# Stable Heterocyclic Primary Nitroso-amines

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Stable primary nitroso-amines are obtained by treating those heterocyclic amines which contain a C=N system adjacent to the amino-group and no labile hydrogen atoms with nitrous acid. The presence of carbon, substituted nitrogen, oxygen, or sulphur atoms in the remaining portion of the heterocyclic ring does not militate against the formation of the nitroso-amines. The relationship between the structure of the primary nitroso*amino-system* and imino, diazoate, and diazonium forms is discussed. Reactions of the nitroso-amines include ready reduction to hydrazines and a thermal arylation which involves a homolytic displacement of the nitroso-amino-group in a reaction similar to the Gomberg–Bachman process.

THE reaction of primary arylamines with nitrous acid which leads to diazonium salts is normally regarded as involving primary nitroso-amines or their conjugate acids as unstable short-lived intermediates. Our interest in heterocyclic hydrazines and their carbonyl derivatives[1] led us to investigate the reactions of five-membered heteroarylamines (I) with nitrous acid in expectation that a route to the heterocyclic hydrazines *via* reduction of the resulting diazonium salts might emerge. The diazotisation procedures we used were simple, involving dropwise addition of aqueous sodium nitrite to the heterocyclic amine in ice-cold concentrated hydrochloric acid. The products were stable crystalline compounds which had a nitroso rather than a diazonium structure. They could have arisen from nitrosation of the primary amino-group or from nitrosation of a ring nitrogen atom. The literature records a number of similar products which were in fact described as heterocyclic primary nitroso-amines and includes those of 1,2,4-thiadiazoles (II) (X = R-C, Y = N, Z = S),[2,3] 1,3,4-thiadiazoles, *e.g.* (IIc),[4] thiazoles (II) (X-Y = CH=CH, Z = S),[5,6] tetrazoles (IIa),[7] 1,3,4-oxadiazoles, *e.g.* (IIb),[8] and triazoles, *e.g.* (IIe),[9] as well as unstable diazohydroxides of pyrazoles,[10] indiazole,[11] and isoxazole.[12] Structural assignments were mainly based on chemical reactions of the nitrosoamino-system and as such were not entirely unequivocal since it was always possible that Fischer-

Hepp[13] type rearrangements of ring nitrosated compounds to exocyclic nitrosoamino-structures (II) had occurred under the reaction conditions. The structural
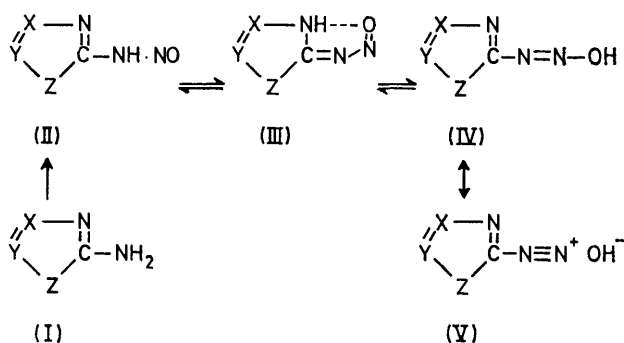


a; X = N, Y = N, Z = NR
b; X = N, Y = C·C$_6$H$_4$R($p$), Z = O
c; X = N, Y = CPh, Z = S
d; X = N·CH$_2$Ph, Y = N, Z = N, X–Y single bond, Z–Y double bond
e; X = N, Y = CPh, Z = NH

SCHEME 1

problem presented by the crystalline compounds which we isolated was two-fold: (a) to decide whether the

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[1] For a review see R. N. Butler and F. L. Scott, *Chem. and Ind.,* 1970, 1216; T. A. F. O'Mahony, R. N. Butler, and F. L. Scott, *J.C.S. Perkin II,* 1972, 1319. See also refs. 16, 18, 19, 23, 24, and 25.

