

## Sulphur Nitrides in Organic Chemistry. Part 8.<sup>1</sup> Reaction of Tetrasulphur Tetranitride with Grignard Reagents and Organolithium Compounds

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The reaction of tetrasulphur tetranitride ( $N_4S_4$ ) (1) with Grignard reagents (2a—h) and organolithium compounds (10a—h) was investigated. It was found that the reaction of (1) with (2) gave the corresponding disulphides (4a—h) in good yields together with 1,5-diaryl-1,3,5,2,4-trithiadiazapenta-2,3-dienes (3a—c), bisarylamino sulphides (5a and b), ammonium thiosulphates (6a—e), and thiosulphonates (7a—d). Reaction of (1) with (10a—f), generated from benzyl sulphides, afforded diaryl disulphides (4a, b, and e) in moderate yields accompanied by *trans*-stilbenes (11a and b) and 1,2-bisphenylthio-1,2-diarylethanes (12a and b). Reaction of (1) with diphenyl(phenylthio)methyl-lithium (10g), gave diphenyl disulphide (4a), the tetraphenylethylene (11c), and benzophenone (13a), while reaction of sulphur with (10g) afforded 1,2-epithio-1,1,2,2-tetraphenylethane (15) in 52% yield besides (4a), (11c), and (13c). Reaction of (1) with 9-phenylthiofluoren-9-yl-lithium (10h) gave (4a), bifluorenylidene (11d), 1,1'-bisphenylthiobifluorenyl (12c), fluorenone (13b), and fluorenylidene-aminosulphenamide (14).

TETRASULPHUR TETRANITRIDE ( $N_4S_4$ ) (1) is known to be susceptible towards attack by nucleophiles and the reaction of (1) with arylmagnesium bromide has been reported<sup>2,3</sup> to give 1,5-diaryl-1,3,5,2,4-trithiadiazapenta-2,3-dienes (3). However, details of the reaction were not given.

As part of our studies on compound (1), we have investigated its reaction with Grignard reagents (2) and the

magnesium bromides (2h) were carried out at room temperature. Reaction mixtures were decomposed in 10% aqueous acetic acid (method A), in externally cooled glacial acetic acid (method B), or in concentrated hydrochloric acid-ethanol (3:7 v/v) (method C). The products, 1,5-diaryl-1,3,5,2,4-trithiadiazapenta-2,3-dienes (3), disulphides (4), bisarylamino sulphides (5), Bunte's salts (6), and thiosulphonates (7), were obtained in the

TABLE I  
Reaction of  $N_4S_4$  (1) with Grignard reagents (2a—h)

Run	Reagent	Decomp. conditions	(2) : (1) (mol/mol)	Products [Yield (mol %) <sup>a</sup> ]				
				(3)	(4)	(5)	(6)	(7)
1	(2a)	A	4	(3a) <sup>b</sup> [8]	(4a) <sup>c</sup> [72]	(5a) <sup>d</sup> [5]	(6a) [18]	
2	(2b)	A	4	(3b) <sup>b</sup> [6]	(4b) <sup>c</sup> [92]	(5b) <sup>d</sup> [19]	(6b) [27]	
3	(2c)	A	4		(4c) <sup>e</sup> [71]		(6c) [59]	
4	(2g)	A	4		(4g) <sup>e</sup> [66]		(6g) [4]	
5	(2h)	A	4		(4h) [30]		(6h) [19]	
6	(2a)	B	4		(4a) [94]	(5a) [trace]		
7	(2b)	B	4	(3b) [34]	(4b) [85]			(7b) <sup>h</sup> [3]
8	(2c)	B	4	(3c) [29]	(4c) <sup>e</sup> [80]			(7c) <sup>e</sup> [6]
9	(2a)	C	2		(4a) [47]			
10	(2a)	C	3		(4a) [63]			
11	(2a)	C	4		(4a) [92]			
12	(2a)	C	6		(4a) [80]			
13	(2b)	C	4		(4b) [98]			(7b) [5]
14	(2c)	C	4		(4c) [72]			(7c) [14]
15	(2d)	C	4		(4d) <sup>d</sup> [63]			
16	(2e)	C	4		(4e) [90]			(7e) <sup>h</sup> [5]
17	(2f)	C	4		(4f) <sup>f</sup> [99]			(7f) <sup>h</sup> [10]
18	(2g)	C	4		(4g) [82]			(7g) <sup>g</sup> [12]

