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Studies on Organic Sulfur Compounds. X.[1] The Reactions of Alkoxycarbonyl Isothiocyanates with *prim*-α-Acetylenic Alcohols[2]

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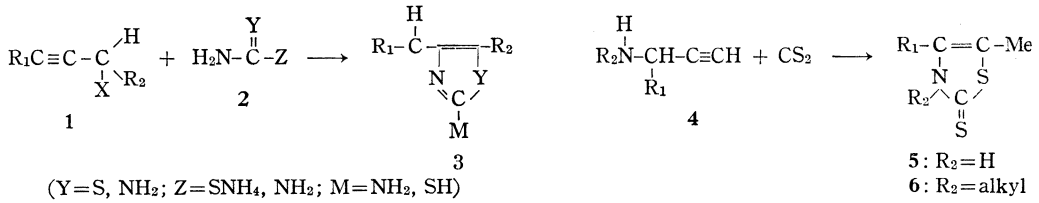
The reactions of alkoxycarbonyl isothiocyanates and *prim*-α-acetylenic alcohols afford N-alkoxycarbonyl-O-acetylenyl thiocarbamates, N-alkoxycarbonyl-S-allenyl thiolcarbamates and 4-alkylidene-2-alkoxycarbonylimino-1,3-oxathiolanes. However, the reaction patterns are dependent on the substituents on the 3-positions of α-acetylenic alcohols: 3-Phenyl-2-propyn-1-ol (**40**) react smoothly with the isothiocyanates to give 1:1 adducts which cyclize immediately to 4-benzylidene-1,3-oxathiolanes (**42**). 2-Butyn-1-ol (**36**) reacts slowly with the isothiocyanates to afford N-alkoxycarbonyl-O-2-butyn-1-yl thiocarbamates (**37**), but these compounds (**37**) cyclize hardly to 4-ethylidene-1,3-oxathiolanes (**39**) even in the presence of a base. In the case of 2-propyn-1-ol (**19**), N-alkoxycarbonyl-O-2-propyn-1-yl thiocarbamates (**24**), N-alkoxycarbonyl-S-allenyl thiolcarbamates (**25**) and 2-alkoxycarbonylimino-4-methylidene-1,3-oxathiolanes (**26**) are obtained. Furthermore, the cyclization mechanisms of α-acetylenyl thiocarbamates (**45**) were confirmed by using N(D)-O-(2-propyn-1-yl)-N-isopropoxycarbonyl thiocarbamate (**43**).

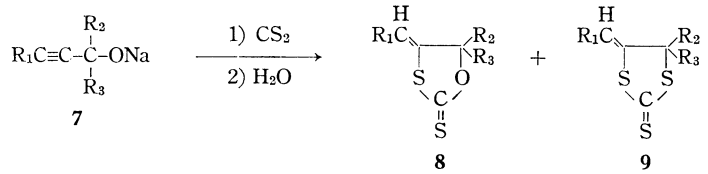
There are many reports concerning the intramolecular cyclization reactions of compounds having both a carbon–carbon triple bond and a nucleophilic radical. 2-Aminothiazole (**3**: Y=S; M=NH_2), 2-thiazolethiol (**3**: Y=S; M=SH), and 2-aminodiazole (**3**: Y=NH; M=NH_2) derivatives are prepared by treatment of α-haloacetylenic compounds (**1**) with thiourea, ammonium dithiocarbamate and guanidine, respectively.[4,5] 4-Methyl-2-thiazolethiols (**5**), and 4-methylthiazoline-2-thiones (**6**) are also obtained by the reactions of propargyl amines (**4**)[6,7] and carbon disulfide. Tomita, Nagano, and Oka[8,9] have reported that in the reactions of sodium α-acetylenic alcoholates (**7**) and carbon disulfide, two five

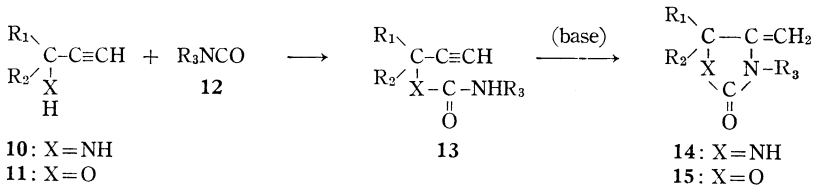


(Y=S, NH_2; Z=SNH_4, NH_2; M=NH_2, SH)

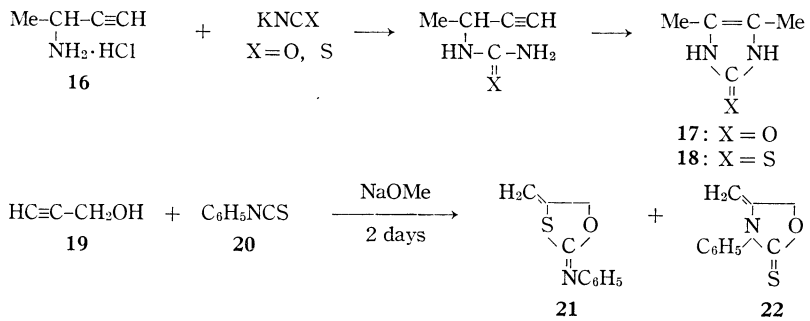
membered hetero compounds [4-alkylidene-1,3-oxathiolane-2-thiones (**8**) and -1,3-dithiolane-2-thiones (**9**)] are obtained. It is known that in the presence of a basic catalyst, propargyl amines (**10**) and propargyl alcohols (**11**) react with isocyanates (**12**) to give 4-methylidene-

1) Part IX: M. Nagano, T. Matsui, J. Tobitsuka, and K. Oyamada, *Chem. Pharm. Bull.* (Tokyo), **20**, 2626 (1972).
2) This was presented at the 5th Sympodium of Organic Sulfur Chemistry, Kiryu, February 1971.
3) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
4) Y. Yura, *Chem. Pharm. Bull.* (Tokyo), **10**, 372 (1962).
5) Y. Yura, *Chem. Pharm. Bull.* (Tokyo), **10**, 376 (1962).
6) Y. Yura, *Chem. Pharm. Bull.* (Tokyo), **10**, 1087 (1962).
7) J.W. Batty and B.C.L. Weedon, *J. Chem. Soc.*, **1944**, 746.
8) K. Tomita, M. Nagano, and H. Oka, *Chem. Pharm. Bull.* (Tokyo), **16**, 914 (1968).
9) K. Tomita and M. Nagano, *Chem. Pharm. Bull.* (Tokyo), **16**, 1324 (1968).





2-imidazolidinones (**14**) and -2-oxazolidinones (**15**), respectively.[10-12] Yura[6] has reported that 4,5-dimethyl-2-imidazoline (**17**) or -2-imidazolethiol (**18**) is prepared by treatment of 3-amino-1-butyne hydrochloride (**16**) with potassium cyanate or potassium thiocyanate, respectively. Furthermore, it has been reported by Shachat, *et al.*[10] that propargyl alcohol (**19**) reacts with phenyl isothiocyanate (**20**) in the presence of sodium methylate to afford two cyclic compounds (**21** and **22**). From these facts, α-acetylenic alcohols would be con-

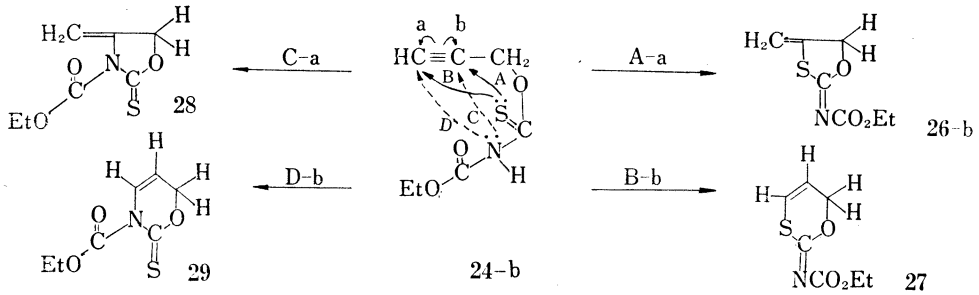


sidered to react with alkoxycarbonyl isothiocyanates to afford the corresponding thiocarbamates or their cyclization products. Nevertheless, we found no reports of such a reaction. The present paper describes on the reactions of some prim-α-acetylenic alcohols and some alkoxycarbonyl isothiocyanates (**23**).

