Preparation and Reactions of cis-1,4-Diphthaloyltetra-az-2-ene
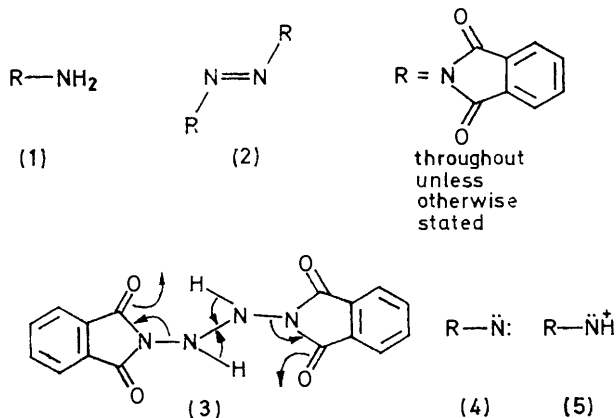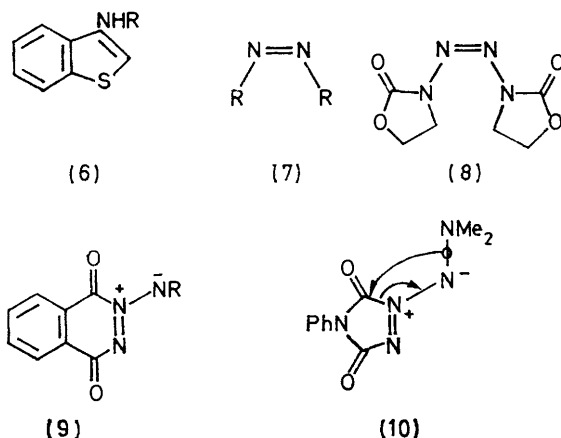
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Oxidation of N-aminophthalimide with lead tetra-acetate in the absence of additives gives mainly trans-1,4-diphthaloyltetra-az-2-ene (2), but in the presence of certain sulphur compounds (benzo[b]thiophen, dibenzo[b,d]-thiophen, and diphenyl sulphide) the corresponding cis-tetra-azene (7) is the major product. Unlike the trans-tetra-azene, the cis-compound undergoes thermolysis in boiling benzene to give N-(o-isocyanatobenzoyl)phthalimide (18), which in the presence of phthalimide anion gives 2-phthalimido-3,1-benzoxazin-4-one (25). Reactions of the two tetra-azenes with sodium methoxide are described, together with a possible mechanistic link with the conversion of (7) into (18).

OXIDATION of 1,1-disubstituted hydrazines provides a simple route to tetra-az-2-enes.[1] The oxidation of N-aminophthalimide (1) with lead tetra-acetate to give the trans-tetra-azene (2) and phthalimide probably involves formation of the tetra-azane (3) and its subsequent oxidation to (2) and fragmentation (3; arrows) to phthalimide;[2] the independently synthesised tetra-azane (3) gives the tetra-azene (2) on oxidation, and phthalimide on warming at 30—40 °C.[3] The tetra-azane (3) could be formed by interaction of phthalimidonitrene (4) or the nitrenium ion (5) with N-aminophthalimide;[2] the frequently cited but unlikely[4] dimerisation of nitrenes is not favoured as a route to (2).

As part of our study of the reaction of the nitrene (4) with aromatic compounds,[5] N-aminophthalimide was oxidised with lead tetra-acetate in the presence of benzo[b]thiophen. This gave the insertion product (6), whose structure was confirmed by an independent synthesis from benzo[b]thiophen-3(2H)-one and N-aminophthalimide (1). However the major product of the oxidation (49% yield) proved to be the cis-tetra-azene (7). Prior to the preliminary communication of

R—NH₂ ... (1)

(2)

R = (throughout unless otherwise stated)

R—N̈: R—N̈H⁺
(4)   (5)

(3)

this result[6] the only reported cis-tetra-azene was compound (8), obtained by heterogeneous oxidation (HgO) of

the corresponding hydrazine.[7] The structure (7) follows from analysis and molecular weight determination, which establish the molecular formula ($C_{16}H_8N_4O_4$), and

(6)   (7)   (8)

(9)   (10)

reduction (H_2 over Pd–C; 20 °C) to phthalimide (>90% yield). The presence of two intact phthalimido-residues is supported by the i.r. spectrum, which is similar to that of the trans-isomer but shows the greater complexity expected for reduced symmetry. Thus the trans-tetra-azene (2) shows two carbonyl bands (1 743 and 1 786 cm⁻¹), and the cis-isomer four such bands (1 728, 1 743, 1 780, and 1 806 cm⁻¹). An alternative structure (9) which could explain much of the chemistry of (7) described below † would be expected to give N-aminophthalimide and the easily isolated phthalohydrazide on reduction.

Further evidence for the cis–trans-relationship of the two tetra-azenes is provided by their similar mass spectra (see below and Experimental section), and similar acid-catalysed rearrangement. Thus on dissolution in trifluoroacetic acid at 20 °C, the cis-isomer (7) is cleanly converted into a 1 : 1 mixture of isatoic anhydride and phthalimide. Although stable under these conditions the trans-tetra-azene gives the same products in boiling acetic acid.[2]

† Structure (9) is analogous to structure (10) proposed[8] for the product obtained by reaction of 4-phenyltriazoline-3,5-dione with 1,1-dimethylhydrazine; compound (10) rearranges to an azide (10; arrows) on warming.

