

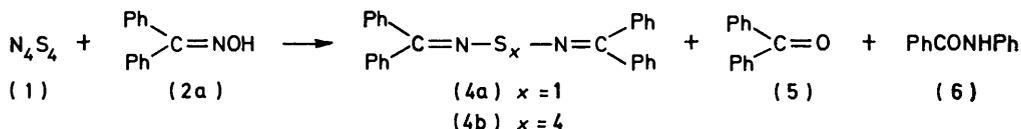
Sulphur Nitrides in Organic Chemistry. Part 5.¹ The Reaction of Tetrasulphur Tetranitride with Oximes and Imines

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The reaction of tetrasulphur tetranitride (N_4S_4) (1) with oximes (2a–d) and imines (3a and b) was carried out under refluxing condition in toluene. It was found that the N–O bond in benzophenone oxime (2a) or fluorenone oxime (2b) was cleaved by (1) to afford the corresponding imino-sulphides such as bis(diphenylmethyleneamino) sulphides (4) or bis(fluorenylideneamino) sulphides (7) together with benzophenone (5) and benzanilide (6), or fluorenone imine (3a), fluorenone (8), and fluorenylideneaminosulphenamide (9), respectively. The reaction of (1) with (3a) was carried out under the same conditions to give the expected bis(fluorenylideneamino) mono-sulphide (7a) together with the trisulphide (7b), (8), and (9). Similarly phenanthrenequinone monoimide (3b) afforded the bis(oxophenanthrenylideneamino) monosulphide (13) in 83% yield. From these results, it can be concluded that imines are probably an intermediate in the formation of the imino-sulphides (4) and (7). In contrast to (2a and b), cyclohexanone oxime (2c) afforded only large amounts of tarry materials. It was also found for the reaction with benzil monoimine (2d) that not only the N–O bond but also the C–C bond of (2d) was cleaved with (1) to afford benzamide (10) and benzonitrile (11) together with 3,4-diphenyl-1,2,5-thiadiazole (12).

THE N–N bond cleavage of hydrazines and the oxidation of hydrazones to give the corresponding amines and azines, respectively, on treatment with tetrasulphur tetranitride (N_4S_4) has previously been reported.² As a logical extension, the formation of imines by N–O bond cleavage in oximes with N_4S_4 (1) is expected and we now report the reaction of (1) with oximes (2) and imines (3).

Reaction of (1) with Oximes (2a and b).—The reaction of (1) with (2a) gave a mixture of bis(diphenylmethyleneamino) sulphides (4) together with benzophenone (5), and benzanilide (6). The mono- (4a) and tetra-sulphide (4b) were separated by fractional recrystallization. The formation of (5) can easily be understood in terms of the hydrolysis of (2a), (4), and/or benzophenone imine which



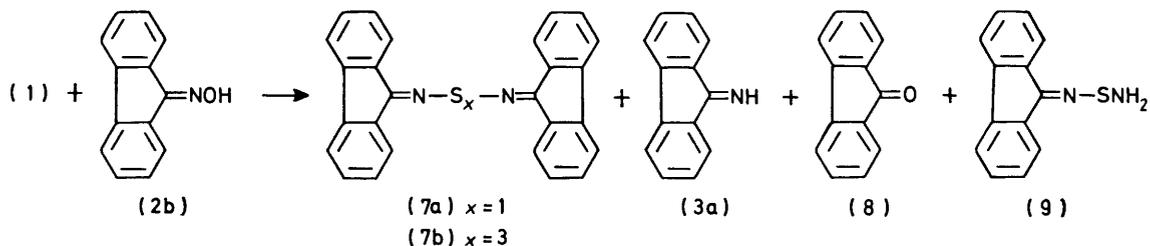
RESULTS AND DISCUSSION

The reaction of (1) with benzophenone oxime (2a), fluorenone oxime (2b), cyclohexanone oxime (2c), benzil mono-oxime (2d), fluorenone imine (3a),³ and phen-

anthrenequinone monoimide (3b)⁴ was carried out and the results are summarized in the Table.

might be an intermediate in the formation of (4). However, the pathway for the formation of (6) is obscure at present.

