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Studies on Organic Sulfur Compounds. VIII.[1] The Reaction of Alkoxycarbonyl Isothiocyanates and 2-Aminothiazole[2]

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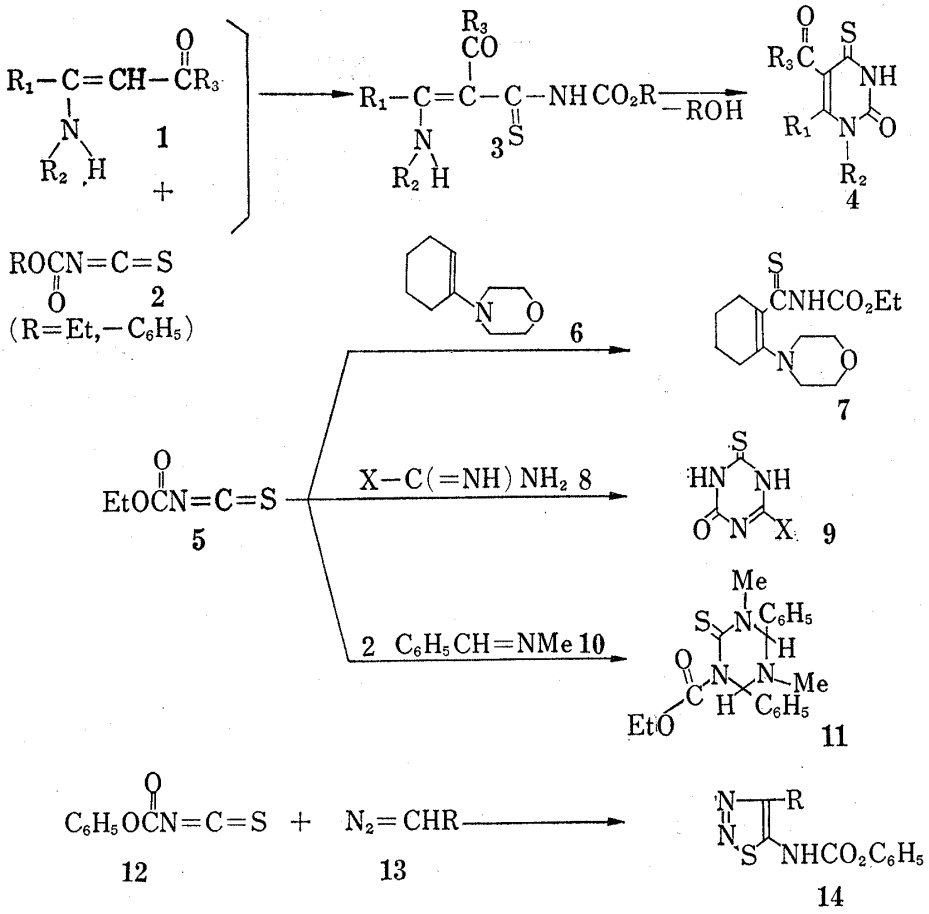
The reactions of some alkoxycarbonyl isothiocyanates (**2**) with 2-aminothiazol (**15**) afforded thiazolo[3,2-*a*]-*S*-triazine-4-thio-2-one (**27**), N-alkoxycarbonyl-N′-(2-thiazolyl)-thuoureas (A), alkyl-N-(2-thiazolyl)carbamates (B), N-alkoxycarbonyl thiocarbamates (C) and thiocyanic acid (**31**). However, in the case using phenoxycarbonyl isothiocyanate (**59**), the corresponding 1:1 adduct of (**59**) and (**15**) could not be obtained, but thiazolo-[3,2-*a*]-s-thiazine-2-thio-4-one (**32**) was isolated, besides the cyclic compound (**27**), thiazolyl carbamate (**60**) and phenol.

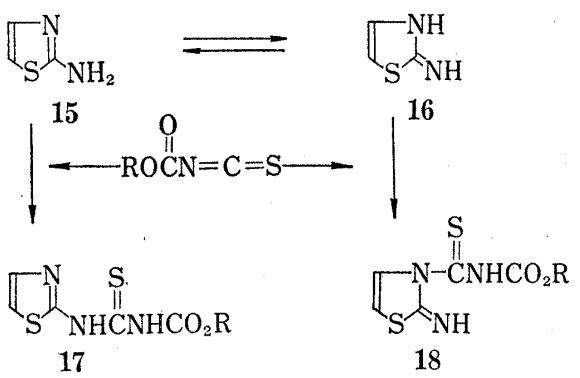
Since ever the synthesis of alkoxycarbonyl isothiocyanates and their addition reactions with some alkyl (or aryl) amines and alkanols were reported by R.E. Doran[4,5] and A.E. Dixon *et al.*,[6–8] until a recent date other studies on the chemical behavior of the alkoxycarbonyl isothiocyanates were rarely found in the literature. However, in 1963 A. Takamizawa *et al.*[9] isolated the two structural isomers, namely alkoxycarbonyl thiocyanates and isothiocyanates, from the reaction mixtures of potassium thiocyanate and chloroformates, and presented physical data for the two isomers. Since then a number of the interesting addition reactions of alkoxycarbonyl isothiocyanates with some enamines, imines, amidines or diazo compounds have been reported. For example, Goerdeler and co-workers[10–12] prepared 4-thiouracils (**4**) from β-aminocrotonic acid derivatives (**1**) and some alkoxycarbonyl isothiocyanates. Lamon[13] obtained 1-(N-carboethoxythiocarbamoyl)-2-(N-morpholino)cyclohexene (**7**) by the addition reaction of 1-(N-morpholino)cyclohexene (**6**) and ethoxycarbonyl isothiocyanate (**5**). Goerdeler and Neuffer[14] reported that ethoxycarbonyl isothiocyanate (**5**) reacted with amidinyl compounds (**8**), namely amidines, isoureas, isothioureas and guanidines, to give s-triazine-4-thio-2-ones (**9**). It was also reported that the isothiocyanate (**5**) formed a six-membered heterocycle (**11**) by means of cycloaddition with benzylidene N-methyl imine.[15] Furthermore, it has been known that 5-phenoxycarbonylamino-1,2,3-thiadiazoles (**14**) could