[2] J. Goerdeler, K. Deselaers, and A. Ginsberg, *Chem. Ber.,* 1960, **93,** 963.

[3] J. Goerdeler and K. Deselaers, *Chem. Ber.,* 1958, **91,** 1025.

[4] M. Freund and C. Meinecke, *Ber.,* 1896, **29,** 2511.

[5] G. T. Morgan and G. V. Morrow, *J. Chem. Soc.,* 1915, **107,** 1294.

[6] P. Schatzmann, *Annalen,* 1891, **261,** 9.

[7] R. Stolle, *J. prakt. Chem.,* 1932, **134,** 282; *Ber.,* 1922, **55,** 1295; 1925, **58,** 2100.

[8] R. Stolle and K. Fehrenbach, *J. prakt. Chem.,* 1929, **122,** 289.

[9] H. Gehlen and J. Dost, *Annalen,* 1963, **665,** 144.

[10] A. Michaelis and H. Bressel, *Annalen,* 1915, **407,** 286.

[11] E. Bamberger, *Annalen,* 1915, **407,** 286.

[12] H. Wieland, *Annalen,* 1903, **328,** 197.

[13] O. Fischer and E. Hepp, *Ber.,* 1886, **19,** 2291.

compounds were primary nitroso-amines or secondary ring nitroso-amines and (b) if the former was the case to decide on the relative importance of the various possible tautomeric forms, (II) ⇌ (III) ⇌ (IV) ↔ (V).

RESULTS AND DISCUSSION

(a) *Structure.*—When the amines (Ia—d) were treated with nitrous acid in an excess of hydrochloric acid, the corresponding stable nitroso-amines (IIa—d) were obtained. Their structures were determined from the following spectroscopic data:

*I.r. spectra.* The i.r. spectra of all the compounds (IIa—d), in the solid state, displayed a band at 1505—1540 $cm^{-1}$ due to the nitroso stretching vibration.[14] Diazonium stretching vibrations [15] at 2220 $cm^{-1}$ were absent. Thus the i.r. data suggest both the presence of a nitroso-form in the products in the solid state and the absence of a diazonium form. The n.m.r. data (see later) confirmed amino-nitrosation, and the i.r. spectra also suggested that form (III) does not contribute significantly and pointed to major contributions from forms (II) and (IV). A band at 1435 $cm^{-1}$ (not present in the amines) is assigned to the OH group of form (IV) from its similarity to the NOH band of oximes. A broadening was observed in the N–H band of the nitroso-amines at 3300—3450 $cm^{-1}$. This may be due to the presence of the OH group of form (IV) but it could also arise from changes in the nature of the hydrogen bonding in the solid state and hence cannot be assigned unequivocally. The i.r. spectra of the tetrazole series (IIa) also showed cyclic $>C=N$ stretching bands at 1650—1630 $cm^{-1}$. Exocyclic $>C=N$ stretching bands for a form such as (III) would be expected at 1660 $cm^{-1}$ by comparison with model compounds, for example (VI).[16] The absence of
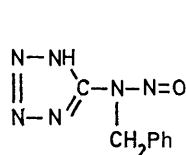


(VII)
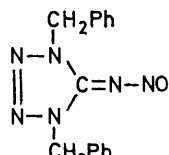
(VI)

this absorption and of any diazonium absorptions suggests that forms (II) and (IV) are the predominant forms present. It was not possible to assign unequivocally the –N=N– stretching vibration (1630—1575 $cm^{-1}$) expected for form (IV) because of overlapping ring absorptions already present in this region.