Similarly the reaction of N_4S_4 with (2b) afforded bis-



anthrenequinone monoimide (3b)⁴ was carried out and the results are summarized in the Table.

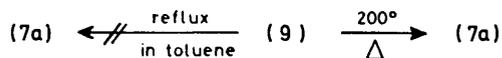
(fluorenylideneamino) mono- (7a) and tri-sulphide (7b) together with (3a), fluorenone (8), and fluorenylideneaminosulphenamide (9).

Reaction of N_4S_4 (1) with oximes (2a–d) and imines (3a and b) in refluxing toluene^a

| Substrate | t/h | Products (mol %) ^b |
|-------------------|-----|--|
| (2a) | 24 | (4a) (5), (4b) (3), (5) (34), (6) (1) |
| (2b) | 5 | (7a) (22), (7b) (10), (3a) (4), (8) (14), (9) (10) |
| (2c) | 5 | Intractable tar |
| (2d) ^c | 6 | (10) (23), (11) (9), (12) (4) |
| (3a) ^c | 5 | (7a) (41), (7b) (14), (8) (25), (9) (0.6) |
| (3b) | 5 | (13) (83) |

^a The molar ratio of (1) and substrate is 1 : 2 unless otherwise indicated. ^b Isolated yields; calculated on the basis of substrates used. ^c The molar ratio of (1) and substrates is 1 : 4.

Although (7a) is stable in ethanolic hydrochloric acid at room temperature for 24 h, it is easily hydrolysed under refluxing conditions to give fluorenone in 70% yield. Compound (9) gave (7a) in quantitative yield on heating



at 200° for 5 min, but not in refluxing toluene. These results show that (9) is not an intermediate in the formation of (7a) in the reaction of (1) with (2b).

It should be noted that (3a), which seems a probable intermediate in the formation of (7) and (9), was isolated in the reaction of (1) with (2b).

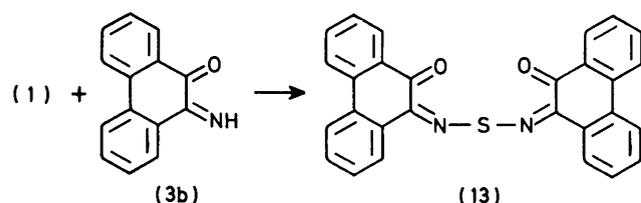
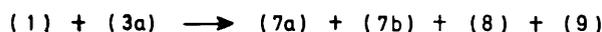
Reaction of (1) with Imines (3a and b).—It has been reported that⁵ the reaction of (1) with pyrrolidine gave dipyrrolidinyl sulphide, though the reaction pathway is not clear. Therefore, the reaction of (1) with imines



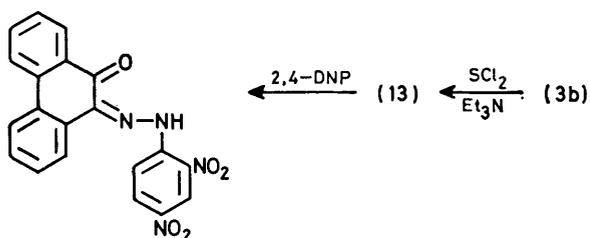
(3a and b) was investigated in order to clarify whether the imines (3) were intermediates in the formation of the imino-sulphides.

As expected, the reaction of (1) with (3a) afforded the same products, (7a and b), (8), and (9), as for the reaction of (1) with (2b). When the molar ratio of (1) to (3a) was changed from 1 : 4 to 1 : 2, the yield of (7a) increased from 41 to 58%.

The reaction with (3b) afforded the expected bis(oxophenanthrenylideneamino) monosulphide (13) in 83% yield. The structure of (13) was established by an



alternative preparation involving the reaction of (3b) with sulphur dichloride in the presence of triethylamine (yield 32%) and by the reaction with 2,4-dinitrophenylhydrazine (2,4-DNP).

