Ring Closures from Enecarbamoyl Thiocyanates. Syntheses of 5,6,7,8-Tetrahydro-4-thio-2,4(1*H*,3*H*)-quinazolinediones and Related Compounds

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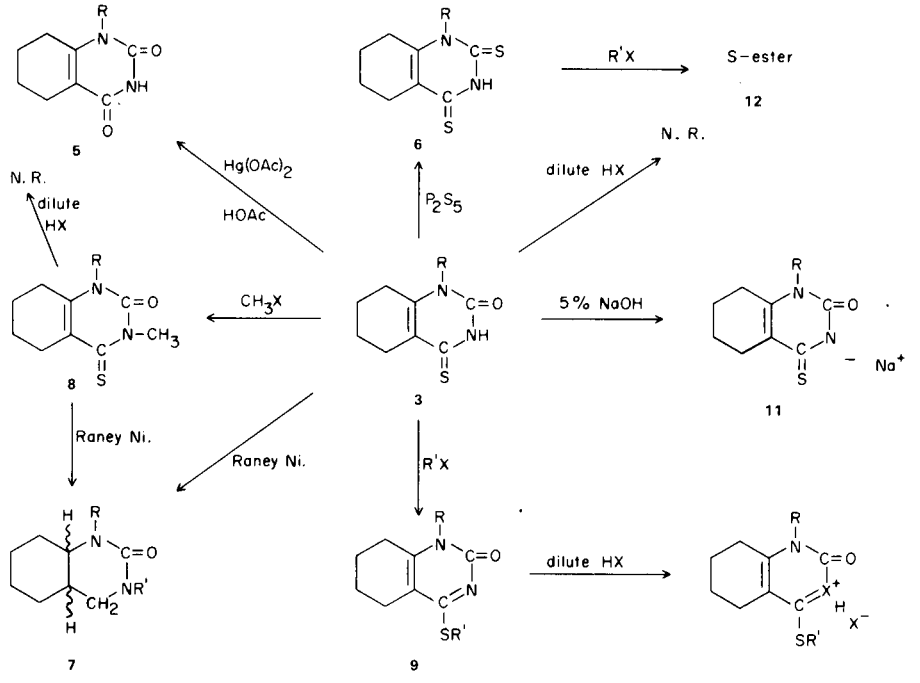
Alkyl (1-cyclohexen-1-yl)carbamoyl chlorides (**1**) react with thiocyanate ion to form enecarbamoyl thiocyanates (**2**). In pyridine solution **2** readily isomerizes to the isothiocyanate **4**, which however is not isolated, but immediately transformed in good yields to tetrahydro-4-thio-2,4(1*H*,3*H*)quinazolinediones (**3**). Various transformations of **3**, including conversion to tetrahydro-2,4(2*H*,4*H*)quinazolinedione (**5**), dithione (**6**), alkylation products (**8** and **9**), sodium salts **11** and Raney nickel degradation to 4,4a,5,6,7,8,8a-octahydro-1-methyl-2(1*H*)quinazolinone (**7**), were carried out to investigate their chemistry and substantiate structural assignments.

The reaction of electrophiles, such as acid chlorides, with enolizable imines can produce enamidic compounds (1,2). *N*-substituted-(1-cyclohexen-1-yl)carbamoyl chlorides (**1**) result if phosgene is employed as the electrophile with cyclohexylidene amines (3).

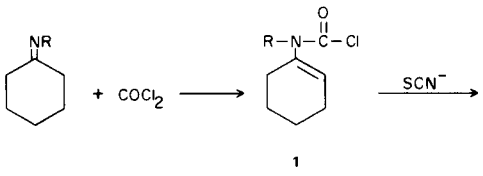
These stable materials possess a labile chlorine, and thus comparison of their reaction behavior towards various nucleophiles would be of interest.

Detailed studies have shown that while dialkyl carbamoyl chlorides react with thiocyanate ion to give only carbamoyl isothiocyanates (4), with subsequent isomerization and dimerization reactions, diphenylcarbamoyl chloride gives solely the corresponding thiocyanate, which can be isomerized to the isothiocyanate only by fusion at elevated temperatures (5).

