Anal. Calcd for $C_{15}H_{14}ClN_3O$: N, 14.6. Found: N, 14.4.

The above salt (0.8 g) was heated at 190-200° for 5 min when the original solid, after melting with effervescence, resolidified. 3,4-Diphenyl-*s*-triazolin-5-one crystallized from methanol as colorless needles: 0.3 g, mp 258-260° (lit.[12] mp 254-256°, 260°), $\lambda_{max}^{CH_3OH}$ 256 mμ (log ε 3.96).

Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.9; H, 4.7; N, 17.7. Found: C, 70.6; H, 4.7; N, 17.95.

Registry No.—$C_{15}H_{14}ClN_3S$, 2254-71-9; picrate of $C_{15}H_{14}ClN_3S$, 13136-10-2; $C_{16}H_{16}ClN_3S$, 13136-11-3; $C_{10}H_{12}ClN_3S$, 13136-12-4; $C_{11}H_{14}ClN_3S$, 13136-13-5; $C_{20}H_{17}BrN_4$, 13136-14-6; $C_{15}H_{15}BrN_4$, 13127-53-2; $C_{15}H_{14}INS$, 13136-15-7; $C_6H_{12}IN_3S$, 2254-72-0; N-amino-N,N′-diphenylbenzamidine, 13136-17-9; N-phenylbenzamide phenylhydrazone, 13136-18-0; N-amino-N-methyl-N′-phenylbenzamidine-*p*-nitrobenzylidene derivative, 13136-19-1; N-amino-N-methyl-N′-phenylbenzamidine hydrobromide, 13136-20-4; 1-acetyl-4-methyl-1-phenylsemicarbazide, 13136-21-5; 1-benzoyl-4-methyl-1-phenylsemicarbazide, 13136-22-6; 1-acetyl-1,4-dimethylsemicarbazide, 13136-23-7; 1-acetyl-1-methyl-4-phenylsemicarbazide, 5790-59-0; 1-benzyl-1,4-dimethylsemicarbazide, 13136-25-9; 1-benzyl-1-methyl-4-phenylsemicarbazide, 13136-26-0; 1-acetyl-1-methyl-4-phenylthiosemicarbazide, 13136-27-1; 1-benzoyl-1,4-dimethylthiosemicarbazide, 13136-28-2; 1-benzoyl-1-methyl-4-phenylthiosemicarbazide, 13136-29-3-1,4-di(*p*-nitrophenyl)thiosemicarbazide, 13136-30-6; 1-benzoyl-2,2-diacetyl-1-phenylhydrazine, 13136-31-7; N-amino-N-methyl-N′-phenylbenzamidine, 13136-32-8; 1,4-diphenyl-3-methyl-*s*-triazoline-5-thione, 13136-33-9; 1-acetyl-1,4-diphenylthiosemicarbazide, 13136-34-0; 1,4-diphenyl-3-methyl-5-methylthio-*s*-triazolium iodide, 13136-35-1; 1,4-diphenyl-3-methyl-5-methylthio-*s*-triazolium chloride, 13136-36-2; biacetyl (1-acetyl-1-methyl)hydrazone, 13136-37-3; biacetyl (1-acetyl-1-methyl)osazone, 13136-38-4; 3,4-diphenyl-2-methyl-*s*-triazol-5-onium chloride, 13136-39-5; 3,4-diphenyl-*s*-triazolin-5-one, 2039-00-1; 1-acetyl-1,4-dimethylthiosemicarbazide, 13136-41-9.

Oxidation of Phenylhydrazones with Manganese Dioxide

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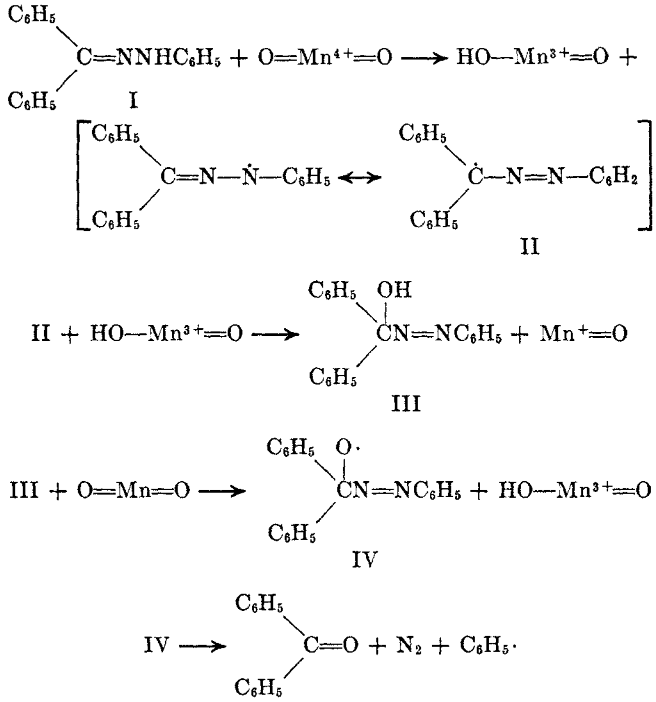
Received January 18, 1967

Benzophenone phenylhydrazone, acetophenone phenylhydrazone, and *p*-bromoacetophenone phenylhydrazone, when oxidized with manganese dioxide, give the corresponding ketones and biphenyl. Aldehyde phenylhydrazones, on the other hand, give a mixture of oxidative dimers, triazoles, and biphenyl, depending on the reaction conditions. Oxidation of benzil osazone gives 2,4,5-triphenyl-1,2,3-triazole, whereas biacetyl and glyoxal osazones give only azoalkanes.

