N-Ethoxycarbonylamidines as Starting Materials and Intermediates in the Synthesis of Heterocyclic Compounds

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Treatment of *N*-ethoxycarbonylthioamides (**1**) with primary aromatic amines yields *N*-aryl-*N'*-ethoxycarbonylamidines (**2**), which thermally cyclize to 2-aryl-4(3*H*)-quinazolinones (**6**). Analogous reactions of **1** with ethyl 3-aminocrotonate and with 2-amino-2-thiazoline lead respectively to ethyl 2-aryl-3,4-dihydro-6-methyl-4-oxo-5-pyrimidinecarboxylates (**10**) and to 2-aryl-6,7-dihydro-4*H*-thiazolo[3,2-*a*]-1,3,5-triazin-4-ones (**14**), presumably through the corresponding *N*-ethoxycarbonylamidines.

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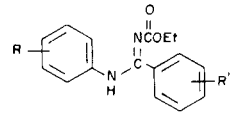
Of the various methods of preparation of 2-substituted 4(3*H*)-quinazolinones (**6**) (1), the thermal decomposition of *N*-alkoxycarbonyl-*N'*-arylamidines (**2**) has not attracted much attention, very likely because of the lack of a convenient and general method of preparation of such amidines (2-4). It was previously found, however, that the *N*-ethoxycarbonyl derivatives of pyrrole- and thiophene-2-thioamide react with aniline to form the corresponding *N*-ethoxycarbonylamidines, which, upon heating in quinoline, smoothly cyclize into 2-(2-pyrrolyl)- and 2-(2-thienyl)-4(3*H*)-quinazolinone, respectively (5). Because of the convenience and efficiency of this reaction sequence, it was decided to explore its possibilities as a general method of preparation of 2-substituted 4(3*H*)-quinazolinones.

The *N*-ethoxycarbonylthioamides (**1**) needed as starting materials are readily obtained by the reaction of aromatic

Table I

N-Aryl-*N'*-ethoxycarbonylamidines (**2**)



