Reactions of 1,2-Dihydro-4*H*-3,1-benzothiazine-2,4-dithiones (Trithioisatoic Anhydrides) with *N*-Substituted Benzylamines and Trialkyl Phosphites

Masahiko Takahashi,* Tomoko Gunji, and Akiko Ichikawa

Department of Materials Science, Faculty of Engineering, Ibaraki University, Hitachi, Ibaraki 316-8511, Japan

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Reactions of 1,2-dihydro-4*H*-3,1-benzothiazine-2,4-dithiones (trithioisatoic anhydrides) **3** with *N*-substituted benzylamines **9** gave 1,2-dihydroquinazoline-4-thiones **10**, *o*-thioureidodithiobenzoic acid **11**, *o*-aminothiobenzamides **12**, 2-amino-3,1-benzothiazine-4-thiones **13**, or quinazoline-2,4-dithiones **14**, depending on the kinds of amine and the reaction solvent. On the other hand, reaction of **3** with trialkyl phosphites afforded dialkyl (1,2-dihydro-2-thioxo-4*H*-3,1-benzothiazin-4-yl)phosphonates **18**.

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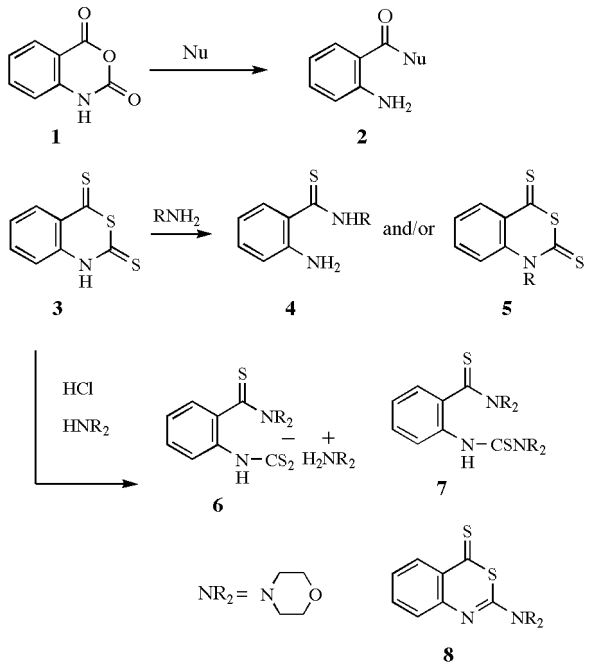
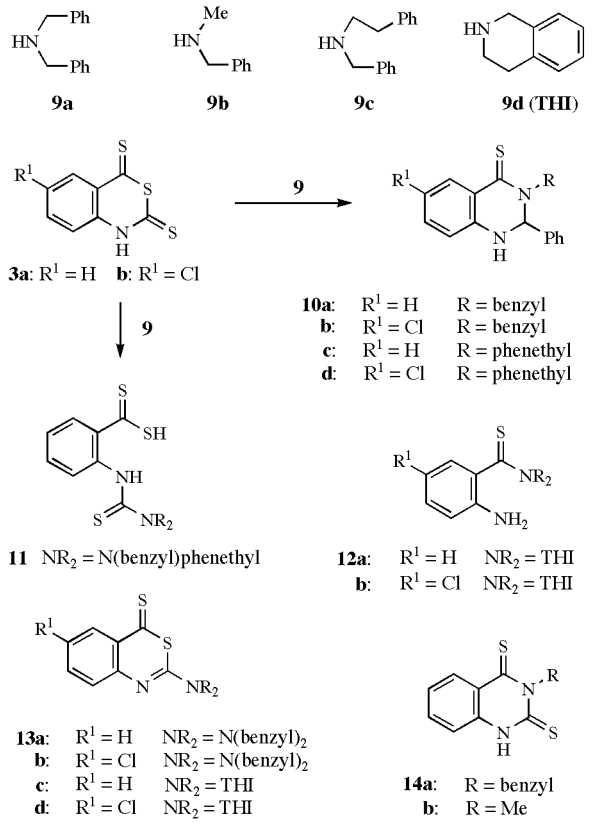
2*H*-3,1-Benzoxazine-2,4-diones (isatoic anhydrides) **1** are readily available and reactive compounds that are useful for the preparation of many aromatic and heterocyclic compounds and have been well documented [1]. Isatoic anhydrides **1** usually undergo nucleophilic attack at the C-4 carbonyl position to give *o*-aminobenzoyl derivatives **2** on loss of carbon dioxide, which are useful for further cyclization to heterocycles (Scheme 1). On the other hand, the reactivities of their sulfur analog, 1,2-dihydro-4*H*-3,1-benzothiazine-2,4-dithiones (trithioisatoic anhydrides) **3** are less known in spite of their interesting structure of a cyclic -NH-CS-S-CS- moiety. Reactions of **3** with primary amines give ring-opened products **4** on loss of carbon disulfide and/or quinazoline-2,4-dithiones **5** with elimination of hydrogen sulfide [2,3]. These reactions have been applied to the synthesis of condensed heterocycles by using bifunctional nucleophiles such as diamines [4], aminoalcohols [5], acid hydrazides [6], and aminoguanizines [7]. However, little is known about the reaction of **3** with secondary amines; the reaction with morpholine has been reported to give a ring-opened morpholinium salt **6** (90%), *o*-(thioureido)thiobenzamides **7** (8%), and 2-amino-3,1-benzothiazine-4-thiones **8** (trace amount) [8]. In the course of our study on the synthesis of heterocycles, we attempted to prepare some *N*,*N*-disubstituted *o*-aminothiobenzamides **4** (Nu = NR_2) by reacting **3** with secondary amines. However, we found that the reaction of **3** with *N*-substituted benzylamines proceeded unexpectedly to give a variety of ring-opened and cyclic compounds depending upon the kinds of substituted benzylamine and reaction solvent. Furthermore, trialkyl phosphites as phosphorus nucleophiles were found to give phosphonate-containing 3,1-benzothiazines. We report here our results of the reaction of **3** with secondary amines **9a-d** bearing benzyl groups and with trialkyl phosphites.