*N.m.r. spectra.* N.m.r. studies of isomerism, due to restricted rotation about the N–N bond of nitroso-amines, are well documented,[17] and it has been established that protons *cis* to the O atom resonate at higher fields than those in the *trans* situation. The spectra of the compounds (IIa; R = PhCH₂) and (IId) each showed

two signals for the benzyl protons as expected: (IIa; R = PhCH₂), τ *cis* 4·56, *trans* 4·36, isomer ratio *cis* : *trans*, *ca.* 1 : 7; (IId), τ *cis* 4·42, *trans* 4·26, isomer ratio *ca.* 1 : 1·5. The small separation of the *cis* and *trans* signals relative to that of N-alkylnitroso-amines (Δτ *ca.* 0·8 p.p.m.) is probably due to the greater distance of the alkyl groups from the nitroso-amine unit in this instance. The model compound (VII) prepared by nitrosation of 5-benzylaminotetrazole also showed two benzyl signals, τ 4·70 and 3·94 (Δτ 0·76 p.p.m.) in good agreement with other work.[17]

*U.v. spectra.* The u.v. spectra (Table 2, Experimental section) were less informative but fully consistent with the foregoing data. The data for methanol as solvent are limited because of paucity of model compounds, but the intensity and position of the band for the imino-compound (VI) are different from the data for the others and consistent with the compounds having a fundamentally different structure. In base the tautomeric forms (II)—(IV) all form the same anion. The similarity between the two measurements in the Table and those for the *anti*-benzenediazoate [$\lambda_{max.}$ 270—280 nm (ε 7—12 × 10³)] are consistent with a similarity in structure and in agreement with Goerdeler's [3] previous conclusions.

(b) *Reactions.*—The nitroso-amines were highly acidic, the tetrazole series having p$K_a$ values of 3·13—3·58. This property provided a useful means of purifying the compounds, namely by extraction with base and reprecipitation by acid (see Experimental section). Their reactions were also consistent with the presence of forms (II) and (IV). Mild reduction of the nitroso-amines with zinc in acetic acid gave the expected hydrazines. These were isolated as their benzaldehyde derivatives, which we have previously prepared unequivocally.[18,19] This reaction further confirms the primary nitroso-amino-structure of the compounds as against a possible ring nitrosated structure. The possibility that a Fischer–Hepp [13] type rearrangement of a ring-nitrosated compound to the primary nitroso-amine structure (II) occurred under these reducing conditions is unlikely and the reduction reactions, coupled with the n.m.r. data, provide conclusive evidence for amino-nitrosation.

When the compounds (IIb and c) were heated under reflux in benzene, homolytic displacement of the nitroso-amino-group occurred, yielding 2,5-diaryl-1,3,4-oxa- and thia-diazoles (VIII) (Scheme 2). Quantities of the parent amine (derived from N–NO bond cleavage) together with equivalent quantities of NO₂ (from the same bond cleavage, NO being oxidised to NO₂) were also obtained with the compounds (IIb). In addition varying quantities of intractable gums were also formed in each case. Photolysis of the nitroso-amine (IIb, R = H) in benzene suspension at 25° was less efficient than the

[14] T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, 1966, **88** 4518; Y. L. Chow and A. C. H. Lee, *Canad. J. Chem.*, 1967, **45**, 311.
[15] J. M. Tedder, *Adv. Heterocyclic Chem.*, 1967, **8**, 1.
[16] F. L. Scott and J. C. Tobin, *J. Chem. Soc.* (C), 1971, 703.

[17] R. K. Harris and R. A. Spragg, *Chem. Comm.*, 1967, 362; A. Mannschreck, H. Munsch, and A. Mattheus, *Angew. Chem. Internat. Edn.*, 1966, **5**, 728; G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, 1964, **86**, 4373.
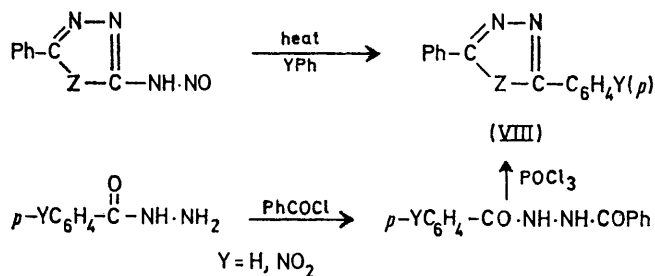[18] J. C. Tobin, A. F. Hegarty, and F. L. Scott, *J. Chem. Soc. (B)*, 1971, 2198.
[19] R. N. Butler, T. M. Lambe, and F. L. Scott, *J.C.S. Perkin I*, 1972, 269.

