isolating stable quinone imine intermediates from these reactions, we have examined the oxidation of both N-phenyl-*p*-phenylenediamine (VII) and N,N'-diphenyl-*p*-phenylenediamine (VIII). Treatment of VII with manganese dioxide gave a 70% yield of N-phenyl-*p*-benzoquinone monoimine (IX), whereas VIII under the same conditions gave a 91% yield of N,N'-diphenyl-*p*-benzoquinone imine (X). Ammonia gas was evolved during the oxidation of VII, but not in the reaction of VIII. The isolation of such quinone imines as IX and X strongly supports the mechanism (Scheme I) that has been suggested for amine oxidation.

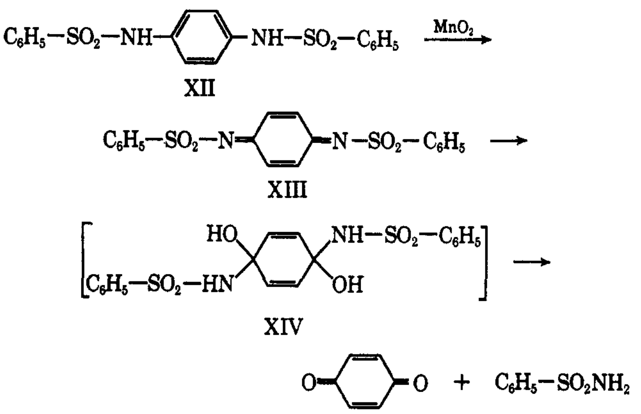
Lithium aluminium hydride reduction of 2,2'-dinitrobiphenyl is reported to give rise to dibenzopyridazine.[10] Under similar conditions, 2,2'-dinitrobiphenyl ether and 2,2'-dinitrobiphenyl sulfide give the corresponding cyclic, seven-membered azo compounds.[11] We have examined the reactions of 2,2'-diaminobiphenyl and 2,2'-diaminobiphenyl sulfide with manganese dioxide, with a view to finding out whether these reactions would lead to the formation of the corresponding cyclic azo compounds. The oxidation of 2,2'-diaminobiphenyl with manganese dioxide gave a 55% yield of dibenzopyridazine and a probable pathway is indicated in Scheme II. 2,2'-Diaminobiphenyl sulfide, on the other hand, gave a 20% yield of 2,2'-bis(*o*-aminothiophenoxy)azobenzene (XI) and none of the cyclic azo compound.

SCHEME II



N,N'-Dibenzenesulfonyl-*p*-phenylenediamine (XII) is oxidized to *p*-benzoquinonebenzenesulfonimide by reagents like silver oxide, sodium chromate, and lead tetraacetate.[9] In the present investigation, we have studied the oxidation of XII using active manganese dioxide. When this oxidation was carried out at room temperature in acetone medium, a 32% yield of N,N'-dibenzenesulfonyl-*p*-benzoquinone imine (XIII) was isolated. The same reaction, in refluxing benzene gave a 37% yield of benzenesulfonamide and a small quantity of benzoquinone. It is apparent that both benzenesulfonamide and benzoquinone are formed from XIII, the initial oxidation product of XII. However, a simple mode of hydrolysis for the conversion of XIII into benzenesulfonamide and benzoquinone is ruled out since XIII is reported to be quite resistant to hydrolysis, both under acid and basic conditions.[9] A more probable pathway would be the hydroxylation of XIII by manganese dioxide (which invariably contains some water) to give the intermediate XIV which is then cleaved to the products as shown in Scheme III. The formation of similar hydroxylated intermediates have been postulated in the oxidation of substituted amines using manganese dioxide.[12]

SCHEME III



If we assume that the oxidation of XII is proceeding through the hydroxylated intermediate XIV, then one would expect that anils will also be oxidized by manganese dioxide by a similar route. In this connection, we have examined the oxidation of benzophenone anil with manganese dioxide which led to benzophenone (50%) and azobenzene (55%). It is pertinent to observe that benzophenone anil is not hydrolyzed by refluxing with water for few hours. Also, the oxidation of benzophenone anil could not be achieved by treatment with dry manganese dioxide from which all water has been removed. We therefore assume that the active manganese dioxide containing small amounts of moisture is actually responsible for this type of oxidation. The reported oxidation of azines to give alde-

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[7] (a) O. Wheeler and D. Gonzalez, *Tetrahedron*, **20**, 189 (1964); (b) O. Wheeler, *Chem. Ind.* (London), 1769 (1965).

