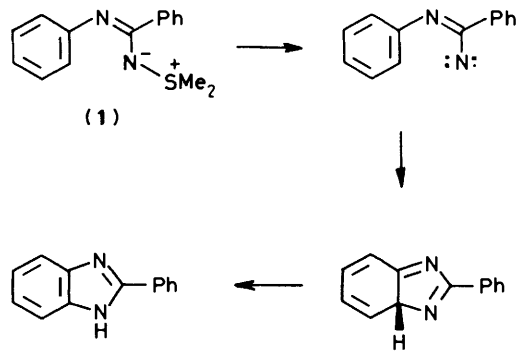
Intramolecular Reaction Between Nitro and Carbodi-imide Groups; A New Synthesis of 2-Arylbenzotriazoles

Peter G. Houghton, David F. Pipe, and Charles W. Rees*
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

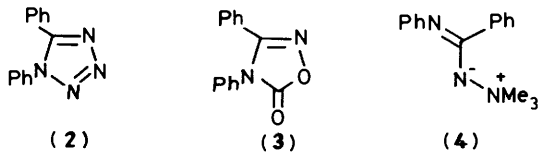
1-(2-Nitrophenyl)-5-phenyltetrazole (**5b**) decomposes when heated to give nitrogen, carbon dioxide, and 2-phenylbenzotriazole (**6**) in high yield. This new molecular rearrangement proceeds *via* 2-nitrophenyl(phenyl)carbodi-imide (**8**). Other precursors of this carbodi-imide, *i.e.* oxadiazolone (**10**), oxadiazolethione (**11**), oxathiadiazole 2-oxide (**12**), and the aminimide (**16**), and carbodi-imide itself, all give 2-phenylbenzotriazole (**6**) on thermolysis, the last three in high yield. This reaction is general for diarylcarbodi-imides with an *ortho* nitro group, and their precursors, and it provides a useful new route to 2-arylbenzotriazoles. A sequence of electrocyclic ring closing and opening reactions (Scheme 5) is proposed as the mechanism of this process. The key intermediate, 2-phenyl-1,2,4-benzotriazin-3-one 1-oxide (**19**), has been isolated from a careful thermolysis of (**12**) in toluene; in solution it is in reversible equilibrium with the ring-opened form (**20**). This new nitro–carbodi-imide group interaction has been extended to the more stable nitrobiphenyl(phenyl)carbodi-imide (**25**) and nitronaphthyl(phenyl)-carbodi-imide (**24**) which, on flash vacuum pyrolysis, give benzimidazo[1,2-*f*]phenanthridine (**29**) and benz[*cd*]indazole 1-oxide (**32**) respectively, in new rearrangements.

We have shown that the photolysis of *N*-arylimidoylsulphimides [*e.g.* (**1**)] provides a good route to 2-substituted benzimidazoles, presumably by generation and cylisation of imidoyl nitrenes to 3a*H*-benzimidazoles and hence to 1*H*-benzimidazoles (Scheme 1).[1] Other routes to the same nitrenes also gives benzimidazoles.[2] These include the photolysis of 1,5-diphenyltetrazole (**2**),[3] the thermolysis of 3,4-diphenyl-1,2,4-oxadiazol-5-one (**3**),[4] and thermolysis of the aminimide (**4**).[5] To learn more about the



(1)

Scheme 1.

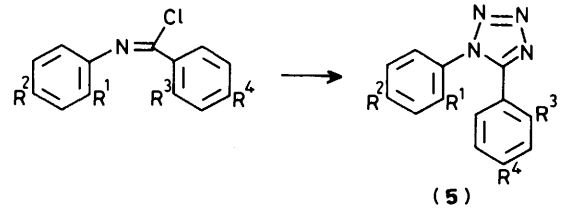


(2) (3) (4)

mechanism of these reactions, particularly about the intermediacy of 3a*H*-benzimidazoles, we studied the photolysis and thermolysis of similar sulphimides and tetrazoles but with the *ortho* positions of the *N*-aryl group substituted.[6] The products could again be rationalised by the formation and rearrangement of 3a*H*-benzimidazole intermediates. When one *ortho* position was substituted by methyl or chlorine, the nitrene cyclised exclusively to the unsubstituted position, as expected. However, when the *ortho* substituent was methoxycarbonyl, cyclisation to the substituted position competed effectively with that to the unsubstituted position.[7] To explore this unexpected directing effect of the ester group further, particularly with respect to possible through-space interaction of its oxygen atoms with the highly electrophilic nitrene, other related groups were introduced into the same *ortho* position. When this group is nitro, thermolysis of the 1-(2-nitrophenyl)-5-phenyltetrazole (**5b**) gave 2-phenylbenzotriazole (**6**) in high yield. We describe here this new mode of decomposition, which is mechanistically interesting and provides a useful synthesis of 2-arylbenzotriazoles, and two extensions of it.[8]

Results and Discussion

Preparation of Tetrazoles.—1,5-Diaryltetrazoles (**5**) were prepared as shown (Scheme 2). The imidoyl chlorides were formed from the anilides and phosphorus pentachloride in hot benzene or toluene, and converted into the tetrazoles with sodium azide in dimethylformamide, essentially by the method of Kabada,[9] in excellent yields (80—90%). Attempted pre-



(5)

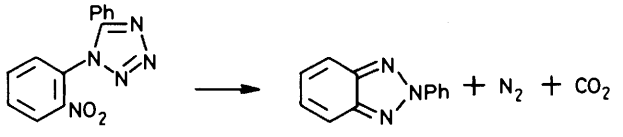
a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = NO_2$, $R^2 = R^3 = R^4 = H$
c; $R^2 = NO_2$, $R^1 = R^3 = R^4 = H$
d; $R^4 = NO_2$, $R^1 = R^2 = R^3 = H$
e; $R^3 = NO_2$, $R^1 = R^2 = R^4 = H$
f; $R^4 = Cl$, $R^1 = R^2 = R^3 = H$
g; $R^1 = NO_2$, $R^2 = R^3 = H$, $R^4 = Cl$
h; $R^1 = R^4 = NO_2$, $R^2 = R^3 = H$
i; $R^1 = R^3 = H$, $R^2 = NO_2$, $R^4 = Cl$
j; $R^1 = R^3 = H$, $R^2 = R^4 = NO_2$
k; $R^1 = R^2 = NO_2$, $R^3 = R^4 = H$
l; $R^1 = CN$, $R^2 = R^3 = R^4 = H$

Scheme 2.

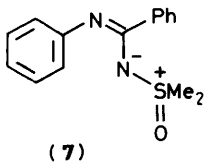
paration of the dinitrophenyltetrazole (**5k**) in this way failed; the imidoyl side-chain was lost and 6-nitrobenzofuroxan was formed in moderate yield. The tetrazole (**5k**) was prepared by treatment of the isolated imidoyl chloride with sodium azide in aqueous acetone solution.[10]

Thermolysis of Tetrazoles.—Thermolysis of 1-(2-nitrophenyl)-5-phenyltetrazole (**5b**) in bromobenzene at 156 °C gave 2-phenylbenzotriazole (**6**) in 80% yield. The same product was obtained (80—90%) from thermolysis in 1,2-dichlorobenzene at 180 °C, 1,2,4-trichlorobenzene at 215 °C, acetophenone at 200 °C, and nitrobenzene at 210 °C. Reaction times varied from several minutes at the highest temperature to several hours at the lowest. The tetrazole (**5b**) decomposed much faster than 1,5-diphenyltetrazole (**5a**) under the same conditions.

Transformation of (**5b**) into (**6**) requires the loss of nitrogen,



(**5b**) (**6**)

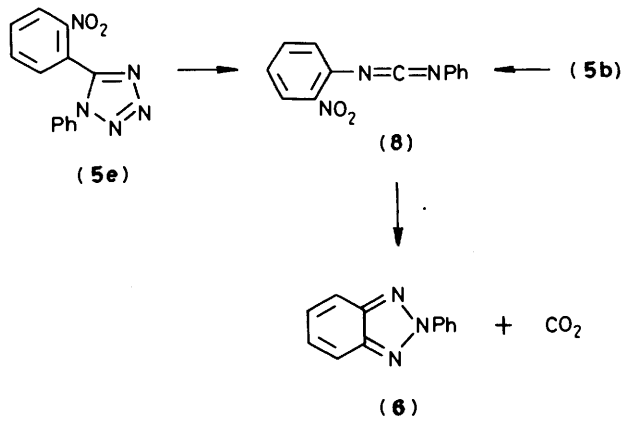


(**7**)

as expected for a tetrazole, and either carbon dioxide or carbon monoxide and oxygen. Direct mass spectral analysis of the evolved gases showed significant increases in the background nitrogen (28.006 15) and carbon dioxide 43.9898) peaks and no peak (27.9949) for carbon monoxide. The evolved gases also gave a positive test for carbon dioxide (lime water) and a negative test for carbon monoxide (palladous chloride). Thermolysis of (**5b**) in dimethyl sulphoxide gave 2-phenylbenzotriazole (**6**) in reduced yield (34%) together with 2-nitroaniline (18%); no imidoylsulphoximide (**7**) could be detected, suggesting that the reaction does not proceed through an imidoyl nitrene or nitrenoid species.

