Studies of Acyl and Thioacyl Isocyanates. XIV.[1] The Reactions of Benzoyl and Thiobenzoyl Isocyanates with Hydrazones

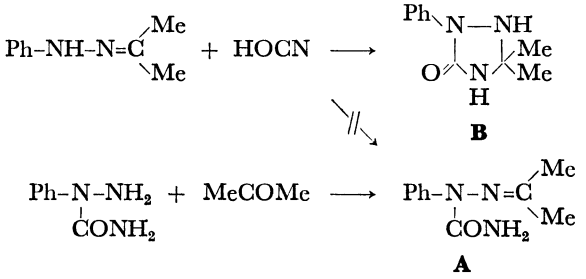
Otohiko TSUGE* and Shuji KANEMASA

Research Institute of Industrial Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

(Received April 30, 1974)

Benzoyl (**1**) and thiobenzoyl isocyanates (**2**) reacted with benzaldehyde arylhydrazones and methylhydrazone to give the corresponding semicarbazones as isolated products respectively. In the reactions with acetone arylhydrazones and methylhydrazone, however, the *s*-triazolidin-5-ones whose structures corresponded to the ring tautomers of semicarbazones, were isolated as sole products from the reaction of **1**, and **2** afforded the (4+2) cycloadducts of **2** to the C=N bond of hydrazones and *s*-triazolidin-5-ones. It has been found that in some cases, the semicarbazones isomerize into their ring tautomers, and the isomerization obeys good first-order kinetics taking into account the equilibrium. Although **1** did not react with *p*-tosyl- and benzoylhydrazones, **2** easily added to both hydrazones to yield the corresponding (4+2) cycloadducts.

In a previous paper[2] dealing with the reactions of benzoyl (**1**) and thiobenzoyl isocyanates (**2**) with hydrazines, we reported that **1** reacted with phenylhydrazine to give 1-phenyl-4-benzoylsemicarbazide, while the reaction of **2** with the same hydrazine gave 1,3-diphenyl-Δ^3-triazolin-5-one under the elimination of hydrogen sulfide. It has been also described that the Δ^3-triazolin-5-one was identical with the hydrolytic product of adducts of **1** to benzaldehyde phenylhydrazone (**3a**) and acetone phenylhydrazone (**4a**), and the adducts would be the corresponding 4-benzoyl-2-phenylsemicarbazones, respectively. It has been clarified by Schildknecht and Hatzmann,[3] however, that an adduct[4,5] of cyanic acid to **4a** is not acetone 2-phenylsemicarbazone (**A**) but its ring tautomer, 3,3-dimethyl-1-phenyl-*s*-triazolidin-5-one (**B**), while a product[6] obtained from 2-phenylsemicarbazide and acetone is the semicarbazone (**A**).

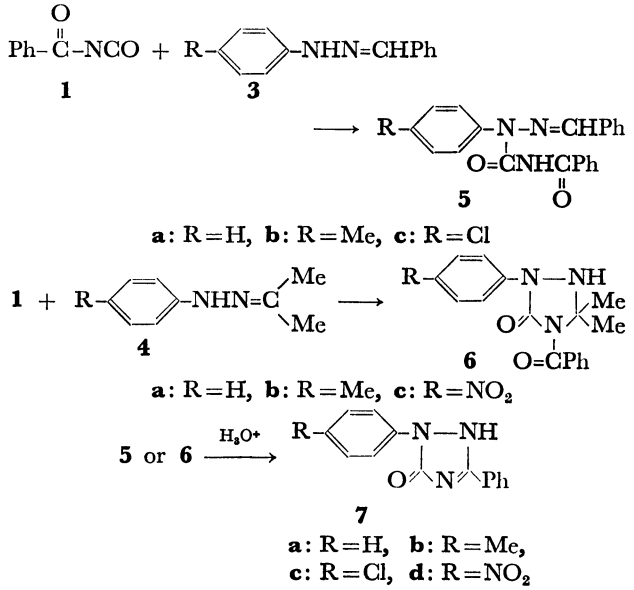


Consequently, we were obliged to reinvestigate whether the products obtained by the reaction of **1** with **3a** and **4a** would be really the corresponding 4-benzoyl-2-phenylsemicarbazones. It has been now proved that the adduct to **4a** is not the semicarbazone but its ring tautomer, although the adduct to **3a** is the semicarbazone. This fact seems to indicate that **1** might react with hydrazone to afford either the semicarbazone or its ring tautomer depending on the nature of carbonyl component of hydrazone. On the other hand, little attention has been paid to the reaction of **2** with hydrazones. Since the reactivity of **2** in 1,4-cycloaddition to C=N bonds is greater than that of **1**,[7-10] the reaction of **2** with hydrazone might be expected to give a (4+2) cycloadduct, besides the semicarbazone and its ring tautomer.

This paper deals with the reactions of **1** and **2** with aryl- and methylhydrazones of benzaldehyde and acetone. In this context, the reactions with *p*-tosyl- and benzoylhydrazones are also described.

