Reactive Intermediates. Part XX.[1] Preparation of Sulphoximides from Sulphoxides and *N*-Amino-lactams, and a Study of their Fragmentation [2]

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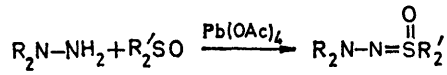
Lead tetra-acetate oxidation of *N*-amino-lactams in the presence of sulphoxides gives sulphoximides in good yields. The sulphoximides undergo photochemical fragmentation to regenerate the sulphoxides and *N*-nitrenes, which can be intercepted by cyclohexene. Vapour phase pyrolysis at 400—500° also results in fragmentation of the sulphoximides, but under these conditions nitrogen is extruded from the heterocyclic systems, and products of ring contraction can be isolated. Thus, phthalimidosulphoximides give benzocyclobutene-1,2-dione.

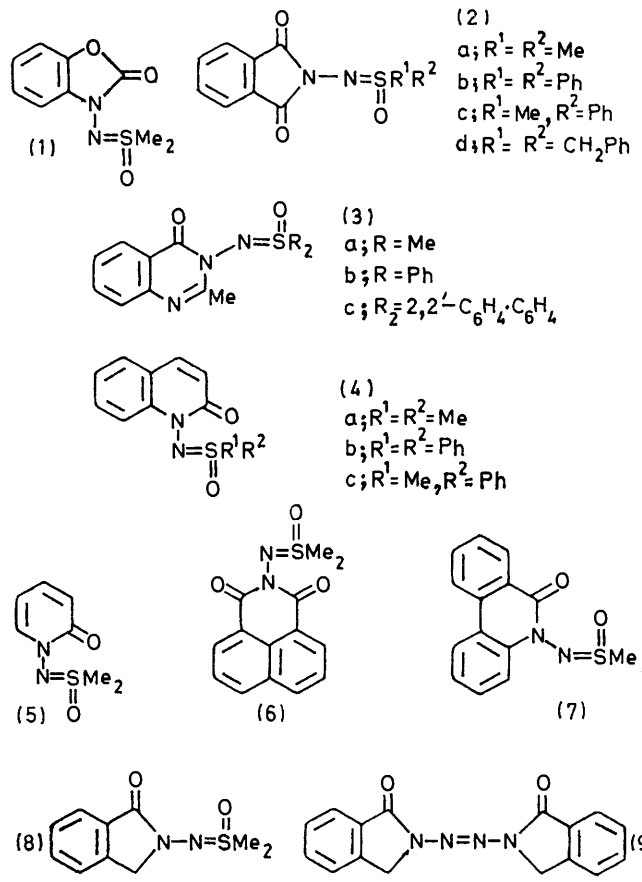
SULPHOXIDES are among the best reagents yet discovered for intercepting nitrene intermediates. *N*-Sulphonylsulphoximides have been isolated from a wide variety of reactions in which sulphonylnitrenes could be involved as intermediates,[3-6] even in systems (such as that involving oxidation of sulphonamides [6]) where other potential nitrene 'traps' fail to react. Acylnitrenes have also been intercepted by sulphoxides.[5,7] There is no direct evidence that all these reactions do involve free nitrene intermediates, but the nitrene mechanism provides a simple general rationalisation of the results. The oxidation of *N*-amino-lactams in the presence of sulphoxides similarly gives sulphoximides (Scheme 1).[2,8] These reactions give good yields with a



SCHEME 1

wide variety of *N*-amino-lactams and sulphoxides, and thus provide a simple and convenient route to the compounds. Reactions of this type have been used to prepare optically active sulphoximides.[4,9] The present paper gives experimental details for the preparation of sulphoximides and discusses their photochemical and thermal fragmentation.

