Photolysis and Thermolysis of *N*-(*N*-Arylimidoyl)sulphimides

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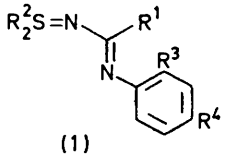
Routes to the imidoylsulphimides (1) are described, starting from either the corresponding amidines or the imidoyl chlorides. Photolysis of the sulphimides involves cleavage of the sulphur–nitrogen bonds and gives 2-substituted benzimidazoles in good yields.

SS-Dimethyl-*N*-(*N*-phenylbenzimidoyl)sulphimide (1a) is decomposed by heating in benzonitrile or decalin under reflux, and gives 2-phenylbenzimidazole, 2-phenylquinazoline, and 2,4,6-triphenyl-1,3,5-triazine. Mechanisms are proposed for the formation of the last two, unexpected products. Similar thermal decomposition of the sulphimides (1b—e) is observed; the thermolysis is markedly catalysed by copper salts.

ORGANIC azides have proved to be versatile reagents in synthesis, both as components in intermolecular reactions and as substrates capable of fragmentation and intramolecular rearrangement. These reactions often involve the elimination of molecular nitrogen and the formation of products formally derived from nitrene intermediates. Sulphimides, $RN{=}SR'_2$, bear some similarity to azides in that the substituted nitrogen atom is nucleophilic and is adjacent to a good leaving group, in this case a sulphide, and sulphimides might therefore be expected to react in the same way as azides in many instances. An example of such parallel behaviour is the generation of ethoxycarbonylnitrene by photolysis of ethyl azidoformate and of *N*-ethoxycarbonyl-*SS*-dimethylsulphimide.[1]



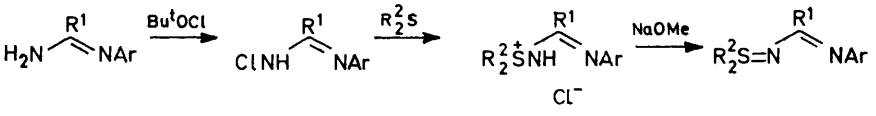
(1)

a; R^1 = Ph, R^2 = Me, R^3 = R^4 = H
b; R^1 = Ph, R^2 = R^3 = Me, R^4 = H
c; R^1 = Ph, R^2 = Me, R^3 = Cl, R^4 = H
d; R^1 = Ph, R^2 = Me, R^3 = H, R^4 = Cl
e; R^1 = Ph, R^2 = CH_2Ph, R^3 = R^4 = H
f; R^1 = Ph, R^2_2 = $[CH_2]_4$, R^3 = R^4 = H
g; R^1 = R^2 = Ph, R^3 = R^4 = H
h; R^1 = R^2 = Ph, R^3 = Me, R^4 = H
j; R^1 = R^2 = Ph, R^3 = Cl, R^4 = H
k; R^1 = R^2 = Me, R^3 = R^4 = H
m; R^1 = CH_2Ph, R^2 = Me, R^3 = R^4 = H

In systems where azides are not readily available, sulphimides might offer some advantages as precursors of nitrenes. Imidoylsulphimides are an example; here the corresponding azides normally exist as their cyclic aromatic valence tautomers, the 1*H*-tetrazoles. Photolysis and thermolysis of 1-aryltetrazoles leads to benzimidazole and carbodi-imide derivatives, these being formally derived from the corresponding imidoylnitrenes. We have prepared a series of *N*-(*N*-arylimidoyl)sulphimides (1) and have investigated their photolysis and thermolysis, in order to compare the reaction conditions and products with those of the corresponding tetrazoles.

We find that the photochemical decomposition of the sulphimides can be rationalised by invoking the imidoylnitrenes but the major pathways of thermal decomposition can not.

Preparation of Sulphimides.—No imidoylsulphimides had been reported when this work was started. In 1974 the preparation of *N*-benzimidoyl-*SS*-dimethylsulphimide (2) was described;[2] this sulphimide was obtained by the reaction of *N*-chlorobenzamidine with dimethyl sulphide, and treatment of the resulting sulphonium salt with base. The guanidine derivative (3) was prepared by a similar route.[3] We have used three methods for preparing imidoylsulphimides. The first (Scheme 1) is analogous to those used for the sulphimides (2) and (3), the *N*-chloroamidine being generated *in situ* by the reaction of the amidine with t-butyl hypochlorite. This method is suitable for *N*-chloro-*N*-arylbenzamidines and dialkyl sulphides but fails with diphenyl sulphide. The second method, which was also used with alkyl sulphides, involves the formation of a sulphonium salt by reaction of the amidine with the complex formed between the sulphide and *N*-chlorosuccinimide (Scheme 2). This method of forming sulphonium salts was first described by Vilsmaier and Sprügel;[4] it has recently been used in the preparation of *N*-arylsulphimides.[5]

