Preparation and Diazotization of Thioanthranilic Acid. Chemistry of 4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine[1a,b]

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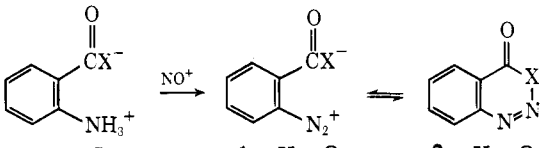
Abstract: Thioanthranilic acid (**3**) was prepared and diazotized in order to study the stability and reactivity of diazoniumthiocarboxylates. Isatoic anhydride and potassium sulfide afforded **3** as a yellow oil, which converted itself after several days to 2-(*o*-aminophenyl)-4*H*-3,1-benzoxazin-4-one. Aprotic diazotization of **3** yielded 4-oxo-3,4-dihydro-3,1,2-benzothiadiazine (**2b**) instead of benzenediazonium-2-thiocarboxylate. Thus, a stable nitrogen-containing product resulted from diazotization of this amino thioacid. Thermolysis of **2b** gave 3*H*-1,2-benzodithiol-3-one (**4**), dithiosalicylide (**5**), and, in the presence of anthracene, triptycene. When a 1-butanol solution of **2b** was irradiated or refluxed, butyl thiosalicylate and bis(*o*-carbobutoxyphenyl) disulfide resulted. Photolysis of **2b** in inert solvents yielded **4**, **5**, and thioxanthone. Irradiation of **2b** as a film in a special cell cooled with liquid nitrogen followed by scanning of the ir spectrum revealed new ir bands assigned to 2-thiobenzpropiolactone and an unknown.

In protic or aprotic diazotizing media aliphatic amino acids provide an array of products.[2] In contrast diazotization of anthranilic acid provides in good yield *o*-benzenediazoniumcarboxylate (**1a**), a compound of low stability.[3] If before diazotization an oxygen atom of anthranilic acid is replaced with a sulfur atom, then *o*-benzenediazoniumthiocarboxylate (**1b**) should result. If sulfur as a nucleophile reacts with the diazonium cation, then 4-oxo-3,4-dihydro-3,1,2-benzothiadiazine (**2b**) might form. The oxygen analog, 4-oxo-3,4-dihydro-3,1,2-benzoxadiazine (**2a**), has not been reported. This paper reports results from research in this area.



X = O, S — **1a**, X = O; b, X = S — **2a**, X = O; b, X = S

Experimental Section

The following were used for spectral data: ultraviolet (uv), Cary 14 spectrophotometer; infrared (ir), Perkin-Elmer 337 grating spectrometer (all bands with absorption in excess of *ca.* 50% are reported); proton magnetic resonance (pmr), Varian A-60 spectrometer (tetramethylsilane is the internal standard; peaks are reported in τ units; multiplicity and integration are placed in parentheses; mass (ms), Hitachi RMU-6E unit (data are reported as per cent intensity in parentheses relative to the largest peak and were obtained at 70 eV, molecular ion = MI). Irradiation source was either a 200- or 500-W Hanovia medium-pressure mercury lamp or 16 GE G25T8 germicidal fluorescent tubes arranged in a circular bank. Samples were degassed with pure dry nitrogen for at least 0.5 hr prior to photolysis. Photolytic reactions do not occur under the same conditions in the dark. Elemental and molecular weight analyses were by Alfred Bernhardt, Mulheim, Germany. Melting points, obtained on a Thomas-Hoover capillary tube apparatus, are uncorrected. The following compounds were purchased from commercial suppliers: *o*-aminothiophenol, anthracene, anthraquinone, *p*-bromophenacyl bromide, carbazole, isatoic anhydride, isoamyl nitrite, thiosalicylic acid, and triptycene.

Thioanthranilic Acid (3).[4] To a solution of potassium hydroxide (10 g, 0.18 mol, in 500 ml of absolute ethanol) saturated with hydrogen sulfide (2.5 hr at 0°) was added isatoic anhydride (28.8 g, 0.175 mol) slowly. Hydrogen sulfide was bubbled through the solution for 25 additional hr at 0°. The hydrogen sulfide stream was discontinued and the solvent evaporated *in vacuo* to provide a tan residue. That part of the residue which was soluble in 430 ml of 1% aqueous sodium hydroxide was treated with Celite (1 g), filtered, and extracted with 200 ml of benzene which was discarded. The aqueous phase was then stirred with 400 ml of chloroform and the two-phase mixture cooled to near 0°. After slowly adjusting the pH of the aqueous phase to 4 (Congo Red) with concentrated hydrochloric acid, the two phases were separated. The aqueous phase was then extracted with additional chloroform. The combined chloroform solutions provided upon work-up 26.8 g (100%) of the thioacid **3** as a yellow-orange oil of low stability: ν_{max}^{neat} 3500, 3370, 2560, 1645, 1625, 1595, 1560, 1495, 1470, 1210, 1160, 945, 870, 790, and 760 cm^{-1}; pmr (CCl_4) τ 2.4–3.6 (m, 4 H), 4.7 (s, 3 H); mass spectrum *m/e* = 153 (MI, 33), 120 (100), 92 (48), 65 (39). *p*-Bromophenacyl thioanthranilate was prepared[5] from thioacid **3** and *p*-bromophenacyl bromide: mp 118.5–120° (from EtOH); ν_{max}^{KBr} 3510, 3390, 1705, 1635, 1590, 1500, 1200, 1160, 985, 915, 810, and 735 cm^{-1}; pmr ($CDCl_3$) τ 2.2–2.9 (m, 6 H), 3.3 (m, 2 H), 4.7 (broad s, 2 H), 5.6 (s, 2 H); mass spectrum 351, 349 (MI, 2, 2), 183 (5), 120 (100), 92 (29), 83 (24), 65 (31).