Alkoxycarbonyl isothiocyanates (**23**) are easily decomposed by bases such as alcoholates, *tret.* amines and inorganic salts.[13,14] Therefore, the mixture of 2-propyn-1-ol(propargyl alcohol; 1.0 mole) and ethoxycarbonyl isothiocyanate (**23-b**; 1.1 mole) was heated at 70—80° on an oil bath for 5 hr without a solvent, and the reaction mixture was chromatographed over silica gel to give N-ethoxycarbonyl-O-(2-propyn-1-yl)thiocarbamate(**24-b**) in 12.3%, N-ethoxycarbonyl-S-(1,2-propadien-1-yl)thiolcarbamate(**25-b**) in 10.2% and 2-ethoxycarbonylimino-4-methylidene-1,3-oxathiolane(**26-b**) in 48.2% yield. Furthermore, the compound (**24-b**) transformed to **25-b** and **26-b** by the same thermal conditions as above. However, a similar phenomenon has been already observed in the rearrangement of α-acetylenyl xanthates to the corresponding allenyl thiolcarbonates.[15] The structures of **24-b** and **25-b** were

10) N. Shachat and J.J. Bagnell, Jr., *J. Org, Chem.*, **28**, 991 (1963).
11) K. Sisido, K. Hukuoka, M. Tuda, and H. Nozaki, *J. Org. Chem.*, **27**, 2663 (1962).
12) N.R. Easton, D.R. Cassady, and R.D. Dillard, *J. Org. Chem.*, **27**, 2927 (1962).
13) A. Takamizawa, K. Hirai, and K. Matsui, *Bull. Chem. Soc. Japan*, **36**, 1214 (1962).
14) J. Goerdeler, *Q. Reports on Sulfur Chemistry*, **5**, 1619 (1970).
15) K. Tomita and M. Nagano, *Chem. Pharm. Bull.* (Tokyo), **16**, 1911 (1968).

determined on the basis of elemental analyses and spectral data. The characteristic infrared (IR) absorption bands of the former compound (**24-b**) were observed at 3400 and 1775 cm^{-1} for a secondary amide [-C(O)NH-], at 3300 and 2120 cm^{-1} for an ethynyl group (HC≡C-); the nuclear magnetic resonance (NMR) spectrum showed a triplet at 8.69 τ for three methyl protons (-$CH_2\underline{C}H_3$, J=7.0 Hz), a triplet at 7.43 τ for one ethynyl proton ($\underline{H}C\equiv C$-, J=2.2 Hz), a quartet at 5.74 τ for two methylene protons (-$C\underline{H}_2CH_3$, J=7.0 Hz) and a doublet at 4.85 τ for two methylene protons (HC≡C-$\underline{C}H_2$, J=2.2 Hz) and approximately at 1.62 τ for one secondary amide proton (>NH). The characteristic IR absorption bands of the latter compound (**25-b**), which would be formed by the [3,3]-sigmatropic rearrangement of **24-b**, were observed at 3400, 1755, and 1685 cm^{-1} for a secondary amide [-C(O)NHC(O)-], and at 1955 cm^{-1} for an allene group (-C=C=C-), and the NMR spectrum showed a triplet at 8.67 τ for three methyl protons (-$CH_3\underline{C}H_3$, J=7.0 Hz), a quartet at 5.72 τ for two methylene protons (-$CH_2\underline{C}H_3$, J=7.0 Hz), a doublet at 4.92 τ for two vinylidene protons (=C=$\underline{C}H_2$, J=6.5 Hz), a triplet at 2.90 τ for one vinylidene proton (-$\underline{H}C$=C=C, J=6.5 Hz), and approximately at 2.05 τ for one secondary amide proton [-C(O)N$\underline{H}$C(O)-]. However, it is not clear why the coupling constants of the protons of the above allene group (**25-b**) are larger than those of general allene compounds.[15] Compound (**26-b**) was indicated as being a 1:1 addition product of **23-b** and **19** by elemental analysis and mass spectrum (MS): M^+=187, and the characteristic IR absorption bands were at 1678 cm^{-1} for a carbonyl group(>C=O), at 1635 cm^{-1} for a carbon-carbon double bond (>C=C<), and at 1580 cm^{-1} for a conjugated carbon-nitrogen double bond [=N-C(O)-]. From these data, four possible structures (**26-b**, **27**, **28**, and **29**), which would be formed by four intramolecular cyclization processes of **24-b**, were considered



for this compound. The NMR spectrum showed a triplet at 8.67 τ for three methyl protons (-$CH_2\underline{C}H_3$, J=7.0 Hz), a quartet at 6.77 τ for two methylene protons (-$\underline{C}H_2CH_3$, J=7.0 Hz), four peaks (a triplet and a doublet) centered at 4.92 τ for one unequivalent methylene proton ($\underline{H}a$>C=, J_1=2.5 Hz, J_2=2.3 Hz), and four peaks (a triplet and a doublet centered at 4.63 τ for one another methylene proton ($\underline{H}a$>C=, J_1=2.5 Hz, J_2=2.3 Hz). The NMR spectrum was more similar to that of the compound (**21**) than that of the compound (**22**) (see Fig. 1). For further confirmation, this compound (**26-b**) was hydrolyzed with one normal hydrogen chloride to give O-acetonyl-N-ethoxycarbonyl-carbamate (**30**) which was also obtained by oxydation of O-acetonyl-N-ethoxycarbonyl-thiocarbamate (**32**). Compound (**21**) was treated with normal hydrogen chloride to afford 4-methylidene-1,3-oxathiolane-2-one (**33**) which was also prepared by oxidation of 4-methylidene-1,3-oxathiolane-2-thione (**34**)[8] with mercuric acetate, but in the case of compound (**22**) the *exo* double bond rearranged to form 5-methyl-1-phenyl-oxazoline-2-thione (**35**). From these data, the structure of **26-b** was consequently confirmed as being 2-ethoxycarbonylimino-4-methylidene-1,3-oxathiolane. The yields of the products in the reactions of alkoxycarbonyl isothiocyanates (**23**) with 2-propyn-1-ol (**19**) are summarized in Table I.

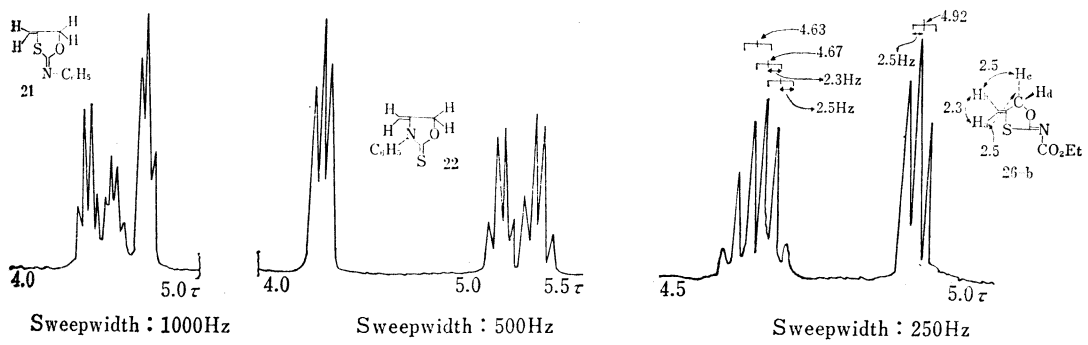


Fig. 1. NMR Spectra ($CDCl_3$) of 4-Methylidene-2-phenylimino-1,3-oxathiolane (**21**), 4-Methylidene-3-phenyl-oxazolidine-2-thione (**22**), and 2-Ethoxycarbonylimino-4-methylidene-1,3-oxathiolane (**26-b**).

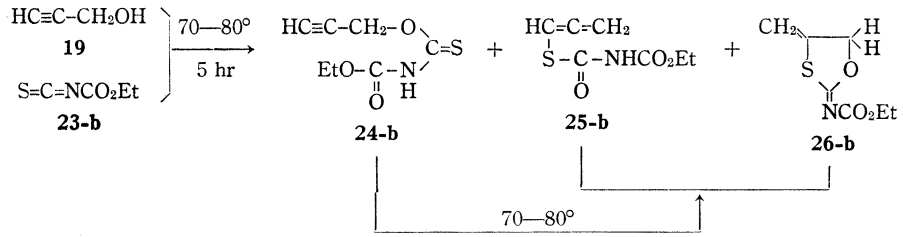


Chart 1

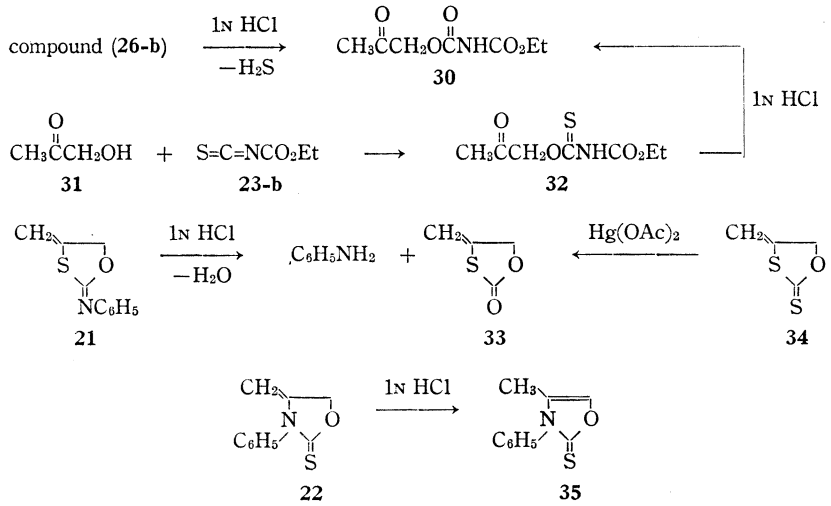


Chart 2

A mixture of 2-butyn-1-ol (**36**) and ethoxycarbonyl isothiocyanate (**23-b**) in carbon tetrachloride was refluxed for 3 hr, and the resulting residue was chromatographed to give only N-ethoxycarbonyl-O-(2-butyn-1-yl)thiocarbamate(**37-b**) in 76.3% yield. The yield of **37-b** under this reaction condition was larger than when no solvent was employed. The adduct (**37-b**) was heated at 120—130° for 3 hr to afford N-ethoxycarbonyl-S-(2,3-butadien-2-yl)thiolcarbamate (**38**) in 21.4% yield. However, when **37-b** was treated with triethyl amine in ethyl alcohol, 2-ethoxycarbonylimino-4-ethylidene-1,3-oxathiolane (**39-b**) was obtained in 55.7% yield. Other alkoxycarbonyl isothiocyanates were reacted with **36** under