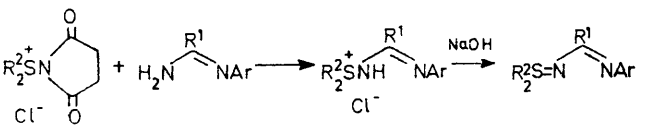


SCHEME 1

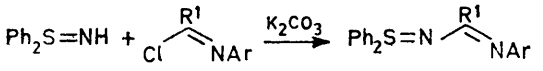
The third method of preparation, which was used for *SS*-diphenylsulphimides, involves the reaction of a benzimidoyl chloride with the sulphimide $Ph_2S{=}NH$

[1] Y. Hayashi and D. Swern, *Tetrahedron Letters*, 1972, 1921.
[2] T. Fuchigami and K. Odo, *Chem. Letters*, 1974, 247.
[3] A. Heesing and G. Imsieke, *Chem. Ber.*, 1974, **107**, 1536.
[4] E. Vilsmaier and W. Sprügel, *Tetrahedron Letters*, 1972, 625.
[5] P. K. Claus, P. Hofbauer, and W. Rieder, *Tetrahedron Letters*, 1974, 3319; see also P. K. Claus, W. Rieder, P. Hofbauer, and E. Vilsmaier, *Tetrahedron*, 1975, **31**, 505.

(Scheme 3). This *N*-unsubstituted sulphimide is readily available from the *N*-*p*-tolylsulphonyl derivative by acidic hydrolysis,[6] or by the amination of diphenyl sulphide.[7]

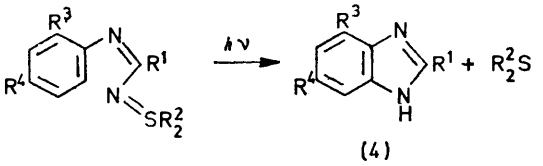


SCHEME 2



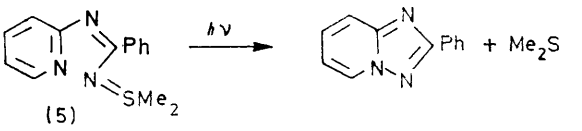
SCHEME 3

Photolysis.—The sulphimides (1) were irradiated in acetonitrile using a medium-pressure mercury lamp. The only products observed were the corresponding



SCHEME 4

sulphide and benzimidazole (Scheme 4). The reaction proceeded readily to give the benzimidazoles (4) in good yields (Table). Photolysis of the *SS*-diphenylsulphimides (1g and h) was rapid. The *SS*-dialkylsulphimides were cleaved more slowly and the yields of benzimidazoles were not optimised. *SS*-Dimethyl-*N*-[*N*-(2-pyridyl)-benzimidoyl]sulphimide (5) gave 2-phenyl-*s*-triazolo-[1,5-*a*]pyridine [8] (90%) (Scheme 5); here, the nitrogen



SCHEME 5

atom of the pyridine ring rather than the β-carbon atom is the site of cyclisation.

These reactions probably involve the generation of imidoylnitrene intermediates and their subsequent cyclisation. 1,5-Diphenyltetrazole has also been observed to give 2-phenylbenzimidazole when photolysed, and the same nitrene intermediate is probably involved in the photolysis of the tetrazole and of the sulphimides (1a, e, f, and g). With the pyridylsulphimide (5) cyclisation on to nitrogen rather than carbon is in accord with the expected electrophilic nature of the nitrene; preferential cyclisation on to nitrogen has been observed in other reactions which are thought to involve nitrene intermediates; for example, the thermolysis of 2-(2-pyridyl)phenyl azide.[9]

It is notable that no products formed by Wolff rearrangement of the proposed imidoylnitrenes are observed. This is also the case in the photolysis of 1,5-diphenyltetrazole,[10] although pyrolysis gives diphenylcarbodi-imide, the Wolff rearrangement product, in good yield.[11]

Thermolysis.—The dimethylsulphimides (1a—d) decomposed slowly when heated in solvents above 150 °C, and were completely converted into products when heated in decalin under reflux for 8—16 h. *SS*-Dimethyl-*N*-(*N*-phenylbenzimidoyl)sulphimide (1a) gave 2-phenylbenzimidazole (9%), 2-phenylquinazoline (19%), and 2,4,6-triphenyl-1,3,5-triazine (65%), each being isolated in the yields quoted and identified by comparison with a specimen prepared by a standard route. Analogous products were isolated in comparable yields from the sulphimides (1b—d).