[8] R. Willstätter, *Ber.*, **37**, 1499 (1904).

[9] R. Adams and A. S. Nagarkatti, *J. Amer. Chem. Soc.*, **72**, 4601 (1950).

[10] G. M. Badger and J. H. Seidler, *J. Chem. Soc.*, 3207 (1951).

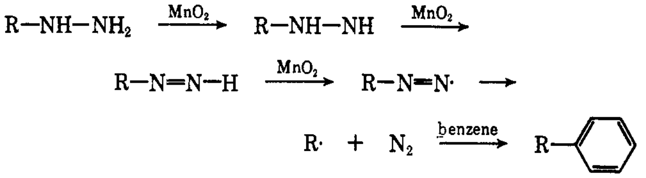
[11] N. L. Allinger and G. A. Youngdales, *J. Amer. Chem. Soc.*, **84**, 1020 (1962).

[12] H. B. Henbest and A. Thomas, *J. Chem. Soc.*, 3032 (1957).

hydes and ketones[13] may also be proceeding through a similar mechanism.

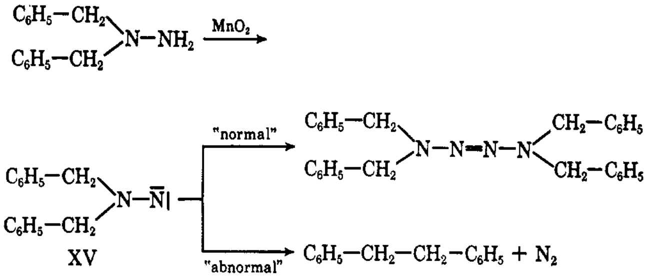
In continuation of our studies, we have examined the reaction of different substituted hydrazines with manganese dioxide. The oxidation of phenylhydrazine, for example, gave a 26% yield of biphenyl, when the reaction was carried out in benzene. Similarly, the oxidation of *p*-nitrophenylhydrazine and 2,4,6-trichlorophenylhydrazine gave *p*-nitrobiphenyl (50%) and 2,4,6-trichlorobiphenyl (39%), respectively. A probable route for this oxidation involves the stepwise removal of hydrogen atoms from the hydrazines by manganese dioxide giving rise to radical intermediates which finally yield aryl radicals by the loss of nitrogen. These aryl radicals can combine with the solvent to give biphenyls (Scheme IV). The formation of biphenyls in the oxidation of phenylhydrazines have also been observed earlier, when either silver oxide or mercuric oxide have been employed.[14]

