Some *trans*-Phenylazo-1,2,4-oxadiazoles

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Some *trans*-phenylazoformamide oximes (4) have been prepared from *trans*-benzenediazocyanides (3) and hydroxylamine, and converted into *trans*-3-phenylazo-1,2,4-oxadiazoles (5) by reaction with amide acetals or trialkyl orthoformates. Some 5-unsubstituted 3-phenylazo-1,2,4-oxadiazoles have been reduced to 3-amino-1-aryl-1,2,4-triazoles (8), but di-imide reduced 3-*p*-chlorophenylazo-1,2,4-oxadiazole to the corresponding hydrazine. Thiocyanogen converted 5-methyl-3-phenylazo-1,2,4-oxadiazole into the corresponding *p*-thiocyanato-compound (5o).

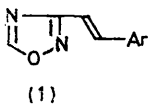
We earlier [1a,b] prepared some *trans*-3-styryl-1,2,4-oxadiazoles (1) by treating cinnamamide oximes (2) with trialkyl orthoformates or other cyclizing reagents. Some of these compounds displayed high anthelmintic activity.[1b] We now report the preparation of some *trans*-3-phenylazo-1,2,4-oxadiazoles (5), and of 3-phenyl-*trans*-5-phenylazo-1,2,4-oxadiazole (7).

We treated some *trans*-benzenediazocyanides (3) [2] with hydroxylamine and obtained *trans*-phenylazoformamide

[1] (*a*) J. A. Claisse, M. W. Foxton, G. I. Gregory, A. H. Sheppard, E. P. Tiley, W. K. Warburton, and M. J. Wilson, *J.C.S. Perkin I*, 1973, 2241; (*b*) J. A. Claisse, G. I. Gregory, and W. K. Warburton, S.Afr.P. 6,801,861 (*Chem. Abs.*, 1970, **72**, 21,696).

[2] N. Campbell, *Ann. Reports*, 1947, **44**, 134.

oximes (4). Longo [3] prepared the amide oximes (4) by extracting the nitriles (3) into ether from a mixture of arenediazonium salt and potassium cyanide and treating the ethereal extract with aqueous hydroxylamine. We have obtained higher overall yields by Longo's method than by first isolating the nitriles.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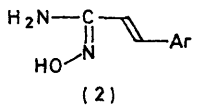
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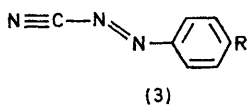
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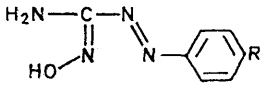
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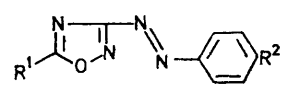

(5)

	R^1	R^2		R^1	R^2
a;	H	H	k;	Me	Br
b;	H	Cl	l;	Me	OMe
c;	H	Br	m;	Me	SMe
d;	H	OMe			O ↑
e;	H	SCN			SMe
f;	H	NO_2	n;	Me	SMe
g;	H	Me	o;	Me	SCN
h;	Me	H	p;	Me	NO_2
i;	Me	Cl	q;	Me	Me
j;	Et	Cl	r;	Et	Me

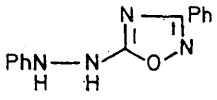
We readily obtained 5-unsubstituted 1,2,4-oxadiazoles by treating the amide oximes (4) with trimethyl or triethyl orthoformate in the presence of boron trifluoride, or with dimethylformamide dimethyl acetal; these reagents had given 3-styryl-1,2,4-oxadiazoles in good yield.[1b] However *trans*-3-*p*-nitrophenylazo-1,2,4-oxadiazole (5f) was obtained from the oxime (4; Ar = *p*-$O_2N{\cdot}C_6H_4$) only when the reaction with dimethylformamide dimethyl acetal was carried out in the presence of acetic acid.

3-Substituted 5-alkyl-1,2,4-oxadiazoles are usually made [4] by thermal cyclization of *O*-acyl amide oximes; they can also be made from amide oximes and orthoesters, for example triethyl orthoacetate.[1a,b] However *trans*-*p*-chlorophenylazoformamide *O*-propionyloxime was not affected by refluxing toluene and the *O*-acetyl analogue decomposed in refluxing acetic anhydride. Moreover, *trans*-*p*-chlorophenylazoformamide oxime was unaffected by triethyl orthoacetate. We finally obtained the 5-alkyl-1,2,4-oxadiazoles (5h—l) and (5p—r) by treating the appropriate amide oxime with dimethylacetamide dimethyl acetal or dimethylpropionamide dimethyl acetal.