Manganese dioxide has been employed in the oxidation of a variety of organic compounds.[2] Quite recently, the oxidation of several organic substrates like phenylcarbinols,[3] diarylmethanes,[4] N-methylanilines,[5] and of N-benzylanilines,[6] employing active manganese dioxide in neutral solvents, has been tried and a free-radical mechanism has been suggested for these reactions. Maier and Heep[7] have reported that hydrazones of aldehydes and ketones are oxidized by manganese dioxide to carbonyl compounds, and they have suggested that diazo ketones are the intermediates in these reactions.

SCHEME I



During the course of the present investigation, we have examined the oxidation of several phenylhydrazones of aldehydes and ketones, employing manganese dioxide. Thus, the oxidation of benzophenone phenylhydrazone (I) in benzene at room temperature gave a mixture of benzophenone (50%) and biphenyl (27%).[8] When the same reaction, however, was carried out in refluxing benzene, higher yields of both benzophenone (65%) and biphenyl (34%) were obtained. The formation of biphenyl suggests that free-radical intermediates are involved in this reaction and a possible route is shown in Scheme I. In this scheme, we assume that manganese dioxide effects the cleavage of the N-H bond of the phenylhydrazone, generating the pseudo-

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[1] To whom enquiries should be addressed.

[2] For a recent review, see, R. M. Evans, *Quart. Rev.* (London), **13**, 60 (1959).

[3] E. F. Pratt and J. F. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961).

[4] E. F. Pratt and S. P. Suskind, *ibid.*, **28**, 638 (1963).

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

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

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

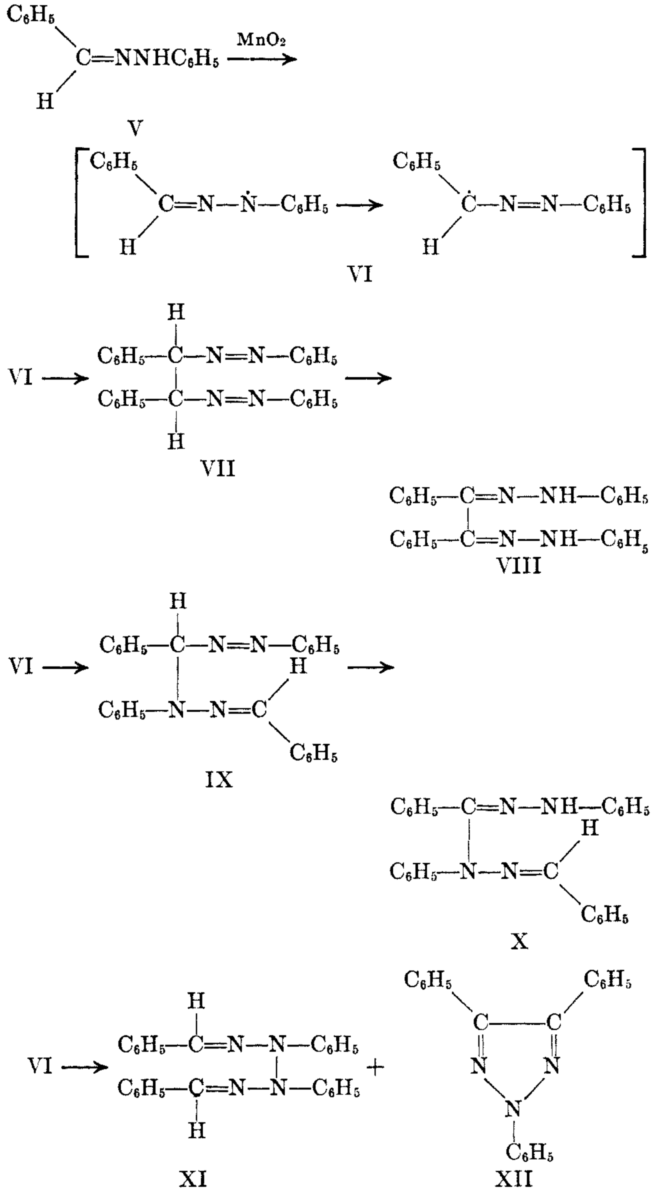
[8] The yields of biphenyl throughout are calculated on the basis that one phenyl radical from the hydrazone combines with the solvent in forming the product.

allylic radical (II). A similar hydrogen-abstraction step is postulated in the lead tetraacetate oxidation of phenylhydrazones.[9] The pseudo-allylic radical (II) can then abstract a hydroxyl group from HOMn═O, produced in the first stage of the reaction, giving the azohydroxy intermediate (III). The conversion of II to III is very similar to the conversion of diphenylmethane to diphenylcarbinol in manganese dioxide oxidation.[4] The azohydroxy compound (IV) can ultimately give rise to benzophenone and phenyl radicals. If phenyl radicals are formed, as suggested in Scheme I, one would expect these radicals to react with the solvent giving rise to substitution products. Our experiments employing different solvents like toluene and cumene justify this assumption. Thus, when benzophenone phenylhydrazone was oxidized in refluxing toluene, benzophenone (65%) and a mixture of methylbiphenyls (32%) were obtained.[10] Similarly, in refluxing cumene, a mixture of isopropylphenyls was obtained. In addition, benzophenone (58%) and a small quantity of benzophenone anil (4%) were also isolated from this run.