Anal. Calcd for $C_{15}H_{12}BrNO_2S$: C, 51.43; H, 3.46; N, 4.00; Br, 22.82; S, 9.15. Found: C, 51.46; H, 3.50; N, 3.93; Br, 22.90; S, 9.35.

After a day or so thioacid **3** deposits a gummy yellow solid which was placed on a silica gel column and eluted with 10% ether–hexane to provide crude 2-(*o*-aminophenyl)-4-oxo-4*H*-3,1-benzoxazine as a bright yellow solid: mp 138–164° dec (from heptane); ν_{max}^{KBr} 3450, 3320, 1760, 1650, 1635, 1605, 1565, 1485, 1460, 1310, 1235, 1220, 1170, 1160, 1150, 1050, 1040, 775, 765, 754, and 685 cm^{-1}; pmr ($CDCl_3$) τ 1.7–1.9 (m, *ca.* 2 H), 2.3–2.8 (m, *ca.* 4.5 H), 3.85 (m, *ca.* 3.8 H); mass spectrum, see Table I. This compound was

(1) (a) Presented in part at the Joint Southeast-Southwest Regional American Chemical Society Meeting, New Orleans, La., Dec. 1970, No. ORGN 349, and at the Seventh Midwest Regional American Chemical Society Meeting, St. Louis, Mo., Oct 1971, No. ORGN 525. (b) Part of this work has been communicated in preliminary form; see A. T. Fanning, Jr., and T. D. Roberts, *Tetrahedron Lett.*, 805 (1971). (c) Abstracted in part from the Ph.D. dissertation of A. T. Fanning, Jr., University of Arkansas, 1972.

(2) (a) D. Van Slyke, *J. Biol. Chem.*, **9**, 185 (1911); **12**, 275 (1912); **83**, 425 (1929); (b) A. T. Austin, *J. Chem. Soc.*, 149 (1950); (c) C. Schmidt, *J. Biol. Chem.*, **82**, 587 (1929); (d) R. C. Neuman, Jr., *J. Org. Chem.*, **29**, 2096 (1964).

(3) (a) M. Stiles and R. Miller, *J. Amer. Chem. Soc.*, **82**, 3802 (1960); (b) see R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, and references therein; (c) F. Logullo, A. Seitz, and L. Friedman in *Org. Syn.*, **48**, 12 (1958).

(4) R. P. Staiger, G. F. Schlaudecker, and E. B. Miller, U. S. Patent 3,123,631 (1964); *Chem. Abstr.*, **60**, 13195 (1964).

(5) Following a procedure described by R. L. Shriner, R. C. Fuson, and D. Y. Curtin in "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1965, p 235.

Table I. Mass Spectra of 2-(*o*-Aminophenyl)-4*H*-3,1-benzoxazin-4-one (**6**), and 2-Phenyl-4*H*-3,1-benzoxazin-4-one (**7**)

6 *m/e* (int)	**7** *m/e* (int)	Tentative assignment
238 (100)	233 (100)	Parent, M
210 (7)	195 (4)	M − CO
194 (13)	179 (48)	M − CO_2
146 (7)	146 (18)	M − substituent at 2[a]
120 (54)	105 (66)	M − C_6H_5CON
90 (11)	90 (13)	M − substituent at 2[a] + C_2O_2
92 (33)	77 (60)	Substituent at 2[a]

[a] The substituent located at position 2 on the benzoxazine ring.

always slightly contaminated with a higher molecular weight (284) compound and was not obtained pure.

4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine (2b). A mixture of freshly prepared thioacid **3** (5.6 g, 0.04 mol) and trichloroacetic acid (0.1 g) in 50 ml of tetrahydrofuran[3e] was added to a solution of isoamyl nitrite (7.5 g, 0.06 mol) in 10 ml of tetrahydrofuran over a 15-min period at 0°. During this addition the initial yellow color of the solution changed to deep red. In an additional hour of stirring the color became red-orange. The reaction mixture was concentrated to 20 ml *in vacuo*, diluted with 200 ml of ice-cold ether and ligroin, and filtered. The resulting solid was dried overnight *in vacuo* to provide a gold-colored solid (2.9 g, 48%) which was purified by column chromatography (silica gel, ether-hexane as eluent) or sublimation (below 60°, 1 mm). The analytical sample of benzothiadiazine **2b**, as bright yellow crystals, mp 105.7–106.3° dec, was prepared by recrystallizing from absolute ethanol: ν_{max}^{KBr} 1670 (sharp), 1600, 1450 (doublet), 1265, 1210, 920, and 770 cm^{-1}; pmr ($CDCl_3$) τ 2.1–2.9 (m); λ_{max}^{MeOH} 306 nm (ϵ 1650); mass spectrum *m/e* 164 (MI, 24), 136 (100), 108 (97), 104 (42), 76 (57).