SCHEME IV



Several 1,1-disubstituted hydrazines have been oxidized with different oxidizing agents such as potassium permanganate, bromine, ferric chloride, quinone, and mercuric oxide[15] to give tetrazenes as major products. Report has also been made of the anomalous type of oxidation of 1,1-disubstituted hydrazines giving rise to symmetrical, substituted bibenzyls and nitrogen.[16] A detailed study of the oxidation of 1,1-disubstituted hydrazine derivatives has been done by several workers.[17] They have observed that if the oxidation is carried out under conditions in which the hydrazine is present in relatively high concentration, *e.g.*, by rapid addition of hydrazine to the oxidizing agent or by the rapid addition of the solid oxidizing agent to the solution of hydrazine, the aminoimido intermediate formed initially dimerizes to the tetrazene in the so-called "normal" manner. If the nitrogen atom in the aminoimido intermediate is lost to yield a stabilized radical, then an alternative "abnormal" pathway is possible, giving rise to fragmentation and recombination of products. For example, the oxidation of 1,1-dibenzylhydrazine gives rise to mainly bibenzyl and nitrogen and an intramolecular process has been suggested as shown in Scheme V. The formation of the tetrazene is explained in terms of the dimerization of the aminoimido intermediate XV or by its reaction with another molecule of unchanged hydrazine to give a tetrazane which is subsequently oxidized to tetrazene.[18] In the present study, the oxidation of several disubstituted hydrazines have been tried using manganese dioxide. Thus, the oxidation of N-aminopiperidine in benzene at room temperature gave a 76% yield of 1,4-bispentamethyleneletetrazene (XVI). Similarly, N-aminohomopiperidine and N-aminomorpholine gave the corresponding tetrazenes XVII and XVIII in 86 and 80% yields, respectively. It is assumed on the basis of analogy, that the oxidation of these hydrazines is proceeding through the aminoimido intermediates which dimerize to the tetrazenes. The loss of nitrogen is not facile in view of the unstable nature of the resultant radicals.

SCHEME V



The oxidation of N,N-diphenylhydrazine with manganese dioxide gave a 76% yield of 1,1,4,4-tetraphenyltetrazene and a small quantity of biphenyl. N,N-Dibenzylhydrazine on the other hand, when oxidized at room temperature in chloroform solution gave a 10% yield of 1,1,4,4-tetrabenzyltetrazene and a 20% yield of bibenzyl. When the same reaction was carried out in refluxing ethanol and with the gradual addition of manganese dioxide to the hydrazine, a 40% yield of bibenzyl was isolated. The formation of bibenzyl could arise from an intramolecular loss of nitrogen from the aminoimido intermediate XV as postulated earlier.

Experimental Section

All melting points are uncorrected and were determined in a Thomas-Hoover melting point apparatus. Infrared spectra were determined on a Perkin-Elmer Infracord spectrometer and uv spectra were obtained on a Cary 14-R spectrophotometer.

Starting Materials.—Active manganese dioxide was prepared by using manganese sulfate dihydrate (280 g) and potassium permanganate (320 g) according to reported procedure.[19] N,N-Diphenyl hydrazine[20] and N-aminomorpholine[21] were prepared by the reduction of N-nitrosodiphenylamine and N-nitrosomorpholine, respectively, using zinc and acetic acid. Dibenzylhydrazine[22] was prepared by the lithium aluminum hydride reduction of N-nitrosodibenzylhydrazine, whereas N-aminopiperidine[23] was prepared by reducing N-nitrosopiperidine employing aluminum amalgam in absolute ethanol. 2,2′-Diaminobiphenyl[24] was prepared by the reduction of the corre-

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[13] G. Mair and U. Heep, *Angew. Chem. Intern. Ed. Engl.*, **4**, 956 (1965).

[14] L. Hardie and R. H. Thomas, *J. Chem. Soc.*, 2512 (1957).

[15] For some of these oxidations, see, (a) E. Fischer, *Ann.*, **190**, 67 (1877); (b) E. Fischer, *ibid.*, **199**, 281 (1879); (c) E. Renouf, *Ber.*, **13**, 2169 (1880); (d) T. Curtius and H. Franzer, *ibid.*, **34**, 552 (1901); H. Wieland and H. Fressel, *Ann.*, **392**, 133 (1912).

[16] See (a) M. Busch and B. Weiss, *Ber.*, **33**, 2701 (1900); (b) H. Duval, *Bull. Soc. Chim. Fr.*, **7**, 728 (1910); (c) J. Kenner and J. Wilson, *J. Chem. Soc.*, 1108 (1927).

[17] For some of these studies, see (a) D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Amer. Chem. Soc.*, **85**, 194 (1963); (b) C. G. Overberger, *Rec. Chem. Progr.*, **21**, 21 (1960); (c) C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **27**, 417 (1962); (d) C. G. Overberger and B. S. Marks, *J. Amer. Chem. Soc.*, **77**, 4097, 4104 (1955); (e) C. G. Overberger, L. C. Palmer, B. S. Marks, and N. R. Byrd, *ibid.*, **77**, 4100 (1955).