Compound No.	R	R'	% Yield (a)	Mp °C (b)	Elemental Analysis, % Calcd. (Found) C	H	N	IR, cm⁻¹ N-H	C=O	¹H-NMR, ppm (c) Aromatic	R	R'	COOEt	NH
2a	H	H	70	108-109 (d)	71.62 (71.75)	6.01 (6.14)	10.44 (10.59)	3310	1660	7.0-7.8 (m, 10)			1.0 (t, 3), 3.9 (q, 2)	9.9 (s, 1)
2b	H	4-Me	95	108-110	72.73 (72.34)	6.43 (6.42)	9.92 (9.92)		1660	6.9-7.7 (m, 9)		2.4 (s, 3),	1.0 (t, 3), 3.8 (q, 2)	9.8 (s, 1)
2c	3-Me	4-Me	54	89-89.5	72.95 (73.02)	6.80 (6.69)	9.45 (9.55)	3270	1660	6.7-7.5 (m, 8)	2.3 (s, 3), (e)	2.4 (s, 3), (e)	1.0 (t, 3), 3.9 (q, 2)	9.8 (s, 1)
2d	4-Me	4-Me	71	114-115.5	72.95 (72.89)	6.80 (6.59)	9.45 (9.58)	3320	1690	7.0-7.6 (m, 8)	2.3 (s, 3), (e)	2.4 (s, 3), (e)	1.0 (t, 3), 3.9 (q, 2)	9.7 (s, 1)
2e	2-MeO	4-Me	51	99-100.5	69.21 (69.32)	6.45 (6.30)	8.97 (9.03)	3420	1680	6.9-7.4 (m, 8)	3.8 (s, 3),	2.4 (s, 3),	1.0 (t, 3), 3.9 (q, 2)	9.2 (s, 1)
2f	4-Cl	4-Me	98	147-148.5	64.46 (64.62)	5.41 (5.23)	8.84 (8.69)	3310	1690	7.2-7.8 (m, 8)		2.3 (s, 3),	1.0 (t, 3), 3.9 (q, 2)	9.9 (s, 1)
2g	H	4-Et	94	89-91	72.91 (73.12)	6.80 (6.91)	9.45 (9.52)	3340	1680	6.9-7.8 (m, 9)		1.2 (t, 3), 2.6 (q, 2)	1.0 (t, 3), 3.9 (q, 2)	9.8 (s, 1)
2h	H	4-i-Pr	88	95-96	73.52 (73.56)	7.14 (7.08)	9.03 (9.03)	3270	1690	7.0-7.8 (m, 9)		1.2 (d, 6), 2.9 (m, 1)	1.0 (t, 3), 3.9 (q, 2)	9.8 (s, 1)
2i	H	4-MeO	84	100-100.5	68.44 (68.60)	6.08 (6.15)	9.39 (9.41)	3300	1660	6.9-7.8 (m, 9)		3.8 (s, 3),	1.0 (t, 3), 3.9 (q, 2)	9.8 (s, 1)
2j	4-Me	4-MeO	60	121.5-122.5	69.21 (69.46)	6.45 (6.19)	8.97 (9.00)	3250	1630	6.9-7.6 (m, 8)	2.3 (s, 3),	3.8 (s, 3)	1.0 (t, 3), 3.9 (q, 2)	9.7 (s, 1)
2k	4-Cl	4-MeO	86	126-127	61.35 (61.49)	5.14 (5.09)	8.42 (8.41)	3320	1690	6.9-7.7 (m, 8)		3.8 (s, 3),	1.0 (t, 3), 3.9 (q, 2)	9.8 (s, 1)
2ℓ	benzo[*c*]	4-MeO	80	134-135	72.40 (72.64)	5.79 (5.58)	8.04 (8.04)	3280	1690	7.0-8.4 (m, 11)		3.8 (s, 3)	1.1 (t, 3), 3.9 (q, 2)	10.0 (s, 1)
2n	H	4-EtO	73	127-128	69.21 (69.18)	6.45 (6.33)	8.97 (8.99)	3220	1660	6.9-7.8 (m, 9)		1.3 (t, 3), 4.1 (q, 2)	1.0 (t, 3), 3.9 (q, 2)	9.8 (s, 1)

(a) Crude or recrystallized product with melting point within 10° of that of the analytically pure compound. (b) Recrystallized from aqueous ethanol. (c) Solutions in hexadeuteriodimethyl sulfoxide. (d) Previously reported as an oil (2). (e) These assignments may be interchanged.

compounds such as benzene, alkylbenzenes, and alkoxybenzenes with ethoxycarbonyl isothiocyanate, in the presence of anhydrous aluminum chloride (6). We have found that treatment of **1** with primary aromatic amines in refluxing ethanol causes evolution of hydrogen sulfide and results in formation of *N*-aryl-*N'*-ethoxycarbonylamidines (**2**) in yields ranging from 51 to 98% (Table I). Best results are obtained when aniline or a *p*-substituted aniline is used, whereas *o*- or *m*-substituted anilines lead to tarry and difficult to crystallize products. Weakly nucleophilic amines, such as *p*-nitroaniline, are essentially inert under the conditions used. Reactions run in tetrahydrofuran, or acetonitrile as solvent give tarry products, whereas reactions in toluene do not allow isolation of amidines **2** but yield directly the corresponding quinazolinones (**6**). In all cases, the reaction progress is followed easily by monitoring the evolution of hydrogen sulfide with lead acetate paper.

The general structure of the products (**2**) is supported by their ir spectra, which contain an absorption band at 1630-1690 cm^{-1} consistent with a conjugated carbonyl group, and their nmr spectra, which exhibit the characteristic pattern of the ester ethyl group, as well as signals corresponding to the protons of the two aromatic rings and their substituents.

