refinements of the atomic coordinates and thermal parameters (anisotropic for I and Cl and isotropic for C, N, and O) converged to $R = 0.07$. Various refinements of the multiplicities of C-7, O, and N in the final stages of the analysis confirmed the presence of the *N*-chloro lactam moiety in **5**.

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**Registry No.**—**3**, 5152-34-1; **4**, 27305-20-0; **5**, 27305-23-3; **6**, 3580-04-9; **7**, 27305-21-1.

**Supplementary Material Available.** Tables of fractional coordinates and temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-2129.

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# Unusual Reaction of 4-Mercapto-1,2,3-benzotriazine with *N*-(2,4-Dibromophenyl)benzohydrazonyl Bromide

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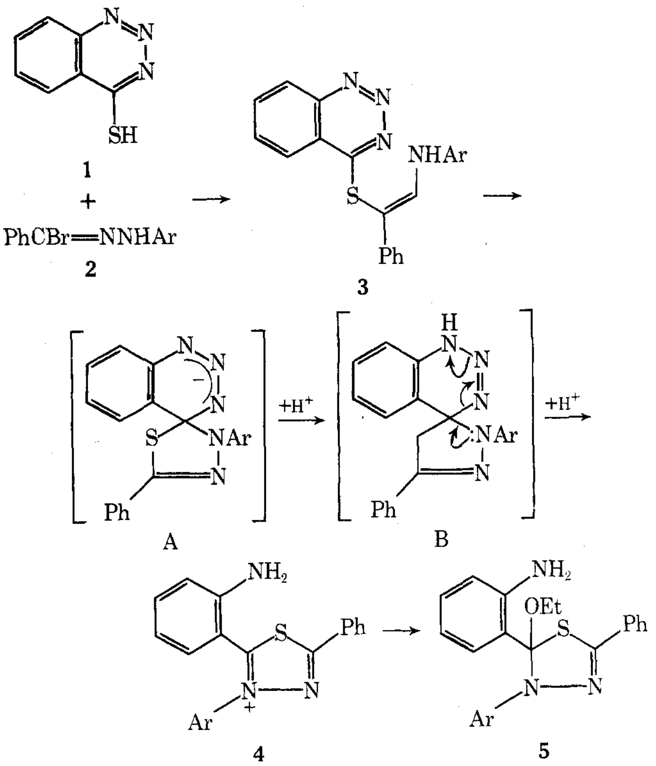
During the course of studies on hydrazonyl halides, we have noted an unusual reaction between 4-mercapto-1,2,3-benzotriazine (**1**), *N*-(2,4,-dibromophenyl)benzohydrazonyl bromide (**2**, Ar = $2,4\text{-}Br_2C_6H_3$), and ethanol in the presence of triethylamine.

Reactions of aryl mercaptans with hydrazonyl halides in the presence of base give aryl thiohydrazonates which are normally stable under the conditions of formation.[1] In the present case we envisage deprotonation by triethylamine of the thiohydrazonate **3** formed from **1** and **2**, followed by intramolecular nucleophilic addition of the anion to C-4 of the triazine.[2] Reversible protonation of the spirocyclic intermediate A at N-1 or N-3 of the triazine to give, e.g., B may now be followed by aromatization of the newly formed ring, opening of the triazine ring with loss of N-3 and N-2 as nitrogen, and protonation of N-1 to give the thiadiazolium ion **4**. We have confirmed[3] that such thiadiazolium ions add ethoxide ion equivalent at C-2(5) when treated with ethanolic sodium ethoxide or ethanol–triethylamine and so progression of **4** to the observed product **5** is readily understood. The ease of reaction is notable in view of the stability of simple aryl thiohydrazonates.[1]

This case and the recently reported[4] formation of 2-(2-aminophenyl)-5-mercapto-1,3,4-thiadiazole from 4-hydrazinoquinazoline and $CS_2$ in the presence of KOH represent unusual Smiles-type rearrangements[5] in which the migrating aryl ring (1,2,3-benzotriazin-4-yl or quinazolin-4-yl) collapses while the cyclic transition state for the migration is consolidated as a new ring (1,3,4-thiadiazole), closure occurring by C–N or C–S bond formation as appropriate.



## Experimental Section

NMR data were obtained with a Varian A-60 spectrometer (tetramethylsilane as internal standard).

4-Mercapto-1,2,3-benzotriazine was conveniently prepared from 1,2,3-benzotriazin-4-one and phosphorus pentasulfide in pyridine or toluene.[6]

**5-(2-Aminophenyl)-4-(2,4-dibromophenyl)-5-ethoxy-2-phenyl-$\Delta^2$-1,3,4-thiadiazoline (5).** A mixture of 1.63 g (0.01 mol) of **1**, 4.33 g (0.01 mol) of **2**,[7] and 30 ml of ethanol was stirred at room temperature and 2 ml of triethylamine was added. There was an immediate evolution of gas. After 30 min, solvent was removed in vacuo and the pale brown solid was washed with water and dried to give 2.8 g (53%) of **5** which crystallized from hexane as fawn needles: mp 136–137°; ir (Nujol–hexachlorobutadiene mulls) 3500 and 3400 (NH), 1600, 1570, 1550, and 1480 (aromatic C=C and C=N),[8] 1460 and 1375 (aliphatic CH), 1325, 1300, 1220, 1150, 1105, 1075, 1060, 1050, 980, 970; 870, 820, 765, 745, 725, and 690 $cm^{-1}$ (aromatic C–H; mono-, 1,2-di-, and 1,2,4-trisubstituted benzene); NMR ($CDCl_3$) $\delta$ 7.90–6.42 (m, 12 H), 4.39 (s, br, 2 NH, exchangeable with $D_2O$), 3.82 (m, 2 H), and 1.35 ppm (t, 3 H).

Anal. Calcd for $C_{22}H_{19}Br_2N_3OS$: C, 49.5; H, 3.6; Br, 30.0; N, 7.9. Found: C, 49.8; H, 3.8; Br, 30.5; N, 7.7.

**Registry No.**—**1**, 2536-88-1; **2** (Ar = $2,4\text{-}Br_2C_6H_3$), 2516-46-3; **5** (Ar = $2,4\text{-}Br_2C_6H_3$), 55298-74-3.

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