Using the preferred reaction conditions employed by



previous investigators (4,5), namely potassium or sodium thiocyanate in boiling acetonitrile, **1** gave a mixture of the carbamoyl thiocyanate **2** and 5,6,7,8-tetrahydro-4-thio-2,4-(1*H*,3*H*)quinazolinedione (**3**). Yields were disappointing (*i.e.* 20% of **2** and 42-48% of **3**).



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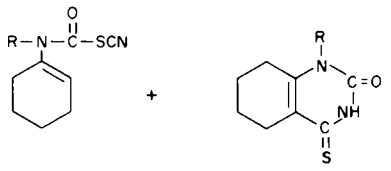
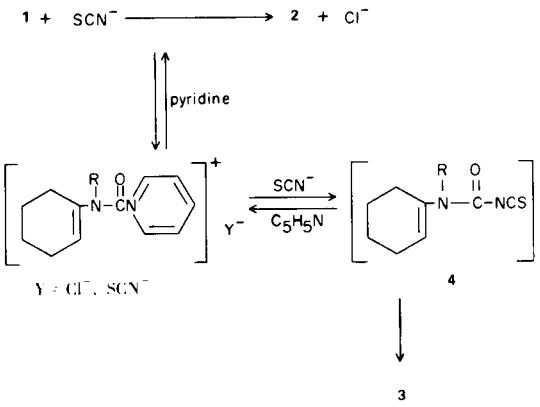


2 3

No intermediate enecarbamoyl isothiocyanate **4** was isolated. Material **2** was readily identified from analyses, molecular weight, nmr and ir spectra, including the characteristic sharp, medium intensity thiocyanate band at 4.62 μ, (see Table III for compliation of pertinent spectra data for key compounds). It seems reasonable to assume that any **4** produced in the reaction was immediately transformed to **3**. Facile intermolecular reaction of aryl and alkyl isothiocyanates (2), (6) and acyl isothiocyanate (7) with cyclic imines have previously been demonstrated. The intramolecular transformation of **4** to **3** would be expected to proceed with even greater ease.

Thiocyanate **2** exhibited the same inertness towards isomerization that had previously been noted for diphenylcarbamoyl thiocyanate (5). Refluxing in neutral solvents, even in the presence of thiocyanate ion, did not produce isomerization. Only by heating **2** considerably above its melting point could isomerization be made to occur (with formation of **3**).

It is not clear whether isomerization of carbamoyl thiocyanates follows predominately a dissociation-recombination or addition-elimination mechanism (5). Nevertheless, it seemed reasonable to conclude that isomerization of **2** to **4** (to form **3**) could be induced by providing a nucleophile which could effectively react with either **1** or **2** to cause their dissociation. Pyridine has been shown to form such complexes with carbamoyl chlorides and further, to occasionally catalyze thiocyanate isomerization (8b). Thus, **1** and **2** could react reversibly with pyridine, thereby promoting formation of **4**. The complete isomerization of **2** to **4** would then depend on the latter's fast, irreversible conversion to **3**.



Preliminary data on the isomerization of **2a** in pyridine is given in Fig. 1. At room temperature the transformation of **2a** to **3a** can be directly and quantitatively observed by measuring with time, the areas under the well separated nmr resonance peaks for NCH_3 from **2a** and **3a** respectively. Pyridine has the added advantage of solubilizing both ammonium thiocyanate and dilute solutions of **3**, so that homogeniety of the reactants and organic products may be maintained.

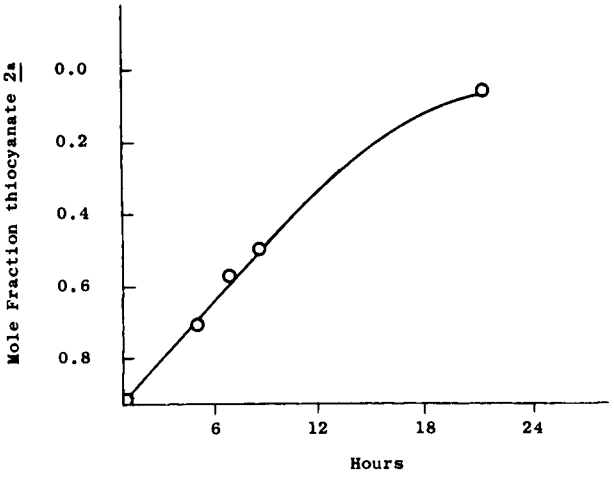


Figure 1 Isomerization of (1-cyclohexen-1-yl)-methylcarbamoyl thiocyanate in pyridine at 25°