Scheme I

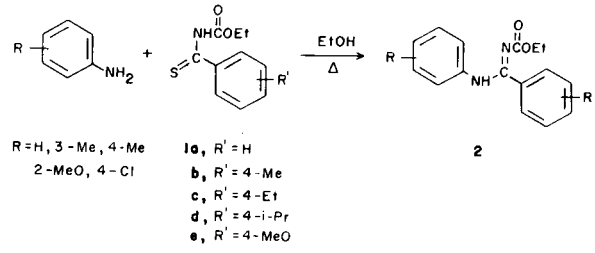
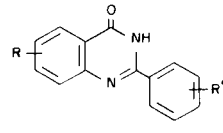


Table II

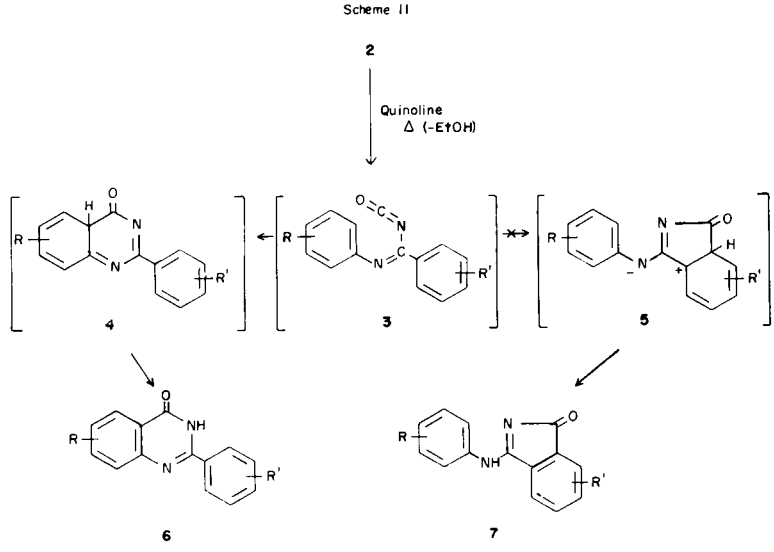
2-Aryl-4(3*H*)-quinazolinones (**6**)



Compound No.	R	R'	% Yield (a)	Mp °C (b)	Elemental Analysis, % Calcd. (Found) C	H	N	IR, cm^{-1} C=O	^{1}H-NMR, ppm (c) Aromatic	R	R'
6a	H	H	84	237.5-238.5 (d)	75.66 (75.81)	4.54 (4.71)	12.60 (12.82)	1660	7.4-7.9 (m, 6), 8.0-8.3 (m, 3) (e)		
6b	H	4-Me	85	240-241 (f)	76.25 (76.04)	5.12 (5.05)	11.85 (11.86)	1660	7.5-8.5 (m, 8)		2.6 (s, 3)
6d	6-Me	4-Me	86 54 (g)	271-272	76.78 (76.49)	5.64 (5.41)	11.19 (11.31)	1690	7.5-8.3 (m, 7)	2.5 (s, 3) (h)	2.6 (s, 3) (h)
6e	8-MeO	4-Me	30 (g)	248-249	72.16 (71.96)	5.29 (5.18)	10.51 (10.52)	1680	7.6-8.2 (m, 7)	4.2 (s, 3)	2.6 (s, 3)
6f	6-Cl	4-Me	49	296-298	66.55 (66.71)	4.10 (3.92)	10.35 (10.21)	1670	7.6-8.5 (m, 7)		2.6 (s, 3)
6g	H	4-Et	86	227-228	76.78 (77.00)	5.64 (5.80)	11.19 (11.37)	1660	7.3-8.3 (m, 8)		1.2 (t, 3), 2.7 (q, 2) (i)
6h	H	4-i-Pr	82	211-213	77.25 (77.21)	6.10 (6.02)	10.60 (10.73)	1680	7.3-8.3 (m, 8)		1.2 (d, 6), 2.8-3.2 (m, 1) (e)
6i	H	4-MeO	76 93 (j)	244-246 (k)	71.42 (71.61)	4.79 (5.01)	11.11 (11.09)	1670	6.6-8.3 (m, 8)		3.8 (s, 3)
6j	6-Me	4-MeO	85	258-259	72.17 (72.09)	5.30 (5.16)	10.52 (10.49)	1680	7.2-7.3 (m, 2), 7.7-8.3 (m, 5)	2.6 (s, 3)	4.0 (s, 3)
6k	6-Cl	4-MeO	85	292-293 (*l*)	62.84 (62.73)	3.87 (3.68)	9.77 (9.74)	1680	6.8-7.0 (m, 2), 7.4-8.0 (m, 5)		3.6 (s, 3)
6*l*	benzo[*f*]	4-MeO	87	311-312	75.49 (75.64)	4.67 (4.66)	9.26 (9.39)	1650	7.3-7.5 (m, 2), 7.9-8.7 (m, 8)		4.1 (s, 3)
6m	8-MeO	4-MeO	37 (m)	229-230	68.07 (68.11)	5.00 (5.13)	9.92 (9.77)	1660	7.1-8.1 (m, 7)	3.9 (s, 3) (h)	4.0 (s, 3) (h)
6n	H	4-EtO	82	248-249.5	72.17 (72.14)	5.30 (5.40)	10.52 (10.68)	1660	7.2-7.3 (m, 2), 7.6-8.4 (m, 6)		1.4 (t, 3), 4.2 (q, 2)