The mode of formation of the benzotriazole (**6**) from the tetrazole (**5b**) was not immediately obvious; nitrogen is lost and the phenyl group has migrated from carbon to nitrogen, but the destruction of the nitro group and particularly the formation of carbon dioxide, presumably from the nitro group oxygen atoms and the tetrazole carbon atom, was surprising. Tetrazole decompositions normally require a higher temperature than that for (**5b**), although an *o*-carboxylic acid group has been shown to lower the decomposition temperature.[11] Thermolysis of the 2,4-dinitrophenyltetrazole (**5k**) was even faster in boiling bromobenzene, producing a good yield of 5-nitro-2-phenylbenzotriazole in 45 min. Under the same conditions 1,5-diphenyltetrazole (**5a**) and 1-(4-nitrophenyl)-5-phenyltetrazole (**5c**) were stable. Heating the *o*-cyano derivative (**5l**) in 1,2,4-trichlorobenzene (215 °C) for 0.5 h produced exclusively a carbodi-imide (see below); at this temperature the unsubstituted compound (**5a**) was still unchanged. Thus an *ortho* electron withdrawing group in the 1-phenyl ring facilitates decomposition of the tetrazole, and this effect is considerably enhanced by a second, conjugated electron-withdrawing group.

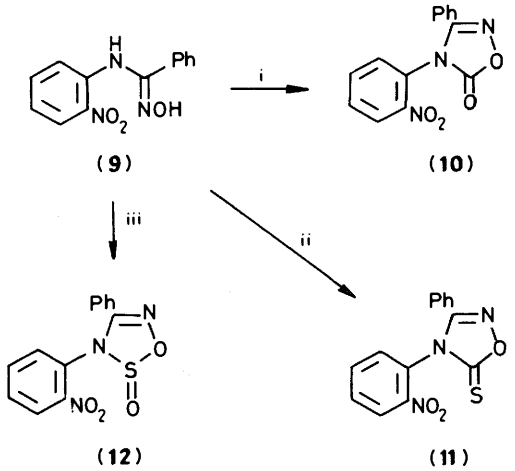
1,5-Diaryltetrazoles are known to decompose thermally to carbodi-imides,[12] and the simplest pathway for the formation of benzotriazole (**6**), nitrogen, and carbon dioxide from tetrazole (**5b**) would appear to involve the carbodi-imide (**8**). This was strongly supported by the observation that 1-phenyl-5-(2-nitrophenyl)tetrazole (**5e**), which could rearrange to the same carbodi-imide (**8**) on loss of nitrogen, did indeed give 2-phenylbenzotriazole (**6**) in high yield on thermolysis in 1,2,4-



(**5e**) (**8**) (**5b**) (**6**)

trichlorobenzene for 9 h; the rearrangement of (**5e**) was slower than that of (**5b**) because the *o*-nitrophenyl group migrates more slowly than the phenyl group. The effects of these and other substituents in the thermolysis of 1,5-diaryltetrazoles (**5**) are detailed in the Experimental section. The presence of an *o*-nitro group in the intermediate carbodi-imide leads to benzotriazoles in high yield. In its absence the carbodi-imide and the urea derived therefrom are isolated, together with the benzimidazole which is formed by imidoyl nitrene cyclisation when the 1-phenyl group does not contain an electron-withdrawing group.

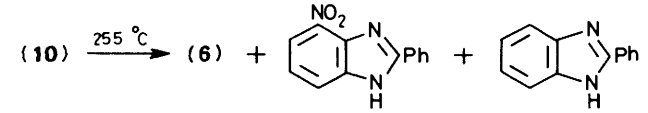
Alternative Generation of the Carbodi-imides.—To provide further support for carbodi-imides as intermediates in the diaryltetrazole decomposition, other carbodi-imide precursors, both cyclic and acyclic, were studied. The oxadiazolone (**10**), oxadiazolethione (**11**), and oxathiadiazole 2-oxide (**12**) could each rearrange to the carbodi-imide (**8**) on extrusion of CO_2, COS, and SO_2 respectively. They were prepared from the amidoxime (**9**), for which an improved preparation is reported, as shown in Scheme 3. Thermolysis of the oxadiazolone (**10**), previously reported[4] to give only 4-nitro-2-phenyl-



(**9**) (**10**) (**12**) (**11**)

Scheme 3. *Reagents:* i, $ClCO_2Et$; ii, $CSCl_2$; iii, $SOCl_2$

benzimidazole (**13**) required a relatively high temperature; it was carried out at 255 °C in diphenyl ether and in the melt, with very similar results. Besides recovered starting material (20%), 2-phenylbenzotriazole (**6**) (10%), 4-nitro-2-phenylbenzimidazole (**13**) (35%) and 2-phenylbenzimidazole (**14**) (3%)

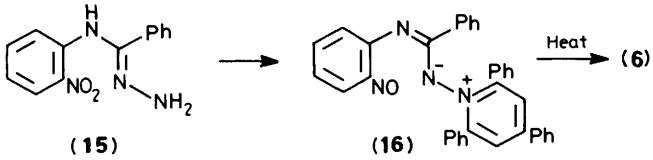


(**10**) → (**6**) + (**13**) + (**14**)

were formed; benzotriazole (**6**) and nitrobenzimidazole (**13**) were the expected products. The small amount of 2-phenylbenzimidazole may have arisen by cyclisation of the imidoyl nitrene to the substituted *ortho* position to give a 3a-nitro-3a*H*-benzimidazole with subsequent loss of the nitro group after it has undergone a [1,5] shift to nitrogen; the *N*-nitro compound could well be hydrolysed during isolation.

The oxadiazolethione (**11**) was also thermally stable, but at the same temperature (255 °C) decomposed to give similar proportions of the same products as the oxadiazolone (**10**). However the oxathiadiazole 2-oxide (**12**) decomposed rapidly in boiling bromobenzene (156 °C) to give 2-phenylbenzotriazole (**6**) in excellent yield. Formation and decomposition of the carbodi-imide (**8**) could be clearly monitored spectroscopically. 3,4-Diaryloxathiadiazole 2-oxides, like (**12**), are known to give carbodi-imides almost quantitatively on heating.[13]

Thermolysis of triphenylpyridinium aminimides has recently been shown to provide a good route to carbodi-imides.[14] The aminimide (**16**) was therefore prepared, from the amidrazone (**15**) and 2,4,6-triphenylpyrylium perchlorate, and then heated in 1,2-dichlorobenzene for 1 h to give 2-phenylbenzotriazole (**6**) in good yield.



(**15**) → (**16**) → (**6**)

Finally, a series of 2-nitrophenyl(aryl)carbodi-imides were prepared in standard ways from the corresponding thioureas, with mercuric oxide or with 2-chloro-1-methylpyridinium iodide (see Experimental section). They were isolated by rapid column chromatography and had a characteristic intense i.r. band at 2 120—2 170 cm^{-1}. The carbodi-imides were pure by t.l.c. and were used immediately, being dissolved in a solvent, usually bromobenzene, and heated to reflux under nitrogen. They gave 2-arylbenzotriazoles in good overall yields from the corresponding thioureas. Reaction times varied from several minutes to several hours depending upon the aryl substitutents.

The symmetrical bis-2-nitrophenylcarbodi-imide was prepared by dimerisation of 2-nitrophenyl isocyanate with 3-methyl-1-phenyl-2,5-dihydrophosphole 1-oxide as catalyst.[15] This carbodi-imide was the only one previously recorded with an *o*-nitro group, but there was no report of its thermal rearrangement.[15]

1-(2-Nitrophenyl)-3-R-carbodi-imides (R = t-butyl, benzyl and 2-pyridyl) did not undergo this thermal rearrangement. Extensive heating in a range of solvents at temperatures up to 215 °C (1,2,4-trichlorobenzene) failed to cause any rearrangement; i.r. monitoring showed that these carbodi-imides were thermally very stable. The stretching vibration at 2 120—2 170 cm^{-1} slowly decreased in intensity, with the formation of tarry material over a period of 24 h.