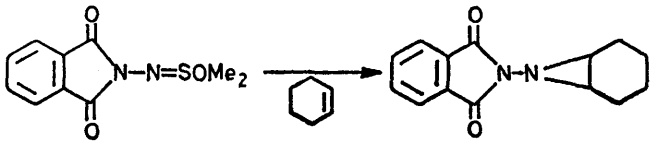
Preparation of Sulphoximides.—The sulphoximides (1)—(6) were prepared by the reaction of Scheme 1. The preparation of compound (7), which was used in the pyrolysis studies, has been reported earlier.[8] The *SS*-dimethylsulphoximides were very easily prepared by carrying out the oxidation of the *N*-amino-lactams in dimethyl sulphoxide as solvent, the excess of dimethyl sulphoxide then being removed by pouring the reaction mixture into water or into ether. Oxidations involving other sulphoxides were carried out in dichloromethane containing a 3—4 molar excess of the sulphoxide. The procedure gave satisfactory yields of sulphoximides in most cases, although chromatography was usually needed to separate the product from the unchanged sulphoxide. This proved to be an obstacle to the isolation of the dibenzylsulphoximide (2d), for which an alternative preparative procedure was devised, involving



slow inverse addition of *N*-aminophthalimide to a mixture of 1 mol. equiv. of dibenzyl sulphoxide and lead tetra-acetate in dichloromethane. This procedure gave the sulphoximide in high yield, and is probably the most satisfactory one for general use.

[1] Part XIX, M. Keating, M. E. Peek, C. W. Rees, and R. C. Storr, preceding paper.
[2] Preliminary communications, D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Comm.*, 1969, 146; T. L. Gilchrist, C. W. Rees, and E. Stanton, *ibid.*, 1971, 801.
[3] D. Carr, T. P. Seden, and R. W. Turner, *Tetrahedron Letters*, 1969, 477; M. Okahara and D. Swern, *ibid.*, p. 3301; H. Kwart and A. A. Khan, *J. Amer. Chem. Soc.*, 1967, **89**, 1950; P. Robson and P. R. H. Speakman, *J. Chem. Soc.* (*B*), 1968, 463.
[4] D. R. Rayner, D. M. von Schritz, J. Day, and D. J. Cram, *J. Amer. Chem. Soc.*, 1968, **90**, 2721.
[5] L. Horner and A. Christmann, *Chem. Ber.*, 1963, **96**, 388.
[6] T. Ohashi, K. Matsunaga, M. Okahara, and S. Komori, *Synthesis*, 1971, 96.
[7] J. Sauer and K. K. Mayer, *Tetrahedron Letters*, 1968, 319.
[8] C. W. Rees and M. Yelland, *J.C.S. Perkin I*, 1972, 77.
[9] S. Colonna and C. J. M. Stirling, *Chem. Comm.*, 1971, 1591.

Photochemical and Thermal Fragmentation.—The sulphoximides were investigated as possible precursors of *N*-nitrenes, as part of a general survey of non-oxidative routes to such nitrenes. It was found that pyrolysis, in the melt, of the dimethylsulphoximide (2a) derived from *N*-aminophthalimide gave phthalimide as the only recognisable product. However, photolysis of the sulphoximide in the presence of cyclohexene resulted in a slow exchange reaction in which an aziridine was formed (Scheme 2). These results



