purified by chromatography (silica gel, diisopropyl ether/hexane). The thione *S*-imides were obtained as red oils, and some of them crystallized on standing at 0 °C. The crystals were carefully washed with dry hexane, yielding analytically pure products.

All the thione *S*-imides synthesized showed typical infrared C=S=N absorptions between 900 and 1000 cm^{-1} and UV absorptions with λ_{max} between 380 and 400 nm ($\log \epsilon \approx 4$). The ^1H NMR signals were all in full accord with the presented structure.

Alternative Procedure (Nonaqueous Workup). Phenyl 2,4,6-Trimethyldithiobenzoate *thiono*-*S*-*tert*-Butylimide (3i). To a solution of *N*-(trimethylsilyl)-*tert*-butylamine (3.0 mmol) in diethyl ether (50 mL) was added at 0 °C *n*-BuLi (1.10 equiv). After the mixture was stirred for 1 h at room temperature, a solution of sulfine **4a** (3.0 mmol) in diethyl ether (10 mL) was added at −78 °C. Then, after the mixture was stirred another hour, trimethylsilyl chloride (3.3 mmol) was added at room temperature. The precipitated lithium chloride was filtered off, and the filtrate was concentrated in vacuo, affording thione *S*-imide **3i** as a yellow oil which crystallized on standing. Washing with hexane gave pure material: IR (KBr) 992 cm^{-1} (C=S=N); ^1H NMR ($CDCl_3$) δ 1.42 (s, 9 H, *t*-C_4H_9), 2.12 (s, 3H, *p*-CH_3), 2.20 (s, 6 H, *o*-CH_3), 6.53 (s, 2 H, *m*-H), 6.90–7.40 (m, 5 H, arom); UV (CH_3OH) λ_{max} 381 nm ($\log \epsilon$ 3.93); mass spectrum, *m/e* 343 (M^+). Due to instability satisfactory elemental analyses were not obtained.

Phenyl 4-Methoxy-2,6-dimethyl-3-isopropyldithiobenzoate *thiono*-*S*-*tert*-Butylimide (31). This compound was prepared as described for **3i** by starting from sulfine **4b**: IR (NaCl) 990 cm^{-1} (C=S=N); ^1H NMR ($CDCl_3$) δ 1.08, 1.17 [d, 6 H, J = 7.5 Hz, $CH(CH_3)_2$], 1.39 (s, 9 H, *t*-C_4H_9), 2.10, 2.18 (s, 6 H, *o*-CH_3), 2.70–3.30 [m, 1 H, $CH(CH_3)_2$], 3.58 (s, 3 H, OCH_3), 6.30 (s, 1 H, *m*-H), 6.90–7.20 (m, 5 H, arom); UV (CH_3OH) λ_{max} 380 nm. Due to instability satisfactory elemental analyses were not obtained.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. **1a**, 68761-21-7; **1b**, 71740-69-7; **1d**, 4104-47-6; **2a**, 85535-32-6; **2b**, 87463-60-3; **3a**, 87463-61-4; **3b**, 87463-62-5; **3c**, 87463-63-6; **3d**, 63609-88-1; **3e**, 87463-64-7; **3f**, 87463-65-8; **3g**, 87481-60-5; **3h**, 87463-66-9; **3i**, 87463-67-0; **3j**, 87463-68-1; **3k**, 87463-69-2; **3l**, 87481-61-6; (*E*,*E*)-**3m**, 87463-70-5; (*E*,*Z*)-**3m**, 87463-71-6; (*E*,*E*)-**3n**, 87463-72-7; (*E*,*Z*)-**3n**, 87463-73-8; (*E*,*E*)-**3o**, 87463-74-9; (*E*,*Z*)-**3o**, 87463-75-0; **3p**, 87463-76-1; (*E*,*Z*)-**3q**, 87463-77-2; (*E*,*E*)-**3r**, 87463-78-3; (*E*,*Z*)-**3s**, 87463-79-4; **3t**, 87463-80-7; **3u**, 87463-81-8; **4a**, 87463-82-9; **4b**, 87463-83-0; **4c**, 87463-84-1; **4d**, 78610-73-8; **4e**, 78594-05-5; **4f**, 87463-85-2; **4g**, 4440-32-8; **5a**, 87463-86-3; **5b**, 87463-87-4; **5c**, 87463-88-5; **5d**, 87463-89-6; **5e**, 87463-90-9.

Supplementary Material Available: The spectroscopic data for compounds **3e–h,j,k,m–t**. (4 pages). Ordering information is given on any current masthead page.

Palladium-Catalyzed Polyhetero-Claisen Rearrangement of 3-(Allylthio)-1,2,4-triazin-5(4*H*)-ones

Masato Mizutani and Yuzuru Sanemitsu*

Takarazuka Research Institute, Sumitomo Chemical Co., Ltd., Takarazuka, Hyogo 665, Japan

Yoshinao Tamaru and Zen-ichi Yoshida*

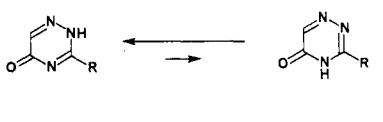
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Received May 17, 1983

The S → N allylic transposition of 3-(allylthio)-1,2,4-triazin-5(2*H*)-ones (**2**) has been performed successfully by catalysis of a palladium(II) salt, where regioselectivities of the rearrangement (N-2 vs. N-4) are highly dependent on the substitution pattern of the allylic moiety. The rearranged products (**3** and **4**) are converted to 6,7-dihydro-4*H*-thiazolo[2,3-*c*][1,2,4]triazin-4-ones (**10**) and 2,3-dihydro-7*H*-thiazolo[3,2-*b*][1,2,4]triazin-7-ones (**11**), respectively, in high yields by treatment with concentrated sulfuric acid in refluxing formic acid.