The synthetic utility of this general route to 2-arylbenzotriazoles, which starts from readily available materials and gives 2-isomers exclusively, has already been demonstrated. 2-Diphenylaminophenyl(2-nitrophenyl)carbodi-imide, prepared from the corresponding thiourea, was heated in bromobenzene for 45 min to give the required 2-(2-diphenylaminophenyl)benzotriazole (**17**) (75%); thus a bulky *ortho*-substituent on the 2-aryl group is well tolerated.[16] Heating the appropriate 5-aryl-1-(2-nitrophenyl)tetrazoles in nitrobenzene gave the 2-methoxy- and 2,6-dimethoxy-phenylbenzotriazoles (**18**; R = H, OMe) which were otherwise difficult to obtain.[17]

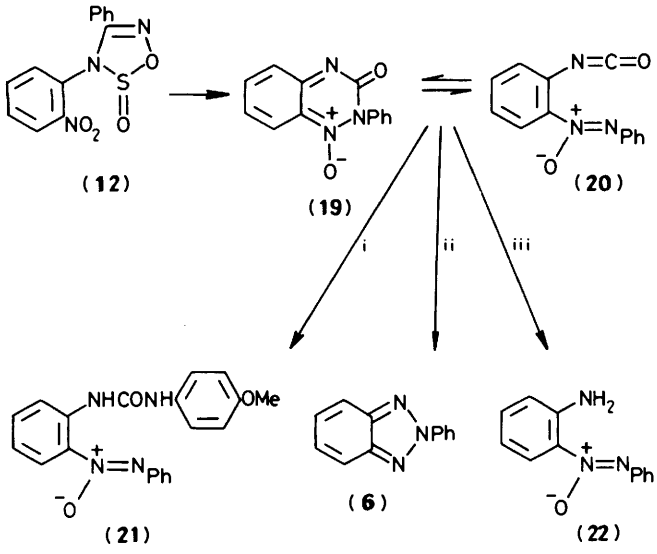
(**17**) (**18**)

Mechanism of the Rearrangement.—With the clear demonstration that 2-nitrophenyl(phenyl)carbodi-imide (**8**) was the key intermediate in the formation of benzotriazole (**6**) it was of interest to uncover the mechanism of this transformation. A major clue came from carefully monitoring the decomposition of oxathiadiazole 2-oxide (**12**), the 'cleanest' source of benzotriazole (**6**), under mild conditions. In some of the decompositions described above a transient red intermediate had been observed, and this red colour persisted in the thermolysis of (**12**) in boiling toluene. Analysis by t.l.c. showed that carbodi-imide (**8**) was formed rapidly (*ca.* 30 min) and was then replaced by the red compound which in turn was replaced, over several hours, by 2-phenylbenzotriazole (**6**). After 3 h, compounds (**12**) and (**8**) had disappeared, the red colour had reached maximum intensity and only a little benzotriazole (**6**) had appeared. Evaporation of the solvent then gave a blood-red solid which was purified by crystallisation from acetone. Further thermolysis of the red solid, in the melt or in bromobenzene, gave the benzotriazole (**6**) quantitatively. I.r. analysis of the coloured intermediate showed different spectra in the solid and liquid phases. There was a strong carbonyl peak at 1 695 cm^{-1} in the solid phase (KBr disc) but this was diminished in solution (CCl_4) and a new absorption at 2 260 cm^{-1}, suggesting an isocyanate group, appeared. The ^1H n.m.r. spectrum showed only aromatic protons. On this evidence the red compound was assigned structure (**19**) in the solid phase and (**20**) in solution. The interconversion of structures (**19**) and (**20**) was reversible. Further support for these structures came from treatment with *p*-anisidine which gave the urea (**21**) (90%), acidic hydrolysis which gave the benzotriazole (**6**) (93%), and basic hydrolysis which gave 2-aminoazoxybenzene (**22**) (71%) Scheme 4). The 1,2,4-benzotriazin-3-one 1-oxide structure (**19**) was finally confirmed for the red solid by *X*-ray crystallography.*

2-Aryl-1,2,4-benzotriazin-3-one 1-oxides have not been reported before, although 2*H*-derivatives have been prepared by base catalysed cyclisation of 2-nitroarylureas.[18] An attempt to synthesise the 2-phenyl compound (**19**) by a similar cyclisation of 2-nitrophenyl(phenyl)urea was unsuccessful. A closely related interconversion, between 6-methyl-2-(*p*-tolyl)-1,2,4-benzotriazin-3-one and the azoisocyanate tautomer, has been reported.[19]

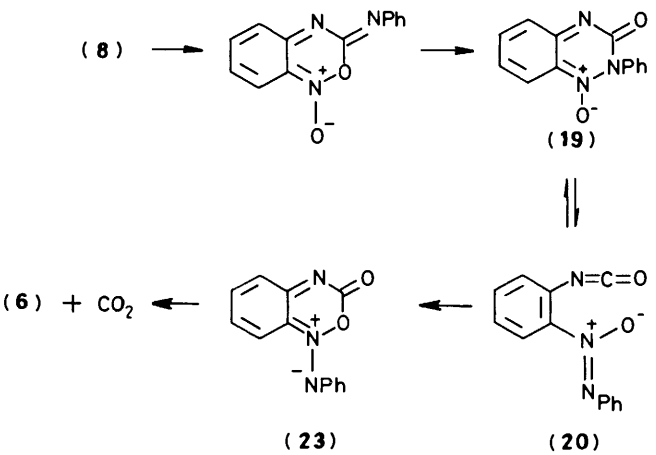
With the identification of the tautomers (**19**) and (**20**) as intermediates in the conversion of carbodi-imide (**8**) into

* Determined by Dr. D. J. Williams of this Department.



Scheme 4. *Reagents:* i, $MeOC_6H_4{\cdot}NH_2$-*p*; ii, heat or dilute aqueous H_2SO_4; iii, dilute aqueous KOH

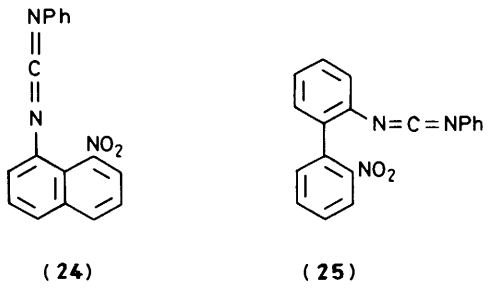
benzotriazole (**6**), an overall mechanism involving a sequence of electrocyclic ring closing and opening reactions can be proposed (Scheme 5). Initial closure of the nitro group onto the



Scheme 5.

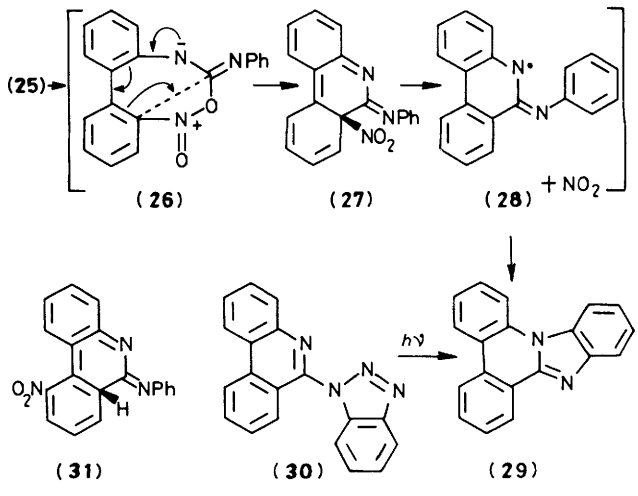
carbodi-imide carbon is followed by a rapid Dimroth-type rearrangement to give (**19**). The isocyanate (**20**) can revert rapidly to (**19**) or, more slowly, cyclise in an alternative way to give (**23**); this now contains an –OCO– structural unit and can readily decompose by breaking of a weak N–O bond to give carbon dioxide and 2-phenylbenzotriazole (**6**), possibly *via* 2-nitrenoazobenzene.

Extensions of this Nitro Group–Carbodi-imide Interaction.— In view of this very efficient interaction between the *ortho* related nitro and carbodi-imide groups, we decided to investigate the analogous naphthalene (**24**) and biphenyl (**25**) compounds in which the two groups are 1,3- and 1,4-related, respectively. The functional groups are not conjugated in (**24**) and are only weakly conjugated, through the biphenyl system, in (**25**). We find that these two compounds undergo different, new thermal rearrangements.