Results and Discussion

Reactions with Benzaldehyde and Acetone Arylhydrazones. Benzoyl isocyanate (**1**) reacted with benzaldehyde phenylhydrazone (**3a**) and with acetone phenylhydrazone (**4a**) to give the corresponding 1 : 1 adducts, **5a** and **6a**, in excellent yields, respectively. The IR spectrum of **5a** showed well-defined absorption bands at 3460 (NH), 1760 (C=O), 1510 and 1490 cm^{-1} (Amide II), and the NMR spectrum in deuteriochloroform ($CDCl_3$) exhibited signals at δ 7.1—8.1 (16H, m, aromatic protons and N=C**H**) and 10.55 ppm (1H, broad, N**H**). On the other hand, the IR spectrum of **6a** showed no bands assignable to Amide II absorptions, but displayed characteristic bands at 3190 (NH), 1740, 1640 (C=O), 1330, and 1310 cm^{-1}. In the NMR spectrum in $CDCl_3$ signals appeared at δ 1.70 (6H, s, C**H**$_3$), 4.6 (1H, broad, N**H**), and 6.9—7.8 ppm (10H, m, aromatic protons). These spectral data indicate that **5a** is an adduct of different type from **6a**, although



Scheme 1.

* To whom correspondence should be addressed.

hydrolyses of both **5a** and **6a** gave the same product, 1,3-diphenyl-Δ^3-*s*-triazolin-5-one (**7a**), whose structure was established by the identification with an authentic sample.[2]

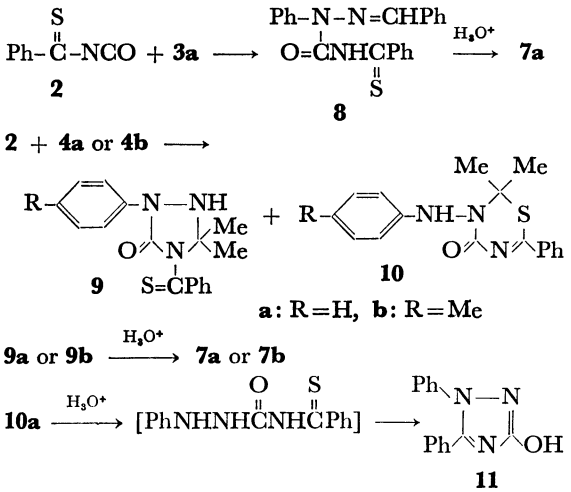
Schildknecht and Hatzmann[3] reported that in the NMR spectra in $CDCl_3$ acetone 2-phenylsemicarbazone (**A**) showed two singlets (each 3H) assignable to two methyls-protons at δ 1.63 and 2.1 ppm, while two methyls-protons of 3,3-dimethyl-1-phenyl-*s*-triazolidin-5-one (**B**) appeared as a singlet (6H) at δ 1.46 ppm. As mentioned above, **6a** exhibited a singlet (6H) due to two methyls-protons in the spectrum.

On the basis of the spectral data and of the results of hydrolysis, the structures of **5a** and **6a** were deduced as benzaldehyde 4-benzoyl-2-phenylsemicarbazone and 4-benzoyl-3,3-dimethyl-1-phenyl-*s*-triazolidin-5-one, respectively.

Similarly, the reaction of **1** with benzaldehyde *p*-tolyl- (**3b**) and *p*-chlorophenylhydrazones (**3c**) gave the corresponding semicarbazones, **5b** and **5c**, while the *s*-triazolidin-5-ones, **6b** and **6c**, were obtained in the reaction with acetone *p*-tolyl- (**4b**) and *p*-nitrophenylhydrazones (**4c**). On treatment with hydrochloric acid, all **5** and **6** were converted into the corresponding Δ^3-*s*-triazolin-5-ones, **7b**—**7d**, in good yields respectively (Scheme 1).

The reaction of thiobenzoyl isocyanate (**2**) with **3a** afforded benzaldehyde 2-phenyl-4-thiobenzoylsemicarbazone (**8**), whose structure was confirmed on the basis of its spectral data. Hydrolysis of **8** gave Δ^3-*s*-triazolin-5-one **7a**. In the reaction with **4a**, however, two 1:1 adducts, **9a** and **10a**, were obtained in 19 and 60% yields, respectively.

The minor product **9a** was deduced to be 3,3-dimethyl-1-phenyl-4-thiobenzoyl-*s*-triazolidin-5-one on the basis of the following evidence. The IR spectrum of **9a** was quite similar to that of **6a**, and in its NMR spectrum two methyls-protons and NH-proton appeared at δ 1.89 (6H, s) and 4.95 ppm (1H, broad), besides aromatic protons. Treatment of **9a** with hydrochloric acid gave Δ^3-*s*-triazolin-5-one **7a**. On the other hand, the IR spectrum of major product **10a** exhibited characteristic bands at 3310 (NH), 1650 (C=O), and 1530 cm^{-1}, and the NMR spectrum showed signals at



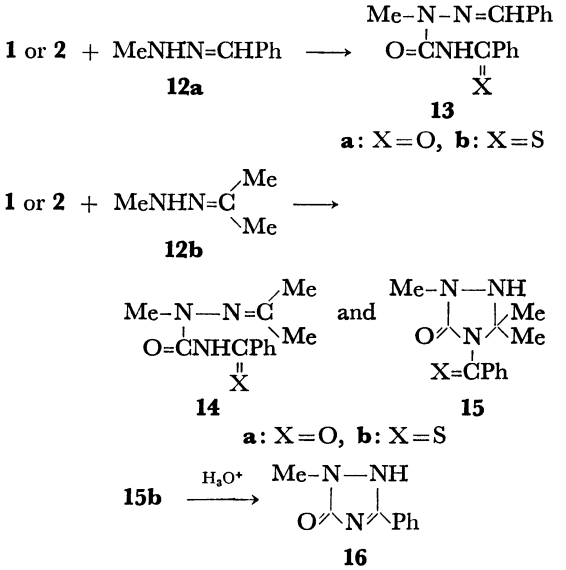
Scheme 2.

