

Synthesis and Decomposition of Some Sulphamoyl Azides

By Rudolph A. Abramovitch* and Koichi Miyashita, Department of Chemistry, University of Alabama, University, Alabama 35486, U.S.A.

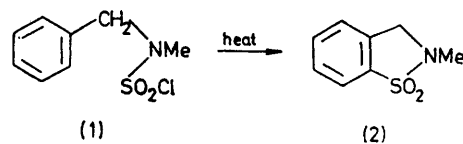
Thermolysis or photolysis of sulphamoyl azides does not lead to sulphamoylnitrenes; complex reactions occur, involving mainly S-N bond cleavage and some C-N cleavage. The intramolecular cyclisation of some intermediate sulphamoyl chlorides are described.

SULPHONYL AZIDES are known to undergo thermolysis to sulphonylnitrenes which, in turn, can undergo a number of interesting reactions.¹ The corresponding sulphamoylnitrenes, RR'NSO₂N, are not known; indeed, until recently, little was known about their potential precursors, the sulphamoyl azides. A number of the latter have been synthesised recently and their hypotensive activity has been studied.² The synthesis of a few sulphamoyl azides and abortive attempts to generate sulphamoylnitrenes are now reported.

Sulphamoyl chlorides were prepared from *N*-lithioamines and sulphuryl chloride. The properties of new compounds in this series are collected in Table 1. A number of by-products were obtained. Thus, *N*-chlorosulphonation of *N*-methylaniline was accompanied by ring chlorination³ to give 2,4,6-trichloro-*N*-methylaniline (5%). Preparation of *N*-benzyl-*N*-methylsulphamoyl chloride (1) (not known when the work was initiated but recently reported²) in ether also led to 2,3-dihydro-*N*-methylbenzothiazole 1,1-dioxide (2) in 6.8% yield.⁴ This could arise from the sulphamoyl chloride, probably during distillation. When the chlorosulphonation was carried out at 75–80 °C in dibutyl ether, some *N*-benzylidene-methylamine (8.5%) was also

obtained [loss of SO₂ and HCl from (1)] together with benzaldehyde formed by hydrolysis. Other by-products were not identified.

N-(Biphenyl-2-yl)-*N*-methylsulphamoyl chloride (3a) could be cyclised readily to 6-methyldibenzo[*c,e*][1,2]-thiazine 5,5-dioxide (4) with aluminium chloride in



benzene. On the other hand, *N*-acetyl-*N*-(biphenyl-2-yl)sulphamoyl chloride (3b) and aluminium chloride in boiling benzene gave 2-acetamidobiphenyl (5) quantitatively. Similarly, *N*-acetyl-*N*-phenylsulphamoyl chloride gave acetanilide. When, however, compound (1) was heated in benzene with anhydrous aluminium chloride, diphenylmethane (6a) (65%) and *N*-methylbenzenesulphonamide (7a) (91%) were obtained. The corresponding reaction of (1) in chlorobenzene gave a mixture of *o*- and *p*-chlorodiphenylmethane (6b) (1 : 3.75)

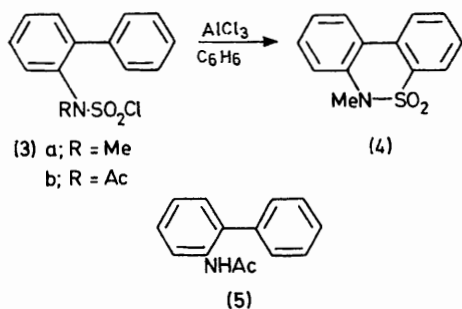
² W. L. Matier, W. T. Comer, and D. Deitchman, *J. Medicin. Chem.*, 1972, **15**, 538.

³ F. Bell, *J. Chem. Soc.*, 1953, 4182.

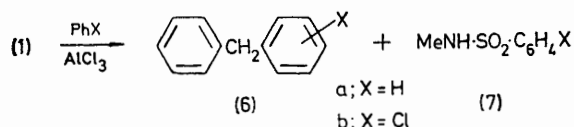
⁴ J. Koetschet and P. Koetschet, *Helv. Chim. Acta*, 1929, **12**, 669.

