General Procedure for Cleavage of Protective Groups Using Ferric Chloride Adsorbed on Silica Gel. A mixture of 5 mmol of a protected hydroxy compound and 0.10 g of $FeCl_3$–SiO_2 reagent in 20 mL of $CHCl_3$ or CH_3COCH_3 was stirred at room temperature. The reaction was monitored by GC or TLC. After completion of the reaction, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The product was purified by distillation, crystallization, or column chromatography.

3-*O*-(*tert*-Butyldimethylsilyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (17). The title compound was obtained as a syrup: IR (neat) 1250 cm^{-1}; ^1H NMR δ 0.16 (s, 6 H), 0.83 (s, 9 H), 1.32 (s, 3 H), 1.50 (s, 3 H), 2.00 (br s, 1 H), 2.51 (br s, 1 H), 3.75–4.40 (m, 6 H), 5.93 (d, J = 3.7 Hz, 1 H). Anal. Calcd for $C_{15}H_{30}O_6Si$: C, 53.86; H, 9.04. Found: C, 53.80; H, 8.97.

Registry No. 1, 100-79-8; 2, 4352-95-8; 3, 4352-98-1; 4, 99605-24-0; 5, 67124-67-8; 6, 99605-25-1; 7, 6226-44-4; 8, 99605-26-2; 9, 582-52-5; 10, 18549-40-1; 11, 16713-80-7; 12, 24807-96-3; 13, 18685-18-2; 14, 22529-61-9; 15, 3162-96-7; 16, 99605-27-3; 17, 99605-28-4; 18, 99605-29-5; 19, 85951-08-2; 20, 5330-64-3; 21, 18325-46-7; 1,2,3-propanetriol, 56-81-5; 2-heptanone, 110-43-0; 2-pentanone, 107-87-9; *trans*-1,2-cyclohexanediol, 1460-57-7; cyclohexanol, 108-93-0; 2-heptanol, 543-49-7; 1-butanol, 71-36-3; cyclohexylmethanol, 100-49-2; methyl α-D-glucopyranoside, 97-30-3; ferric chloride, 7705-08-0.

Reinvestigation on the Adducts Derived from *N*-Alkyloxaziridine and Phenyl Isothiocyanate

Mitsuo Komatsu,* Yoshiki Ohshiro, Toshio Agawa, Mineo Kuriyama, Noritake Yasuoka, and Nobutami Kasai*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

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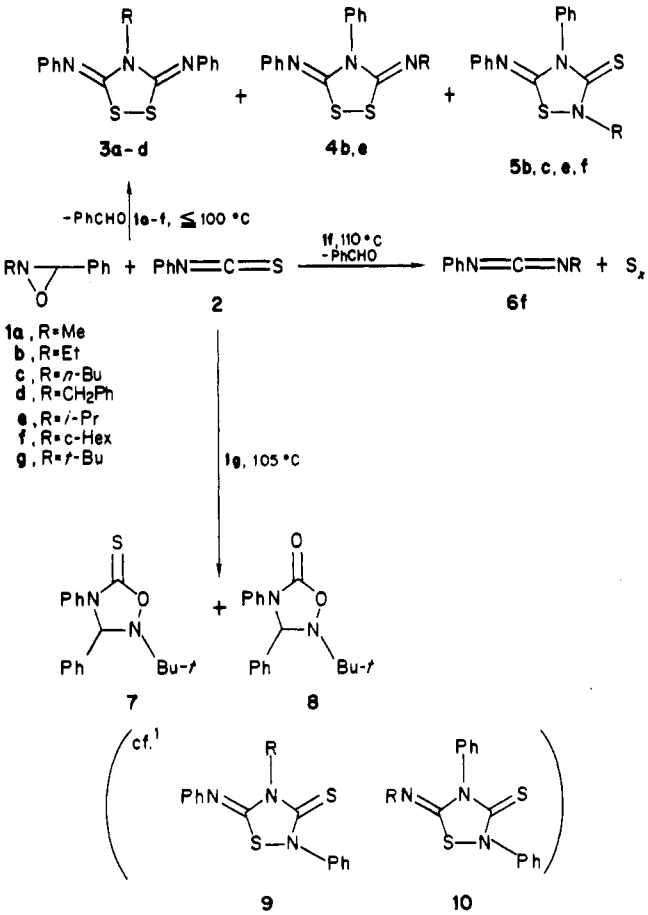
Previously we reported reactions of *N*-alkyloxaziridines **1** with sulfur-containing heterocumulenes such as carbon disulfide and phenyl isothiocyanate (**2**) leading to heterocyclic compounds or to another heterocumulene with incorporation of an alkylnitrene moiety.[1] The reaction of **1f** (R = c-Hex) with **2**, for example, afforded thiadiazolidine derivative **5f** at 90 °C but *N*-cyclohexyl-*N'*-phenylcarbodiimide (**6**) at 110 °C as illustrated in Scheme I. When the N-substituent of **1** was a *tert*-butyl group (**1g**), 1:1 cycloadducts **7** and **8** were isolated. However, the structures of the products **3** and **5** were assigned as thiadiazolidines **9** and **10**, respectively, in the preceding paper.[1] Similar reactions, viz., alkyl azides with isothiocyanates, were extensively studied by L'abbé et al., who assigned structures of the products mainly by ^{13}C NMR[2] and revealed rearrangement reactions among the products.[3]

