

A Convenient Synthesis of 2-Substituted 1,3,5-Trithians

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Summary A convenient new route to 2-substituted 1,3,5-trithians by reaction of $S(CH_2SH)_2$ and aldehydes in acetic acid has been developed.

RECENT reports^{1,2} on the synthesis of 2-substituted trithians (by treatment of 1,3,5-trithian with butyl-lithium followed by reaction with an electrophile) and on their subsequent use as aldehyde-protecting and/or -activating groups prompts this report of a simple alternative synthesis for this potentially useful class of molecule.

$SH)_2$ † (0.02 moles) was stirred at 25°, and concentrated sulphuric acid was added dropwise over several minutes; the reaction mixture was stirred for ½ h at 25° and worked-up by pouring it on to ice. The precipitated solid was collected by vacuum filtration.

The amount of sulphuric acid used in these reactions can be critical. In several cases an excess of sulphuric acid led to complete polymerization. The Table shows the conditions for the reaction and some of the physical data of the products.

Physical and synthetic data for 2-R-1,3,5-trithians

Compound ^a	ml H ₂ SO ₄	% Yield	M.p.	Work-up procedure	H _A	NMR δ(SiMe ₄) H _B	H _C
(1)	3	91	Hexane 85—87° ^b	A ^e	4.14(q, 1) ^g	3.80(d, 2)	4.29(d, 2)
(2)	3	89	2:1 Hexane-acetone 137—138°	A	5.30(s, 1) ^h	3.78(d, 2)	4.46(d, 2)
(3)	1	69	140—141° ^{c,d}	A	5.54(s, 1) ^h	3.82(d, 2)	4.43(d, 2)
(4)	0.25	90	2:1 Hexane-acetone 110—111°	A	5.76(s, 1) ^h	4.16(d, 2)	4.69(d, 2)
(5)	4	88	1:2 Hexane-acetone 141—142°	B ^f	5.41(s, 1) ^h	4.02(d, 2)	4.67(d, 2)
(6)	3	93	1:2 Hexane-acetone 181—183°	A	5.50(s, 1) ^h	3.85(d, 2)	4.48(d, 2)
(7)	2	83	1:2 Hexane-acetone 129-S-131°	A	5.51(s, 1) ^h	4.10(d, 2)	4.72(d, 2)

^a All compounds gave satisfactory analytical data. Full i.r., n.m.r., and mass spec. data are in agreement with the assigned structures.

^b Lit. (86—86.3°).³

^c Precipitated from methanol with hexane.

^d Compound (3) turns pink when exposed to light. Its acetyl derivative is light-stable; m.p. 159—160° (ethanol).

^e The reaction mixture is poured into 30 g of ice and the solid formed collected by vacuum filtration.

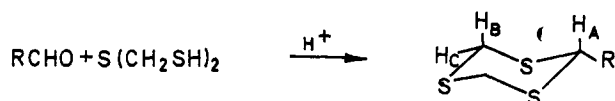
^f The reaction mixture is poured into 300 ml of iced 20% K₂CO₃ and the solid formed collected by vacuum filtration.

^g CCl₄.

^h Acetone.

The following general procedure was used. A mixture of acetic acid (30 ml), aldehyde (0.02 moles), and $S(CH_2-$

Attempts to prepare these compounds by stirring the aldehyde and sulphide in benzene with a trace of acid followed by benzene-water azeotrope were not as successful as the above procedure which has been demonstrated to proceed in high yield for many classes of aldehydes.



R = (1) Me; (2) Ph; (3) C₆H₄-OH-*o*; (4) 2-furfuryl; (5) C₆H₄-NMe₂-*p*; (6) C₆H₄-NO₂-*p*; (7) 3,4-methylenedioxyphenyl.

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² D. Seebach, *Syn.*, 1969, **4**, 17.

³ E. J. Corey and D. Seebach, unpublished results reported in ref. 2.

Identification of S₄⁺ in Sulphur-Oleum Solutions

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Summary The radical formed on dissolving sulphur in 60% oleum is shown to be S₄⁺ by e.s.r. studies with sulphur enriched to 91.8% in ³³S.