1) Part VII: M. Nagano and K. Tomita, *Chem. Pharm. Bull.* (Tokyo), **20**, 2308 (1972).
2) The 90th Annual Meeting of Pharmaceutical Society of Japan, Sapporo, 1970. Preliminary Report, p. II-30.
3) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
4) R.E. Doran, *J. Chem. Soc.*, **69**, 324 (1890).
5) R.E. Doran, *J. Chem. Soc.*, **79**, 906 (1901).
6) A.E. Dixon, *J. Chem. Soc.*, **75**, 375 (1899).
7) A.E. Dixon and J. Taylor, *J. Chem. Soc.*, **89**, 892 (1906).
8) A.E. Dixon and J. Taylor, *J. Chem. Soc.*, **93**, 906 (1908).
9) A. Takamizawa, K. Hirai, and K. Matsui, *Bull. Chem. Soc., Japan*, **36**, 1214 (1963).
10) J. Goerdeler and H. Horn, *Chem. Ber.*, **96**, 526 (1963).
11) J. Goerdeler and H. Keuser, *Chem. Ber.*, **97**, 3106 (1904).
12) J. Goerdeler and J. Gnad, *Chem. Ber.*, **98**, 1531 (1965).
13) R.W. Lamon, *J. Heterocycl. Chem.*, **5**, 837 (1968).
14) J. Goerdeler and J. Neuffer, *Chem. Ber.*, **104**, 1606 (1971).
15) J. Goerdeler and D. Wobig, Angew. *Chem.*, **79**, 272 (1967).

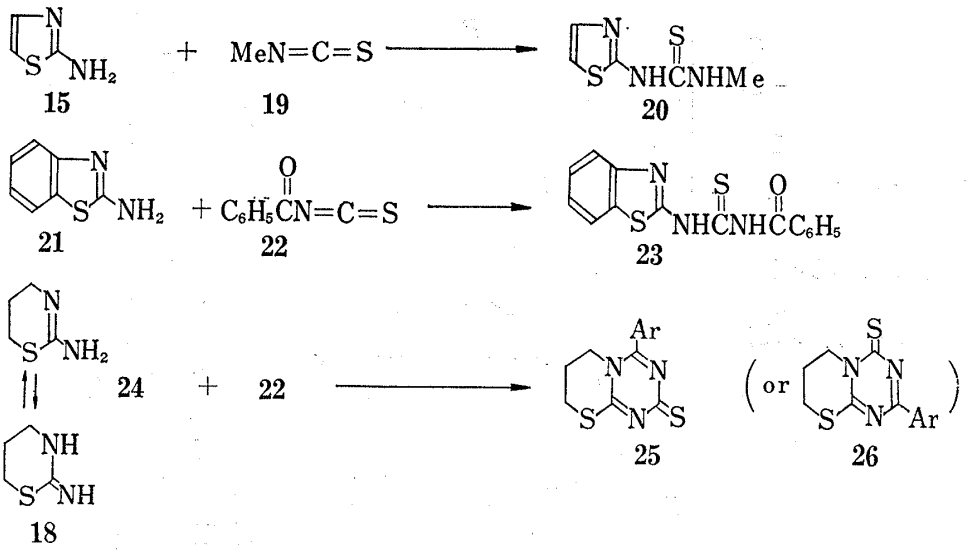


be prepared by 1,2-cycloaddition of phenoxycarbonyl isothiocyanate (**12**) and diazocompounds (**13**).[16]

There are no reports concerning the reactions of 2-aminoazoles and alkoxycarbonyl isothiocyanates. The present paper describes the reactions of some alkoxycarbonyl isothiocyanates and 2-aminothiazole. This amine may possibly exist in two forms, namely in an amino (**15**) and an imino form (**16**), in some solvents.[17] Supposedly then the addition reaction of alkoxycarbonyl isothiocyanates with 2-aminothiazole could afford two structually isomeric adducts (**17** and **18**). However, it is known that treatment of 2-aminothiazole (**15**) and 2-aminobenzothiazole (**21**) with methyl isothiocyanate (**19**) and benzoyl isothiocyanate (**22**) gave the corresponding adducts (**20**[18] and **23**[19]) respectively. Schobel *et al.*[19] reported also that the reaction of benzoyl isothiocyanate (**22**) with 2-aminopentiazoline (**24**) afforded a

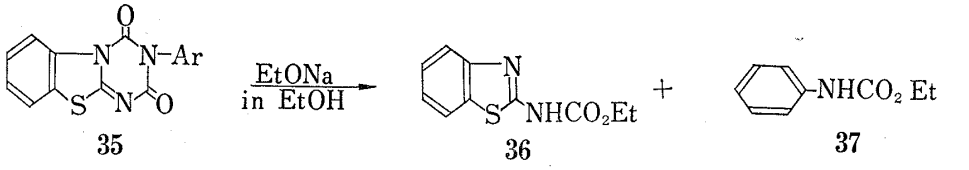


16) J. Goerdeler and G. Gnad, *Chem. Ber.*, **99**, 1618 (1966).
17) A.R. Katritzky and T.M. Lagowski, "The Principles of Heterocyclic Chemistry," Methuen, London, 1967.
18) Japan patent, 33080 (October 24, 1970).
19) A. Schobel and K.H. Magosch, *Libigs Ann. Chem.* **742**, 85 (1970).



bicyclic compound, whose structure was not confirmed to be either of the two isomers (**25** and **26**).