We were unable to obtain either a diazocyanide or an azoformamide oxime from *p*-methylthioaniline or *p*-methylsulphinylaniline, and had to prepare the oxadiazole (5m) from (5o). Treating *trans*-3-phenylazo- or 5-methyl-3-phenylazo-1,2,4-oxadiazole (5a or h) in glacial acetic acid with the thiocyanogen (prepared *in situ* from sodium thiocyanate and bromine) gave in each case the *p*-thiocyanato-compound. 5-Methyl-*trans*-3-*p*-thiocyanatophenylazo-1,2,4-oxadiazole (5o) was converted smoothly into the methylthio-compound (5m) by methanolic sodium methoxide in the presence of methyl iodide, and peracetic acid in methylene chloride converted (5m) into the sulphoxide (5n). The thiocyanation of (5a and h), even under forcing conditions, is interesting, for direct thiocyanation is usually limited to aromatic amines, phenols, and particularly reactive hydrocarbons.[5]

5-Chloro-3-phenyl-1,2,4-oxadiazole reacted with phenylhydrazine to give the hydrazine (6); oxidation of this by manganese dioxide gave 3-phenyl-*trans*-5-phenylazo-1,2,4-oxadiazole (7). 3-Chloro-5-phenyl-1,2,4-oxadiazole did not react with phenylhydrazine.

In an attempt to obtain a 3-hydrazino-1,2,4-oxadiazole we reduced (5b) catalytically, but 2 mol. equiv. of hydrogen were rapidly taken up, and the product was the aminotriazole (8; R = Cl). Reduction of (5f) with acidic titanous chloride similarly gave the triazole (8; R = NO_2). However (5b) was smoothly reduced by di-imide to give 3-*p*-chlorophenylhydrazino-1,2,4-oxadiazole. Reduction of the nitro-compound (5f) by sodium hydrosulphide in aqueous methanol was evidently accompanied by ring fission, for the product was the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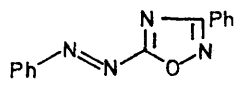
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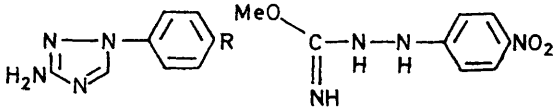
(8) (9)

imidate (9). The aminotriazole structure assigned to the reduction product (8) is supported by elemental analysis, molecular weight, and i.r. and n.m.r. spectra {(8; R = Cl) has $\nu_{max.}$ ($CHBr_3$) 3480 and 3380 cm^{-1} (NH_2), τ [$(CD_3)_2SO$] 1·12 (CH), 4·25 (2H, not coupled, NH_2), and 2·18 and 2·42 (C_6H_4)}. The formation of the triazole (8) can be explained in terms of saturation of the N=N bond and reductive fission [6] of the O–N bond of the oxadiazole, with subsequent cyclodehydration.

We have assigned the *trans*-configuration to all the cyanides, amide oximes, and oxadiazoles described here. Although *cis*-benzenediazocyanides can be isolated by working carefully at low temperatures,[7] they readily change into the more stable *trans*-isomers. The m.p.s of the nitriles (3; R = Cl, Br, or OMe) agree with those of the known *trans*-compounds. We obtained the

[3] G. Longo, *Gazzetta*, 1933, **63**, 923.
[4] F. Eloy, *Fortschr. chem. Forsch.*, 1965, **4**, 807, 812.
[5] J. L. Wood, *Org. Reactions*, 1946, **3**, 240.
[6] G. Palazzo, *Ann. Chim.* (*Italy*), 1961, **51**, 130.
[7] R. J. W. Le Fèvre and H. Vine, *J. Chem. Soc.*, 1938, 431; see also J. Suszko and T. Ignasiak, *Bull. Acad. polon. Sci. Ser. Sci. chim.*, 1970, **18**, 669.

nitrile (3; R = Me) as a solid, m.p. 75°, by a modification of the method of Le Fèvre and Northcott,[8] who, however, obtained it only as an oil. We have assumed that it has the *trans*-structure.