δ 1.80 (6H, s, CH_3) and 6.5 ppm (1H, broad, NH), besides aromatic protons. Hydrolysis of **10a** afforded 3-hydroxy-1,5-diphenyltriazole (**11**), whose structure corresponds to that of the compound derived from 1-phenyl-4-thiobenzoylsemicarbazide with the elimination of hydrogen sulfide. The structure of **11** was confirmed by the identification with an authentic sample.[2] On the basis of the above observations, the structure of **10a** was deduced as 3-anilino-2,2-dimethyl-6-phenyl-2,3-dihydro-4H-1,3,5-thiadiazin-4-one, which corresponds to the (4+2) cycloadduct of **2** to the C=N bond of **4a**.

Similarly, **2** reacted with **4b** to give the corresponding *s*-triazolidin-5-one **9b** and 2,3-dihydro-4*H*-1,3,5-thiadiazin-4-one **10b** in 32 and 29% yields, respectively.

Reactions with Benzaldehyde and Acetone Methylhydrazones. The reactions of both isocyanates **1** and **2** with benzaldehyde methylhydrazone (**12a**) afforded the corresponding semicarbazones **13a** and **13b**, whose structures were confirmed on the basis of their spectral data, in good yields respectively.

By the IR and NMR spectroscopic studies it was found that the crystals obtained from the reaction of **1** with acetone methylhydrazone (**12b**) were a mixture of the corresponding semicarbazone **14a** and its ring tautomer **15a**, but no **14a** could be isolated and **15a** was obtained as the sole pure compound from the mixture. Furthermore, the relative amount of **15a** was increased with an increase in the reaction time. Similar phenomena were observed in the reaction of **2** with **12b**, and *s*-triazolidin-5-one **15b**, which on hydrolysis gave 1-methyl-3-phenyl-Δ^3-*s*-triazolin-5-one (**16**), was only isolated (Scheme 3).



Scheme 3.

The above observations indicate that semicarbazones **14a** and **14b** isomerize into the corresponding ring tautomers **15a** and **15b**, respectively. Consequently, the isomerization was followed by the NMR spectroscopy.

Isocyanate **1** was mixed with **12b** in chloroform at −70 °C, and the NMR spectrum of the reaction mix-

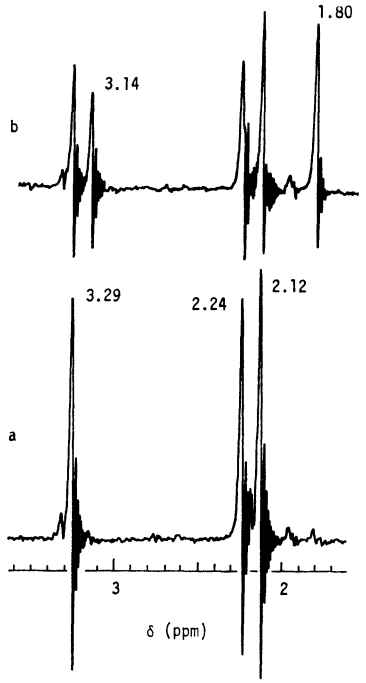


Fig. 1. NMR spectra of the reaction system **1**—**12b** in chloroform at 36.0 °C. a: Pure **14a**. b: A mixture of **14a** and **15a** (44%) after 2.5 hr.

ture was immediately measured at a constant temperature. For example, the NMR spectrum at 36.0 °C is illustrated in Fig. 1-a: three singlets appear at δ 2.12, 2.24, and 3.29 ppm in the same intensity. The singlets at δ 2.12 and 2.24 ppm can be assigned as two methyls-protons of isopropylidene group and that at δ 3.29 is ascribable to the *N*-methyl-protons in the semicarbazone **14a**.[11] The spectrum changes with time. As shown in Fig. 1-b, the initial three singlets decrease in intensity in the same ratio, and new two singlets with the relative intensity of 2: 1 show up at δ 1.80 and 3.14. These new two singlets can be assigned as the 3,3-dimethyls- and *N*-methyl-protons in the *s*-triazolidin-5-one **15a**, respectively. Furthermore, it was found by the IR spectrum that the crude product obtained from the reaction of **1** with **12b** at 0 °C was composed of **14a** and **15a**, and the microanalysis of the product agreed with that of a 1: 1 adduct of **1** to **12b**. These facts indicate clearly that the initial semicarbazone **14a** isomerizes into its ring tautomer **15a**. It was also established that both the isomerizations at 36.0 and 54.0 °C give the equilibrium composition composed of 40% of **14a** and 60% of **15a** after some time.

The first-order rate of the isomerization of **14a** taking into account the equilibrium may be expressed as follows:

$$dx/dt = k(a-x) - k'x \quad (1)$$

where a is the initial concentration of **14a**, x is the concentration of **14a** consumed after t s, and k and k' are the rate constants of the consumption and the formation of **14a** respectively.