Despite the synthetic utility of S → N allylic rearrangement (a general structural transformation: N=CS-CC=C → S=CNCC=C) this rearrangement is one of the least studied polyhetero-Claisen rearrangement,[1] perhaps because the higher temperatures required can lead to side reactions (e.g., double-bond migration of allylic moiety to vinyl sulfides, deallylation, etc.). Furthermore there are no structure–reactivity correlations to permit general use of this rearrangement. For example, 2-(allylthio)benzimidazoles,[2] 2-(allylthio)benzthiazoles,[3] and 2-(allylthio)-imidazolines[4] undergo the S → N allylic rearrangement, while 5-(allylthio)pyrimidines[5] and 8-(allylthio)caffeines[2] are reported not to give the rearranged products.

Scheme I



1,2,4-Triazin-5-ones are of interest in view of their biological activities (for example, metribuzin[6] is a potent herbicide). In this paper we describe the S → N allylic rearrangement of 3-(allylthio)-1,2,4-triazin-5(2*H*)-ones **2**.

(1) For comprehensive review, see: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. (b) Bennet, G. B. *Synthesis* **1977**, 589. (c) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.

(2) Krivozheiko, K. M.; Kolesova, M. B.; El'tsov, A. V. *Biol. Akt. Soedin.* **1968**, 300.

(3) Takahashi, T.; Kaji, A.; Hayami, J. *Bull. Inst. Chem. Res., Kyoto Univ.* **1973**, *51*, 163.

(4) Kohn, H.; Arceneaux, J. H. *J. Org. Chem.* **1977**, *42*, 2339.

(5) Fourrey, J. L.; Estrabaud, E.; Jouin, P. *J. Chem. Soc., Chem. Commun.* **1975**, 993.

(6) 3-(Methylthio)-4-amino-6-*tert*-butyl-1,2,4-triazin-5(4*H*)-one; Draber, W.; Dickore, K.; Büchel, K. H.; Trebst, A.; Pistorius, E. *Naturwissenshaften* **1968**, *55*, 446.

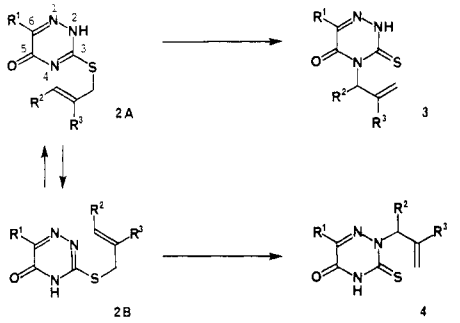
0022-3263/83/1948-4585$01.50/0

Table I. Palladium-Catalyzed S → N Rearrangement of 3-(Allylthio)-1,2,4-triazin-5(2*H*)-ones (2)

entry	triazinone 1	conditions[a]	product (% yield)[b]	ratio of 3/4[c]
1	2a	THF, reflux, 3 h	3a (76), 4a (10)	88:12
2	2b	THF, reflux, 1 h	3b (79), 4b (11)	88:12
3	2c	THF, room temp, 8 h	3c + 4c (88)	95:5
4	2d	THF, reflux, 2 h	3d (27), 4d (65)	30:70
5	2e	THF, reflux, 2.5 h	3e + 4e (100)	29:71
6	2f	dioxane, reflux, 12 h	3f (46), 4f (16)	74:26

[a] For entries 1–5, 1 mol % of $PdCl_2(PhCN)_2$ is used. For entry 6, 10 mol % of $PdC_2(PhCN)_2$ is used. [b] Yields refer to the isolated ones. [c] Ratios are deduced from the isolated yields of 3 and 4. For entries 3 and 5, the ratios are calculated from the isolated yields of 10 and 11 (see Table II).

Scheme II



	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	Ph	H	H
d	H	CH_3	H
e	Ph	CH_3	H
f	H	H	CH_3

These reactions were performed successfully by an application of the palladium(II)-catalyzed method reported previously from these laboratories.[7] We also describe a novel and high-yield acid-catalyzed cyclization of the rearranged products 3 and 4 to the fused heterocyclic systems 10 and 11.

Results and Discussion

3-(Alkylthio)-1,2,4-triazin-5(2*H*)-ones exist as a mixture of tautomers **1A** and **1B** (Scheme I). Spectroscopic analysis[8] indicates that **1A** is the main tautomer, and alkylation of the salts of 1 occurs at the N-2 nitrogen atom (vide infra, Scheme III).[9]

It was our premise that S → N allylic rearrangement of 3-(allylthio)-1,2,4-triazin-5(2*H*)-one (**2a–f**, Scheme II) would provide a route to the N-4 alkylated products predominantly, via the main tautomer **2A**.

Pd(II)-Catalyzed S → N Allylic Rearrangement. Thermal rearrangement of 2 was first examined. The reaction was very slow, and at high temperatures they either decomposed (**2a**, at 150–160 °C, neat) or provided a mixture of N-4 and N-2 alkylation products nonselectively in low yield (from **2c**, **3c**, and **4c** in a ratio 57:43 in 63% yield based on a 65% conversion, 170 °C for 6 h in Decalin). In marked contrast to these results, the S → N allylic rearrangement was found to proceed smoothly at 25–65 °C in the presence of a catalytic amount of $PdCl_2(PhCN)_2$ to provide the rearranged products in high yields. The results together with the reaction conditions are summarized in Table I, which reveals that the regioselectivity is highly dependent on the substitution pattern of the allylic moiety. As expected, when $R^2 = R^3 = H$, N-4 alkylation took place selectively, irrespective of the substituents R^1. When $R^2 = CH_3$ and $R^3 = H$, the reaction proceeded with similar ease, however, with reversed selectivity, providing predominantly the N-2 products. In the former cases the results seem to reflect the distribution of tautomers **2A** and **2B** under the reaction conditions. The reversed selectivity in the latter cases might be explained in terms of a pseudo-A(1,3) interaction[10] between C-5 carbonyl oxygen and the terminal methyl group in a chairlike transition state, leading to a C-4 alkylation product. The kinetic nature of product distribution is apparent from the following observations. (1) No isomerization of **3b** to **4b**, or vice versa, was observed under the rearrangement conditions. (2) Only methallyl type products and no traces of crotyl type products were obtained (entries 4 and 5 in Table I). This complete allylic inversion indicates that the reaction proceeded in a intramolecular fashion. The rearrangement of **2f** was exceptionally slow, resulting in a low regioselectivity and low yield. All these results are in good accordance with those observed for the Pd(II)-catalyzed S → N allylic rearrangements of thioimidates reported previously from these laboratories and support the mechanism proposed therein.[7a,11]