thermolysis, 95% of the compound being recovered unchanged after 3 h irradiation, 2% of compound (VIII; $Z = O$, $Y = H$) also being isolated. A similar phenylation reaction was observed when compound (IIa;

Ph-C $\overset{N-N}{\underset{Z-C-NH\cdot NO}{||}}$ $\xrightarrow[\text{YPh}]{\text{heat}}$ Ph-C $\overset{N-N}{\underset{Z-C-C_6H_4Y(p)}{||}}$

(VIII)

$\uparrow$ POCl$_3$

$p$-YC$_6$H$_4$-$\overset{O}{\overset{||}{C}}$-NH·NH$_2$ $\xrightarrow{\text{PhCOCl}}$ $p$-YC$_6$H$_4$-CO·NH·NH·COPh

Y = H, NO$_2$

SCHEME 2

$R = Ph$) was heated in benzene, and yielded 1,5-diphenyltetrazole. The nitroso-amine (IIa; $R = Ph$), however, was less labile than the compounds (IIb and c) and more prolonged heating was required for an appreciable reaction. We regard these phenylation reactions as examples of Gomberg–Bachman processes [20] involving homolysis of the diazohydroxide forms (IV) into R·, N$_2$, and ·OH. The homolytic nature of the process was confirmed when compound (IIb; $R = H$) was heated under reflux in nitrobenzene. The main product (37%) was 2-$p$-nitrophenyl-5-phenyl-1,3,4-oxadiazole (VIII; $Z = O$, $Y = NO_2$), which was isolated along with parent amine (Ib) (20%) and large quantities of gum. There was no evidence for meta-substitution and t.l.c. of the products did not show a spot comparable to that of an authentic sample of the meta-product. Attempts to separate the resins from any 2-$o$-nitrophenyl-5-phenyl-1,3,4-oxadiazole which may have been formed were not successful; if this product is present, it must be in small proportion. The structures of the 2,5-diaryloxadiazoles (VIII; $Z = O$) were established by unequivocal preparation from the appropriate benzohydrazides (Scheme 2).

(c) *Nitrosation* versus *Diazotisation.*—When the amine (Ie) was treated with nitrous acid as already described, the product was a diazonium salt which showed a strong diazonium band at 2220 cm$^{-1}$ and exploded violently at 76° on gentle heating. (It should be handled with care since it exploded on some occasions when touched with a spatula.) When the compound was treated *in situ* with azide ion, the expected azide was obtained. When the diazotisation was carried out in fluoroboric acid, a stable diazonium fluoroborate was formed. Previously, with a similar 1,2,4-triazole system where the 1-proton was replaced by an aryl substituent, Gehlen [9] readily obtained primary nitroso-amines. Similarly, diazotisation of 5-aminotetrazoles (Ia; $R = H$) leads to the well known tetrazole-5-diazonium salts.[21]

Our observations, coupled with those of others,[2–9]