The oxidation of acetophenone phenylhydrazone in refluxing benzene gave a 40% yield of acetophenone and 25% of biphenyl. Similarly, *p*-bromoacetophenone phenylhydrazone gave *p*-bromoacetophenone (43%) and biphenyl (30%). However, when benzophenone 2,4-dinitrophenylhydrazone was oxidized, only a 4% yield of benzophenone could be isolated in addition to a trace of biphenyl. The poor yields in this case are to be expected, since nitro compounds are not readily oxidized by manganese dioxode.[11]

Benzaldehyde phenylhydrazone has been oxidized by several reagents like amyl nitrite,[12] mercuric oxide,[13] sodium ethoxide and iodine,[14] oxygen,[15] and ammonical silver nitrate in dimethylformamide.[16] The products from these oxidations have been characterized as substances of molecular formula $C_{26}H_{22}N_4$ and there exists considerable controversy as to the number and identity of the oxidative dimers formed.[16] In our study of the oxidation of benzaldehyde phenylhydrazone using active manganese dioxide, different products were obtained depending upon whether the reactions were carried out in benzene at room temperature or at elevated temperatures. For example, the room-temperature oxidation of benzaldehyde phenylhydrazone gave a 31% yield of 1,2-(bisphenylazo)-1,2-diphenylethane (VII) and 60% yield of N^{α},$N^{\beta'}$-diphenyl-N^{β}-benzalbenzhydrazidine (X). The identity of VII has been established beyond doubt on the basis of elemental analysis and spectral data. The infrared spectrum of this compound did not show the presence of any N-H band. Similarly, the ultraviolet spectrum of a freshly prepared solution in chloroform showed two absorption bands at 270 mμ (ϵ 22,000) and 400 mμ (ϵ 394), in agreement with the earlier reported values for this compound.[16,17]

SCHEME II



When the oxidation of benzaldehyde phenylhydrazone was carried out in refluxing benzene, four products could be isolated. These were biphenyl (17%), benzil osazone (VII, 12%), 2,4,5-triphenyl-1,2,3-triazole (XII, 44%, and 2,3-diphenyl-1,4-dibenzaltetrazene (XI, 14%). The electronic spectrum of XI showed three bands at 233, 260, and 340 mμ in intensities which indicate the presence of two phenylhydrazone chromophores. The nmr spectrum showed a multiplet centered around τ 2.8 (22 H) which includes the phenyl protons and two CH═N protons. The CH═N proton signal appears to be buried in the aromatic proton multiplet and such cases have been reported earlier.[16,18]

The formation of products like biphenyl VII, VIII, X, and XI from benzaldehyde phenylhydrazone can be explained by the path shown in Scheme II. Coupling of the pseudo-allylic radical (VI) can take place

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[9] D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Am. Chem. Soc.*, **83**, 747 (1961).

[10] For phenylation reactions using toluene, see W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1798 (1934); R. L. Dannley and B. Zaremsky, *J. Am. Chem. Soc.*, **77**, 1588 (1955).

[11] O. H. Wheeler and D. Gonzalez, *Tetrahedron*, **20**, 189 (1964).

[12] (a) E. Bamberger and W. Pemsel, *Ber.*, **36**, 57 (1903); (b) H. v. Pechmann, *ibid.*, **26**, 1045 (1893).

[13] (a) G. Minnunni, *Gazz. Chim. Ital.*, **22**, 217 (1892); (b) G. Minnunni and E. Rap, *ibid.*, **26**, 442. 446 (1896).

[14] (a) H. Ingle and H. H. Mann, *J. Chem. Soc.*, **67**, 60 (1895); (b) E. Bamberger and J. Grob, *Ber.*, **34**, 523 (1901).