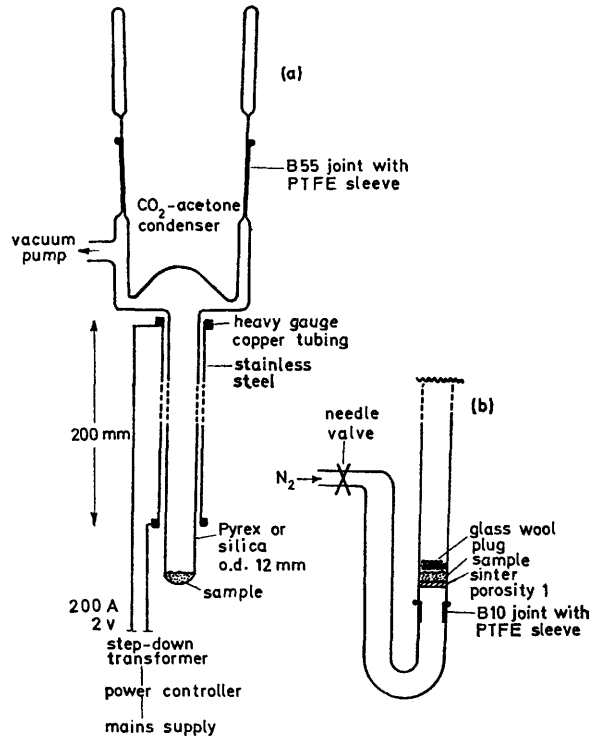
SCHEME 2

closely parallel those obtained with the sulphoximide derived from tetraphenyl-2-pyridone,[8] and the photochemical exchange reaction parallels that observed with phthalimidoaziridines, the mechanism of which has been investigated.[10] By analogy with these results, it appears likely that the photochemical exchange reaction involves a reversible cleavage of the sulphoximide to phthalimidonitrene and dimethyl sulphoxide, the nitrene then being intercepted by the cyclohexene.

In view of the apparent distinction between those *N*-nitrenes which undergo ready fragmentation and those in which the nitrogen is retained,[11] it was of interest to discover the fate of the nitrenes derived from these *N*-amino-lactams when they were generated at high temperature and at low pressure in the vapour phase. Under such conditions the nitrenes would presumably undergo unimolecular decomposition. Accordingly, the flash vacuum pyrolysis of some of the sulphoximides was investigated.

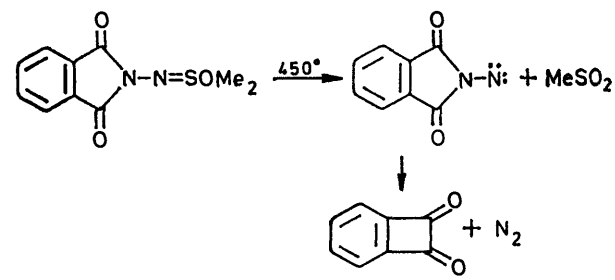
The apparatus used is shown in the Figure; the simpler version (a) consists of a quartz or Pyrex tube, closed at one end, with a connection to a vacuum pump at the open end, and a carbon dioxide–acetone condenser fitted at this end by means of a ground glass joint and polytetrafluoroethylene (PTFE) sleeve. The bottom 3 cm of the tube is heated in an oil-bath or an air-bath, the remaining portion being surrounded by a heating jacket of low thermal capacity. The sample in the bottom of the tube (50—500 mg) is heated under vacuum at a temperature such that it vaporises fairly rapidly (5—30 min). The temperature of the pyrolysis oven can be varied up to 1000°. For involatile compounds an entrainment pyrolysis technique is used, as shown in (b). A slow stream of nitrogen is passed through the apparatus and facilitates the vaporisation of the solid.

In this apparatus, pyrolysis of the sulphoximides proceeded cleanly and in high yield at 400—500°. From the dimethylsulphoximide (2a), two products were isolated: phthalimide (48%) and benzocyclobutene-1,2-dione (35%). The latter product is the



Vacuum pyrolysis apparatus

one to be expected if phthalimidonitrene undergoes fragmentation in the vapour phase, with loss of nitrogen (Scheme 3). This reaction is directly analogous to that



SCHEME 3

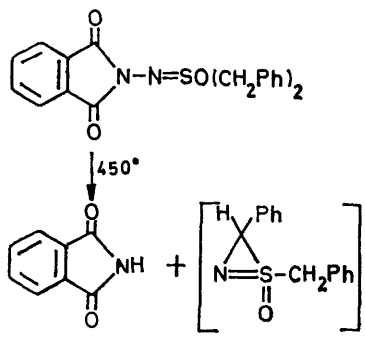
of isoindolinylnitrenes,[12,13] which results in the loss of nitrogen and the formation of products derived from *o*-xylylene and benzocyclobutene. There is evidence, from the stereochemistry of the products, that the extrusion of nitrogen from isoindolinylnitrenes is concerted.[13] No such stereochemical criterion exists in the case of phthalimidonitrene, and the question of the mechanism of the extrusion must therefore remain