Scheme 1



We prepared **3** from **1** and phosphorus pentasulfide in refluxing 1,2,4-trimethylbenzene [2,9]. The reaction of **3** with dibenzylamine **9a** in dioxane at reflux gave an unexpected product (42%), whose structure was assigned to be 3-benzyl-2-phenyl-1,2,3,4-tetrahydroquinazoline-4-thione **10a** on the basis of spectral data (Scheme 2). However, 2-dibenzylamino-4*H*-3,1-benzothiazine-4-thione **13a** (33%) and 3-benzyl-1,2,3,4-tetrahydroquinazoline-2,4-dithione **14a** (38%) were obtained when treated in methanol and in ethyl acetate instead of dioxane, respectively. The reaction of **3** with other secondary amines **9b-d** bearing a benzyl moiety was also examined. In aprotic solvents such as dioxane, 1,2,4-trimethylbenzene, or ethyl acetate, **10**, *o*-(amino)thiobenzamides **12**, or **14** were produced. On the other hand, the formation of *o*-thioureidodithiobenzoic acid **11** or 4-amino-1,3-benzothiazin-4-thiones **13** was observed in methanol. Treatment of **11** with a catalytic amount of *p*-toluenesulfonic acid monohydrate in refluxing methanol gave the starting **3a** in 65% yield. These results are summarized in Table 1.

Scheme 2



in the reactions of **3a** with **9a** and **b**, the benzyl group was selectively eliminated to give **14a** and **b**, respectively. This may be explained as follows. The cyclization of **15** by nucleophlic attack of thioamide nitrogen at the dithiocarbamic acid group would give the second zwitter ionic intermediate **16**. Rearrangement of the benzyl groups from the nitrogen atom to the sulfur atom may result in the formation of the third intermediate **17**, which would become **14** on extrusion of *o*-methylbenzenethiol. On the other hand, nucleophilic attack of **9** at the C-2 thiocarbonyl group (path b) would give **11**, which may cyclize to yield **13**. It is also possible that **13** was directly produced by the addition of **9** to the C-2 thiocarbonyl followed by elimination of hydrogen sulfide without ring-opening of **3**.