Recently, we reexamined cyclic adducts **3b** etc. by means of X-ray diffraction and also by ^{13}C NMR and determined the molecular structures of the products **3** and **5**: the formerly proposed structures **9** and **10** were not correct. Structures of cycloadducts **7** and **8** (R = *t*-Bu) were correct, judging from their spectral and analytical data or identification with an authentic sample.[1]

Scheme I



A careful workup of the reaction of **1b** (R = Et) with **2** carried out at 80 °C in benzene afforded not only the adducts **3b** and **5b** but also a third isomeric cycloadduct (**4b**), previously a contaminant of **3b**.[4] Conclusive evidence for the structures of **3b** and **5b** has been obtained by X-ray crystallography.[5] Clearly, the molecule assigned as **9b** (R = Et) was found to be 4-ethyl-3,5-bis(phenylimino)-1,2,4-dithiazolidine (**3b**, Figure 1) and **10b** (R = Et) to be 2-ethyl-4-phenyl-5-(phenylimino)-1,2,4-thiadiazolidine-3-thione (**5b**, Figure 1). ^{13}C NMR spectra of compounds **3b** and **5b** were in good agreement with X-ray data.

Efforts to obtain suitable crystals of **4b** for X-ray analysis failed. In the ^1H NMR spectrum of **4b**, the methylene protons appear in higher field than those of **3b** by ca. 1 ppm. The ^{13}C NMR spectrum clearly shows that the structure of **4b** is not symmetrical and no thione carbon[3] but two types of imino carbons were observed. The IR spectrum of **4b** exhibited rather weak absorption due to the C=N bond at 1615 cm^{-1}, while relatively wide absorption of the C=N bond of **3b** was observed at around 1580 cm^{-1}. These data as well as that of mass spectrum supported the 3,5-bis(imino)-1,2,4-dithiazolidine structure of **4b**.

Similarly we reexamined the cycloadducts having other *N*-alkyl substituents by NMR and IR spectral data (Table

(1) Komatsu, M.; Ohshiro, Y.; Yasuda, K.; Ichijima, S.; Agawa, T. *J. Org. Chem.* **1974**, *39*, 957.
(2) L'abbé, G. *Tetrahedron* **1982**, *38*, 3537; *J. Heterocycl. Chem.* **1984**, *21*, 627 and references cited therein.
(3) L'abbé, G.; Van Loock, E.; Velherst, G.; Toppet, S. *J. Org. Chem.* **1975**, *40*, 607. L'abbé, G.; Velherst, G.; Toppet, S. *Ibid.* **1977**, *42*, 1159.

(4) A trace amount of a cycloadduct consisting of PhN=C=S, PhN=C=NEt, and NEt was isolated and the structure was determined to be 2,4-diethyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine by spectral analysis: mp 82–83 °C; IR (Nujol) 1620 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H, Me), 1.37 (t, 3 H, Me), 2.95 (q, 2 H, CH_2), 4.06 (q, 2 H, CH_2), 6.7–7.4 (m, 10 H, 2 Ph); ^{13}C NMR ($CDCl_3$) 148.0 (s, PhN=), 148.2 (s, PhN=), 150.0 (s, C=N), 153.3 ppm (s, C=N); MS, m/e 324 (M^+). Anal. Calcd for $C_{18}H_{20}N_4S$: C, 66.35; H, 6.21; N, 17.27; S, 9.88. Found: C, 66.74; H, 6.17; N, 17.29; S, 9.85.
(5) For details: Kuriyama, M.; Yasuoka, N.; Kasai, N.; Komatsu, M.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.*, in contribution.

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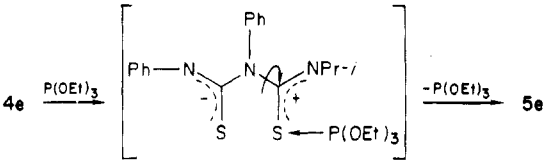
Table I. Reassignment of the Adducts from Oxaziridine 1 and Phenyl Isothiocyanate (2)

oxaziridine 1		yield (%) of products		
	R	3	4	5
1a	Me	6		
1b	Et	21	2	4
1c	*n*-Bu	8		
1d	CH_2Ph	7		
1e	*i*-Pr		36	1
1f	*c*-Hex		*a*	58

[a] The product was detected by IR spectra, but could not be purified.

II), and the structures reported there[1] were corrected as listed in Table I.