[1] P. A. S. Smith in 'Open-chain Nitrogen Compounds,' Benjamin, New York, 1966, vol. 2, p. 346.

[2] L. Hoesch and A. S. Dreiding, Helv. Chim. Acta, 1975, 58, 980.

[3] D. J. Anderson, T. L. Gilchrist, and C. W. Rees, Chem. Comm., 1971, 800.

[4] T. L. Gilchrist and C. W. Rees in ' Carbenes, Nitrenes, and Arynes,' Nelson, London, 1969, p. 96.

[5] D. W. Jones, J.C.S. Perkin I, 1972, 225, 2728; J.C.S. Chem. Comm., 1972, 884; 1973, 67.

[6] D. W. Jones, Chem. Comm., 1970, 1084.

[7] P. S. Forgione, G. S. Sprague, and H. J. Troffkin, J. Amer. Chem. Soc., 1966, 88, 1079.

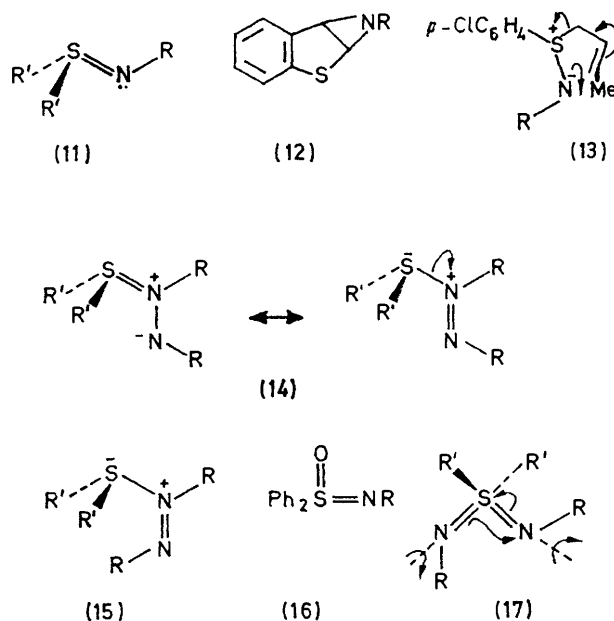[8] K. H. Koch and E. Farr, Angew. Chem. Internat. Edn., 1970, 9, 634.

Dibenzo[b,d]thiophen and diphenyl sulphide also divert the oxidation of N-aminophthalimide (1) to the cis-tetra-azene. In these cases the yield is improved, presumably owing to the absence of a secondary reaction leading to products of type (6). However the cis-tetra-azene is contaminated with small and variable amounts of the trans-isomer, so that for preparative purposes oxidation in the presence of benzo[b]thiophen is preferred. The success of these oxidations favours an intermediate sulphimide (11) rather than an intermediate aziridine (12) in the benzo[b]thiophen reaction. The related sulphimide (11; R′ = Me) has been prepared by addition of N-aminophthalimide (1) to lead tetra-acetate and dimethyl sulphide at —75 °C.* Replacement of dimethyl sulphide by diphenyl sulphide in this procedure gives the cis-tetra-azene in good yield and none of the sulphimide (11; R′ = Ph). Other evidence for a sulphimide intermediate was obtained by the isolation of both the cis-tetra-azene and sulphenamides from the reaction of allyl aryl sulphides with phthalimidonitrene.[9] Here the intermediate sulphimide (13) is in part trapped by rapid 2,3-sigmatropic shift (13; arrows) to a sulphenamide.

The intermediacy of a sulphimide like (11; R′ = Ph) readily explains formation of cis- rather than trans-tetra-azene. The indicated S–N bond rotamer would be preferred on steric grounds, and its reaction with the nitrene (4) † to give the species (14) rather than (15) might also be sterically preferred. Loss of diphenyl sulphide from (14) could then give the cis-tetra-azene. Reaction of the sulphimide (11) with the nitrene giving (14) is related to the reaction of carbenes with sulphoxides, where attack is at oxygen rather than sulphur.[10] The reaction of nitrenes with sulphoxides generally proceeds by attack at sulphur;[11] thus diphenyl sulphoxide and the nitrene (4) give the sulphoximide (16).[12] There is insufficient evidence to exclude other mechanisms for cis-tetra-azene formation. It is possible that the sulphimide (11; R′ = Ph) reacts with the nitrene (4) at sulphur to give the sulphodi-imide (17), which by the indicated conrotatory closure to a three-membered ring followed by non-linear cheletropic extrusion of diphenyl sulphide gives the cis-tetra-azene. There is however little precedent for such a sequence; thermolysis of the sulphoximide (16) gives Ph₂SO and the nitrene (4) rather than Ph₂S and the nitroso-compound RNO.[12] It is also possible that the sulphimide (11; R′ = Ph) is unstable in the presence of a proton source (acetic acid), the reaction between (11; R′ = Ph) and its N-protonated conjugate acid leading to (7). Analogy for such a sequence may be found in the base-catalysed conversion of a benzyldiphenylsulphonium salt into cis- and trans-stilbene,[13a] the formation of tetra-az-2-enes in

the reaction of 1,1-disubstituted hydrazines with di-sulphonylsulphodi-imides,[13b] and the conversion of a sulphoximide related to (16) into a tetra-az-2-ene in hot ethanol.[12]