Next, we turned our attention to phosphorus nucleophiles. Recently, Huang *et al*. reported a desulfurization reaction of trithio-1,8-naphthalic anhydride, which has a similar trithioanhydride moiety in the molecule, with triethyl phosphite, giving three types of dimer [10]. There has been no reaction of **3** with phosphorus nucleophiles. Thus, we examined the reaction with phosphorus compounds as nucleophiles in the next step. Triphenylphosphine afforded no isolable product. However, reflux of a mixture of **3** and trialkyl phosphite in dioxane gave the pale yellow products dialkyl (1,2-dihydro-4*H*-1,3-benzothiazin-4-yl)phosphonates **18** in 20-39% yields (Scheme 4). In the case of **3a**, two products were formed; one product was finally assigned as **18a** (20%) and the other as 2-methylthio-4*H*-3,1-benzothiazine-4-thione **19** (21%). The structure of

Table 1

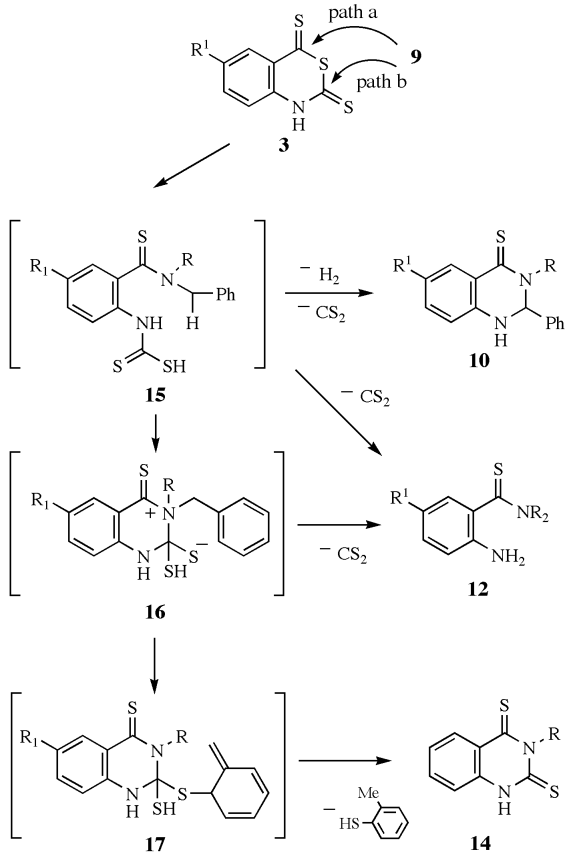
Reaction Products **10** – **14** from **3** and **9**

	Solvent	**9a**	**9b**	**9c**	**9d**
3a	Dioxane	**10a** (42%)	-	-	**12a** (30%)
	Methanol	**13a** (33%)	-	**11** (89%)	**13c** (58%)
	1,3,5-Trimethylbenzene		**14b** (80%)	**10c** (13%)	-
	Ethyl acetate	**14a** (38%)	-	-	-
3b	Dioxane	**10b** (15%)	-	**10d** (14%)	**12b** (20%)
	Methanol	**13b** (16%)	-	-	**13d** (71%)

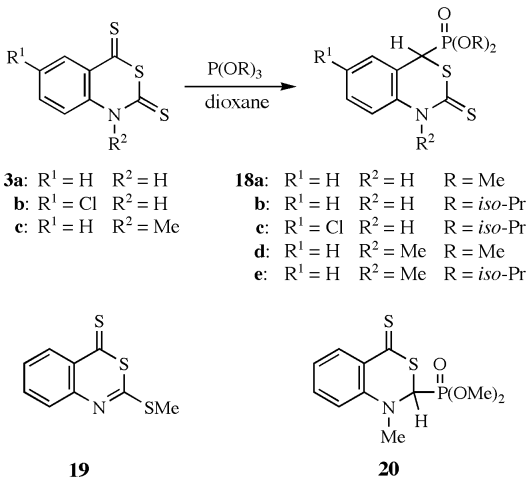
It is possible that these products are produced by the nucleophilic attack of **9** at the C-4 carbon (path a) or at the C-2 carbon (path b) of **3** (Scheme 3). In path a, the reaction of **3** with **9** would result in ring-opening to give the first intermediate **15**. The formation of **10** can be explained by oxidative cyclization between the amino group and the benzyl group with loss of carbon disulfide. Auto-oxidation by a radical mechanism was presumed due to the ease of occurrence of radical species at the benzyl position, and this was confirmed by a decrease in the yield in the reaction of **3a** with **9a** in the presence of the radical scavenger galvinoxyl (9% yield) or diphenylpicrylhydrazyl (28%). Elimination of carbon disulfide from **15** may yield *o*-aminothiobenzamides **12**. It is interesting that