* R. A. Abramovitch and R. G. Sutherland, *Fortschr. Chem. Forsch.*, 1970, **16**, 1; R. A. Abramovitch and W. D. Holcomb, *J. Amer. Chem. Soc.*, 1975, **97**, 676.

(80.6%) and a mixture of the *N*-methylchlorobenzene-sulphonamides (7b) (32%). These products could arise by intermolecular attack of (1) on the solvent followed



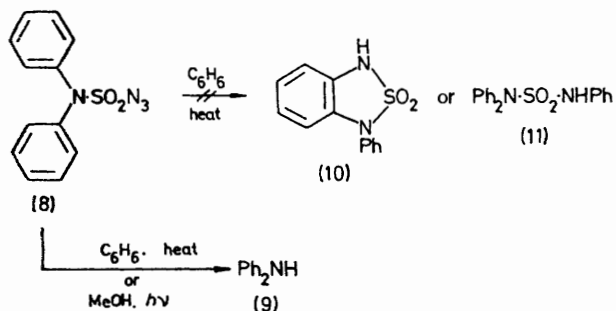
by heterolysis to give a benzyl cation, but other pathways are also conceivable. No intramolecular cyclisation



product (2) appeared to be formed from (1) in the presence of aluminium chloride.

The sulphamoyl azides were prepared from the chlorides and sodium azide. The properties of new azides are collected in Table 2.

Thermolysis of *NN*-dimethylsulphamoyl azide⁵ in dry benzene at 130 °C gave as many as eleven products, none of which were identified, and no evidence for nitrene formation was obtained. Since intramolecular aromatic substitution by arylnitrenes takes place more easily than intermolecular substitution,⁶ and formation of five- and seven-membered rings by intramolecular substitution by a sulphonylnitrene is known,^{6,7} an attempt was made to detect the formation of sulphamoylnitrenes by intramolecular substitution with sulphamoyl azides.



Thermolysis of *NN*-diphenylsulphamoyl azide (8) in benzene gave diphenylamine (9) (54%) and an unidentified purple product. No intra- (10) or intermolecular (11) substitution product from a hoped-for

⁵ W. B. Hardy and F. H. Adams, U.S.P. 2,863,866/1958 (*Chem. Abs.*, 1959, **53**, 7988e).

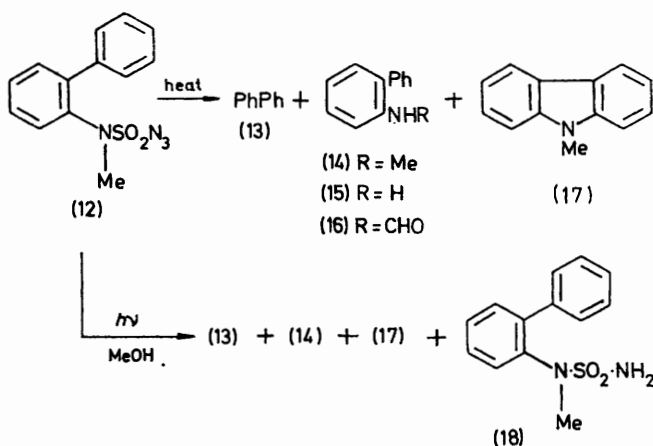
⁶ R. A. Abramovitch, in 'Organic Reactive Intermediates,' ed. S. P. McManus, Academic Press, New York, 1973, p. 127.

⁷ R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *J. Amer. Chem. Soc.*, 1969, **91**, 1219.

sulphamoylnitrene was detected. Photolysis of (8) in methanol gave (9) (38%) and a dark violet solid which was not identified but is probably derived from the diphenylaminyl radical.⁸

Since the lack of formation of (10) *via* a nitrene intermediate might be due to the necessary involvement of a highly strained benzaziridine,⁷ the cyclisation of *N*-(biphenyl-2-yl)-*N*-methylsulphamoyl azide (12) was attempted. Thermolysis of (12) in dry benzene at 130–135 °C gave biphenyl (13) (2%), 2-methylaminobiphenyl (14) (12%), 2-aminobiphenyl (15) (13%), and 2-formamidobiphenyl (16) (13%). No products of intramolecular cyclisation or of intermolecular attack upon solvent benzene were detected. Similar results were obtained when the reaction was carried out in dry, degassed cyclohexane in the presence of hydroquinone (the latter was recovered quantitatively).