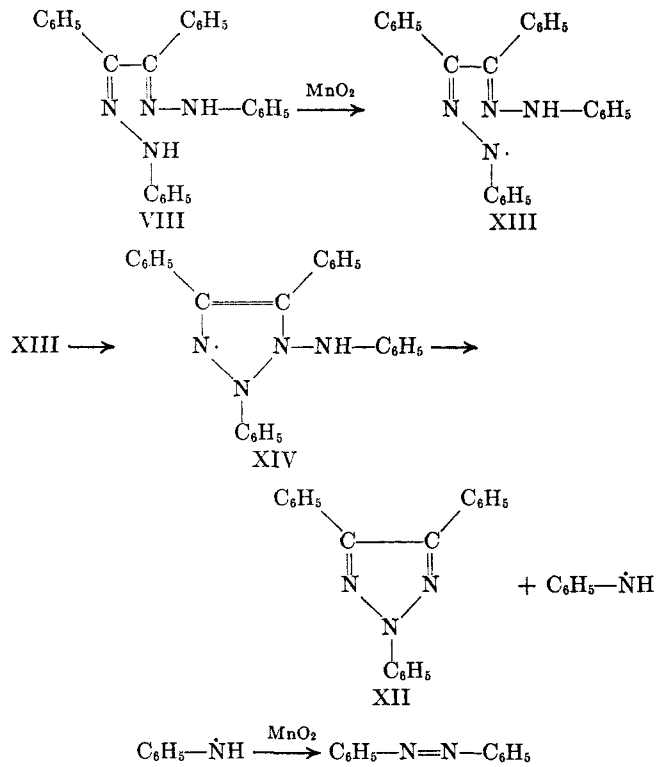
[15] (a) H. Stobbe and R. Nowak, *ibid.*, **46**, 2887 (1913); (b) M. Busch and H. Kunder, *ibid.*, **49**, 2345 (1916).

[16] T. W. Milligan and B. C. Minor, *J. Org. Chem.*, **27**, 4663 (1962).

[17] For the ultraviolet spectrum of azo compounds, see (a) A. Burawoy, *J. Chem. Soc.*, 1865 (1937); (b) ref 9.

[18] D. Y. Curtin, J. A. Gourse, W. H. Richardson, and K. L. Rinehart, Jr., *J. Org. Chem.*, **24**, 93 (1959).

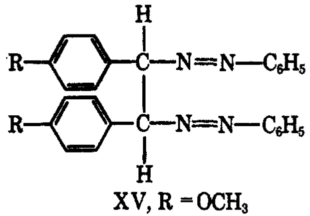
SCHEME III



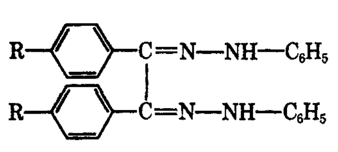
in several ways. For example, C–C coupling gives the bisphenylazoalkane (VII), a C–N coupling leads to product (IX), and an N–N coupling gives the tetrazene (XI). From our experiments involving benzaldehyde phenylhydrazone, it has not been possible to isolate any C–N coupling product corresponding to IX. However, the isolation of $N^{\alpha},N^{\beta'}$-diphenyl-N^{α}-benzalhydrazidine (X) in good yields (60%) during the room-temperature oxidation suggests that IX is formed in this reaction which rapidly isomerizes to X. Similarly, one can explain the formation of benzil osazone (VIII) as occurring owing to the isomerization of the bisazoalkane (VII). It is known that phenylazoalkanes are converted into phenylhydrazones, under the influence of acids, bases, and radical initiators.[19] We have observed that a chloroform solution of the bisazoalkane (VII) is slowly isomerized to benzil osazone (VIII) even at room temperature. The two absorption bands (277 and 400 $m\mu$) due to the azo chromophore in the electronic spectrum of a freshly prepared solution of VII gradually disappear and two new bands (290 and 340 $m\mu$), characteristic of the phenylhydrazone chromophore, appear. This isomerization is more facile in the presence of a trace of acid and it has been possible for us to isolate benzil osazone (VIII) in 50% yield, on refluxing a chloroform solution of VII with a few drops of HCl.

It is not very clear how the triazole is formed in the oxidation of benzaldehyde phenylhydrazone. Benzil osazone under acidic condition is reported to give triazole (XII).[20] With a view to finding out whether triazole (XII) is formed from benzil osazone under our experimental conditions, we have examined the oxidation of VIII using manganese dioxide. When the reaction was carried out in benzene at room temperature, a 33% yield of triazole (XII) and a trace of biphenyl were formed. In addition, the presence of azobenzene could be detected in the mother liquor (ultraviolet spectrum and tlc identification). Increased yields of triazole XII (85%) and biphenyl (21%) were obtained, when the reaction was carried out in refluxing benzene. A probable route for the formation of XII through radical intermediates XIII and XIV is indicated in Scheme III.

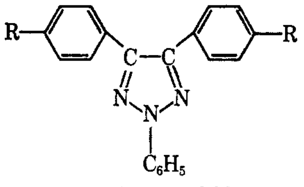
We have examined the oxidation of few other aldehyde phenylhydrazones like anisaldehyde phenylhydrazone and *p*-tolualdehyde phenylhydrazone. The room-temperature oxidation of anisaldehyde phenylhydrazone in benzene gave exclusively 1,2-(bisphenylazo)-1,2-dianisylethane (XV, 84%). In refluxing benzene, however, three products could be isolated which include biphenyl (10%), anisil osazone (XVI, 12%), and 2-phenyl-4,5-dianisyl-1,2,3-triazole (XVII, 7%).