Table I. Yields of Isolated Products in the Reactions of Alkoxycarbonyl Isothiocyanates (**23**) with 2-Propyn-1-ol (**19**)

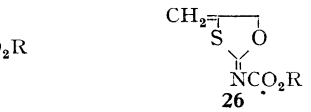
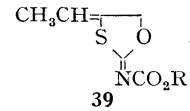
$S{=}C{=}NCO_2R$ **23**	$HC{\equiv}C\text{-}CH_2\text{-}O$ $ROC\text{-}N\text{-}C{=}S$ $\|\ \ \ \|$ $O\ \ H$ **24**	$HC{=}C{=}CH_2$ $S\text{-}C\text{-}NHCO_2R$ $\|$ O **25**	 **26**
23-a: R=Me	**24-a**: 14.9 (%)	**25-a**: 10.3 (%)	**26-a**: 55.4 (%)
23-b: R=Et	**24-b**: 12.3 (%)	**25-b**: 10.2 (%)	**26-b**: 48.2 (%)
23-c: R=*n*-Pr	**24-c**: 10.2 (%)	**25-c**: 9.4% (%)	**26-c**: 49.3 (%)
23-d: R=iso-Pr	**24-d**: 9.8 (%)	**25-d**: 8.2 (%)	**26-d**: 44.1 (%)
23-e: R=*n*-Bu	**24-e**: 12.1 (%)	**25-e**: 5.3 (%)	**26-e**: 41.8 (%)
23-f: R=iso-Bu	**24-f**: 14.9 (%)	not isolated	**26-f**: 32.1 (%)

Table II. Yields of 2-Butyn-1-yl-N-alkoxycarbonyl-thiocarbamates (**37**) and Their Cyclization Products (**39**)

$CH_3C{\equiv}C\text{-}CH_2OC(=S)NHCO_2R$ **37**	Et_3N in EtOH	 **39**
R=Me (**37-a**): 82.9 (%)	⟶	R=Me (**39-a**): 60.2 (%)
R=Et (**37-b**): 76.3 (%)		R=Et (**39-b**): 55.7 (%)
R=*n*-Pr (**37-c**): 58.4 (%)		R=*n*-PR (**39-c**): 42.3 (%)
R=iso-Pr (**37-d**): 60.2 (%)		R=iso-Pr (**39-d**): 42.6 (%)
R=*n*-Bu (**37-e**): 21.9 (%)		R=*n*-Bu (**39-e**): 22.5 (%)
R=iso-Bu (**37-f**): 22.4 (%)		R=iso-Bu (**39-f**): 23.3 (%)

similar reaction conditions as above, and then the resulting addition compounds (**37**) were treated with triethyl amine to afford the corresponding cyclization compounds (**39**). The yields of **37** and **39** are summarized in Table II.

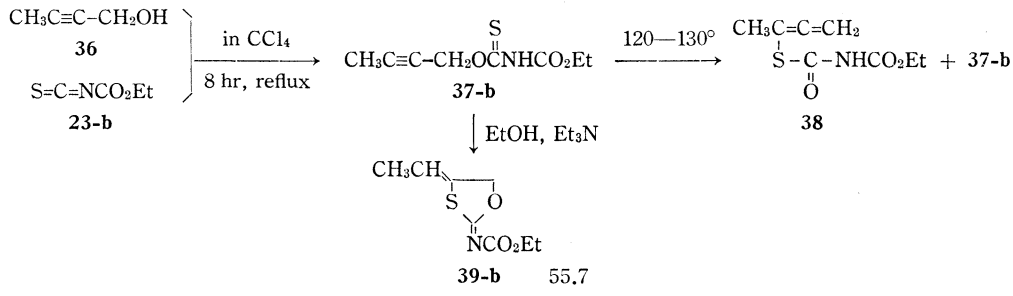
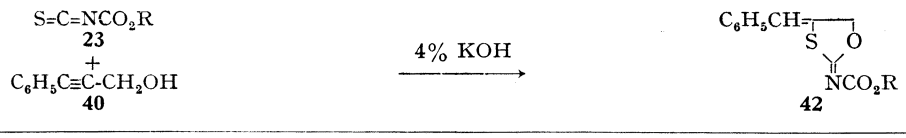


Chart 3

3-Phenyl-2-propyn-1-ol (**40**) was reacted with ethoxycarbonyl isothiocyanate (**23-b**) at 50—70° for 5 hr with no solvent, and then the reaction mixture was chromatographed over silica gel to give N-ethoxycarbonyl-O-(3-phenyl-2-propyn-1-yl)thiocarbamate (**41**) in 5.7% and 4-benzylidene-2-ethoxycarbonylimino-1,3-oxathiolane(**42-b**) in 71.5% yield. However, the adduct (**41**) was so unstable that on treatment with 4% potassium hydroxide at room temperature, it cyclized immediately to form **42-b**. The reaction mixtures of other alkoxycarbonyl isothiocyanates and **40** were treated with 4% potassium hydroxide under the same

TABLE III. Yields of 4-Benzylidene-2-alkoxycarbonylimino-1,3-oxathiolanes (**42**)



R=Me (**23-a**)	**42-a**: 90.3 (%)
R=Et (**23-b**)	**42-b**: 86.9 (%)
R=*n*-Pr (**23-c**)	**42-c**: 72.3 (%)
R=iso-Pr (**23-d**)	**42-d**: 72.4 (%)
R=*n*-Bu (**23-e**)	**42-e**: 68.5 (%)
R=iso-Bu (**23-f**)	**42-f**: 69.0 (%)

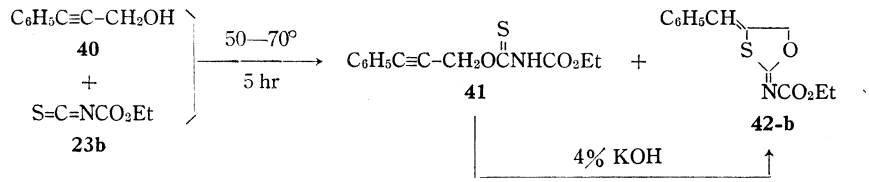


Chart 4

reaction conditions as above. The yields of the corresponding cyclic compounds (**42**) are summarized in Table III.

The reaction patterns of alkoxycarbonyl isothiocyanates (**23**) with prim-α-acetylenic alcohols were dependent on the substituent groups at the 3-position of the alcohols. 3-Phenyl-2-propyn-1-ol (**40**) reacted smoothly with alkoxycarbonyl isothiocyanates (**23**) to give 1:1 adducts which cyclized readily to **42** in the presence of a base. On the contrary, 2-butyn-1-ol (**36**) reacted slowly with the isothiocyanates (**23**) to afford 1:1 adducts (**37**), and these adducts hardly underwent intramolecular cyclization. However, in the reactions of 2-propyn-1-ol (**19**) with the isothiocyanates, the corresponding 1:1 adducts (**24**), the [3,3]-sigmatropic rearrangement products (**25**) and the five membered cyclic compounds (**26**) were obtained. On the other hand, the larger the alkyl groups of alkoxycarbonyl isothiocyanates (**23**) were, the lower the yields of reaction products were.

For further confirmation of the mechanism of the formation of the 4-alkylidene-2-ethoxycarbonylimino-1,3-oxathiolanes (**46**), N(D)-O-(2-propyn-1-yl)isopropoxycarbonyl-thiocarba-

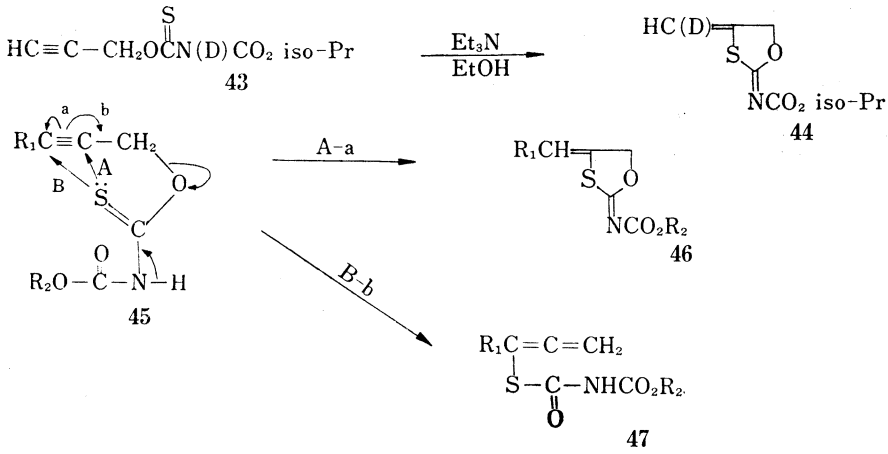


Chart 5

mate (**43**), which was prepared by the treatment of O-(2-propyn-1-yl)isopropoxycarbonyl-thiocarbamate (**24-d**) with heavy water (D_2O), was heated in triethyl amine to afford 2-isopropoxycarbonylimino-4-D-methylidene-1,3-oxathiolane (**44**). The structures of the compounds (**43** and **44**) were confirmed on the basis of elemental analyses and spectral data. From above experimental data, it became clear that O-acetylenyl-N-alkoxycarbonyl-thiocarbamates (**45**) should cyclize intramolecularly to give the products (**46**) *via* course A-a, and on the other hand, the allenes (**47**) would be formed by [3,3]-sigmatropic rearrangement of the compound (**45**) *via* course B-b (Chart 5).