The observed facile formation of **3** from **2** in pyridine as shown in Fig. 1 holds for preparing macro amounts of **3** from **1**. The latter is added to a solution of ammonium thiocyanate in pyridine and the homogeneous mixture refluxed for about 15-30 minutes. On cooling, the contents can simply be poured into water and high purity **3** filtered off in yields of *ca.* 80% (see Table II and Experimental for examples).

The structure of **3** as 1-substituted-5,6,7,8-tetrahydro-4-thio-2,4(1*H*,3*H*)quinazolinedione is verified by a number of considerations. Elemental analyses, molecular weight,

TABLE I

1-Substituted 5,6,7,8-Tetrahydro-4-thio-2,4-(1*H*,3*H*)-quinazolinediones (3)

Material	R	M.p. °C	Yield	Molecular Formula	Analysis Calcd. C	H	N	Found C	H	N
3a	CH_3	252-258 (a)	85	$C_9H_{12}N_2OS$	55.07	6.16	14.27	54.91	6.14	14.38
3b	C_2H_5	204-206	75	$C_{10}H_{14}N_2OS$	57.11	6.71	13.32	57.32	6.59	13.39
3c	$(CH_3)_2CH$	255-259	72	$C_{11}H_{16}N_2OS$	58.90	7.19	12.49	59.75	7.07	12.78
3d	$(CH_3)_2CHCH_2$	196-196.5	85	$C_{12}H_{18}N_2OS$	60.47	7.61	11.75	60.69	7.46	11.60
3e	cyclohexyl	204-213	57	$C_{14}H_{20}N_2OS$	63.60	7.62	10.60	63.56	7.76	10.51
3f	$C_6H_5CH_2$	219-227	76	$C_{15}H_{16}N_2OS$	66.15	5.92	10.28	65.91	5.91	9.37
3g	C_6H_5	278-280 (b)	84	$C_{14}H_{14}N_2OS$	65.09	5.46	10.84	65.30	5.45	10.70
3h	$3,4(Cl)_2C_6H_3$	205 dec.	89	$C_{14}H_{12}Cl_2N_2OS$	51.39	3.70	8.56	51.73	3.91	8.53

(a) Ref. 9 gives m.p. 241-245° dec. (b) *ibid.*, m.p. 287-294°

TABLE II

Alkylation Products of 1-Substituted 5,6,7,8-Tetrahydro-4-thio-2,4-(1*H*,3*H*)-quinazolinediones (8, 9)

Material	R	R′	M.p. °C	Yield	Molecular Formula	Analyses Calcd. C	H	N	Found C	H	N
8	CH_3	CH_3	167-169	<20	$C_{10}H_{14}N_2OS$	57.11	6.71	13.32	57.12	6.91	13.26
9a	CH_3	CH_3	150-151	>50	$C_{10}H_{14}N_2OS$	57.11	6.71	13.32	57.08	6.76	13.54
9b	CH_3	C_2H_5	158-159	69	$C_{11}H_{16}N_2OS$	58.90	7.19	12.49	59.08	7.25	12.59
9c	CH_3	n-C_3H_7	128-129		$C_{12}H_{18}N_2OS$	60.47	7.61	11.75	60.60	7.72	11.76
9d	CH_3	$(CH_3)_2CH$	169-170	50	$C_{12}H_{18}N_2OS$	60.47	7.61	11.75	60.26	7.70	11.75
9e	CH_3	n-C_4H_9	72-75	70	$C_{13}H_{20}N_2OS$	61.87	7.99	11.10	61.67	8.04	11.25
9f	CH_3	n-C_6H_{13}	66-68	66	$C_{15}H_{24}N_2OS$	64.25	8.63	9.99	64.07	8.58	10.02
9g	CH_3	n-C_8H_{17}	74-75	73	$C_{17}H_{28}N_2OS$	66.19	9.15	9.08	66.12	8.90	8.91
9h	CH_3	n-$C_{10}H_{21}$	70-71	98	$C_{19}H_{32}N_2OS$	67.81	9.58	8.32	68.00	9.74	8.35
9i	CH_3	$C_6H_5CH_2$	166	94	$C_{16}H_{18}N_2OS$	67.10	6.34	9.78	67.02	6.40	9.38
9j	CH_3	$H_2C{=}CHCH_2$	133-134	87	$C_{12}H_{16}N_2OS$	60.99	6.82	11.85	61.05	6.90	11.77
9k	C_2H_5	n-C_3H_7	116-117	95	$C_{13}H_{20}N_2OS$	61.87	7.99		62.37	8.08	
9l	C_2H_5	$CH_2{=}CClCH_2$	88-90	65	$C_{13}H_{17}ClN_2OS$	54.82	6.02	9.84	55.01	5.82	9.72