If the concentration of **15a** at the equilibrium is x_e,

$$k(a-x_e) - k'x_e = 0 \quad (2)$$

From Eqs. (1) and (2), the rate of the consumption of **14a** may be given by:

$$dx/dt = ka(x_e-x)/x_e \quad (3)$$

Equation (3) then gives:

$$\ln [x_e/(x_e-x)] = kat/x_e$$

As illustrated in Fig. 2, the plots of $\ln[x_e/(x_e-x)]$ *vs.* the reaction times at various temperatures show straight lines. The rate constants k at 30.5, 36.0, 45.5, and 54.0 °C were 4.2×10^{-5}, 9.3×10^{-5}, 2.2×10^{-4}, and 4.0×10^{-4} s^{-1}, respectively. The plots of the logarithm of the rate constants against reciprocal absolute temperatures showed the straight line. The rate of isomerization of **14a** in benzene at 36.0 °C was measured, and the rate constant k was found to be 1.1×10^{-4} s^{-1}: little solvent effect was observed.

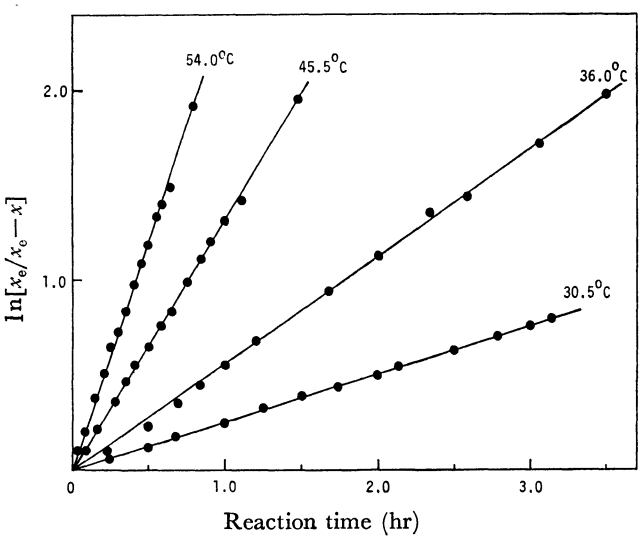


Fig. 2. Plots of the first-order function *vs.* reaction time at various temperatures in the reaction system **1**—**12b**.

The energy parameters calculated on the basis of the above observations are given in Table 1.

It was also clarified by the NMR spectroscopic study that acetone 4-benzoyl-2-phenylsemicarbazone is initially formed in the reaction of **1** with acetone phenylhydrazone (**4a**), and isomerizes into its ring tautomer **6a** with reaction time. The isomerization obeys good first-order kinetics, and the energy parameters and the concentration of **6a** at the equilibrium are also summarized in Table 1.

Table 1. Energy parameters

Parameter[a]	Reaction system	
	1—**12b**	**1**—**4a**
E_a(kcal/mol)	19.2	18.6
A(s^{-1})	3.39×10^9	2.14×10^9
$\Delta H^{\ddagger}_{25}$(kcal/mol)	18.6	18.0
$\Delta S^{\ddagger}_{25}$(cal/mol·deg)	−17.0	−17.7
$\Delta F^{\ddagger}_{25}$(kcal/mol)	23.67	23.27
x_e (%) in $CHCl_3$	60	*ca.* 100

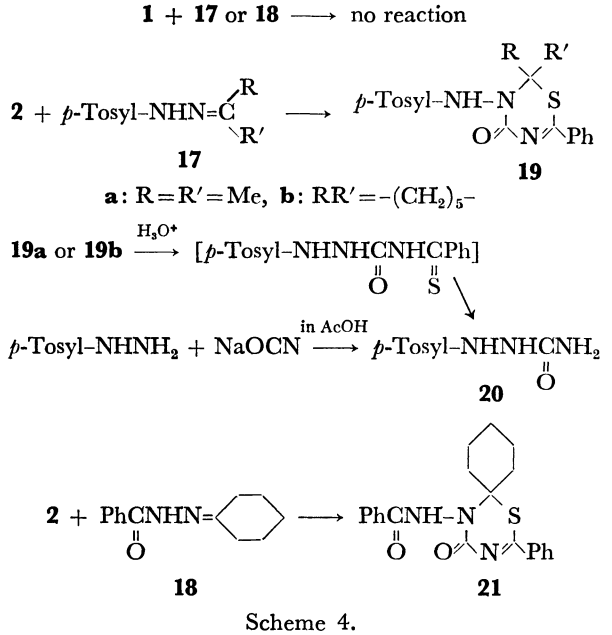
a) E_a: Activation energy; A: Frequency factor; $\Delta H^{\ddagger}_{25}$: Enthalpy of activation at 25 °C; $\Delta S^{\ddagger}_{25}$: Entropy of activation at 25 °C; $\Delta F^{\ddagger}_{25}$: Free energy of activation at 25 °C; x_e: Concentration of *s*-triazolidin-5-one **15a** or **6a** at the equilibrium.

However, semicarbazones **13a** and **13b** did not isomerize into their ring tautomers and were recovered quantitatively even at 80 °C.

Reactions with p-*Tosyl- and Benzoylhydrazones.* On the basis of the results mentioned above, it could be viewed that **1** attacks exclusively the more basic nitrogen atom, and **2** reacts with the more and/or the less basic nitrogen atom of hydrazone. It is then expected that both **1** and **2** would give the (4+2) cycloadducts as predominant products in the reaction with hydrazones having electronwithdrawing groups such as *p*-tosyl and benzoyl.

However, **1** did not react with *p*-tosylhydrazones, **17a** and **17b**, and cyclohexanone benzoylhydrazone (**18**) even when the reaction was carried out under reflux in benzene.

The reaction of **2** with *p*-tosylhydrazones, **17a** and **17b**, afforded the corresponding (4+2) cycloadducts, **19a** and **19b**, whose structures were confirmed on the basis of their spectral data and of the result of hydrolysis.