[18] See, for example (a) R. L. Hinnman and K. L. Hamm, *ibid.*, **81**, 3294 (1959); (b) C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **21**, 2423 (1962); (c) C. G. Overberger, J. Kesselin, and P. T. Huang, *J. Amer. Chem. Soc.*, **81**, 3779 (1959); (d) C. G. Overberger, J. G. Lombardino and R. G. Hiske, *J. Amer. Chem. Soc.*, **80**, 6430 (1958); (e) ref 16b–d.

[19] E. F. Pratt and T. McGovern, *J. Org. Chem.*, **29**, 1540 (1964).

[20] E. Fischer, *Ann.*, **190**, 175 (1877).

[21] I. V. Podgornaya and I. Ya. Postovskii, *Zh. Obshch. Khim.*, **34** (1), 33 (1964); *Chem. Abstr.*, **60**, 10676 (1964).

[22] C. G. Overgerger, *J. Amer. Chem. Soc.*, **77**, 4100 (1955).

[23] H. G. Kazmirowski and H. Goldhahn, East German Patent, 23,001 (1962); *Chem. Abstr.*, **58**, 6746 (1963).

[24] P. A. S. Smith and B. B. Brown, *J. Amer. Chem. Soc.*, **75**, 6335 (1953).

sponding dinitro compound using Raney nickel as catalyst. 2,2′-Diaminobiphenylsulfide,[11] on the other hand, was prepared by the reduction of 2,2′-dinitrobiphenylsulfide using zinc and calcium chloride in ethanol. *p*-Benzoquinonesulfonimide[9] was prepared by lead tetraacetate oxidation of *p*-phenylenedibenzenesulfonamide. All other starting materials were obtained commercially.

Oxidation of *o*-Phenylenediamine.—A mixture of *o*-phenylenediamine (2 g, 0.009 mol) and manganese dioxide (10 g) was refluxed in dry benzene (150 ml) for 4 hr. Ammonia gas was evolved during the course of the reaction which was identified by the usual qualitative tests. Removal of the unchanged manganese dioxide and the solvent gave a residue which was chromatographed on alumina. Elution with benzene gave 0.7 g (35%) of 2,2′-diaminoazobenzene (III) which melted at 134°, after recrystallization from a mixture (1:1) of benzene and petroleum ether (bp 60–80°). The identity of this compound was confirmed by a mixture melting point with an authentic sample,[6] and also by comparison of the ir spectra. The ultraviolet spectrum of this compound in methanol showed the following absorption maxima: 245 mμ (ϵ 30,750), 312 (12,000), and 442 (11,500). Further elution of the alumina column with a mixture of benzene and ethanol gave a dark red polymeric material, which on treatment with dilute hydrochloric acid, followed by treatment with sodium hydroxide, gave a further yield (0.3 g, 15%) of 2,2′-diaminoazobenzene (III). No other identifiable product could be obtained from this material.

In a repeat experiment, a solution of 2 g (0.009 mol) of *o*-phenylenediamine in 250 ml of benzene was gradually added to a stirred suspension of manganese dioxide (10 g) in benzene (200 ml), over a period of 12 hr. Removal of the solvent and unchanged manganese dioxide gave a dark red polymeric material which showed a C=O band absorption at 1675 cm^{-1}. Work-up of this mixture, employing chromatography over alumina, gave 0.25 g (13%) of 2,2′-diaminoazobenzene, mmp 134°.

In a repeat run, employing the same quantities of starting materials, but carrying out the reaction in refluxing benzene, a 21% yield of ammonia was evolved, as measured by absorption in a standard solution of hydrochloric acid.