The formation of 2-phenylbenzimidazoles is most simply rationalised by postulating a cleavage of the sulphimides into nitrenes and dimethyl sulphide, as in the photochemical reactions. The sulphimide (5) was considerably less stable than the other *SS*-dimethylsulphimides, and gave 2-phenyl-*s*-triazolo[1,5-*a*]pyridine when heated in toluene under reflux. This lower stability probably indicates nucleophilic participation by the nitrogen of the pyridine ring in the cleavage of the sulphimide. Such participation, which is observed in the thermal decomposition of aromatic azides bearing neighbouring nucleophilic groups, may also operate in

Benzimidazoles isolated from photolysis of imidoylsulphimides †

		Benzimidazole (4)			
Sulphimide	Photolysis time (h)	Yield (%)	M.p. (°C)	Lit. m.p.	Ref.
(1a)	5	30	288—290	288	*a*
(1a)	21	96	288—290	288	*a*
(1b)	15	68	249—251	251—252	*a*
(1c)	19	72	229—231	227—228	*b*
(1d)	23	72	208—210	210	*c*
(1e)	17	38	288—290	288	*a*
(1f)	18	67	288—290	288	*a*
(1g)	3	73	288—290	288	*a*
(1h)	4	95	248—250	251—252	*a*
(1j)	21	73	229—231	227—228	*b*
(1k)	16	61	176—177	172—174	*d*
(1m)	15	53	188	187	*e*

† Sulphimide (0.5 mmol) in acetonitrile (100 ml) and 100 W medium-pressure mercury immersion lamp with Hanau M68 filter; yields for recrystallised products.

[a] M. W. Partridge and H. A. Turner, *J. Chem. Soc.*, 1958, 2086. [b] F. Montanari and R. Passerini, *Boll. Sci. Fac. Chim. ind. Bologna*, 1953, **11**, 42 (*Chem. Abs.*, 1954, **48**, 6436). [c] B. A. Poraĭ-Koshits, L. S. Efros, and O. F. Ginzburg, *J. Gen. Chem.* (*U.S.S.R.*), 1949, **19**, 1545. [d] E. C. Wagner and W. H. Millett, *Org. Synth.*, Coll. Vol. II, 1943, p. 65. [e] B. A. Poraĭ-Koshits, L. S. Efros, and O. F. Ginzburg, *J. Gen. Chem.* (*U.S.S.R.*), 1947, **17**, 1768.

[6] N. Furukawa, T. Omata, T. Yoshimura, T. Aida, and S. Oae, *Tetrahedron Letters*, 1972, 1619.

[7] Y. Tamura, K. Sumoto, H. Matsushima, H. Taniguchi, and M. Ikeda, *J. Org. Chem.*, 1973, **38**, 4324.

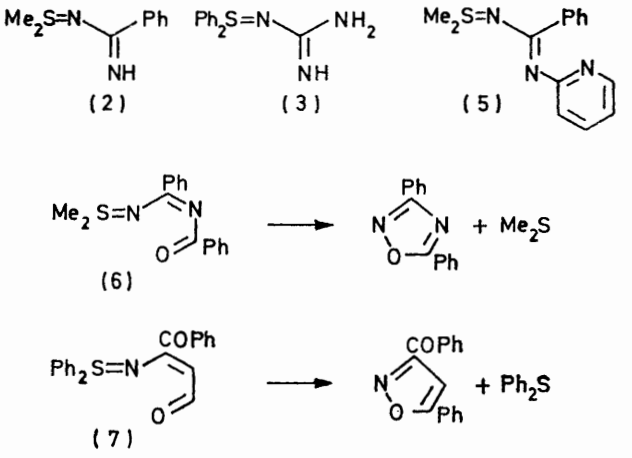
[8] K. T. Potts, H. R. Burton, and J. Bhattacharyya, *J. Org. Chem.*, 1966, **31**, 260.

[9] R. A. Abramovitch and K. A. H. Adams, *Canad. J. Chem.*, 1961, **39**, 2516.

[10] W. Kirmse, *Angew. Chem.*, 1959, **71**, 537.

[11] P. A. S. Smith and E. Leon, *J. Amer. Chem. Soc.*, 1958, **80**, 4647.

the ready conversion of the sulphimides (6) [2] and (7) [7] into heterocyclic products.