Scheme 4.

Hydrolyses of both **19a** and **19b** afforded 1-*p*-tosylsemicarbazide (**20**), which was identical with an authentic sample prepared from *p*-tosylhydrazine and cyanic acid.

Similarly, **2** reacted with benzoylhydrazone **18** to give the corresponding (4+2) cycloadduct **21** (Scheme 4).

Experimental

All melting and boiling points are uncorrected. The IR spectra were measured as KBr disks, and NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as an internal reference.

Materials. Benzoyl isocyanate (**1**) was prepared by the reported method.[12] Thiobenzoyl isocyanate (**2**): a solution of 1.0 g of 2-phenylthiazoline-4,5-dione in 10 ml of xylene was heated at 120 °C, giving a reddish violet solution of **2** which was used *in situ*.[13] This solution is referred to as the standard solution of **2**.

Hydrazones were prepared by the reaction of the corresponding hydrazine with carbonyl coumpounds. Benzaldehyde phenyl- (**3a**), mp 152 °C [lit,[14] mp 152.5 °C]; *p*-tolyl- (**3b**), mp 125 °C [lit,[15] mp 125 °C]; *p*-chlorophenylhydrazone (**3c**), mp 129—130 °C [lit,[16] mp 127 °C]; acetone phenyl- (**4a**)- mp 32 °C [lit,[17] mp 21 °C]; *p*-tolyl- (**4b**), mp 51—52 °C [lit,[18] mp 50—52 °C]; *p*-nitrophenylhydrazone (**4c**), mp 149 °C [lit,[19] mp 148—148.5 °C]; benzaldehyde methylhydrazone (**12a**), viscous liquid, NMR ($CDCl_3$) δ: 2.76 (3H, s, N-C**H**$_3$), 5.61 (1H, s, =C**H**), 7.1—7.6 (6H, m, aromatic and N**H**); acetone methylhydrazone (**12b**), bp 115—117 °C, NMR ($CDCl_3$) δ: 1.73, 1.89 (each 3H, s, C**H**$_3$), 2.85 (3H, s, N-C**H**$_3$), 4.32 (1H, broad, N**H**); acetone *p*-tosyl- (**17a**), mp 150 °C [lit,[20] mp 153 °C]; cyclohexanone *p*-tosylhydrazone (**17b**), mp 158 °C [lit,[20] mp 156 °C]; cyclohexanone benzoylhydrazone (**18**), mp 158—159 °C [lit,[21] mp 158—159 °C].

Reaction of 1 with 3a. To a solution of 2.0 g of **3a** in 20 ml of benzene was added 1.5 g of **1** at 0 °C, and then the reaction mixture was stirred at room temperature for 30 min: during which time crystals precipitated. Filtration gave 1.4 g of crystals. The filtrate was evaporated *in vacuo* to leave 2.0 g of crystals. Recrystallization of the combined crystals (3.5 g, 97%) from ethanol afforded 4-benzoyl-2-phenylsemicarbazone (**5a**), mp 164 °C, as colorless needles.

Found: C, 73.32; H, 5.01; N, 12.33%. Calcd for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24%.

Similarly, **1** reacted with **3b** and **3c** under the same conditions, giving the corresponding semicarbazones quantitatively.

4-Benzoyl-2-*p*-tolylsemicarbazone (**5b**): mp 175—176 °C, colorless needles.

Found: C, 74.21; H, 5.20; N, 11.75%. Calcd for $C_{22}H_{19}N_3O_2$: C, 73.93; H, 5.36; N, 11.75%.

IR: 3380 (NH), 1755 (C=O), 1500 and 1480 cm^{-1} (Amide II).

4-Benzoyl-2-*p*-chlorophenylsemicarbazone (**5c**): mp 177—178 °C, colorless needles.

Found: C, 67.02; H, 4.12; N, 11.14%. Calcd for $C_{21}H_{16}N_3O_2Cl$: C, 66.75; H, 4.24; N, 11.13%.

IR: 3380 (NH), 1750 (C=O), 1500 and 1480 (Amide II).

Reaction of 1 with 4b. To a solution of 4.0 g of **4b** in 20 ml of benzene was added 3.6 g of **1** at 0 °C, and the reaction mixture was stirred at room temperature for 30 min. The mixture was concentrated *in vacuo* to give resinous material, which on trituration with petroleum ether (bp 35—50 °C) crystallized. Recrystallization from ethanol gave 6.8 g (90%) of 4-benzoyl-3,3-dimethyl-1-*p*-tolyl-*s*-triazolidin-5-one (**6b**), mp 161—162 °C (decomp.), as colorless prisms.

Found: C, 70.17; H, 6.22; N, 13.55%. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58%.

IR: 3250 (NH), 1750, 1655 (C=O) and 1320 cm^{-1}. NMR ($CDCl_3$) δ: 1.70 (6H, s, C**H**$_3$), 2.28 (3H, s, -C_6H_4C**H**$_3$), 4.1 (1H, broad, N**H**), 7.0—7.7 (9H, m, aromatic protons).

Similarly, the reaction of **1** with **4a** and **4c** under the same conditions gave the corresponding *s*-triazolidin-5-ones in almost quantitative yields, respectively.

4-Benzoyl-3,3-dimethyl-1-phenyl-*s*-triazolidin-5-one (**6a**): mp 140.5—141 °C (decomp.), colorless prisms.

Found: C, 69.31; H, 6.02; N, 14.12%. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.13; H, 5.80; N, 14.23%.