In a different run, 2 g (0.009 mol) of *o*-phenylenediamine and manganese dioxide (10 g) were heated at *ca.* 110° in the absence of any solvent. Vigorous evolution of ammonia was observed during the reaction. Work-up of the mixture by treatment with benzene and chromatography of the benzene extract over alumina gave 0.45 g (22%) of 2,2′-diaminoazobenzene, mmp 134°.

Oxidation of *p*-Phenylenediamine.—A mixture of *p*-phenylenediamine (2 g, 0.009 mol) and manganese dioxide (10 g) in dry benzene (175 ml) was stirred for 6 hr. Evolution of ammonia could be detected during the reaction. Removal of the solvent and unchanged manganese dioxide gave an impure product, which on fractional crystallization from a mixture (1:1) of benzene and ethanol gave 0.8 g of impure *p,p*′-diaminoazobenzene, mp 246–250°. Chromatography over alumina, employing a mixture (1:1) of benzene and ethyl acetate gave a pure sample (0.6 g, 30%) of *p,p*′-diaminoazobenzene, mmp 250–251°. The identity of this compound was further confirmed by a comparison of its ir and uv spectra with those of an authentic sample.[25,26]

From the mother liquor 0.04 g (2%) of *p*-benzoquinone was isolated which melted at 114–115° (mixture melting point). Its ir and uv spectra were identical with those of an authentic sample.

In a repeat run, employing the same quantities of starting materials, but carrying out the reaction in refluxing benzene, a 25% (0.5 g) yield of *p,p*′-diaminoazobenzene was obtained. Vigorous evolution of ammonia was observed during the reaction. No other product could be isolated from this run.

Oxidation of N-Phenyl-*p*-phenylenediamine.—A mixture of N-phenyl-*p*-phenylenediamine (VII) (2 g, 0.01 mol) and manganese dioxide (8 g) was refluxed in benzene for 4 hr. Unchanged manganese dioxide was removed and the organic matter was chromatographed on alumina to give 1.4 g (70%) of N-phenyl-*p*-benzoquinone monoimine (IX): mp 99–100° after recrystallization from benzene; uv spectrum (methanol), λ_{max} 264 mμ (ϵ 18,000), 288 (16,000) and 450 (3100); ir spectrum (KBr), ν_{max} 1660 cm^{-1} (C=O).

The melting point and uv data are in agreement with those reported for this compound in the literature.[27,28]

Anal. Calcd for $C_{12}H_9NO$: C, 78.8; H, 4.9; N, 7.6. Found: C, 79.3; H, 5.2; N, 7.6.

Oxidation of N,N′-Diphenyl-*p*-phenylenediamine.—Treatment of a mixture of N,N′-diphenyl-*p*-phenylenediamine (0.5 g, 0.0018 mol) with manganese dioxide (2.5 g) in refluxing benzene (50 ml) for 3 hr and work-up in the usual manner, employing chromatography on alumina, gave 0.45 g (91%) of N,N′-diphenyl-*p*-benzoquinone imine (X), mp 187°.[29]

Oxidation of 2,2′-Diaminobiphenyl.—A mixture of 2,2′-diaminobiphenyl (2 g, 0.01 mol) and manganese dioxide (16 g) was refluxed in benzene (125 ml) for 4 hr. Removal of the solvent and unchanged manganese dioxide gave a red-brown viscous mass, which was chromatographed on alumina. Elution with a mixture (3:1) of benzene and petroleum ether (bp 60–80°) gave 0.5 g of unchanged 2,2′-diaminobiphenyl, mmp 78°. Further elution of the column with benzene gave 0.8 g (55%) of dibenzopyridazine, which melted at 157° after recrystallization from benzene. The identity of this compound was established by a mixture melting point determination and also by a comparison of its ir spectrum with that of an authentic sample.[10]

Oxidation of 2,2′-Diaminobiphenyl Sulfide.—Treatment of a mixture of 2,2′-diaminobiphenyl sulfide (1 g, 0.0047 mol) and manganese dioxide (5 g) in refluxing benzene (75 ml) for 6 hr and work-up in the usual manner gave a deep red, viscous material. Chromatography over alumina, employing benzene gave 0.2 g (20%) of *o,o*′-bis(*o*-aminothiophenoxy)azobenzene (XI): mp 202° dec after recrystallization from benzene; uv spectrum (methanol), λ_{max} 240 mμ (ϵ 47,000) and 315 (21,000) and 420 (12,500); ir spectrum (KBr), ν_{max} 3480, 3400 cm^{-1} (NH_2).