The carbodi-imides were prepared in high yield from the corresponding thioureas by treatment with 2-chloro-1-methylpyridinium iodide and triethylamine, as before. They were thermally much more stable than the analogous benzene derivative (**8**), presumably because the initial, favourable electrocyclic reaction proposed for (**8**) is not possible in (**24**) and would have a much higher activation energy in (**25**). The carbodi-imides were unchanged when heated for several hours in boiling 1,2,4-trichlorobenzene, and they gave complex mixtures when heated in the melt at 270 °C under nitrogen; they were therefore subjected to flash vacuum pyrolysis.

Pyrolysis of compound (**25**) at 750 °C and 0.015 mmHg gave benzimidazo[1,2-*f*]phenanthridine (**29**) in 45% yield after chromatographic purification. The identity of this pentacyclic product was confirmed by an independent synthesis. Since none of the literature preparations[20] of (**29**) was entirely suitable, we devised a simple alternative route to it: condensation of 6-chlorophenanthridine with 2-nitroaniline, reduction of the nitro group, and diazotisation of the resulting amine readily gave the phenanthridinylbenzotriazole (**30**) and photolysis of this gave the required product (**29**). Formation of (**29**) from carbodi-imide (**25**), with the formal loss of nitrous acid, suggests closure of the carbodi-imide group onto the nitro-bearing carbon of the biphenyl to give tetrahedral intermediate (**27**). This intermediate could readily dissociate into nitrogen dioxide and the highly stabilised organic radical (**28**), which could cyclise once more to give, after aromatisation, the observed product (**29**) (Scheme 6). Collapse of the carbodi-imide to give



Scheme 6.

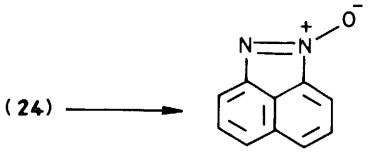
intermediate (**27**) might be expected to be accompanied by similar collapse to the unsubstituted *ortho* position, to give the isomeric intermediate (**31**), which in turn would be expected to give a nitro derivative of product (**29**) or, more likely, 6-anilino-

10-nitrophenanthridine. Neither of these products was detected in the pyrolysate, the latter by direct comparison with an authentic specimen, prepared from 10-nitrophenanthridone.[21]

This apparent selectivity for closure onto the nitro-bearing position suggests some attractive interaction between the carbodi-imide and nitro groups, the extreme of which would be O–C bond formation to give the intermediate (**26**), by a process exactly analogous to that proposed above as the first step in the transformation of the phenylcarbodi-imide (**8**). The intermediate (**26**) could then rearrange to (**27**), as shown, possibly *via* a fused tetracyclic system. Interaction between the carbodi-imide and nitro groups could also be favoured by the known propensity for 2,2′-substituted biphenyls to adopt the *cisoid* conformation in the gaseous and condensed phases.[22]

Some evidence for the decisive influence of the nitro group in the pyrolysis of (**25**) was found in the flash vacuum pyrolysis of the compound with the nitro group omitted: when biphenyl-2-yl(phenyl)carbodi-imide was pyrolysed under exactly the same conditions as (**25**), it was recovered largely unchanged and only 4% of the cyclisation product, 6-anilinophenanthridine, was obtained. Thus the nitro group in (**25**) controls the direction of ring closure and provides a lower energy pathway for it, as in the mechanism proposed.

The naphthylcarbodi-imide (**24**) was also pyrolysed at 750 °C and 0.015 mmHg, but on a smaller scale (10 mg) since it sublimed very slowly. It gave benz[*cd*]indazole 1-oxide (**32**) in good yield (70%) though the other volatile component, probably phenyl isocyanate, was not identified. The *N*-oxide (**32**) could reasonably be formed by transfer of oxygen from



nitro to carbodi-imide, as proposed above; but since the *peri* nitrogen atoms are not now conjugated, and because the molecular geometry allows, they interact through space to form an N–N bond, with the elimination of phenyl isocyanate.

Conclusion

There are many, usually catalysed, reactions which involve neighbouring group participation in *ortho* substituted nitrobenzene derivatives and which are useful in heterocyclic syntheses.[23] To these may now be added the nitro-carbodi-imide interactions described here. Intramolecular nucleophilic attack by the nitro group oxygen upon the carbodi-imide carbon, to form 6-, 7-, and 8-membered ring intermediates appears to be general. After this initial attack, reactions of the benzene (**8**), naphthalene (**24**), and biphenyl (**25**) derivatives diverge, to form 5-membered heterocyclic products by different pathways.

Experimental

I.r. spectra were recorded for liquids as thin films and for solids as Nujol mulls unless otherwise stated on Perkin Elmer 527 and 298 spectrophotometers, and calibrated against polystyrene. U.v. spectra were recorded on a Pye Unicam SP800 spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Bruker WM 250 (operating at 250 MHz) or on a Perkin Elmer R32 (operating at 90 MHz). Mass spectra were recorded using a VG Micromass 7070B mass spectrometer operating at 70 eV using a direct insertion probe. Silica gel H (Merck, type 60) was used for column chromatography, pressure being applied at 5—10 lb in^{-2}. Silica gel GF_{254} (Merck) was used for thin layer chromatography (t.l.c.) and PF_{254} (Merck) for preparative layer chromatography (p.l.c.). Ether refers to diethyl ether and petroleum refers to light petroleum, b.p. 40—60 °C, unless stated otherwise. Solvents were dried by standard procedures. Melting points were determined on a Kofler hot stage apparatus and are uncorrected.

Preparation of the Tetrazoles (**5**).—*N*-Arylimidoyl chlorides were prepared from the corresponding amide by stirring a solution of the amide in toluene with phosphorus pentachloride (1.1 mol equiv.) at room temperature. If necessary for complete reaction, the solution was heated under reflux for 1 h. The solvent was removed under reduced pressure and the imidoyl chloride was used without further purification, except for *N*-(2,4-dinitrophenyl)benzimidoyl chloride, m.p. 118—120 ° (lit.,[24] 117.5—120.5 °C). The *N*-imidoyl chloride (0.012 mol) in dry DMF (15 ml) was added dropwise over a period of 45 min to an excess of finely ground sodium azide (0.024 mol) in dry DMF (15 ml) with vigorous stirring. The reaction temperature was kept below 25 °C during the addition. When the addition was complete the suspension was stirred for a further 45 min. Sufficient water to dissolve any inorganic salts and then to cause turbidity (1—10 ml) was added and the mixture was stored in the cold room (5 °C) for 1—4 days. The crystals produced were filtered off, washed with water, and recrystallised from ethanol. The following were prepared: 1,5-diphenyltetrazole (**5a**), m.p. 145—146 °C (lit.,[9] 145—146 °C); 1-(2-nitrophenyl)-5-phenyltetrazole (**5b**), m.p. 167—169 °C (lit.[9] 168—169 °C); 1-(4-nitrophenyl)-5-phenyltetrazole (**5c**), m.p. 153.5—155 °C (lit.,[9] 155—157 °C); 5-(4-nitrophenyl)-1-phenyltetrazole (**5d**), m.p. 181—183 °C (lit.,[9] 182—183 °C); 5-(2-nitrophenyl)-1-phenyltetrazole (**5e**), m.p. 175—177 °C (lit.,[9] 179—181 °C); 5-(4-chlorophenyl)-1-phenyltetrazole (**5f**), m.p. 155—157 °C (lit.,[12] 155.5 °C); 5-(4-chlorophenyl)-1-(4-nitrophenyl)tetrazole (**5i**), m.p. 187—188 °C (lit.,[25] 188—189 °C); 1,5-bis(4-nitrophenyl)tetrazole (**5j**), m.p. 264 °C decomp. (lit.,[26] 262 °C); 5-(4-*chlorophenyl*-1-(2-*nitrophenyl*)*tetrazole* (**5g**) (58%), m.p. 163—164 °C (ethanol) (Found: C, 51.8; H, 2.6; N, 23.2. $C_{13}H_8ClN_5O_2$ requires C, 51.8; H, 2.7; N, 23.2%); $\nu_{max.}$ 1 600, 1 520, 1 340s, 1 090, 850, 820, 780, and 730s; $\lambda_{max.}$($CHCl_3$) 249 nm (20 330); δ($CDCl_3$) 7.26—7.64 (5 H, m), 7.75—7.95 (2 H, m), and 8.19—8.35 (1 H, m); *m/z* 301 (M^+), 273, 153 (base), 139, and 125; 1-(2-*nitrophenyl*)-5-(4-*nitrophenyl*)*tetrazole* (**5h**) (46%), m.p. 210—212 °C (ethanol) (Found: C, 50.1; H, 2.6; N, 26.9. $C_{13}H_8N_6O_4$ requires C, 50.0; H, 2.6; N, 26.9%); $\nu_{max.}$ 1 610, 1 540s, 1 520s, 1 345s, and 860 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 267 nm (24 950); δ[$(CD_3)_2SO$] 8.12 (4 H, br m) and 8.17 (4 H, q); *m/z* 313 (M^+ + 1), 284, 240, 164, 150, 134, 120, and 90 (base); 1-(2,4-dinitrophenyl)-5-phenyltetrazole (**5k**), m.p. 183 °C (decomp.) (lit.,[10] 183 °C), by the method of Bianchetti,[10] but with 1:1 acetone–water as solvent in place of acetone; and 2-(5-phenyltetrazol-1-yl)benzonitrile (**5l**).[7]