(a) Crude or recrystallized product with melting point within 10° of that of the analytically pure compound. (b) Recrystallized from *N,N*-dimethylformamide. (c) Solutions in trifluoroacetic acid, unless otherwise specified. (d) Lit (2) mp 230-232°. (e) Solution in hexadeuteriodimethylsulfoxide. (f) Lit (15) mp 241°. (g) One-pot procedure. (h) These assignments may be interchanged. (i) Solution in hexadeuteriodimethyl sulfoxide/trifluoroacetic acid. (j) Cyclization in the absence of solvent. (k) Lit (15) mp 247°. (*l*) Lit (16) mp 291-292°. (m) Cyclization without crystallization and purification of **2m**.

Scheme II

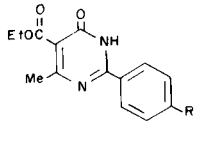


When an *N*-aryl-*N'*-ethoxycarbonylamidine (**2**) is boiled briefly in quinoline, ethanol is evolved and the corresponding 2-aryl-4(3*H*)-quinazolinone (**6**) is formed in 49-88% yield (Table II). Presumably, elimination of ethanol yields an imidoyl isocyanate (**3**), which undergoes cyclization to form the observed product (Scheme I). The formation of quinazolinones by cyclization of imidoyl isocyanates is well documented in the literature (7-9). As in the already published results, we have not observed formation of a different product (**7**) resulting from the alternative mode of cyclization of **3**. This is probably due to the fact that formation of **7** must proceed through an unstable dipolar intermediate (**5**), whereas formation of the isolated product (**6**) involves a more stable neutral intermediate (**4**). Cyclization of *N*-ethoxycarbonyl-*N'*-(3-methylphenyl)-4-methylbenzamidine (**2c**) yields a mixture of two products corresponding to ring closure *o*- and *p*- to the methyl group of the benzene ring undergoing annelation. The nmr spectrum of this mixture shows that the product resulting from ring closure at the *p*-position is formed in only a slight excess (~10% over its isomer). Apparently a methyl substituent does not hinder cyclization at its *o*-position substantially. Thermolysis of *N*-ethoxycarbonyl-*N'*-(2-naphthyl)-4-methoxybenzamidine (**2ℓ**) yields the benzo-[*f*]quinazolinone **6ℓ** in 87% yield. These cyclizations most likely are simple thermal processes, since they proceed equally well when diphenyl ether is used instead of quinoline, or when an amidine **2** is heated at 50-70° above its melting point, in the absence of a solvent. Also, as mentioned earlier, reactions of **1** with aromatic amines in refluxing toluene lead directly to the quinazolinones ("one-pot" preparations), although in low yield (30-54%).