Anal. Calcd for $C_{24}H_{20}N_4S_2$: C, 67.3; H, 4.6; N, 13.1. Found: C, 67.79; H, 4.6; N, 12.7.

Oxidation of N,N′-Dibenzenesulfonyl-*p*-phenylenediamine (XII).—A solution of XII (2 g, 0.005 mol) in dry acetone (175 ml) was stirred with manganese dioxide (12 g) for 5 hr. Removal of the solvent and excess of manganese dioxide gave a greenish yellow viscous mass which showed the presence of a C=O absorption band at 1675 cm^{-1} in the infrared spectrum. Extraction with hot benzene and fractional crystallization from the same solvent gave 0.6 g (32%) of N,N′-dibenzenesulfonyl-*p*-benzoquinone imine, mmp 178°.

In a repeat experiment, 2 g (0.005 mol) of XII and 16 g of manganese dioxide were refluxed in 200 ml of benzene for 6 hr. Work-up of the mixture as in the previous case, gave 0.6 g (37%) of benzenesulfonamide, mmp 151°, and 0.3 g (50%) of benzoquinone, identified through its infrared spectrum.

Oxidation of N,N′-Dibenzenesulfonyl-*p*-benzoquinone Imine (XIII).—Refluxing a mixture of XIII (0.5 g, 0.005 mol) and manganese dioxide (5 g) in dry benzene (100 ml) for 4 hr and work-up in the usual manner gave 0.1 g (25%) of benzenesulfonamide, mmp 151°. A brown polymeric material which showed a sharp carbonyl peak at 1675 cm^{-1} was isolated from the mother liquor.

Oxidation of Benzophenone Anil.—A mixture of benzophenone anil (1 g, 0.004 mol) and active manganese dioxide (30 g) was refluxed in benzene (150 ml) for 8 hr. Water formed during the reaction was collected in a Dean-Stark water separator. Removal of the unchanged manganese dioxide and solvent gave an orange red solid, which was chromatographed over alumina. Elution with petroleum ether (bp 60–80°) gave 0.19 g (55%) of azobenzene, mmp 65°. Further elution with benzene gave 0.3 g of unchanged benzophenone anil, mmp 113°. Elution with ethanol gave a product which on treatment with 2,4-dinitrophenylhydrazine gave 0.71 g of benzophenone 2,4-dinitrophenylhydrazone, mmp 230°.

In a second experiment, a mixture of benzophenone anil (1 g, 0.004 mol) and dry manganese dioxide[30] (30 g) was refluxed in dry benzene (200 ml) for 6 hr. Work-up of the mixture gave 0.9 g (90%) of unchanged benzophenone anil, mmp 113°.

Oxidation of Phenylhydrazines.—In a typical run, 2 g of the hydrazine and 5 g of active manganese dioxide was stirred in refluxing benzene (50 ml) for 4 hr. After removal of the inorganic

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(25) O. N. Witt and E. Koptshni, *Ber.* **45**, 1136 (1912).

(26) W. R. Brode and I. L. Seldini, *J. Amer. Chem. Soc.*, **77**, 2762 (1955).

(27) R. Wilstätter and C. L. Moore, *Ber.*, **40**, 668 (1907).

(28) C. J. Podersen, *J. Amer. Chem. Soc.*, **79**, 5014 (1957).

(29) W. L. Semon, U. S. Patent, 2,118,826 (1938); *Chem. Abstr.*, **32**, 5411 (1938).