Decomposition of (12) in boiling dry degassed acetonitrile in the presence of hydroquinone led to quantitative recovery of the latter and to more than twenty



products (as indicated by t.l.c.). The only new product identified, in addition to (13) (13%) and (14) (10%), was *N*-methylcarbazole (17) (1.8%). Photolysis of the azide in methanol gave compounds (13) (1%), (14) (25%), and (17) (1%). In addition, *N*-biphenyl-2-yl-*N*-methylsulphamide (18) (8.4%) was obtained and characterised by its analysis and spectral properties. This may perhaps arise by hydrogen abstraction from solvent by a triplet sulphamoylnitrene or, more likely, from a hydrogen-bonded azide.^{9,10}

The routes to compounds (14)–(17) can all be visualised as involving the radical *o*-PhC₆H₄·NMe, resulting from homolytic cleavage of the sulphamoyl N–S bond. That biphenyl (13) arises from hydrogen-abstraction by a biphenyl radical and not from solvent benzene is obvious from the fact that it is obtained in acetonitrile and in methanol as well. Photolysis in the presence of

⁸ W. A. Waters, 'The Chemistry of Free Radicals,' Clarendon Press, Oxford, 1946, p. 66; H. Wieland and C. Müller, *Ber.*, 1913, **46**, 3304.

⁹ W. Lwowski and E. Scheiffele, *J. Amer. Chem. Soc.*, 1965, **87**, 4359.

¹⁰ M. T. Reagen and A. Nickon, *J. Amer. Chem. Soc.*, 1968, **90**, 4096.

chlorine¹¹ and thermolysis¹² of arenesulphonyl chlorides and thermolysis of sulphonyl azides are known to lead to radicals, and it appears that C-N bond cleavage is a minor reaction in the decomposition of (12). The above pathways are clearly more favoured than N-N₂ bond dissociation that would result in nitrene formation.

EXPERIMENTAL

Sulphamoyl Chlorides.—The general method is illustrated in the following examples.

N-Acetyl-N-(biphenyl-2-yl)sulphamoyl chloride (3b). To a solution of 2-acetamidobiphenyl (6.33 g) in ether (150 ml) was added a solution (13.9 ml) of *n*-butyl-lithium (1.1 equiv.) in hexane. The mixture was heated at 100–110 °C for 1 h (at 85 °C a white precipitate separated). Sulphuryl chloride (4.45 g) was added at room temperature over 5 min. The precipitate was filtered off and washed with dry benzene and the washings and filtrate were combined.

except in dry ether (50 ml) and with heating at 38–42 °C for 5 h. Distillation of the product gave the chloride (1.95 g, 17.7%), b.p. 110° at 0.7 mmHg, and 2,3-dihydro-*N*-methylbenzothiazole 1,1-dioxide (0.60 g, 6.8%), b.p. 147° at 0.7 mmHg, m.p. 125–126.5° (lit.,⁴ 122–123°) (Found: C, 52.5; H, 5.1. Calc. for C₉H₉NO₂S: C, 52.45; H, 4.9%); ν_{\max} (KBr) 1 390 and 1 165 cm⁻¹ (SO₂); δ (CDCl₃) 7.95–7.28 (4 H, m, ArH), 4.34 (2 H, s, CH₂), and 2.95 (3 H, s, NCH₃); *m/e* 185 (2%), 184 (8), 183 (34, M⁺), 182 (55), and 42 (100).

Sulphamoyl Azides.—The general method is illustrated by the following synthesis.

NN-Diphenylsulphamoyl azide. A mixture of diphenylsulphamoyl chloride (1.37 g) and sodium azide (0.425 g) in acetone (50 ml) and water (8 ml) was stirred vigorously at room temperature for 20 h. The acetone was evaporated off at room temperature and the residue was extracted with dichloromethane, dried (MgSO₄), and evaporated to give the *azide* (1.33 g, 97.5%), m.p.