XV, R = OCH$_3$
XVIII, R = CH$_3$



XVI, R = OCH$_3$
XIX, R = CH$_3$

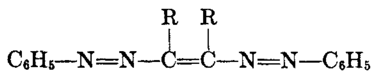


XVII, R = OCH$_3$
XX, R = CH$_3$

The oxidation of *p*-tolualdehyde phenylhydrazone in benzene at room temperature gave the expected 1,2-(bisphenylazo)-1,2-di-*p*-tolylethane (XVIII) in 90% yield. In refluxing benzene, the products were biphenyl (8%) and 2-phenyl-4,5-di-*p*-tolyl-1,2,3-triazole (XX, 15%).

As in the case of 1,2-(bisphenylazo)-1,2-diphenylethane (VII), both the bisazo compounds XV and XVIII underwent isomerization in chloroform solution to the corresponding osazones XVI and XIX.

In continuation of our study concerning the oxidation of osazones, we have examined the oxidation of both biacetyl osazone and glyoxal osazone, using manganese dioxide. Oxidation of biacetyl osazone at room temperature gave exclusively α,β-(bisbenzeneazo)butylene (XXI, 90%). In refluxing benzene, a 14% yield of



$$C_6H_5{-}N{=}N{-}\overset{R}{C}{=}\overset{R}{C}{-}N{=}N{-}C_6H_5$$

XXI, R = CH$_3$
XXII, R = H

biphenyl and an unidentified product, which analyzes for $C_{16}H_{16}N_4$, were obtained. Unlike the case of benzil osazone, none of the expected triazole could be isolated from this run. Similarly, the room-temperature oxidation of glyoxal osazone gave a 94% yield of α,β-(bisazobenzene)ethylene (XXII). No other product including any triazole could be isolated.

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(19) A. J. Bellamy and R. D. Guthrie, *J. Chem. Soc.*, 3528 (1965).

(20) H. Biltz and R. Weiss, *Ber.*, 3519 (1902).

Experimental Section

Manganese Dioxide.—Active manganese dioxide (85 g) was prepared by way of a reported procedure,[6] employing manganese sulfate monohydrate (140 g) and potassium permanganate (160 g).

Oxidation of Benzophenone Phenylhydrazone. A. In Benzene at Room Temperature.—Benzophenone phenylhydrazone (2 g, 0.007 mole) and manganese dioxide (10 g) were stirred in dry benzene (100 ml) for 24 hr. Removal of the inorganic material and of the solvent gave a product, which was chromatographed on alumina. Elution with petroleum ether (bp 60–80°) gave 0.28 g (27%) of biphenyl, mp 70° (mixture melting point). Further elution of the alumina column with a mixture of benzene and chloroform (1:1) gave a viscous liquid, which on distillation under reduced pressure gave 0.66 g (50%) of benzophenone, identified through its 2,4-dinitrophenylhydrazone, mp 239° (mixture melting point).

B. In Refluxing Benzene.—In a second run, benzophenone phenylhydrazone (2 g, 0.007 mole) and manganese dioxide (12 g) were refluxed in dry benzene for 6 hr. Work-up as in the previous case gave 0.38 g (34%) of biphenyl and 0.84 g (63%) of benzophenone.

C. In Refluxing Toluene.—A mixture of benzophenone phenylhydrazone (5 g, 0.01 mole) and manganese dioxide (30 g) was refluxed in dry toluene (250 ml) for 4 hr. Work-up of the mixture gave an impure liquid which when chromatographed on alumina using petroleum ether (bp 60–80°) gave 1.3 g of a yellow oil. Distillation of this oil under reduced pressure gave 1.0 g (32%) of a mixture of methylbiphenyls: bp 80–87° (1 mm), λ_{max} (ethanol) 243 mμ (ϵ 17,520). The infrared spectrum showed three absorption bands at 825, 793, and 775 cm^{-1}, characteristic of a mixture of methylbiphenyls (*ortho*, *meta*, and *para*).[21]

Anal. Calcd for $C_{13}H_{12}$: C, 92.85; H, 7.1 Found: C, 92.8; H, 7.2.

Elution of the alumina column with benzene gave a product (2.3 g) which on recrystallization from petroleum ether (bp 60–80°) gave 2.15 g (65%) of benzophenone, mp 48° (mixture melting point).

D. In Refluxing Cumene.—In a similar run, benzophenone phenylhydrazone (5 g, 0.18 mole) and manganese dioxide (30 g) were refluxed in cumene (250 ml). Removal of the inorganic material and of the solvent gave an oil which was chromatographed on alumina. Elution with petroleum ether (bp 60–80°) gave a liquid (1.5 g) which on distillation gave a mixture of isopropylbiphenyls (1.27 g, 35%): bp 85–105° (0.2 mm), λ_{max} (ethanol) 248 mμ (ϵ 19,000). The infrared absorption spectrum showed three bands at 841, 805, and 765 cm^{-1} characteristic of a mixture of biphenyls.[21]

Anal. Calcd for $C_{15}H_{16}$: C, 91.8; H, 8.1. Found: C, 91.5; H, 8.0.

Elution of the alumina column with benzene gave 2.5 g of a viscous liquid which was further chromatographed on alumina to give 0.19 g (4%) of benzophenone anil, mp 113° (mixture melting point) and 1.94 g (58%) of benzophenone, mp 48° (mixture melting point).