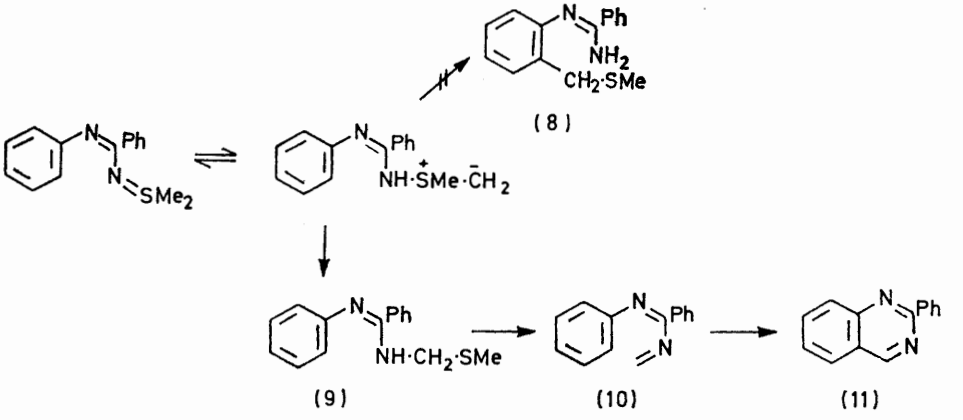


The mechanism of formation of the 2-phenylquinazolines is more complex, as one carbon atom of the sulphide is incorporated into the heterocycle. Evidence that this carbon atom, C-4 of the quinazoline, comes from the sulphide, was obtained by examining the products of thermolysis of *SS*-dibenzyl-*N*-(*N*-phenylbenzimidoyl)sulphimide (1e). These products included 2-phenylbenzimidazole (7%) and 2,4-diphenylquinazoline (38%), the *S*-benzyl group becoming the *C*-phenyl group at position 4 of the quinazoline.

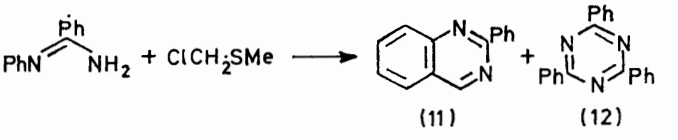
Two mechanisms were considered for the formation of the quinazolines, and these are outlined in Scheme 6. In the first, the sulphimide is converted into the amidine (8) by a rearrangement equivalent to a vinylogous Sommelet–Hauser rearrangement. This is then envisaged to cyclise by intramolecular displacement of the methylthio-group. The mechanism had to be discounted when a specimen of the amidine (8), synthesised independently from 2-(methylthiomethyl)aniline and methyl thiobenzimidate hydriodide,[12] was found not to give any 2-phenylquinazoline under the conditions of the thermolysis.

The second mechanism involves a Stevens rearrangement as the first step. Stevens rearrangement has been proposed as a first step in the thermolysis of some *N*-acylsulphimides.[13] The amidine (9) thus formed may then be converted into a Schiff's base (10) by thermal elimination of methanethiol. 2-Phenylquinazoline (11) can then be formed by electrocyclic ring closure and dehydrogenation.

An attempt was made to synthesise the proposed intermediate (9) by heating together *N*-phenylbenzamidine and chloromethyl methyl sulphide. In the conditions required to bring about reaction (decalin solvent and a sealed tube at 200 °C) the amidine (9) was not detected, but both 2-phenylquinazoline and 2,4,6-triphenyl-1,3,5-triazine (12) were isolated from the reaction mixture (Scheme 7). The amidine (9) is therefore a possible precursor of both these products. The triazine is known to be a product of the trimerisation of benzonitrile in the presence of various catalysts, but it is unlikely that it is formed from benzonitrile in the thermolysis of these sulphimides: the yield of triazine was not increased, but somewhat decreased, when the thermolysis was carried out in benzonitrile rather than in decalin.



SCHEME 6



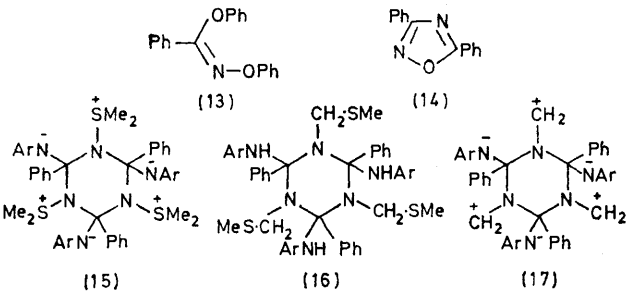
SCHEME 7

It was unexpected to find the *s*-triazine (12) as the major product (55—65%) of thermolysis of the *N*-benzimidoylsulphimides (1a—c), and only a tentative mechanism for its formation can be proposed at present. This formation of (12) is reminiscent of its formation in

[12] P. Reynard, R. C. Moreau, and N. H. Thu, *Compt. rend.*, 1961, **253**, 2540.

[13] H. Kise, G. F. Whitfield, and D. Swern, *Tetrahedron Letters*, 1971, 1761; D. Swern, G. F. Whitfield, H. S. Beilan, and D. Saika, *J. Org. Chem.*, 1974, **39**, 2148; S. Oae, T. Matsuda, T. Tsujihara, and N. Furukawa, *Bull. Chem. Soc. Japan*, 1972, **45**, 3586.

the thermolysis or photolysis of various formal ' adducts ' of benzonitrile, such as benzamidoxime,[14] the iminoether (13),[15] and the diphenyloxadiazole (14),[16] though in these reactions the yield of triazine is very low. Formation of triazine (12) from (13) and (14) was



(13) (14)

(15) (16) (17)

thought to result from the trimerisation of some activated nitrile species such as PhĊ=N̈. This seems very unlikely in our high yield reactions, which formally involve trimerisation of the benzimidoylsulphimides (1) or, more likely, the derived Stevens rearrangement products [*e.g.* (9)] or Schiff's bases [*e.g.* (10)], with loss of the elements of $ArN{=}SMe_2$, $ArNH{\cdot}CH_2{\cdot}SMe$, or $ArN{=}CH_2$, respectively; no products derived from these fragments were isolated, however. These trimerisations would give (15), (16), or (17), respectively, though it is possible that some of the elimination steps may occur before ring closure. Nothing is known about the timing of the individual steps, some of which may be reversible, but ultimate formation of the *s*-triazine as the major thermolysis product is presumably related to its great thermodynamic stability.