SULPHUR dissolves in oleum to produce a variety of species and two distinct radicals, R¹ and R², are detected in e.s.r. spectra.¹ R¹ is observed at all SO₃ concentrations while R²

is only seen when the SO_3 concentration is below *ca.* 40%. Studies at 77 K show that R^1 is axially symmetric and R^2 is not. From e.s.r. experiments with sulphur containing 10% of ^{33}S , McNeil, Murray, and Symons² proposed that R^1 was S_3^+ in the form $[\text{S}_2(\text{HS}_2\text{O}_6)_2(\text{HS}_2\text{O}_7)_2]^+$. More recently, Gillespie and Passmore,³ and Giggenbach⁴ have suggested that the radical R^1 is S_4^+ . However, no direct evidence for this assignment has been presented.

In the hopes of obtaining more conclusive evidence of the identity of R^1 and R^2 we have studied their e.s.r. spectra using sulphur enriched to 91.8% ^{33}S .† Spectra in 60% and 20% oleum, taken with a Varian E-12 spectrometer are given in Figures 1 and 2. The 13-line spectrum of R^1 ‡

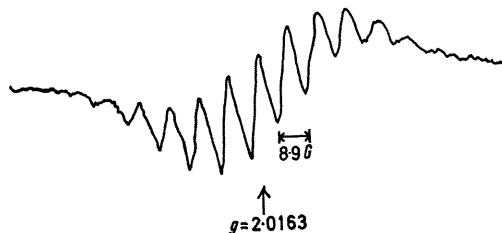


FIGURE 1. E.s.r. spectrum of sulphur containing 91.8% ^{33}S in 60% oleum. The solution contained *ca.* 0.2–0.3 mg S in 1 ml oleum.



FIGURE 2. E.s.r. spectrum of sulphur containing 91.8% ^{33}S in 20% oleum. The solution contained *ca.* 0.2–0.3 mg S in 1 ml oleum.

confirms the presence of 4 equivalent sulphur atoms. To obtain the g value and the magnetic hyperfine coupling constant, allowing for the presence of more than one isotopic species, we have computer-simulated the observed spectra. Satisfactory agreement is found with $g = 2.0163$, $A_{\text{iso}} = 8.87$ G and a half-linewidth at half height of about 4 G.§ The most abundant species (^{33}S)₄ is responsible for the peaks observed. The next abundant species, (^{33}S)₃³²S, produces the slight inflections between the peaks. In Figure 2, R^2 appears as one broad resonance superimposed on the spectrum of R^1 . Since hyperfine splittings in R^2 are not resolved, we have not attempted to separate the signals from the two species.

The results for R^1 are fully consistent with its previous identification as S_4^+ . The e.s.r. results do not distinguish between square-planar, puckered, or tetrahedral geometries. However, S_4^+ is a precursor to the recently identified species S_4^{2+} .^{5,6} S_4^{2+} has a m.c.d. spectrum⁵ analogous to that of Se_4^{2+} whose structure has been shown by X-ray diffraction to be square-planar.⁷ Hence, S_4^+ is most likely square-planar. The small value of A shows that the unfilled orbital has little s character, which is consistent with its being the antibonding π -orbital of a square-planar ring.

In the absence of resolved hyperfine structure in the e.s.r. spectrum of R^2 we are unable to derive any conclusions about its identity. Since the resonance line has been broadened in comparison with the ^{32}S spectrum the presence of sulphur is confirmed.

Gillespie and Passmore,³ and Giggenbach⁴ attribute the blue colour of sulphur solutions in oleum to S_3^{2+} and S_4^+ respectively. Our work does not resolve this disagreement.

While this paper was with the referees Stillings, Symons, and Wilkinson⁸ reported e.s.r. spectra of 10 and 25% ^{33}S -enriched sulphur in 60% oleum and interpreted them in terms of a S_3^+ species. Both the number and relative intensities of the lines in our spectrum are definitely inconsistent with this assignment.

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† Obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee.

‡ The outermost peaks are more clearly seen than in Figure 1 under higher sensitivity.

§ There appears to be a real change in g value from the ^{32}S species ($g = 2.013$).

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