indicate that an essential structural requirement for the formation of stable primary nitroso-amines is a heteroaromatic amine containing a C=N system adjacent to the amino-group and no labile hydrogen atoms. In the remaining portion of the ring the presence of carbon, substituted nitrogen, oxygen, or sulphur atoms does not militate against the formation of stable primary nitroso-amines. The nitrosoamino-system may theoretically exist in the forms (II)—(V) and stabilisation via hydrogen bonding as in form (III) seems an attractive explanation for the extra stability. Such an imino-form has previously been considered to exert a stabilising influence on the intermediates in the reaction of 2-aminopyridine with nitrous acid.[22] However, our data preclude this as the primary source of stability for the present five-membered heterocyclic systems. The influence of a labile H atom in destabilising the nitroso-amines is of interest. We tentatively suggest that the stability of the diazoate form is a critical factor in deciding between the formation of a primary nitroso-amine and of a diazonium salt. If in the equilibrium between forms (II) and (IV) the diazoate form acquires extra stabilisation through hydrogen bonding with the cyclic C=N system, diazonium salt formation may be inhibited. [Such an –O–H · · ·N= intramolecular hydrogen bond would be expected to be stronger than the N–H · · · O= bond of form (III).] The presence of an acidic H atom would facilitate isomerisation to the more reactive non-hydrogen bonded forms, thus enhancing diazonium salt formation.

EXPERIMENTAL

M.p.s were measured with an Electrothermal apparatus. I.r. spectra were measured with Perkin-Elmer spectrophotometers (models 137E and 257) with sodium chloride optics. Solids were examined as KBr discs. U.v. spectra were measured on a Unicam SP 800 spectrophotometer. N.m.r. spectra were measured on a Varian HA100 spectrometer at 25° with deuteriochloroform as solvent. Microanalysis were carried out by Mrs. K. M. Duggan and Miss D. Healy of this Department.

The preparation of the heterocyclic amines has previously been described.[16,23–25] 2-Amino-5-phenyl-1,3,4-thiadiazole was obtained by the dehydration of 1-benzoylthiosemicarbazide in syrupy phosphoric acid at 120°.

(i) *Preparation of Primary Nitroso-amines.*—(a) 2-*Aryl*-5-*nitrosoamino*-1,3,4-*oxadiazoles* (IIb). Typically, a well stirred ice-cold suspension of the amine (Ib; $R = MeO$) (8·0 g) and sodium nitrite (10·5 g) in water (100 ml) was treated slowly (30 min) with 10% hydrochloric acid (100 ml) and the mixture was stirred for 3 h at 5°. Unchanged starting amine (2·4 g, 30%) was separated from the yellow solid by stirring in aqueous sodium carbonate (20%). Acidification of the yellow alkaline solution with dilute hydrochloric acid yielded 2-p-*methoxyphenyl*-5-*nitrosoamino*-1,3,4-*oxadiazole* (IIb; $R = MeO$) (3·75 g, 41%), m.p. 110°

[20] W. Bachman and R. A. Hoffman, *Org. Reactions*, 1944, **2**, 224.
[21] F. R. Benson, ' Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, London, 1967, vol. 8, p. 1.
[22] A. Albert, ' Heterocyclic Chemistry,' Athlone Press, University of London, 1968 (2nd edn.), p. 82.

[23] F. L. Scott, T. M. Lambe, and R. N. Butler, *Tetrahedron Letters*, 1971, 2669.
[24] T. M. Lambe, R. N. Butler, and F. L. Scott, *Chem. and Ind.*, 1971, 996.
[25] F. L. Scott, D. A. Cronin, and J. K. O'Halloran, *J. Chem. Soc. (C)*, 1971, 2769.

(Found: C, 49·5; H, 3·6; N, 25·7. $C_9H_8N_4O_3$ requires C, 49·1; H, 3·65; N, 25·45%).

Nitroso-amines prepared in a similar manner are listed in Table 1. All of these nitroso-amines could be purified by careful reprecipitation from aqueous sodium carbonate with hydrochloric acid, and the substituted 1-phenyltetrazol-5-yl derivatives could also be satisfactorily recrystallised from aqueous ethanol. The $pK_a$ values (Table 1) were measured

identical (mixture m.p. and i.r. spectra) with a sample prepared unequivocally.[25] When the diazotisation was carried out with fluoroboric acid, a yellowish stable *diazonium fluoroborate* was formed, m.p. 250° (decomp.) (Found: C, 37·6; H, 2·65; N, 27·45. $C_8H_6BF_4N_5$ requires C, 37·3; H, 2·3; N, 27·15%).