The nitriles (3; R = Cl, Br, Me, or MeO) all reacted with hydroxylamine to give amide oximes that were obtained stereochemically pure (i.r. and n.m.r. spectra), as were also the amide oximes (4; R = H, Cl, Me, or NO_2) that we prepared without isolating the intermediate nitriles. The oxadiazoles (5) were also obtained stereochemically pure, and it is highly probable that they, also, are *trans*-compounds.

EXPERIMENTAL

U.v. spectra were measured for solutions in ethanol. T.l.c. was carried out on Merck Kieselgel F_{254} plates in benzene containing various proportions of ethyl acetate. ^1H N.m.r. spectra were recorded at 60 MHz.

trans-*Toluene*-p-*diazocyanide*.—*p*-Toluidine, dissolved in water (100 ml) and 10N-hydrochloric acid (20 ml), was stirred at 0—4°, and sodium nitrite (7·0 g) in water (15 ml) was added dropwise. The solution was filtered and added to ice (200 g). Sodium carbonate (5·5 g) in water (50 ml) was added, the solution was stirred with light petroleum (b.p. 80—100°; 1200 ml) at 0°, and potassium cyanide (16·5 g) in water (35 ml) was added dropwise. After 30 min the petroleum layer was separated, dried (Na_2SO_4), left at room temperature for 16 h, evaporated to 300 ml, and finally cooled to −45°, giving a sticky solid (6·0 g, 41%). Recrystallization from acetone–ethanol (1 : 2 v/v) at −30° gave trans-*toluene*-p-*diazocyanide*, m.p. 75°, $\lambda_{max.}$ 342 and 233 nm (ε 10,600 and 5800) (Found: C, 66·6; H, 4·8; N, 28·3. $C_8H_7N_3$ requires C, 66·2; H, 4·8; N, 28·9%).

The following compounds were prepared similarly: *trans*-*p*-chlorobenzenediazocyanide (38%), m.p. 100—101° (lit.,[7] 105°); *trans*-*p*-bromobenzenediazocyanide (15%), m.p. 132—133° (lit.,[7] 132°); *trans*-*p*-methoxybenzenediazocyanide (89%), m.p. 113° (decomp.) (lit.,[9], 120—121°).

trans-p-*Chlorophenylazoformamide Oxime*.—*trans*-*p*-Chlorobenzenediazocyanide (1·0 g) in methanol (25 ml) was mixed with hydroxylamine (450 mg) in dry methanol (7 ml). After 15 min the red suspension was refrigerated, then filtered, giving the *amide oxime* (0·81 g, 68%), m.p. 214°, $\lambda_{max.}$ 304 and 228 nm (ε 10,000 and 8700) (Found: C, 42·3; H, 3·7; Cl, 17·6; N, 28·3. $C_7H_7ClN_4O$ requires C, 42·3; H, 3·55; Cl, 17·9; N, 28·2%). The O-*propionyl derivative* had m.p. 188° (decomp.) (from toluene) (Found: C, 47·2; H, 4·4; Cl, 13·9; N, 21·9. $C_{10}H_{11}ClN_4O_2$ requires C, 47·2; H, 4·3; Cl, 14·0; N, 22·0%).

Similarly were prepared: trans-p-*bromophenylazoformamide oxime* (82%), m.p. 206° (decomp.), $\lambda_{max.}$ 305 and 226·5 nm (ε 10,800 and 8900) (Found: C, 34·7; H, 2·9; Br, 32·3; N, 22·9. $C_7H_7BrN_4O$ requires C, 34·5; H, 2·9; Br, 32·9; N, 23·1%); trans-p-*methoxyphenylazoformamide oxime* (29%), m.p. 162—164° (decomp.) (from aqueous ethanol), $\lambda_{max.}$ 354·5 and 241·5 nm (ε 16,900 and 7900) (Found: C, 49·2; H, 5·2; N, 28·8. $C_8H_{10}N_4O_2$ requires C, 49·5; H, 5·2; N, 28·9%); *trans*-*p*-tolylazoformamide oxime (90%), m.p. 166° (lit.,[3] 164°) (Found: C, 53·8; H, 5·4; N, 31·6. Calc. for $C_8H_{10}N_4O$: C, 54·0; H, 5·6; N, 31·5%).