Experimental[16]

General Method for Reactions of Alkoxycarbonyl Isothiocyanates (23) and 2-Propyn-1-ol (19)——The mixtures of 0.022 mole of alkoxycarbonyl isothiocyanates (**23**) and 0.02 mole of 2-propyn-1-ol (**19**) were stirred at room temperature for 1 hr, was heated at 70—80° in nitrogen atomosphere for 5 hr on an oil bath. The reaction mixtures, without further treatment with a base or an acid, was eluted with benzene–AcOEt on silica gel. The isolated products were recrystallized from a suitable solvent.

Reaction of Methoxycarbonyl Isothiocyanate (23-a) and 2-Propyn-1-ol (19)——2.85 g of **23-a** was reacted with 1.12 g of **19** by the general method to afford three products (**24-a**, **25-a** and **26-a**). O-2-Propynyl-N-methoxycarbonyl-thiocarbamate (**24-a**), 0.57 g, colorless needles from ether–pet. ether, mp 53—55°. *Anal.* Calcd. for $C_6H_7O_3NS$: C, 41.62; H, 4.08; N, 8.09; S, 18.48. Found: C, 41.27; H, 4.59; N, 7.99; S, 18.46. IR ν_{max}^{Nujol} cm^{-1}: 3320 and 2120 (HC≡C–), 3220 and 1772 [–C(O)NHC(S)–]. NMR ($CDCl_3$)τ(J=Hz): 7.40 (1H, t, J=2.8), 6.18 (3H, s), 4.84 (2H, d, J=2.8), *ca.* 1.61 (1H, broad). N-Methoxycarbonyl-S-1,2-propadien-1-yl-thiolcarbamate (**25-a**), 0.36 g, colorless needles from ether–pet. ether, mp 106—108°. *Anal.* Calcd. for $C_6H_7O_3NS$: C, 41.62; H, 4.08; N, 8.09; S, 18.48. Found: C, 41.41; H, 4.12; N, 7.76; S, 18.56. IR ν_{max}^{Nujol} cm^{-1}: 2200 (–C=C=C–), 3175, 1754 and 1655 [–C(O)NHC(O)–]. NMR ($CDCl_3$)τ(J=Hz): 7.17 (3H, s), 4.90 (2H, d, J=6.5), 3.68 (1H, t, J=6.5), *ca.* 1.71 (1H, broad). 2-Methoxycarbonylimino-4-methylidene-1,3-oxathiolane (**26-a**), 1.91 g, colorless needles from benzene–*n*-hexane. mp 89—90°. *Anal.* Calcd. for $C_6H_7O_3NS$: C, 41.62; H, 4.08; N, 8.09; S, 18.48. Found: C, 41.76; H, 4.11; N, 7.96; S, 18.60. IR ν_{max}^{Nujol} cm^{-1}: 1688 (>C=O), 1630 (>C=C<), 1572 (>C=N–). NMR ($CDCl_3$) τ (J=Hz): 6.15 (3H, s), 4.88 for two equivalent ring methylene protons (–$\underline{CH_2}$–; t, J=2.5), 4.88 for one nonequivalent exo methylene proton ($\frac{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3), 4.65 for another nonequivalent exo methylene proton ($\frac{Ha}{\underline{Hb}}$>=; t, d, J_1=2.5, J_2=2.3).

Reaction of Ethoxycarbonyl Isothiocyanate (23-b) and 2-Propyn-1-ol (19)——2.89 g of **23-b** was reacted with 1.12 g of **19** by the general method to afford three products (**24-b**, **25-b** and **26-b**): O-2-Propynyl-N-ethoxycarbonyl-thiocarbamate (**24-b**), 0.46 g, pale yellow needles from ether–pet. ether, mp 50—52°. *Anal.* Calcd. for $C_7H_9O_3NS$: C, 44.92; H, 4.84; N, 7.48; S, 17.12. Found: C, 44.62; H, 4.95; N, 7.36; S, 16.82. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300 and 2120 (HC≡C–), 3400 and 1770 [–C(O)NHC(S)–]. NMR ($CDCl_3$)τ(J=Hz): 8.69 (3H, t, J=7.0), 7.43 (1H, t, J=2.2), 5.74 (2H, q, J=7.0), 4.85 (2H, d, J=2.2), *ca.* 1.62 (1H, broad). UV λ_{max}^{EtOH} mμ (ε): 259 (7500). N-Ethoxycarbonyl-S-1,2-propadien-1-yl-thiolcarbamate (**25-b**), 0.382 g, colorless needles from ether–pet. ether, mp 78—80°. *Anal.* Calcd. for $C_7H_9O_3NS$: C, 44.92; H, 4.84; N, 7.48; S, 17.12. Found: C, 44.93; H, 5.00; N, 7.43; S, 16.97. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1955 (–C=C=C–), 3400, 1755 and 1675 [–C(O)NHC(O)–]. NMR ($CDCl_3$) τ (J=Hz): 8.67 (3H, t, J=7.0), 5.72 (2H, q, J=7.0), 4.92 (2H, d, J=7.0), 2.90 (1H, t, J=7.0), *ca.* 2.05 (1H, broad). UV $\lambda_{max}^{Dioxane}$ mμ (ε): 238 (6500). 2-Ethoxycarbonylimino-4-methylidene-1,3-oxathiolane (**26-b**), 1.80 g, colorless needles from *n*-hexane, mp 108—109°. *Anal.* Calcd. for $C_7H_9O_3NS$: C, 44.92; H, 4.84; N, 7.48; S, 17.12. Found: C, 45.07; H, 4.93; N, 7.46; S, 17.04. Mass Spectrum *m/e*: M$^+$=187. IR ν_{max}^{Nujol} cm^{-1}: 1677 (>C=O), 1637 (>C=C<), 1580 (>C=N–). NMR ($CDCl_3$) τ(J=Hz): 8.67 (3H, t, J=7.0), 6.77 (2H, q, J=7.0), 4.92 (2H, t, J=2.5), 4.63 for one nonequivalent exo methylene proton ($\frac{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3), 4.67 for another nonequivalent exo methylene proton ($\frac{Ha}{\underline{Hb}}$>=; t, d, J_1=2.5, J_2=2.3). UV λ_{max}^{EtOH} mμ (ε): 259.5 (6700).

Hydrolysis of 2-Ethoxycarbonylimino-4-methylidene-1,3-oxathiolane (26-b)——A suspension of 1.87 g of 26-b in 20 ml of 1N HCl was refluxed for 1 hr, neutrallized with sat. $NaHCO_3$, and extracted with $CHCl_3$. $CHCl_3$ layer was washed with H_2O, and dried over anhyd. Na_2SO_4. Solvent was removed under reduced pressure, and then the residual solid was recrystallized from benzene–*n*-hexane to afford O-acetonyl-N-ethoxycarbonyl-carbamate (**30**) as colorless needles of mp 85—87°, 1.30 g (68.5%). Mass Spectrum *m/e*:

16) All melting and boiling points were uncorrected. NMR spectra were obtained in the specified solvents on a Varian A-60 and Varian HA-100 spectrometer with tetramethylsilane as an internal standard. Mass spectra were determined on a JEOL JMS-OISG spectrometer.

M^+=189. *Anal.* Calcd. for $C_7H_{11}O_5N$: C, 44.44; H, 5.86; N, 7.41. Found: C, 44.45; H, 5.62; N, 7.51. IR ν_{max}^{Nujol} cm^{-1}: 3170 [–C(O)NHC(O)–], 1810, 1728 and 1715 for three carbonyl groups. NMR ($CDCl_3$)τ(J=Hz): 8.68 (3H, t, J=7.0), 7.82 (3H, s), 5.71 (2H, q, J=7.0), 5.28 (2H, s), *ca.* 2.64 (1H, broad).

Preparation of O-Acetonyl-N-ethoxycarbonyl-carbamate (30)——a) A solution of 1.48 g of acetol (**31**),[17] and 2.90 g of ethoxycarbonyl isothiocyanate (**23-b**) in 60 ml of AcOEt was refluxed for 1 hr, the solvent was removed under reduced pressure, and the resulting residue was eluted with benzene on silica gel. The isolated solid was recrystallized from *n*-hexane to afford 1.04 g of O-acetonyl-N-ethoxycarbonyl-thiocarbamate (**32**) as pale yellow needles of mp 68—69°. *Anal.* Calcd. for $C_7H_{13}O_4NS$: C, 40.58; H, 6.32; N, 6.76; S, 15.44. Found: C, 40.67; H, 6.41; N, 6.80; S, 15.16. IR ν_{max}^{Nujol} cm^{-1}: 3260 (NH), 1776 and 1730 for two carbonyl groups. NMR ($CDCl_3$)τ(J=Hz): 8.66 (3H, t, J=7.0), 7.75 (3H, s), 5.71 (2H, q, J=7.0), 4.85 (2H, s), *ca.* 1.95 (1H, broad). b) A suspension of 0.2 g of **32** in 10 ml of 1N HCl was refluxed for 2 hr, neutralized with sat. $NaHCO_3$ aqueous, and extracted with $CHCl_3$. $CHCl_3$ layer was washed with H_2O, and dried over anhyd. Na_2SO_4. The solvent was removed, and the residue was recrystallized from *n*-hexane–benzene to afford 0.1 g of O-acetonyl-N-ethoxycarbonyl-carbamate (**30**).