18d, as an example, was assigned as follows: the ms spectrum and elemental analysis confirmed the molecular formula $C_{11}H_{14}NO_3PS_2$, and the ^{1}H nmr spectrum showed the presence of a CH-PO(OMe)$_2$ moiety. However, clear differentiation of the structures of **18d** and the isomeric **20** on the basis of these data was difficult. The structure was finally detemined by the ^{13}C nmr spectrum of **18d**, which showed the presence of C=S carbon at 191.54 ppm, corresponding to the C_4-carbon of **3c** (189.85 ppm in deuteriochloroform). The coupling constants of $^1J_{PC}$=153.4 Hz, $^2J_{PC}$=6.3 Hz, $^3J_{PC}$=3.2 and $^3J_{PC}$=3.1 Hz are in accordance with the structure of dimethyl (1,2-dihydro-1-methyl-2-thioxo-4*H*-3,1-benzothiazin-4-yl)phophonate **18d**, excluding the alternative structure **20**. The presence of

Scheme 3



Scheme 4



hydrogen at the C-4 position of **18** is unexpected. The formation of olefins by the reaction of 1,2-thiocarbonate or 1,2-trithiocarbonate with trialkyl phosphite was reported by Corey *et al.* [11]. On the other hand, Rameriz *et al.* reported the formation of biphthalyl in the reaction of phthalic ahydride with trialkyl phosphite, while dialkyl phthalide-3-phosphonate was formed in the reaction of a mixture of dialkyl phosphite and trialkyl phosphite [12]. This was explained by partial hydrolysis of trialkyl phosphite to dialkyl phosphite followed by atttack of dialkyl phoshite on the intermediate carbene. When the reaction of **3a** with trimethyl phosphite was carried out in the presence of one drop of acetic acid as a proton donor, the yield of **18a** was increased from 20% to 29%, suggesting that the C-4 proton is derived from some proton donor in the solution. However, in contrast to Rameriz's experiment, the reaction of **3** in the mixture of trialkyl phosphite and dialkyl phosphite did not proceed smoothly, and most of the starting materials were recovered. Although the reaction mechanism for the formation of **18** remains obscure at present, new phosphorus derivatives of trithioisatoic anhydrides were obtained in this reaction.

In conclusion, we have found that the reaction of trithioisatoic anhydrides with secondary amines bearing benzyl groups gave various kinds of products depending on the solvents and substituents and that the reaction with trialkyl phosphite afforded derivatives with phosphonate groups at the C-4 position. These results show that trithioisatoic anhydrides have potential as starting materials for the synthesis of other heterocycles or new derivatives of 3,1-benzothiazines.

EXPERIMENTAL

Melting points were determined with a MRK MEL-TEMP II and are uncorrected. Ir spectra were recorded using JASCO A-102 and FT/IR-420 spectrophotometers. Ms and ^{1}H-nmr spectra were recorded using a JEOL JMS DX-300 spectrometer and a JEOL GSX-400 spectrometer, respectively. Microanalyses were performed using a YANAKO CHN-Corder MT-5.

3-Benzyl-2-phenyl-1,2,3,4-tetrahydroquinazoline-4-thione (**10a**).

A mixture of **3a** (211 mg, 1.0 mmole) and **9a** (384 mg, 2.0 mmoles) in dioxane (5 ml) was refluxed for 24 hours. After evaporation of the solvent, methanol was added to the yellow oily residue to afford a crystalline product, which was collected by filtration to give yellow needles **10a** (137 mg, 42%), mp 178-179 °C (methanol); ir (potassium bromide): 3280, 1615, 1585, 1510, 1485, 1220 cm^{-1}; ^{1}H nmr (dimethylsulfoxide-d$_6$): δ 4.44 (d, J = 15.2 Hz, 1H, PhC*H*$_2$), 6.03 (d, J =3 .2 Hz, 1H, C$_2$-H), 6.36 (d, J = 15.2 Hz, 1H, PhC*H*$_2$), 6.66-8.19 (m, 14H), 7.85 (d, J = 3.2 Hz, 1H, NH); ms: m/z 330 (M$^+$, 56), 237 (100), 225 (59), 193 (54).

Anal. Calcd. for $C_{21}H_{18}N_2S$: C, 76.35; H, 5.49; N, 8.48. Found: C, 76.34; H, 5.51; N, 8.64.

6-Chloro-3-benzyl-2-phenyl-tetrahydroquinazoline-4-thione (**10b**).