trans-p-*Nitrophenylazoformamide Oxime*.—*p*-Nitroaniline (27·6 g) was stirred with 10N-hydrochloric acid (40 ml), and sodium nitrite (14·5 g) in water (20 ml) was added dropwise at 0°. The product was extracted into ether, and the extract was shaken with aqueous hydroxylamine [from hydroxylamine hydrochloride (27·8 g) and 20% (w/v) sodium hydroxide]. The amide oxime separated as a brown solid (23·8 g). Extraction of the ethereal solution with 5N-hydrochloric acid and neutralization of the extract with sodium acetate gave more amide oxime (5·4 g). The two crops were dissolved in 4N-sodium hydroxide and the filtered solution when neutralized with sodium acetate gave the amide oxime (23·8 g, 57%), m.p. 166° (decomp.), forming orange *needles*, m.p. 170° (decomp.) (from ethanol), $\lambda_{max.}$ 386 and 286 nm (ε 10,900 and 14,000) (Found: C, 40·4; H, 3·4; N, 33·3. $C_7H_7N_5O_3$ requires C, 40·2; H, 3·4; N, 33·5%). *trans*-Phenylazoformamide oxime (29%), m.p. 126° (from water) (lit.,[3] m.p. 126°) was prepared similarly.

trans-3-*Phenylazo*-1,2,4-*oxadiazole* (5a).—Phenylazoformamide oxime (1·82 g) was mixed with triethyl orthoformate (15 ml) and boron trifluoride–ether complex (2 drops). The mixture was heated on a steam-bath for 1 h, then evaporated to dryness under reduced pressure. The residue was recrystallized from 95% methanol (charcoal) to give the *oxadiazole* (1·395 g, 72%), m.p. 87°, $\lambda_{max.}$ 305 nm (ε 17,400) (Found: C, 55·5; H, 3·4; N, 32·6. $C_8H_6N_4O$ requires C, 55·2; H, 3·5; N, 32·6%).

Similarly were prepared: trans-3-p-*chlorophenylazo*-1,2,4-*oxadiazole* (5b) (70%), m.p. 136° (from methanol), $\lambda_{max.}$ 316 and 231 nm (ε 18,700 and 10,000) (Found: C, 46·6; H, 2·8; Cl, 16·95; N, 26·6. $C_8H_5ClN_4O$ requires C, 46·1; H, 2·4; Cl, 17·0; N, 26·85%); trans-3-p-*bromophenylazo*-1,2,4-*oxadiazole* (5c) (57%), m.p. 136—137° (from ethanol), $\lambda_{max.}$ 320 and 232·5 nm (ε 16,300 and 9600) (Found: C, 37·7; H, 2·0; Br, 31·3; N, 22·6. $C_8H_5BrN_4O$ requires C, 38·0; H, 2·0; Br, 31·6; N, 22·3%); trans-3-p-*tolylazo*-1,2,4-*oxadiazole* (5 g) (48%), m.p. 102° [from methanol–light petroleum (b.p. 60—80°)], $\lambda_{max.}$ 321·5 and 231 nm (ε 16,900 and 9500) (Found: C, 57·1; H, 4·3; N, 29·7. $C_9H_8N_4O$ requires C, 57·4; H, 4·3; N, 29·8%).

trans-3-p-*Nitrophenylazo*-1,2,4-*oxadiazole* (5f).—*p*-Nitrophenylazoformamide oxime (2·0 g) was heated under reflux in benzene (300 ml) with glacial acetic acid (2·0 ml), then dimethylformamide dimethyl acetal (4 ml) was added. After 90 min the benzene was removed and the residue was recrystallized from 95% methanol (charcoal), giving the *oxadiazole* (1·48 g, 78%), m.p. 190°, $\lambda_{max.}$ 298 nm (ε 21,500) (Found: C, 43·8; H, 2·3; N, 32·2. $C_8H_5N_5O_3$ requires C, 43·8; H, 2·3; N, 32·2%).

trans-3-p-*Methoxyphenylazo*-1,2,4-*oxadiazole* was similarly prepared except that the acetic acid was omitted (15% yield after chromatography on silica); m.p. 130—131°, $\lambda_{max.}$ 350 and 243 nm (ε 18,900 and 9400) (Found: C, 53·0; H, 4·0; N, 27·4. $C_9H_8N_4O_2$ requires C, 52·9; H, 4·0; N, 27·4%).