In the cyclization reactions described so far, an amidine (**2**) derived from an *N*-ethoxycarbonylthioamide (**1**) and an aromatic amine is thermolyzed to form a 2-substituted 4(3*H*)-quinazolinone (**6**). The heterocyclic ring of the pro-

Table III

Ethyl 2-Aryl-3,4-dihydro-6-methyl-4-oxo-5-pyrimidinecarboxylates (**10**)



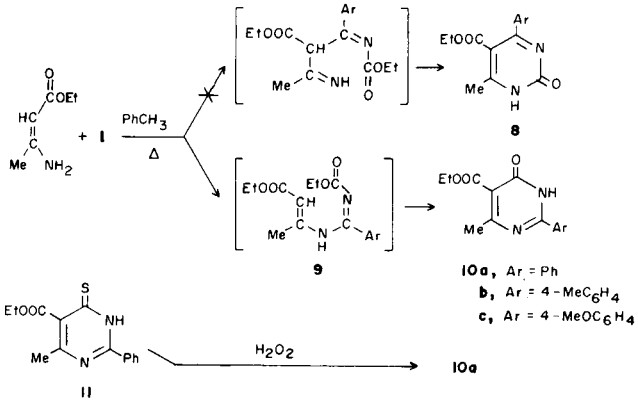
Compound No.	R	% Yield (a)	Mp °C (b)	Elemental Analysis, % Calcd. (Found) C	H	N	IR, cm⁻¹ C=O	¹H-NMR, ppm (c) Aromatic	R	COOEt	Me
10a	H	36	177.5-178.5	65.11 (65.23)	5.46 (5.56)	10.85 (10.78)	1710, 1650	7.4-7.6 (m, 3), 8.2-8.4 (m, 2)		1.4 (t, 3), 4.4 (q, 2)	2.5 (s, 3)
10b	Me	41	188.5-189	66.16 (66.16)	5.92 (5.72)	10.28 (10.28)	1710, 1650	7.3 (d, 2), 8.2 (d, 2)	2.4 (s, 3) (d)	1.4 (t, 3), 4.5 (q, 2)	2.5 (s, 3) (d)
10c	MeO	42	174-175.5	62.49 (62.19)	5.59 (5.46)	9.73 (9.73)	1700, 1650	7.0 (d, 2), 8.3 (d, 2)	3.9 (s, 3)	1.4 (t, 3), 4.4 (q, 2)	2.5 (s, 3)

(a) Crude or recrystallized product with melting point within 10° of that of the analytically pure compound. (b) Recrystallized from ethanol or 2-propanol. (c) Solutions in deuteriochloroform. (d) These assignments may be interchanged.

duct incorporates the formally "enamine" component of the aromatic amine, *i.e.*, its nitrogen atom and two carbon atoms of the benzene ring. This suggests the possibility of using primary enamines, instead of aromatic amines, for the preparation of amidines to be cyclized. However, when *N*-ethoxycarbonylthioamides (**1**) are allowed to react with ethyl 3-aminocrotonate in refluxing toluene, ethyl 2-aryl-3,4-dihydro-6-methyl-4-oxo-5-pyrimidinecarboxylates (**10**, Table III), are obtained as products. As for the previously mentioned reactions in toluene, the presumed intermediate amidines (**9**) lose ethanol under the reaction conditions to form the isolated products (Scheme II). In spite of the long time required for their completion (5-10 days) and their low yields (36-42%), these reactions may be considered of value as one-step syntheses of variously substituted pyrimidine derivatives. The structure assigned to the products (**10**) is supported by their ir spectra, which contain bands at 1710 and 1650 cm^{-1} corresponding to the ester and amide carbonyls, and their nmr spectra, which exhibit the expected signals for the ethyl, methyl and aryl groups. An alternative structure (**8**) is eliminated by the finding that **10a** is identical with the product of the hydrogen peroxide oxidation of an authentic sample of ethyl 3,4-dihydro-6-methyl-2-phenyl-4-thioxo-5-pyrimidinecarboxylate (**11**) (10,11).