4-Benzoyl-3,3-dimethyl-1-*p*-nitrophenyl-*s*-triazolidin-5-one (**6c**): mp 203.5 °C (decomp.), pale yellow prisms.

Found: C, 59.95; H, 4.52; N, 16.52%. Calcd for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.74; N, 16.46%.

IR: 3230 (NH), 1750, 1660 (C=O) and 1320 cm^{-1}.

Hydrolysis of 5a. A solution of 0.3 g of **5a** in 10 ml of 15% hydrochloric acid was heated at 100 °C for 1 hr. After cooling, filtration gave crystals. Recrystallization from

ethanol afforded 0.24 g (100%) of 1,3-diphenyl-Δ^3-*s*-triazolin-5-one (**7a**), mp 230—231 °C, which was identical with an authentic sample.[2]

Similarly, hydrolysis of **5b**, **5c**, and **6a—6c** with hydrochloric acid afforded the corresponding Δ^3-*s*-triazolin-5-ones in good yields, respectively. 1-*p*-Tolyl- (**7b**), mp 232.5 °C [lit,[2] mp 232.5 °C], 1-*p*-chlorophenyl- (**7c**), mp 273 °C [lit,[2] mp 273 °C], and 1-*p*-nitrophenyl-3-phenyl-Δ^3-*s*-triazolin-5-one (**7d**), mp 329—330 °C [lit,[2] mp 329—330 °C], were identified with the respective authentic samples.[2]

Reaction of 2 with 3a. To a standard solution of **2** was added 1.0 g of **3a** at 0 °C: crystals precipitated immediately. Filtration gave pale yellow crystals, which on recrystallization from ethanol afforded 1.5 g (79% yield based on 2-phenylthiazoline-4,5-dione used) of 2-phenyl-4-thiobenzoylsemicarbazone (**8**), mp 163—163.5 °C (decomp.), as pale yellow prisms.

Found: C, 70.38; H, 4.62; N, 11.48%. Calcd for $C_{21}H_{17}N_3OS$: C, 70.18; H, 4.77; N, 11.69%.

IR: 3400 (NH), 1720 (C=O) and 1460 cm^{-1} (Amide II). NMR ($CDCl_3$) δ: 7.1—7.9 (16H, m, aromatic and N=C**H**), 11.5 (1H, broad, N**H**).

Reaction of 2 with 4a. To a standard solution of **2** was added 0.78 g of **4a** at 0 °C, and the reaction mixture was stirred at room temperature for 1 hr: during which time crystals appeared. Filtration gave crystals, which on recrystallization from acetone afforded 0.97 g (60%) of 3-anilino-2,2-dimethyl-6-phenyl-2,3-dihydro-4*H*-1,3,5-thiadiazin-4-one (**10a**), mp 124—125 °C (decomp.), as yellow prisms.

Found: C, 65.54; H, 5.40; N, 13.72%. Calcd for $C_{17}H_{17}N_3OS$: C, 65.58; H, 5.50; N, 13.50%.

The filtrate was concentrated *in vacuo* below 15 °C to leave a residue, which on trituration with diethyl ether gave crystals. Recrystallization from ethanol afforded 0.31 g (19%) of 3,3-dimethyl-1-phenyl-4-thiobenzoyl-*s*-triazolin-5-one (**9a**), mp 141 °C (decomp.), as yellow needles.

Found: C, 65.64; H, 5.26; N, 13.77%. Calcd for $C_{17}H_{17}N_3OS$: C, 65.58; H, 5.50; N, 13.50%.

IR: 3270 (NH), 1720 (C=O) and 1350 cm^{-1}.

Similarly, the reaction of **2** with **4b** afforded the corresponding 1:1 adducts, **9b** and **10b**, in 32 and 29% yields, respectively.

3,3-Dimethyl-4-thiobenzoyl-1-*p*-tolyl-*s*-triazolidin-5-one (**9b**): mp 151.5—152 °C (decomp.), yellow needles.

Found: C, 66.69; H, 5.90; N, 13.00%. Calcd for $C_{18}H_{19}N_3OS$: C, 66.44; H, 5.89; N, 12.92%.

IR: 3260 (NH), 1720 (C=O), 1340 and 1330 cm^{-1}. NMR ($CDCl_3$) δ: 1.90 (6H, s, C**H**$_3$), 2.30 (3H, s, $-C_6H_4CH_3$), 5.05 (1H, broad, N**H**), 7.0—7.8 (9H, m, aromatic protons).

2,2-Dimethyl-3-*p*-methylanilino-6-phenyl-2,3-dihydro-4*H*-1,3,5-thiadiazin-4-one (**10b**): mp 115—116 °C (decomp.), yellow prisms.

Found: C, 66.58; H, 5.93; N, 12.89%. Calcd for $C_{18}H_{19}N_3OS$: C, 66.44; H, 5.89; N, 12.92%.

IR: 3310 (NH), 1660 (C=O), 1550 and 1520 cm^{-1}. NMR ($CDCl_3$) δ: 1.80 (6H, s, C**H**$_3$), 2.26 (3H, s, $-C_6H_4CH_3$), 6.4 (1H, broad, N**H**), 6.8—7.6 (7H, m, aromatic protons), 8.0—8.3 (2H, m, *o*-protons of 6-phenyl).