Structure Determination of the Rearranged Products 3 and 4. The thiones 3 and 4 in entries 1, 2, 4, and 6 in Table I were separated and purified by means of careful column chromatography over silica gel. The ratio of 3 and 4 was obtained on the basis of the isolated yields of products. The mixtures of products in entries 3 and 5 were hardly separable by column chromatography in any solvent systems examined, and the ratios were deduced from the isolated yields of 10 and 11 (vide infra).

In the mass spectra, both 3 and 4 have the same parent peak as the starting triazinone 2. In the ^1H NMR spectra, the signals for their allylic methylene protons resonated in the region of δ 4.65–5.04 (except **3d** and **4d**). In the spectra of the crotyl type products (**3d** and **4d**), no allylic methylene protons appeared and only allylic methine protons were observed. These results clearly indicate that 3 and 4 are the rearranged products. However, we met difficulties in discrimination of these isomers, because the pairs of 3 and 4 did not show characteristic absorptions in IR, ^1H NMR, and mass spectra. Accordingly the structures of **3a** and **4a** were determined on the basis of

(7) (a) Tamaru, Y.; Kagotani, M.; Yoshida, Z. *J. Org. Chem.* **1980**, *45*, 5221. (b) Tamaru, Y.; Kagotani, M.; Yoshida, Z. *Tetrahedron Lett.* **1981**, *22*, 4245.

(8) (a) Jonáš, J.; Gut, J. *Collect. Czech. Chem. Commun.* **1962**, *27*, 1886. (b) Uchytilová, V.; Fiedler, P.; Prystaš, M.; Gut, J. *Ibid.* **1971**, *36*, 1955. (c) Pitha, J.; Fiedler, P.; Gut. J. *Ibid.* **1966**, *31*, 1864. (d) Lee, J.; Paudler, W. W. *J. Heterocycl. Chem.* **1972**, *9*, 995. (e) Brown, D. J.; Jones, R. L. *Aust. J. Chem.* **1972**, *25*, 2711.

(9) Daunis, J.; Jacquier, R.; Viallefont, P. *Bull. Soc. Chim. Fr.* **1971**, 3658. For example, see the conversion from 9 to 8 (Scheme III).

(10) (a) Johnson, F. *Chem. Rev.* **1968**, *68*, 375. (b) Hart, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 397 and his extensive current works. (c) Wilsen, S. R.; Missa, R. N. *J. Org. Chem.* **1980**, *45*, 5079. (d) Overman, L. E.; Yokomitsu, T. *Ibid.* **1980**, *45*, 5229.

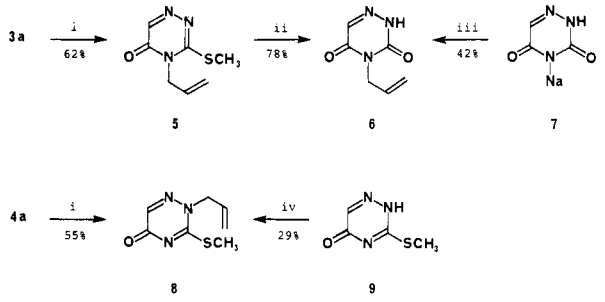
(11) (a) Overman, L. E. *J. Am. Chem. Soc.* **1980**, *102*, 865. (b) Henry, P. M. *Ibid.* **1972**, *94*, 5200.

Table II. Acid-Catalyzed Cyclization of 4- or 2-Allyl-3-thio-1,2,4-triazine-3,5(2*H*,4*H*)-diones 3 and 4

entry	triazinedione 3 and 4	rctn time,[a] h	product 10 and 11 (% isolated yield)	UV spectra of 10 and 11, λ_{max}^{EtOH}, nm (ϵ)
1	**3a**	4	**10a** (97)	211 (11 200), 296 (5400)
2	**4a**	2.5	**11a** (78)	233 (19 000)
3	**3b**	5	**10b** (100)	212 (11 300), 293 (7000)
4	**3c** + **4c**[b]	1	**10c** (79)	207 (17 200), 244 (10 000), 325 (17 200)
			11c (4)	202 (14 700), 234 (20 500), 306 (13 700)
5	**3c** + **4c**[c]	2	**10c** (46), **11c** (35)	
6	**3d**	2	**10d** (93)	trans 214 (15 000), 299 (7700)
			(trans/cis = 1:4)[f]	cis 212 (11 800), 296 (6400)
7[d]	**4d**	3.5	**11d** (95)	trans 236 (22 300)
			(trans/cis = 1:2)[f]	cis 235 (22 800)
8	**3e** + **4e**[e]	2.5	**10e** (22)	trans 206 (17 900), 245 (10 500), 326 (17 800)
			(trans/cis = 1:4)[f]	cis 205 (14 800), 245 (7900), 327 (13 800)
			11e (54)	trans 206 (11 400), 240 (15 600), 310 (10 300)
			(trans/cis = 1:2)[f]	cis 204 (13 400), 237 (17 500), 307 (11 900)
9	**3f**	2	**10f** (100)	212 (10 400), 297 (5400)
10	**4f**	2	**11f** (87)	234 (23 300)

[a] Reaction conditions are as follows: A mixture of the substrate and concentrated H_2SO_4 in HCOOH is refluxed for an indicated period of time. [b] A mixture of products in entry 3, Table I is used. [c] A mixture of products obtained by a thermal rearrangement of **2c** is used. [d] 10-Camphorsulfonic acid is used in place of sulfuric acid. [e] A mixture of products in entry 5, Table I is used. [f] Trans/cis ratios are calculated on the basis of their integral in ^1H NMR spectra.