The *s*-triazine was not formed under our conditions from *N*-phenylbenzamidine, which might have arisen by hydrolysis of the sulphimide (1a). Somewhat surprisingly, the triazine was also not formed from *N*-benzoyl-*SS*-dimethylsulphimide, which by analogy was expected to eliminate dimethyl sulphoxide.

Following the analogy drawn earlier between sulphimides and azides, the possibility of catalysis in the thermal decomposition of our sulphimides was considered. Copper(II) salts did significantly lower the temperature at which *SS*-dimethyl-*N*-(*N*-phenylbenzimidoyl)sulphimide (1a) decomposed. Although the sulphimide decomposed slowly in boiling xylene, the decomposition was enhanced in the presence of anhydrous copper(II) sulphate, the quinazoline (11) (27%) and the triazine (12) (25%) being isolated after 10 h. The sulphimide (1a) was unchanged in boiling toluene (23 h) but in the presence of copper(II) acetylacetonate (10%) it was extensively decomposed; the quinazoline (11) (16%), but none of the triazine (12), was isolated. In spite of the lower temperatures and some apparent selectivity in the catalysed decompositions, the reactions were no cleaner and the yields no higher than in the uncatalysed thermolyses, and this catalysis was therefore not investigated further.

The course of the thermal decomposition of these sulphimides is in contrast with that of the corresponding aminimide, $Me_3\overset{+}{N}{-}\bar{N}C(Ph){=}NPh$, which is reported to give 2-phenylbenzimidazole in good yield when it is pyrolysed.[17] The difference is presumably related to a greater tendency for Stevens rearrangement in the sulphimides.

EXPERIMENTAL

M.p.s were determined on a Kofler block. I.r. spectra were recorded for Nujol mulls on a Pye Unicam SP 200 spectrometer. N.m.r. spectra were recorded on a Varian HA-100 instrument with tetramethylsilane as internal reference. Mass spectra were recorded on an A.E.I. MS12 or MS902 instrument operating at 70 eV. Preparative layer chromatography was carried out on Kieselgel PF254 (Merck).

Preparation of Sulphimides.—Three general procedures were used.

Method A. Freshly prepared t-butyl hypochlorite (2.16 g, 0.02 mol) in dry dichloromethane (10 ml) was added dropwise over 20 min to a solution of the amidine (0.02 mol) (prepared by the general method of Short *et al.*[18]) in dichloromethane (40 ml), stirred at −60 °C. After a further 20 min, the sulphide (0.024 mol) was added rapidly. The mixture was stirred for 40 min at −60 °C, then sodium methoxide [from sodium (0.024 mol) and methanol (10 ml)] was added. After 1 h at −60 °C the mixture was allowed to warm up to room temperature and was washed with water, dried, and evaporated to yield the crude sulphimide (80—90%), which was recrystallised from pentane–dichloromethane. The following sulphimides were prepared: SS-*dimethyl*-N-(N-*phenylbenzimidoyl*)*sulphimide* (1a) (60%) from *N*-phenylbenzamidine;[19] m.p. 167—169° (Found: C, 69.9; H, 6.3; N, 10.9. $C_{15}H_{16}N_2S$ requires C, 70.3; H, 6.3; N, 10.9%); δ ($CDCl_3$) 2.72 (6 H) and 6.5—7.4 (10 H, m); *m/e* 256 (76), 209 (20), 195 (54), 180 (99), 91 (60), and 77 (100); *m** (256 ⟶ 209) 170.6, *m** (209 ⟶ 180) 155.1; SS-*dimethyl*-N-[N-(2-*tolyl*)*benzimidoyl*]*sulphimide* (1b) (67%) from *N*-2-tolylbenzamidine;[20] m.p. 170—172° (Found: C, 70.7; H, 6.9; N, 10.3. $C_{16}H_{18}N_2S$ requires C, 71.1; H, 6.7; N, 10.4%); δ ($CDCl_3$) 2.22 (3 H), 2.75 (6 H), and 6.3—7.4 (9 H, m); *m/e* 270; N-[N-(2-*chlorophenyl*)*benzimidoyl*]-SS-*dimethylsulphimide* (1c) (65%) from *N*-2-chlorophenylbenzamidine;[21] m.p. 172—174° (Found: C, 61.8; H, 5.2; N, 9.8. $C_{15}H_{15}ClN_2S$ requires C, 62.0; H, 5.2; N, 9.6%); δ ($CDCl_3$) 2.80 (6 H) and 6.3—7.4 (9 H, m); *m/e* 292 (15), 290 (40), and 214 (100); N-[N-(4-*chlorophenyl*)*benzimidoyl*]-SS-*dimethylsulphimide* (1d) (62%) from *N*-4-chlorophenylbenzamidine;[20] m.p. 180—182° (Found: C, 62.1; H, 5.4; N, 9.7%); δ ($CDCl_3$) 2.76 (6 H) and 6.5—7.4 (9 H, m); *m/e* 292 (37) and 290 (100); SS-*dibenzyl*-N-(N-*phenylbenzimidoyl*)*sulphimide* (1e) (67%) from *N*-phenylbenzamidine; m.p. 122—124° (Found: C, 79.4; H, 6.0; N, 6.8. $C_{27}H_{24}N_2S$ requires C, 79.4; H, 5.9; N, 6.9%); δ ($CDCl_3$) 4.25 (4 H) and 6.6—7.6 (20 H, m); *m/e* 408 (2),