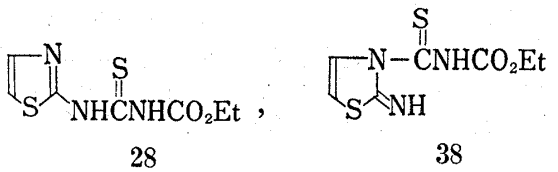
The mixture of equimolar amounts of 2-aminothiazole (**15**) and ethoxycarbonyl isothiocyanate (**5**) in ethyl acetate was allowed to stand overnight at room temperature and refluxed for one hour to afford four products (**27**, **28**, **29**, **30**) and thiocyanic acid (**31**). The molecular formula of the compound (**27**) was expressed as $C_5H_3N_3OS_2$ by the elemental analysis and mass spectrum (MS): $M^+=185$, and the infrared (IR) spectrum showed a carbonyl bond at 1680 cm^{-1} and a double bond at 1645 cm^{-1}. The nuclear magnetic resonance (NMR) spectrum consisted of a pair of doublets at 2.70 and 1.90 τ (two ring protons, $J=5.0$ Hz) and a signal approximately at -3.05 τ (one amide proton, broad). From these data, the structure of the compound (**27**) was regarded as a condensed ring structure (Chart 1). Gizycki and Oertel[20] obtained two carbamates (**36** and **37**) by the alcoholysis of benzothiazolo[3,2-*a*]-*s*-triazine-2,4-dione (**35**) with ethyl alcohol and sodium ethoxide. According to this method,



the above compound (**27**) was treated with methyl alcohol to afford methyl-N-(2-thiazolyl)-carbamate (**33**) in 80% yield, whose IR and NMR spectrum coincided with those of the sample obtained from 2-aminothiazole and methyl chloroformate (**34**). From this experiment the structure of compound (**27**) was consequently confirmed as thiazolo[3,2-*a*]-*s*-triazine-4-thio-2-one. Compound (**28**) was regarded as 1:1 reaction adduct of 2-aminothiazole (**15**) and ethoxycarbonyl isothiocyanate (**5**) on the basis of the elemental analysis and spectral data. The NMR spectrum consisted of three methyl protons (triplet, $J=7.0$ Hz) at 9.64 τ, two methylene protons (quartet, $J=7.0$ Hz) at 5.64 τ, two ring protons (a pair of doublets, $J=$ 3.6 Hz) at 2.90 and 2.38 τ, and two broad protons approximately at 1.62 and -2.46 τ. From these data, it was supposed that the possible structure of the addition product was **28** or **38**. However, this compound was heated at 180—190° for 20 minutes on an oil bath to afford the thiazolo[3,2-*a*]-*s*-triazine-2-thio-4-one (**32**). The IR spectrum of the compound (**32**) showed an amide group at 3150, 1755, and 1740 cm^{-1} [-C(S)NHC(O)-], and the NMR spectrum con-

20) U.V. Gizycki and G. Oertel., *Angew. Chem. internal. Edit.* **7**, 380 (1968).

sisted of ring protons (a pair of doublets, $J=$ 5.0 Hz) at 2.56 and 2.14 τ, and one broad proton approximately at $-2.56\,\tau$. From this experiment, the structure of the compound (**28**) was consequently confirmed as N-ethoxycarbonyl-N′-(2-thiazolyl)thiourea. The IR spectrum and melting point of ethyl-N-(2-thiazolyl)carbamate (**29**) agreed with those of the authentic compound prepared by the treatment of 2-aminothiazole (**15**) with ethyl chloroformate (**39**).[21] The IR spectrum of-N-ethoxycarbonyl thiocarbamate (**30**) coincided with that of the sample obtained by the addition reaction of ethoxycarbonyl isothiocyanate (**5**) with ethyl alcohol. Thiocyanic acid (**31**) formed in the reaction of **15** and **5** was ascertained by the color reaction with ferric chloride.