Anal. Calcd for C_7H_4NOS: C, 51.21; H, 2.45; N, 17.06; S, 19.53; mol wt, 164. Found: C, 51.45; H, 2.03; N, 17.03; S, 19.50; mol wt (osmometry), 161.

Alternatively, the above reaction can be conducted in absolute ethanol containing hydrochloric acid as the catalyst. Either procedure gives yields of 50–70%.

Thermolysis of 4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine (2b). *Caution! Samples heated above 180° may explode.* The tip of a tube containing thiadiazine **2b** (0.166 g, 0.001 mol) under nitrogen was placed in a bath at 174° for 1 hr. Periodically the tube was submerged to a further depth so that the sublimed solid was reheated. The gummy yellow residue was chromatographed on a column of silica gel. Elution with carbon tetrachloride gave 9 mg of 3*H*-1,2-benzodithiol-3-one (**4**)[6] (5%, based on reacted starting compound). Benzene–ether eluted 22 mg of benzothiadiazine (**2b**) and 31 mg of dithiosalicylide[6] (**5**) (23% based on reacted starting compound). The yellow residue did not elute with any solvent and was discarded.

3*H*-1,2-Benzodithiol-3-one (4), a yellow solid, was prepared by refluxing an aqueous acidic solution of thiosalicylic acid saturated with hydrogen sulfide:[7] mp 73–74° (lit.[7] 77°), $\nu_{max}^{CCl_4}$ 1680, 1595, 1450, 1260, 1065, and 890 cm^{-1}; pmr ($CDCl_3$) τ 2.1–2.8 (m); mass spectrum *m/e* 168 (MI, 100), 140 (26), 104 (32), 96 (31), 76 (21). **Dithiosalicylide (5)** and **trithiosalicylide** as white solids were prepared[8] from thiosalicylic acid and phosphorus pentoxide. **Dithiosalicylide** had mp 179–182° (lit.[8] 176–177°); ν_{max}^{KBr} 1680, 1580, 1465, 1440, 1265, 1205, 925, 870, 765, 745, and 650 cm^{-1}; pmr ($CDCl_3$) τ 2.70 (s), 2.73 (s); mass spectrum *m/e* 272 (MI, 10), 136 (100), 108 (35), 82 (10), 69 (22). **Trithiosalicylide** had mp 257–259° (lit.[8] 257–258°); ν_{max}^{KBr} 1685, 1580, 1565, 1465, 1440, 1280, 1260, 1205, 1060, 945, 900, 865, 760, 740, 700, and 655 cm^{-1}; pmr ($CDCl_3$) τ 2.35 (s); mass spectrum *m/e* 408 (MI, 0.3), 272 (30), 136 (100), 108 (30), 82 (7), 69 (15).

Thermolysis of 4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine (2b) in the Presence of Anthracene. Gas evolution occurred during addition (1 hr) of a solution of thiadiazine **2b** (1.64 g, 0.01 mol) in 25 ml of triglyme to a solution of anthracene (1.78 g, 0.01 mol) in 25 ml of triglyme maintained at 205° under nitrogen. The mixture was heated 2 additional hr and cooled, and the resulting white solid was filtered: 1.53 g, mp 212–215° (lit.[9] for anthracene, 216.2–216.4°). The residual tan oil, obtained by vacuum distilling the triglyme from the above filtrate, was refluxed 0.75 hr with a solution of maleic anhydride (2.93 g, 0.03 mol) in 50 ml of xylene. To this solution was then added 100 ml of 1 *N* sodium hydroxide, and the mixture was refluxed an additional hr. After the mixture was cooled, the organic layer was separated and worked up to yield a tan solid which was chromatographed on a Florisil column. Elution of this column with 10% ether–hexane gave a mixture of triptycene[6] and carbazole[6] (40 mg, *ca.* 5%) followed by dithiol **4** (90 mg, 12%). Elution with 20% ether–hexene yields salicylide **5** (290 mg, 39%). Finally, methanol eluted a dark viscous oil (330 mg, 44%) which was chromatographed on an alumina column. Elution of the alumina column with ether–ethyl acetate provided a yellow oily solid which on sublimation (90°, 0.5 mm) gave 20 mg of anthraquinone.[6] The nonvolatile oily residue from the sublimation gave ν_{max}^{neat} 1720, 1675, 1585, 1470, 1280, 1265, 1250, 1195, 1120, 1055, 1035, 930, 745, and 690 cm^{-1}; pmr ($CDCl_3$) τ 1.8–2.9 (m), 5.4–5.5 (m), 6.1–6.9 (m).

When this experiment was repeated with 5 equiv of anthracene for each equivalent of thiadiazine **2b**, the carbazole–triptycene fraction increased to 22%.