TABLE III

Pertinent Spectral Properties of Tetrahydroquinazolinediones and Related Materials

Material	R	R′	IR (a) (μ) and Uv λ max (e) (Ethanol) (s,strong; m,medium; w,weak)	Nmr (δ) (Deuteriochloroform) (b)
2a	CH_3		4.62 w (SCN); 5.8 s (C=O); 6.0 w (C=C)	3.10 NCH_3; 6.04 =C*H*
3a	CH_3		5.9 s (C=O); 6.3 s; 245, (3,200); 340 (c), (16,000)	3.28 (pyridine) NCH_3
5a	CH_3		5.9-6.1 s (C=O)	3.25 (d_6DMSO) NCH_3
6a	CH_3		6.3 s	3.71 (pyridine) NCH_3
10a	CH_3		6.02 (C=O), 6.21	3.74 (pyridine) NCH_3
7a	CH_3	H	6.08 s (C=O)	2.80 (CCl_4) NCH_3); 7.30 (N*H*)
7b	CH_3	CH_3		2.80 (CCl_4) $(NCH_3)_2$
8	CH_3	CH_3	5.98 s; 6.22 s; 251, (5700); 338, (17,000)	3.44 NCH_3; 3.81 NCH_3
9a	CH_3	CH_3	6.05 s (C=O); 6.3 m; 270, (12,000); 315, (12,400)	3.48 NCH_3; 2.52 SCH_3
12a	CH_3	CH_3	6.30 s	3.97 NCH_3; 2.60 SCH_3
9d	CH_3	$(CH_3)_2CH$	6.08 s (C=O); 6.28 m	3.44 NCH_3; 4.20 $SCH(CH_3)_2$
9j	CH_3	CH_2=$CHCH_2$	6.08 s (C=O); 6.3 m	3.42 NCH_3; 3.88 SCH_2CH=CH_2
12b	CH_3	CH_2=$CHCH_2$	6.1 w (C=C); 6.3 s	3.92 NCH_3; 4.00 SCH_2CH=CH_2
9i	CH_3	$C_6H_5CH_2$	6.1 s (C=O); 6.25 m	3.45 NCH_3; 4.45 $SCH_2C_6H_5$
12c	CH_3	$C_6H_5CH_2$	6.3 (s)	3.92 NCH_3; 4.52 $SCH_2C_6H_5$

(a) Solvent either chloroform or carbon tetrachloride. (b) Unless otherwise noted. (c) Ref. 9 gives 245 (4,100) and 340 (20,100).

nmr and ir spectra (Table III) are all consistent with the assigned structure. Moreover chemical transformations of **3** as well as the preparation of a positional isomer, 5,6,7,8-tetrahydro-1-methyl-2-thio-2,4(1*H*,3*H*)quinazolinedione (**10**) serve to substantiate structural assignments. In addition, during the course of this investigation, an alternate synthesis of **3** was reported (9). Comparable physical constants were found for the two compounds common to both studies.