[14] G. Leandri and P. Rebora, *Ann. Chim.* (*Italy*), 1956, **46**, 953.
[15] E. C. Taylor and F. Kienzle, *J. Org. Chem.*, 1971, **36**, 233.
[16] H. Newman, *Tetrahedron Letters*, 1968, 2417.
[17] R. F. Smith and T. A. Craig, *Tetrahedron Letters*, 1973, 3941.
[18] P. Oxley, M. W. Partridge, and W. F. Short, *J. Chem. Soc.*, 1947, 1110.
[19] F. C. Cooper and M. W. Partridge, *Org. Synth.*, 1956, **36**, 64.
[20] F. C. Cooper and M. W. Partridge, *J. Chem. Soc.*, 1953, 255.
[21] P. Oxley and W. F. Short, *J. Chem. Soc.*, 1949, 449.

318 (4), and 91 (100); SS-*dimethyl*-N-[N-(2-*pyridyl*)*benzimidoyl*]*sulphimide* (5) (35%) from *N*-2-pyridylbenzamidine;[18] m.p. 170—172° (Found: C, 65.7; H, 6.1; N, 16.1. $C_{14}H_{15}N_3S$ requires C, 65.4; H, 5.8; N, 16.3%); δ ($CDCl_3$) 2.80 (6 H) and 6.2—8.3 (9 H, m); SS-*dimethyl*-N-(N-*phenylacetimidoyl*)*sulphimide* (1k) (84%) from *N*-phenylacetamidine[18] as a hygroscopic gum which did not crystallise; δ ($CDCl_3$) 1.91 (3 H), 2.68 (6 H), and 6.7—7.4 (5 H, m); *m/e* 194 (75), 147 (38), 118 (100), and 77 (75); *m** (194 → 147) 111.3, *m** (147 → 118) 94.7, *m** (118 → 77) 50.2, *picrate*, m.p. 187—189° (Found: C, 45.3; H, 4.2; N, 16.3. $C_{16}H_{17}N_5O_7S$ requires C, 45.3; H, 4.0; N, 16.5%); SS-*dimethyl*-N-(N,2-*diphenylacetimidoyl*)-*sulphimide* (1m) (63%) from *N*,2-diphenylacetamidine;[20] m.p. 105—106° (Found: C, 71.1; H, 6.6; N, 10.4. $C_{16}H_{18}N_2S$ requires C, 71.1; H, 6.7; N, 10.4%); δ ($CDCl_3$) 2.60 (6 H), 3.58 (2 H), and 6.5—7.4 (10 H, m); *m/e* 270 (82), 179 (97), and 91 (100).

Method B. The sulphide (0.02 mol) in dry dichloromethane (5 ml) was added dropwise during 5 min to *N*-chlorosuccinimide (2.67 g, 0.02 mol) in dichloromethane (50 ml) at 0 °C. A precipitate appeared. After 10 min, the amidine (0.018 mol) in dichloromethane (20 ml) was added slowly. The mixture was stirred for 0.5 h at 0 °C and for 0.5 h at room temperature, during which time the precipitate redissolved. The solution was washed with aqueous sodium hydroxide (10%; 50 ml) and water, dried, and evaporated to leave the crude sulphimide (*ca.* 80%), which was crystallised from pentane–dichloromethane. The following sulphimides were prepared: *SS*-dimethyl-*N*-(*N*-phenylbenzimidoyl)sulphimide (1a) (60%), m.p. 167—169°; N-(N-*phenylbenzimidoyl*)-SS-*tetramethylenesulphimide* (1f) (65%), m.p. 131—133° (Found: C, 72.0; H, 6.5; N, 9.7. $C_{17}H_{18}N_2S$ requires C, 72.3; H, 6.4; N, 9.9%); δ ($CDCl_3$) 1.7—2.7 (4 H, m), 3.0—3.6 (4 H, m), and 6.4—7.5 (10 H, m); *m/e* 282 (M^+).

