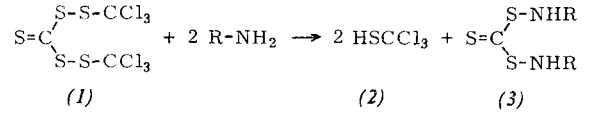
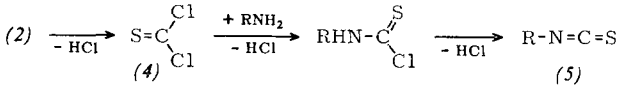
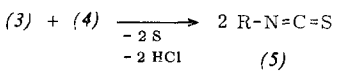
Like thiophosgene, the ester *(1)* also reacts in aqueous suspension with amines, giving isothiocyanates *(5a)–(5d)*; only 3 moles of amine per mole of ester are needed since the *N,N'*-disubstituted trithiodiperoxycarbondiamides *(3)* (which have been identified[2]) also yield isothiocyanates on reaction with thiophosgene *(4)*.



(1) *(2)* *(3)*



(4) *(5)*



(5)

	R	Yield (%)
(5a)	Benzyl	80
(5b)	Phenyl	75
(5c)	*p*-Tolyl	80
(5d)	*p*-Chlorophenyl	72

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Reaction of D-Glucosamine with Carbon Disulfide

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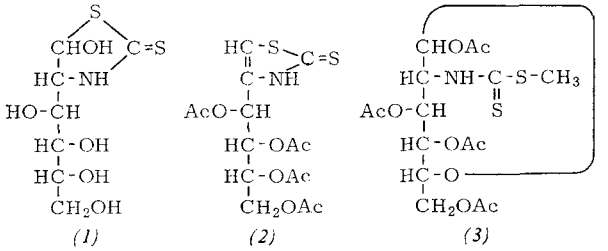
D-Glucosamine and CS_2 in methanol give 5-hydroxy-4-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)thiazolidine-2-thione *(1)* in 80% yield.



(1) *(2)* *(3)*

5-Hydroxythiazolidines appear not to have been described previously. The product *(1)* is precipitated as a mixture of about 80% of the α-form and 20% of the β-form. The mixture has $[\alpha]_D^{20} = 108°$ ($c = 1$; in dimethylformamide) and decomposes from 146 °C. With the calculated amount of acetic anhydride in pyridine at 0 °C it gives the penta-*O*-acetyl derivative which can be separated into its anomers by fractional crystallization from ethyl acetate:

α-5-Acetoxy-4-(D-*arabino*-1,2,3,4-tetraacetoxybutyl)thiazolidine-2-thione, $[\alpha]_D^{20} = +238°$ ($c = 1$; in dimethylformamide), m.p. 137–138 °C.

β-5-Acetoxy-4-(D-*arabino*-1,2,3,4-tetraacetoxybutyl)thiazolidine-2-thione, $[\alpha]_D^{20} = -218°$ ($c = 1$; in dimethylformamide), m.p. 165–168 °C.

When boiled for 16 hr in anhydrous pyridine, both these compounds afford D-*arabino*-1,2,3,4-tetraacetoxybutyl-Δ^4-thiazoline-2-thione *(2)*, $[\alpha]_D^{20} = -37°$ ($c = 1$; in dimethylformamide), m.p. 169–170 °C[1].

The thiazolidinethione ring in compound *(1)* can be easily opened. Use of methyl iodide + triethylamine in pyridine leads to an α,β-mixture of 2-deoxy-2-[methylthio(thiocarbonyl)amino]-D-glucopyranoses, isolated as the crystalline 1,3,4,6-tetra-*O*-acetyl derivative *(3)*, m.p. 143–145 °C (decomp.), $[\alpha]_D^{20} = +100°$ ($c = 1$; in dimethylformamide). Compound *(1)* can be titrated as an acid with alkali; salts of 2-deoxy-2-[methylthio(thiocarbonyl)amino]-D-glucopyranose are thus obtained, form which *(1)* is regenerated on acidification. The yellow Cu(II) salt of *(1)* is practically insoluble in all solvents. Compound *(1)* is stable in glacial acetic acid, but in boiling 2 N hydrochloric acid it affords glucosamine hydrochloride quantitatively. The structures of all the products are proved by, *inter alia*, elemental analyses, molecular-weight determinations, and IR and NMR spectra.

Formation of 5-hydroxythiazolidine-2-thiones appears to be a general reaction of α-amino carbonyl compounds with CS_2.

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[1] *J. C. Jochims*, *A. Seelinger*, and *G. Taigel*, Chem. Ber., in press.

Cyclododecasulfur, S_{12}

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In sulfur melts innumerable forms of sulfur, S_x, with $x = 8$ to about 10^6, coexist in hitherto unelucidated equilibria. Nevertheless, only two definite structures have so far been isolated, namely cyclooctasulfur, S_8 (crystallizing as S_α, S_β, and S_γ), and cyclohexasulfur, S_6 (S_ρ)[1]. Recently[2] we developed a process for the planned synthesis of rings or chains of identical atoms and used it to obtain the unstable molecules S_6 and S_{10}, of which the latter, being extremely, unstable, was insufficiently characterized. We have now prepared a new, surprisingly stable modification of sulfur, *viz.* cyclododecasulfur, S_{12}:

$$H_2S_x + Cl_2S_y \rightarrow 2\,HCl + S_{12}$$
$$(x + y = 12)$$

S_{12} is formed, together with polymeric sulfur, from sulfanes and chlorosulfanes ($x + y = 12$) in CS_2-ether mixtures by use of the dilution principle. It forms small, pale yellowish rectangular prisms from benzene, which melt at 148 °C (with decomposition), *i.e.* appreciably higher than all previously known forms of sulfur; the resolidified melt consists of S_8, m.p. 119 °C, which is formed by way of polymeric sulfur. The solubility of S_{12} in benzene, about 0.4 g/l, is too low for vapor-pressure osmometric or ebullioscopic determination of the molecular weight. On concentration of its solutions in carbon disulfide, S_{12} separates as colorless plates with a circular indentation in the centers of the large faces and containing solvent which they rapidly lose with disintegration, but the solubility in carbon disulfide is also remarkably low (*ca.* 2 g/l), so that vapor-pressure osmometric determination of the molecular weight gives values between 377 and 390 (theory 384).