Table III lists a number of alkylation products prepared from **3**, **5** and **6**. With one exception **3** is alkylated solely on sulfur. This has been established by comparing the similar chemical shifts conferred by sulfide in esters derived from the dithione, **6** (Table III). In only one example was it possible to isolate an alkylation product from **3** other than **9**; methylation gave a small amount of **8**. The nmr chemical shift for the NCH_3 group in this compound is downfield and could be interpreted as arising either from NCH_3 or OCH_3 resonances. Similarly the ir spectra shows two strong absorptions in the 6 μ region, which could arise from a thioamide I band (10) and either a carbonyl or imino group from *N* or *O* methylated material respectively. It would seem more reasonable however to assign the higher frequency absorption at 5.98 μ to a carbonyl (*i.e.* **8**) rather than imino group. The uv spectra for **8** closely resembles **3a**, rather than **9a**.

Chemical properties of **8** are akin to **3** also. Although **9** is soluble in dilute acid and forms hygroscopic salts when precipitated with hydrogen chloride from ether solution, **8** is identical to **3** in its ability to dissolve only in concentrated acid; indeed the successful separation of **8** from **9a** is dependent on this difference in properties. Finally, both **3** and **8** can be degraded with Raney Nickel to form **7** (R′ = H, CH_3 respectively).

The remaining data in Table III is consistent with the assigned structures. Noteworthy are the consistent low field resonances of the NCH_3 group when adjacent to thionosulfur, as in materials **6**, **10**, and possibly **12**. Simi-

lar diamagnetic anisotrophy of a *cis* thiono sulfur has been revealed before (10). Where the *N*-methyl group is adjacent to a carbonyl group, as in **3a**, **5**, **7**, **8**, **9**, **11**, the NCH_3 resonance is consistently upfield.

EXPERIMENTAL

All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Infracord; nmr spectra were recorded by a Varian A-60; mass spectroscopy was measured (direct solids inlet) by a Perkin-Elmer 270 mass spectrometer; and uv was taken by a Bausch and Lomb Spectronic 505. Melting points are corrected.

The preparation of *N*-(1-cyclohexen-1-yl)-*N*-alkylcarbamoyl chlorides have been previously described (3).

(1-Cyclohexen-1-yl)methylcarbamoyl Thiocyanate (**2a**).

(1-Cyclohexen-1-yl)methylcarbamoyl chloride (8.6 g., 0.05 mole) was dissolved in acetonitrile with sodium thiocyanate (4.1 g., 0.05 mole), and the mixture refluxed for fifty minutes. The material was cooled and filtered. The filtrate was vacuum treated to remove solvent, and the residue washed with ether. The material was again filtered and the ether filtrate evaporated to give an oil which solidified on scratching. The material was recrystallized from methylcyclohexane-heptane (charcoal) to give **2a**, m.p. 75-76°. The combined solids from filtration were washed with water and air-dried to give **3a** (see below). Yields of **2a** and **3a** by this method were 20% and 42% respectively.

Anal. Calcd. for $C_9H_{12}N_2OS$ (**2**): C, 55.07; H, 6.16. Found: C, 54.92; H, 6.08.

Specific preparations of **3a**, **8**, **9a**, **9j**, will suffice to give the information necessary for the preparation of the compounds included in Tables I and II.

5,6,7,8-Tetrahydro-1-methyl-4-thio-2,4(1*H*,3*H*)quinazolinedione (**3a**).

(1-Cyclohexen-1-yl)methylcarbamoyl chloride (8.6 g., 0.05 mole) was placed in a dropping funnel and added to a solution of ammonium thiocyanate (4 g., 0.05 mole) dissolved in 80 ml. of pyridine. The mixture was heated to reflux. Precipitate commenced to form at room temperature which thickened as the temperature was raised. The material was heated at reflux (115°) for 15 minutes, then the mixture was cooled. Nmr of the supernatant liquid indicated that complete reaction had taken place with the typical spectral absorption of **3a**. The mixture was filtered to give a light yellow solution, while the 2.5 g. of white residue collected proved to be entirely ammonium chloride (2.7 g. of theory). The filtrate was vacuum treated to remove most of the solvent. The pyridine contaminated solid was washed with water, made *ca.* pH 5 with a small amount of concentrated hydrochloric acid and washed on the filter several times with water. After drying for one hour under vacuum at 80°, the light yellow powdery product weighed 8.3 g. (85% yield). Other preparations of this material and homologs could be carried out by directly pouring the pyridine slurry of ammonium chloride directly into several times its volume of cold water, then filtering off the solid product.