<sup>a</sup> Yields were calculated based upon (1). <sup>b</sup> See refs. 2 and 3. <sup>c</sup> C. N. Yianios and J. V. Kavabinos, *J. Org. Chem.*, 1963, **28**, 3246. <sup>d</sup> J. Troeger and W. Voightlaender-Tetzner, *J. prakt. Chem.*, 1894, **54**, 520. <sup>e</sup> T. J. Wallace, *J. Amer. Chem. Soc.*, 1964, **86**, 2018. <sup>f</sup> M. Furukawa, S. Tsuji, Y. Kojima, and S. Hayashi, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 1965. <sup>g</sup> Y. Miura, N. Mahita, and M. Kinoshita, *Bull. Chem. Soc. Japan*, 1977, **50**, 482. <sup>h</sup> G. Bulmer and F. G. Mann, *J. Chem. Soc.*, 1945, 680.

organolithium compounds (10a—h), and the results are now reported.

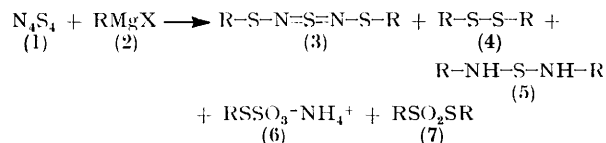
### RESULTS AND DISCUSSION

*Reaction of (1) with Grignard Reagents (2a—h).*—The reactions of compound (1) with phenyl- (2a), *p*-chlorophenyl- (2b), *p*-bromophenyl- (2c), *o*-tolyl- (2d), *p*-tolyl- (2e), *p*-methoxyphenyl- (2f), benzyl- (2g), and cyclohexyl-

yields shown in Table I. While the yields of (3), (5), (6), and (7) were dependent on the decomposition conditions, the disulphides (4a—g) were formed in good yields in every case.

The reported products<sup>2,3</sup> (3a—c) were isolated only when the reaction mixtures of (1) with (2a—c) were decomposed in acetic acid (methods A and B). Though compounds (3b) and (5b) were stable in 10% aqueous

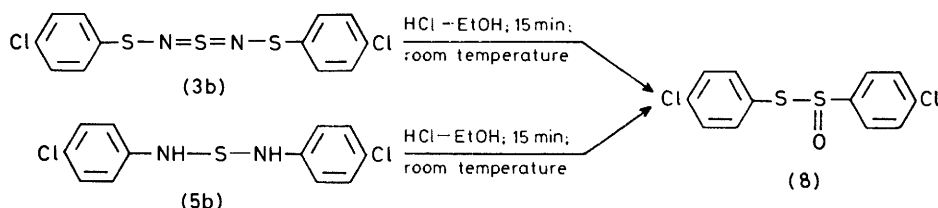
acetic acid at 70 °C, they were easily hydrolysed in 10% ethanolic hydrochloric acid to give the thiosulphinates (8) <sup>4</sup> in 76 and 88% yields, respectively. Products (5),



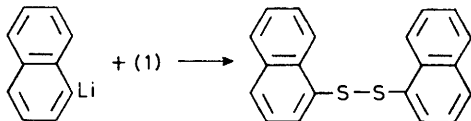
a; R = Ph  
b; R = *p*-ClC<sub>6</sub>H<sub>4</sub>  
c; R = *p*-BrC<sub>6</sub>H<sub>4</sub>  
d; R = *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
e; R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
f; R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
g; R = PhCH<sub>2</sub>  
h; R = cyclo-C<sub>6</sub>H<sub>11</sub>

(6), and (7) are now considered to be formed *via* the trithiadiazapentadienes (3).

Many preparations of disulphides are known and the



reaction of (1) with Grignard reagents (2) presents another method for preparing diaryldisulphides (4a—g), especially when the reaction mixtures are decomposed according to method C.