28 38

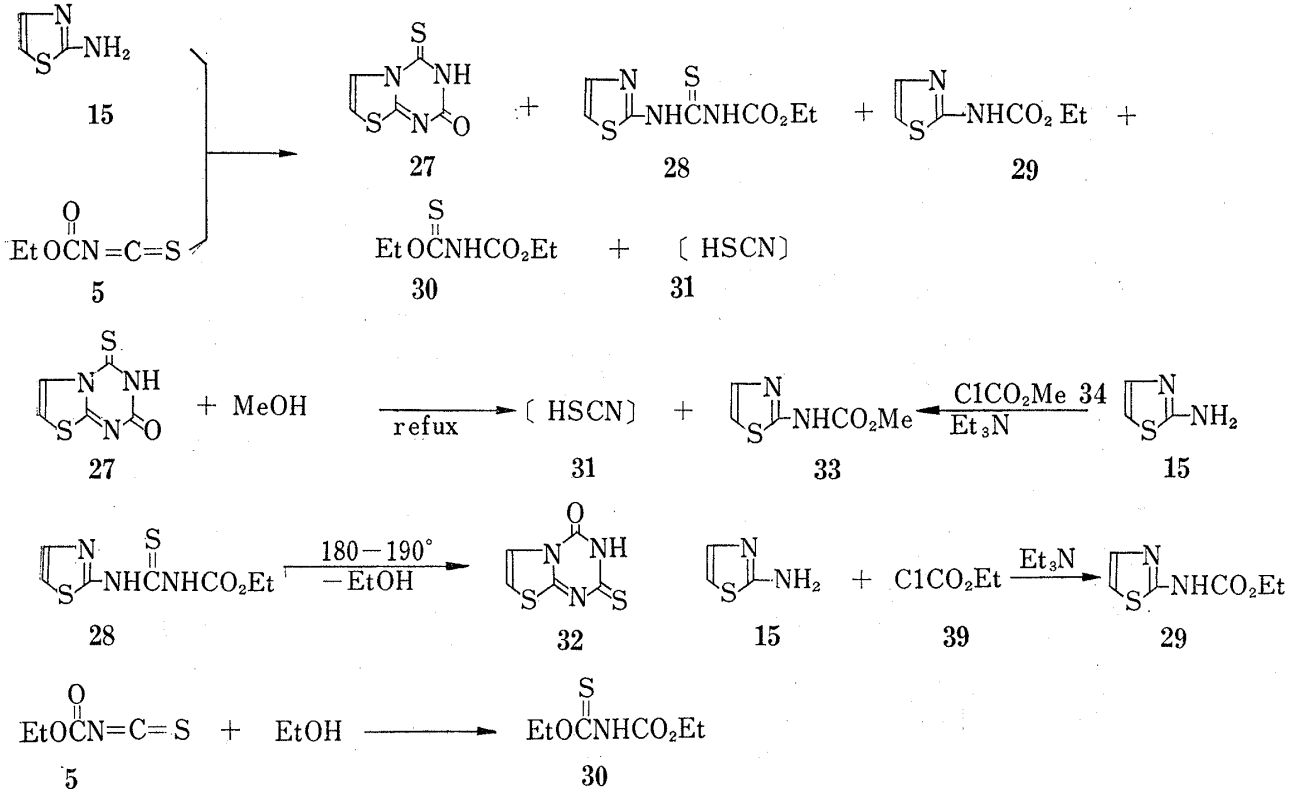
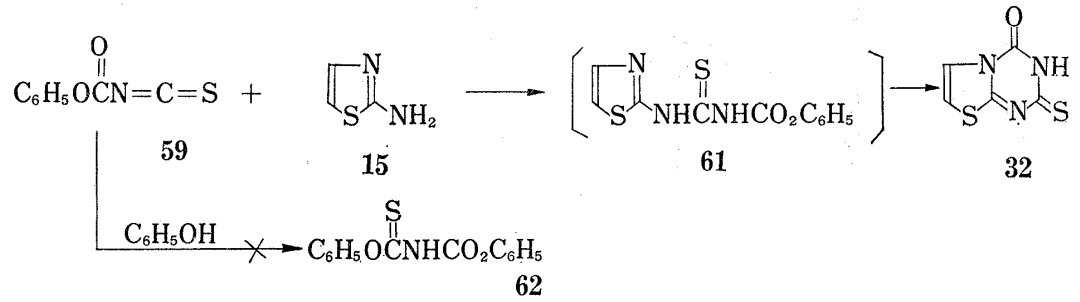


Chart 1

Other alkoxycarbonyl isothiocyanates (methoxy-, *n*-propoxy-, isopropoxy-, *n*-butoxy-, and isobutoxycarbonyl isothiocyanate) reacted with 2-aminothiazole (**15**) under similar reaction conditions to those of **15** and ethoxycarbonyl isothiocyanate (**5**) to give five products,



21) U.S.A. patent 2850503 (Sept. 2, 1958).

namely N-alkoxycarbonyl-N′-(2-thiazolyl)thioureas (A), alkyl-N-(2-thiazolyl)carbamates (B), the cyclic compound (**27**), alkyl alkoxycarbonyl thiocarbamates (C) and thiocyanic acid (**31**) in each case. However, in the case of phenoxycarbonyl isothiocyanate (**59**), the corresponding 1:1 adduct of **59** and **15** could not be obtained, but thiazolo[3,2-*a*]-*s*-triazine-2-thio-4-one

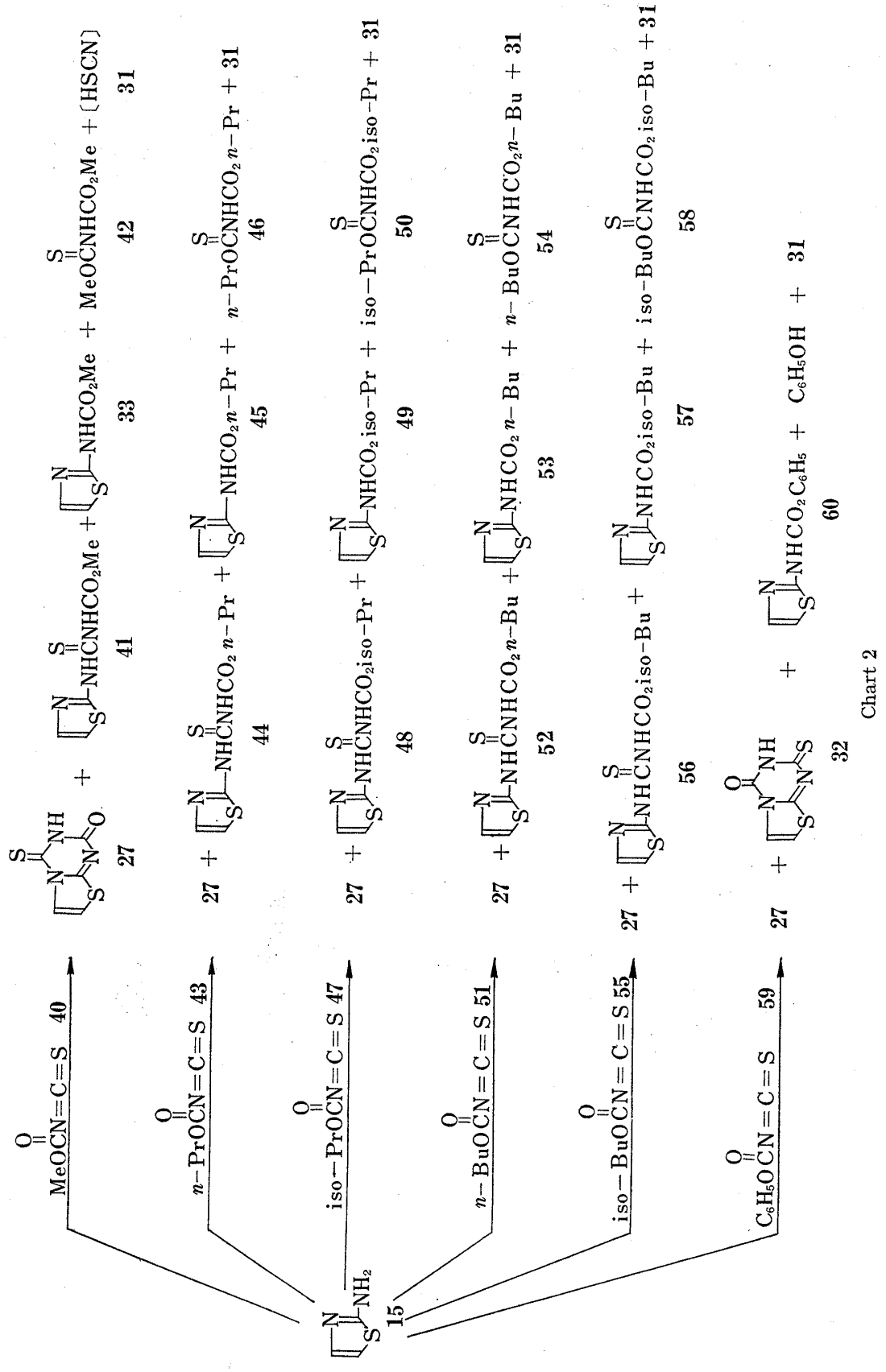
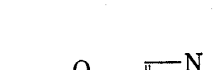
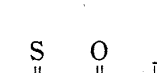
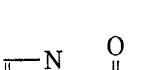
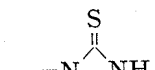
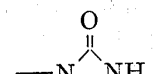