Reaction of 4-Methylidene-2-phenylimino-1,3-oxathiolane (21)[10] with 1N HCl——A suspension of 0.8 g of **21** in 10 ml of 1N HCl was refluxed for 30 minutes, neutralized with sat. $NaHCO_3$ aqueous, and extracted with ether. Ether layer was washed with H_2O, and dried over anhyd. Na_2SO_4. After removal of ether, the residual oil was distilled to afford 0.2 g of 4-methylidene-1,3-oxathiolane-2-one (**33**)* as a pale yellow oil of bp 80—90° (0.3 mmHg). *Anal.* Calcd. for $C_4H_4O_2S$: C, 41.39; H, 3.47; S, 27.57. Found: C, 41.26; H, 3.45; S, 27.78. IR $\nu_{max}^{liq.}$ cm^{-1}: 1750 (>C=O), 1630 for an exo carbon-carbon double bond ($\frac{H}{H}$>C=C–). NMR ($CDCl_3$)τ(J=Hz): 4.99 (2H, t, J=2.1), 4.74 for one nonequivalent exo methylene proton ($\frac{Ha}{Hb}$>=; t, d, J_1=J_2=2.1), 4.65 for another nonequivalent exo methylene proton ($\frac{Ha}{Hb}$>=; t, d, J_1=J_2=2.1). *0.5 g of the compound (**33**) was also obtained by treatment of 1.32 g of 4-methylidene-1,3-oxathiolane-2-thione (**34**)[8] with mercury acetate (4.0 g) in $CHCl_3$.

Reaction of 4-Methylidene-3-phenyl-oxazolidine-2-thione (22) and 1N HCl——A suspension of 0.19 g of **22** in 10 ml of 1N HCl was refluxed for 30 min, was neutralized with sat. $NaHCO_3$ aqueous solution. The precipitated solid was collected by filtration and recrystallized from benzene to afford 0.15 g of 4-methyl-oxazoline-2-thione (**35**) as colorless needles of mp 99—100°. *Anal.* Calcd. for $C_{10}H_9ONS$: C, 62.82; H, 4.75; N, 7.33; S, 16.74. Found: C, 62.65; H, 4.77; N, 7.17; S, 16.74. IR ν_{max}^{Nujol} cm^{-1}: 1660 for a carbon-carbon double bond. NMR ($CDCl_3$)τ(J=Hz): 8.01 (3H, d, J=2.0), 2.78 (1H, q, J=2.0), 2.83—2.28 for five aromatic protons (m).

Reaction of *n*-Propoxycarbonyl Isothiocyanate (23-c) and 2-Propyn-1-ol (19)——2.9 g of **23-c** was reacted with 1.12 g of **19** by the general method to afford three products (**24-c**, **25-c** and **26-c**). O-2-Propynyl-N-*n*-propoxycarbonyl-thiocarbamate (**24-b**), 0.41 g, colorless needles from benzene–*n*-hexane, mp 48—50°. *Anal.* Calcd. for $C_8H_{11}O_3NS$: C, 47.76; H, 5.51; N, 6.96; S, 15.90. Found: C, 47.50; H, 5.60; N, 6.61; S, 16.06. IR ν_{max}^{Nujol} cm^{-1}: 3300 and 2100 (HC≡C–), 3230 and 1755 [–C(O)NHC(S)–]. NMR ($CDCl_3$)τ(J=Hz): 9.04 (3H, t, J=7.0), 8.31 (2H, q, t, J_1=J_2=7.0), 7.43 (1H, t, J=2.8), 5.84 (2H, t, J=7.0), 4.85 (2H, d, J=2.8), *ca.* 1.50 (1H, broad). S-1,2-Propadien-1-yl-N-*n*-propoxycarbonyl-thiolcarbamate (**25-c**), 0.38 g, colorless needles from benzene, mp 65—66°. *Anal.* Calcd. for $C_8H_{11}O_3NS$: C, 47.76; H, 5.51; N, 6.96; S, 15.90. Found: C, 47.51; H, 5.67; N, 6.79; S, 16.17. IR ν_{max}^{Nujol} cm^{-1}: 3200, 1755 and 1655 [–C(O)NHC(O)–], 1945 (–C=C=C–). NMR ($CDCl_3$)τ(J=Hz): 9.04 (3H, t, J=7.0), 8.28 (2H, q, t, J_1=J_2=7.0), 5.80 (2H, t, J=7.0), 4.94 (2H, d, J=6.5), 3.70 (1H, t, J=6.5), *ca.* 5.70 for one secondary amide proton (broad). 4-Methylidene-2-*n*-propoxycarbonylimino-1,3-oxathiolane (**26-c**), 2.0 g, colorless needles from *n*-hexane–benzene, mp 74—75°. *Anal.* Calcd. for $C_8H_{11}O_3NS$: C, 47.76; H, 5.51; N, 6.96; S, 15.90. Found: C, 47.50; H, 5.68; N, 6.97; S, 16.05. IR ν_{max}^{Nujol} cm^{-1}: 1695 (>C=O), 1633 (>C=C–), 1579 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 9.15 (3H, t, J=7.0), 8.27 (2H, q, t, J_1=J_2=7.0), 5.84 (2H, t, J=7.0), 4.93 (2H, t, J=2.5) 4.67 for one nonequivalent exo methylene proton ($\frac{Ha}{Hd}$>=; t, d, J_1=2.5, J_2=2.3), 4.61 for another nonequivalent exo methylene proton ($\frac{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3).

Reaction of Isopropoxycarbonyl Isothiocyanate (23-d) and 2-Propyn-1-ol (19)——2.9 g of **23-d** was reacted with 1.12 g of **19** by the general method to afford three products (**24-d**, **25-d** and **26-d**). O-2-Propynyl-N-isopropoxycarbonyl-thiocarbamate (**24-d**) 0.4 g, colorless needles from *n*-hexane–benzene, mp 82—84°. *Anal.* Calcd. for $C_8H_{11}O_3NS$: C, 47.76; H, 5.51; N, 6.96; S, 15.90. Found: C, 47.56; H, 5.37; N, 6.46; S, 16.35. IR ν_{max}^{Nujol} cm^{-1}: 3300 and 2120 (HC≡C–), 3220 and 1758 [–C(S)NHC(O)–]. NMR ($CDCl_3$) τ(J=Hz): 8.68 (6H, d, J=6.8), 7.42 (1H, t, J=2.5), 5.01 (1H, q, q, J_1=J_2=6.8), 4.82 (2H, d, J=2.5), *ca.* 1.66 (1H, broad). S-1,2-Propadien-1-yl-N-isopropoxycarbonyl-thiolcarbamate (**25-b**), 0.33 g, colorless needles from *n*-hexane–benzene, mp 43—46°. *Anal.* Calcd. for $C_8H_{11}O_3NS$: C, 47.76; H, 5.51; N, 6.96;

17) P.A. Leven and A. Walti, *Org. Syn.*, Collect. II. p 5.

S, 15.90. Found: C, 47.58; H, 5.39; N, 6.85; S, 16.23. IR ν_{max}^{Nujol} cm^{-1}: 3230, 1750 and 1665 [-C(O)NHC(O)-], 1945 (-C=C=C-). NMR ($CDCl_3$)τ(J=Hz): 8.68 (6H, d, J=7.0), 4.06 (1H, q, q, J_1=J_2=7.0), 4.04 (2H, d, J=6.5), 3.65 (1H, t, J=6.5), *ca.* 1.72 (1H, broad). 4-Methylidene-2-isopropoxycarbonylimino-1,3-oxathiolane (**26-d**), 1.79 g, colorless needles from *n*-hexane–benzene, mp 64—65°. *Anal.* Calcd. for $C_8H_{11}O_3NS$: C, 47.76; H, 5.51; N, 6.96; S, 15.90. Found: C, 47.57; H, 5.61; N, 6.83; S, 16.16. IR ν_{max}^{Nujol} cm^{-1}: 1680 (>C=O), 1632 (>C=C<), 1572 (>C=N-). NMR ($CDCl_3$) τ(J=Hz): 8.67 (6H, d, J=7.0), 4.99 (2H, t, J=2.5), 4.67 for one nonequivalent exo methylene proton ($\overset{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3), 4.62 for another nonequivalent methylene proton ($\overset{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3).

Reaction of *n*-Butoxycarbonyl Isothiocyanate (23-e) and 2-Propyn-1-ol (19)——3.5 g of **23-e** was reacted with 1.12 g of **19** by the general method to afford three products (**24-e, 25-e** and **26-e**). O-2-Propynyl-N-*n*-butoxycarbonyl-thiocarbamate (**24-e**), 0.52 g, pale yellow oil, $n_D^{21.3}$=1.5194. *Anal.* Calcd. for $C_9H_{13}O_3NS$: C, 50.23; H, 6.08; N, 6.51; S, 14.86. Found: C, 50.61; H, 6.31; N, 6.81; S, 14.81. IR $\nu_{max}^{liq.}$ cm^{-1}: 3300 and 2100 (HC≡C-), 1780 (>C=O). NMR ($CDCl_3$)τ(J=Hz): 9.06 (3H, t, J=6.5), 8.90—7.95 (4H, m), 5.79 (2H, t, J=6.5), 7.46 (1H, t, J=2.5), 4.84 (2H, d, J=2.5), *ca.* 1.60 (1H, broad). S-1,2-Propadien-1-yl-N-*n*-butoxycarbonyl-thiolcarbamate (**25-e**), 0.29 g, colorless needles from *n*-hexane, mp 50—51°. *Anal.* Calcd. for $C_9H_{13}O_3NS$: C, 50.23; H, 6.08; N, 6.51; S, 14.86. Found: C, 49.87; H, 6.10; N, 6.27; S, 14.81. IR ν_{max}^{Nujol} cm^{-1}: 3200, 1752 and 1660 [-C(O)NHC(O)-], 1940 (-C=C=C-). NMR ($CDCl_3$)τ(J=Hz): 9.06 (3H, t, J=6.5), 0.93—7.99 (4H, m), 5.76 (2H, t, J=6.5), 4.90 (2H, d, J=6.5), 3.68 (1H, t, J=6.5), *ca.* 1.50 (1H, broad). 2-*n*-Butoxycarbonylimino-4-methylidene-1,3-oxathiolane (**26-e**), 1.78 g, colorless needles from *n*-hexane–benzene, mp 49—50°. *Anal.* Calcd. for $C_9H_{11}O_3NS$: C, 50.23; H, 6.08; N, 6.51; S, 14.86. Found: C, 50.06; H, 6.16; N, 6.45; S, 15.01. IR ν_{max}^{Nujol} cm^{-1}: 1685 (>C=O), 1632 (>C=C<), 1570 (>C=N-). NMR ($CDCl_3$)τ(J=Hz): 9.06 (3H, t, J=6.5), 8.92—7.98 (4H, m), 5.80 (2H, t, J=6.5), 4.88 (2H, t, J=2.5), 4.65 for one nonequivalent exo methylene ($\overset{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3), 4.60 for another nonequivalent exo methylene proton ($\overset{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3).