(11)   (12)   (13)

(14)

(15)   (16)   (17)

The explosive nitrogen loss observed on heating the tetra-azene (7) to 160 °C prompted an investigation of its thermolysis. Addition of small portions of (7) to a vessel held at 160 °C gave the isocyanate (18), $v_{max.}$ 2 300 cm⁻¹, characterised as the urethane (19) formed with ethanol, and by reaction with water to give isatoic anhydride and phthalimide. Formation of the isocyanate (18) can be most economically represented as in

(18)   (19)   (20)
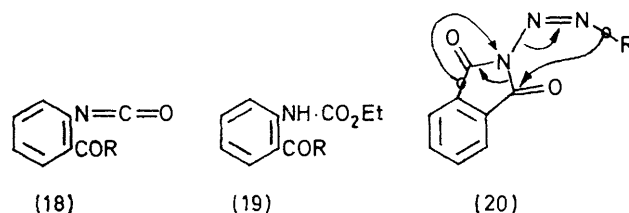
(20), where the cis-disposition of the groups allows one phthalimido-group to function as an internal nucleophile triggering Curtius-type rearrangement in the other phthalimido-group. This mechanism would explain the stability of the trans-tetra-azene under the same conditions. The expression (20) need not imply a concerted process; the acyl azide (21) could be an intermediate which subsequently undergoes Curtius rearrangement to

[9] R. S. Atkinson and S. B. Awad, J.C.S. Chem. Comm., 1975, 651.
[10] R. Oda, M. Mieno, and Y. Hayashi, Tetrahedron Letters, 1967, 2363.
[11] J. Sauer and K. K. Mayer, Tetrahedron Letters, 1968, 319.
[12] D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, J.C.S. Perkin I, 1972, 1317.
[13] (a) A. W. Johnson, V. J. Hruby, and J. R. Williams, J. Amer. Chem. Soc., 1964, 86, 918; (b) G. Kresze in ' Organic Sulphur Chemistry,' ed. C. J. M. Stirling, Butterworths, London, 1975.

* The preparation of compound (11; R′ = Me) was described by Professor C. W. Rees (Tilden Lecture, London, 2nd May, 1974). We thank Dr. T. L. Gilchrist for experimental details of the work of Dr. J. Harris prior to its publication.

† Whether the nitrene (4), its conjugate acid (5), or a lead salt RNHPb(OAc)₃ is the actual intermediate in these reactions is an open question.

(18). The mass spectrum of the tetra-azene (7) includes a peak at $M - 42$ which is most readily explained by loss of N_3 from ionised (21).* A related reaction of (7) may be induced by an external nucleophile. Reaction with 1 equiv. of sodium methoxide in 1,2-dimethoxy-ethane at 0—5 °C affords a crude product showing strong

(21)   (22)
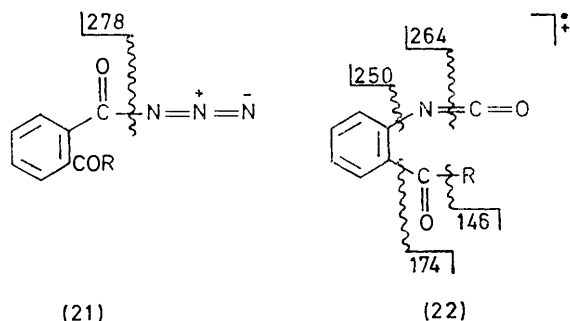
i.r. absorption at 2 130 cm⁻¹ consistent with the presence of the azide (21; R = OMe). On warming the petroleum-soluble portion of this product the band at 2 130 cm⁻¹ is in part replaced by a band at *ca.* 2 300 cm⁻¹,

(23)   (24) R' = H
                (26) R' = Me

(25)   (27)   (28)
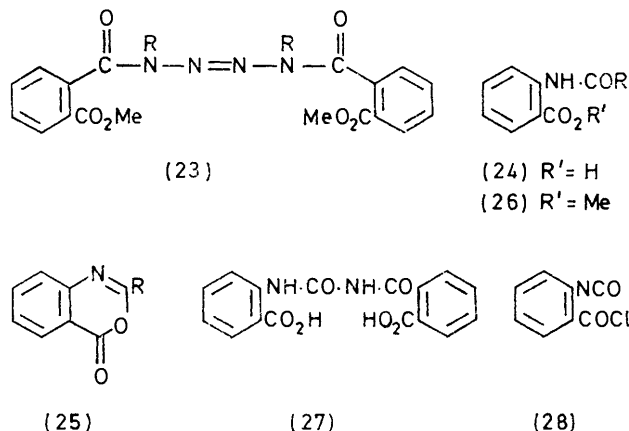
suggesting Curtius rearrangement to (18; R = OMe). Subsequent treatment with methanol gives dimethyl

e.g. (21; R = O₂C·CF₃), would account for the reaction of the tetra-azene (7) with CF₃·CO₂H to give isatoic anhydride and phthalimide. The intermediate (18; R = O₂C·CF₃) could well give isatoic anhydride in the presence of CF₃·CO₂H.