(iii) *Reactions of Primary Nitroso-amines.* (a) *Reduction.* A stirred suspension of compound (IIb; R = H) (6·0 g) and

TABLE 1

Primary nitroso-amines

| Compound [M.p. (°C)] | Found (%) | | | Formula | Required (%) | | |
|---|---|---|---|---|---|---|---|
| | C | H | N | | C | H | N |
| Compounds (IIa) [a] | | | | | | | |
| R = | | | | | | | |
| Ph (110°) [b] | 44·35 | 3·05 | 44·6 | $C_7H_6N_6O$ | 44·2 | 3·2 | 44·2 |
| p-MeC₆H₄ (118) [c] | 46·85 | 3·9 | 41·4 | $C_8H_8N_6O$ | 47·05 | 3·95 | 41·15 |
| p-ClC₆H₄ (130) [d] | 37·1 | 2·5 | 37·0 | } $C_7H_5ClN_6O$ | 37·45 | 2·25 | 37·4 |
| m-ClC₆H₄ (115) [e] | 37·2 | 2·5 | 36·9 | | | | |
| p-NO₂·C₆H₄ (122) [f] | 35·4 | 2·5 | 41·95 | $C_7H_5N_7O_3$ | 35·75 | 2·15 | 41·7 |
| p-BrC₆H₄ (137) | 31·4 | 1·85 | 31·0 | $C_7H_5BrN_6O$ | 31·25 | 1·85 | 31·25 |
| p-MeO·C₆H₄ (129) | 43·9 | 3·8 | 38·3 | $C_8H_8N_6O_2$ | 43·65 | 3·65 | 38·15 |
| PhCH₂ (87) [g] | 47·2 | 3·9 | 40·9 | $C_8H_8N_6O$ | 47·05 | 3·95 | 41·15 |
| p-MeC₆H₄CH₂ (100) | 49·75 | 4·6 | 38·25 | $C_9H_{10}N_6O$ | 49·55 | 4·6 | 38·5 |
| p-ClC₆H₄CH₂ (67) | 40·3 | 3·25 | 35·0 | $C_8H_7ClN_6O$ | 40·5 | 2·95 | 35·4 |
| p-BrC₆H₄CH₂ (85) | 34·1 | 2·4 | 29·55 | $C_8H_7BrN_6O$ | 33·95 | 2·45 | 29·7 |
| Compounds (IIb) [h] | | | | | | | |
| R = | | | | | | | |
| H (106) (lit.,[8] 106) | 50·2 | 3·2 | 29·05 | $C_8H_6N_4O_2$ | 50·5 | 3·15 | 29·45 |
| Me (98) | 53·3 | 3·9 | 27·8 | $C_9H_8N_4O_2$ | 52·95 | 3·9 | 27·45 |
| Pr^i (89) | 56·5 | 5·15 | 24·2 | $C_{11}H_{12}N_4O_2$ | 56·9 | 5·15 | 24·15 |
| (IIc) (104) [i] | 46·7 | 2·9 | 27·05 | $C_8H_6N_4OS$ | 46·6 | 2·9 | 27·2 |
| (IId) [j] | 47·05 | 4·25 | 40·95 | $C_8H_8N_6O$ | 47·05 | 3·95 | 41·15 |

[a] Yields were greater than 70% unless otherwise stated. [b] $pK_a$ 3·46. [c] $pK_a$ 3·54. [d] $pK_a$ 3·38. [e] $pK_a$ 3·28. Yield 52%, $pK_a$ 3·13. [f] $pK_a$ 3·58; exploded at m.p. [g] Yields 43—61%; starting amine recovered (30—40%); exploded at m.p. [i] Yield 55% (Found, S, 15·4. Required, S, 15·5%); exploded at m.p. [j] Brown oil, isolated by ethereal extraction of the acidified sodium carbonate solution; yield, 50%.

by titrating solutions of the nitroso-amines to half neutralisation in a medium of constant ionic strength (a 1M-solution of KCl in 80 : 20 v/v water–ethanol) at 25° using a Radiometer Copenhagen pH meter 25 and an autoburette ABU 12.