*Reaction of (1) with Organolithium Compounds (10a—h).*—The reaction of compound (1) with organolithium

Expecting formation of the 1,1'-bisarythio disulphides (9), we carried out, at room temperature, the reaction of the sulphur-stabilized organolithium compounds (10a—h) (generated *in situ* from thioanisole, phenyl benzyl, phenyl *p*-chlorobenzyl, *p*-chlorophenyl benzyl, phenyl *p*-methylbenzyl, *p*-methylphenyl benzyl, phenyl benzhydryl, and phenyl fluorene-9-yl sulphides) with compound (1). The results are summarized in Table 2.

The expected compound (9) was not obtained and the corresponding disulphides (4a, b, and e) were obtained in poor-to-moderate yields in the reaction with (10a—f) as well as small amounts of *trans*-stilbenes (11a and b) and/or 1,2-bisphenylthio-1,2-diarylethanes (12a and b). In the reaction of (1) with (10g), the yield of (4a) decreased (to 14%). Benzophenone (13a) was isolated in 31%

yield accompanied by tetraphenylethylene (11c) in 11% yield.

The reaction of compound (1) with (10h) afforded the disulphide (4a), bifluorenylidene (11d), 1,1'-bisphenylthiobifluorenyl (12c), fluorenone (13b), and fluorenylidenediaminosulphenamide (14).

We investigated the reaction of sulphur with (10g) in order to check the participation of sulphur, which could be formed by decomposition of (1) during the reaction. Compounds (4a), (11c), and (13a) were formed in 14, 26, and 18% yields, respectively; however, the major product of this reaction was found to be the tetraphenyl

TABLE 2  
Reaction of N<sub>4</sub>S<sub>4</sub> (1) with organolithium compounds (10a—h)

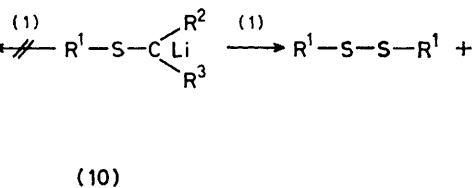
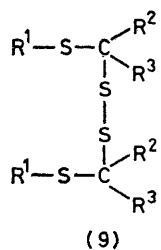
Run	Reagent	(10) : (1) (mol/mol)	Products [Yield (mol %) <sup>a</sup> ]				
			(4)	(11)	(12)	(13)	(14)
1	(10a)	4	(4a) [12]				
2	(10a)	2	(4a) [20]				
3	(10a)	1	(4a) [22]				
4	(10b)	4	(4a) [26]	(11a) [1]	(12a) [3] <sup>e</sup>		
5	(10b)	2	(4a) [43]	(11a) [1]	(12a) [4]		
6	(10b)	1	(4a) [33]	(11a) [trace]	(12a) [8]		
7	(10c)	2	(4a) [33]	(11b) [6]			
8	(10d)	2	(4b) [29]	(11a) [1]			
9	(10e)	2	(4a) [24]		(12b) [7]		
10	(10f)	2	(4e) [22]				
11	(10g)	2	(4a) [14]	(11c) <sup>b</sup> [11]		(13a) [31]	
12	(10h)	2	(4a) [33]	(11d) [20]	(12c) [32]	(13b) [19] <sup>e</sup>	(14) <sup>d</sup> [13]

<sup>a</sup> Yields were calculated based upon (1). <sup>b</sup> See ref. 6. <sup>c</sup> L. Benati, M. Ticco, and A. Tundo, *Gazzetta.*, 1962, 92, 1204, 1213 (*Chem. Abs.*, 1965, 59, 6293f; 1964, 58, 13830c). <sup>d</sup> S. Mataka, K. Takahashi, S. Isni-i, and M. Tashiro, *J.C.S. Perkin I*, 1979, 2905.

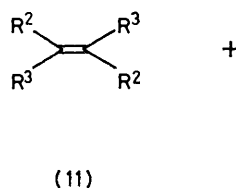
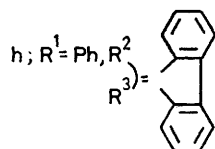
compounds has not been reported. We first carried out the reaction of (1) with  $\alpha$ -naphthyl-lithium at room temperature and obtained the corresponding disulphide <sup>5</sup> in 19% yield. When the reaction was carried out at -70 °C, a large amount of unchanged N<sub>4</sub>S<sub>4</sub> was obtained.

episulphide (15).<sup>6</sup> This suggests that sulphur does not participate in the reaction of (1) with (10g).