Oxidation of Acetophenone Phenylhydrazone.—A mixture of acetophenone phenylhydrazone (4 g, 0.18 mole) and manganese dioxide (24 g) was refluxed in benzene (200 ml) for 4 hr. Work-up of the mixture in the usual manner and chromatography of the products over alumina gave 0.73 g (25%) of biphenyl, mp 70° (mixture melting point), and 0.88 g (40%) of acetophenone, identified through its 2,4-dinitrophenylhydrazone, mp 249° (mixture melting point).

Oxidation of *p*-Bromoacetophenone Phenylhydrazone.—*p*-Bromoacetophenone phenylhydrazone (3 g, 0.1 mole) and manganese dioxide (18 g) were refluxed in benzene (150 ml) for 4 hr. Work-up as in the previous case gave 0.45 g of biphenyl (30%) and 0.9 g (43%) of *p*-bromoacetophenone, mp 52° (mixture melting point).

Oxidation of Benzophenone 2,4-Dinitrophenylhydrazone.—A mixture of 4 g (0.1 mole) of benzophenone 2,4-dinitrophenylhydrazone and 24 g of manganese dioxide was refluxed in dry benzene for 4 hr. Work-up of mixture gave 0.02 g of biphenyl and 0.08 g (4%) of benzophenone.

Oxidation of Benzaldehyde Phenylhydrazone. A. In Benzene at Room Temperature.—A mixture of 2 g (0.1 mole) of benzaldehyde phenylhydrazone and 10 g of manganese dioxide in 100 ml of benzene was stirred at room temperature for 24 hr. Removal of the inorganic material and evaporation of the solvent gave 1.8 g of a yellow solid which on recrystallization from benzene gave 1.15 g (60%) of N$^{\alpha}$,N$^{\beta'}$-diphenyl-N$^{\beta}$-benzalbenzhydrazidine (X), mp 201–202°. The identity of this compound was confirmed by a comparison of its in infrared spectrum with that of an authentic sample.[16]

From the mother liquour, a second compound was isolated which on recrystallization from chloroform gave 0.6 g (31%) of 1,2-(bisbenzeneazo)-2,3-diphenylethane (VII), mp 184–185°.

Anal. Calcd for $C_{26}H_{22}N_4$: C, 80.0; H, 5.6; N, 14.4. Found: C, 80.1; H, 5.8; N, 14.3.

The electronic spectrum of VII in ethanol showed two absorption maxima, λ_{max} 268 mμ (ϵ 22,000) and 400 mμ (ϵ 398). Its infrared spectrum did not show the presence of any N–H band.

B. In Refluxing Benzene.—Benzaldehyde phenylhydrazone (2.5 g, 0.12 mole) and manganese dioxide (15 g) were refluxed in benzene (100 ml) for 6 hr. Work-up of the mixture gave a product which was chromatographed on alumina. Elution with petroleum ether (bp 60–80°) gave 0.34 g (17%) of biphenyl, mp 70° (mixture melting point). Elution of the column with a mixture of petroleum ether (bp 60–80°) and benzene (1:1) gave an orange-red solid which on recrystallization from ethanol gave 0.3 g (12%) of benzil osazone (VIII), mp 225° (mixture melting point), and 0.8 g (44%) of 2,4,5-triphenyl-1,2,3-triazole (XII), mp 120° (mixture melting point). Identities of these products were further confirmed by a comparison of their infrared spectra with those of authentic samples.[20]

Further elution of the alumina column with benzene–petroleum ether mixture (2:1) gave 0.25 g (14%) of 2,3-diphenyl-1,4-dibenzaltetrazene (XI), which melted at 184–185°, after recrystallization from a benzene–ethanol mixture.

Anal. Calcd for $C_{26}H_{22}N_4$: C, 80.0; H, 5.6; N, 14.4. Found: C, 80.2; H, 5.7; N, 14.3%.

The ultraviolet spectrum of XI was characterized by the following maxima: 233 mμ (ϵ 33,000), 260 (39,000), and 340 (36,000). Its infrared spectrum showed no N–H band, but two strong absorptions at 1590 and 1485 cm^{-1} characteristic of >C=N vibrations were observed. The nmr spectrum ($CDCl_3$) showed a single multiplet centered around τ 2.8, due to phenyl protons (22 H).

Oxidation of Anisaldehyde Phenylhydrazone. A. In Benzene at Room Temperature.—A mixture of 2 g (0.08 mole) of anisaldehyde phenylhydrazone and 10 g of manganese dioxide in 100 ml of benzene was stirred at room temperature for 24 hr. Work-up as in the previous cases gave 1.8 g (94%) of crude 1,2-(bisphenylazo)-1,2-dianisylethane (XV), mp 161–163°. Recrystallization from benzene gave 1.6 g (84%) of pure product, mp 165°.

Anal. Calcd for $C_{28}H_{26}N_4O_2$: C, 74.6; H, 5.7; N, 12.4. Found: C, 74.35; H, 5.7; N, 12.4.