TABLE 1
Properties of new sulphamoyl chlorides R¹R²NSO₂Cl

R ¹	R ²	M.p. (°C)	Formula	Calc. (%)		Found (%)		Yield (%)
				C	H	C	H	
Ph	Ph	90–91	C ₁₂ H ₁₀ ClNO ₂ S	53.8	3.7	53.9	3.85	51
<i>o</i> -C ₆ H ₄ Ph	Me	110–111	C ₁₃ H ₁₂ ClNO ₂ S ^a	55.4	4.3	55.3	4.4	63.9
<i>o</i> -C ₆ H ₄ Ph	Ac	99–100	C ₁₄ H ₁₂ ClNO ₂ S ^b	54.3	3.9	54.2	4.0	43.8
Biphenyl-2,2'-diyl		126–127	C ₁₂ H ₈ ClNO ₂ S ^c	54.2	3.0	54.35	3.2	66.3

^a *m/e* 281 (M⁺, 2%) and 182 (*o*-PhC₆H₄NMe⁺, 100). ^b *m/e* 245 (M⁺ - SO₂, 59%) and 160 (100). ^c *m/e* 265 (M⁺, 6.5%) and 167 (C₁₂H₈NH⁺, 100).

TABLE 2
Properties of new sulphamoyl azides R¹R²N·SO₂N₃

R ¹	R ²	M.p. (°C)	Formula	Calc. (%)		Found (%)		Yield (%)
				C	H	C	H	
Ph	Ph	77–78	C ₁₂ H ₁₀ N ₄ O ₂ S ^a	52.55	3.6	52.7	3.3	97.5
<i>o</i> -C ₆ H ₄ Ph	Me	101	C ₁₃ H ₁₂ N ₄ O ₂ S ^b	54.2	4.2	54.3	4.35	92

^a *m/e* 274 (M⁺, 14%) and 168 (Ph₂N⁺, 100). ^b *m/e* 288 (M⁺, 4%), 260 (M⁺ - N₂, 0.5), and 182 (*o*-PhC₆H₄NMe⁺, 100).

Evaporation left a dark brown residue (9.76 g) which was purified by preparative t.l.c. on silica gel (benzene as developer) to give the *sulphamoyl chloride* (4.06 g, 43.8%), m.p. 99–100°; ν_{\max} (KBr) 1 725 (Ac) and 1 399 and 1 152 cm⁻¹ (SO₂N). Starting material (3.91 g, 42.4%) was recovered.

N-Benzyl-N-methylsulphamoyl chloride. (A) *In di-n-butyl ether.* A solution of *N*-methylbenzylamine (6.15 g) in dry di-*n*-butyl ether was treated with a solution of *n*-butyl-lithium (1.1 equiv.) in hexane (23.3 ml) and then heated at 75–80 °C for 1 h. Sulphuryl chloride (7.40 g) was added over 8 min; the solid was filtered off, washed with ice-cold aqueous sodium hydrogen carbonate, and dissolved in benzene, and the solution was dried (MgSO₄). The filtrate was evaporated and the residue was distilled to give the chloride (4.23 g, 32.6%), b.p. 113–114° at 0.6 mmHg (lit.,² 155–159° at 8.0 mmHg). Evaporation of the benzene solution and fractional distillation gave benzaldehyde (0.35 g), b.p. 30–35° at 0.45 mmHg, and *N*-benzylidenemethylamine (0.51 g, 8.5%), b.p. 121–123° at 0.45 mmHg,¹³ both identical with authentic samples.

(B) *In ether.* The reaction was carried out as above

¹¹ B. Miller and C. Walling, *J. Amer. Chem. Soc.*, 1957, **79**, 4187; O. P. Studzinskii, A. V. El'tsov, N. I. Rtishchev, and G. V. Fomin, *Russ. Chem. Rev.*, 1974, **43**, 155.

77–78° (from light petroleum); ν_{\max} (KBr) 2 123 (N₃) and 1 384 and 1 167 cm⁻¹ (SO₂).

6-Methyl-dibenzo[c,d][1,2]thiazine 5,5-Dioxide.—A solution of *N*-(biphenyl-2-yl)-*N*-methylsulphamoyl chloride (0.282 g) and anhydrous aluminium chloride (0.15 g) in dry benzene (10 ml) was boiled under reflux for 10 h. It was then cooled and decomposed with 5% hydrochloric acid. The organic layer was washed with brine, dried (MgSO₄), and evaporated to give compound (4) (0.205 g, 83.6%), m.p. 110–111° (from benzene-light petroleum) (lit.,¹⁴ 112°); ν_{\max} (KBr) 1 328 and 1 175 cm⁻¹ (SO₂); δ (CDCl₃) 8.10–7.08 (8 H, m, ArH) and 3.40 (3 H, s, NCH₃); *m/e* 245 (M⁺, 93.5%) and 180 (100).