[10] T. L. Gilchrist, C. W. Rees, and E. Stanton, *J. Chem. Soc.* (*C*), 1971, 988.
[11] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc.* (*C*), 1970, 576.
[12] W. Baker, J. F. W. McOmie, and D. R. Preston, *J. Chem. Soc.*, 1961, 2971; L. A. Carpino, *J. Amer. Chem. Soc.*, 1962, **84**, 2196; *J. Org. Chem.*, 1969, **34**, 461.
[13] L. A. Carpino, *Chem. Comm.*, 1966, 494.

open. One result which might be taken as evidence against a concerted mechanism is that the corresponding naphthalimidosulphoximide (6) was found to undergo an exactly analogous reaction, giving naphthalimide (41%) and acenaphthenequinone (55%); a concerted mechanism is not possible in this system. Nitrogen was also extruded from the sulphoximide (7), giving fluorenone (10%), although the major product was phenanthridone (80%).

The lactams formed in these pyrolyses result from N–N bond cleavage in the sulphoximides and hydrogen transfer from the *S*-methyl groups. This view is supported by the pyrolysis of the diphenylsulphoximide (2b), which gave a much higher yield of benzocyclobutenedione (68%), and no phthalimide. [This reaction of the readily prepared sulphoximide (2b) constitutes a good synthesis of benzocyclobutenedione, though the chromatographic separation from diphenyl sulphoxide, the only other reaction product, requires care.] Conversely, in a case when hydrogen transfer is facilitated, as in the dibenzylsulphoximide (2d), no benzocyclobutenedione was detected, the N–N bond cleavage and formation of phthalimide being the only reaction observed.

The nature of the sulphur-containing products generated in this hydrogen transfer process is intriguing. From the dibenzylsulphoximide (2d) the primary product would have the molecular formula $C_{14}H_{13}NOS$ (a possible structure is suggested in Scheme 4); however, several attempts to isolate a product other than phthalimide from the reaction were unsuccessful.



SCHEME 4

These sulphoximide pyrolyses show that it is possible to extrude nitrogen even from 'rigid' *N*-nitrenes such as phthalimidonitrene, though the activation energy must be considerably higher than for the corresponding isoindolinylnitrenes, which extrude nitrogen at ambient temperatures.

An attempt was made to extend the work to the preparation and pyrolysis of the sulphoximide (8) derived from *N*-aminophthalimidine; by analogy with the other results, this was thought to be a likely precursor of benzocyclobutenone. Phthalimidine was *N*-aminated with chloramine, and the sulphoxide (8) was prepared, but was found to be extremely labile. On attempted recrystallisation from ethanol, it was converted into the tetrazene (9) (the stereochemistry about the N=N bond was not established). This type of reaction was not observed with any of the other sulphoximides which we have prepared, and we cannot account for the unusual lability of this sulphoximide, unless it simply reflects the greater stability of the *N*-nitrene.

EXPERIMENTAL

Preparation of Sulphoximides.—N-(2,3-*Dihydro*-2-*oxobenzoxazol*-3-*yl*)-SS-*dimethylsulphoximide* (1). 3-Aminobenzoxazol-2(3*H*)-one [11] (0·5 g, 3 mmol) was dissolved in dry dimethyl sulphoxide (15 ml) and lead tetra-acetate (1·5 g, 3·4 mmol) was added during 5 min. The mixture was poured into water (150 ml) and extracted with chloroform (5 × 50 ml). The extract was washed with water, dried, and evaporated, and the residue was crystallised to give the *sulphoximide* (1) (0·45 g, 60%), m.p. 164—165° (from chloroform–petroleum) (Found: C, 48·2; H, 4·4; N, 12·3; S, 14·1. $C_9H_{10}N_2O_3S$ requires C, 47·8; H, 4·5; N, 12·4; S, 14·0%; *M*, 226); $\nu_{max.}$ 1760, 1480, 1209, 1102, 1092, and 1040 cm^{-1}; *m/e* 226, 150, 135, 120, 92, and 78.