Table 2 summarises u.v. data for some of the nitroso-amines.

TABLE 2

| Compound | Solvent | $\lambda_{max.}$/nm ($\varepsilon \times 10^{-3}$) |
|---|---|---|
| (IIa; R = Ph) | ⎫ | 245 (4·15) |
| (IIa; R = PhCH₂) | ⎪ MeOH | 245 (4·70) |
| (VII) | ⎬ | 265 (4·20) |
| (VI) | ⎭ | 284 (9·9) |
| (IIa; R = Ph) | 0·1N-NaOH | 276 (9·5) |
| (IIa; R = PhCH₂) | 0·1N-NaOH | 273 (7·5) |

(ii) 3-*Phenyl*-1,2,4-*triazole*-5-*diazonium salts.*—A well stirred suspension of the triazolylamine (Ie) (500 mg) and sodium nitrite (650 mg) in water (15 ml) was treated slowly (30 min) with 20% hydrochloric acid (10 ml) and the mixture was stirred for 30 min. Unchanged amine was removed from the yellowish solid by the procedure already described, and on acidification of the alkaline solution explosive 3-*phenyl*-1,2,4-*triazole*-5-*diazonium chloride* separated (550 mg, 85%), m.p. 76° (violent explosion), $\nu_{max.}$ 2220 cm⁻¹ (diazonium band). When the compound was treated *in situ* with azide ion, 5-azido-3-phenyl-1,2,4-triazole was formed.[25]

zinc dust (7·0 g) in water (100 ml) was treated slowly (15 min) with 10% acetic acid (200 ml) at 10°. The mixture was stirred for a further 8 h, after which undissolved zinc was removed. When benzaldehyde (3·2 g) in ethanol (100 ml) was added slowly with stirring, 2-(benzylidenehydrazino)-5-phenyl-1,3,4-oxadiazole separated. This compound and a range of its *para*-substituted derivatives have previously been reported (*cf.* ref. 19). Similar treatment of the nitroso-amine (IIc) yielded 2-(*benzylidenehydrazino*)-5-*phenyl*-1,3,4-*thiadiazole* (75%), m.p. 250—251° (Found: C, 64·35; H, 4·05; N, 19·85. $C_{15}H_{12}N_4S$ requires C, 64·3; H, 4·3; N, 20·0%). Similar treatment of the tetrazolyl nitroso-amines (IIa) yielded 5-arylmethylenehydrazino-1-phenyl-, 1-benzyl-, and 2-benzyl-tetrazoles. These compounds have been described previously.[18]

(b) *Gomberg–Bachman arylation reactions.* 2,5-Diphenyl-1,3,4-*oxadiazole* (VIII; Z = O, Y = H). A solution of compound (IIb; R = H) (1·5 g) in benzene (100 ml) was heated under reflux for 30 min during which a colour change from light yellow to dark brown occurred along with the evolution of brown fumes of $NO_2$. The solution was cooled and, after removal of the amine (Ib; R = H) (20%) which had separated, evaporated at 40° under reduced pressure. The residue was leached with ether in a Soxhlet apparatus for 3 h; evaporation of the ethereal solution gave compound (VIII; Z = O, Y = H) (1·03 g, 60%), m.p. 138° (from