Reaction of *N*-Acetyl-*N*-phenylsulphamoyl Chloride with Aluminium Chloride.—A solution of the chloride (0.25 g) in dry benzene (5 ml) was cooled in a solid CO₂-acetone bath and treated with anhydrous aluminium chloride (0.15 g) over 3 min. The mixture was stirred vigorously at room temperature for 10 min (no HCl detected during

¹² P. J. Bain, E. J. Blackman, W. Cummings, S. A. Hughes, E. R. Lynch, E. B. McCall, and R. J. Roberts, *Proc. Chem. Soc.*, 1962, 186; A. J. Neale, T. J. Rawlings, and E. B. McCall, *Tetrahedron*, 1965, **21**, 1299.

¹³ C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 1929, 1199.

¹⁴ F. Ullmann and C. Gross, *Ber.*, 1910, **43**, 2694.

this time), and boiled under reflux overnight. The mixture was decomposed with 5% hydrochloric acid and worked up as for (4). The product was purified by preparative t.l.c. on silica gel. Development with benzene showed the presence of four minor impurities. The major product was acetanilide (0.12 g, 81.6%), identical with an authentic sample.

Reaction of N-Acetyl-N-(biphenyl-2-yl)sulphamoyl Chloride with Aluminium Chloride.—Carried out as above (except that no t.l.c. was necessary), this gave 2-acetamidobiphenyl (96.4%), identical with an authentic sample.

Reaction of N-Benzyl-N-methylsulphamoyl Chloride with Aluminium Chloride.—(A) *In dry benzene.* The sulphamoyl chloride (2.83 g) was added dropwise at room temperature to a suspension of anhydrous aluminium chloride in benzene (10 ml) over 10 min. The mixture was boiled for 6 h, cooled, and decomposed with cold 5% hydrochloric acid. The benzene layer was washed with brine, dried (MgSO₄), and evaporated. The residue (3.98 g) was fractionally distilled to give diphenylmethane (1.41 g, 65.2%), b.p. 89–90° at 1.25 mmHg, and *N*-methylbenzenesulphonamide (1.86 g, 90.7%), b.p. 150–152° at 1.25 mmHg (lit.,¹⁵ 152–154° at 1 mmHg), both identical with authentic samples.

(B) *In dry chlorobenzene.* The sulphamoyl chloride (1.10 g) in chlorobenzene (5 ml) was added dropwise to a suspension of aluminium chloride (0.734 g) in chlorobenzene (10 ml) cooled in solid CO₂-acetone and the mixture was stirred vigorously. The temperature of the mixture was kept below 0 °C for 2 h, then at 0–15 °C for 3 h, and the mixture was then decomposed with ice. Work-up as above followed by preparative t.l.c. on silica gel and development with benzene gave: (a) a mixture (0.82 g, 80.6%) of *o*- and *p*-chlorodiphenylmethane (ratio estimated to be 1 : 3.75 on the basis of the methylene n.m.r. peaks at δ 3.96 and 3.75) and (b) a mixture of *N*-methylchlorobenzenesulphonamides (0.33 g, 32.3%); ν_{max} 3 290 (s, NH) and 1 330 and 1 162 cm⁻¹ (SO₂); *m/e* 205 (*M*⁺, 22%), 175 (*M* – MeNH, 26), and 111 (100) (*o*-Cl, lit.,¹⁶ m.p. 94.5°; *p*-Cl, lit.,¹⁷ m.p. 62–64°).

Decomposition of NN-Diphenylsulphamoyl Azide.—(A) *Thermolysis.* The azide (0.3 g) in dry benzene was boiled under reflux for 4 days. Evaporation gave a dark residue which was purified by preparative t.l.c. on silica gel. Development with benzene–light petroleum (1 : 2 v/v) gave diphenylamine (0.1 g, 54%), m.p. 51–53°, identical with an authentic sample, and an unidentified reddish-violet solid (0.151 g).