Thermolysis of 4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine (2b) in 1-Butanol. Slow gas evolution occurred during refluxing of a solution of thiadiazine **2b** (0.5 g, 0.003 mol) in 1-butanol (50 ml) for 67 hr. After the solvent was distilled, hexane was added to the residue to provide a trace of a white solid, 0.03 g: ν_{max}^{KBr} 3150–2750, 1630, 1465, 1340, 890, 785, and 745 cm^{-1}. The hexane solution was evaporated to yield a yellow semisolid: pmr ($CDCl_3$) τ 2.0–3.1 (m, 9.2 H), 5.3 (s, 0.6 H), 5.6–5.9 (m, 4 H), 8.0–9.3 (m, 13.2 H). A solution of this semisolid in ether was extracted with 10% sodium hydroxide. Work-up of the aqueous phase gave butyl thiosalicylate as a gummy liquid: ν_{max}^{neat} 2600–2500 (w), 1705, 1255, 1100–1020, 800, and 740 cm^{-1}; pmr ($CDCl_3$) τ 2.0–3.0 (m, 4 H), 5.3 (s, 1 H), 5.7 (m, 2 H), 8.2–9.2 (m, 7 H); mass spectrum *m/e* 212 (1), 211 (3), 210 (MI, 14), 154 (5), 153 (4), 138 (5), 137 (16), 136 (100), 109 (7), 108 (7), 65 (7). Work-up of the ether phase gave bis(*o*-carbobutoxyphenyl) disulfide as a colorless solid: mp 79.5–81° (lit.[10] 82–83°); ν_{max}^{neat} 1705 (doublet), 1580, 1560, 1460, 1435, 1305, 1285, 1265, 1255, 1140, 1105, 1060, 1035, 745, and 685 cm^{-1}; pmr ($CDCl_3$) τ 1.9–2.9 (m, 8 H), 5.6 (t, J = 6, 4 H), 7.9–9.1 (m, 14 H); mass spectrum *m/e* 418 (MI, 57), 208 (24), 168 (21), 153 (100).

Irradiation of 4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine (2b) in 1-Butanol at Low Temperatures. A 1-butanol (400 ml) solution of thiadiazine **2b** (1.1 g, 0.006 mol) which was immersed in Dry Ice–acetone was irradiated with a 500-W medium-pressure mercury lamp through a quartz apparatus for 2 hr. A slow stream of pure dry nitrogen stirred the solution. On work-up (see the similar thermolysis above), 90% of the product was a mixture of butyl thiosalicylate (54%) and bis-(*o*-carbobutoxyphenyl) disulfide (46%). The remaining 10% coated the wall of the vessel during the irradiation and is apparently polymeric.

Irradiation of 4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine (2b) in Acetonitrile and Benzene. Gas evolved (40 ml) and a yellow precipitate formed during photolysis of thiadiazine **2b** (0.29 g, 0.0018 mol) in 350 ml of acetonitrile with a 250-W medium-pressure mercury lamp shielded with a Corex filter.[11] The solvent was removed *in vacuo* and the residue, which included the precipitate, was chromatographed on a silica gel column. The following were obtained: dithiol **4** (17 mg, 6%, from 2% ether–hexane), thioxanthone[6] (23 mg, 8%, from 4% ether–hexane), a mixture of di- and trithiosalicylide (65 mg, 23%, from ether–hexane), and a gold-colored powder (180 mg, from 10% methanol–ether; mp 77–98°; ν_{max}^{KBr} 1700, 1200, 905, and 760 cm^{-1}; pmr ($CDCl_3$) τ 2.0–3.0 (m); mass spectrum *m/e* 448 (MI, 0.6), 272 (24), 136 (100), 108 (31), 105 (18), 77 (11), 69 (18). Repetition of this experiment in benzene[12] afforded the same products with two exceptions: the gold-colored

(6) Physical properties agree with those of an authentic sample prepared in the laboratory or purchased from commercial suppliers. Anthraquinone and carbazole are impurities in anthracene.

(7) Following S. Smiles and E. W. McClelland, *J. Chem. Soc.*, 86 (1922).

(8) Following W. Baker, A. S. El-Nawawy, and W. D. Ollis, *ibid.*, 3163 (1952).

(9) "Handbook of Chemistry and Physics," 48th ed, R. Weast, Ed., Chemical Rubber Co., Cleveland, Ohio, 1967, p C-121.

(10) F. Gaildi, R. Ponci, and A. Baruffine, *Farmaco, Ed. Sci.*, **14**, 216 (1959); *Chem. Abstr.*, **54**, 13836 (1960).

(11) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 687.

(12) For 9 hr with a 550-W Hanovia lamp, 38 hr with a circular bank of 16 GE G25T8 fluorescent tubes.

powder was absent and a nonvolatile oil, with ir bands at 1700, 1200, and 900 cm^{-1}, appeared. The oil slowly decomposed.

Low-Temperature Irradiation of 4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine (2b). A thin film of thiadiazine **2b** on a sodium chloride wafer in a special liquid nitrogen cooled apparatus[13] was irradiated with Hanovia 500-W medium-pressure mercury source. In spectra taken at these temperatures, bands at 1670, 1600, 920, 780, 770 cm^{-1} decrease, while bands at 2040, 1805, and 1580 cm^{-1} increase. After 1 hr no further change was noted (see Figure 1). When the cell was warmed to room temperature over a 14.5-hr period, the ir spectrum had changed to resemble that of a mixture of di- and trithiosalicylide. Thin layer chromatographic analysis showed three spots: the starting compound (small amount), dithiosalicylide (small amount), and an immobile residue (large amount).