Although the *trans*-tetra-azene (2) is unchanged by heating at 160 °C, a reaction similar to the thermal rearrangement of the *cis*-isomer (7) is observed with sodium ethoxide in boiling ethanol, which gives ethyl *o*-ethoxycarbonylphenylcarbamate (19; R = OEt) and phthalimide. A likely intermediate step in this process involves the opening of *both* phthalimido-rings, for reaction of (2) with sodium methoxide at 0—5 °C followed by addition of acetic acid gives the tetra-azene (23; R = H). Unlike known tetra-azenes this compound is only disubstituted; with diazomethane it gives the tetrasubstituted product (23; R = Me). Recently compound (23; R = H) was prepared by reaction of the tetra-azene (2) with boiling methanol and shown to give methyl *o*-methoxycarbonylphenylcarbamate and phthalimide on heating.[2] Reaction of both isomers (2) and (7) with sodium methoxide presumably proceeds *via* an intermediate anion (Scheme 1). In the case of the *trans*-isomer the anion and/or its conjugate acid is sufficiently long-lived to undergo further ring opening leading to (23; R = H). Perhaps because of a greater relief of steric strain the anion from the *cis*-tetra-azene fragments to phthalimide anion and the acyl azide (21; R = OMe). More rapid fragmentation of the anion from the *cis*-tetra-azene could be due to the *trans*-periplanar arrangement of nitrogen lone pair and leaving phthalimido-group not possible in the anion from the *trans*-tetra-azene.

Decomposition of the *cis*-tetra-azene (7) also occurs in boiling benzene. In our first experiments, formation of the isocyanate was detected by appearance of i.r. absorption at *ca.* 2 300 cm⁻¹. However after boiling overnight to complete decomposition of the tetra-azene (7) only the benzoxazinone (25) was obtained. This was characterised by hydrolysis (HCl–HOAc) to a mixture


dimethyl phthalate
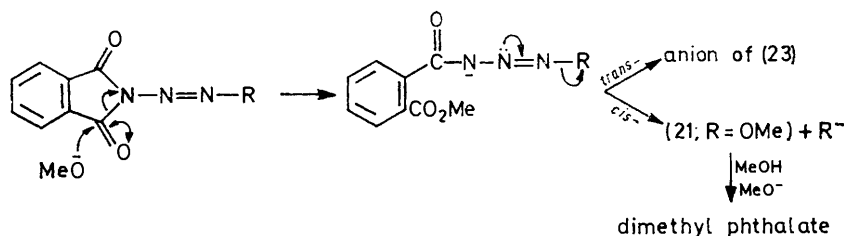
SCHEME 1

phthalate, methyl *o*-methoxycarbonylphenylcarbamate, and phthalimide. The dimethyl phthalate presumably arises by methanolysis of the azide (21; R = OMe); in agreement, reactions of the tetra-azene (7) with 2 equiv. of sodium methoxide in methanol at 0 °C give only dimethyl phthalate and phthalimide.

Schmidt rearrangement of a species related to (21),

of the acid (24) and the dicarboxylic acid (27); the former (24) was converted by aqueous pyridine into

* The other features of the mass spectrum of the tetra-azene (7) parallel its thermal breakdown. The spectrum is similar to that of the isocyanate (18), which fragments by the cleavages shown in (22). Since the spectrum of the *trans*-tetra-azene differs from that of (7) only in the intensities of some peaks, interconversion of ionised *cis*- and *trans*-tetra-azenes is likely.

isatoic anhydride and phthalimide, whereas the latter (27) gave the known dimethyl ester [14] with diazomethane. Although we first suggested a sequence involving a 1,5-phthalimido-shift and electrocyclic ring closure for the conversion of (18) into (25),[6] we now favour a mechanism involving catalysis by an unidentified nucleophile (X⁻) (Scheme 2). The conversion of (18) into (25) is capricious, as befits catalysis by an impurity. Carefully purified *cis*-tetra-azene partly decomposes to the isocyanate (18) in boiling benzene over 18 h without formation of (25). After removal of the unchanged tetra-azene the isocyanate is stable in boiling benzene even in the presence of phthalimide, but addition of a catalytic amount of potassiophthalimide leads to a rapid formation of (25). These observations are in better accord with the mechanism of Scheme 2 in
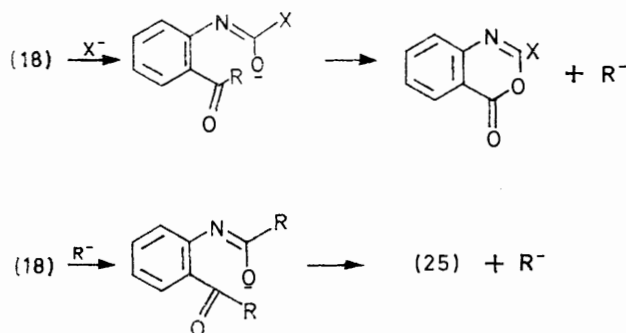
SCHEME 2