Scheme III[a]



[a] (i) $CH_3I/NaOCH_3$, room temperature, (ii) concentrated HCl/EtOH, reflux, (iii) CH_2=$CHCH_2Br/HOCH_2CH_2OH$, 80 °C, (iv) CH_2=$CHCH_2Br/n$-BuLi, THF, reflux.

Scheme IV

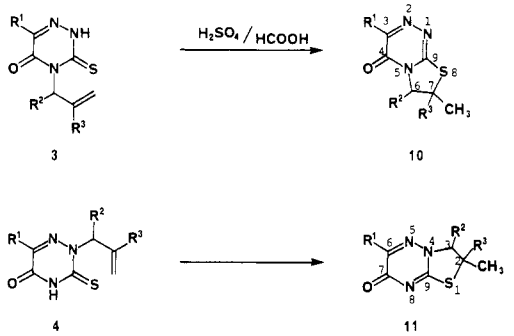
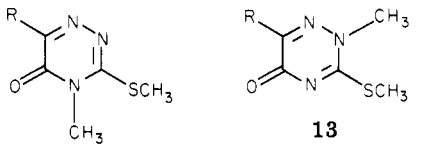


Table III. Ultraviolet Spectral Data of 1,2,4-Triazin-5-ones[15]



compd	R	λ_{max}^{EtOH}, nm (ϵ)
12a	H	230 (5800), 296 (7600)
12b	Ph	211 (14 600), 250 (7000), 334 (14 000)
13a	H	236 (24 500)
13b	Ph	210 (8600), 245 (10 300), 325 (13 000)

the following chemical conversions (Scheme III).

S-Methylation of **3a** followed by acid hydrolysis afforded **6** identical with 4-allyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione prepared by allylation of **7**.[12] Treatment of **4a** with methyl iodide furnished **8** whose structure was confirmed by comparison with an authentic sample prepared by the reaction of **9**[13] with allyl bromide. Though rather laborious, the structures of other derivatives of **3** and **4** may be determined by a similar sequence.

Another basis for distinguishing of **3** and **4** is comparison of UV spectra of S-methylated products, e.g., **5** and **8**, respectively. These S-alkylated isomers are known to show characteristic ultraviolet spectra (vide infra). Although these S-alkylated derivatives of **3** and **4** should be readily separable,[14] this method is unsuitable for estimation of the product ratios of **3** to **4** in entries 3 and 5 (Table I) due to the low yields in the transformation of **3a** to **5** and **4a** to **8** (Scheme III).

In order to circumvent these problems, we developed a new cyclization reaction of **3** and **4** to provide the fused heterocyclic compounds **10** and **11**, respectively, in high yield.

Triazines **3** and **4** or a mixture of them were found to cyclize smoothly by a catalysis of sulfuric acid in refluxing formic acid to provide the thiazolotriazinones **10** and **11**, respectively, or an easily separable mixture of them (Scheme IV), in high yields (Table II). Accordingly the ratios of the isolated yields of **10c**, **11c** and **10e**, **11e** can be used to estimate the product ratios of **3c**, **4c** and **3e**, **4e**, respectively.

The cyclized structures of **10** and **11** were deduced from the analytical and spectral data. The mass spectra of **10** and **11** indicated the same parent peak as the corresponding starting material **3** and **4**, respectively. In the ^1H NMR spectra, accompanied with disappearance of the olefinic protons, characteristic new doublet signals (except **10f** and **11f**) due to methyl protons appeared in the region of δ 1.41–1.60. Singlets at δ 1.65 and 1.70 were observed for **10f** and **11f**, respectively. These results clearly indicate the exclusive formation of the five-membered rings and not the six-membered ones.

The structures of **10** and **11** were easily discernible by comparison of their UV spectra. As shown in Table III,

(12) Gut, J.; Prystaš, M.; Jonáš, J.; Sorm, F. *Collect. Czech. Chem. Commun.* **1961**, *26*, 974.
(13) Restivo, A. R.; Dondzila, F. A. *J. Org. Chem.* **1962**, *27*, 2281.
(14) Unpublished results. The R_f values of 4-methyl-1,2,4-triazin-5-(4*H*)-ones are generally larger than those of 2-methyl-1,2,4-triazin-5-(2*H*)-ones.

the 3,4-disubstituted triazinones **12** shows the absorption maxima uniformly at the longer wavelengths compared with those of 2,3-disubstituted **13**.[15] The bicyclic derivatives **10** and **11** showed the extremely similar absorption shapes and maxima to **12a,b** and **13a,b**, respectively (Table II).

The acid-catalyzed cyclization of **3d** and **3e** provided **10d** and **10e** as diastereomeric mixtures, respectively, in a ratio of 4:1. Similarly **4d** and **4e** were converted to give **11d** and **11e** as diastereomeric mixtures, respectively, in a ratio of 2:1. Each diastereomer was separated by means of careful column chromatography over Fertigsäure Kieselgel 60 (Merck; N-hexane–acetone gradient). The main portions of these diastereomers were determined to be the cis isomers on the basis of the higher field resonances of two methyl carbons compared with those of the minor products in the ^{13}C NMR spectra.[16]

In comparison with the presently available synthetic methods, which show drawbacks from the standpoint of yields,[17] limited availability of the starting materials,[18] or low regioselectivity,[19] the efficiency of the present method is apparent from the high structural flexibility and the unique regioselectivity as well as its high yield with the lack of side products.