Hydrolysis of 10a. A solution of 1.5 g of **10a** in 20 ml of methanol was refluxed with concentrated hydrochloric acid (5 ml) for 30 min. The mixture was concentrated *in vacuo* to leave a residue, which on trituration with aqueous ethanol gave crystals. Recrystallization from ethanol afforded 0.79 g (69%) of 3-hydroxy-1,5-diphenyl-*s*-triazole (**11**), mp 290 °C [lit,[2] mp 290 °C], as colorless needles.

Reaction of 1 with 12a. To a solution of 1.34 g of **12a** in 10 ml of benzene was added 1.47 g of **1** at 0 °C, and then the reaction mixture was stirred at room temperature for 30 min. The mixture was concentrated *in vacuo* to leave a residue, which on trituration with petroleum ether (bp 40—60 °C) gave crystals. Recrystallization from a mixture of benzene and petroleum ether (bp 60—80 °C) afforded 2.4 g (86%) of benzaldehyde 4-benzoyl-2-methylsemicarbazone (**13a**), mp 137—138 °C (decomp.), as colorless needles.

Found: C, 68.54; H, 5.23; N, 14.90%. Calcd for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.38; N, 14.94%.

IR: 3450 (NH), 1745 (C=O), 1510 and 1490 cm^{-1} (Amide II). NMR ($CDCl_3$) δ: 3.43 (3H, s, N–C**H**$_3$), 7.3—8.0 (11H, m, aromatic and N=C**H**), 10.45 (1H, broad, N**H**).

Similarly, the reaction of a standard solution of **2** with **12a** gave the 2-methyl-4-thiobenzoylsemicarbazone **13b**, mp 146—147 °C (decomp.), in 74% yield.

Found: C, 64.61; H, 4.95; N, 13.94%. Calcd for $C_{16}H_{15}N_3OS$: C, 64.63; H, 5.09; N, 14.14%.

IR: 3370 (NH), 1735 (C=O) and 1505 cm^{-1} (Amide II). NMR ($CDCl_3$) δ: 3.41 (3H, s, N–C**H**$_3$), 7.3—7.9 (11H, m, aromatic and N=C**H**), 11.4 (1H, broad, N**H**).

Reaction of 1 with 12b. To a solution of 0.86 g of **12b** in 15 ml of benzene was added 1.47 g of **1**, and then the reaction mixture was stirred at room temperature for 10 hr. The mixture was concentrated *in vacuo* to leave a residue, which on trituration with petroleum ether (bp 40—60 °C) gave crystals. The crystals were washed with benzene and then diethyl ether to afford 1.65 g (71%) of 4-benzoyl-1,3,3-trimethyl-*s*-triazolidin-5-one (**15a**), mp 105.5—107 °C (decomp.).

Found: C, 61.78; H, 6.33; N, 18.27%. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.78; H, 6.48; N, 18.02%.

IR: 3230 (NH), 1735 and 1645 cm^{-1} (C=O). NMR ($CDCl_3$) δ: 1.80 (6H, s, C**H**$_3$), 3.14 (3H, s, N–C**H**$_3$), 4.5 (1H, broad, N**H**), 7.3—7.9 (5H, m, aromatic protons).

Similarly, the reaction of a standard solution of **2** with **12b** at 0 °C for 10 min afforded 67% yield of the corresponding *s*-triazolidin-5-one **15b**, mp 106.5—107.5 °C (decomp.), as yellow needles.

Found: C, 57.97; H, 5.89; N, 17.09%. Calcd for $C_{12}H_{15}N_3OS$: C, 57.82; H, 6.07; N, 16.86%.

IR: 3240 (NH) and 1735 cm^{-1} (C=O).

Hydrolysis of 15b. A solution of 0.2 g of **15b** in 10 ml of methanol was stirred with concentrated hydrochloric acid (1 ml) at room temperature for 1 hr: during which time hydrogen sulfide evolved and the mixture turned into a colorless solution. The solution was concentrated *in vacuo* to leave crystals, which on recrystallization from ethanol afforded 0.13 g (93%) of 1-methyl-3-phenyl-Δ^3-*s*-triazolin-5-one (**16**), mp 216.5—217.5 °C, as colorless needles.

Found: C, 61.89; H, 4.96; N, 24.19%. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99%.

IR: 2800—3140 (NH) and 1690 cm^{-1} (C=O). NMR ($CDCl_3$) δ: 3.56 (3H, s, N–C**H**$_3$), 7.4—8.0 (5H, m, aromatic protons), 11.1 (1H, broad, N**H**).

General Kinetic Method. After a solution of **1** in benzene or chloroform was mixed with equimolar amount of **12b** or **4a** at −70 °C, a part of the solution was quickly transferred into a NMR-measurement tube and then the variation in the semicarbazone/*s*-triazolidin-5-one ratio was followed by the NMR spectrum at a constant temperature.

Reaction of 2 with 17a. A standard solution of **2** was heated with 1.09 g of **17a** at 50—70 °C for 5 min, and then the mixture was stirred at room temperature for 1 hr: during which time crystals precipitated. Recrystallization from a mixture of benzene and petroleum ether (bp 60—80 °C) afforded 1.38 g (73%) of 2,2-dimethyl-6-phenyl-3-*p*-tosylamino-2,3-dihydro-4*H*-1,3,5-thiadiazin-4-one (**19a**), mp 149

°C (decomp.), as colorless needles.

Found: C, 55.76; H, 4.91; N, 10.67%. Calcd for $C_{18}H_{19}N_3O_3S_2$: C, 55.52; H, 4.92; N, 10.79%.