5,6,7,8-Tetrahydro-1,3-dimethyl-4-thio-2,4(1*H*,3*H*)quinazolinedione (**8a**).

Compound **3a** (4 g., 0.0204 mole) was placed in methanol and to this was added 4.4 g. of 25 percent sodium methoxide in methanol. This mixture was treated with 2.7 g. of methyl sulfate, then let stand *ca.* one hour. The methanol was partially removed under vacuum and the residue mixed with water. The solid precipitate was filtered off and recrystallized from aqueous methanol to give 0.35 g. (8% yield).

5,6,7,8-Tetrahydro-1-methyl-4-(methylthio)-2(1*H*)quinazolinone (**9a**).

Material **3a** (4 g., 0.0204 mole) was mixed with an equivalent amount of sodium methoxide in methanol, heated to 60°, then cooled to room temperature. Methyl iodide (3.6 g., 0.025 mole) was added and the material heated for 1 1/2 hours at reflux. The solvent was removed under vacuum and water added to the residue to give an acidic clear solution. Upon making the solution basic with alkali, 3.5 g. of solid **9a** was recovered (82% yield). Recrystallization was effected from methylcyclohexane-toluene (charcoal).

5,6,7,8-Tetrahydro-2-(allylthio)-1-methyl-2(1*H*)quinazolinone (**9j**).

Material **4a** (5 g., 0.0256 mole) was placed in 50 ml. of glyme and 5.7 g. of 25% solution of sodium methoxide in methanol was added. Allyl bromide (3.3 g., 0.027 mole) was added and the mixture heated at reflux for three hours. The solvents were evaporated and water added, and the mixture made basic ($pH > 11$). The solution was filtered and air-dried to give 5.2 g. (87% yield). The material was recrystallized from methylcyclohexane-toluene.

5,6,7,8-Tetrahydro-1-methyl-2,4(1*H*,3*H*)quinazolinedione (**5a**).

Material **3a** (2.0 g., 0.01 mole) was mixed with 0.02 mole of mercuric acetate in 40 ml. of glacial acetic acid. The mixture was refluxed *ca.* seven hours, then permitted to stand 14 hours. The black precipitate was removed by filtration and the filtrate vacuum treated to remove the bulk of the acid solvent. The residue was mixed with a saturated salt solution and the resulting crystals removed by centrifuge. The crystals were initially dried on a clay plate and then in a vacuum oven at 75°. The material was recrystallized from acetone (charcoal) to give colorless needles, m.p. 232-233°.

Anal. Calcd. for $C_9H_{12}N_2O_2$: C, 59.88; H, 6.71; N, 15.55. Found: C, 59.66; H, 6.73; N, 15.52.

5,6,7,8-Tetrahydro-1-methyl-2,4(1*H*,3*H*)quinazolinedithione (**6a**).

Material **3a** (20 g., 0.1 mole) was placed in 200 ml. of *o*-dichlorobenzene. To this mixture was added 10 g. of phosphorus pentasulfide, and the solution heated to reflux at 180° for 1.5 hours. The material was cooled and the solids removed by filtration. The residue was treated with 5 percent caustic and the resulting solution filtered through clay, then acidified with 5 percent hydrochloric acid. The precipitate was removed by filtration and washed with more water, then dried at 80° to give 17.6 g. of **6a**, m.p. 250-259°.

Anal. Calcd. for $C_9H_{12}N_2S_2$: C, 50.91; H, 5.70; S, 30.20. Found: C, 50.86; H, 5.72; S, 30.08.

cis or *trans*-3,4,4a,5,6,7,8,8a-Octahydro-1-methyl-2(1*H*)quinazolinone (**7a**).