Method C. *SS*-Diphenylsulphimide was prepared by the method of Oae *et al.*[6] from *SS*-diphenyl-*N*-*p*-tolylsulphonylsulphimide. To a solution of *SS*-diphenylsulphimide (0.438 g, 2 mmol) in acetonitrile (20 ml) at room temperature was added the appropriate imidoyl chloride (2 mmol) in acetonitrile (15 ml). Anhydrous potassium carbonate (0.4 g, 2.8 mmol) was added and the mixture was stirred for 5 h. It was then poured into water (200 ml) and the sulphimide was extracted with chloroform (2 × 100 ml). The crude products were crystallised from ethanol. The following sulphimides were prepared: SS-*diphenyl*-N-(N-*phenylbenzimidoyl*)*sulphimide* (1g) (50%), m.p. 141—143° (Found: C, 78.7; H, 5.5; N, 7.1. $C_{25}H_{20}N_2S$ requires C, 78.9; H, 5.3; N, 7.4%); δ ($CDCl_3$) 6.3—7.9 (m); *m/e* 380 (M^+); SS-*diphenyl*-N-[N-(2-*tolyl*)*benzimidoyl*]*sulphimide* (1h) (40%); m.p. 138° (Found: C, 78.9; H, 5.8; N, 7.0. $C_{26}H_{22}N_2S$ requires C, 79.2; H, 5.6; N, 7.1%); δ ($CDCl_3$) 1.72 (3 H) and 6.2—8.0 (19 H, m); *m/e* 394 (M^+); N-[N-(2-*chlorophenyl*)*benzimidoyl*]-SS-*diphenylsulphimide* (1j) (22%), m.p. 165—167° (Found: C, 72.0; H, 4.7; N, 6.8. $C_{26}H_{19}ClN_2S$ requires C, 72.4; H, 4.6; N, 6.8%); δ ($CDCl_3$) 6.3—8.0 (m); *m/e* 416 (8), 414 (19), and 186 (100).

Thermolysis of SS-*Dimethyl*-N-(N-*phenylbenzimidoyl*)-*sulphimide* (1a).—(a) *In decalin.* The sulphimide (200 mg) was heated in decalin (25 ml) at 190 °C for 16 h. The products were separated by preparative layer chromatography (silica; chloroform–acetone, 9 : 1). They were 2,4,6-triphenyl-1,3,5-triazine (55 mg, 65%), m.p. and mixed m.p. 235—236°, 2-phenylquinazoline (30 mg, 19%), m.p. and mixed m.p. 100—101° (lit.,[22] 101°), and 2-phenylbenzimidazole (15 mg, 9%), m.p. 288—290°.

(b) *In benzonitrile.* The sulphimide (890 mg) and benzonitrile (40 ml) were heated under reflux for 16 h. The products, isolated as in (a), were 2,4,6-triphenyl-1,3,5-triazine (160 mg, 45%), 2-phenylquinazoline (115 mg, 20%), and 2-phenylbenzimidazole (44 mg, 10%).

(c) *In xylene with copper*(II) *sulphate.* The sulphimide (100 mg) and anhydrous copper(II) sulphate (10 mg) were heated in xylene (10 ml) under reflux for 10 h. 2,4,6-Triphenyl-1,3,5-triazine (10 mg, 25%) and 2-phenylquinazoline (22 mg, 27%) were isolated.

(d) *In toluene with copper*(II) *acetylacetonate.* In the absence of a catalyst, the sulphimide was recovered (98%) after being heated in toluene under reflux for 23 h. In the presence of copper(II) acetylacetonate (12 mg), the sulphimide (100 mg) in toluene (10 ml) gave, after heating for 23 h, 2-phenylquinazoline (13 mg, 16%) as the only identified product. After 65 h, 2-phenylquinazoline (12 mg, 14%) was again the only product isolated.

Thermolysis of Other Sulphimides.—(a) SS-*Dimethyl*-N-[N-(2-*tolyl*)*benzimidoyl*]*sulphimide* (1b). The sulphimide (700 mg) was heated in decalin (30 ml) under reflux for 16 h and gave 2,4,6-triphenyl-1,3,5-triazine (150 mg, 56%), 4-methyl-2-phenylbenzimidazole (50 mg, 10%), m.p. 248—250°, and 8-*methyl*-2-*phenylquinazoline* (145 mg, 25%), m.p. 42—45° (Found: M^+, 220.1000. $C_{15}H_{12}N_2$ requires *M*, 220.0998); δ ($CDCl_3$) 2.85 (3 H), 7.3—7.8 (6 H, m), 8.6—8.8 (2 H, m), and 9.42 (1 H).