The following compounds were prepared as just described from the appropriate amide oxime and dimethylacetamide dimethyl acetal or dimethylpropionamide dimethyl acetal:[10] 5-*methyl*-trans-3-*phenylazo*-1,2,4-*oxadiazole* (5h) (86%),

[8] R. J. W. Le Fèvre and J. Northcott, *J. Chem. Soc.*, 1949, 333.

[9] L. A. Kazitsyna, E. S. Kozlov, and O. A. Reutov, *Doklady Akad. Nauk S.S.S.R.*, 1969, **160**, 600 (*Chem. Abs.*, 1965, **62**, 13,069).

[10] H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Annalen*, 1961, **641**, 22, 28.

m.p. 109° (from aqueous methanol), $\lambda_{max.}$ 307 and 224·5 nm (ε 17,300 and 9900) (Found: C, 57·6; H, 4·4; N, 30·0. $C_9H_8N_4O$ requires C, 57·5; H, 4·3; N, 29·8%); *5-methyl*-trans-3-p-*tolylazo*-1,2,4-*oxadiazole* (5q) (87·5%), m.p. 139° (from methanol), $\lambda_{max.}$ 321 and 231 nm (ε 17,100 and 9300) (Found: C, 59·4; H, 5·1; N, 27·8. $C_{10}H_{10}N_4O$ requires C, 59·4; H, 5·1; N, 27·7%); trans-3-p-*chlorophenylazo*-5-*methyl*-1,2,4-*oxadiazole* (5i) (77%), m.p. 163—164° (from methanol), $\lambda_{max.}$ 317·5 and 230 nm (ε 18,100 and 10,100) (Found: C, 48·4; H, 3·1; Cl, 15·9; N, 25·3. $C_9H_7ClN_4O$ requires C, 48·6; H, 3·2; Cl, 15·9; N, 25·2%); trans-3-p-*methoxyphenylazo*-5-*methyl*-1,2,4-*oxadiazole* (5l) (93%), m.p. 151° (from methanol), $\lambda_{max.}$ 350 and 244·5 nm (ε 20,100 and 9400) (Found: C, 54·9; H, 4·6; N, 25·9. $C_{10}H_{10}N_4O_2$ requires C, 55·1; H, 4·6; N, 25·7%); trans-3-p-*chlorophenylazo*-5-*ethyl*-1,2,4-*oxadiazole* (5j) (75%), m.p. 109° (from methanol), $\lambda_{max.}$ 318 and 230·5 nm (ε 18,300 and 10,200) (Found: C, 50·7; H, 4·0; Cl, 15·0; N, 23·7. $C_{10}H_9ClN_4O$ requires C, 50·7; H, 3·8; Cl, 15·0; N, 23·7%); *5-ethyl*-trans-3-p-*tolylazo*-1,2,4-*oxadiazole* (5r) (91%), m.p. 97° (from aqueous methanol), $\lambda_{max.}$ 322 and 231·5 nm (ε 18,900 and 9200) (Found: C, 60·7; H, 5·6; N, 25·8. $C_{11}H_{12}N_4O$ requires C, 61·1; H, 5·6; N, 25·9%).

trans-3-p-*Thiocyanatophenylazo*-1,2,4-*oxadiazole* (5e).—A solution of *trans*-3-phenylazo-1,2,4-oxadiazole (2·74 g) and sodium thiocyanate dihydrate (4·72 g) in glacial acetic acid (11 ml) was cooled to 0°. Bromine (0·88 ml; 2·57 g) was added with stirring during 10 min. The mixture was stirred at 18° for 1 h, and at 60° for 1·5 h, cooled, and poured into water (75 ml). The solution was filtered, and the product was isolated with ethyl acetate, leaving a yellow solid, which was recrystallized from aqueous methanol, giving the p-*thiocyanato-compound* (1·01 g, 28%), m.p. 160—161°, $\lambda_{max.}$ 326 and 232 nm (ε 17,000 and 9500), τ ($CDCl_3$) 0·72 (CH) and 1·80 and 2·22 (ABq, *J* 9 Hz, *p*-C_6H_4) (Found: C, 46·8; H, 2·3; N, 30·5; S, 13·9. $C_9H_5N_5OS$ requires C, 46·8; H, 2·2; N, 30·3; S, 13·8%).