SS-*Dimethyl*-N-*phthalimidosulphoximide* (2a). Lead tetra-acetate (9·74 g, 22 mmol) was added in portions to a solution of *N*-aminophthalimide [14] (3·24 g, 20 mmol) in anhydrous dimethyl sulphoxide (20 ml). After the solution had been stirred for 10 min it was poured into ether (600 ml). The precipitate was collected and extracted with boiling chloroform (300 ml). Evaporation of the extract to small bulk gave the *sulphoximide* (2a) (3·5 g, 74%), m.p. 208—210° (Found: C, 50·2; H, 4·1; N, 11·7; S, 13·6. $C_{10}H_{10}N_2O_3S$ requires C, 50·4; H, 4·2; N, 11·8; S, 13·5%; *M*, 238); $\nu_{max.}$ 1708, 1203, 1188, 1041, and 880 cm^{-1}; $\lambda_{max.}$ (EtOH) 227 (log ε 4·3), 294 (3·1), and 302 nm (3·1); *m/e* 238, 147, 104 (base), and 76.

SS-*Diphenyl*-N-*phthalimidosulphoximide* (2b). *N*-Aminophthalimide (5·0 g, 0·31 mmol) and diphenyl sulphoxide (25 g., 1·24 mmol) were stirred in dichloromethane (80 ml). Lead tetra-acetate (15·0 g, 0·34 mmol) was added in portions. After 10 min the mixture was filtered and the solid washed with dichloromethane. The combined filtrate and washings were evaporated and the residue was purified by column chromatography (deactivated basic alumina) to give the *sulphoximide* (2b) (3·0 g, 27%), m.p. 220—221° (from ethanol) (Found: C, 66·7; H, 3·8; N, 7·7; S, 8·9. $C_{20}H_{14}N_2O_3S$ requires C, 66·4; H, 3·8; N, 7·7; S, 8·8%; *M*, 362); $\nu_{max.}$ ($CHCl_3$) 1720, 1450, 1372, 1095, 1085, and 1008 cm^{-1}; *m/e* 362, 202, 185 (base), 162, 147, 104, and 76.

S-*Methyl*-S-*phenyl*-N-*phthalimidosulphoximide* (2c). By a procedure similar to that described for the sulphoximide (2b), *N*-aminophthalimide (4·6 mmol) and methyl phenyl sulphoxide (13 mmol) gave the *sulphoximide* (2c) (20%), m.p. 153° (from ethanol) (Found: C, 59·6; H, 4·0; N, 9·1; S, 10·6. $C_{15}H_{12}N_2O_3S$ requires C, 60·0; H, 4·0; N, 9·3; S, 10·7%); $\nu_{max.}$ ($CHCl_3$) 1720, 1375, 1113, 1090, 1035, and 1010 cm^{-1}.

SS-*Dibenzyl*-N-*phthalimidosulphoximide* (2d). Powdered *N*-aminophthalimide (1·62 g, 10 mmol) was added during 1 h to a stirred mixture of dibenzyl sulphoxide (2·3 g, 10

[14] H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 1937, 16.

mmol) and lead tetra-acetate (4·9 g, 11 mmol) in dichloromethane (100 ml). The mixture was stirred for a further 15 min, then filtered, and the solids were washed with dichloromethane. Evaporation of the filtrate and washings gave a yellow oil which solidified when triturated with ether. Crystallisation gave the *sulphoximide* (2d) (3·0 g, 77%), m.p. 147—150° (from ethanol) (Found: C, 67·3; H, 4·7; N, 7·4; S, 8·4. $C_{22}H_{18}N_2O_3S$ requires C, 67·7; H, 4·65; N, 7·2; S, 8·2%); $\nu_{max.}$ 1720, 1220, 1025, 890, 720, and 700 cm^{-1}; τ ($CDCl_3$) 5·54 (4H), 2·72 (10H, m), and 2·41 (4H, m).