A mixture of **3b** (737 mg, 3.0 mmoles) and **9a** (1.48 g mg, 7.5 mmoles) in dioxane (15 ml) was refluxed for 24 hours. After the usual workup, the product **10b** (164 mg, 15%) was obtained as yellow needles, mp 153-154 °C (hexane); ir (potassium bromide): 3260, 1615, 1505, 1545, 1325, 1205 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 4.13 (d, J = 15.2 Hz, 1H), 4.69 (br s, 1H), 6.45 (d, J = 8.4 Hz, 1H), 6.68 (d, J = 15.2 Hz, 1H), 7.2-8.5 (m,

13H); ms: m/z 366 (M^++2, 11), 364 (M^+, 42), 331 (100), 259 (40), 227 (37).

Anal. Calcd. for $C_{21}H_{17}ClN_2S$: C, 69.12; H, 4.70; N, 7.68. Found: C, 69.00; H, 4.86; N, 7.70.

3-Phenethyl-2-phenyl-1,2,3,4-tetrahydroquinazoline-4-thione (**10c**).

A mixture of **3a** (211 mg, 1.0 mmole) and **9c** (350 mg, 1.7 mmoles) in 1,2,4-trimethylbenzene (5 ml) was refluxed for 24 hours. After evaporation of the solvent, the oily residue was separated by column-chromatography (silica gel-benzene) to give **10c** (45 mg, 13%), yellow needles, mp 115-118 °C; ir (potassium bromide): 3388, 1610, 1496, 1317, 1240, 1186, 1153 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.98-3.05 (m, 1H), 3.16-3.24 (m, 1H), 3.45-3.52 (m, 1H), 4.92-4.99 (m, 1H), 6.50 (d, J = 8.0 Hz, 1H), 6.83-7.32 (m, 14H), 8.49 (d, J = 8.0 Hz, 1H); ms: m/z 344 (M^+, 41), 311 (18), 238 (41), 221 (94), 207 (100), 193 (38), 165 (38).

Anal. Calcd. for $C_{22}H_{20}N_2S$: C, 76.70; H, 5.85; N, 8.13. Found: C, 76.57; H, 5.88; N, 8.13.

6-Chloro-3-phenethyl-2-phenyl-1,2,3,4-tetrahydroquinazoline-4-thione (**10d**).

The compound **10d** (14%) was obtained from **3b** and **9c** in dioxane in the same manner as described above. Yellow needles, mp 159-161°C (benzene-hexane); ir (potassium bromide): 3384, 1606, 1494, 1223, 1186, 1086 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.00-3.03 (m, 1H), 3.16-3.24 (m, 1H), 3.44-3.51 (m, 1H), 4.90-4.97 (m, 1H), 6.47 (d, J = 8.4 Hz, 1H), 7.14-8.49 (m, 13H); ms: m/z 380 (M^++2, 15), 378 (M^+, 36), 345 (17), 255 (100), 241 (87).

Anal. Calcd. for $C_{22}H_{19}ClN_2S$: C, 69.73: H, 5.05; N, 7.39. Found: C, 70.01; H, 5.32; N, 7.58.

o-(*N'*-Benzyl-*N'*-phenethyl)thioureidodithiobenzoic Acid (**11**).

A mixture of **3a** (211 mg, 1.0 mmole) and **9c** (254 mg, 1.2 mmoles) in methanol (10 ml) was refluxed for 2 hours. The precipitates were collected by filtration to give **11** (375 mg, 89%), red prisms, mp 168-169 °C (methanol); ir (potassium bromide): 2756, 1598, 1550, 1473, 1443, 1423, 1209, 1147 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.92 (t, J = 8.0 Hz, 2H), 3.15 (t, J = 8.0 Hz, 2H), 4.17 (s, 2H), 7.08-8.43 (m, 14H); ms: m/z 211 (M^+-211, 5), 178 (6), 120 (72), 91 (100).

Anal. Calcd. for $C_{23}H_{22}N_2S_3$: C, 65.36; H, 5.25; N, 6.63. Found: C, 65.13; H, 5.32; N, 6.62.

Treatment of **11** with a catalytic amount of *p*-toluenesulfonic acid monohydrate in refluxing methanol gave the starting **3a** in 65% yield.

N-(2-Aminothiobenzoyl)-1,2,3,4-tetrahydroisoquinoline (**12a**).