Thermolysis of the Tetrazoles (**5**).—All were conducted in an atmosphere of nitrogen. Freshly distilled solvents (1 ml per 50 mg tetrazole) were used, under vigorous reflux. The solvents used were bromobenzene, b.p. 156 °C, 1,2-dichlorobenzene, b.p. 180 °C, and 1,2,4-trichlorobenzene, b.p. 215 °C. At the end of the reflux period the solvent was removed by short-path distillation and the products were purified by column chromatography and crystallisation. Unstable carbodi-imides were hydrolysed by refluxing in dioxane–30% aqueous hydrochloric acid for 1 h.

(*a*) 1,5-Diphenyltetrazole (**5a**) in trichlorobenzene for 40 min was almost unchanged; apart from starting material there was only a trace of high R_F material.

(*b*) 1-(2-Nitrophenyl)-5-phenyltetrazole (**5b**) (140 mg) in bromobenzene for 20 h gave 2-phenylbenzotriazole (**6**) (81 mg, 80%), m.p. and mixed m.p. 108—109 °C. In dichlorobenzene for 30 min (**5b**) (152 mg) gave (**6**) (101 mg, 91%) and in trichlorobenzene for 30 min, (**5b**) (200 mg) gave (**6**) (134 mg, 92%).

(*c*) 5-(2-Nitrophenyl)-1-phenyltetrazole (**5e**) (500 mg) in bromobenzene for 24 h was almost unchanged, showing only a faint fluorescent blue spot by t.l.c. corresponding to (**6**). In dichlorobenzene for 24 h, (**5e**) (200 mg) gave (**6**) (7.5 mg, 5%) and starting material (161 mg, 81%), and in trichlorobenzene for 9 h (**5e**) (500 mg) gave (**6**) (272 mg, 75%).

(*d*) 5-(4-Chlorophenyl)-1-(2-nitrophenyl)tetrazole (**5g**) (500 mg) in bromobenzene for 24 h gave 2-(4-chlorophenyl)-benzotriazole (213 mg, 56%), m.p. 169—170 °C (lit.,[27] 170—171 °C) and (**5g**) (35 mg, 7%) was recovered. In dichlorobenzene for 4 h, (**5g**) (200 mg) gave the same benzotriazole (124 mg, 82%) and in trichlorobenzene for 2.5 h, (**5g**) (500 mg) gave the same benzotriazole (320 mg, 84%).

(*e*) 1-(2-Nitrophenyl)-2-(4-nitrophenyl)tetrazole (**5h**) (100 mg) in bromobenzene for 24 h was unchanged. In dichlorobenzene for 5.5 h, (**5h**) (200 mg) gave 4-nitro-2-(4-nitrophenyl)benzimidazole, m.p. 284—285 °C, (121 mg, 66%) and 2-(4-nitrophenyl)benzotriazole (20 mg, 13%), m.p. 284 °C (lit.,[28] 282 °C). In trichlorobenzene for 5 min, (**5h**) gave a yellow solution from which a pale yellow solid crystallised. Recrystallisation from ethanol–dimethylformamide gave 2-(4-nitrophenyl)benzotriazole (110 mg, 72%).

(*f*) 1-(2,4-Dinitrophenyl)-5-phenyltetrazole (**5k**) (112 mg) in bromobenzene for 45 min gave 5-nitro-2-phenylbenzotriazole (51 mg, 60%), m.p. 175—177 °C (lit.,[29] 176.6—177 °C).

(*g*) 2-(5-Phenyltetrazol-1-yl)benzonitrile (**5l**) (50 mg) in trichlorobenzene for 30 min gave a solution showing only one component by t.l.c. The i.r. spectrum showed an intense band at 2 140 cm^{-1} indicating the product to be 2-cyanophenyl(phenyl)-carbodi-imide. The solvent was removed and the remaining oil was heated (Wood's metal bath) to 268 °C. The yellow oil darkened, but after 20 min at 268 °C the t.l.c. analysis and the i.r. spectrum showed no change; the carbodi-imide was still present.

(*h*) 5-(4-Chlorophenyl)-1-phenyltetrazole (**5f**) was unchanged in bromobenzene (24 h) and largely unchanged in dichlorobenzene (24 h); the tetrazole was recovered (77%) from the latter experiment. In trichlorobenzene for 48 h, (**5f**) (300 mg) gave (i) 4-chlorophenyl(phenyl)carbodi-imide (87 mg, 33%) as an oil (pure by t.l.c.), $\nu_{max.}$ 2 120 cm^{-1}; (ii) 2-(4-chlorophenyl)-benzimidazole (39 mg, 15%), m.p. 292 °C (lit.,[30] 296 °C); and (iii) a (disproportionation) mixture of 4-chlorophenyl(phenyl)-urea and bis-4-chlorophenylurea as shown by the i.r. spectrum ($\nu_{max.}$ 3 380 and 1 650 cm^{-1}) and the mass spectrum which showed *m/z* 280 (M^+) with a two-chlorine isotope pattern superimposed on *m/z* 246 (M^+) with a one-chlorine isotope pattern.

(*i*) 5-(4-Nitrophenyl)-1-phenyltetrazole (**5d**) was unchanged in bromobenzene (24 h) and largely unchanged in dichlorobenzene (24 h); the tetrazole (73%) was recovered from the latter experiment. In trichlorobenzene for 48 h, (**5d**) (300 mg) gave (i) 2-(4-nitrophenyl)benzimidazole (90 mg, 34%), m.p. 325 °C (lit.,[31] 329 °C), (ii) 4-nitrophenyl(phenyl)carbodi-imide[32] (25 mg, 9%) as an oil, pure by t.l.c., $\nu_{max.}$ 2 130 cm^{-1}, and (iii) a mixture (58 mg) of 4-nitrophenyl(phenyl)urea and bis-4-nitrophenylurea, $\nu_{max.}$ 3 280 and 1 635 cm^{-1}.

(*j*) 1-(4-Nitrophenyl)-5-phenyltetrazole (**5c**) (353 mg) in dichlorobenzene for 24 h gave 4-nitrophenyl(phenyl)carbodi-imide (110 mg, 35%).

(*k*) 5-(4-Chlorophenyl)-1-(4-nitrophenyl)tetrazole (**5i**) (300 mg) in trichlorobenzene for 7 h gave, after hydrolysis of the thermolysis product, 4-chlorophenyl(4-nitrophenyl)urea (266 mg, 92%), m.p. 295—305 °C (ethanol) (lit.,[33] 250 °C); $\nu_{max.}$ 3 380, 3 340, 1 735, 1 630, 1 600, 1 540, 1 335, 1 300, 1 180, and 1 110 cm^{-1}; *m/z* 291 (M^+), 273, 164, 153, 138 (base), 127, and 108.

(*l*) 1-(2-Nitrophenyl)-5-phenyltetrazole (**5b**) (266 mg) in dimethyl sulphoxide (6 ml) was heated to reflux for 4 h. After evaporation of solvent, the residue, pre-adsorbed onto silica, was chromatographed on silica with petroleum and then petroleum–dichloromethane (up to 20%) to give an oil which was subject to preparative layer chromatography on silica with ethyl acetate (10%) in chloroform to give 2-phenylbenzotriazole (**6**) (66 mg, 34%) and 2-nitroaniline (26 mg, 18%).

N-(2-*Nitrophenyl*)*benzamide Oxime* (**9**).—The following is an improved modification of the literature method.[34] A solution of sodium ethoxide (from sodium 1 g, 0.043 mol) in dry DMF (10 ml) was added to a solution of dried hydroxylamine hydrochloride (3 g, 0.043 mol) in dry DMF (15 ml). The resulting mixture was filtered and the filtrate added to a solution of *N*-(2-nitrophenyl)benzimidoyl chloride (0.017 mol) in dry diethyl ether (100 ml), and stirred magnetically for 26 h at room temperature. The ether was then removed under reduced pressure; water was gradually added, firstly to dissolve the precipitated salts and then to induce crystallisation of the product. As soon as the mixture became permanently cloudy the addition of water was stopped and the mixture chilled. The resulting solid was filtered off, washed with a small amount of 10% dichloromethane in petroleum and dried to yield *N*-(2-nitrophenyl)benzamide oxime (**9**) (3.56 g, 81%) as yellow prisms, m.p. 185 °C (lit.,[34] 184—185 °C).