Reaction of Isobutoxycarbonyl Isothiocyanate (23-f) and 2-Propyn-1-ol (19)——3.5 g of **23-f** was reacted with 1.12 g of **19** by the general method to afford two products (**24-f** and **26-f**): O-2-Propynyl-N-isobutoxycarbonyl-thiocarbamate (**24-f**), 0.64 g, colorless needles from *n*-hexane–benzene, mp 52—54°. *Anal.* Calcd. for $C_9H_{13}O_3NS$: C, 50.23; H, 6.09; N, 6.51; S, 14.86. Found: C, 50.08; H, 6.28; N, 6.20; S, 14.89. IR ν_{max}^{Nujol} cm^{-1}: 2230 and 2120 (HC≡C-), 3230 and 1770 [-C(S)NHC(O)-]. NMR ($CDCl_3$)τ(J=Hz): 9.04 (6H, t, J=7.0), 8.02 (1H, q, q, t, J_1=J_2=J_3=7.0), 7.44 (1H, t, J=3.0), 6.00 (2H, d, J=7.0), 4.83 (2H, d, J=3.0), *ca.* 1.72 (1H, broad). 2-Isobutoxycarbonylimino-4-methylidene-1,3-oxathiolane (**26-f**), 1.38 g, colorless needles from *n*-hexane–benzene, mp 53—54.°. *Anal.* Calcd. for $C_9H_{13}O_3NS$: C, 50.23; H, 6.09; N, 6.51; S, 14.86. Found: C, 49.89; H, 6.17; N, 6.24; S, 14.89. IR ν_{max}^{Nujol} cm^{-1}: 1685 (>C=O), 1632 (>C=C<), 1570 (>C=N-). NMR ($CDCl_3$)τ(J=Hz): 9.02 (6H, d, J=7.0), 7.98 (1H, q, q, t, J_1=J_2=J_3=7.0), 6.01 (2H, d, J=7.0), 4.89 (2H, t, J=2.5), 4.66 for one nonequivalent exo methylene proton ($\overset{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3), 4.60 for another nonequivalent exo methylene proton ($\overset{Ha}{Hb}$>=; t, d, J_1=2.5, J_2=2.3).

General Method for Preperation of N-Alkoxycarbonyl-O-2-butynyl-thiocarbamates (37)——A solution of 0.01 mole of 2-butyn-1-ol (**36**), 0.011 mole of alkoxycarbonyl isothiocyanates (**23**) in 50 ml of tetra chloromethane was refluxed for 8 hr, and the solvent was evaporated. The resulting solid was recrystallized from a suitable solvent.

Reaction of Methoxycarbonyl Isothiocyanate (23-a) and 2-Butyn-1-ol (36)——1.3 g of **23-a** was reacted with 0.7 g of **36** by the general method, and the resulting solid was recrystallized from *n*-hexane to afford 1.55 g of O-2-butynyl-N-methoxycarbonyl-thiocarbamate (**37-a**) as colorless needles of mp 90—92°. Mass Spectrum *m/e*: M^+=187. *Anal.* Calcd. for $C_7H_9O_3NS$: C, 44.91; H, 4.85; N, 7.48; S, 17.13. Found: C, 45.00; H, 5.00; N, 7.23; S, 16.98. IR ν_{max}^{Nujol} cm^{-1}: 3190 and 1758 [-C(S)NHC(O)-], 2220 (-C≡C-). NMR ($CDCl_3$) τ(J=Hz): 8.10 (3H, t, J=2.5), 6.18 (3H, s), 4.88 (2H, q, J=2.5), *ca.* 1.44 (1H, broad).

Reaction of Ethoxycarbonyl Isothiocyanate (23-b) and 2-Butyn-1-ol (36)——1.45 g of **23-b** was reacted with 0.7 g of **36** by the general method, and the resulting solid was recrystallized form isopropyl ether to afford 1.75 g O-2-butynyl-N-ethoxycarbonyl-thiocarbamate (**37-b**) as colorless needles of mp 85.87°. Mass Spectrum *m/e*: M^+=201. *Anal.* Calcd. for $C_6H_{11}O_3NS$: C, 47.76; H, 5.51; N, 6.96; S, 15.65. Found: C, 47.65; H, 5.64; N, 7.00; S, 15.77. IR ν_{max}^{Nujol} cm^{-1}: 3200 and 1775 [-C(S)NHC(O)-], 2210 (-C≡C-). NMR ($CDCl_3$) τ(J=Hz): 8.70 (3H, t, J=7.0), 8.12 (3H, t, J=2.8), 5.70 (2H, q, J=7.0), 4.90 (1H, q, J=2.8), *ca.* 1.62 (1H,broad). *1.45 g (0.011 mole) of **23-b** was reacted with 0.7 g (0.01 mole) of **36** at 50—70° in nitrogen atmosphere to give 1.16 g (58.0%) of **37-b**.

Reaction of *n*-Propoxycarbonyl Isothiocyanate (23-c) and 2-Butyn-1-ol (36)——1.6 g of **23-c** was reacted with 0.7 g of **36** by the general method. The resulting solid was recrystallized from *n*-hexane–benzene to afford 1.26 g of O-2-butynyl-N-isopropoxycarbonyl-thiocarbamate (**37-c**) as colorless needles of mp 70—71°. Mass Spectrum *m/e*: M^+=215. *Anal.* Calcd. for $C_9H_{13}O_3NS$: C, 50.21; H, 6.09; N, 6.51; S, 14.90.

Found: C, 50.03; H, 6.16; N, 6.61; S, 14.87. IR ν_{max}^{Nujol} cm^{-1}: 3210 and 1766 [–C(S)NHC(O)–], 2230 (–C≡C–). NMR ($CDCl_3$)τ(J=Hz): 9.03 (3H, t, J=6.8), 8.29 (2H, q, t, J_1=J_2=6.8), 8.10 (3H, t, J=2.8), 5.84 (2H, t, J=6.8), 4.99 (2H, q, J=2.8), *ca.* 1.59 (1H, broad).

Reaction of Isopropoxycarbonyl Isothiocyanate (23-d) and 2-Butyn-1-ol (36)——1.6 g of **23-d** was reacted with 0.7 g of **36** by the general method, and then the resulting solid was recrystallized from *n*-hexane–benzene to afford 1.39 g of O-2-butynyl-N-isopropoxycarbonyl-thiocarbamate (**37-d**) as colorless needles of mp 88—90°. Mass Spectrum *m/e*: M$^+$=215. *Anal.* Calcd. for $C_9H_{13}O_3NS$: C, 50.21; H, 6.09; N, 6.91; S, 14.90. Found: C, 50.29; H, 6.35; N, 6.52; S, 14.55. IR ν_{max}^{Nujol} cm^{-1}: 3200 and 1760 [–C(S)NHC(O)–], 2230 (–C≡C–). NMR ($CDCl_3$)τ(J=Hz): 8.71 (6H, d, J=7.0), 8.10 (3H, t, J=2.8), 5.00 (1H, q, q, J_1=J_2=7.0), 4.88 (2H, q, J=2.8), *ca.* 1.65 (1H, broad).

Reaction of *n*-Butoxycarbonyl Isothiocyanate (23-e) and 2-Butyn-1-ol (36)——1.75 g of **23-e** was reacted with 0.7 g of **36** by the general method, and then the resulting solid was recrystallized from *n*-hexane to afford 0.5 g of N-*n*-butoxycarbonyl-O-2-butynyl-thiocarbamate (**37-e**) as colorless needles from *n*-hexane of mp 43—44°. Mass Spectrum *m/e*: M$^+$=229. *Anal.* Calcd. for $C_{10}H_{15}O_3NS$: C, 52.38; H, 6.59; N, 6.11; S, 13.98. Found: C, 52.18; H, 6.67; N, 6.20; S, 13.97. IR ν_{max}^{Nujol} cm^{-1}: 3200 and 1772 [–C(S)NHC(O)–], 2230 (–C≡C–). NMR ($CDCl_3$)τ(J=Hz): 9.07 (3H, t, J=6.5), 8.91—8.00 (4H, m), 8.13 (3H, t, J=2.8), 5.82 (2H, t, J=6.5), 4.90 (2H, q, J=2.8), *ca.* 1.75 (1H, broad).