Chart 2

(**32**) was isolated, besides the cyclic compound (**27**), phenyl-N-(2-thiazolyl)carbamate (**60**) and phenol. Seemingly the postulated 1:1 adduct (**61**) cyclized easily to **32** by the elimination of phenol, and the phenol was unreactive with isothiocyanates to form the addition product (**62**).

Table 1. The Isolated Yields of the Products in the Reaction of Alkoxycarbonyl Isothiocyanates and 2-Aminothiazole.

R	$S{=}C{=}NCOR$	 (A)	 (B)	 **27**	 **32**	 (C)	HSCN	ROH
Me	**40**	**41** 38.6%	33 6.4%	40.5%		**42** 2.6%	+	
Et	**5**	**28** 50.0%	**29** 7.0%	29.0%		**30** 2.8%	+	
n-Pr	**43**	**44** 51.1%	**45** 8.1%	18.9%		**46** 3.4%	+	
iso-Pr	**47**	**48** 50.5%	**49** 8.6%	22.6%		**50** 3.4%	+	
n-Bu	**51**	**52** 54.0%	**53** 17.5%	18.6%		**54** 3.0%	+	
iso-Bu	**55**	**56** 46.2%	**57** 15.1%	25.9%		**58** 0.6%	+	
C_6H_5	**59**		**60** 20.4%	48.4%	21.6%		+	PHOH 87.0%

Experimental[22]

Reactants——Alkoxy- and phenoxycarbonyl isothiocyanates were prepared according to published papers.[7-9]

General Method for Reaction of Alkoxycarbonyl Isothiocyanates and 2-Aminothiazole——To a solution of 2-aminothiazole (0.01 mole) in AcOEt (30 ml), a solution of alkoxycarbonyl isothiocyanates in AcOEt (20 ml) was added dropwise at 0—5°, and the mixture was allowed to stand overnight. After the reaction solution was refluxed for 1 hr, the reaction mixture was washed with aqueous $NaHCO_3$ and H_2O, and dried over anhyd. Na_2SO_4. After removal of the solvent under reduced pressure, the residue was eluted with AcOEt–benzene on silica gel, and the isolated compounds were refined by recrystallization or distillation.

Reaction of Ethoxycarbonyl Isothiocyanate (5) with 2-Aminothiazole (15)——Ethoxycarbonyl isothiocyanate (1.31 g) was treated with 2-aminothiazole (1.0 g) to afford four compounds (**27**, **28**, **29**, and **30**). Thiazolo[3,2-*a*]-s-triazine-4-thio-2-one (**27**), 0.55 g, pale yellow needles from acetone, mp 268—270° (dec). *Anal.* Calcd. for $C_5H_3ON_3S_2$: C, 32.44; H, 1.63; N, 22.70; S, 34.50. Found: C, 32.57; H, 1.55; N, 22.73; S, 34.12. Mass Spectrum: $M^+=185$. IR ν_{max}^{Nujol} cm^{-1}: 3150 (NH), 1680 (>C=O), 1645 (>C=C< or –C=N–). NMR (DMSO-d_6) τ (J=Hz): 2.70 (1H, d., J=5.0), 1.90 (1H, d., J=5.0), *ca.* −3.05 (1H.). N-Ethoxycarbonyl-N′-(2-thiazolyl)thiourea (**28**), 1.15 g, pale yellow needles from ethyl acetate, mp 179—181° (dec). *Anal.* Calcd. for $C_7H_9O_2N_3S_2$: C, 36.37; H, 3.92; N, 18.18; S, 27.56. Found: C, 36.14; H, 4.07; N, 18.21; S, 27.52. IR ν_{max}^{Nujol} cm^{-1}: 3130 (>NH), 1728 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 9.64 (3H, t., J=7.0), 5.64 (2H, q., J=3.6), 2.38 (1H, d., J=3.6), 1.62 (1H), *ca.* −2.46 (1H). UV λ_{max}^{EtOH} mμ (ε): 229 (8400), 260 (16900), 306 (11200). Ethyl-N-(2-thiazolyl)carbamate (**29**)*[1], 0.12 g, colorless needles, from *n*-hexane-benzene, mp 156—157°. *Anal.* Calcd. for $C_6H_8O_2N_2S$: C, 41.86; H, 4.68; N, 16.28; S, 18.59. Found: C, 41.77; H, 4.86; N, 16.22; S, 18.59. IR ν_{max}^{Nujol} cm^{-1}: 3178 (>NH), 1730 (>C=O). UV λ_{max}^{EtOH} mμ (ε): 256 (9100). NMR ($CDCl_3$) τ (J=Hz): 8.61 (3H, t., J=7.5), 5.63 (2H, q., J=7.5), 3.04 (1H, d., J=3.8), 2.58 (1H, d., J=3.8), *ca.* −2.47 (1H). *[1]The compound (**29**) was also prepared by the reaction of 2-aminothiazole (**15**) and ethyl chloroformate (**39**) in the presence of triethyl amine.[21] Ethyl ethoxycarbonyl thiocarbamate