4-(2-*Nitrophenyl*)-3-*phenyl*-1,2,4-*oxadiazol*-5-*one* (**10**).—This was prepared by the literature method,[4] m.p. 126 °C.

4-(2-*Nitrophenyl*)-3-*phenyl*-1,2,4-*oxadiazole*-5-*thione* (**11**).—To a solution of *N*-(2-nitrophenyl)benzamide oxime (**9**) (1.07 g, 4 mmol) in dry benzene (300 ml) at room temperature was added thiophosgene (460 mg, 4 mmol). A few drops of triethylamine were then added and the mixture stirred at room temperature for 1.5 h. The solvent was evaporated and the residue purified by chromatography on silica using dichloromethane–petroleum (1:1) to give 4-(2-*nitrophenyl*)-3-*phenyl*-1,2,4-*oxadiazole*-5-*thione* (**11**) as a pale yellow solid (949 mg, 77%), m.p. 126—128 °C (aqueous ethanol) (Found: C, 56.1; H, 3.0; N, 13.9. $C_{14}H_9N_3O_5$ requires C, 56.2; H, 3.0; N, 14.0%); $\lambda_{max.}(CHCl_3)$ 222 (ε 12 000), 248 (ε 23 000), and 285.5 nm (ε 24 000); $\nu_{max.}$ 1 610, 1 530, 1 350, 1 265, 1 170, 850, 785, and 690 cm^{-1}; $\delta(CDCl_3)$ 8.35—7.10 (m); *m/z* 299 (M^+).

3-(2-*Nitrophenyl*)-4-*phenyl*-1,2,3,5-*oxathiadiazole* 2-*Oxide* (**12**).—To a solution of *N*-(2-nitrophenyl)benzamide oxime (**9**) (1 g, 4 mmol) in dry benzene (300 ml) was added thionyl chloride (460 mg, 4 mmol). The mixture was stirred at room temperature for 1 h, filtered and the solvent removed without heating. The pale yellow solid was crystallised from ethanol, with the minimum of heating, to yield 3-(2-*nitrophenyl*)-4-*phenyl*-1,2,3,5-*oxathiadiazole* 2-*oxide* (**12**) (811 mg, 67%), m.p. 102—103 °C (Found: C, 51.2; H, 2.85; N, 13.7. $C_{13}H_9N_3O_4S$ requires C, 51.5; H, 3.0; N, 13.85%); $\lambda_{max.}(CHCl_3)$ 242 nm (ε 10 500); $\nu_{max.}$ 1 530, 1 350, 1 205, 845, 770, and 695 cm^{-1}; $\delta(CDCl_3)$ 8.06—7.33 (m); *m/z* 303 (M^+).

N-(2-*Nitrophenyl*)*benzamidrazone* (**15**).—A solution of *N*-(2-nitrophenyl)benzimidoyl chloride (0.02 mol) in dry DMF (25 ml) was added very slowly (*ca.* 65 min) (in order to avoid dimerisation) to a magnetically stirred solution of hydrazine hydrate (1.5 g, 1.5 ml, 0.03 mol) and triethylamine (2 g, 2.74 ml, 0.02 mol) in dry DMF (25 ml) at a temperature of *ca.* 50 °C. After addition was complete, the mixture was stirred overnight at room temperature. Water was then added to give separation of

a dark red oil. Cooling and trituration produced an orange solid which was filtered off, dried and purified by chromatography on silica using dichloromethane–petroleum (1:4) to give N-(2-*nitrophenylbenzamidrazone* (**15**) (3.2 g, 63%), m.p. 105—107 °C (Found: C, 61.0; H, 4.7; N, 21.9; $C_{13}H_{12}N_4O_2$ requires C, 60.9; H, 4.7; N, 21.9%); $\nu_{max.}$ 3 420, 3 340, 1 625, 1 570, 1 410, and 1 260 cm^{-1}; δ($CDCl_3$) 9.00 (s, 1 H, NH), 8.30 (dd, 1 H, Ar*H*), 7.77—6.62 (m, 8 H, Ar*H*), and 5.70 (s, 2 H, NH_2); *m/z* 256 (M^+).

N^2-(2,4,6-*Triphenylpyridinio*)-N^1-(2-*nitrophenyl*)*benzamidinide* (**16**).—This was prepared from the amide hydrazone (**15**) by the literature method,[14] m.p. 168—170 °C (benzene–petroleum b.p. 80—100 °C) (Found: C, 80.6; H, 5.2; N, 9.2. $C_{36}H_{26}N_4O_2 \cdot C_6H_6$ requires C, 80.7; H, 5.2; N, 9.0%); $\lambda_{max.}$(EtOH), 221 (ε 24 000), and 303 nm (ε 24 600); $\nu_{max.}$ 1 625, 1 600, 1 580, 1 510, 1 460, 1 375, 1 140, and 695 cm^{-1}; δ($CDCl_3$) 7.90—7.10 (m), *m/z* 546 (M^+).

Thermolysis of Alternative Precursors.—General procedure. The precursor was dissolved in the appropriate solvent (1 ml per 50 mg of compound) and heated in a Wood's metal bath preheated to *ca.* 10—15 °C higher than the boiling point of the solvent. The reactions were monitored by t.l.c. and after completion, the solvent was removed and the products separated by column or p.l.c.

(*a*) 4-(2-*Nitrophenyl*)-3-*phenyl*-1,2,4-*oxadiazol*-5-*one* (**10**).—(i) A solution of the oxadiazolone (**10**) (245 mg) in diphenyl ether was heated for 24 h to give 2-phenylbenzotriazole (**6**) (19 mg, 10%), starting material (**10**) (44 mg, 18%), 4-nitro-2-phenylbenzimidazole (**13**) (71 mg, 34%) and 2-phenylbenzimidazole (**14**) (5 mg, 3%). (ii) The oxadiazolone (**10**) (200 mg) was heated in the melt at 255 °C for 7 h to give 2-phenylbenzotriazole (**6**) (13 mg, 9%), starting material (**10**) (38 mg, 19%), 4-nitro-2-phenylbenzimidazole (**13**) (62 mg, 37%) and 2-phenylbenzimidazole (**14**) (6 mg, 4%).

(*b*) 4-(2-*Nitrophenyl*)-3-*phenyl*-1,2,4-*oxadiazole*-5-*thione* (**11**). (i) A solution of the thione (**11**) (190 mg) in diphenyl ether was heated for 6 h to give 2-phenylbenzotriazole (**6**) (5 mg, 4%), starting material (**11**) (25 mg, 13%), 4-nitro-2-phenylbenzimidazole (**13**) (38 mg, 25%), and 2-phenylbenzimidazole (**14**) (16 mg, 13%). (ii) The thione (**11**) (193 mg) was heated in the melt at 255 °C for 4 h to give 2-phenylbenzotriazole (**6**) (11 mg, 9%), an unidentified gum (37 mg), 4-nitro-2-phenylbenzimidazole (**13**) (10 mg, 7%), and 2-phenylbenzimidazole (**14**) (5 mg, 4%).

(*c*) 3-(2-*Nitrophenyl*)-4-*phenyl*-1,2,3,5-*oxathiadiazole* 2-*oxide* (**12**). (i) Thermolysis of the 2-oxide (**12**) (248 mg) in the melt at 135—140 °C for 1 h gave 2-phenylbenzotriazole (**6**) (103 mg, 64%). (ii) A solution of the 2-oxide (**12**) (195 mg) in bromobenzene was heated for 1 h to give 2-phenylbenzotraizole (**6**) (116 mg, 90%). (iii) A solution of the 2-oxide (**12**) (97 mg) in dry toluene was heated for 50 min to give 2-nitrophenyl(phenyl)-carbodi-imide (**8**) (12 mg, 15%) and 2-nitrophenyl(phenyl)urea (23 mg, 28%).

(*d*) N^2-(2,4,6-*Triphenylpyridinio*)-N^1-(2-*nitrophenyl*)*benzamidinide* (**16**). A solution of the amidinide (**16**) (255 mg) in 1,2-dichlorobenzene was heated for 1 h to give 2-phenylbenzotriazole (**6**) (61 mg, 67%) and 2,4,6-triphenylpyridine (143 mg, 95%) m.p. 137 °C.

