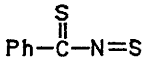
Arylimine Polysulphides

By YUKIHIKO SASAKI and FREDRIC P. OLSEN*
(*Department of Chemistry, McMaster University, Hamilton, Ontario, Canada*)

Summary Tetrasulphur tetranitride on reaction with benzylamines leads to arylimine polysulphides as does sulphur with benzylamines in the presence of lead oxide.

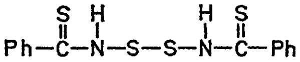
REACTION of tetrasulphur tetranitride with benzylamine gave a yellow solid characterized by Schenck[1] as the thioamide of thiobenzoic acid, (I). Levi[2] obtained the same material by treating sulphur with benzylamine in the presence of lead(II) oxide, but assigned the structure to be either thiobenzamide disulphide, (II), or *NN'*-dibenzylcyclotetrasulphurdi-imide (III). We have isolated this material from both of the above reactions and find its properties to be inconsistent with all three previously suggested structures. It should be formulated as benzylidenimine tetrasulphide (IV), the first example of an arylimine polysulphide. The two reactions have been found to give convenient synthetic routes to several members of this new class of compound.

(IV) was characterised by elemental analysis (consistent with any of the four structures) and osmometric molecular weight [consistent with (II), (III), and (IV)]. The ^{1}H n.m.r. spectrum (in CCl_4), with a sharp singlet at δ − 7·87 (1H) and a multiplet at −7·05 to − 7·48 (5H), clearly eliminates structures (I) and (III). The i.r. spectrum showed no absorption above 3100 cm.$^{-1}$ as would have been expected for the N–H group of (II), but did have a weak band at 1630 cm.$^{-1}$ assignable to a C=N. The n.m.r. chemical



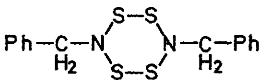
$Ph-\overset{S}{\overset{\|}{C}}-N=S$

(I)

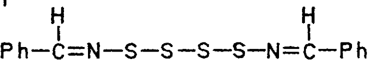


$Ph-\overset{S}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-S-S-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-Ph$

(II)



(III)



$Ph-\overset{H}{\overset{|}{C}}=N-S-S-S-S-N=\overset{H}{\overset{|}{C}}-Ph$

(IV)

shift of the low-field singlet is in good agreement with that expected for the benzyl proton in (IV). Thermal decomposition leading to elemental sulphur and triphenyl-*s*-triazine, also supports structure (IV).

In the tetrasulphur tetranitride–benzylamine reaction in the absence of solvent, (IV) [R_F 0·46 (silica gel–carbon disulphide), with 0·80 for sulphur] accounts for 68% of the sulphur in the starting tetrasulphur tetranitride. Other products include elemental sulphur, benzylidenimine trisulphide (m.p. 125—126°; n.m.r.: singlet at δ − 8·42, multiplet at −7·24 to −7·84; R_F 0·40; 5% of all sulphur), and benzylidenimine disulphide (m.p. 100—100·5°; n.m.r.: singlet at δ − 8·14, multiplet at −7·24 to −7·84; R_F 0·36; 7% of all sulphur), as well as ammonia and *N*-benzylidene benzylamine. The overall reaction is:

$$S_4N_4 + 8PhCH_2{\cdot}NH_2 \rightarrow PhCH{:}NS_nN{:}CHPh + 3PhCH{:}NCH_2Ph + 7NH_3 + (4 - n)S \qquad (n = 2\text{—}4)$$

Electron-withdrawing groups on the aromatic ring of the starting amine decrease the yield of tetrasulphide (*p*-Cl; 48%). In this reaction the substituted imine monosulphide (7%) was isolated together with elemental sulphur. Electron-releasing groups favour formation of the tetrasulphide (*p*-OMe; 73%). α-Methyl benzylamine does not give analogous imine polysulphides, while with phenylhydrazine, tetrasulphur tetranitride yields elemental sulphur (63%), diphenyl disulphide (16%), and diphenyl monosulphide (7%) as the main sulphur-containing products. The yield of imine polysulphide is decreased in the presence of solvents (pyridine, dimethylformamide, triethylamine, benzene, or an excess of benzylamine). In the last case, this arises from further reaction of the imine polysulphide with the excess of amine.

In the benzylamine–sulphur–lead oxide reaction the tetrasulphide accounts for about 1/3 of the total sulphur with substantially more di- and tri-sulphides than in the tetrasulphur tetranitride reaction. The products are conveniently separated by column chromatography on silica gel and/or by fractional crystallization from methanol. The relative difficulty of obtaining tetrasulphur tetranitride as a starting material makes the sulphur–amine reaction the more convenient synthetic route.

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[1] R. Schenck, *Annalen*, 1896, **290**, 171.

[2] T. G. Levi, *Gazzetta*, 1931, **61**, 294.