Experimental Section

Melting points were determined in capillary tubes with a Mettler FP 61 instrument and are uncorrected. Short-path (bulk-to-bulb) distillations were carried out in a Kugelrohr apparatus. Microanalyses were obtained with a Perkin-Elmer 240 or 240B instrument. Measurement of infrared spectra were made on a Hitachi 260-10 spectrometer. Proton magnetic resonances (^1H NMR) spectra were measured at 60 MHz on a Hitachi R-24B NMR spectrometer, at 90 MHz on a Hitachi R-900 spectrometer, and at 200 MHz on a Varian XL-200 instrument with tetramethylsilane as an internal standard. ^{13}C NMR spectra at 200 MHz were taken on a Varian XL-200 instrument with $CDCl_3$ as an internal standard. Mass spectra were run on a Shimadzu LKB-9000B instrument. Ultraviolet spectra were obtained with a Hitachi 220 spectrometer. Infrared and mass spectra and analytical data for individual compounds **2–6**, **8**, **10**, and **11** are recorded in Supplementary Pages (see paragraph at the end of the paper).

3-(Allylthio)-1,2,4-triazin-5(2*H*)-ones (2a–f). (A) General Procedure for Preparation of 3-(Allylthio)-1,2,4-triazin-5-(2*H*)-ones (2a, 2d, 2f). To a stirred solution of thiosemicarbazide (6.40 g, 70.2 mmol) in 80% aqueous EtOH (80 mL) at 70 °C was added glyoxylic acid (5.64 g, 76.2 mmol) in 80% aqueous EtOH (36 mL). After the reaction mixture was stirred at the same temperature for 5 min, a solution of NaOH (3.12 g, 78 mmol) dissolved in H_2O (20 mL) and alkenyl halide [allyl bromide (**2a**), *trans*-crotyl chloride (**2d**), methallyl chloride (**2f**); 79.8 mmol] were added. The reaction mixture was refluxed for 3 h. The solvent was removed in vacuo and the residue was dissolved in $CHCl_3$ and then washed with H_2O. The organic extract was dried over $MgSO_4$ and concentrated to give a crystalline product, which was recrystallized from *n*-hexane–acetone to furnish pure product (**2a**, **2d**, **2f**).

2a: mp 128.6 °C; yield 46.4%; ^1H NMR ($CDCl_3$) δ 4.86 (d, J = 6.0 Hz, 2 H), 5.03–6.21 (m, 3 H), 7.67 (s, 1 H).

2d: mp 106.9 °C; yield 39.6%; ^1H NMR ($CDCl_3$) δ 1.65 (d, J = 4.8 Hz, 3 H), 3.75 (d, J = 5.4 Hz, 2 H), 5.39–6.02 (m, 2 H), 7.60 (s, 1 H).

2f: mp 116.7 °C; yield 24.7%; ^1H NMR ($CDCl_3$) δ 1.74 (s, 3 H), 3.81 (s, 2 H), 4.80 (s, 1 H), 4.93 (s, 1 H), 7.60 (s, 1 H).

(B) General Procedure for Preparation of 3-(Allylthio)-1,2,4-triazin-5(2H)-ones (2b, 2c, 2e). To a stirred solution of 3-thio-1,2,4-triazine-3,5(2*H*,4*H*)-dione [R^1 = CH_3 (**2b**), R^1 = Ph (**2c**, **2e**); 10 mmol] and sodium methoxide (10 mmol) in MeOH (30 mL) was added alkenyl bromide [allyl bromide (**2b**, **2c**), *trans*-crotyl bromide (**2e**); 11 mmol] at room temperature. The reaction mixture was stirred overnight at the same temperature. After removal of MeOH under reduced pressure, the residue was partitioned between $CHCl_3$ and H_2O. After the residue was dried over $MgSO_4$, the organic extract was evaporated to give crude product **2**, which was recrystallized from EtOH to yield pure compound **2**.

2b: mp 185.2 °C; yield 77.7%; ^1H NMR (Me_2SO-d_6) δ 2.07 (s, 3 H), 3.75 (d, J = 6.0 Hz, 2 H), 4.92–5.39 (m, 2 H), 5.52–6.19 (m, 1 H).

2c: mp 194.2 °C; yield 69.0%; ^1H NMR (Me_2SO-d_6), δ 3.86 (d, J = 6.0 Hz, 2 H), 5.00–6.18 (m, 3 H), 7.22–7.52 (m, 3 H), 7.77–8.15 (m, 2 H).

2e: mp 172.8 °C dec; yield 52.1%; ^1H NMR (Me_2SO-d_6) δ 1.64 (d, J = 4.8 Hz, 3 H), 3.76 (d, J = 6.0 Hz, 2 H), 5.40–5.73 (m, 2 H), 7.21–7.50 (m, 3 H), 7.75–8.09 (m, 2 H).

S → N Allylic Rearrangement. (A) Thermal Rearrangement of 3-(Allylthio)-1,2,4-triazin-5(2*H*)-ones. The suspensions of **2c** (630 mg, 2.57 mmol) over Decalin (20 mL) was heated at 170 °C for 6 h. The reaction mixture was purified twice by column chromatography (silica gel, *n*-hexane–acetone gradient), yielding a mixture (260 mg) of 3-thio-4-allyl-6-phenyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (**3c**) and 2-allyl-3-thio-6-phenyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (**4c**) and the starting material (220 mg). The yield of the rearranged products was 63% on the basis of 65% conversion.

Thermal treatment of **2a** (neat at 150–160 °C) provided intractable mixture of products. The absence of **3a** and **4a** was thoroughly checked by TLC.