(30) Dry manganese dioxide was prepared by refluxing the hydrated form of active manganese dioxide in toluene for 12 hr and removing the water in a Dean–Stark separator.

material and the solvent, the product formed in each case was recrystallized from suitable solvents.

Oxidation of phenylhydrazine (2 g, 0.019 mol) gave a mixture of biphenyl (0.75 g, 26%), mp 70°, and azobenzene (40 mg, 3%), mp 65°.

p-Nitrophenylhydrazine (2 g, 0.013 mol) gave *p*-nitrobiphenyl (1.3 g, 50%), mp 113°, after recrystallization from ethanol.

2,4,6-Trichlorophenylhydrazine (2 g, 0.009 mol) on oxidation gave 2,4,6-trichlorobiphenyl (0.9 g, 39%), mmp 62°[31] after recrystallization from dilute acetic acid.

Oxidation of Hydrazines.—In a typical experiment a mixture of the hydrazine and manganese dioxide (1:2.5) in 75 ml of dry benzene was stirred at room temperature for 1 hr. The products were purified by chromatography over alumina using benzene and by recrystallization from suitable solvents.

N-Aminopiperidine (2.5 g, 0.025 mol) gave 1.9 g (76%) of 1,4-bispentamethylenetetrazene (XVI): mp 44° after recrystallization from dilute ethanol; uv spectrum of XVI (cyclohexane), λ_{max} 288 mμ (ϵ, 11,630); ir spectrum (KBr), ν_{max} 2930, 2800, 1460, 1442, 1365, 1320, 1290, 1265, 1160, 1125, 1082, 1066, 1030, 1025, 986, 970, 925, 868, 770, and 695 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}N_4$: C, 61.2; H, 10.2; N, 28.5. Found: C, 60.8; H, 10.6; N, 28.4.

Oxidation of N-aminohomopiperidine (3 g, 0.026 mol) gave 2.5 g (86%) of 1,4-bishexamethylenetetrazene (XVII), which melted at 62–63° after recrystallization from ethanol: uv spectrum of XVII (cyclohexane), λ_{max} 290 mμ (ϵ 12,610); ir spectrum (KBr), ν_{max} 2930, 2850, 1460, 1442, 1365, 1280, 1240, 1200, 1120, 1110, 1070, 1060, 1005, 986, 965, 912, 885, 865, 820, and 715 cm^{-1}.

Anal. Calcd for $C_{12}H_{24}N_4$: C, 64.28; H, 10.7; N, 25.0. Found: C, 64.06; H, 10.30; N, 25.14.

N-Aminomorpholine (2 g, 0.019 mol) of oxidation gave 1.6 g (80%) of 1,4-bis(3-oxapentamethylenetetrazene (XVIII): mp 157° after recrystallization from ethanol: uv spectrum of XVIII (cyclohexane), λ_{max} 284 mμ (ϵ 10,150); ir spectrum (KBr), ν_{max} 3000, 2910, 1460, 1400, 1380, 1275, 1220, 1190, 1140, 1120, 1100, 1080, 1020, 990, 935, 870, and 779 cm^{-1}.

Anal. Calcd for $C_8H_{16}O_2N_4$: C, 48.0; H, 8.0; N, 28.0. Found: C, 48.04; H, 8.2; N, 28.09.

N,N-Diphenylhydrazine (0.6 g, 0.003 mol) gave 0.45 g (76%) of 1,1,4,4-tetraphenyltetrazene: mp 123° dec (lit.[32] mp 123°); uv spectrum (cyclohexane), λ_{max} 285 mμ (ϵ 13,900), 304 (15,140) and 360 (14,860); ir spectrum (KBr), ν_{max} 3010, 1590, 1490, 1450, 1345, 1325, 1295, 1090, 1280, 1010, 1100, 1065, 1020, 995, 938, and 890 cm^{-1}.

Anal. Calcd for $C_{24}H_{20}N_4$: C, 79.1; H, 5.9; N, 15.3. Found: C, 79.29; H, 5.6; N, 15.0.