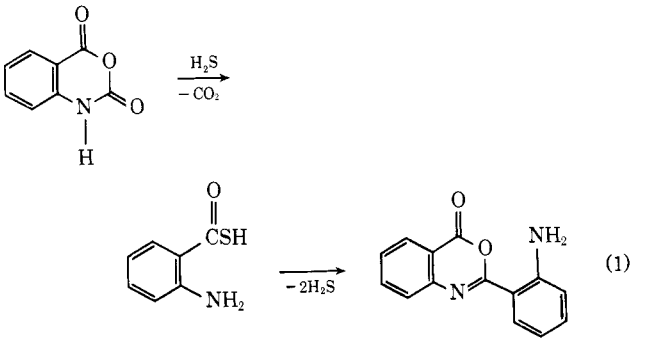
1,2,3-Benzothiadiazole, a white solid, mp 37–37.5° (lit.[14] 35°), was prepared by diazotization of 2-aminobenzenethiol.[14] The ir spectrum of 1,2,3-benzothiadiazole did not change when a thin film was irradiated at low temperatures in the same manner as that described above for thiadiazine **2b**. During photolysis in the same apparatus at room temperature, the ir spectrum gradually changed to that of thianthrene. This was confirmed by mixing the solid remaining after irradiation with concentrated sulfuric acid to yield a purple solution.[15]

Irradiation of Dithiosalicylide (0.5 g, 0.002 mol) in 350 ml of acetonitrile in a water-cooled immersion apparatus with a Hanovia 200-W medium-pressure mercury lamp through a Corex filter[11] for 4 hr under nitrogen caused 20 mg of a yellow precipitate to form: ν_{max}^{KBr} 1695, 1580, 1560, 1460, 1435, 1275, 1260, 1195, 1125, 1035 890, 760, 750, 705, and 640 cm^{-1}. The filtrate from the reaction mixture was evaporated to yield a brown powder which was chromatographed on a silica gel column. Elution with hexane gave 3 mg of a deep yellow oil: $\nu_{max}^{CCl_4}$ 1695, 1590 (doublet), 1450 (doublet), 1275, 1260, 1240, 1130, 1070, 1025, 890, 725 cm^{-1}. Thin layer chromatographic analysis of this oil revealed four spots, none of which had a R_f value which corresponded to that of dithiol **4**. Further elution of the silica gel column with benzene, methylene chloride, and ether afforded only starting compound, salicylide **5**.

Results and Discussion

According to an abbreviated report,[4] isatoic anhydride and hydrogen sulfide afford thioanthranilic acid (**3**) as a yellow solid, mp 130–155°. Such a precipitate was obtained in this work by first bubbling hydrogen sulfide through a dimethylformamide solution of isatoic anhydride and triethylamine, then diluting with water, and finally storing the mixture for several days. Analysis of spectral data for this solid, however, cause its structure to be assigned as 2-(*o*-aminophenyl)-4*H*-3,1-benzoxazin-4-one (**6**) rather than thioacid **3** (eq 1). The proton magnetic resonance spectrum has an eight-proton absorption in the aromatic proton area and a broad two proton peak assigned to N–H absorption. The infrared spectrum has absorption at 3450 and 3320 cm^{-1} and thus supports NH_2 as a structural feature rather than NH_3^+, as expected for thioacid **3**. Sharp carbonyl absorption at 1760 cm^{-1} is also characteristic of benzoxazin-4-ones[16] rather than thiocarboxylate anions, as in the zwitterion **3**. The mass spectrum of this solid has a parent peak at *m/e* 238 and a fragmentation pattern characteristic of benzoxazin-4-ones[17] (see Table I).

Unfortunately, the limited data of the earlier patent[4] make it impossible to accurately assign a structure to the reported compound. However, in this laboratory a solid with the same color and melting point range has been assigned as benzoxazine **6** (see below for data on thioanthranilic acid). An instructive explanation for the formation of benzoxazine **6** is that thioacid **3** forms, but undergoes self-acylation and elimination of 2 equiv of hydrogen sulfide to yield the yellow solid (eq 1).



(1)

If the reaction medium can be altered so that the product is rapidly obtained, thioacid **3** should be isolable. Accordingly, ethanol was substituted for dimethylformamide as solvent and the reaction mixture was rapidly worked up. Solubility of the sodium salt in water was used as an aid in purification. The product, an oil, did not crystallize under any conditions and slowly decomposed to benzoxazine **6** at room temperature. Therefore, characterization and all transformations were rapidly carried out with fresh samples. The infrared spectrum of the oil has absorption at 3500 and 3370 cm^{-1} (assigned to NH_2), 2560 cm^{-1} (assigned to SH), and 1645 cm^{-1} (assigned to C=O). A four-proton multiplet at τ 2.4–3.6 in the pmr spectrum arises from aromatic hydrogens. A broad three-proton singlet at τ 4.7 is apparently a combined absorption of NH_2 and SH. The mass spectrum is easily rationalized as fragmentation of thioanthranilic acid (see Experimental Section).