The electronic spectrum of a freshly prepared solution of XV in chloroform showed two absorption maxima: λ_{max} 269 mμ (ϵ 32,630) and 400 mμ (ϵ 545). After keeping the solution for several hours at room temperature (25°), the absorption positions shifted to 280 and 340 mμ. The infrared spectrum of a freshly prepared solution of XV did not show any N–H band, but on keeping the solution for 2 hr, an N–H absorption at 3330 cm^{-1} appeared.

B. In Refluxing Benzene.—In a second run 5 g (0.21 mole) of anisaldehyde phenylhydrazone and 30 g of manganese dioxide were refluxed in 250 ml of dry benzene for 4 hr. The mixture was worked up as usual by chromatography on alumina. Elution with petroleum ether gave 0.35 g (10%) of biphenyl, mp 70° (mixture melting point). Further elution of the column with benzene gave a product, which on recrystallization from a mixture of ethanol and benzene (1:1) gave 0.58 g (12%) of anisil osazone (XVI), mp 197°.

Anal. Calcd for $C_{28}H_{26}N_4O_2$: C, 74.6; H, 5.7; N, 12.4. Found: C, 74.1; H, 5.6; N, 12.2.

The ultraviolet spectrum of XVI was characterized by the following absorption maxima: 288 mμ (ϵ 38,370) and 340 mμ (ϵ 51,080). The identity of this material was further confirmed by a comparison of its infrared spectrum with that of an authentic sample.[22]

From the mother liquor 0.32 g of a pale yellow solid separated out, which on repeated crystallization from ethanol gave 0.28 g (7%) of 2-phenyl-4,5-dianisyl-1,2,3-triazole (XVII), mp 133°.

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(21) C. S. Rondestvedt, Jr., and H. S. Blanchard, *J. Am. Chem. Soc.*, **77**, 1769 (1955).

(22) H. Biltz and A. Wienands, *Ann.*, **308**, 8 (1899).

Anal. Calcd for $C_{22}H_{19}N_3O_2$: C, 73.9; H, 5.3; N, 11.7. Found: C, 74.3; H, 5.3; N, 11.65.

The ultraviolet spectrum of XVII showed the following absorption maxima: 225 mμ (ε 27,620), 280 (32,540), and 300 (33,980). The infrared spectrum showed absorption bands at 975, 998 cm^{-1} characteristic of triazoles.[23]

Oxidation of *p*-Tolualdehyde Phenylhydrazone. A. In Benzene at Room Temperature.—A mixture of *p*-tolualdehyde phenylhydrazone (2 g, 0.09 mole) and manganese dioxide (10%) were stirred at room temperature in dry benzene (100 ml) for 24 hr. Removal of unchanged manganese dioxide and of the solvent gave 1.8 g of a yellow solid which on recrystallization from benzene yielded 1.7 g (90%) of 1,2-(bisphenylazo)-1,2-ditolylethane (XVIII), mp 170–171°.

Anal. Calcd for $C_{28}H_{26}N_4$: C, 80.3; H, 6.2; N, 13.3. Found: C, 80.02; H, 6.0; N, 13.27.

The ultraviolet spectrum of a freshly prepared solution of XVIII in chloroform was characterized by the following absorption maxima: 270 mμ (ε 30,300) and 400 mμ (ε 490). On keeping this solution for several days there was a shift in the positions of the bands and the new maxima were observed at 290 mμ (ε 30,000) and 339 mμ (ε 38,500). The infrared spectrum of a, freshly prepared solution ($CHCl_3$) did not show any N–H band, but an N–H band appeared, after keeping the solution for 1 day.

B. In Refluxing Benzene.—In a similar experiment 5 g of *p*-tolualdehyde phenylhydrazone (0.2 mole) and 30 g of manganese dioxide were refluxed in 250 ml of dry benzene for 4 hr. Work-up of the mixture in the usual manner and chromatography on alumina employing petroleum ether (bp 60–80°) gave 0.3 g (8%) of biphenyl, mp 70° (mixture melting point). Further elution of the alumina column with petroleum ether gave a red, viscous solid, which on repeated crystallizations from ethanol gave 0.4 g (15%) of 2-phenyl-4,5-di-*p*-tolyl-1,2,3-triazole (XX), mp 142°.

Anal. Calcd for $C_{22}H_{19}N_3$: C, 81.2; H, 5.8; N, 12.9; mol wt, 325. Found: C, 80.8; H, 5.8; N, 12.7; mol wt, 320.

The ultraviolet spectrum of XX in ethanol showed two absorption maxima: 220 mμ (ε 17,487) and 290 mμ (ε 31,034). The infrared spectrum showed the triazole absorptions[23] at 980 and 988 cm^{-1}.

Further elution of the column with benzene–petroleum ether mixture (1:1) gave 0.3 g of a yellow, polymeric material from which no pure product could be isolated.

Isomerization of 1,2-(Bisphenylazo)-1,2-dianisylethane.—A solution of 100 mg (0.2 mole) of 1,2-(bisphenylazo)-1,2-dianisylethane in a mixture of 15 ml of chloroform and 8 ml of ethanol with 2 drops of 5% HCl was refluxed for 18 hr. Removal of the solvent and recrystallization of the product from a mixture of benzene and ethanol gave 50 mg (50%) of anisil osazone (XVI), mp 197° (mixture melting point). The identity of this compound was further confirmed by a comparison of the infrared spectrum with that of an authentic sample.