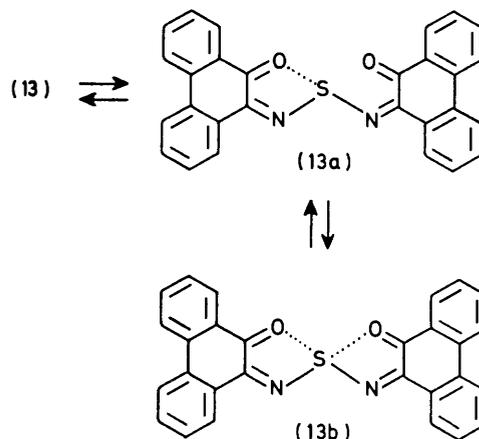


These results suggest that the reaction of (1) with imines is a useful method for the preparation of imino-monosulphides such as (7a) and (13).

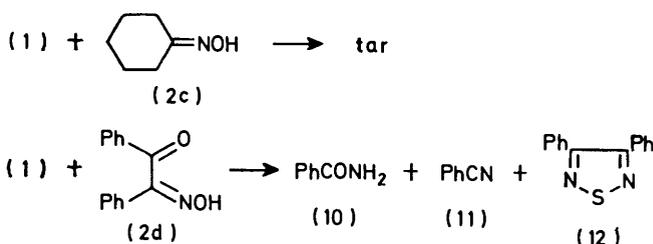
There are two possible structures involving one or two partial bonds^{6,7} between sulphur and oxygen in (13). In the i.r. spectrum of (13), two weak peaks ascribable to $\nu_{\text{C=O}}$ appear at 1640 and 1600 cm^{-1} . This seems to support the presence of partial bonds.

Reaction of (1) with Oximes (2c and d).—In contrast to (2a and b), the reaction with (2c) afforded only a large amount of intractable tar, while the reaction with (2d) gave benzamide (10), benzonitrile (11), and 3,4-diphenyl-

1,2,5-thiadiazole⁸ (12). The formation of (10) and (11) suggest that not only the N-O bond but also the C-C bond of (2d) was cleaved with (1) under the conditions used.



Reaction Pathway.—Based on the above results, the Scheme is postulated to rationalize the reaction of (1) with oximes (2a, b, and d). Nucleophilic attack by the oxygen atom of (2a and b) on the sulphur atom of (1) gives the intermediate A and a subsequent hydrogen



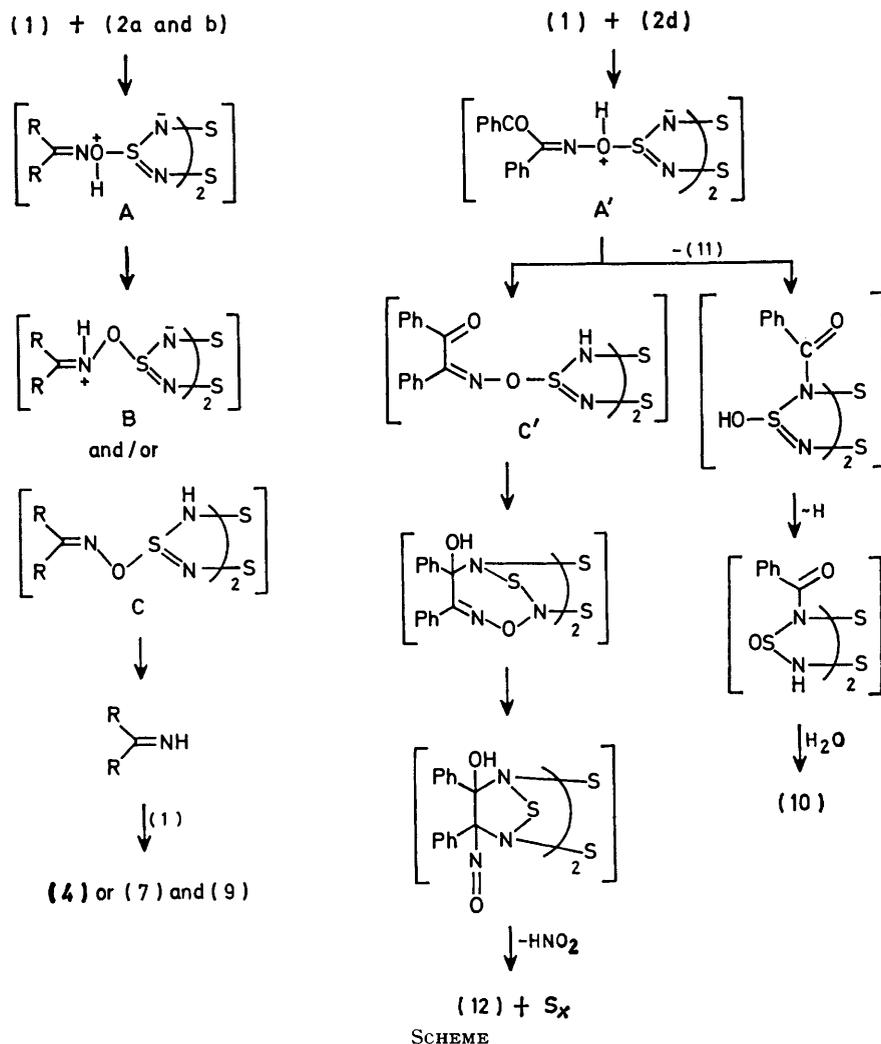
shift affords the intermediate B and/or C, from which the imines are formed. In the reaction with (2d), the intermediate A' is formed initially; however, the products are produced through the complex reaction pathway shown in the Scheme.

