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Preparation of Milligram Quantities of Tetrasulphur Tetranitride and Tetrasulphur Dinitride by a Method Suitable for Isotopic Labelling

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In the course of our research into the identity of the free radical formed from strained olefins with tetrasulphur tetranitride [1] and with tetrasulphur dinitride [2], we required milligram quantities of the sulphur–nitrogen compounds. In order to detect the presence of sulphur in the radicals it was necessary to label the sulphur–nitrogen compounds with sulphur-33 which should produce extra splittings in the ESR spectra. An earlier publication [3] described the production of milligram quantities of tetrasulphur tetranitride but this method required the use of about a gram of sulphur as starting material; even using sulphur labelled with 50% sulphur-33, the method would be far too costly to use. A second method [4] is inefficient and is also inconvenient. We have devised a method which employs a starting weight of sulphur of about 1–2 mg.

Experimental

About 1 mg of sulphur plus about 2.5 mg of bromine were put into a small borosilicate tube and sealed under vacuum. After heating for 24 hours at 50 °C, 1.5 cm^3 of carbon tetrachloride was added to the contents of the tube. A stream of dry gaseous ammonia was bubbled into this solution of sulphur bromide, the solution being shaken throughout. The solution became deep orange and the ammonia was passed in until a pH of 8 was reached. The ammonium bromide was filtered off and the filtrate contained tetrasulphur tetranitride and tetrasulphur dinitride; washing the precipitated ammonium bromide with carbon tetrachloride did not improve the yield. It has been pointed out [3] that the theoretical yield of tetrasulphur tetranitride is 33% according to the equation:

$$6S_2Br_2 + 16NH_3 \rightarrow S_4N_4 + 8S + 12NH_4Br$$

However, we found the carbon tetrachloride solution to contain the dinitride and the tetranitride in the ratio of about 3:1. There is no mention in any of the published methods [4–7] for the preparation of tetrasulphur tetranitride of tetrasulphur dinitride being an important by-product. We estimate that the spent reaction mixture contains 50% sulphur, 30% tetrasulphur dinitride, 10% tetrasulphur tetranitride and 10% S_7NH. No rigorous attempts have been made to optimise the experimental conditions. Obviously, it would be interesting to study the reaction mechanism in detail. Separations of the components of our reaction mixture were carried out by thin-layer chromatography using 0.25 mm "polygram" silica gel paper supplied by Macherey, Nagel and Co. A good separation was obtained after 3 hours using carbon tetrachloride as solvent, the bright orange spot of S_4N_2 being ahead of the yellow spot of S_4N_4 which was ahead of the yellow spot of S_8. Identification of the spots was made by preparing larger scale authentic samples of tetrasulphur tetranitride and of tetrasulphur dinitride by the published procedures in reference 8 and in references 6 and 7 respectively. The identity and purity of these samples were checked using the following spectroscopic techniques (i) infra-red absorption; (ii) mass spectrometry; (iii) electronic absorption.

Infra-red Spectroscopy

Spectra were obtained using a Perkin Elmer 577 grating infra-red spectrometer. The results obtained are listed in Table I and they are in good agreement with previously-published data.

TABLE I. Infrared Spectra.

S_4N_2[a]		S_4N_4[a]		
KBr disc of oil	Liquid[b]	CsI disc	Solid[c]	Solid[d]
1030s	1034s	928s	925	928
928s	930m	769m	–	768
630s	628s	760m	–	764
621m	620s	728m	719	728
467m	468m	701s	696	702
373m	373s	622m	–	–
–	318m	552s	557	552
–	264w	548w	552	–
		527m	–	530
		515w	–	520
		346s	347	–

[a] Bands measured in cm^{-1}: s = strong, m = medium, w = weak. [b] Reference [9]. [c] Reference [10]. [d] Reference [3].

Mass Spectrometry

Spectra were recorded with a V. G. Micromass 12 electron ionisation mass spectrometer having a mass

TABLE II. Mass Spectra.

Ionising voltage	S_4N_2					
	SN^+	S_2^+	S_2N^+	$S_2N_2^+$	S_3N^+	$S_4N_2^+$
25	9	50	11	4	9	17
30	15	48	11	5	7	13
70	25	39	11	6	8	12

Ionising voltage	S_4N_4						
	SN^+	S_2N^+	$S_2N_2^+$	S_3N^+	$S_3N_2^+$	$S_3N_3^+$	$S_4N_4^+$
25	52	9	14	1	1	20	4
30	43	11	15	1	1	24	6
70	51	10	14	1	1	20	4

range of 2–900 m/e. The data in Table II give the percentage of total ionisation and ions not containing sulphur and/or nitrogen have been ignored.

Ultraviolet/Visible Absorption Spectroscopy

Spectra of hexane solutions of S_4N_4 and S_4N_2 were obtained using a Unicam SP800 ultraviolet spectrophotometer. In accordance with previous work [7, 9] we obtained absorption bands at 377 and 455 nm for S_4N_2 in hexane. However, we did not obtain a maximum at 220 nm as reported by Adkins and Turner [7] but there is a plateau below this wavelength having an extinction coefficient of 3400 M^{-1} cm^{-1}. The ultraviolet/visible spectrum of S_4N_4 does not appear to be in the literature; in hexane we found a single maximum at 256 nm having a molar extinction coefficient of 14,400 M^{-1} cm^{-1}. The longer wavelength bands of both S_4N_4 and S_4N_2 provide the most useful means of measuring their concentrations.

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