(B) Pd(II)-Catalyzed S → N Allylic Rearrangement. General Procedure. A THF or dioxane solution of **2** (1 mmol) and $PdCl_2(PhCN)_2$ (indicated amounts in Table I) was stirred under the conditions presented in Table I. After evaporation of the solvent, the residue was directly subjected to a column purification (silica gel, *n*-hexane–acetone gradient). In entries 1, 2, 4, and 6 in Table I, the spectroscopically pure compounds **3** and **4** were obtained (**3** was eluded first). In entries 3 and 5, mixtures of **3** and **4** were not separable.

3a: mp 103.4 °C (*n*-hexane–acetone); ^1H NMR ($CDCl_3$) δ 4.92 (d, J = 6.0 Hz, 2 H), 5.14–5.54 (m, 2 H), 5.63–6.18 (m, 1 H), 7.58 (s, 1 H).

4a: mp 139.6 °C (*n*-hexane–acetone); ^1H NMR ($CDCl_3$) δ 5.01 (d, J = 6.0 Hz, 2 H), 5.17–5.57 (m, 2 H), 5.76–6.43 (m, 1 H), 7.68 (s, 1 H).

3b: mp 106.8 °C (*n*-hexane–acetone); ^1H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 4.96 (d, J = 6.0 Hz, 2 H), 5.14–5.54 (m, 2 H), 5.64–6.31 (m, 1 H).

4b: mp 82.9 °C (*n*-hexane–*i*-PrOH); ^1H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 4.93 (d, J = 6.0 Hz, 2 H), 5.11–5.48 (m, 2 H), 5.69–6.43 (m, 1 H).

3d: mp 103.6 °C (*n*-hexane–acetone); ^1H NMR ($CDCl_3$) δ 1.56 (d, J = 6.0 Hz, 3 H), 5.00–5.46 (m, 2 H), 5.84–6.46 (m, 2 H), 7.39 (s, 1 H).

4d: mp 134.3 °C (*n*-hexane–acetone); ^1H NMR ($CDCl_3$) δ 1.46 (d, J = 6.0 Hz, 3 H), 5.05–5.48 (m, 2 H), 5.60–6.36 (m, 2 H), 7.60 (s, 1 H).

3f: mp 145.1 °C (*n*-hexane–acetone); ^1H NMR ($CDCl_3$) δ 1.82 (s, 3 H), 4.65–5.00 (m, 4 H), 7.60 (s, 1 H).

(15) Daunis, J.; Guindo, Y.; Jacquier, R.; Viallefont, P. *Bull. Soc. Chim. Fr.* **1972**, 1511.

(16) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 NMR Spectroscopy", 2nd Ed.; Wiley: New York, 1980. (c) Gaudemer, A. "Stereochemistry: Fundamentals and Method"; Kagan, H. B., Ed.; Georg Thime: Stuttgart, 1977; Vol. 1.

(17) (a) Ibrahim, E. S.; Shamseldine, S. A.; Soliman, F. S. G.; Labouta, I. M. *Pharmazie*, **1979**, *34*, 7. (b) Doleschall, G.; Hornyak, G.; Hornyak-Hamori, M.; Lempert, K.; Wolfer, A. *Acta. Chim. Acad. Sci. Hung.* **1967**, *53*, 385. (c) Doleschall, G.; Hornyak, G.; Lang, L.; Lempert, K.; Zauer, K. *Ibid.* **1968**, *57*, 191.

(18) For the synthesis of the type of compound **10**, to our knowlege, there is only one method, which consists of a condensation of 2-hydrazinothiazoles with α-keto acids. (a) Doleschall, G.; Lempert, K. *Acta Chim. Acad. Sci. Hung.* **1967**, *53*, 397. (b) Le Count, D. J.; Taylor, P. J. *Tetrahedron* **1975**, *31*, 433.

(19) Nyitrai, J.; Bekassy, S.; Lempert, K. *Acta Chim. Acad. Sci. Hung.* **1967**, *53*, 309. 3-Methyl-6,7-dihydro-4*H*-thiazolo[2,3-*c*][1,2,4]triazin-4-one and 6-methyl-2,3-dihydro-7*H*-thiazolo[3,2-*b*][1,2,4]triazin-7-one are obtained in a ratio 4:6 by the reaction of 3-thio-6-methyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione and 1,2-dibromoethane.

4f: mp 147.9 °C (*n*-hexane–acetone); ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 3 H), 4.74–5.04 (m, 4 H), 7.60 (s, 1 H).

Isomerization of 3b and 4b with Pd(II) Salt. Treatment of **3b** (46 mg, 0.25 mmol) with $PdCl_2(PhCN)_2$ (2 mg, 0.005 mmol) in refluxing THF (5 ml) for 10 h resulted in a complete recovery of the starting material, as judged from ^{1}H NMR and TLC. Under the similar conditions, **4b** afforded the same result.

3-(Methylthio)-4-allyl-1,2,4-triazin-5(4*H*)-one (5). Into a stirred solution of sodium (57 mg, 2.48 mmol) in CH_3OH was added **3a** (350 mg, 2.07 mmol) at room temperature. After 5 min, the reaction mixture was treated with methyl iodide (194 μL, 3.11 mmol) and was stirred at the same temperature for 3 h. Usual extractive workup with $CHCl_3$ and removal of the solvent gave crude **5**, which was purified by column chromatography (silica gel, *n*-hexane–acetone gradient) to afford pure **5** (220 mg, 62% yield based on 93% conversion) and recovered **3a** (23 mg). An analytically pure sample of **5** was obtained by distillation: bp 135–138 °C (0.32 mmHg); ^{1}H NMR ($CDCl_2$) δ 2.72 (s, 3 H), 4.66 (d, *J* = 5.4 Hz, 2 H), 5.15–5.52 (m, 2 H), 5.62–6.25 (m, 1 H), 8.28 (s, 1 H).