Isomerization of 1,2-(Bisphenylazo)-1,2-ditolylethane.—1,2-(Bisphenylazo)-1,2-ditolylethane (100 mg, 0.2 mmole) was refluxed in a mixture of chloroform (30 ml) and ethanol (10 ml) with 3 drops of 5% HCl for 18 hr. Removal of the solvent gave a product which on recrystallization from ethanol gave 35 mg (35%) of *p*-tolyl osazone (XIX), mp 180°.

Anal. Calcd for $C_{28}H_{26}N_4$: C, 80.3; H, 6.2; N, 13.3. Found: C, 79.8; H, 6.19; N, 13.4.

The ultraviolet spectrum of XIX showed the following absorption maxima: 290 mμ (ε 30,000) and 339 mμ (ε 39,000). The infrared spectrum showed an N–H peak at 3330 cm^{-1}.

Oxidation of Benzil Osazone. A. In Benzene at Room Temperature.—A mixture of 2 g (0.005 mole) of benzil osazone and 10 g of manganese dioxide was stirred in 100 ml of benzene at room temperature for 24 hr. Work-up of the mixture in the usual way gave a product which was chromatographed on alumina employing petroleum ether to give 0.05 g of biphenyl (0.5%), mp 70° (mixture melting point). Further elution with petroleum ether gave a product which on fractional crystallization from ethanol gave 0.5 g (33%) of 2,4,5-triphenyl-1,2,3-triazole (XII), mp 120° (mixture melting point).

The mother liquor showed the presence of azobenzene as identified on a tlc plate. In addition, the ultraviolet spectrum of the mother liquor showed absorption bands similar to those of azobenzene.

B. In Refluxing Benzene.—In a similar experiment 2 g (0.005 mole) of benzil osazone and 25 g of manganese dioxide were refluxed in 100 ml of dry benzene for 6 hr. Work-up of the mixture as in the previous case gave 0.35 g (21%) of biphenyl, mp 70° (mixture melting point), and 1.3 g (85%) of XII, mp 120° (mixture melting point).

Oxidation of Biacetyl Osazone. A. In Benzene at Room Temperature.—A mixture of 2 g (0.007 mole) of biacetyl osazone and 10 g of manganese dioxide in 100 ml of benzene was stirred for 24 hr. Removal of the solvent and unchanged manganese dioxide gave a deep violet solid, which after several crystallizations from ethanol gave 1.72 g (90%) of α,β-bisbenzeneazobutylene (XXI), mp 159° (mixture melting point). The ultraviolet spectrum of XXI in alcohol showed the following absorption maxima: 240 mμ (ε 57,000), 375 (76,000), 390 (75,000), and 488 (1750), in agreement with those of an authentic sample.[24]

B. Refluxing Benzene.—In a repeat run, 2.5 g (0.009 mole) of biacetyl osazone and 15 g of manganese dioxide were refluxed in 100 ml of dry benzene for 4 hr. Work-up of the mixture in the usual manner and chromatography on alumina using petroleum ether gave 0.38 g (14%) of biphenyl, mp 70° (mixture melting point). Elution of the column with a mixture benzene and petroleum ether gave a product which after several recrystallization from cyclohexane gave a yellow solid, mp 127°.

Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.7; H, 6.06; N, 21.2. Found: C, 72.3; H, 5.7; N, 21.2.

The ultraviolet spectrum of this product showed two absorption maxima: λ_{max} 219 mμ (ε 13,410) and 339 mμ (ε 17,800). No N–H band was visible in the infrared spectrum.

Oxidation of Glyoxal Osazone.—A mixture of 2 g (0.008 mole) of glyoxal osazone and 10 g of manganese dioxide in 100 ml of benzene was stirred at room temperature for 24 hr. Removal of the unchanged manganese dioxide and of the solvent gave 1.8 g (94%) of α,β-bisbenzeneazoethylene (XXII), mp 143–145° dec. Two recrystallizations from ethanol gave a pure product melting at 149° dec. There was no depression in the melting point on admixture with an authentic sample of XXII.[25]

Registry No.—VII, 2572-14-7; XI, 10591-67-0; XV, 10591-68-1; XVI, 6266-37-1; XVII, 10591-70-5; XVIII, 10591-71-6; XIX, 10591-72-7; XX, 10591-73-8; benzophenone phenylhydrazone, 574-61-8; acetophenone phenylhydrazone, 583-11-9; *p*-bromoacetophenone phenylhydrazone, 10591-75-0; benzophenone 2,4-dinitrophenylhydrazone, 1733-62-6; benzaldehyde phenylhydrazone, 588-64-7; anisaldehyde phenylhydrazone, 622-73-1; *p*-tolualdehyde phenylhydrazone, 2829-25-6; benzil osazone, 1695-80-3; biacetyl osazone, 2861-48-5; glyoxal osazone, 1534-21-0.

Acknowledgment.—We thank Mr. A. H. Siddiqui for help in microanalysis.

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