The Preparation of Thioureas.—General procedure. To a vigorously stirred solution of the appropriate 2-nitrophenyl isothiocyanate[35] (0.01 mol) in dry benzene (10 ml) was added a solution of freshly distilled (or crystallised) amine (0.01 mol) in dry benzene (5 ml). The solution was stirred at room temperature for 5 min. If a solid was not produced the solution was warmed on a water-bath (80 °C) for 10 min. On cooling a precipitate was formed. The mixture was stirred for a further 30 min, filtered and the solid crystallised.

2-Nitrophenyl(phenyl)thiourea, 2-nitrophenyl (4-nitrophenyl)thiourea, and 2-nitrophenyl(*p*-tolyl)thiourea had the literature properties. 2,6-*Dimethylphenyl*(2-*nitrophenyl*)*thiourea* (84%), m.p. 171—173 °C (ethanol) (Found: C, 59.8; H, 5.0; N, 13.9. $C_{15}H_{15}N_3O_2S$ requires C, 59.8; H, 5.0; N, 13.9%; $\nu_{max.}$ 3 350, 3 160, 1 610, 1 550, 1 520, 1 460, 1 265, 1 210, 855, 780, 725, and 710 cm^{-1}; δ([$^2H_6$]acetone) 2.37 (s, 6 H), 9.02 (m, 7 H), and 9.15—9.59 (br s, NH, D_2O exchangeable); *m/z* 300 (M^+ − 1), 255 (base), 163, 138, and 130.

2-*Nitrophenyl*-(2,4,6-*trimethylphenyl*)*thiourea* (72%), m.p. 175—177 °C (Found: C, 60.8; H, 5.45; N, 13.3. $C_{16}H_{17}N_3O_2S$ requires C, 60.9; H, 5.4; N, 13.3%); $\nu_{max.}$ 3 340, 3 130, 1 615, 1 535, 1 350, 1 270, 1 230, 860, 790, and 750 cm^{-1}; *m/z* 314 (M^+ − 1), 269 (base), and 177.

4-*Methoxyphenyl*(2-*nitrophenyl*)*thiourea* (92%), m.p. 165—167 °C (ethanol) (Found: C, 55.4; H, 4.3; N, 13.8. $C_{14}H_{13}N_3O_3S$ requires C, 55.4; H, 4.3; N, 13.9%); $\nu_{max.}$ 3 180, 1 610, 1 590, 1 520, 1 455, 1 350, 1 250, 1 170, 1 030, 830, 785, and 745 cm^{-1}; *m/z* 303 (M^+), 285, 269, 257, 180, 165 (base), 150, 138, and 108.

4-*Methoxy*-2-*nitrophenyl*(*phenyl*)*thiourea* (62%), m.p. 159—161 °C (Found: C, 56.2; H, 4.2; N, 14.2. $C_{14}H_{13}N_3O_3S$ requires C, 55.4; H, 4.3; N, 13.9%); $\nu_{max.}$ 3 340, 3 100, 1 605, 1 550, 1 535, 1 380, 1 370, 1 230, 1 040, and 860 cm^{-1}; δ([$^2H_6$]acetone) 3.90 (s, 3 H), 7.00—8.10 (m, 9 H), and 9.03—9.67 (br m, 2 H); *m/z* 303 (M^+) 257, 168, 138, 135, and 93 (base).

2-*Nitrophenyl*(*t-butyl*)*thiourea* (93%), m.p. 155—165 °C (ethanol) (Found: C, 52.3; H, 6.0; N, 16.6. $C_{11}H_{15}N_3O_2S$ requires C, 52.15; H, 6.0; N, 16.6%); $\nu_{max.}$ 3 280, 3 220, 1 610, 1 565, 1 510, 1 470, 1 350, 1 270, 1 190, 865, 780, and 720 cm^{-1}; *m/z* 254 (M^+ − 1), 219, 207, 189, 163, 151, 138, and 133.

Benzyl(2-*nitrophenyl*)*thiourea* (72%), m.p. 119.5—121 °C (Found: C, 58.7; H, 4.6; N, 14.6. $C_{14}H_{13}N_3O_2S$ requires C, 58.5; H, 4.6; N, 14.6%); $\nu_{max.}$ 3 240, 3 180, 1 610, 1 595, 1 510, 1 480, 1 460, 1 350, 975, 780, 740, and 700 cm^{-1}; δ([$^2H_6$]acetone) 4.96 (s, 2 H) and 7.42—9.80 (m, 11 H); *m/z* 287 (M^+) 241, 220, 180, 164, 106, and 91 (base).

2-*Nitrophenyl*(2-*pyridyl*)*thiourea* (75%), m.p. 191—192 °C (Found: C, 52.7; H, 3.71; N, 20.1. $C_{12}H_{10}N_4O_2S$ requires C, 52.5; H, 3.7; N, 20.4%); $\nu_{max.}$ 3 240, 1 610, 1 550, 1 520, 1 485, 1 350, 1 325, 1 260, 1 190, 1 155, and 775 cm^{-1}; δ([$^2H_6$]-acetone) 7.14—7.86 (m); *m/z* 274 (M^+) 242, 228, 196, 168, 136, 120, and 78 (base).

4-*Methoxy*-2-*nitrophenyl*(2-*pyridyl*)*thiourea* (29%), m.p. 199—201 °C (Found: C, 51.10; H, 3.9; N, 18.3. $C_{13}H_{12}N_4O_3S$ requires C, 51.3; H, 4.0; N, 18.4%); $\nu_{max.}$ 3 250, 1 610, 1 590, 1 530, 1 385, 1 325, 1 280, 1 240, 1 190, 1 155, 1 030, and 780 cm^{-1}; δ($^2H_6$]acetone) 3.89 (s, 3 H) and 7.04—8.70 (m, 9 H); *m/z* 304 (M^+) 258, 226, 168, 136, 120, and 78 (base).

2′-*Nitrobiphenyl*-2-*yl*(*phenyl*)*thiourea.*—A mixture of 2-amino-2′-nitrobiphenyl (200 mg, 0.95 mmol), thiophosgene (125 mg, 0.95 mmol), concentrated hydrochloric acid (1 ml) in water (5 ml) and toluene (5 ml) was refluxed for 2.5 h. The cooled mixture was separated, the organic phase washed once with water, dried over magnesium sulphate and the solvent removed. The isothiocyanate thus formed was dissolved in benzene to which was added aniline (88.5 mg, 0.95 mmol). The solution was heated on a water-bath for 2 min and the solvent removed. Addition of petroleum (5 ml) followed by trituration produced a yellow solid which was crystallised from ethanol to give 2′-*nitrobiphenyl*-2-*yl*(*phenyl*)*thiourea* (150 mg, 45%), m.p. 155—156 °C (Found: C, 65.1; H, 4.3; N, 12.0. $C_{19}H_{15}N_3O_2S$ requires C, 65.3; H, 4.4; N, 11.8%); $\nu_{max.}$ 3 360, 3 150, 1 530, 1 360, 1 240, 885, 790, 770, and 755 cm^{-1}; δ([$^2H_6$]-DMSO) 7.03—8.08 (m, 13 H), 9.12 (s, 1 H), and 9.50 (s, 1 H); *m/z* 350 (M^+ + 1), 315, 303, 285, 269, 256, 167, 135, and 93.

8-*Nitro*-1-*naphthyl(phenyl)thiourea*.—1-Amino-8-nitronaphthalene (1 g, 5.3 mmol), thiophosgene (0.69 g, 5.3 mmol), concentrated hydrochloric acid (1 ml) in water (10 ml) and toluene (10 ml) were refluxed for 1.75 h. The cooled organic phase was separated and washed with water, dried over sodium sulphate and the solvent removed. The red oil was dissolved in benzene (5 ml) to which aniline (0.5 g, 5.3 mmol) was added. A yellow solid separated and on crystallisation from ethanol–dimethylformamide gave 8-*nitro*-1-*naphthyl(phenyl)thiourea* (1.7 g, 42%), m.p. 186—188 °C (Found: C, 63.2; H, 4.1; N, 12.8. $C_{17}H_{13}N_3O_2S$ requires C, 63.1; H, 4.1; N, 13.0%); $\nu_{max.}$ 3 320, 3 160, 1 515, 1 375, 1 240, 825, 765, 755, and 740 cm^{-1}; δ([$^2H_6$]-DMSO) 7.20—8.43 (m, 11 H), 9.26 (br, s, 1 H, D_2O exchangeable) and 9.82 (br s, 1 H, D_2O exchangeable); *m/z* 277 [$M^+ - 46$ (NO_2)], 230, 184, 172, 140, and 93 (base).