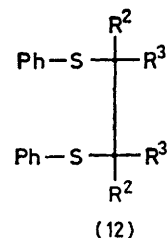
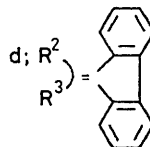
Though the pathway of the reactions is obscure, the formation of thiobenzophenone in the reaction of (1) with (10g) is suggested from the following observations: (i)



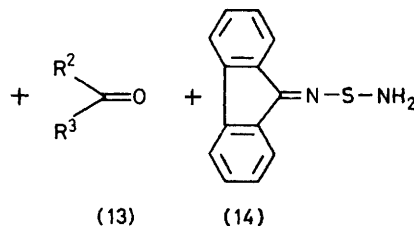
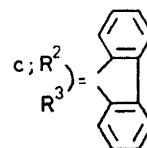
- a;  $R^1 = \text{Ph}, R^2 = R^3 = \text{H}$   
 b;  $R^1 = R^2 = \text{Ph}, R^3 = \text{H}$   
 c;  $R^1 = \text{Ph}, R^2 = \text{H}, R^3 = p\text{-ClC}_6\text{H}_4$   
 d;  $R^1 = p\text{-ClC}_6\text{H}_4, R^2 = \text{H}, R^3 = \text{Ph}$   
 e;  $R^1 = \text{Ph}, R^2 = \text{H}, R^3 = p\text{-MeC}_6\text{H}_4$   
 f;  $R^1 = p\text{-MeC}_6\text{H}_4, R^2 = \text{H}, R^3 = \text{Ph}$   
 g;  $R^1 = R^2 = R^3 = \text{Ph}$



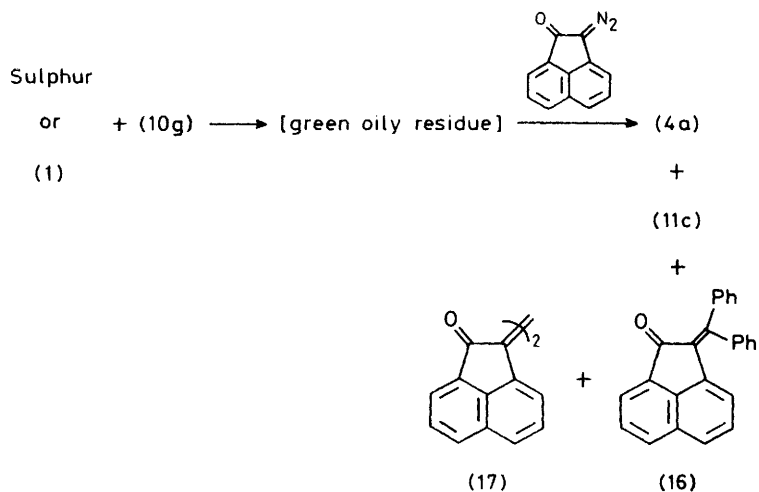
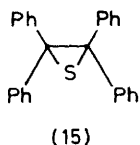
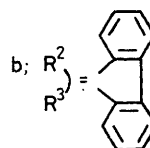
- a;  $R^2 = \text{Ph}, R^3 = \text{H}$   
 b;  $R^2 = p\text{-ClC}_6\text{H}_4, R^3 = \text{H}$   
 c;  $R^2 = R^3 = \text{Ph}$



- a;  $R^2 = \text{Ph}, R^3 = \text{H}$   
 b;  $R^2 = p\text{-MeC}_6\text{H}_4, R^3 = \text{H}$



- a;  $R^2 = R^3 = \text{Ph}$



an unstable green band appeared on the column during chromatography of the mixture from the reaction of (1) or sulphur with (10g), and (ii) 2-diphenylmethylenecenaphthen-1-one (16)<sup>7</sup> was formed in 63% yield when the green oily material obtained through column chromatography in the dark, was heated under reflux in toluene in the presence of 2-diazoacenaphthen-1-one.