EXPERIMENTAL

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

M.p.s were determined on a Yanagimoto micro-apparatus and are uncorrected. 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.

Reaction of (1) with (2a).—A mixture of (2a) (1970 mg) and (1) (920 mg) in toluene (20 ml) was refluxed and then subjected to column chromatography on silica gel (Wako gel C-300), using benzene as eluant, to afford the sulphides (4), benzophenone (5) (617 mg, 34%), benzanilide (6) (28 mg, 1%), and a large amount of tar. Pure samples of (4a and b) were obtained by fractional recrystallization in 5% (103 mg) and 3% (74 mg) yields, respectively: (4a), yellow prisms (from hexane), m.p. 167° (lit.,⁹ 162°) (Found: C, 79.55; H, 5.1; N, 7.05. Calc. for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{S}$: C, 79.55; H, 5.15; N, 7.1%); bis(diphenylmethyleneamino) tetrasulphide; (4b), pale yellow prisms (from hexane), m.p.



108—109° (Found: C, 63.95; H, 4.1; N, 5.7. $C_{26}H_{20}N_2S_4$ requires C, 63.95; H, 4.15; N, 5.75%; m/e 488 (M^+), 456, 424 ($M^+ - 2S$, m^* 368.3), and 392.

Reaction of (1) with (2b).—A mixture of (2b) (980 mg) and (1) (460 mg) in toluene (20 ml) was heated at reflux for 5 h, and allowed to stand overnight at room temperature to give *bis*(fluorenylideneamino) monosulphide (7a) (455 mg, 22%). The filtrate was further allowed to stand overnight to afford a solid which, on washing with cold 10% NaOH aqueous solution, gave the imine (3a) (38 mg, 4%). The filtrate was evaporated and the residue was chromatographed on alumina using benzene as eluant to give fluorenone (8) (134 mg, 14%) and *bis*(fluorenylideneamino) trisulphide (7b) (227 mg, 10%). *Fluorenylideneamino*-sulphenamide (9) was obtained using $CHCl_3$ as eluant. Compound (7a) gave dark green prisms (from toluene), m.p. >300° (Found: C, 80.05; H, 4.2; N, 7.2. $C_{26}H_{16}N_2S$ requires C, 80.05; H, 4.15; N, 7.2%); m/e 388 (M^+); (7b) formed pale yellow prisms (from toluene), m.p. 205—207° (decomp.) (Found: C, 68.85; H, 3.55; N, 6.15. $C_{28}H_{16}N_2S_3$ requires C, 69.0; H, 3.55; N, 6.2%); (9) afforded yellow needles (from benzene), m.p. 170° (Found: C, 68.9; H, 4.4; N, 12.25. $C_{13}H_{10}N_2S$ requires C, 69.0; H, 4.45; N, 12.4%); m/e 226 (M^+); ν_{NH} (KBr) 3 360 and 3 200 cm^{-1} .