In an analogous manner, *N*-ethoxycarbonylthioamides react with 2-amino-2-thiazoline in refluxing ethanol with evolution of hydrogen sulfide and formation of 2-aryl-6,7-dihydro-4*H*-thiazolo[3,2-*a*]-1,3,5-triazin-4-ones (**14**) in good yields (69-85%) (Table IV). Once again, under the reaction conditions, the anticipated amidines (**13**) cyclize with loss of ethanol to the isolated products (Scheme III). Because of the relatively low reaction temperature, formation of an imidoyl isocyanate intermediate is unlikely in these cases, which more probably involve cyclization of **13** by direct

Scheme III



Scheme IV

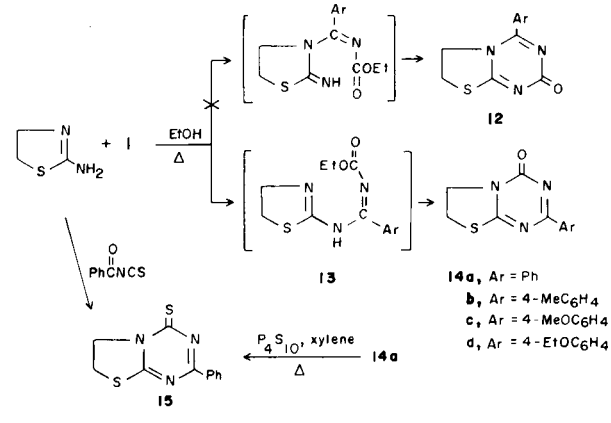
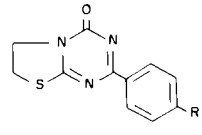


Table IV

2-Aryl-6,7-dihydro-4*H*-thiazolo[3,2-*a*]-1,3,5-triazin-4-ones (**14**)



Compound No.	R	% Yield (a)	Mp °C	Elemental Analysis, % Calcd. (Found) C	H	N	IR, cm^{-1} C=O	^{1}H-NMR, ppm (b) Aromatic	R	CH_2CH_2
14a	H	78	235.5-236.5 (c)	57.13 (57.12)	3.92 (4.17)	18.17 (18.04)	1680	7.5-7.7 (m, 3), 8.3-8.4 (m, 2)		3.6 (t, 2), 4.6 (t, 2)
14b	Me	69	242-243 (d)	58.76 (58.92)	4.51 (4.69)	17.13 (16.93)	1680	7.4 (d, 2), 8.2 (d, 2)	2.5 (s, 3)	3.8 (t, 2), 4.7 (t, 2)
14c	MeO	85	213.5-215 (e)	55.16 (55.22)	4.24 (4.33)	16.08 (16.01)	1680	7.1 (d, 2), 8.3 (d, 2)	3.9 (s, 3),	3.6 (t, 2), 4.4 (t, 2)
14d	EtO	81	208.5-210.5 (f)	56.71 (56.74)	4.76 (4.99)	15.26 (15.28)	1680	6.9 (d, 2), 8.5 (d, 2)	1.4 (t, 3), 4.1 (q, 2)	3.5 (t, 2) 4.6 (t, 2)

(a) Crude or recrystallized product with melting point within 10° of that of the analytically pure compound. (b) Solutions in deuteriochloroform for **14a,b,d**, in hexadeuteriodimethylsulfoxide for **14c**. (c) Recrystallized from ethanol. (d) Recrystallized from chloroform. (e) Recrystallized from 1-propanol (f) Recrystallized from 1-butanol.

nucleophilic attack of the ring nitrogen at the ester carbonyl. The structure assignment (**14**) for the products is consistent with their ir (conjugated carbonyl band at 1680 cm^{-1}) and nmr spectra (signals corresponding to CH_2CH_2, but not to CH_2CH_3 protons). Because of the ability of 2-amino-2-thiazoline, however, to act as a nucleophile through either its amino group, or its ring nitrogen atom (12), an isomeric structure **12** is in principle also possible. The assigned structure (**14**) is supported by the fact that treatment of **14a** with phosphorus pentasulfide in refluxing xylene yields thione **15**, identical with one of the products of the reaction of 2-amino-2-thiazoline with benzoyl isothiocyanate, the structure of which has been established (13).