Material **3a** (1 g., 0.005 mole) was heated 8 hours in 2-propanol with 15 g. of Raney Nickel. The material was filtered through a fluted filter twice, then the filtrate vacuum treated to remove solvent. The residue (0.6 g.) was an oil which solidified on scratching and cooling. Recrystallization from heptane (charcoal) gave 0.4 g. of crystals, m.p. 105-106°. The nmr was consistent with the structure (see Table III). Mass spectrum (70 eV) important m/e (rel intensity) (possible fragmentation mode): 168 (60) (parent molecular ion); 167 (16) (168-H); 126 (8) (168-NCO); 125 (100) (168-HNCO); 111 (63) (168-CH_3NCO) (125-CH_2); 82 (12) (111-CH_2NH).

Anal. Calcd. for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65. Found: C, 64.56; H, 9.65; N, 16.68.

cis or *trans*-3,4,4a,5,6,7,8,8a-Octahydro-1,3-dimethyl-2(1*H*)quinazolinone (**7b**).

Raney Nickel treatment of **8** in similar fashion to that given above, gave a colorless oil that would not crystallize, nmr (see Table III); mass spectrum (70 eV) important m/e (rel intensity) (possible fragmentation mode): 182 (68) (parent molecular ion); 181 (40) (182-H); 140 (7) (182-NCO); 139 (73) (181-NCO); 126 (11) (140-CH_2); 125 (100) (182-CH_3NCO); 82 (10) (125-CH_3N and CH_2).

5,6,7,8-Tetrahydro-1-methyl-4 or 2(methylthio)-2 or 4(1*H*)quinazolinethione (**12a**).

Dithione **6** (2.12 g., 0.01 mole) was placed in 50 ml. of dimethyl sulfoxide and 0.01 mole of 25% sodium methoxide in methanol was added. To this mixture was added 1.4 g. of methyl iodide. After stirring at room temperature for *ca.* five hours, the mixture was poured into 300 ml. of ice-water. Sodium chloride was added to the colloidal suspension and the mixture allowed to stand two days before filtering. The solid collected was recrystallized from a mixture fo toluene and methylcyclohexane (charcoal) to give 0.5 g. of yellow solid, m.p. 160-175° dec.

Anal. Calcd. for $C_{10}H_{14}N_2S_2$: C, 53.06; H, 6.23; N, 12.38. Found: C, 53.00; H, 6.02; N, 12.23.

4 or 2-(Allylthio)-5,6,7,8-tetrahydro-1-methyl-2 or 4(1*H*)quinazolinethione (**12b**).

Dithione **6** (2.12 g., 0.01 mole) was reacted with an equivalent amount of 3-chloropropene in the presence of sodium methoxide, in similar fashion to preparation of **12a**. Recrystallization (charcoal) from carbon tetrachloride afforded yellow crystals, m.p. 118-120°.

Anal. Calcd. for $C_{12}H_{16}N_2S_2$: C, 57.10; H, 6.39; N, 11.10; S, 25.41. Found: C, 57.32; H, 6.38; N, 11.08; S, 25.33.

4 or 2-(Benzylthio)-5,6,7,8-tetrahydro-1-methyl-2 or 4(1*H*)quinazolinethione (**12c**).

Dithione **6** (0.7 g., 0.0055 mole) reacted in dimethylsulfoxide with equimolar amount of α-chlorotoluene and sodium methoxide, in similar fashion to the preparation of **12c**. Recrystallization from methanol gave a yellow solid, m.p. 157-165°.

Anal. Calcd. for $C_{16}H_{18}N_2S_2$: C, 63.54; H, 6.00. Found: C, 63.17; H, 6.16.

5,6,7,8-Tetrahydro-1-methyl-4-thio-2,4(1*H*,3*H*)quinazolinedione, Sodium Salt, Monohydrate (**11**).

Material **3a** (3 g., 0.0153 mole) was stirred in methanol and 3.26 g. of a 25% solution of sodium methoxide in methanol was added, whereupon the solution became clear. After stirring several minutes, the few residual solid particles were filtered off, and methanol removed under vacuum. The solid was dried at 80° under vacuum to give 3.0 g. or 83% yield.

Anal. Calcd. for $C_9H_{11}NaN_2OS \cdot H_2O$: C, 45.75; H, 5.55. Found: C, 45.18; H, 5.49.

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