22) All melting and boiling points were uncorrected. NMR spectra were obtained in the specified solvents on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Mass spectrum was determined on a JEOL JMS-OISG spectrometer.

(**30**)*2, 0.05 g, pale yellow needles from *n*-hexane, mp 40—42°. *Anal.* Calcd. for $C_6H_{11}ON_3S$: C, 40.68; H, 6.26; N, 7.91; S, 18.06. Found: C, 40.35; H, 6.32; N, 7.99; S, 18.16. IR ν_{max}^{Nujol} cm^{-1}: 3225 (NH), 1775 (>C=O). UV λ_{max}^{EtOH} mμ (ε): 253.5 (15800). NMR ($CDCl_3$) τ (J=Hz): 8.68 (3H, t., J=7.0), 8.56 (3H, t., J=7.0), 5.74 (2H, q., J=7.0), 5.34 (2H, q., J=7.0), *ca.* 1.44 (1H). *2The compound (**30**) was easily prepared by the reaction of ethoxycarbonyl isothiocyanate (**5**) and EtOH.[5]

Methanolysis of Thiazolo[3,2-*a*]-*s*-triazine-4-thio-2-one (27)——The compound (**27**) (1.85 g) was refluxed in MeOH (100 ml) for 6 hr and the solvent was removed under reduced pressure. The residual solid was recrystallized from *n*-hexane-benzene to afford 1.26 g of methyl N-(2-thiazolyl)carbamate (**33**).

Preparation of Thiazolo[3,2-*a*]-*s*-triazine-2-thio-4-one (32)——N-Ethoxycarbonyl-N'-(2-thiazolyl)-thiourea (**28**) was heated at 180—190° for 20 minutes under N_2 gas, and the residual solid was recrystallized from acetone to give 0.37 g of the compound (**32**) as pale yellow needles of mp 229—232° (dec). *Anal.* Calcd. for $C_5H_3ON_3S_2$: C, 32.44; H, 1.63; N, 22.70; S, 34.50. Found: C, 32.36; H, 1.75; N, 22.89; S, 34.23. Mass spectrum: M^+=185. IR ν_{max}^{Nujol} cm^{-1}: 3150 (NH), 1755 and 1740 (>C=O). NMR (DMF) τ (J=Hz): 2.56 (1H, d., J=5.0), 2.14 (1H, d., J=5.0), *ca.* −2.56 (1H).

Reaction of Methoxycarbonyl Isothiocyanate (40) and 2-Aminothiazole (15)——Methoxycarbonyl isothiocyanate (1.29 g) was treated with 2-aminothiazole (1.0 g) to afford two compounds (**41** and **42**) besides 0.75 g of the compound (**27**) and 0.102 g of the compound (**33**). N-Methoxycarbonyl-N'-(2-thiazolyl)thiourea (**41**), 0.82 g, pale yellow needles from ethyl acetate, mp 169—171° (decomp.). *Anal.* Calcd. for $C_6H_7O_2N_3S_2$: C, 33.19; H, 3.25; N, 19.35; S, 29.49. Found: C, 33.41; H, 3.40; N, 19.43; S, 29.89. IR ν_{max}^{Nujol} cm^{-1}: 3175 (NH), 1724 (>C=O). UV λ_{max}^{EtOH} mμ (ε): 229 (8900), 260 (16900), 306 (11500). NMR ($CDCl_3$) τ (J=Hz): 6.10 (3H, s.), 2.90 (1H, d., J=4.0), 2.39 (1H, d., J=4.0), *ca.* 1.35 (1H), *ca.* −2.72 (1H). Methyl methoxycarbonyl thiocarbamate (**42**), 0.04 g, colorless needles from *n*-hexane, mp 45—46°. *Anal.* Calcd. for $C_4H_7ON_3S$: C, 32.22; H, 4.73; N, 9.40; S, 21.50. Found: C, 32.30; H, 4.80; N, 9.15; S, 21.39. UV λ_{max}^{EtOH} mμ (ε): 253 (16700). NMR ($CDCl_3$) τ (J=Hz): 6.19 (3H, s.), 5.85 (3H, s.), *ca.* 1.51 (1H).