which phthalimide anion (R⁻), released by initial attack of the unidentified nucleophile (X⁻), acts as a chain carrier in the conversion of (18) into (25). Analogy for the second part of this sequence is provided by the preparation of (25) by reaction of *o*-isocyanatobenzoyl chloride (28) [15] with potassiophthalimide.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified i.r. spectra refer to Nujol mulls, and n.m.r. spectra to solutions in deuteriochloroform measured with a Varian A60A spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument. Petroleum refers to light petroleum (b.p. 60—80°) and chromatography on silica to short-column chromatography [16] over Kieselgel G (Merck). The phrase 'work-up in the usual way' refers to dilution with dichloromethane, washing with water, drying (MgSO₄), and evaporation under reduced pressure on a water-bath.

Oxidation of N-*Aminophthalimide in the Presence of* Benzo[b]*thiophen.*—Lead tetra-acetate (3.65 g) was added in small portions over 10 min to a stirred mixture of N-aminophthalimide (1.25 g) and benzo[b]thiophen (1.5 g) in dichloromethane (20 ml) at 0—5 °C. Work-up in the usual way and trituration with benzene gave a crystalline solid (0.61 g, 48%). Purification by dissolving in dichloromethane at the b.p., cooling to 0—5 °C, and adding ethanol

gave cis-1,4-*diphthaloyltetra-az-2-ene* (7), m.p. 160—161° (decomp.) [Found: C, 60.2; H, 2.5; N, 17.5%; *M* (osmometer), 304. C₁₆H₈N₄O₄ requires C, 60.0; H, 2.5; N, 17.5%; *M*, 320], ν_max. 1 728, 1 753, 1 790, and 1 806 cm⁻¹, *m/e* 320 (0.1%, *M*⁺), 292 (30), 278 (2.2), 264 (5), 250 (6.7), 248 (1), 222 (1.1), 220 (1.4), 174 (4.4), 147 (33), 146 (100), 118 (0.55), 104 (33), 90 (33), and 76 (33%), *m** 237.7 (292 ⟶ 264) and 214 (292 ⟶ 250). Accurate mass *m/e* 278.045 26 corresponded to C₁₆H₈NO₄ (*M* − N₃) (required 278.045 33) and not C₁₆H₈N₃O₃ (required 278.056 6). The insolubility of this compound and its decomposition in CF₃·CO₂H and (CD₃)₂SO prevented determination of its n.m.r. spectrum. The absence of i.r. absorption at 960m and 980w cm⁻¹ shows the absence of the related *trans*-tetra-azene.

The benzene mother-liquor left after removal of the tetra-azene (7) was chromatographed on silica in benzene–ether (4 : 1), which eluted 3-(*phthalimidoamino*)benzo[b]-*thiophen* (6), m.p. 201—203° [from ethanol (charcoal)] (Found: C, 65.1; H, 3.7; N, 9.55; S, 11.15. C₁₆H₁₀N₂O₄S requires C, 65.3; H, 3.4; N, 9.5; S, 10.9%), ν_max. 3 400, 1 786, and 1 725 cm⁻¹, δ 6.62 (2 H, s, 1 H exch. D₂O), 7.2—7.56 (2 H, m, aromatic), and 7.6—8.05 (6 H, m, aromatic, including AA′BB′ of the phthaloyl group). The same product (mixed m.p. and i.r. spectrum) was obtained by heating benzo[b]thiophen-3(2H)-one [17] and N-aminophthalimide in boiling ethanol (2 h) followed by chromatographic isolation as described above.

Oxidation of N-*Aminophthalimide in the Presence of Diphenyl Sulphide.*—Lead tetra-acetate (7.3 g; dried by pressing on filter papers) was added in small portions over 15—20 min to a stirred mixture of N-aminophthalimide (2.5 g), diphenyl sulphide (4 ml), and dichloromethane (40 ml) at 0 °C. After stirring for a further 10 min the product was worked up in the usual way. The semi-crystalline product was triturated with benzene, and the crystals were filtered off and washed with a little warm benzene. This tetra-azene (1.82 g, 72% yield) was shown to be substantially pure by i.r. spectroscopy (only very weak bands at 960 and 980 cm⁻¹) and by the absence of *trans*-tetra-azene crystals left after decomposition of the *cis*-tetra-azene at *ca.* 160 °C. However the process can yield a product more heavily contaminated with *trans*-tetra-azene; this is not purified by crystallisation from CH₂Cl₂–EtOH. The yield of *cis*-tetra-azene is unchanged by reducing the quantity of diphenyl sulphide to 0.4 g per 0.625 g of N-aminophthalimide, or by adding N-aminophthalimide in portions over 10—15 min to a mixture of diphenyl sulphide and lead tetra-acetate stirred at 0—5 °C.

Oxidation in the presence of dibenzo[b,d]thiophen gave the *cis*-tetra-azene in 58% yield.