Reaction of Isobutoxycarbonyl Isothiocyanate (23-f) and 2-Butyn-1-ol (36)——1.75 g of **23-f** was reacted with 0.7 g of **36** by the general method, and then the resulting solid was recrystallized from *n*-hexane to afford 0.51 g of O-2-butynyl-N-isobutoxycarbonyl-thiocarbamate as colorless needles of mp 50—51°. Mass Spectrum *m/e*: M$^+$=229. *Anal.* Calcd. for $C_{10}H_{15}O_3NS$: C, 52.38; H, 6.59; N, 6.11; S, 13.98. Found: C, 52.08; H, 6.51; N, 5.89; S, 13.98. IR ν_{max}^{Nujol} cm^{-1}: 3210 and 1765 [–C(S)NHC(O)–], 2230 (–C≡C–). NMR ($CDCl_3$)τ(J=Hz): 9.02 (6H, d, J=7.0), 8.11 (3H, t, J=3.0), 8.08 (1H, t, d, d, J_1=J_2=J_3=7.0), 6.08 (2H, d, J=7.0), 4.94 (2H, q, J=3.0), *ca.* 1.62 (1H, broad).

General Cyclization Method of N-Alkoxycarbonyl-O-2-butynyl-thiocarbamates (37)——A solution of 0.01 mole of **37** in 50 ml of EtOH involving 0.01 mole of Et_3N was refluxed for 1 hr, and EtOH was removed under reduced pressure. The residual solid was recrystallized from a suitable solvent.

Synthesis of 4-Ethylidene-2-methoxycarbonylimino-1,3-oxathiolane (39-a)——1.87 g of O-2-butynyl-N-methoxycarbonyl-thiocarbamate (**37-a**) was treated with Et_3N in EtOH according to the general method to afford 1.12 g of **39-a** as colorless prisms (*n*-hexane–benzene) of mp 102—104°. *Anal.* Calcd. for $C_7H_9O_3NS$: C, 44.91; H, 4.85; N, 7.48; S, 17.13. Found: C, 44.70; H, 5.02; N, 7.21; S, 17.23. IR ν_{max}^{Nujol} cm^{-1}: 1698 (>C=O), 1640 (>C=C<), 1585 (>C=N–). NMR ($CDCl_3$) τ(J=Hz): 8.29 (3H, d, t, J_1=7.0, J_2=2.0), 6.14 (3H, s), 4.95 (2H, d, q, J_1=2.2, J_2=2.0), 4.25 (1H, q, t, J_1=7.0, J_2=2.2).

Synthesis of 4-Ethylidene-2-ethoxycarbonylimino-1,3-oxathiolane (39-b)*——2.01 g of O-2-butynyl-N-ethoxycarbonyl-thiocarbamate (**37-b**) was treated with Et_3N according to the general method to afford 1.12 g of **39-b** as colorless prisms (isopropyl ether) of mp 104—105°. *Anal.* Calcd. for $C_8H_{11}O_3NS$: C, 47.74; H, 5.50; N, 6.96; S, 15.93. Found: C, 47.60; H, 5.41; N, 7.03; S, 15.80. IR ν_{max}^{Nujol} cm^{-1}: 1685 (>C=O), 1640 (>C=C<), 1590 (>C=N–). UV λ_{max}^{EtOH} mμ (ε): 266 (6400). NMR ($CDCl_3$)τ(J=Hz): 8.66 (3H, t, J=7.0), 8.20 (3H, d, t, J_1=7.0, J_2=2.0), 5.73 (2H, q, J=7.0), 4.96 (2H, d, q, J_1=2.2, J_2=2.0), 4.26 (1H, q, t, J_1=7.0, J_2=2.2). *2.01 g of **37-b** was heated at 120—130° for 3 hr on an oil bath, and then the reaction mixture was eluted with benzene on silica gel column to afford 0.82 g of **37-b** and 0.43 g (21.4%) of S-2,3-butadien-2-yl-N-ethoxycarbonyl-thiolcarbamate (**38**) as colorless needles of mp 74—75°. *Anal.* Calcd. for $C_8H_{11}O_3NS$: C, 47.76; H, 5.51; N, 6.96; S, 15.91. Found: C, 47.80; H, 5.60; N, 6.63; S, 16.17. IR ν_{max}^{Nujol} cm^{-1}: 3180, 1742 and 1656 [–C(O)NHC(O)–], 1945 (–C=C=C–). NMR ($CDCl_3$)τ(J=Hz): 8.68 (3H, t, J=7.0), 7.90 (3H, t, J=3.5), 5.73 (2H, q, J=7.0), 5.62 (2H, q, J=3.5), *ca.* 1.97 (1H, broad).

Synthesis of 4-Ethylidene-2-*n*-propoxycarbonylimino-1,3-oxathiolane (39-c)——2.16 g of O-2-butynyl-N-*n*-propoxycarbonyl-thiocarbamate (**27-c**) was treated with Et_3N according to the general method to afford 0.91 g of **39-c** as colorless needles (*n*-hexane–benzene) of mp 73—75°. *Anal.* Calcd. for $C_9H_{13}O_3NS$: C, 50.21; H, 6.09; N, 6.51; S, 14.90. Found: C, 50.06; H, 6.43; N, 6.27; S, 15.24. *IR ν_{max}^{Nujol} cm^{-1}: 1695 (>C=O), 1590 (>C=N–). *The absorption bands of a carbon-carbon double bond (>C=C<) are not clear. NMR ($CDCl_3$)τ(J=Hz): 9.08 (3H, t, J=7.0), 8.25 (2H, q, t, J_1=J_2=7.0), 8.20 (3H, d, t, J_1=7.0, J_2=1.8), 5.83 (2H, t, J=7.0), 4.95 (2H, d, q, J_1=2.0, J_2=1.8), 4.25 (1H, q, t, J_1=7.0, J_2=2.0).

Synthesis of 4-Ethylidene-2-isopropoxycarbonylimino-1,3-oxathiolane (39-d)——2.16 g of O-2-butynyl-N-isopropoxycarbonyl-thiocarbamate (**27-d**) was treated with Et_3N according to the general method to afford 0.92 g of **39-d** as colorless needles (*n*-hexane–benzene) of mp 74—76°. *Anal.* Calcd. for $C_9H_{13}O_3NS$: C, 50.21; H, 6.09; N, 6.51; S, 14.90. Found: C, 49.88; H, 6.04; N, 6.59; S, 14.86. *IR ν_{max}^{Nujol} cm^{-1}: 1690 (>C=O), 1590 (–C=N–). *The absorption bands of a carbon-carbon double bond (–C=C–) are not clear. NMR ($CDCl_3$)τ(J=Hz): 8.67 (6H, d, J=6.4), 8.20 (3H, d, t, J_1=7.0, J_2=1.9), 4.98 (2H, d, q, J_1=2.0, J_2=1.9), 4.26 for (1H, q, t, J_1=7.0, J_2=2.0).

Synthesis of 2-*n*-Butoxycarbonylimino-4-ethylidene-1,3-oxathiolane (39-e)——2.3 g of N-*n*-Butoxycarbonyl-O-2-butynyl-thiocarbamate (**37-e**) was treated with Et_3N according to the general method to afford 0.515 g of **39-e** as colorless needles (pet. ether) of mp 35—37°. *Anal.* Calcd. for $C_{10}H_{15}O_3NS$: C, 52.38; H, 6.59; N, 6.11; S, 13.98. Found: C, 52.18; H, 6.78; N, 6.12; S, 14.13. IR ν_{max}^{Nujol} cm^{-1}: 1685 (>C=O), 1640

(>C=C–), 1560 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 9.09 (3H, t, J=6.0), 8.95—8.01 (4H, m), 8.22 (3H, d, t, J_1=7.0, J_2=1.9), 5.81 (2H, t, J=6.0), 4.97 (2H, q, t, J_1=7.0, J_2=2.0), 4.27 (1H, q, t, J_1=7.0, J_2=2.0).

Synthesis of 2-Isobutoxycarbonylimino-4-ethylidene-1,3-oxathiolane (39-f)——2.3 g of N-isobutoxycarbonyl-O-2-butynyl-thiocarbamate (**37-f**) was treated with Et_3N according to the general method to afford 0.535 g of **39-f** as colorless needles (pet. ether) of mp 41—43°. *Anal.* Calcd. for $C_{10}H_{11}O_3NS$: C, 52.38; H, 6.59; N, 6.11; S, 13.98. Found: C, 52.03; H, 6.50; N, 6.17; S, 13.95. IR ν_{max}^{Nujol} cm^{-1}: 1684 (>C=O), 1632 (>C=C<), 1583 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 9.03 (6H, d, J=6.5), 8.21 (3H, d, t, J_1=7.0, J_2=1.9), 7.92 (1H, q, q, t, J_1=J_2=J_3=6.5), 6.01 (2H, d, J=6.5), 4.97 (2H, d, t, J_1=2.0, J_2=1.9), 4.24 (1H, q, t, J_1=7.0, J_2=2.0).