5-Methyl-trans-3-p-*thiocyanatophenylazo*-1,2,4-*oxadiazole* (5o) was prepared similarly (34% yield); m.p. 163—164° (from methanol), $\lambda_{max.}$ 326·5 and 232·5 nm (ε 17,500 and 9200), τ ($CDCl_3$) 1·81 and 2·30 (ABq, *J* 8·5 Hz, *p*-C_6H_4) and 7·30 (CH_3) (Found: C, 48·7; H, 3·0; N, 28·6; S, 13·2. $C_{10}H_7N_5OS$ requires C, 49·0; H, 2·9; N, 28·5; S, 13·1%). The mother liquors yielded trans-3-p-*bromophenylazo*-5-*methyl*-1,2,4-*oxadiazole* (5k), m.p. 165—166°, $\lambda_{max.}$ 320·5 and 232 nm, τ ($CDCl_3$) 1·97 and 2·27 (ABq, *J* 8·5 Hz) and 7·28 (CH_3) (Found: C, 40·4; H, 2·7; Br, 29·5; N, 21·1. $C_9H_7BrN_4O$ requires C, 40·5; H, 2·6; Br, 29·9; N, 21·0%).

5-Methyl-trans-3-p-*methylthiophenylazo*-1,2,4-*oxadiazole* (5m).—The preceding thiocyanate (4·14 g) was stirred in methanol (1·5 l) containing methyl iodide (1·5 ml, 3·415 g). A solution prepared by dissolving sodium (490 mg) in methanol (80 ml) was added in one portion at room temperature. The solution was left for 90 min, then 2N-hydrochloric acid (20 ml) and water (100 ml) were added, and the methanol was removed under reduced pressure, giving the methylthio-compound (3·81 g, 96·4%), m.p. 160—161°. A *sample* recrystallized from toluene–light petroleum (b.p. 80—100°) had m.p. 164—165°, $\lambda_{max.}$ 380 and 257 nm (ε 16,100 and 9700) (Found: C, 51·3; H, 4·3; N, 24·2; S, 13·4. $C_{10}H_{10}N_4OS$ requires C, 51·3; H, 4·3; N, 23·9; S, 13·7%).

5-Methyl-trans-3-p-*methylsulphinylphenylazo*-1,2,4-*oxadiazole* (5n).—The preceding compound (2·0 g) in methylene chloride (200 ml) was stirred at −5°, and part of a solution of '40%' peracetic acid (Laporte) (3 ml) in methylene chloride (100 ml) was added in portions. The reaction was monitored by t.l.c. After 55 ml had been added, the solvent was removed, and the residue was stirred with light petroleum (b.p. 40—60°; 100 ml), then recrystallized from toluene (75 ml), giving the *sulphoxide* (1·79 g, 84%), m.p. 172—173°, $\lambda_{max.}$ 315 and 229 nm (ε 15,500 and 8800) (Found: C, 47·8; H, 4·0; N, 22·4; S, 13·0. $C_{10}H_{10}N_4O_2S$ requires C, 48·1; H, 4·0; N, 22·4; S, 12·8%).

3-Phenyl-5-phenylhydrazino-1,2,4-*oxadiazole* (6).—5-Chloro-3-phenyl-1,2,4-oxadiazole (987 mg) and phenylhydrazine (1·90 g) were stirred in toluene (20 ml) at room temperature for 18 h. The solid that separated was washed with light petroleum (b.p. 40—60°), then with water, leaving the *hydrazino-compound* (898 mg, 65%), m.p. 177° (decomp.), $\lambda_{max.}$ 234 nm (ε 30,800), τ [$(CD_3)_2SO$] −0·30 and 1·71 (NH·NH) (Found: C, 66·8; H, 4·8; N, 22·3. $C_{14}H_{12}N_4O$ requires C, 66·6; H, 4·8; N, 22·2%).

3-Phenyl-5-phenylazo-1,2,4-*oxadiazole* (7).—Compound (6) was dissolved in acetone (20 ml) and dimethyl sulphoxide (20 ml) and stirred with active [11] manganese dioxide (3·67 g) for 75 min. The solution was filtered and the acetone was removed under reduced pressure. Water was added giving the *phenylazo-compound* (450 mg, 93%), m.p. 135—136°, $\lambda_{max.}$ 329·5 and 234·5 nm (ε 19,300 and 19,000) (Found: C, 67·2; H, 4·1; N, 22·5. $C_{14}H_{10}N_4O$ requires C, 67·2; H, 4·0; N, 22·4%).