Oxidation of N-*Aminophthalimide in the Absence of a Trap.*—Oxidation of the title compound (1.25 g) as for oxidation in the presence of benzo[b]thiophen, and work-up in the usual way, gave *trans*-diphthaloyltetra-az-2-ene (2) (0.82 g), m.p. 294—299° (decomp.; rapid heating); i.r. spectrum unchanged by crystallisation from CH₂Cl₂–PhH, and CH₂Cl₂–Me₂CO; *m/e* 320 (34%, *M*⁺), 292 (4), 278 (16), 264 (1), 250 (4), 248 (2), 220 (1.2), 174 (80), 147 (54), 146 (60), 130 (3.4), 118 (14), 104 (70), 90 (100), and 76 (80%), *m** 241.5 (320 ⟶ 278) and 95.36 (146 ⟶ 118), ν_max. 1 743 and 1 786 cm⁻¹ (lit.,[2] 1 744 and 1 788 cm⁻¹), δ(CF₃·CO₂H) 7.8—8.3 (AA′BB′).

[14] J. Bredt and H. Hof, *Ber.*, 1900, **33**, 21.
[15] H. Ulrich, B. Tucker, and A. R. R. Sayigh, *J. Org. Chem.*, 1967, **32**, 4052; Y. Ikawura, H. Uno, and S. Kang, *ibid.*, 1966, **31**, 142.

[16] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.
[17] R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1970, 1926.

Hydrogenolysis of cis-1,4-*Diphthaloyltetra-az-2-ene.*—The tetra-azene (100 mg) and palladium–charcoal (10%; 40 mg) in ethyl acetate (10 ml) were shaken in hydrogen (17 h). Evaporation of the filtered solution gave phthalimide (90 mg), identical (m.p., mixed m.p., and i.r. spectrum) with an authentic sample.

Reaction of the cis-*Tetra-azene* (7) *with Trifluoroacetic Acid.*—The *cis*-tetra-azene (50 mg) and trifluoroacetic acid (2 ml) were kept at 20 °C (18 h). Evaporation of the acid under reduced pressure gave a crystalline solid. The i.r. spectrum of this product was identical with that of a 1 : 1 mixture of phthalimide and isatoic anhydride.

Thermolysis of the cis-*Tetra-azene* (7).—The *cis*-tetra-azene (150 mg) was added in small portions to a test-tube maintained at 165—170 °C; vigorous nitrogen loss accompanied each addition. The product crystallised from benzene–petroleum to give N-(o-*isocyanatobenzoyl*)*phthalimide* (18), m/e 292 (30%, M^+), 264 (6, M — CO), 250 (8, M — NCO), 248 (6, M — CO_2), 220 (5, M — CO — CO_2), 174 (3), 146 (100), 130 (4), 118 (3.5), 104 (11), 90 (30), 86 (14), 84 (2.1), and 76 (40%); m^* 238.7 (292 —→ 264) and 214.04 (292 —→ 250), $\nu_{max.}$ 2 300, 1 800, 1 740, 1 700, and 1 604 cm^{-1}. The isocyanate was further characterised as the *urethane* (19), formed by brief boiling with ethanol, m.p. 142—144° (from ethanol) (Found: C, 63.6; H, 4.25; N, 8.35%; M^+, 384.131. $C_{18}H_{14}N_2O_5$ requires C, 63.9; H, 4.2; N, 8.3%; M, 384.132), $\nu_{max.}$ 3 450, 1 800, 1 740, 1 675, 1 606, and 1 580 cm^{-1}, δ 1.32 (3 H, t, J 7 Hz, CH_3), 4.26 (2 H, q, J 7 Hz, CH_2), 7.09 (1 H, m, aromatic), 7.5—8.2 (6 H, m, aromatic), 8.53 (1 H, m, aromatic), and 10.08br (1 H, s, NH).

Reaction of the Urethane (19) *with Sodium Ethoxide.*—The foregoing urethane (20 mg) and sodium ethoxide solution [1 ml of a solution from sodium (14 mg) and ethanol (10 ml)] were stirred at 20 °C (2 h). Addition of dilute acetic acid gave 2-*ethoxycarbonyl*-2'-*ethoxycarbonylaminodibenzoamide* (18 mg), m.p. 150—154° (Found: M^+, 384.131. $C_{20}H_{20}N_2O_6$ requires M, 384.132), $\nu_{max.}$ 3 390, 3 330, 1 710, 1 680, and 1 590 cm^{-1}, δ 1.0—1.5 (6 H, 6 lines, two CH_3 triplets, J 7 Hz), 3.87—4.5 (4 H, 6 lines, two CH_2 quartets, J *ca.* 7 Hz), 7.03 (1 H, m, aromatic), 7.28—8.18 (7 H, m, aromatic and NH), 8.34 (1 H, dd, J 8 and <1 Hz, aromatic), and 9.67br (1 H, NH). The same product was formed on heating (19) in boiling ethanol (48 h).