4-Allyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (6). (A) From 5. A solution of **5** (150 mg, 0.82 mmol) in 35% HCl (1 mL) and EtOH (3 mL) was heated under reflux for 1 h. After removal of the solvent, the residue was purified by crystallization from *n*-hexane–EtOH to give pure **6** (97 mg, 78% yield): mp 119.3 °C (*n*-hexane–acetone); ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 4.40 (d, *J* = 5.4 Hz, 2 H), 4.95–5.35 (m, 2 H), 5.49–6.15 (m, 1 H), 7.25 (s, 1 H).

(B) From 6-Azauracil Sodium Salt Monohydrate (7). In ethylene glycol (15 mL), **7** (3.06 g, 20 mmol) was treated with allyl bromide (2.6 mL, 30 mmol) at 80 °C for 5 h. The solvent was removed in vacuo to leave a slightly white solid, which was washed with $CHCl_3$ (30 mL)–MeOH (20 mL). After filtration and washing with $CHCl_3$ (50 mL), the combined filtrates were evaporated to provide a crude material, which was subjected to a column purification (silica gel, *n*-hexane–acetone gradient) to afford **6** (1.29 g, 42% yield).

2-Allyl-3-(methylthio)-1,2,4-triazin-5(2*H*)-one (8). (A) From 4a. In a similar way to **5**, treatment of **4a** (100 mg, 0.59 mmol) with methyl iodide provided **8** (57 mg, 55% yield based on 96% conversion) and the starting material **4a** (4 mg). Analytically pure material was afforded by distillation: bp 132–142 °C (0.3 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.59 (s, 3 H), 4.65 (d, *J* = 5.4 Hz, 2 H), 5.11–5.48 (m, 2 H), 5.66–6.29 (m, 1 H), 7.55 (s, 1 H).

(B) From 3-(Methylthio)-1,2,4-triazin-5(2*H*)-one (9). A solution of **9** (300 mg, 2.09 mmol) in THF (10 mL) and HMPA (1.5 mL) was cooled to −20 °C, and then to this stirred solution was added *n*-BuLi (1.6 M in *n*-hexane, 2.30 mmol). After being stirred at the same temperature for 30 min, the reaction mixture was treated with allyl bromide (230 μL, 2.72 mmol) and was stirred over the range of −20 °C to room temperature overnight. Usual extractive workup with $CHCl_3$ and evaporation of the solvent provided crude **8**, which was purified by column chromatography (silica gel, *n*-hexane–acetone gradient) to give pure **8** (110 mg, 29% yield).

Acid-Catalyzed Cyclization of 4- or 2-Allyl-3-thio-1,2,4-triazine-3,5(2*H*,4*H*)-dione (10 or 11). General Procedure. A solution of **3**, **4** or the mixture of **3** and **4** (1 mmol), and concentrated sulfuric acid (118 mg, 1.2 mmol) in 2 mL of formic acid was refluxed over an indicated period of time. The mixture was neutralized with aqueous $NaHCO_3$ and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated to dryness in vacuo to afford the product **10**, **11**, or the mixture of **10** and **11**. This mixture was easily separated by column chromatography (silica gel, *n*-hexane–acetone gradient; **10** was less polar than **11**). In entries 6–8 in Table II, careful separation of the mixture by column chromatography [Fertigsäure Kieselgel 60 (Merck), *n*-hexane–acetone gradient] provided pure diastereomers. The trans isomer was eluded first. Analytically pure materials except *trans*-**10e** were obtained by recrystallization from *n*-hexane–acetone.

10a: mp 111.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (d, *J* = 6.0 Hz, 3 H), 3.77–4.65 (m, 3 H), 8.08 (s, 1 H).

11a: mp 128.7 °C; ^{1}H NMR ($CDCl_3$) δ 1.60 (d, *J* = 6.0 Hz, 3 H), 3.87–4.80 (m, 3 H), 7.50 (s, 1 H).

10b: mp 110.4 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (d, *J* = 6.0 Hz, 3 H), 2.39 (s, 3 H), 3.72–4.64 (m, 3 H).

10c: mp 152.6 °C; ^{1}H NMR ($CDCl_3$) δ 1.63 (d, *J* = 6.0 Hz, 3 H), 3.90–4.33 (m, 2 H), 4.45–4.78 (m, 1 H), 7.40–7.61 (m, 3 H), 8.13–8.36 (m, 2 H).

11c: mp 158.2 °C; ^{1}H NMR ($CDCl_3$) δ 1.63 (d, *J* = 6.0 Hz, 3 H), 3.94–4.27 (m, 2 H), 4.46–4.77 (m, 1 H), 7.33–7.53 (m, 3 H), 8.01–8.19 (m, 2 H).

***trans*-10d**: mp 92.4 °C; ^{1}H NMR ($CDCl_3$) δ 1.54 (d, *J* = 6.6 Hz, 3 H), 1.56 (d, *J* = 7.1 Hz, 3 H), 3.48 (dq, *J* = 1.2, 7.1 Hz, 1 H), 4.79 (dq, *J* = 1.2, 6.6 Hz, 1 H), 8.24 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.8 (6-Me), 23.1 (7-Me), 45.0 (C_7), 64.7 (C_6), 146.7 (C_3), 151.5 (C_4), 161.9 (C_9).

***cis*-10d**: mp 123.1 °C; ^{1}H NMR ($CDCl_3$) δ 1.41 (d, *J* = 6.5 Hz, 3 H), 1.51 (d, *J* = 6.9 Hz, 3 H), 4.31 (dq, *J* = 6.9, 6.9 Hz, 1 H), 5.01 (dq, *J* = 6.5, 6.9 Hz, 1 H), 8.19 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.7 (6-Me), 12.9 (7-Me), 42.8 (C_7), 60.1 (C_6), 146.9 (C_3), 150.7 (C_4), 162.4 (C_9).