Since elemental analysis was not possible because of the instability of thioacid **3**, a stable, solid derivative was desired to complete the characterization. Benzyl chloride and thioacid **3** gave an oil which could not be easily purified or crystallized. *p*-Bromophenacyl bromide and thioacid **3** give a sharply melting solid which, when analyzed, had the correct percentages for the elements of *p*-bromophenacyl thioanthranilate. Correct infrared and proton magnetic resonance spectra (see Experimental Section) completed the assignment of structure not only to the derivative, but thioacid **3** as well. Thus, thioanthranilic acid can be prepared and characterized but must be rapidly used in any further manipulations.

Diazotization of Amino Thioacids. If diazotization of thioacid **3** should proceed like that of anthranilic acid, then benzenediazonium-2-thiocarboxylate (**1b**) would be expected. The stability of diazoniumthiocarboxylate **1b** relative to benzenediazonium-2-carboxylate (**1a**) is of direct interest in this work. Instead, diazotization of thioacid **3** provides a stable, yellow solid which has properties not expected in a diazoniumthiocarboxylate. Detonation and decomposition do not readily occur at room temperature or below 180°. The compound can be sublimed or purified by column

(13) E. L. Wagner and D. F. Horning, *J. Chem. Phys.*, **18**, 296 (1950). Infrared spectra can be obtained at the temperature of liquid nitrogen without disturbing the sample. We thank Professor O. L. Chapman for bringing this reference to our attention.

(14) P. Jacobsen and H. Janssen, *Justus Liebigs Ann. Chem.*, **277**, 221 (1938).

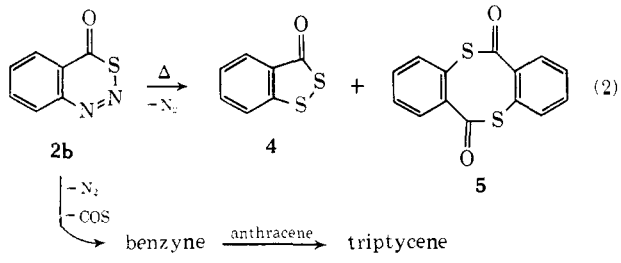
(15) K. P. Zeller, H. Meier, and E. W. Muller, *Tetrahedron Lett.*, 537 (1971).

(16) M. Kurihara and N. Yoda, *Bull. Chem. Soc. Jap.*, **39**, 1942 (1966).

(17) G. J. K. Gibson, A. S. Lindsey, and H. M. Paisley, *J. Chem. Soc. C*, 1792 (1967).

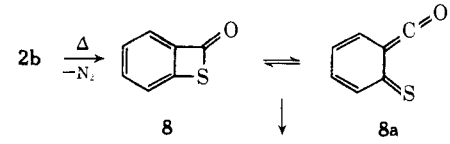
chromatography without apparent decomposition. In contrast to diazoniumcarboxylate **1a**, this solid is soluble in organic solvents and virtually insoluble in water. Elemental analysis and molecular weight determination ascertain that $C_6H_4N_2OS$ is the empirical and molecular formula. Rather than broad absorption at 1530 cm^{-1}, which is characteristic of thiocarboxylate anion, the infrared spectrum has a sharp, strong band at 1670 cm^{-1}, assigned to thioester. Absorptions normally assigned to $-N_2^+$ in the 2280-cm^{-1} region and NH_2 in the 3400-cm^{-1} area are absent. As expected, only aromatic proton absorption is observed in the pmr spectrum. Thus, the structure of the stable, yellow solid is assigned as 4-oxo-3,4-dihydro-3,1,2-benzothiadiazine (**2b**). The mass spectral fragmentation pattern is easily rationalized as being derived from thiadiazine **2b** (see Experimental Section). Thus a stable, nitrogen-containing compound results from diazotization of thioanthranilic acid.

Chemistry of 4-Oxo-3,4-dihydro-3,1,2-benzothiadiazine (2b). The initial question to be answered concerning the chemistry of thiadiazine **2b** involved the leaving ability of nitrogen and carbonoxy sulfide. Since samples did not detonate or explode below 180°, experiments could be carried out safely. If both groups leave simultaneously or nearly so, benzyne will form and ultimately yield a dimer, biphenylene, or trimer, triphenylene, or be captured by the environment.[3] Other reaction paths suggested by the mass spectral fragmentation pattern for thiadiazine **2b** give benzocyclopropenone,[18] 2-thiobenzpropiolactone,[19] and benzothiirene as unstable intermediates which might dimerize to anthraquinone, dithiosalicylide, and thianthrene,[15] respectively. When samples of thiadiazine **2b** were heated until gas evolution occurred, two sulfur-containing products, salicylide (**5**), and dithiol (**4**), were identified by comparing physical and spectral properties with those of authentic samples (eq 3). Apparently nitrogen is easily lost; but carbonoxy sulfide is not. Perhaps a higher reaction temperature would aid benzyne formation. Accordingly, thiadiazine **2b** was added to solutions of anthracene maintained at 205°. *Since gas evolution was vigorous,* **2b** *was added in small portions.* In addition to dithiol **4** and salicylide **5**, triptycene was isolated in low yield. When the reaction was repeated with a fivefold excess of anthracene, the yield of triptycene was increased to only 20%. Thus, benzyne or some intermediate which transfers, the elements of benzyne, does form, but in low yield (eq 2).