Reaction of the cis-*Tetra-azene* (7) *with Sodium Methoxide.*—(a) The tetra-azene (160 mg) in 1,2-dimethoxyethane (2 ml) was stirred at 0—5 °C with sodium methoxide (27 mg) (30 min). The supernatant liquid was decanted and evaporated to dryness at 20 °C under high vacuum. The i.r. spectrum of the product (film) showed a strong peak at 2 130 cm^{-1}. The product in petroleum (6 ml) was heated on a steam-bath (5 min). The i.r. spectrum of the product obtained by evaporation showed $\nu_{max.}$ 2 130 and 2 240 cm^{-1}. Boiling with methanol (30 min) gave a crude product which was chromatographed on silica in benzene–ether (9 : 1). Elution with the same solvent gave first methyl *o*-methoxycarbonylphenylcarbamate (26; R = OMe) (12 mg) and then dimethyl phthalate (12 mg). Elution with benzene–ether (4 : 1) gave phthalimide (24 mg). The products had i.r. spectra identical with those of authentic samples.

(b) The *cis*-tetra-azene (320 mg) in methanol (2 ml) at 0—5 °C was treated with sodium methoxide in methanol [1.1 ml of a solution prepared from sodium (460 mg) and methanol (10 ml)] over 2 h. Work-up by addition of acetic acid and evaporation at 40 °C under reduced pressure

followed by work-up in the usual way gave a mixture of phthalimide (110 mg) and dimethyl phthalate (168 mg). These were separated by employing the insolubility of the former in petroleum, and identified by i.r. comparison with authentic samples.

Reaction of the trans-*Tetra-azene* (2) *with Sodium Methoxide.*—The tetra-azene (320 mg) in methanol (2 ml) at 0—5 °C was treated with sodium methoxide as in (b) above. The white precipitate that formed on addition of acetic acid with scratching was crude trans-1,4-*bis*-(o-*methoxycarbonylbenzoyl*)*tetra-az-2-ene* (23; R = H) (350 mg), m.p. 111—115° (decomp.). One crystallisation from methanol at 0—5 °C raised the m.p. to 158—165° (decomp.) (Found: C, 56.35; H, 4.25; N, 14.85. $C_{18}H_{16}N_4O_6$ requires C, 56.25; H, 4.2; N, 14.6%), $\nu_{max.}$ 3 200, 1 725, 1 670, 1 600, and 1 585 cm^{-1}; δ[(CD$_3$)$_2$SO] 12.90br (2 H, s, HNCO), 7.80 (2 H, apparent s, aromatic), 7.7—7.4 (6 H, m, aromatic), and 3.82 (6 H, s, OCH$_3$). The same product was formed in comparable yield when only 1 mol. equiv. of sodium methoxide was employed.

Reaction of the Tetra-azene (23; R = H) *with Diazomethane.*—With ethereal diazomethane at 0—5 °C (42 h) the tetra-azene (23; R = H) (50 mg) gave 1,4-*bis*-(o-*methoxycarbonylbenzoyl*)-1,4-*dimethyltetra-az-2-ene* (23; R = Me) (37 mg), m.p. 163—165° (from methanol) [Found: C, 58.2; H, 4.85; N, 13.7%; M (osmometer), 495; M^+, 412.139. $C_{20}H_{20}N_4O_6$ requires C, 58.25; H, 4.9; N, 13.6%; M, 412.138], $\nu_{max.}$ 1 730, 1 675, 1 605, and 1 587 cm^{-1}, δ 2.97 (6 H, s, 2 × NCH$_3$), 3.8 (6 H, s, 2 × OCH$_3$), 7.2—7.7 (6 H, m, aromatic), and 7.9—8.1 (2 H, m, aromatic), m/e 412 (11.5%, M^+), 320 (27.5), 305 (6.7), 296 (9.2), 288 (5.7), 261 (7.6), 248 (5.8), 245 (5.0), 223 (10.3), 217 (8.3), 192 (10.1), 181 (6.2), 177 (27.8), 175 (15), 164 (32.1), 163 (100), 162 (23.2), 161 (100), and 160 (19.2%). The same product was obtained as follows. The tetra-azene (2) in dichloromethane was shaken with portions of 2N-sodium hydroxide until addition of concentrated hydrochloric acid to the aqueous extract gave no precipitate. The precipitate (hydrochloride?), $\nu_{max.}$ 3 150, 2 360—2 700, 1 650—1 720, 1 605, and 1 587 cm^{-1}, with ethereal diazomethane in the presence of methanol at 0—5 °C over 48 h, gave compound (23; R = Me) identical (mixed m.p. and i.r. spectrum) with the sample previously prepared.

Reaction of the trans-*Tetra-azene* (2) *with Sodium Ethoxide in Hot Ethanol.*—The tetra-azene (250 mg) in boiling ethanol (10 ml) was treated with a solution of sodium ethoxide [from sodium (18 mg) and ethanol (1.0 ml)] and the mixture was boiled under reflux (15 min). The product was evaporated under reduced pressure on a water-bath, acidified with hydrochloric acid (2N), and extracted into dichloromethane. Extraction of the organic layer with 2N-sodium hydroxide and acidification of the extract gave phthalimide (40 mg), identical (i.r. spectrum) with an authentic sample. Evaporation of the dried (MgSO$_4$) dichloromethane solution gave ethyl *o*-ethoxycarbonylphenylcarbamate, identical (i.r. and n.m.r. spectra) with an authentic sample.