Reaction of *n*-Propoxycarbonyl Isothiocyanate (43) and 2-Aminothiazole (15)——*n*-Propoxycarbonyl isothiocyanate (1.6 g) was reacted with 2-aminothiazol (1.0 g) to give three compounds (**44**, **45**, and **46**) besides (**27**) (0.35 g). N-*n*-Propoxycarbonyl-N'-(2-thiazolyl)thiourea (**44**), 1.28 g, pale yellow needles from ethyl acetate, mp 154—156° (decomp.). *Anal.* Calcd. for $C_8H_{11}O_2N_3S_2$: C, 39.19; H, 4.52; N, 17.14; S, 26.10. Found: C, 39.53; H, 4.66; N, 17.27; S, 25.70. IR ν_{max}^{Nujol} cm^{-1}: 3150 (NH), 1726 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 9.01 (3H, t., J=7.1), 8.12 (2H, q., t., J_1=7.1, J_2=7.0), 5.76 (2H, t., J=7.0), 2.96 (1H, d., J=4.0), 2.40 (1H, d., J=4.0), *ca.* 1.54 (1H), *ca.* −2.66 (1H). UV λ_{max}^{EtOH} mμ (ε): 228 (9500), 260 (17200), 305 (11200). *n*-Propyl N-(2-thiazolyl)carbamate (**45**), 0.15 g, colorless needles from *n*-hexane, mp 139—140°. *Anal.* Calcd. for $C_7H_{10}O_2N_2S$: C, 45.16; H, 5.41; N, 15.05; S, 17.19. Found: C, 45.26; H, 5.58; N, 15.27; S, 17.27. IR ν_{max}^{Nujol} cm^{-1}: 3200 (NH), 1730 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 8.92 (3H, t., J=7.0), 8.15 (2H, q., t., J_1=J_2=7.0), 5.60 (2H, t., J=7.0), 2.86 (1H, d., J=4.0), *ca.* −3.38 (1H). UV λ_{max}^{EtOH} mμ (ε): 255.7 (9200). *n*-Propyl N-*n*-propoxycarbonyl thiocarbamate (**46**), 0.06 g, pale yellow oil, bp 110—115°/0.7 mmHg (bath temp.). *Anal.* Calcd. for $C_8H_{15}NO_3S$: C, 46.82; H, 7.37; N, 6.83; S, 15.59. Found: C, 46.73; H, 7.43; N, 6.80; S, 15.52. IR $\nu_{max}^{Liq.}$ cm^{-1}: 2250 (NH), 1770 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 9.03 (3H, t., J=7.0), 8.96 (3H, t., J=7.0), 8.03 (2H, q., t., J_1=J_2=7.0), 8.28 (2H, q., t., J_1=J_2=7.0), 5.85 (2H, t., J=7.0), 5.50 (2H, t., J=7.0), *ca.* 1.64 (1H).

Reaction of Isopropoxycarbonyl Isothiocyanate (47) and 2-Aminothiazole (15)——Isopropoxycarbonyl isothiocyanate (1.6 g) was reacted with 2-aminothiazole (1.0 g) to afford three compounds (**48**, **49**, and **50**) besides (**27**) (0.42 g). N-Isopropoxycarbonyl-N'-(2-thiazolyl)thiourea (**48**), 1.27 g, colorless needles from ethyl acetate, mp 146—147° (dec). *Anal.* Calcd. for $C_8H_{11}O_2N_3S_2$: C, 39.19; H, 4.52; N, 17.14; S, 26.10. Found: C, 39.45; H, 4.51; N, 17.34; S, 25.92. IR ν_{max}^{Nujol} cm^{-1}: 3150 (NH), 1720 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 8.68 (6H, d., J=6.8), 4.92 (1H, q., q., J_1=J_2=6.8), 2.98 (1H, d., J=3.9), 2.40 (1H, d., J=3.9), *ca.* 1.46 (1H), *ca.* −2.90 (1H). UV λ_{max}^{EtOH} mμ (ε): 228.5 (9800), 260 (17900), 305 (11000). Isopropyl N-(2-thiazolyl)carbamate (**49**), 0.16 g, colorless needles from *n*-hexane, mp 127—128°. *Anal.* Calcd. for $C_7H_{10}N_2O_2S$: C, 45.16; H, 5.41; N, 15.05; S, 17.19. Found: C, 45.24; H, 5.56; N, 15.13; S, 17.38. IR ν_{max}^{Nujol} cm^{-1}: 3200 (NH), 1740 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 8.58 (6H, d., J=7.0), 4.71 (1H, q., q., J_1=J_2=7.0), 2.88 (1H, d., J=4.0), 2.35 (1H, d., J=4.0), *ca.* −3.33 (1H). UV λ_{max}^{EtOH} mμ (ε): 256 (9400). Isopropyl N-isopropoxycarbonyl thiocarbamate (**50**), 0.07 g, pale yellow oil, 103—115°/0.6 mmHg (bath temp.). *Anal.* Calcd. for $C_8H_{15}N_3O_3S$: C, 46.82; H, 7.37; N, 6.83; S, 15.59. Found: C, 46.67; H, 7.50; N, 6.99; S, 15.75. IR ν_{max}^{Nujol} cm^{-1}: 3280 (NH), 1773 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 8.90 (3H, d., J=7.0), 8.82 (3H, d., J=7.0), 5.01 (1H, q., q., J_1=J_2=7.0), 4.37 (1H, q., q., J_1=J_2=7.0), *ca.* 1.83 (1H). UV λ_{max}^{EtOH} mμ (ε): 255 (13700).

Reaction of *n*-Butoxycarbonyl Isothiocyanate (51) and 2-Aminothiazole (15)——*n*-Butoxycarbonyl isothiocyanate (1.75 g) was reacted with 2-aminothiazole (1.0 g) to afford three compounds (**52**, **53**, and **54**) besides (**27**) (0.27 g). N-*n*-Butoxycarbonyl-N'-(2-thiazolyl)thiourea (**52**), 1.40 g, colorless needles from ethyl acetate, mp 115—116° (dec). *Anal.* Calcd. for $C_9H_{13}O_2N_3S_2$: C, 41.70; H, 5.06; N, 16.21; S, 24.68. Found: C, 41.76; H, 5.19; N, 16.41; S, 24.55. IR ν_{max}^{Nujol} cm^{-1}: 3150 (NH), 1730 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 9.06 (3H, t., J=6.0), 7.94—9.02 (4H, m.), 5.50 (2H, t., J=6.0), 3.00 (1H, d., J=4.0), 2.22 (1H, d., J=4.0), *ca.* 1.30 (1H, m.), *ca.* −2.95 (1H, m.). UV λ_{max}^{EtOH} mμ (ε): 229 (9300), 259.5 (16900), 306 (11100). *n*-Butyl N-(2-thiazolyl)carbamate (**53**), 0.35 g, colorless needles from *n*-hexane, mp 122—124°. *Anal.*