EXPERIMENTAL

Melting points were determined in capillaries with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer using mineral oil mulls. The ^1H nmr spectra were obtained on a Varian EM360 spectrometer using solutions in the indicated solvents and tetramethylsilane as internal standard.

N-Aryl-*N'*-ethoxycarbonylamidines (**2**).

A mixture of 0.010 mole of an *N*-ethoxycarbonylthioamide (**1**), 0.020 mole of an aromatic amine, and 20 ml of ethanol was refluxed until the evolution of hydrogen sulfide had stopped, as indicated by lead acetate paper (14). After removal of the solvent by distillation under reduced pressure, the residue was triturated with petroleum ether (bp 60-80°) and recrystallized from aqueous ethanol. In the cases of **2i** and **2n**, the reaction mixture (at the end of the hydrogen sulfide evolution) was subjected to steam distillation and the residue was recrystallized from aqueous ethanol. Yields and physical properties of **2** are given in Table I.

2-Aryl-4(3*H*)-quinazolinones (**6**).

A. General Method.

A mixture of 0.30 to 1.0 g of an *N*-aryl-*N'*-ethoxycarbonylamidine (**2**) and 2 to 6 ml of quinoline was boiled in a small, open flask until the temperatue of the escaping vapor reached 150-160° (2-4 minutes). The resulting mixture was cooled, diluted with petroleum ether (bp 60-80°), and filtered to yield the crude **6**, which was recrystallized from *N,N*-dimethylformamide. Yields and physical properties of **6** are given in Table II.

B. In Diphenyl Ether.

Amidine **2i** (0.30 g, 1.0 mmole) was heated in 1 ml of diphenyl ether, and the product was treated as described above to yield 0.22 g (88%) of quinazolinone **6i**, mp 245-246°.

C. In the Absence of Solvent.

Amidine **2i** (0.35 g, 1.2 mmoles) was heated in an oil bath at 150-170° for 1.5 hours. The resulting solid was treated with petroleum ether (bp 60-80°) to yield 0.28 g (93%) of quinazolinone 6i, mp 240-242°.

D. One-pot Method.

A mixture of 0.010 mole of an *N*-ethoxycarbonylthioamide (**1**), 0.012 mole of an aromatic amine, and 10 ml of toluene was refluxed until the evolution of hydrogen sulfide had stopped (several days). The solid that precipitated on cooling was washed with cold methanol and recrystallized from *N,N*-dimethylformamide.

E. Without Purificiation of Amidine **2**.

A solution of 0.35 g (1.5 mmoles) of **1e** and 0.50 g (4.1 mmoles) of *o*-anisidine in 5 ml of ethanol was refluxed until the evolution of hydrogen sulfide had stopped. After distillation of the solvent under reduced pressure, the oily residue was steam distilled to remove the excess of the amine. The new residue was treated with ethyl ether, the resulting mixture was filtered, and the filtrate was evaporated to an oil. Heating of this with quinoline and further treatment as described under A yielded a crude solid, which was washed with cold ethanol to afford 0.10 g of quinazolinone **6m**, mp 228-229°. Concentration of the washings gave an additional 0.05 g of **6m**, mp 226-227° (total yield, 37%).

Ethyl 2-Aryl-3,4-dihydro-6-methyl-4-oxo-5-pyrimidinecarboxylates (**10**).