(b) N-[N-(2-*Chlorophenyl*)*benzimidoyl*]-SS-*dimethylsulphimide* (1c). The sulphimide (725 mg) was heated in decalin (30 ml) under reflux for 16 h and gave 2,4,6-triphenyl-1,3,5-triazine (140 mg, 54%), 4-chloro-2-phenylbenzimidazole (100 mg, 17%), m.p. 227—229°, and 8-*chloro*-2-*phenylquinazoline* (140 mg, 22%), m.p. 95—97° (Found: M^+, 242.0430/240.0459. $C_{14}H_9ClN_2$ requires *M*, 242.0425/240.0454); δ ($CDCl_3$) 7.3—8.1 (6 H, m), 8.6—8.8 (2 H, m), and 9.48 (1 H).

(c) N-[N-(4-*Chlorophenyl*)*benzimidoyl*]-SS-*dimethylsulphimide* (1d). The sulphimide (290 mg) was heated in decalin (15 ml) for 16 h and gave 5-chloro-2-phenylbenzimidazole (40 mg, 17%), m.p. 206—208°, and 6-*chloro*-2-*phenylquinazoline* (40 mg, 16%), m.p. 158—160° (Found: M^+, 242.0432/240.0461); δ ($CDCl_3$) 7.4—8.2 (6 H, m), 8.5—8.7 (2 H, m), and 9.44 (1 H).

(d) SS-*Dibenzyl*-N-(N-*phenylbenzimidoyl*)*sulphimide* (1e). The sulphimide (810 mg) was heated in decalin (40 ml) under reflux for 16 h and gave 2-phenylbenzimidazole (30 mg, 7%), m.p. 288—289°, and 2,4-diphenylquinazoline (210 mg, 38%), m.p. 115—116° (lit.,[23] 119—120°).

(e) SS-*Dimethyl*-N-[N-(2-*pyridyl*)*benzimidoyl*]*sulphimide* (5). The sulphimide (100 mg) was heated in toluene (20 ml) under reflux for 96 h and gave 2-phenyl-*s*-triazolo[1,5-*a*]-pyridine (46 mg, 60%), m.p. 134—136° (lit.,[8] 138°).

N-(2-*Methylthiomethylphenyl*)*benzamidine* (8).—(a) 2-(*Methylthiomethyl*)*aniline*. *SS*-Dimethyl-*N*-phenylsulphimide was the product isolated (90%) when aniline was

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[24] P. G. Gassman and G. D. Gruetzmacher, *J. Amer. Chem. Soc.*, 1974, **96**, 5487.
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treated with t-butyl hypochlorite, dimethyl sulphide, and sodium methoxide at −60 °C, according to the method of Gassman and Gruetzmacher.[24] The sulphimide was then rearranged to 2-methylthiomethylaniline by treatment with triethylamine in boiling toluene; the product was isolated (65%) by distillation; b.p. 85—90° at 0.3 mmHg (lit.,[25] 90° at 0.2 mmHg).

(b) *Methyl thiobenzimidate hydriodide.* This was prepared from iodomethane (1.42 g, 0.01 mol) and thiobenzamide (1.37 g, 0.01 mol) in acetic anhydride (15 ml) at room temperature. The product was filtered off and crystallised to give the hydriodide (1.6 g, 58%), m.p. 163—165° (from ethanol) (lit.,[12] 167°).

(c) The hydriodide (558 mg, 2 mmol) and 2-(methylthiomethyl)aniline (306 mg, 2 mmol) were heated in acetonitrile (25 ml) under reflux for 4 h. The solvent was evaporated off to leave a yellow oil which was dissolved in dichloromethane (35 ml). This solution was shaken with water (2 × 50 ml) and the aqueous extracts were treated with aqueous ammonia (*d* 0.880; 30 ml). The precipitate was extracted by shaking the mixture with dichloromethane (3 × 25 ml) and the solvent was evaporated off. Crystallisation of the resulting solid gave N-(2-*methylthiomethylphenyl*)*benzamidine* (40 mg, 8%), m.p. 93—94° (from ether–hexane) (Found: C, 70.0; H, 6.5; N, 10.7. $C_{15}H_{16}N_2S$ requires C, 70.3; H, 6.3; N, 10.9%); δ ($CDCl_3$) 2.02 (3 H), 3.66 (2 H), 4.6br (2 H), and 6.7—8.1 (9 H, m); *m/e* 256 (M^+), 241, and 210.

Attempted Pyrolysis of the Amidine (8).—The amidine was recovered (60%) after heating in decalin under reflux for 47 h. No 2-phenylquinazoline was detected.

N-*Phenylbenzamidine and Chloromethyl Methyl Sulphide.*—*N*-Phenylbenzamidine (392 mg, 2 mmol) and chloromethyl methyl sulphide (234 mg, 2.4 mmol) were heated in decalin (8 ml) in a sealed tube at 200 °C for 18 h. A great deal of charring occurred. The residue was extracted with dichloromethane (2 × 25 ml) and this gave an oil (80 mg) when evaporated. Preparative layer chromatography (silica; chloroform) gave 2,4,6-triphenyl-1,3,5-triazine (16 mg, 10%) and 2-phenylquinazoline (15 mg, 5%).

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