3-p-*Chlorophenylhydrazino*-1,2,4-*oxadiazole*.— *trans*-3-*p*-Chlorophenylazo-1,2,4-oxadiazole (255 mg) was dissolved in warm ethanol (10 ml). Palladium–charcoal (10%; 17 mg) was added, followed by hydrazine hydrate (91%; 0·2 ml), dropwise, with stirring. The mixture was stirred for 1·5 h more, then poured into water (100 ml). Isolation with chloroform and recrystallization from aqueous methanol gave the *hydrazino-compound* as orange needles (200 mg, 88%), m.p. 132—133°, $\lambda_{max.}$ 294 and 243·5 nm (ε 1700 and 13,700), $\nu_{max.}$ ($CHBr_3$) 3350 cm^{-1} (NH), τ [$(CD_3)_2SO$] 1·54 (CH), 2·82 and 3·19 (ABq, *J* 9 Hz, aromatic), and 1·95 and 3·32 (NH·NH) (Found: C, 45·5; H, 3·4; Cl, 16·6; N, 27·0. $C_8H_7ClN_4O$ requires C, 45·6; H, 3·35; Cl, 16·8; N, 26·6%).

3-Amino-1-p-*chlorophenyl*-1,2,4-*triazole* (8; R = Cl).—*trans*-3-*p*-Chlorophenylazo-1,2,4-oxadiazole (5·96 g) in methanol (400 ml) was hydrogenated over 5% palladium–charcoal (1·07 g) (uptake 2 mol. equiv. in 80 min). Filtration and concentration to 60 ml gave the *triazole* (3·77 g, 68%), m.p. 206—207°, $\lambda_{max.}$ 276 nm (ε 15,000) (Found: C, 49·6; H, 3·9; Cl, 17·7; N, 29·2%; *M* (Rast), 183. $C_8H_7ClN_4$ requires C, 49·4; H, 3·6; Cl, 18·2; N, 28·8%; *M*, 194·6).

3-Amino-1-p-*nitrophenyl*-1,2,4-*triazole* (8; R = NO_2).—*trans*-3-*p*-Nitrophenylazo-1,2,4-oxadiazole (100 mg) was stirred in 5N-hydrochloric acid (50 ml), and acidic titanium(II) chloride solution (15% w/v; 2 ml) was added during 90 min. The suspension was heated to 70°, the resulting solution was cooled, and the pH was adjusted to 7 (solid Na_2CO_3). The product was isolated with ethyl acetate and recrystallized from ethyl acetate–methanol, giving the *triazole* as yellow needles (69 mg, 80%), m.p. 301° (decomp.), $\lambda_{max.}$ 238·5 and 334·5 nm (ε 9200 and 13,200), $\nu_{max.}$ (Nujol) 1320 and 1492 (NO_2), 3440 and 3335 (NH_2), and 840 cm^{-1} (*p*-C_6H_4), τ [$(CD_3)_2SO$] 0·90 (CH), 4·04 (NH_2), and 1·60 and

[11] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1948, 426.

2·01 (ABq, J 9 Hz, p-C_6H_4) (Found: C, 45·1; H, 3·3; N, 32·6. $C_8H_7N_5O_2$ requires C, 46·8; H, 3·4; N, 34·2%).

Methyl p-*Nitrophenylazoformimidate* (9).—*trans*-3-*p*-Nitrophenylazo-1,2,4-oxadiazole (200 mg) was dissolved in hot methanol (50 ml), and sodium sulphide nonahydrate 0·31 g) in water (2 ml) was added dropwise with stirring during 15 min. The solution was left for 1 h, then evaporated to dryness. The residue was recrystallized from aqueous methanol to give the *imidate* as deep red plates (80 mg, 46%), m.p. 165—166°, $\lambda_{max.}$ 411 and 240·5 nm (ε 7600 and 13,800), τ [$(CD_3)_2SO$] 6·27 (OCH_3), 3·88 (2H, NH), 1·01 (C=NH), and 1·98 and 3·18 (ABq, J 9·5 Hz, p-C_6H_4) (Found: C, 45·7; H, 4·8; N, 27·5. $C_8H_{10}N_4O_3$ requires C, 45·7; H, 4·8; N, 26·7%).

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