A mixture of **3a** (633 mg, 3.0 mmoles) and **9d** (599 mg, 4.5 mmoles) in dioxane (15 ml) was refluxed for 1 hour. After evaporation of the solvent, the residue was chromatographed on silica gel with chloroform to give an oily product **12a** (240 mg, 30%), which was solidified on addition of a small amount of methanol, white powder, mp 99-100 °C (methanol); ir (potassium bromide): 3450, 3350, 1620, 1500, 1440, 1290, 1240, 1220 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.87-3.12 (m, 2H), 3.75 (br s, 2H), 4.47-4.70 (m, 2H), 5.32 (d, J = 18.2 Hz, 1H), 5.49 (d, J = 18.2 Hz, 1H), 6.70-7.27 (m, 8H); ms: m/z 268 (M^+, 45), 235 (27), 136 (49), 132 (100).

Anal. Calcd. for $C_{16}H_{16}N_2S$: C, 71.60;H, 6.01; N, 10.44. Found: C, 71.59; H, 6.11; N, 10.51.

N-(2-Amino-5-chlorothiobenzoyl)-1,2,3,4-tetrahydroisoquinoline (**12b**).

The compound **12b** (20%) was obtained from **3b** and **9d** in dioxane in a similar manner as described above, white powder, mp 124-125 °C (methanol); ir (potassium bromide): 3423, 3316, 1620, 1486, 1444, 1290, 1204, 1186 cm^{-1}: ^1H nmr (deuteriochloroform): δ 2.89-3.11 (m, 2H), 3.99 (br s, 2H), 4.41-4.69 (m, 2H), 5.33 (d, J = 17.8 Hz, 1H), 5.42 (d, J = 17.8 Hz, 1H), 6.64-7.27 (m, 7H); ms: m/z 304 (M^++2, 12), 302 (M^+, 33), 269 (29), 170 (28), 132 (100).

Anal. Calcd. for $C_{16}H_{15}ClN_2S$: C, 63.63; H, 4.99; N, 9.25. Found: C, 63.43; H, 5.12; N, 9.33.

2-Dibenzylamino-4*H*-3,1-benzothiazine-4-thione (**13a**).

A mixture of **3a** (422 mg, 2.0 mmoles) and **9a** (807 mg, 4.1 mmoles) in methanol (20 ml) was refluxed for 24 hours. The precipitates formed were collected by filtration to give **13a** (246 mg, 33%), orange needles, mp 103-104 °C (MeOH); ir (potassium bromide): 1560, 1520, 1460, 1440, 1360, 1230, 1200 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.81 (s, 4H), 7.18-8.62 (m, 14H). MS: m/z 374 (12, M^+), 223 (63), 267 (17), 178 (33), 91 (100).

Anal. Calcd. for $C_{22}H_{18}N_2S_2$: C, 70.55; H, 4.84; N, 7.48. Found: C, 70.59; H, 4.89; N, 7.69.

6-Chloro-2-dibenzylamino-4*H*-3,1-benzothiazine-4-thione (**13b**).

The compound **13b** (16%) was prepared from **3b** and **9a** in methanol in the same manner as described above. Orange needles, mp 141-142 °C (hexane); ir (potassium bromide): 1550, 1520, 1465, 1425, 1195 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.80 (s, 4H), 7.25-8.56 (m, 13H); ms: m/z 410 (M^++2, 5), 408 (M^+, 11), 317 (57), 212 (30), 91 (100).

Anal. Calcd. for $C_{22}H_{17}ClN_2S_2$: C, 64,61; H, 4.19; N, 6.85. Found: C, 64.72; H, 4.33: N, 6.90.

2-(1,2,3,4-Tetrahydroqunolin-2-yl)-4*H*-3,1-benzothiazine-4-thione (**13c**).

A mixture of **3a** (211 mg, 1.0 mmole) and **9d** (266 mg, 2.0 mmoles) in methanol (10 ml) was refluxed for 3 hours. After evaporation of the solvent, the residue was separated by column chromatography (silica gel-hexane/chloroform) to give **13c** (180 mg, 58%), unstable orange oil; ir (neat): 2975, 1520, 1445, 1325, 1225 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.25-4.47 (m, 2H), 4.72-5.09 (m, 2H), 5.23 (d, J = 18.0 Hz, 1H), 5.38 (d, J = 18.0 Hz, 1H), 6.98-8.32 (m, 8H); ms: m/z 310 (M^+, 42), 132 (100), 118 (44), 104 (40).