#### EXPERIMENTAL

**CAUTION.**— $N_4S_4$  is explosive and should be handled with care.

M.p.s were determined on a Yanagimoto micro melting-point apparatus. I.r. spectra were measured as KBr pellets on a Nippon Bunko IR spectrophotometer. Mass spectra were obtained on a Hitachi R-4 mass spectrometer at 70 eV using a direct inlet system. N.m.r. spectra were measured at 60 MHz with a Hitachi R-20 n.m.r. spectrometer with  $Me_4Si$  as an internal standard in  $CDCl_3$ . Column chromatography was carried out on silica gel (Wako gel, C-300) unless otherwise stated. Hexane (A), hexane-benzene (1 : 1) (B), benzene (C), chloroform (D), and ethanol (E) were used as eluants.

**Reaction of Tetrasulphur Tetranitride (1) with Grignard Reagents (2a—h).**—In a typical procedure, a solution of (2b) [prepared from p-chlorobromobenzene (5.6 g) and magnesium ribbon (700 mg) in anhydrous ether (60 ml) was added to a solution of (1) (1.29 g) in dry benzene (120 ml) at room temperature over 45 min. The mixture was poured into 10% aqueous acetic acid (300 ml) (method A), into externally cooled acetic acid (300 ml) (method B), or into a mixture of concentrated hydrochloric acid (30 ml) and ethanol (70 ml). The organic layer was separated, washed with water ( $2 \times 150$  ml), and dried ( $Na_2SO_4$ ). Solvents were removed *in vacuo* and the residue was subjected to column chromatography.

Compounds (3), (4), and (5) were obtained from fraction A, compound (7) was isolated from the fraction C, and compound (6) was obtained from fraction E. The physical properties of new compounds are as follows. 1,5-Bis-(4-bromophenyl)-1,3,5,2,4-trithiadiazapenta-2,3-diene (3c) formed dark red needles, m.p. 163—164 °C (from hexane) (Found: C, 33.3; H, 1.8; N, 6.4.  $C_{12}H_8Br_2N_2S_3$  requires C, 33.04; H, 1.85; N, 6.4%), *m/e* 438, 436, and 434 ( $M^+$ ); dicyclohexyl disulphide (4h) was a liquid (Found: C, 62.4; H, 9.65.  $C_{12}H_{22}S_2$  requires C, 62.54; H, 9.6%); the ammonium thiosulphates (6a—e) afforded plates (from benzene-ethanol) and showed broad bands at  $\nu_{max}$ . 3 300—3 000  $cm^{-1}$  ascribable to ammonium salts: ammonium S-phenyl thiosulphate (6a) had m.p. 183—185 °C (Found: C, 34.55; H, 4.35; N, 6.7.  $C_6H_9NO_3S_2$  requires C, 34.77; H, 4.4; N, 6.76%); ammonium S-p-chlorophenyl thiosulphate (6b) had m.p. 225—230 °C (Found: C, 29.7; H, 3.3; N, 5.7.  $C_6H_8ClNO_3S_2$  requires C, 29.8; H, 3.36; N, 5.8%); ammonium S-p-tolyl thiosulphate (6e) had m.p. 180—182 °C (Found: C, 37.9; H, 4.8; N, 5.9.  $C_7H_{11}NO_3S_2$  requires C, 38.0; H, 5.0; N, 6.3%); ammonium S-benzyl thiosulphate (6g) had m.p. 154—162 °C (Found: C, 37.9; H, 5.0; N, 6.3.  $C_7H_{11}NO_3S_2$  requires C, 38.0; H, 5.0; N, 6.3%); and ammonium S-cyclohexyl thiosulphate (6h) had m.p. 130—137 °C (Found: C, 33.5; H, 6.9; N, 6.3.  $C_6H_{15}NO_3S_2$  requires C, 33.8; H, 7.1; N, 6.8%).

**Hydrolysis of Compounds (3b) and (5b).**—A mixture of (3b) (420 mg) and concentrated hydrogen chloride (5 ml) in benzene (50 ml) was stirred at room temperature for 15 min.