(B) *Photolysis.* The azide (1.02 g) in methanol (200 ml) in a Pyrex vessel was irradiated for 4.5 h at 300 nm. Evaporation gave a dark violet solid which was separated by pre-

parative t.l.c. to give diphenylamine (0.227 g, 38.3%), starting azide (0.213 g, 21%), and unidentified violet and blue solids (0.455 mg).

Decomposition of N-(Biphenyl-2-yl)-N-methylsulphamoyl Azide.—(A) *Thermolysis in dry benzene.* The azide (1.44 g) in benzene (10 ml) was heated in a sealed tube at 130–135 °C for 10 h. The solvent was evaporated off to give a dark brown solid which, on treatment with acetone, gave a mixture of white solids (100 mg) which were not identified. The filtrate was evaporated and the residue was separated into six bands by preparative t.l.c. (light petroleum–benzene, 1 : 1 v/v). Material from each band was collected and subjected once again to t.l.c. to give biphenyl (20 mg, 2.6%), m.p. 69–71°, *m/e* 154 (*M*⁺, 100%); 2-methylaminobiphenyl (107 mg, 11.7%) (lit.,^{18a} b.p. 115–116° at 2 mmHg); starting material (30 mg, 2%); 2-amino-biphenyl (110 mg, 13%); and 2-formamidobiphenyl (130 mg, 12.8%) (lit.,^{18a} m.p. 75°). All the products were identical (i.r. and n.m.r.) with authentic samples.

(B) *Thermolysis in dry, degassed cyclohexane.* The azide (1.44 g) and hydroquinone (0.55 g) in degassed cyclohexane (10 ml) were heated under oxygen-free nitrogen in a sealed tube at 100–105 °C for 14 h. Work-up as above gave biphenyl (40 mg, 5.2%), 2-methylaminobiphenyl (0.16 g, 17%), starting azide (0.23 g, 15.9%), 2-amino-biphenyl (10 mg, 1.1%), 2-formamidobiphenyl (20 mg, 1.9%), and hydroquinone (0.55 g, 100%).

(C) *Thermolysis in dry, degassed acetonitrile.* When carried out as above at the b.p. of the solvent containing 1 equiv. of hydroquinone the thermolysis gave biphenyl (12.9%), *N*-methylcarbazole (1.8%), m.p. 84–86° [identical with an authentic sample (lit.,^{18b} m.p. 87°)], 2-methylaminobiphenyl (23%), starting azide (10.3%), and numerous (>15) unidentified minor fractions.

(D) *Photolysis in methanol.* The azide (1.44 g) in methanol (200 ml) was irradiated at 300 nm for 20 h under oxygen-free nitrogen. Work-up gave biphenyl (30 mg, 3.8%), *N*-methylcarbazole (10 mg, 1.0%), 2-methylaminobiphenyl (0.23 g, 25.1%), starting azide (50 mg, 3.4%), and *N*-biphenyl-2-yl-*N*-methylsulphamide (0.11 g, 8.4%) (Found: C, 59.25; H, 5.5. C₁₃H₁₄N₂O₂S requires C, 59.55; H, 5.35%); m.p. 80–81°; ν_{max} (KBr) 3 500, 3 320, and 3 210 (NH₂, NH), and 1 346 and 1 168 cm⁻¹ (SO₂); δ (CDCl₃) 7.60–7.20 (9 H, m, ArH), 4.07 (2 H, s, NH₂), and 3.03 (3 H, s, NCH₃); *m/e* 262 (*M*⁺, 8) and 183 (*M*⁺ – SO₂NH, 100).

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¹⁵ T. L. Cairns and J. C. Sauer, *J. Org. Chem.*, 1955, **20**, 627.

¹⁶ N. N. Dykhanov, T. Ryzhkova, and A. M. Khaletskii, *Ukrain. khim. Zhur.*, 1969, **35**, 821 (*Chem. Abs.*, 1970, **72**, 43066e).

¹⁷ E. L. Eliel and K. W. Nelson, *J. Org. Chem.*, 1955, **20**, 1657.

¹⁸ Heilbron's 'Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, vol. 1, 1965, (a) p. 90; (b) p. 552.