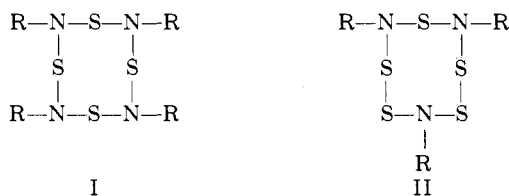


# Substituted Cyclic Sulfur-Nitrogen Compounds from Reaction of Primary Amines with Sulfur Dichloride

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Chromatographic separation of the products of reaction of benzylamine and  $\beta$ -phenylethylamine with sulfur dichloride has led to the isolation of  $(C_6H_5CH_2N)_3S_5$  and  $(C_6H_5CH_2CH_2N)_3S_5$ . Similar treatment of the reaction of ethylamine with sulfur dichloride has shown the compound  $(C_2H_5N)_4S_4$  to be a stable, colorless, crystalline solid and not an unstable, colored oil as earlier reported.

REACTIONS OF primary amines with sulfur dichloride have been reported to yield, in addition to polymeric materials, small amounts of crystalline solids of composition  $(RN)_4S_4$  and  $(RN)_3S_5$  possessing structures I and II, respectively (1, 3).



With methylamine, both compounds were obtained (3). With benzylamine and  $\beta$ -phenylethylamine, only the compounds corresponding to structure I were isolated (1). The reaction of ethylamine with sulfur dichloride was reported to yield an unstable oil of composition  $(C_2H_5N)_4S_4$  to which structure I was assigned (2).

Using the same technique as that reported for methylamine, we have repeated the reactions of benzylamine,  $\beta$ -phenylethylamine and ethylamine with sulfur dichloride. By elution chromatography of the petroleum ether soluble reaction products on neutral aluminum oxide, isolation of

the benzyl and  $\beta$ -phenylethyl derivatives of structure II was achieved in 1-2% yields. Similarly, the ethyl derivative of structure I was obtained as a colorless, crystalline solid. No ethyl derivative of structure II was isolated.

The infrared spectra of the materials are consistent with the proposed structures. The proton nuclear magnetic resonance spectrum of  $(C_2H_5N)_4S_4$  was found to consist of a 1:2:1 triplet of relative intensity 3 at -1.32 ppm (relative to tetramethylsilane) and a 1:3:3:1 quartet of relative intensity 2 at -3.67 ppm ( $J=7$  cps).

Suggested names for the compounds herein reported are:  $(C_2H_5N)_4S_4$ , 2,4,6,8-tetraethyl-1,3,5,7,2,4,6,8-tetrathiatrazocine;  $(C_6H_5CH_2N)_3S_5$ , 2,5,8-tribenzyl-1,3,4,6,7,2,5,8-pentathiatriazocine; and  $(C_6H_5C_2H_4N)_3S_5$ , 2,5,8-tris( $\beta$ -phenylethyl)-1,3,4,6,7,2,5,8-pentathiatriazocine.

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Table I. Properties of Derivatives

	Melting point, °C.	Analysis <sup>b</sup>				Mol. Wt. <sup>a</sup>
		%C	%H	%N	%S	
$(C_2H_5N)_4S_4$	143	31.97	6.71	18.64	42.68	300.4
$(C_6H_5CH_2N)_3S_5$	150	32.18	6.95	18.85	42.66	303
		53.02	4.45	8.83	33.70	475.7
		53.00	4.50	8.78	33.80	466
$(C_6H_5C_2H_4N)_3S_5$	89	55.67	5.26	8.12	30.96	517.8
		55.58	5.27	7.90	30.86	494

<sup>a</sup> Mechrolab Osometer. <sup>b</sup> First line calculated, second line found.