The benzene layer was separated, washed with water (50 ml), and dried ( $Na_2SO_4$ ). Removal of solvent afforded the thiosulphinate (8) (280 mg). Similarly, (5b) (616 mg) gave (8) (545 mg) as pale yellow prisms, m.p. 112 °C (from ethanol) (lit.<sup>4</sup> 99—102 °C) (Found: C, 47.4; H, 2.65. Calc. for  $C_{12}H_{82}ClOS_2$ : C, 47.5; H, 2.66%).

**Reaction of (1) with  $\alpha$ -Naphthyl-lithium.**—A solution of  $\alpha$ -naphthyl-lithium [prepared from  $\alpha$ -bromonaphthalene (2.9 g) and lithium metal (200 mg) in anhydrous ether (60 ml) was added dropwise to a solution of (1) (1.2 g) in anhydrous benzene at room temperature over 40 min. The mixture was then poured into 10% aqueous acetic acid (300 ml). The organic layer was treated as in the reaction of (1) with (2).  $\alpha$ -Naphthyl disulphide<sup>5</sup> (420 mg) was isolated from fraction A.

**Reaction of (1) with Lithium Sulphides (10a—h).**—**Reaction with Compound (10a).** A solution of (1) (1.29 g) in anhydrous THF (40 ml) was added dropwise at room temperature over 40 min to a solution of (10a) [prepared from thioanisole (1.87 g), Dabco (1.7 g), and butyl-lithium (15% solution in hexane; 10 ml)] in anhydrous THF (40 ml). The reaction mixture was poured into ice-water (300 ml) and the organic layer was treated as described above. Fraction A afforded a yellow liquid, which was distilled *in vacuo* to remove unchanged thioanisole (1.4 g). Compound (4a) (310 mg) was obtained from the residue.

**Reaction with Compounds (10b—h).** In a typical procedure, the reaction of (1) (1.2 g) with (10b) [prepared from benzyl phenyl sulphide (1.5 g), Dabco (900 mg), and butyl-lithium (15% solution in hexane; 10 ml)] was carried out and treated as described above. Compounds (4) and (11a—c) were obtained from fraction A, compounds (11d) and (12) were isolated from fraction B, and compounds (13) and (14) were obtained from fractions C and D respectively. 1,2-Bisphenylthio-1,2-di-p-tolyethane (12b) formed needles, m.p. 207.5—209 °C (from ethanol) (Found: C, 78.6; H, 6.35.  $C_{28}H_{26}S_2$  requires C, 78.8; H, 6.14%),  $\delta$  2.20 (s, 6 H,  $CH_3$ ), 4.50 (s, 2 H, CH), and 6.9—7.1 (m, 18 H, aromatic); 9,9'-bisphenylthio-9,9'-bifluorenyl (12c) formed prisms, m.p. 229—231 °C (from hexane-benzene) (Found: C, 83.5; H, 4.75.  $C_{38}H_{26}S_2$  requires C, 83.5; H, 4.8%); *m/e* 437 ( $M^+$  — PhS), 360 ( $M^+$  —  $Ph_2S$ ), and 328 ( $M^+$  —  $Ph_2S_2$ ).

**Reaction of Sulphur with Compound (10g).**—The reaction of sulphur (1.02 g) and compound (10g) [prepared from benzhydryl phenyl sulphide (2.2 g), Dabco (1.8 g), and n-butyl-lithium (15% solution in hexane; 10 ml)] was carried out and the products were treated as described above. Compound (4a) (120 mg) was isolated from fraction A. A mixture of (11c) and (15) was obtained from fraction B; the products were separated by washing with ether which readily dissolves (15). Compound (13a) was obtained from fraction C and determined as its 2,4-dinitrophenyl-hydrazone (500 mg).

Repetition of the reaction followed by column chromatography in the dark gave a green oil which was then heated under reflux in toluene (30 ml) in the presence of  $\alpha$ -diazoacenaphthenone (1.0 g) for 4 h. The toluene was evaporated off *in vacuo* and the residue was subjected to column chromatography. The disulphide (4a) (1.5 g) was obtained from fraction A, tetraphenylethylene (11c) (980 mg) and the ketone (16) (400 mg) were isolated from fraction B, and diacenaphthylidenedione (17)<sup>6</sup> (120 mg) and unchanged  $\alpha$ -diazoacenaphthenone (620 mg) were obtained from fraction C.

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