6-Chloro-2-(1,2,3,4-tetrahydroisoquinolin-2-yl)-4*H*-3,1-benzothiazine-4-thione (**13d**).

A mixture of **3b** (246 mg, 1.0 mmole) and **9d** (260 mg, 2.0 mmoles) in methanol (10 ml) was refluxed for 13 hours. After the same work-up as **13c**, unstable orange oil **13d** (243 mg, 71%) was obtained; ir (neat): 2950, 1500, 1445, 1405, 1320, 1290, 1220, 1150 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.78-3.92 (m, 1H), 4.28-4.72 (m, 1H), 4.80-5.10 (m, 2H), 5.23 (d, J = 18.0 Hz, 1H), 5.30 (d, J = 18.0 Hz, 1H), 7.02-8.17 (m, 7H); ms: m/z 346 (M^++2, 10), 344 (M^+, 23), 132 (100), 117 (39), 104 (52).

3-Benzyl-1,2,3,4-tetrahydroquinazoline-2,4-dithione (**14a**).

A mixture of **3a** (211 mg, 1.0 mmole) and **9a** (484 mg, 3.0 mmoles) in ethyl acetate (5 ml) was refluxed for 13 hours. After

collection of the yellow precipitates (32 mg) by filtration, the filtrate was evaporated. The residue was washed with acetone and the additional precipitates (76 mg) were collected by filtration. The combined product **14a** (108 mg, 38%) was recrystallized from chloroform-hexane to give yellow needles, mp 230-231 °C; ir (potassium bromide): 2956, 1615, 1536, 1648, 1146, 1109 cm^{-1}; ^1H nmr (dimethyl sufoxide-d_6): δ 6.38 (br s, 2H), 7.20-8.35 (m, 9H), 13.54 (s, 1H); ms: m/z 284 (M^+, 100), 251 (54), 162 (17), 135 (18).

Anal. Calcd. for $C_{15}H_{12}N_2S_2$: C, 63.34; H, 4.25; N, 9.85. Found: C, 63.35; H, 4.47; N, 9.81.

3-Methyl-tetrahydroquinazoline-2,4-dithione (**14b**).

A mixture of **3a** (422 mg, 2.0 mmoles) and **9b** (484 mg, 4.0 mmoles) in 1,2,4-trimethylbenzene (4 ml) was refluxed for 24 hours. The precipitates formed were collected by filtration to give **14b** (334 mg, 80%), mp 278-280 °C (methanol), which was identical with the sample prepared in 48% yield from **3a** (211 mg, 1.0 ml) and 50% dimethylamine (1.8 ml, 13 mmol) by warming at 60 °C for 5 hours.

Dimethyl (1,2-Dihydro-2-thioxo-4*H*-3,1-benzothiazin-4-yl)phosphonate (**18a**) and 2-Methylthio-4*H*-3,1-benzothiazine-4-thione (**19**).

A mixture of **3a** (422 mg, 2.0 mmoles) and trimethyl phosphite (1.18 ml, 10 mmoles) in dioxane (5 ml) was refluxed for 18 hours. After evaporation of the solvent the solid residue was washed with benzene and recrystallized from benzene-methanol to give **18a** (116 mg, 20%), pale yellow needles, mp 170-172 °C (benzene-methanol); ir (potassium bromide): 3153, 2947, 1525, 1492, 1352, 1253, 1059, 1015 cm^{-1}; ms: m/z 289 (M^+, 62), 225 (7), 194 (15), 180 (100), 148 (31); ^1H nmr (dimethylsulfoxide-d_6): δ 3.58 (d, $^3J_{PH}$=10.8 Hz), 3.65 (d, $^3J_{PH}$=10.8 Hz, 3H), 5.02 (d, $^2J_{PH}$=17.6 Hz, 1H), 7.19-7.39 (m, 4H).

Anal. Calcd. for $C_{10}H_{12}NO_3PS_2$: C, 41.52; H, 4.18; N. 4.84. Found: C, 41.42; H, 4.16; N, 4.71.

The filtrate after washing and filtration was collected and chromatographed on silica gel with chloroform-ethyl acetate-methanol to give **19** (96 mg, 21%), orange needles, mp 106-107 °C (hexane); ir (potassium bromide): 1556, 1524, 1453, 1231, 1221, 1015 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.70 (s, 3H), 7.26-8.65 (m, 4H); ms: m/z 225 (M^+, 58), 178 (100), 134 (13), 102 (25).