Formation of Carbodi-imides and Conversion into Benzotriazoles.—Method A. To a solution of the thiourea (1 mmol) in a suitable solvent (methylene chloride or acetone) was added mercuric oxide (2 mmol) and an excess of magnesium sulphate as desiccant. The suspension was vigorously stirred until t.l.c. showed complete consumption of starting material. The metal salts were filtered off and the solvent removed to give the carbodi-imide, which was thermolysed without purification as described under Method B.

Method B.[36] To a solution of the thiourea (1 mmol) in dry acetonitrile (10 ml) was added 2-chloro-1-methylpyridinium iodide (1.2 mmol). Triethylamine (2 mmol) was added to the rapidly stirred suspension; a clear solution was formed, followed by the precipitation of a solid. When the reaction was complete (t.l.c.) the solvent was removed and the residue suspended in dry methylene chloride (*ca.* 3 ml), loaded onto a chromatography column (Silica H–petroleum) and eluted with petroleum (100 ml) under hand pump pressure. The column was then eluted with methylene chloride–petroleum (1:1) which rapidly removed the carbodi-imide from the column as a fast running band. The carbodi-imides were in contact with the silica for very short periods (*ca.* 2—5 min). The solvent was removed and the carbodi-imide thermolysed without purification by dissolution in freshly distilled bromobenzene and refluxing of the solution under nitrogen until all the carbodi-imide was consumed (t.l.c.). The solvent was removed under reduced pressure and the resulting solid was purified by column chromatography (silica H, gradient elution) and crystallisation to give: 2-phenylbenzotriazole, m.p. 109—110 °C (50%, method A); 2-(*p*-tolyl)-benzotriazole, m.p. 119—121 °C (lit.,[27] 120—121 °C) (43%, method B); 2-(4-methoxyphenyl)benzotriazole, m.p. 111—113 °C (lit.,[27] 108—110 °C) (55%, method B); 2-(2,6-*dimethylphenyl*)*benzotriazole*, m.p. 91—94 °C (59%, method A) (Found: C, 75.3; H, 5.9; N, 18.8; $C_{14}H_{13}N_3$ requires C, 75.3; H, 5.9; N, 18.8%); $\nu_{max.}$ 1 340, 1 275, 1 230, 970, 815, 790, and 755 cm^{-1}; δ($CDCl_3$) 1.90 (s, 6 H), 7.06—7.60 (m, 5 H,), and 7.82—8.05 (m, 2 H); *m/z* 223 (M^+), 207, 195, 118, and 91; 2-(2,4,6-*trimethylphenyl*)*benzotriazole*, m.p. 117 °C (73%, method B) (Found: C, 75.7; H, 6.4; N, 17.7. $C_{15}H_{15}N_3$ requires C, 75.9; H, 6.4; N, 17.7%); $\nu_{max.}$ 1 345, 1 285, 1 275, 1 225, 970, 860, and 740 cm^{-1}; δ($CDCl_3$) 1.86 (s, 6 H), 2.30 (s, 3 H), 6.96 (s, 2 H), 7.35—7.46 (m, 2 H), and 7.80—8.00 (m, 2 H); *m/z* 237 (M^+, base) 222, and 209.

Bis(2-nitrophenyl)carbodi-imide, prepared by the method of Campbell *et al.*[15] was thermolysed in the melt at 165 °C for 5 min to give 2-(2-nitrophenyl)benzotriazole, m.p. 127—130 °C (lit.,[37] 132.8—133.8 °C) (84%).

Preparation and Reaction of 2-*Phenyl*-1,2,4-*benzotriazin*-3-*one* 1-*Oxide* (**19**).—A solution of 3-(2-nitrophenyl)-4-phenyl-1,2,3,5-oxathiadiazole 2-oxide (**12**) (200 mg) in dry toluene (15 ml) was heated under reflux for 3 h. The solvent was evaporated and the residue crystallised from acetone to give 2-*phenyl*-1,2,4-*benzotriazin*-3-*one* 1-*oxide* (**19**) (81 mg, 51%) as deep red needles, m.p. 120—124 °C (Found: C, 65.1; H, 3.9; N, 17.4. $C_{13}H_9N_3O_2$ requires C, 65.3; H, 3.8; N, 17.6%); $\nu_{max.}$(CCl_4) 2 260, 1 695, and 1 610 cm^{-1}; (KBr) 1 690, 1 610, 1 470, 1 445, and 1 350 cm^{-1}; δ([$^2H_6$]-DMSO), 8.02—6.56 (m); *m/z* 195. A few crystals of (**19**) were heated in the melt at 145 °C for 5 min. T.l.c. showed quantitative conversion into 2-phenylbenzotriazole (**6**). Addition of dilute sulphuric acid to (**19**) (100 mg) followed by the extraction of the resultant colourless mixture with hexane gave 2-phenylbenzotriazole (75 mg, 93%). Warming of a solution of (**19**) (57 mg) in 10% aqueous potassium hydroxide on a steam-bath for 5 min gave *o*-aminoazoxybenzene (**22**) (71%) and a little 2-phenylbenzotriazole.

A solution of (**19**) (200 mg) and *p*-anisidine (103 mg) in dry benzene (15 ml) was heated under reflux for 15 min. The product was recrystallised from ethanol to give 2-*azoxyphenyl*(4-*methoxyphenyl*)*urea* (**21**) (277 mg, 91%), m.p. 183—184 °C (Found: C, 66.1; H, 5.0; N, 15.4. $C_{20}H_{18}N_4O_3$ requires C, 66.3; H, 5.0; N, 15.5%); $\lambda_{max.}$($CHCl_3$), 244 (ε 13 500), and 3.19 nm (ε 6 600); $\nu_{max.}$ 3 270, 1 665, 1 590, 1 380, 1 250, 760, and 725 cm^{-1}; δ($CDCl_3$) 9.90 (s, 1 H, NH), 8.70—6.50 (m, 14 H), and 3.80 (s, 3 H, OMe); *m/z* 362 (M^+).

8-*Nitro*-1-*naphthyl(phenyl)carbodi-imide* (**24**).—The carbodi-imide (**24**), prepared from the thiourea (method B), was sublimed through a quartz tube at 750 °C/0.015 mmHg. After 5 h, 10 mg of (**24**) had sublimed. An orange compound was washed with methylene chloride from the cold finger and removal of the solvent gave a solid which was crystallised from petroleum (60—80 °C) to give benz[1,8-*cd*]indazole 1-oxide (**32**) (4 mg), m.p. 145 °C (lit.,[38] 156—157 °C); *m/z* 170 (M^+).

2′-*Nitrobiphenyl*-2-*yl(phenyl)carbodi-imide* (**25**).—The carbodi-imide (**25**) (248 mg), prepared from the thiourea (method B), was sublimed through a quartz tube at 750 °C/0.015 mmHg, to give a polar solid (90 mg) which crystallised from petroleum–dichloromethane and then sublimed to give benzimidazo[1,2-*f*]phenanthridine (**29**) (45%) identical with an authentic specimen prepared as follows.

Benzimidazo[1,2-f]*phenanthridine* (**29**).—Equimolar amounts of 6-chlorophenanthridine, 2-nitroaniline, and sodium carbonate were intimately mixed and heated in the melt at 240—250 °C under nitrogen for 20 min. Chromatography gave 2-*nitro*-N-*phenanthridin*-6-*yl*)*aniline* as an orange solid, m.p. 167—169 °C (Found: C, 72.0; H, 4.1; N, 13.2. $C_{19}H_{14}N_3O_2$ requires C, 72.4; H, 4.2; N, 13.3%); δ($CDCl_3$) 7.05 (t, 1 H), 7.48—7.99 (m, 6 H), 8.20—8.57 (m, 5 H), and 9.55 (d, 1 H); *m/z* 315 (M^+). Reduction of the nitro compound and diazotisation of the resulting amine using standard conditions gave 1-*phenanthridin*-6-*ylbenzotriazole*, m.p. 215—217 °C (Found: C, 76.8; H, 4.1; N, 18.8. $C_{19}H_{12}N_4$ requires C, 77.0; H, 4.1; N, 18.8%), *m/z* 296 (M^+), 268. Photolysis (254 nm) of the benzotriazole in acetonitrile gave benzimidazo[1,2-*f*]phenanthridine (**29**), m.p. 151—153 °C (lit.,[20] 151—152 °C); $\nu_{max.}$ 3 350, 1 530, 1 440, 1 370, 1 260, 775, and 730 cm^{-1}; δ($CDCl_3$) 7.27 (s), 7.45—8.94 (m); *m/z* 268 (M^+), 164 and 134.

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