***trans*-11d**: mp 127.1 °C; ^{1}H NMR ($CDCl_3$) δ 1.59 (d, *J* = 6.5 Hz, 3 H), 1.61 (d, *J* = 6.8 Hz, 3 H), 3.62 (dq, *J* = 6.8, 6.9 Hz, 1 H), 4.20 (dq, *J* = 6.5, 6.9 Hz, 1 H), 7.56 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.4 (3-Me), 19.7 (2-Me), 44.7 (C_2), 68.6 (C_3), 142.0 (C_6), 161.1 (C_7), 168.0 (C_9).

***cis*-11d**: mp 109.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.48 (d, *J* = 7.0 Hz, 3 H), 1.49 (d, *J* = 6.8 Hz, 3 H), 4.18 (dq, *J* = 6.8, 7.0 Hz, 1 H), 4.65 (dq, *J* = 6.8, 6.8 Hz, 1 H), 7.55 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.1 (3-Me), 15.3 (2-Me), 41.9 (C_2), 65.0 (C_3), 142.0 (C_6), 161.2 (C_7), 168.3 (C_9).

***trans*-10e**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.57 (d, *J* = 6.5 Hz, 3 H), 1.58 (d, *J* = 7.2 Hz, 3 H), 3.48 (dq, *J* = 1.1, 7.2 Hz, 1 H), 4.86 (dq, *J* = 1.1, 6.5 Hz, 1 H), 7.38–7.56 (m, 3 H), 8.15–8.30 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.0 (6-Me), 23.3 (7-Me), 45.6 (C_7), 65.0 (C_6), 128.3 (C_2, or C_3, Ph), 129.0 (C_2, or C_3, Ph), 130.6 (C_4, Ph), 132.4 (C_1, Ph), 151.6 (C_4), 152.7 (C_3), 160.5 (C_9).

***cis*-10e**: mp 120.3 °C; ^{1}H NMR ($CDCl_3$) δ 1.42 (d, *J* = 6.6 Hz, 3 H), 1.46 (d, *J* = 7.7 Hz, 3 H), 4.28 (dq, *J* = 6.8, 7.7 Hz, 1 H), 5.03 (dq, *J* = 6.6, 6.8 Hz, 1 H), 7.40–7.54 (m, 3 H), 8.12–8.23 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.8 (6-Me), 13.1 (7-Me), 43.4 (C_7), 60.5 (C_6), 128.2 (C_2, or C_3, Ph), 128.8 (C_2, or C_3, Ph), 130.4 (C_4, Ph), 132.4 (C_1, Ph), 150.8 (C_4), 152.8 (C_3), 161.0 (C_9).

***trans*-11e**: mp 168.4 °C; ^{1}H NMR ($CDCl_3$) δ 1.60 (d, *J* = 6.7 Hz, 3 H), 1.63 (d, *J* = 6.4 Hz, 3 H), 3.64 (dq, *J* = 6.7, 6.9 Hz, 1 H), 4.25 (dq, *J* = 6.4, 6.9 Hz, 1 H), 7.38–8.52 (m, 3 H), 8.08–8.18 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.5 (3-Me), 19.7 (2-Me), 44.6 (C_2), 68.9 (C_3), 128.1 (C_2, or C_3, Ph), 128.7 (C_2, or C_3, Ph), 130.5 (C_4, Ph), 132.2 (C_1, Ph), 147.4 (C_6), 160.4 (C_7), 166.1 (C_9).

***cis*-11e**: mp 173.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.45 (d, *J* = 7.2 Hz, 3 H), 1.50 (d, *J* = 6.7 Hz 3 H), 4.15 (dq, *J* = 6.9, 7.2 Hz, 1 H), 4.65 (dq, *J* = 6.7, 6.9 Hz, 1 H), 7.36–7.51 (m, 3 H), 8.05–8.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.1 (3-Me), 15.2 (2-Me), 41.7 (C_2), 65.3 (C_3), 128.0 (C_2, or C_3, Ph), 128.6 (C_2, or C_3, Ph), 130.3 (C_4, Ph), 132.1 (C_1, Ph), 147.4 (C_6), 160.4 (C_7), 166.2 (C_9).

10f: mp 165.6 °C; ^{1}H NMR ($CDCl_3$) 1.65 (s, 6 H), 4.10 (s, 2 H), 8.20 (s, 1 H).

11f: mp 156.1 °C; ^{1}H NMR ($CDCl_3$) 1.70 (s, 6 H), 4.21 (s, 2 H), 7.52 (s, 1 H).

Acknowledgment. We are indebted to Mr. K. Moriguchi and Mr. K. Watanabe for obtaining NMR spectra and for discussion therein.

Registry No. **2a**, 87450-63-3; **2b**, 87450-64-4; **2c**, 87450-65-5; **2d**, 87450-66-6; **2e**, 87450-67-7; **2f**, 87450-68-8; **3a**, 87450-69-9; **3b**, 87450-70-2; **3d**, 87450-71-3; **3f**, 87450-72-4; **4a**, 87450-73-5; **4b**, 87450-74-6; **4d**, 87450-75-7; **4f**, 87450-76-8; **5**, 87450-77-9; **6**, 79944-17-5; **7**, 17121-89-0; **8**, 87450-78-0; **9**, 18060-72-5; **10a**, 87450-79-1; **10b**, 87450-80-4; **10c**, 87450-81-5; *trans*-**10d**, 87450-82-6; *cis*-**10d**, 87450-83-7; *trans*-**10e**, 87450-84-8; *cis*-**10e**, 87450-85-9; **10f**, 87450-86-0; **11a**, 87450-87-1; **11c**, 87450-88-2; *trans*-**11d**, 87450-89-3; *cis*-**11d**, 87450-90-6; *trans*-**11e**, 87450-91-7; *cis*-**11e**, 87450-92-8; **11f**, 87450-93-9; $PdCl_2(PhCN)_2$, 14220-64-5.

Supplementary Material Available: Table listing the IR and mass spectra and physical data (3 pages). Ordering information is given on any current masthead page.