Anal. Calcd. for $C_9H_7NS_3$: C, 47.97; H, 3.13; N, 6.22. Found: C, 47.94; H, 3.12; N, 3.12.

Diisopropyl (1,2-Dihydro-2-thioxo-4*H*-3,1-benzothiazin-4-yl)phosphonate (**18b**).

This compound, prepared in a similar manner as that of **18a**, was obtained in 22% yield as pale yellow powders, mp 190-192 °C (benzene); ir (potassium bromide): 3163, 1525, 1492, 1345, 1234, 992 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.13-1.42 (m, 12H), 4.02 (d, $^2J_{PH}$=18.8 Hz, 1H), 4.70-4.93 (m, 2H), 7.11-7.29 (m, 4H), 11.18 (br s, 1H); ms: m/z 345 (M^+, 32), 261 (31), 180 (100), 136 (25).

Anal. Calcd. for $C_{14}H_{20}NO_3PS_2$: C, 48.68; H, 5.84; N, 4.06. Found: C, 48.61; H, 5.82; N, 4.20.

Diisopropyl (6-Chloro-1,2-dihydro-2-thioxo-4*H*-3,1-benzothiazin-4-yl)phosphonate (**18c**).

This compound, prepared in a similar manner as that of **18a**, was obtained in 24% yield as pale yellow prisms, mp 177-179 °C (methanol-hexane); ir (potassium bromide): 3454, 2979, 1523, 1487, 1353, 1239, 1000 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.13-1.64 (m, 12H), 3.92 (d, $^2J_{PH}$=18.8 Hz, 1H), 4.74-4.97 (m, 2H), 7.16-7.26 (m, 3H), 11.61 (br s, 1H); ms: m/z 379 (M^+, 40), 337 (46), 295 (14), 214 (100), 182 (19).

Anal. Calcd. for $C_{14}H_{19}ClNO_3PS_2$: C, 44.27; H, 5.04; N, 3.69. Found: C, 44.17; H, 5.04; N, 3.69.

Dimethyl (1,2-Dihydro-1-methyl-2-thioxo-4*H*-3,1-benzothiazin-4-yl)phosphonate (**18d**).

This compound, prepared in a similar manner as that of **18a**, was obtained in 39% yield as orange powders, mp 136-138 °C (benzene-hexane); ir (potassium bromide): 2908, 1468, 1362, 1257, 1041, 1009 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.72 (d, $^3J_{PH}$=10.8 Hz, 3H), 3.81 (d, $^3J_{PH}$=11.2 Hz, 3H), 3.94 (s, 3H), 3.96 (d, $^2J_{PH}$=18.8 Hz, 1H), 7.19-7.43 (m, 4H); ^{13}C nmr (deuteriochloroform): δ 40.18, 41.27 (d, $^1J_{PC}$=153.4 Hz), 54.07 (d, $^2J_{PC}$=6.3 Hz), 54.90 (d, $^2J_{PC}$=6.3 Hz), 118.36 (d, $^3J_{PC}$=3.2 Hz), 120.89, 125.60 (d, $^3J_{PC}$=3.1 Hz), 128.31, 129.32 (d, $^2J_{PC}$=6.3 Hz), 140.97, 191.54; ms: m/z 303 (M^+, 46), 194 (100), 153 (24), 117 (26).

Anal. Calcd. for $C_{11}H_{14}NO_3PS_2$: C, 43.56; H, 4.65; N, 4.62. Found: C, 43.68; H, 4.89; N, 4.73.

Diisopropyl (1,2-Dihydro-1-methyl-2-thioxo-4*H*-3,1-benzothiazin-4-yl)phosphonate (**18e**).

This compound, prepared in a similar manner as that of **18a**, was obtained in 32% yield as thin yellow needles, mp 109-110 °C (benzene-hexane); ir (potassium bromide): 2978, 2906, 1468, 1354, 1254, 1111, 1016, 989 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.15-1.33 (m, 12H), 3.82 (d, $^2J_{PH}$=18.8 Hz, 1H), 3.92 (s, 3H), 4.58-4.82 (m, 2H), 7.17-7.41 (m, 4H), ms: m/z 359 (M^+, 37), 194 (86), 165 (48), 134 (52), 123 (100).

Anal. Calcd. for $C_{15}H_{22}NO_3PS_2$; C, 50.12; H, 6.17; N, 3.90. Found: C, 50.34; H; 6.30; N, 3.96.

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