Hydrolysis of (7a).—Compound (7a) (100 mg) was heated to reflux in concentrated hydrochloric acid (3 ml) and ethanol (7 ml) for 1.5 h, the mixture was left overnight at room temperature, and then poured into water (100 ml) to give fluorenone (65 mg, 70%), which was collected by filtration.

Reaction of (1) with (2d).—A mixture of (1) (230 mg) and benzil mono-oxime (2d) (1 120 mg) in toluene (20 ml) was refluxed for 6 h and then chromatographed on silica gel using benzene as eluant to afford benzamide (10) (141 mg, 23%), benzonitrile (11) (40 mg, 9%), and 3,4-diphenyl-1,2,5-thiadiazole (12) (49 mg, 4%) which formed prisms (from hexane), m.p. 83—84° (lit.,⁸ 85—86°).

Reaction of (1) with (3a).—A mixture of imine (3a) (684 mg) and (1) (176 mg) in toluene (10 ml) was refluxed for 5 h and then left overnight at room temperature. The precipitate of (7a) (310 mg, 41%) was collected by filtration. Column chromatography of the filtrate on alumina using benzene as eluant gave (7b) (120 mg, 14%), (8) (170 mg, 25%), and (9) (5 mg, 0.6%). When a mixture of (3a) (950 mg) and (1) (460 mg) was treated and worked up as above, (7a) (600 mg, 58%) was obtained.

Reaction of (1) with (3b).—A mixture of (3b) (1 000 mg) and (1) (440 mg) in toluene (10 ml) was refluxed for 5 h and left at room temperature. The precipitate of *bis*-

(10-oxophenanthren-9-ylideneamino) sulphide (13) was collected by filtration, dark green needles (from toluene), m.p. $>300^{\circ}$; $\nu_{\text{C=O}}$ (KBr) 1 640 and 1 600 cm^{-1} (Found: C, 75.5; H, 3.65; N, 6.35. $\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ requires C, 75.65; H, 3.65; N, 6.3%).

Preparation of (13) from (3b) and Sulphur Dichloride.—To a stirred mixture of (3b) (446 mg) and triethylamine (0.2 ml) in CCl_4 (10 ml) was added dropwise at room temperature a solution of SCl_2 (0.14 ml) in CCl_4 (2 ml). The mixture was stirred for an additional 1 h and the precipitate was filtered off and then washed with water to afford (13) (152 mg, 32%).

Reaction of (13) with 2,4-Dinitrophenylhydrazine.—A mixture of (13) (500 mg) and 2,4-dinitrophenylhydrazine (435 mg) in ethanol (50 ml) was refluxed for 4.5 h and was allowed to stand at room temperature. The precipitate

of phenanthrequinone mono-2,4-dinitrophenylhydrazone (575 mg, 67%) was collected by filtration.

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REFERENCES

- ¹ Part 4, S. Mataka, K. Takahashi, and M. Tashiro, *J. Heterocyclic Chem.*, 1977, **14**, 963.
- ² M. Tashiro and S. Mataka, *Chem. Letters*, 1976, 627.
- ³ A. Kliegel, *Ber.*, 1910, **43**, 2497.
- ⁴ R. Anchütz and G. Shultz, *Annalen*, 1879, **196**, 51.
- ⁵ R. Schenk, *Annalen*, 1896, **290**, 171.
- ⁶ P. Yate and D. R. Moore, *J. Amer. Chem. Soc.*, 1953, **80**, 5577.
- ⁷ A. Atkinson, A. G. Brewster, S. V. Ley, R. S. Osborn, D. Rogers, D. J. Williams, and K. A. Woods, *J.C.S. Chem. Comm.*, 1977, 325 and references cited therein.
- ⁸ V. Bertini and P. Pino, *Angew. Chem.*, 1966, **78**, 493.
- ⁹ K. Hunger, *Chem. Ber.*, 1967, **100**, 2214.