A mixture of 0.80 g (3.8 mmoles) of **1a**, 0.65 g (5.0 mmoles) of ethyl 3-aminocrotonate and, 10 ml of toluene was refluxed until evolution of hydrogen sulfide had stopped (5.5 days). Cooling of the reaction mixture, filtration, and washing of the precipitate with cold methanol gave 0.35 g (36%) of **10a**, mp 167-170°.

Similarly, 2.23 g (0.010 mole) of **1b**, 1.4 g (0.011 mole) of ethyl 3-aminocrotonate, and 10 ml of toluene were refluxed for 10 days. Upon cooling of the mixture, there was obtained 0.30 g of **10b**, mp 185-186°. Concentration of the filtrate gave two more crops of **10b**: 0.45 g, mp 186-187° and 0.35 g, mp 180-183° (total yield, 41%).

Finally, from 1.2 g (5.0 mmoles) of **1e**, 0.70 g (5.4 mmoles) of ethyl 3-aminocrotonate, and 10 ml of toluene refluxed for 5 days, there was obtained 0.60 g (42%) of **10c**, mp 161-165°.

Physical constants of **10** are shown in Table III.

Oxidation of Ethyl 3,4-Dihydro-6-methyl-2-phenyl-4-thioxo-5-pyrimidinecarboxylate (**11**) to **10a**.

A solution of 0.50 g of thione **11** (10,11) in 15 ml of 3% hydrogen peroxide and 10 ml of 10% aqueous sodium hydroxide was heated to its boiling point and then chilled. Acidification with concentrated hydrochloric acid precipitated a colorless solid, mp 177.5-178.5°. This was found to be identical in all respects with **10a**.

2-Aryl-6,7-dihydro-4*H*-thiazolo[3,2-*a*]-1,3,5-triazin-4-ones (**14**).

A mixture of 0.58 g (2.8 mmoles) of **1a**, 0.30 g (2.9 mmoles) of 2-amino-2-thiazoline, and 15 ml of ethanol was refluxed until evolution of hydrogen sulfide had stopped (16 hours). Chilling and filtration of the resulting mixture followed by washing of the precipitate with cold ethanol afforded 0.50 g (78%) of **14a**, mp 230-235°.

In a similar manner, 2.23 g (0.010 mole) of **1b**, 1.2 g (0.012 mole) of 2-amino-2-thiazoline, and 10 ml of ethanol were refluxed overnight to yield 1.7 g (69%) of **14b**, mp 232-235°.

From 1.2 g (5.0 mmoles) of **1c**, 1.0 g (0.010 mole) of 2-amino-2-thiazoline, and 20 ml of ethanol, upon refluxing overnight, there was obtained 1.1 g (85%) of **14c**, mp 210-213°.

Finally, 1.25 g (4.9 mmoles) of **1d**, 1.0 g (0.010 mole) of 2-amino-2-thiazoline, and 50 ml of ethanol were refluxed for 5 hours and then allowed to stand at room temperature overnight to yield 1.1 g (81%) of **14d**, mp 208-210°.

Physical constants of **14** are given in Table IV.

6,7-Dihydro-2-phenyl-4*H*-thiazolo[3,2-*a*]-1,3,5-triazine-4-thione (**15**).

A mixture of 0.50 g (2.2 mmole) of **14a**, 2.0 g of phosphorus pentasulfide, and 25 ml of xylene was refluxed for 24 hours. After it had been cooled, the resulting mixture was thoroughly mixed with 200 ml of ethyl ether. Filtration followed by removal of the solvents from the filtrate by distillation yielded a residue, which was boiled successively with several portions of chloroform. The chloroform solution was concentrated to give 0.20 g (37%) of crude product, mp 238-243°. The pure substance was obtained by recrystallization from chloroform, mp 242.5-243.5°. This was found to be identical in all respects with an authentic sample of **15** [lit (13) mp 242°].

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(14) Although in some cases this test was negative after only 3-4 hours, the reaction mixtures were routinely allowed to reflux overnight to ensure completion of the reaction. For compound **2e**, a 3-day refluxing period was found necessary.

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