Oxidation of N,N-Dibenzylhydrazine.—N,N-Dibenzylhydrazine (0.5 g, 0.0024 mol) was treated with manganese dioxide (2.2 g) in chloroform (50 ml) at room temperature for 1 hr. Removal of the unchanged manganese dioxide gave a product which was chromatographed over alumina. Elution with petroleum ether (bp 60–80°) and recrystallization from ether gave 15 mg (10%) of 1,1,4,4-tetrabenzyltetrazene, mmp 99°. Further elution of the alumina column with a mixture of benzene and petroleum ether gave 85 mg (20%) of bibenzyl, mmp 52°.

In a second experiment, a mixture (0.5 g, 0.0024 mol) of N,N-dibenzylhydrazine and 1.8 g of manganese dioxide was refluxed in absolute ethanol (70 ml) for 1 hr. Work-up of the mixture in the usual manner gave 0.21 g (49%) of bibenzyl, mmp 52°. None of the tetrazene could be isolated from this run.

Registry No.—Manganese dioxide, 1313-13-9; *o*-phenylenediamine, 95-54-5; *p*-phenylenediamine, 106-50-3; N-phenyl-*p*-phenylenediamine, 101-54-2; N,N'-diphenyl-*p*-phenylenediamine, 74-31-7; 2,2'-diaminobiphenyl, 1454-80-4; 2,2'-diaminobiphenyl sulfide, 5873-51-8; XI, 16504-18-0; XII, 16504-19-1; XIII, 1050-82-4; benzophenone anil, 574-45-8; phenylhydrazine, 100-63-0; *p*-nitrophenylhydrazine, 100-16-3; 2,4,6-trichlorophenylhydrazine, 5329-12-4; N-aminopiperidine, 2213-43-6; XVI, 2081-14-3; N-aminohomopiperidine, 5906-35-4; XVII, 16504-24-8; N-aminomorpholine, 4319-49-7; XVIII, 16504-26-0; N,N-diphenylhydrazine, 530-50-7; 1,1,4,4-tetraphenyltetrazene, 16504-27-1; N,N-dibenzylamine, 5802-60-8.

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Some Aspects of Vinyl Azide Chemistry. Thermally Induced Reactions

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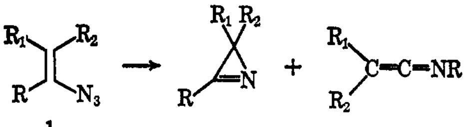
A comparison of the chemistry of terminal and internal vinyl azides is presented. On decomposition, internal vinyl azides formed azirines while terminal vinyl azides did not. The nature of the products from the latter azides depended upon the substituents on the carbon β to the azido group. In solvents other than ethanol, 9-(azidomethylene)fluorene gave 9-(N,N-fluorenylideneaminomethylene)fluorene, while 2-azido-1,1-diphenylethylene and 1-azido-2-phenylpropene formed indole derivatives. The latter two compounds when decomposed in ethanol produced dihydropyrazines at the expense of indole formation. Possible mechanisms for these reactions are considered. In addition, the geminal vinyl diazide, 9-diazidomethylenefluorene, was found to form 9-azido-9-fluorenecarbonitrile while the vicinal diazide, 2,3-diazido(N-phenyl)maleimide, gave N,N-bis(cyanocarbonyl)aniline.

The decomposition of vinyl azides has been the subject of several recent investigations.[1] The majority of these studies has dealt exclusively with internal[2] vinyl azides 1. It was found that on photolysis or thermolysis this type of azide consistently lost nitrogen and



1 2 3

rearranged to azirines 2 in good yield usually accompanied by small amounts of iminoketenes 3.[1a–c]

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[2] By internal, we mean vinyl azides in which a substituent other than hydrogen is bonded to the carbon bearing the azide group. When a hydrogen atom is bonded to the azide bearing carbon, we will refer to the compound as a terminal vinyl azide.