Rearrangement of the Isocyanate (18) *in Boiling Benzene.*—The *cis*-tetra-azene (100 mg; recrystallised 5 × from CH$_2$Cl$_2$–EtOH at 0—5 °C) and benzene (6 ml; dried over sodium) were boiled under reflux in scrupulously clean and dry apparatus (18 h). After removal of unchanged *cis*-tetra-azene (30 mg) by filtration, evaporation left the pure isocyanate (18) (i.r. spectrum). Addition of fresh benzene (7 ml) and boiling under reflux (18 h) either alone or in the

presence of phthalimide (5 mg) led to unchanged (18); addition of potassiophthalimide (10 mg) and boiling under reflux (18 h) gave 2-*phthalimido*-3,1-*benzoxazin*-4-*one* (25) (60 mg), m.p. 196—198° (from ethanol) [Found: C, 65.65; H, 2.8; N, 9.4; M (osmometer), 286. $C_{16}H_8N_2O_4$ requires C, 65.75; H, 2.8; N, 9.6%; M, 290], δ 7.53 (1 H, m), 7.63—8.13 (6 H, m), and 8.25 (1 H, m), $v_{max.}$ 1 785, 1 768, 1 734, and 1 640 cm^{-1}. The rearrangement of (18) into (25) may occur in the absence of potassiophthalimide, in the presence of an unidentified impurity.

Acidic Hydrolysis of the Benzoxazinone (25).—The benzoxazinone (60 mg) in glacial acetic acid (3 ml) and hydrochloric acid (10 drops) was kept at 20 °C (18 h). The crystalline acid (24) (25 mg) that separated was filtered off; $v_{max.}$ 3 280, 2 700—2 400, 1 793, 1 755, and 1 688 cm^{-1}. This was directly converted into the *methyl ester* (26) by reaction in tetrahydrofuran with ethereal diazomethane; m.p. 165 and 198° (decomp.) (from benzene–petroleum) (Found: M^+, 324.075. $C_{17}H_{12}N_2O_5$ requires M, 324.075), $v_{max.}$ 3 270, 1 808, 1 780, 1 700, 1 612, and 1 595 cm^{-1}, δ 4.0 (3 H, s, OCH$_3$), 7.08 (1 H, m, aromatic), 7.25—8.2 (6 H, m, aromatic), 8.68 (1 H, dd, J 8 and 1 Hz, aromatic), and 11.9lbr (1 H, s, NH). An attempt to obtain the n.m.r. spectrum of the acid (24) in pyridine–D$_2$O gave a 1 : 1 mixture of isatoic anhydride and phthalimide (i.r. and n.m.r. spectra).

The acetic acid liquor left after removal of the acid (24) was kept at 20 °C for 24 h, and the diacid (27) (10 mg) was filtered off and directly converted into its dimethyl ester (CH$_2$N$_2$); m.p. 164—166° (from methanol) (lit.,[14] 140—142°), $v_{max.}$ 3 230, 3 120, 1 724, 1 700sh, 1 688, and 1 585 cm^{-1}, δ 3.88 (3 H, s, OCH$_3$), 3.99 (3 H, s, OCH$_3$), 6.9—8.25 (7 H, m, aromatic), 8.27 (1 H, dd, J 8 and 1 Hz, aromatic),

9.48br (1 H, s, NH), and 12.3br (1 H, s, NH). The same di-ester was formed from (26) in boiling methanol over 30 min.

Reaction of Phthalimide with Sodium Methoxide–Bromine. —The m.p. discrepancy observed in the preceding experiment led us to repeat the experiment of Bredt and Hof.[14] Phthalimide (3.7 g) was added to a solution of sodium methoxide [from sodium (1.15 g) and methanol (20 ml)] which was stirred at 0—5 °C, and bromine (4 g) in methanol (7 ml) was added over 10 min. The product was kept at 0—5 °C (30 min), and then at room temperature (1.5 h), and diluted with water. Attempted extraction into dichloromethane led to separation of a crystalline solid (2.95 g), m.p. 137—139° raised to 160—162° by one crystallisation from methanol. This product was identical (mixed m.p. and i.r. spectrum) with that described above.

Reaction of the Benzoxazinone (25) *with Sodium Ethoxide.* —The benzoxazinone (40 mg) was treated with sodium ethoxide (6.3 mg) in ethanol (2 ml) at 20 °C (1.5 h). The product was diluted with water, acidified with hydrochloric acid (2N), and extracted into dichloromethane, and the organic layer was washed with sodium hydroxide solution (2N) and water, and dried (MgSO$_4$). Evaporation gave ethyl *o*-ethoxycarbonylphenylcarbamate (20 mg), identical (i.r. spectrum) with authentic material.

2-*Phthalimido*-3,1-*benzoxazin*-4-*one*.— *o*-Isocyanatobenzoyl chloride [15] (363 mg) and potassiophthalimide (370 mg) in benzene (3 ml) were boiled under reflux (18 h). Chromatography of the product over silica in benzene–ether (9 : 1) gave the benzoxazinone (25) (130 mg), identical (m.p., mixed m.p., and i.r. spectrum) with the sample already described.