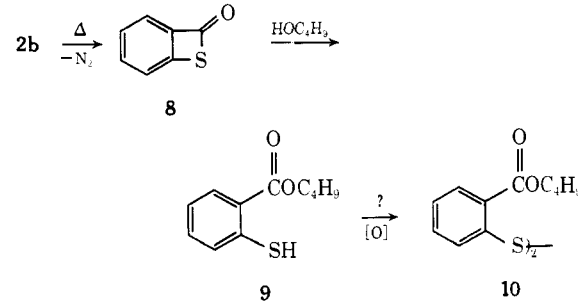
(2)

An instructive explanation for the above result involves 2-thiobenzpropiolactone (**8**)[19] as an intermediate. Initially, thiadiazine **2b** may lose nitrogen to form lactone **8**, which yields dithiol **4** and salicylide **5** by direct reaction or from its ring-opened tautomer, ketene **8a** (eq 3). At higher temperatures, a fraction of thiadiazine **2b** or lactone **8** fragments to benzyne which can be trapped by reaction with anthracene to yield triptycene.



(3)

In a recent communication Chapman and McIntosh[19] reported not only several infrared bands of lactone **8**, but also reaction of lactone **8** above −40° with methanol to afford methyl *o*-mercaptobenzoate. If lactone **8** is an intermediate in the thermal decomposition of thiadiazine **2b**, the same reaction type should occur. Thus, thiadiazine **2b** was refluxed in 1-butanol (*ca.* 118°) until gas evolution ceased. The two products, dithiol **4** and salicylide **5**, which were previously isolated from thermolysis of thiadiazine **2b** were not formed in detectable amounts! Instead, butyl *o*-mercaptobenzoate (**9**) as a gummy liquid and bis(*o*-carbobutoxyphenyl) disulfide (**10**) as a colorless liquid resulted, as if lactone **8** had formed first and then reacted with 1-butanol (eq 4).



(4)

The gummy liquid was characterized as the mercapto ester **9** by its spectral data (see Experimental Section). The expected absorptions in the infrared, pmr, and mass spectra were noted. Assignment of the disulfide structure to the colorless solid was based on melting point and infrared, pmr, and mass spectral data (see Experimental Section). Since efforts were not made to exclude oxygen from the work-up procedure, disulfide **10** probably forms from mercapto ester **9**. Similar oxidations are documented.[20]

In order to duplicate the conditions of Chapman and McIntosh[19] more closely, thiadiazine **2b** was irradiated in 1-butanol at −78° and allowed to slowly warm to room temperature. The same two butyl esters resulted. Further, irradiation of a thin film of thiadiazine **2b** in a special low-temperature cell[13] (this cell allows scanning of the infrared spectrum without raising the temperature) caused lactone **8** to form as is evidenced by the appearance of an intense peak at 1803 cm^{-1}, identical with that reported by Chapman and McIntosh[19] (see Figure 1).

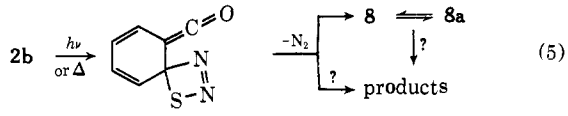
(18) M. S. Ao, E. M. Burgess, A. Schauer, and E. A. Taylor, *Chem. Commun.*, 220 (1969); J. Adamson, D. L. Forster, L. Gilchrist, and C. W. Rees, *ibid.*, 221 (1969).

(19) O. L. Chapman and C. L. McIntosh, *J. Amer. Chem. Soc.*, **92**, 7001 (1970).

(20) Reference 5, p 888.

If both the thermolysis and photolysis of thiadiazine **2b** are proceeding through the same intermediate, namely thiolactone **8**, then irradiation in inert solvents should mainly provide the same products as thermolysis in inert solvents. Such is the case. Irradiation at room temperature in acetonitrile or benzene provides mainly dithiol **4** and dithiosalicylide, **5**, In addition, small yields of trithiosalicylide and thioxanthone are found and are attributed to difference in temperature and concentration. Formation of trithiosalicylide can be rationalized as trimerization of thiolactone **8** or reaction of **8** with salicylide **5**. The latter compound, thioxanthone, contains the elements of benzyne and thiolactone **8** and suggests that benzyne may be an intermediate in photolysis.

Alternative explanations of these data are possible and, among others, involve possible formation of ketene **11** which fragments to **8** or **8a** or reacts directly to give the observed products (eq 5). Current re-

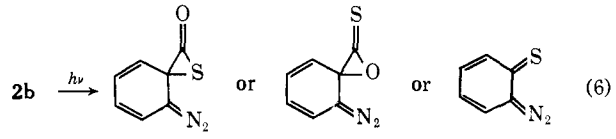


(5)

11

search is designed to ascertain what role, if any, such intermediates play in this chemistry.