IR: 3220 (NH) and 1685 cm^{-1} (C=O). NMR ($CDCl_3$) δ: 1.74, 2.01 (each 3H, s, CH_3), 2.42 (3H, s, $-C_6H_4CH_3$), 7.2—8.1 (10H, m, aromatic and NH).

Similarly, **2** reacted with **17b** to give 63% yield of the corresponding 2,3-dihydro-4*H*-1,3,5-thiadiazin-4-one **19b**, mp 151.5—152 °C (decomp.), as colrless prisms.

Found: C, 59.01; H, 5.36; N, 9.80%. Calcd for $C_{21}H_{23}N_3O_3S_2$: C, 58.73; H, 5.40; N, 9.79%.

IR: 3250 (NH) and 1685 cm^{-1} (C=O). NMR ($CDCl_3$) δ: 2.40 (3H, s, $-C_6H_4CH_3$), 1.5—2.7 (10H, m, CH_2), 7.0—8.1 (10H, m, aromatic and NH).

1-p-Tosylsemicarbazide (20). i) A solution of 0.5 g of **19a** in 10 ml of methanol was refluxed with concentrated hydrochloric acid (5 ml) for 30 min. The mixture was concentrated *in vacuo* to leave crystals, which on recrystallization from ethanol gave 0.21 g (72%) of **20** as colorless prisms, mp 243 °C (decomp.).

Found: C, 41.72; H, 4.73; N, 18.63%. Calcd for $C_8H_{11}N_3O_3S$: C, 41.92; H, 4.84; N, 18.34%.

IR: 3480, 3390, 3060 (NH), 1650 (C=O) and 1170 cm^{-1} (SO_2).

Similarly, hydrolysis of **19b** (0.8 g) with concentrated hydrochloric acid (10 ml) at 100 °C for 5 hr gave 0.43 g (100%) of **20**.

ii) To a suspension of 0.8 g of *p*-tosylhydrazine in 10 ml of acetic acid was slowly added 2.0 g of sodium cyanate at room temperature. The mixture was heated at 70—80 °C for 10 min, and then stirred at room temperature for 1 hr. After it was poured into ice-water, filtration gave crystals, which on recrystallization from ethanol afforded 0.75 g (76.5 %) of **20**, mp 243 °C (decomp.).

Reaction of 2 with 18. To a standard solution of **2** was added 1.13 g of **18** at 0 °C, and the mixture was then stirred at room temperature for 1 hr: during which time crystals precipitated. Recrystallization from benzene afforded 1.5 g (76%) of the 2,3-dihydro-4*H*-1,3,5-thiadiazin-4-one **21**, mp 158.5—159 °C (decomp.), as yellow needles.

Found: C, 66.55; H, 5.75; N, 10.86%. Calcd for $C_{21}H_{21}N_3O_2S$: C, 66.48; H, 5.58; N, 11.08%.

IR: 3320 (NH), 1695 and 1665 cm^{-1} (C=O). NMR ($CDCl_3$) δ: 1.2—1.9 (6H, m, CH_2), 1.9—2.5 (4H, m, CH_2), 7.0—8.2 (10H, m, aromatic protons), 9.91 (1H, s, NH).

This work was supported in part by a Grant-in-Aid of Industrial Scientific Research from the Asahi Glass Co., Ltd. for which the authors' thanks are due.

References

1) Part XIII of this series: O. Tsuge and S. Kanemasa, *J. Org. Chem.*, **38**, 2972 (1973).
2) O. Tsuge, S. Kanemasa, and M. Tashiro, *Tetrahedron*, **24**, 5205 (1968).
3) H. Schildknecht and G. Hatzmann, *Ann. Chem.*, **724**, 226 (1969).
4) A. Arnold, *Ber.*, **30**, 1015 (1897).
5) R. C. Goodwin and J. R. Bailey, *J. Amer. Chem. Soc.*, **46**, 2827 (1924).
6) L. Rolla, *Gazz. chim. ital.*, **38, I**, 327 (1908).
7) O. Tsuge and K. Sakai, This Bulletin, **45**, 1534 (1972).
8) O. Tsuge and S. Kanemasa, *ibid.*, **45**, 2877 (1972).
9) O. Tsuge and S. Kanemasa, *ibid.*, **45**, 3591 (1972).
10) O. Tsuge and S. Kanemasa, *Tetrahedron*, **28**, 4737 (1972).
11) The NMR spectrum of semicarbazone **12b** exhibited three singlets ascribable to two methyls-protons of isopropylidene group and *N*-methyl-protons at δ 1.73, 1.89, and 2.85 ppm, respectively.
12) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **27**, 4361 (1962); *ibid.*, **28**, 1805 (1963).
13) J. Goerdeler and H. Schenk, *Chem. Ber.*, **98**, 2954 (1965).
14) E. Fischer, *Ann. Chem.*, **190**, 67 (1877).
15) H. von Pechmann and P. Runge, *Ber.*, **27**, 1693 (1894).
16) J. T. Hewitt, *J. Chem. Soc.*, **63**, 868 (1893).
17) W. Theilacker and H. J. Tomuschat, *Ber.*, **88**, 1086 (1955).
18) J. Raschen, *Ann. Chem.*, **239**, 223 (1887).
19) E. Bamberger and H. Sternitzki, *Chem. Ber.*, **26**, 1291 (1893).
20) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, **1952**, 4735.
21) O. Tsuge, M. Tashiro, and K. Hokama, *Kogyo Kagaku Zasshi*, **71**, 1203 (1968).