Calcd. for $C_8H_{12}O_2N_2S$: C, 47.99; H, 6.04; N, 13.99; S, 15.97. Found: C, 47.72; H, 6.23; N, 14.06; S, 16.08. IR ν_{max}^{Nujol} cm^{-1}: 3170 (NH), 1725 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 8.98 (3H, t., J=6.8), 8.82—7.86 (4H, m.), 5.58 (2H, t., J=7.0), 2.86 (1H, d., J=4.0), 2.34 (1H, d., J=4.0), *ca.* −3.30 (1H). UV λ_{max}^{EtOH} mμ (ε): 256 (9400). *n*-Butyl N-*n*-Butoxycarbonyl thiocarbamate (**54**), 0.08 g, pale yellow oil, bp 130—135°/1.0 mmHg (bath temp.). *Anal.* Calcd. for $C_{10}H_{19}NO_3S$: C, 51.49; H, 8.21; N, 6.01; S, 13.72. Found: C, 51.59; H, 8.30; N, 6.06; S, 13.62. IR $\nu_{max}^{Liq.}$ cm^{-1}: 3250 (NH), 1780 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 9.06 (3H, t., J=6.0), 9.04 (3H, t., J=6.0), 9.04—7.90 (8H, m.), 5.84 (2H, t., J=6.0), 5.46 (2H, t., J=6.0), *ca.* 1.62 (1H). UV λ_{max}^{EtOH} mμ (ε): 254 (13500).

Reaction of Isobutoxycarbonyl Isothiocyanate (55) and 2-Aminothiazole (15)——Isobutoxycarbonyl isothiocyanate (1.75 g) was reacted with 2-aminothiazole (1.0 g) to afford three compounds (**56**, **57**, and **58**) besides (**27**) (0.48g). N-Isobutoxycarbonyl-N′-(2-thiazolyl)thiourea (**56**), 1.20 g, colorless needles from *n*-hexane-benzene, mp 135° (decomp.). *Anal.* Calcd. for $C_9H_{13}O_2N_3S_2$: C, 41.70; H, 5.06; N. 16.21; S, 24.68. Found: C, 41.70; H, 5.22; N, 16.12; S, 24.44. IR ν_{max}^{Nujol} cm^{-1}: 3150 (NH), 1730 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 9.05 (6H, d., J=7.0), 8.00 (1H, q., q., t., J_1=J_2=J_3=7.0), 5.95 (2H, d., J=7.0), 2.96 (1H, d., J=4.0), *ca.* 1.40 (1H), *ca.* −2.88 (1H). UV λ_{max}^{EtOH} mμ (ε): 229 (9600), 260 (17400), 305 (11500). Isobutyl N-(2-thiazolyl)carbamate (**57**), 0.3 g, colorless needles from *n*-hexane, mp 108—109°. *Anal.* Calcd. for $C_8H_{12}O_2N_2S$: C, 47.99; H, 6.04; N, 13.99; S, 15.97. Found: C, 47.75; H, 6.27; N, 13.97; S, 16.03. IR ν_{max}^{Nujol} cm^{-1}: 3200 (NH), 1730 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 8.95 (6H, d., J=7.0), 7.88 (1H, q., q., t., J_1=J_2=J_3=7.0), 5.77 (2H, d., J=7.0), 2.85 (1H, d., J=4.0), 2.30 (1H, d., J=4.0), *ca.* −3.38 (1H). UV λ_{max}^{EtOH} mμ (ε): 256 (9200). Isobutyl N-isobutoxycarbonyl thiocarbamate (**58**), 0.15 g, pale yellow oil, bp 130—135°/1.0 mmHg (bath temp.). *Anal.* Calcd. for $C_{10}H_{19}O_3NS$: C, 51.49; H, 8.21; N, 6.01; S, 13.72. Found: C, 51.70; H, 8.61; N, 6.29; S, 13.69. IR $\nu_{max}^{Liq.}$ cm^{-1}: 3250 (NH), 1770 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 9.03 (6H, d., J=6.5), 8.94 (6H, d., J=6.5), 8.16 (1H, q., q., t., J_1=J_2=J_3=6.5)., 7.87 (1H, q., q., t., J_1=J_2=J_3=6.5), 6.04 (2H, d., J=6.5), 5.68 (2H, d., J=6.5), *ca.* 1.46 (1H). UV λ_{max}^{EtOH} mμ (ε): 254 (13900).

Reaction of Phenoxycarbonyl Isothiocyanate (59) and 2-Aminothiazole (15)——Phenoxycarbonyl isothiocyanate (1.79 g) was reacted with 2-aminothiazole (1.0 g) to afford compound (**60**) besides (**27**) (0.94 g), (**32**) (0.4 g) and phenol (0.82 g), whose IR spectrum agreed with that of the authentic sample. Phenyl N-(2-thiazolyl)carbamate (**60**), 0.43 g, colorless needles from *n*-hexane, mp 178—180°. *Anal.* Calcd. for $C_{10}H_8O_2N_2S$: C, 54.55; H, 3.66; N, 21.72; S, 14.53. Found: C, 54.84; H, 3.90; N, 12.91; S, 14.33. IR ν_{max}^{Nujol} cm^{-1}: 3170 (NH), 1740 (>C=O). NMR ($CDCl_3$) τ (J=Hz): 2.82 (1H, d., J=4.0), 2.20 (1H, d., J=4.0), 2.80—2.20 (5H, m.), *ca.* −3.96 (1H).

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