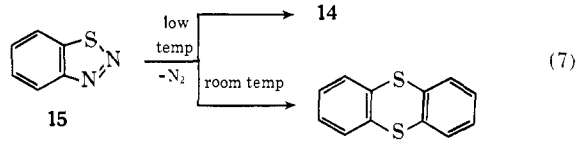
In addition to the infrared absorption at 1803 cm^{-1} which develops when thiadiazine **2b** is irradiated at low temperatures, another band not reported by Chapman and McIntosh[19] appears at 2050 cm^{-1}. Such absorption is most easily assigned to the diazo group,[21] $=N_2$, and causes speculative formulas **12**, **13**, and **14** to be drawn as possible structures (eq 6). An alter-



(6)

12 13 14

native source of diazothione **14** might be benzothiadiazole (**15**). Low-temperature irradiation of solid films might isomerize diazole **15** to diazothione **14**. However, when this reaction was attempted and monitored by scanning the infrared spectrum, no change was noted. Irradiation of a solid film of diazole **15** at room temperature gave thianthrene[16] (eq 7). Other



(7)

15

experiments in progress seek to clarify the structure which causes the novel absorption at 2050 cm^{-1}.

Formation of dithiol **4** may appear to be an anomaly since two sulfur atoms are present. However, several sources of singlet D sulfur atoms[22] are present. Reaction of these sulfur atoms with thiolactone **8** should provide dithiol **4**. Alternately, salicylide **6** may fragment by free radical processes to yield dithiol **4**, carbon monoxide, and benzyne (eq 8). However, when sal-

(21) D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry," McGraw-Hill, New York, N. Y., 1966, p 59.
(22) E. Leppin and K. Gollnick, *J. Amer. Chem. Soc.*, **93**, 2848 (1971).

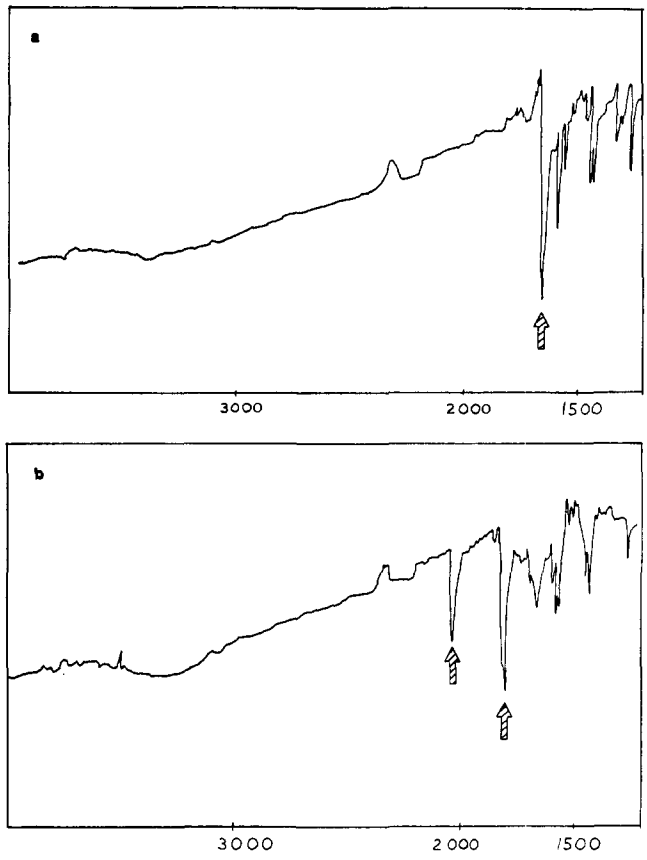
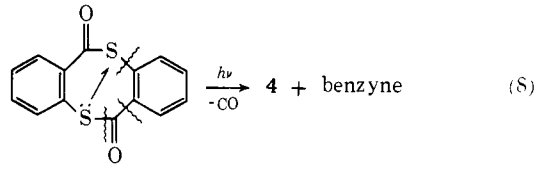


Figure 1. Infrared spectrum of thiadiazine **2b**: (a) at ~−180°; (b) after 1 hr of irradiation at ~−180° (Pyrex filter).

icylide **5** was irradiated under the previous reaction conditions, dithiol **4** was not formed. Mainly starting material was recovered.



(8)

5

In summary, thiadiazine **2b** affords several products when heated or irradiated, all of which may be rationalized as being derived from 2-thiobenzpropiolactone **8**. Two lines of proof have been presented that **8** is indeed formed by thermolysis and photolysis of thiadiazine **2b**: (1) an infrared absorption band which matches that reported[19] for **8** develops in irradiated samples of **2b** and (2) products which form from irradiation or thermolysis of **2b** are those expected based on chemistry previously reported for **8**. Thus, thiadiazine **2b** is proposed as a useful source of thiolactone **8**.

Acknowledgments. Appreciation is extended to the National Science Foundation for its Research Instruments Grants (GP-6978 and GP-8286). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Comments by the referees, especially on formation of **4**, are acknowledged. Stimulating discussions with W. L. Meyer are appreciated.