N-(3,4-*Dihydro*-2-*methyl*-4-*oxoquinazolin*-3-*yl*)-SS-*dimethylsulphoximide* (3a). This was prepared from 3-amino-2-methylquinazoline [11] and dimethyl sulphoxide by a procedure analogous to that described for the sulphoximide (2a). The yellow *sulphoximide* (3a) (90%) had m.p. 176—178° (from ethanol) (Found: C, 52·4; H, 5·15; N, 16·8; S, 12·7. $C_{10}H_{13}N_3O_2S$ requires C, 52·6; H, 5·2; N, 16·7; S, 12·8%); $\nu_{max.}$ 1670, 1595, 1210, and 1050 cm^{-1}.

N-(3,4-*Dihydro*-2-*methyl*-4-*oxoquinazolin*-3-*yl*)-SS-*diphenyl sulphoximide* (3b). This was prepared by a procedure analogous to that described for the sulphoximide (2b). The *sulphoximide* (3b) (64%) had m.p. 137—138° (from ethanol) (Found: C, 66·9; H, 4·5; N, 11·3. $C_{21}H_{17}N_3O_2S$ requires C, 67·2; H, 4·6; N, 11·2%); $\nu_{max.}$ 1670, 1600, 1230, 1090, and 770 cm^{-1}.

SS-*Biphenyl*-2,2′-*diyl*-N-(3,4-*dihydro*-2-*methyl*-4-*oxoquinazolin*-3-*yl*)*sulphoximide* (3c). This was prepared, from dibenzothiophen *S*-oxide, by a procedure analogous to that described for the sulphoximide (2b). The *sulphoximide* (3c) (13%) had m.p. 238—240° (from ethanol) (Found: C, 67·5; H, 4·0; N, 11·5; S, 8·4. $C_{21}H_{15}N_3O_2S$ requires C, 67·55; H, 4·05; N, 11·3; S, 8·6%); $\nu_{max.}$ 1670, 1600, 1210, 980, and 760 cm^{-1}.

N-(1,2-*Dihydro*-2-*oxoquinolin*-1-*yl*)-SS-*dimethylsulphoximide* (4a). This was prepared from 1-amino-2-quinolone [11] and dimethyl sulphoxide by a procedure analogous to that described for sulphoximide (2a). The *sulphoximide* (4a) (52%) had m.p. 200—201° (from ethanol) (Found: C, 56·0; H, 5·3; N, 11·7. $C_{11}H_{12}N_2O_2S$ requires C, 55·9; H, 5·1; N, 11·7%); $\nu_{max.}$ 1650, 1590, 1210, 1030, and 750 cm^{-1}.

N-(1,2-*Dihydro*-2-*oxoquinolin*-1-*yl*)-SS-*diphenylsulphoximide* (4b). This was prepared by a procedure analogous to that described for sulphoximide (2b). The *sulphoximide* (4b) (45%) had m.p. 162—163° (from ethanol) (Found: C, 70·3; H, 4·5; N, 8·05; S, 9·0. $C_{21}H_{16}N_2O_2S$ requires C, 70·0; H, 4·5; N, 7·8; S, 8·9%); $\nu_{max.}$ 1660, 1610, 1330, 1250, 1170, 1100, 745, and 680 cm^{-1}.

N-(1,2-*Dihydro*-2-*oxoquinolin*-1-*yl*)-S-*methyl*-S-*phenylsulphoximide* (4c). This was prepared by a procedure analogous to that described for sulphoximide (2b). The *sulphoximide* (4c) (32%) had m.p. 158—159° (from ethanol) (Found: C, 64·5; H, 4·7; N, 9·4; S, 10·5. $C_{16}H_{14}N_2O_2S$ requires C, 64·6; H, 4·7; N, 9·4; S, 10·85%); $\nu_{max.}$ 1660, 1230, 1180, 750, and 680 cm^{-1}.

N-(1,2-*Dihydro*-2-*oxo*-1-*pyridyl*)-SS-*dimethylsulphoximide* (5). This was prepared from 1-amino-2-pyridone [15] and dimethyl sulphoxide by a procedure analogous to that described for the sulphoxide (2a). The *sulphoximide* (5) (36%) had m.p. 122—123° (from ethanol) (Found: C, 82·3; H, 5·0; N, 5·5. $C_7H_{10}N_2O_2S$ requires C, 82·5; H, 5·0; N, 5·8%).