Reaction of Ethoxycarbonyl Isothiocyanate (23-b) and 3-Phenyl-2-propyn-1-ol (40)——A mixture of 1.45 g of **23-b** and 1.32 g of **40** was heated at 50—70° for 5 hr on an oil bath. The reaction mixture was eluted with benzene on silica gel column to give two products (**41** and **42-b**): O-3-Phenyl-2-propynyl-N-ethoxycarbonyl-thiocarbamate (**41**), 1.88 g, n_D^{20}: 1.5890, pale yellow oil. *Anal.* Calcd. for $C_{13}H_{13}O_3NS$: C, 59.31; H, 4.98; N, 5.32; S, 12.16. Found: C, 59.53; H, 5.26; N, 5.17; S, 11.63. IR $\nu_{max}^{liq.}$ cm^{-1}: 3270 and 1770 [–C(S)NHC(O)–], 2230 (>C=C–). NMR ($CDCl_3$)τ(J=Hz): 8.69 (3H, t, J=7.0), 5.74 (2H, q, J=7.0), 4.60 (2H, s), 2.82—2.35 for five aromatic protons (m), *ca.* 1.64 (1H, broad). UV $\lambda_{max}^{dioxane}$ mμ (ε): 246 (20200), 256 (21000). 2-Ethoxycarbonylimino-4-benzylidene-1,3-oxathiolane (**42-b**), 0.15 g, colorless needles from *n*-hexane–benzene, mp 96—97°. Mass Spectrum *m/e*: M^+=263. *Anal.* Calcd. for $C_{13}H_{13}O_3NS$: C, 59.31; H, 4.98; N, 5.32, S, 12.16. Found: C, 59.26; H, 4.95; N, 5.42; S, 12.15. IR ν_{max}^{Nujol} cm^{-1}: 1680 (>C=O), 1650 (>C=C<), 1575 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 8.60 (3H, t, J=7.0), 5.74 (2H, q, J=7.0), 4.75 (2H, d, J=2.0), 3.35 (1H, t, J=2.0), 2.82—2.47 for five aromatic protons (m). UV λ_{max}^{EtOH} mμ (ε): 271 (15300).

Cyclization Reaction of 41——To benzene (200 ml) solution of 2.63 g of **41**, 4%KOH aqueous (10 ml) was added at room temperature, and the mixture was stirred for 30 minutes at room temperature. The organic layer was washed with H_2O, dried over anhyd. Na_2SO_4, and then the solvent was removed under reduced pressure. The resulting solid was recrystallized from isopropyl ether to afford 2.17 g of **42-b**.

General Method for Preparation of 2-Alkoxycarbonylimino-4-benzylidene-1,3-oxathiolanes (42)——The mixture of 0.011 mole of alkoxycarbonyl isothiocyanates (**23**) and 0.01 mole of 3-phenyl-2-propyn-1-ol (**40**) was heated at 50—70° in nitrogen atmosphere for 5 hr, and then to the reaction mixture 200 ml of benzene and 4% KOH aqueous (10 ml) were added and stirred at room temperature for 30 minutes. The organic layer was washed with H_2O, and dried over anhyd. Na_2SO_4. After removal of benzene under reduced pressure, the resulting solid was recrystallized from a suitable solvent.

Synthesis of 4-Benzylidene-2-methoxycarbonylimino-1,3-oxathiolane (42-a)——1.31 g of methoxycarbonyl isothiocyanate (**23-a**) was reacted with 1.32 g of **40**, and the reaction mixture was treated with 4% KOH by the general method to give 2.25 g of **42-a**, colorless needles from *n*-hexane–benzene, mp 106—108°. *Anal.* Calcd. for $C_{12}H_{11}O_3NS$: C, 57.83; H, 4.45; N, 5.62; S, 12.84. Found: C, 57.63; H, 4.74; N, 5.71; S, 13.13. IR ν_{max}^{Nujol} cm^{-1}: 1690 (>C=O), 1640 (>C=C–), 1575 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 6.15 (3H, s), 4.74 (2H, d, J=2.3), 3.32 (1H, t, J=2.3), 2.81—2.44 for five aromatic protons (m).

Synthesis of 4-Benzylidene-2-ethoxycarbonylimino-1,3-oxathiolane (42-b)——The reaction of ethoxycarbonyl isothiocyanate (**23-b**, 1.45 g) with 1.32 g of **40** afforded 2.29 g of **42-b**.

Synthesis of 4-Benzylidene-2-*n*-propoxycarbonylimino-1,3-oxathiolane (42-c)——The reaction of *n*-propoxycarbonyl isothiocyanate (**23-c**; 1.59 g) with 1.32 g of **40** afforded 2.06 g of **42-c**, colorless needles from *n*-hexane–benzene, mp 86—88°. *Anal.* Calcd. for $C_{14}H_{15}O_3NS$: C, 60.64; H, 5.45; N, 5.05; S, 11.54. Found: C, 60.62; H, 5.77; N, 5.02; S, 11.65. IR ν_{max}^{Nujol} cm^{-1}: 1695 (>C=O), 1635 (>C=C<), 1588 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 9.02 (3H, t, J=7.0), 6.25 (2H, q, t, J_1=J_2=7.0), 5.82 (2H, t, J=7.0), 4.75 (2H, d, J=2.3), 3.33 (1H, t, J=2.3), 2.87—2.45 for five aromatic protons (m).

Synthesis of 4-Benzylidene-2-isopropoxycarbonylimino-1,3-oxathiolane (42-d)——The reaction of isopropoxycarbonyl isothiocyanate (**23-d**, 1.59 g) with 1.32 g of **40** afforded 2.01 g of **42-d**, colorless needles from *n*-hexane–benzene, mp 93—94°. *Anal.* Calcd. for $C_{14}H_{15}O_3NS$: C, 60.64; H, 5.45; N, 5.05; S, 11.54. Found: C, 60.70; H, 5.46; N, 5.09; S, 11.82. IR ν_{max}^{Nujol} cm^{-1}: 1675 (>C=O), 1635 (>C=C<), 1580 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 2.67 (6H, d, J=6.5), 5.03 (1H, q, q, J_1=J_2=6.5), 4.75 (2H, d, J=2.1), 3.33 (1H, t, J=2.1), 2.86—2.47 for five aromatic protons (m).

Synthesis of 4-Benzylidene-2-*n*-butoxycarbonylimino-1,3-oxathiolane (42-e)——The reaction of *n*-butoxycarbonyl isothiocyanate (**23-e**, 1.73 g) with 1.32 g of **40** afforded 1.99 g of **42-e**, colorless needles from isopropyl ether, mp 58—59°. *Anal.* Calcd. for $C_{15}H_{17}O_3NS$: C, 61.85; H, 5.88; N, 4.81; S, 10.98. Found: C, 61.64; H, 6.00; N, 4.70; S, 10.97. IR ν_{max}^{Nujol} cm^{-1}: 1692 (>C=O), 1630 (>C=C<), 1580 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 9.06 (3H, t, J=7.0), 8.95—7.98 (4H, m), 5.78 (2H, t, J=7.0), 4.75 (2H, d, J=2.1), 3.34 (1H, t, J=2.1), 2.80—2.44 for five aromatic protons (m).

Synthesis of 4-Benzylidene-2-isobutoxycarbonylimino-1,3-oxathiolane (42-f)——The reaction of isobutoxycarbonyl isothiocyanate (**23-f**, 1.73 g) with 1.32 g of **40** afforded 2.02 g of **42-f**, colorless needles from *n*-hexane–benzene, mp 79—81°. *Anal.* Calcd. for $C_{15}H_{17}O_3NS$: C, 61.85; H, 5.88; N, 4.81; S, 10.98. Found: C, 61.77; H, 5.91; N, 4.56; S, 10.98. IR ν_{max}^{Nujol} cm^{-1}: 1680 (>C=O), 1640 (>C=C<), 1590 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 9.03 (6H, d, J=7.0), 8.02 (1H, q, q, t, J_1=J_2=J_3=7.0), 5.99 (2H, d, J=7.0), 4.74 (2H, d, J=2.3), 3.32 (1H, t, J=2.3), 2.84—2.49 for five aromatic protons (m).

Synthesis of O-2-Propynyl-N-isopropoxycarbonyl-N(D)-thiocarbamate (43)——4.02 g (0.02 mole) of **24-d** was suspended in D_2O (50 ml), and stirred for 5 hr at room temperature. After removal of D_2O under reduced pressure, the residual solid was recrystallized from isopropyl ether to afford 3.2 g of **43** as colorless needles of mp 82—83°. *Anal.* Calcd. for $C_8H_{12}O_3NS$: C, 47.50; H, 5.98; N, 6.92; S, 15.85. Found: C, 47.33; H, 5.62; N, 6.92; S, 15.84. IR ν_{max}^{Nujol} cm^{-1}: 3250, 2100 for a ethynyl group (HC≡C–), 2320 for Nitrogen-Deuterium bond (>N–D: strong), 1755 (>C=O). NMR (CCl)τ(J=Hz): 8.70 (6H, d, J=6.7), 7.52 for one ethynyl proton (HC≡C–; t, J=2.5), 5.00 (1H, q, q, J_1=J_2=6.7), 4.90 for two methylene protons (–C≡C–CH_2–O–; d, J=2.5).

Cyclization Reaction of 43 to C(D)-4-Methylidene-2-isopropoxycarbonylimino-1,3-oxathiolane (44)——A solution of 2.02 g of **43** in 30 ml of triethyl amine was refluxed for 30 minutes, and triethyl amine was removed under reduced pressure. The resulting solid was recrystallized from isopropyl ether to afford 0.8 g of **44** as colorless needles of mp 64—65°. *Anal.* Calcd. for $C_8H_{12}O_3NS$: C, 47.50; H, 5.58; N, 6.92; S, 15.85. Found: C, 47.78; H, 5.98; N, 6.86; S, 15.85. IR ν_{max}^{Nujol} cm^{-1}: 1675 (>C=O), 1570 (>C=N–). NMR ($CDCl_3$)τ(J=Hz): 8.68 (6H, d, J=7.0), 4.98 (1H, q, q, J_1=J_2=7.0), 4.92 for two ring methylene protons (d, J=2.3), 4.67 for one exo methylene proton ($\begin{matrix}H\\D\end{matrix}$>C=C–; t, J=2.3).

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