hexane) (lit.,[26] 138°) (Found: C, 75·45; H, 4·4; N, 12·55. Calc. for $C_{14}H_{10}N_2O$: C, 75·65; H, 4·5; N, 12·6%), identical (mixture m.p. and i.r. spectra) with a sample prepared unequivocally.[26] No further crystalline products were isolated. Irradiation of compound (IIb; R = H) (1·0 g) in benzene (600 ml) at 25° under nitrogen with a Hanovia lamp yielded only 2% of compound (VIII; Z = O, Y = H) after 3 h; 95% of the nitroso-amine was recovered unchanged. When 2-nitrosoamino-5-phenyl-1,3,4-thiadiazole (IIc) was heated under reflux (30 min) in benzene, the corresponding 2,5-diphenyl derivative (VIII; Z = S, Y = H) [27] (50%), m.p. 140° (from hexane) (Found: C, 70·5; H, 4·05; N, 11·85; S, 13·5. Calc. for $C_{14}H_{10}N_2S$: C, 70·6; H, 4·2; N, 11·75; S, 13·45%) was obtained. Substantially less $NO_2$ and greater quantities of gums were formed and the amine (Ic) was not detected. When 5-nitrosoamino-1-phenyltetrazole (IIa; R = Ph) was heated under reflux in benzene for 11 h, 1,5-diphenyltetrazole (62%), m.p. 144° (from n-hexane) (lit.,[28] 144°) (Found: C, 70·15; H, 4·44; N, 25·1. Calc. for $C_{13}H_{10}N_4$: C, 70·25; H, 4·55; N, 25·2%) was obtained. This was identical (mixture m.p. and i.r. spectra) with a sample prepared unequivocally.[28]

*Pyrolysis in nitrobenzene.* A solution of the nitroso-amine (IIb; R = H) (1 g) in nitrobenzene (20 ml) was heated at 100° for 1 h and evaporated under reduced pressure to 4 ml. The amine (Ib; R = H) (250 mg, 25%) separated (filtrate A). Addition of ether (100 ml) to the filtrate A

yielded 2-p-*nitrophenyl*-5-*phenyl*-1,3,4-*oxadiazole* (VIII; Z = O, R = $NO_2$) (420 mg, 30%) (filtrate B), m.p. 208—209° (from ethanol) (Found: C, 62·55; H, 3·5; N, 16·05. $C_{14}H_9N_3O_3$ requires C, 62·9; H, 3·35; N, 15·75%). Further work-up of the filtrate B yielded only intractable gums. T.l.c. of the products over fluorescent silica gel with benzene–methanol (85 : 15) gave no spot corresponding to that of 2-*m*-nitrophenyl-5-phenyl-1,3,4-oxadiazole. The $R_F$ value of compound (VIII; Z = O, R = $NO_2$) under these conditions was 0·69.

*Synthesis of* 2-p-*Nitrophenyl*-5-*phenyl*-1,3,4-*oxadiazole* (VIII; Z = O; R = $NO_2$).—A stirred suspension of *p*-nitrobenzohydrazide (5·3 g) in pyridine (100 ml) was treated slowly (15 min) with benzoyl chloride; the mixture was heated under reflux for 30 min, cooled and poured into ice-cold water to yield a white precipitate of 1-*benzoyl*-2-(p-*nitrobenzoyl*)*hydrazine* (8·5 g, quantitative), m.p. 243—245° (from ethanol) (Found: C, 58·9; H, 4·1; N, 15·0. $C_{14}H_{11}N_3O_4$ requires C, 58·95; H, 3·85; N, 14·7%). A solution of this hydrazine (2·0 g) in phosphoryl chloride (8 ml) was heated under reflux for 8 h, cooled, and poured carefully into ice-cold water to yield white crystals of compound (VIII; Z = O, R = $NO_2$) (1·7 g, 88%), m.p. 208—209° (from ethanol), identical (mixture m.p. and i.r. spectra) with that obtained from the pyrolysis of compound (IIb; R = H) in nitrobenzene.

[26] R. Stolle, *J. Prakt. Chem.*, 1904, **69**, 145.
[27] B. Holmberg, *Arkiv Kemi*, 1944, **17A**, 1.

[28] J. Vaughan and P. A. S. Smith, *J. Org. Chem.*, 1958, **23**, 1909.