SS-*Dimethyl*-N-*naphthalimidosulphoximide* (6). This was prepared from *N*-aminonaphthalimide [16] and dimethyl sulphoxide by a procedure analogous to that described for the sulphoximide (1). The *sulphoximide* (6) (29%) had m.p. 205° (from ethanol) (Found: C, 58·1; H, 4·4; N, 10·0; S, 11·2. $C_{14}H_{12}N_2O_3S$ requires C, 58·3; H, 4·2; N, 9·7; S, 11·1%); $\nu_{max.}$ 1702, 1664, 1237, 1203, 1066, 1056, 889, and 775 cm^{-1}; τ ($CDCl_3$) 6·64 (6H) and 2·40—1·40 (6H, m).

N-(5,6-*Dihydro*-6-*oxophenanthridin*-5-*yl*)-SS-*dimethylsulphoximide* (7). This was available from the work of Rees and Yelland.[8]

SS-*Dimethyl*-N-*phthalimidin*-2-*ylsulphoximide* (8). (*a*) To phthalimidine (10·0 g, 75 mmol) in dry dichloromethane (150 ml) was added sodium hydride (50% dispersion in oil; 5·4 g, 112 mmol). When gas evolution had ceased, chloramine (0·15M in dichloromethane; 750 ml) was added. After 60 h the brown precipitate was filtered off and the filtrate evaporated. The semi-solid residue was triturated with petroleum. Crystallisation then gave N-*aminophthalimidine* (4·5 g, 40%), m.p. 96° (from benzene–petroleum) (Found: C, 64·4; H, 5·4; N, 18·7%; *m/e*, 148. $C_8H_8N_2O$ requires C, 64·8; H, 5·4; N, 18·9%; *M*, 148); $\nu_{max.}$ (Nujol) 3280, 3257, 3148, 1706, 1465, 1450, 958, 729, and 721 cm^{-1}; $\lambda_{max.}$ (EtOH) 222 (log ε 4·0), 229 (3·9), 272 (3·5), and 279 nm (3·4); τ ($CDCl_3$) 5·53 (4H) and 2·80—2·00 (4H, m); τ ($CDCl_3$–D_2O) 5·53 (2H) and 2·80—2·00 (4H, m); benzylidene derivative, m.p. 206° (lit.,[17] 206°).

(*b*) Lead tetra-acetate (3·0 g, 6·75 mmol) was added to *N*-aminophthalimidine (1·0 g, 6·75 mmol) in dry dimethyl sulphoxide (15 ml). The mixture was poured into dichloromethane (200 ml) and washed with water (2 × 200 ml). The organic solution was evaporated to leave a yellow oil which rapidly crystallised to give SS-*dimethyl*-N-*phthalimidin*-2-*ylsulphoximide* (8) (0·8 g, 53%), m.p. 160° (decomp., then crystals form in melt, m.p. >320°); $\nu_{max.}$ 1685, 1210, 1196, 1176, 1040, 982, and 733 cm^{-1}; τ ($CDCl_3$) 6·76 (6H), 5·38 (4H), 2·70—2·40 (3H, m), and 2·30—2·00 (1H, m); *m/e* (no parent peak at 224), 148, 147, 133, 132, 118, 90, and 78 (base). Attempted recrystallisation from ethanol gave 2,2′-*azophthalimidine* (9), plates m.p. >320° (Found: C, 65·3; H, 4·0; N, 19·0%; *m/e*, 292. $C_{16}H_{12}N_4O_2$ requires C, 65·75; H, 4·1; N, 19·2%; *M*, 292); $\nu_{max.}$ 1720, 1470, 1454, 1366, 1212, and 741 cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 5·63 (4H), 3·30—2·80 (6H, m), and 2·75—2·50 (2H, m).

Photolysis of SS-*Dimethyl*-N-*phthalimidosulphoximide in the Presence of Cyclohexene.*—The sulphoximide (0·50 g, 2·1 mmol) in acetonitrile (15 ml) containing cyclohexene (15 ml) was irradiated (Rayonet reactor; 254 nm lamps; quartz vessel) for 24 h. The solvent was removed and the residue purified by column chromatography (deactivated basic alumina). Ether–petroleum (1 : 1) eluted 7-phthalimido-7-azabicyclo[4,1,0]heptane (105 mg, 20%), m.p. 135° (lit.,[11] 137°), identical with a specimen prepared by the oxidation of *N*-aminophthalimide in cyclohexene.

Vacuum Pyrolysis of Sulphoximides.—For a general description of the apparatus and the method used see Discussion section.

[15] H. Erlenmeyer and K. Hoergerle, *Helv. Chim. Acta*, 1956, **39**, 1203.

[16] L. A. Carpino, A. A. Santilli, and R. W. Murray, *J. Amer. Chem. Soc.*, 1960, **82**, 2728.

[17] A. Darapsky and P. Heinrichs, *J. prakt. Chem.*, 1936, **146**, 307.

SS-*Dimethyl*-N-*phthalimidosulphoximide* (2a). The title compound (238 mg) was sublimed at 205° and 0·4 mm Hg (N_2 flow rate 5 ml min^{-1}) and pyrolysed at 450°. The pale yellow solid (135 mg) which collected on the condenser was separated by preparative layer chromatography (p.l.c.) (silica; 20 × 20 × 0·1 cm; ether). This gave (i) bicyclo[4,2,0]octa-1,3,5-triene-7,8-dione (benzocyclobutene-1,2-dione) (46 mg, 35%), m.p. 130—132° (from cyclohexane) (lit.,[18] 130—131°), $\nu_{max.}$ (Nujol) 1795, 1780, 1735, 1590, 1280, 1170, 1140, 940, 855, and 780 cm^{-1} (identical with the published [18] spectrum), and (ii) phthalimide (70 mg, 48%).

SS-*Diphenyl*-N-*phthalimidosulphoximide* (2b). The sulphoximide (162 mg) was pyrolysed at 420° by sublimation at 220° and 0·01 mm Hg. The pyrolysate, a pale yellow solid (140 mg), was separated by p.l.c., and gave (i) benzocyclobutenedione (40 mg, 68%), (ii) diphenyl sulphoxide (70 mg, 77%), and (iii) unchanged sulphoximide (5 mg, 3%).

SS-*Dibenzyl*-N-*phthalimidosulphoximide* (2d). The compound (256 mg) was sublimed at 150—170° and 0·5 mm Hg (N_2 flow rate 5 ml min^{-1}) and the vapour was pyrolysed at 450°. The pyrolysate (211 mg) was a solid at −70° but appeared partly to decompose on warming to room temperature, and also appeared to be hygroscopic. Analysis by t.l.c. showed several components but benzocyclobutenedione and dibenzyl sulphoxide were not detected. P.l.c. (silica; ether–petroleum 1 : 1) gave only phthalimide (77 mg, 80%). Rapid p.l.c. on alumina also gave only phthalimide.

SS-*Dimethyl*-N-*naphthalimidosulphoximide* (6). The sulphoximide (138 mg) was vaporised at 220° and 0·005 mmHg, and the vapour pyrolysed at 450°. The pyrolysate was separated by p.l.c. and gave (i) acenaphthenequinone (35 mg, 55% based on starting material consumed), m.p. and mixed m.p. 255—258°, (ii) naphthalimide (28 mg, 41% based on starting material consumed), and (iii) starting material (6) (39 mg).

N-(5,6-*Dihydro*-6-*oxophenanthridin*-5-*yl*)-SS-*dimethylsulphoximide* (7). The sulphoximide (50 mg) was vaporised at 180—210° and 0·1 mmHg, and the vapour pyrolysed at 400°. T.l.c. of the pyrolysate showed phenanthridone and fluorenone, but no benzo[*c*]cinnoline or biphenylene. The pyrolysate was washed with dichloromethane, and phenanthridone (27 mg, 80%) was filtered off. The filtrate on evaporation gave fluorenone (3 mg, 10%).

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