The previously reported chemical properties of the dithiazolidine **4e** (R = *i*-Pr) are now explained better with the corrected structure. For example, reduction of **4e** with $LiAlH_4$ giving *N,N'*-diphenylthiourea is understood without the postulated rearrangement during the reaction.[1] Rearrangement of dithiazolidine **4e** to thiadiazolidinethione **5e** (R = *i*-Pr) in the presence of triethyl phosphite



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is also reasonably explained in terms of the corrected structures.

Furthermore, evidence for rearrangement of **4** to **3** during the reaction was observed when monitored by ^1H NMR. Formation of dithiazolidine **4b** occurred at the very early stage of the reaction. The amount of **4b** increased to some extent and then started to decrease. While thiadiazolidinethione **5b** increased steadily, dithiazolidine **3b** appeared much later than **4b** and gradually became the main product. A similar type of rearrangement of 3-(benzoylimino)-5-(methylimino)-4-phenyl-1,2,4-dithiazolidine to 3-(benzoylimino)-4-methyl-5-(phenylimino)-1,2,4-dithiazolidine in the presence of benzoyl isothiocyanate has been reported.[6]

Table II. ^1H and ^{13}C NMR Data of Compounds 3, 4, and 5[a]

compd	R	mp (°C) [color of crystals]	^1H NMR ($CDCl_3$), δ	^{13}C NMR ($CDCl_3$), ppm
3b	Et	156.5-157.5 [pale yellow]	4.31 (NCH_2)	153.4 (C=N), 149.2
3c	*n*-Bu	95-96 [pale yellow]	4.27 (NCH_2)	153.7 (C=N), 149.2
4b	Et	169-170 [pale yellow]	3.33 (NCH_2)	153.9 (C=N), 150.3 (C=N), 149.3, 139.8
4e	*i*-Pr	166.5-167 [pale yellow]	3.47 (NCH)	153.9 (C=N), 149.1 (C=N), 147.9, 139.4
5b	Et	153-154 [colorless]	4.07 (NCH_2)	177.0 (C=S), 153.8 (C=N), 150.0, 137.8
5c	*n*-Bu	115-116 [colorless]	4.00 (NCH_2)	177.7 (C=S), 154.1 (C=N), 149.2, 138.1
5e	*i*-Pr	196.5-197 [colorless]	5.41 (NCH)	176.6 (C=S), 154.1 (C=N), 150.5, 137.6
5f	c-Hex	208-209 [colorless]	5.03 (NCH)	176.3 (C=S), 150.3 (C=N), 147.5, 137.5

[a] For compounds **3a** and **3d**, see ref 3.

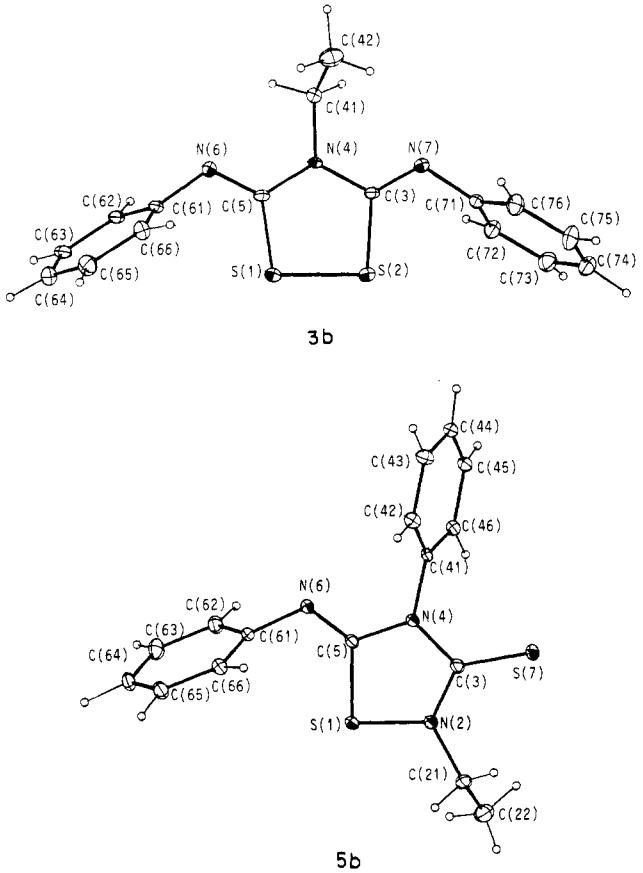
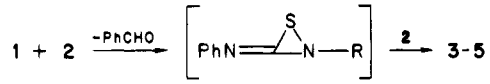


Figure 1. ORTEP drawings for **3b** and **5b**.[5]

In spite of the above structural reassignment, the results do not deny assumption of formation of the thiaziridine-imine intermediate **12** from oxaziridine **1** and isothiocyanate **2** with loss of benzaldehyde.[1] The intermediate also well explains formation of carbodiimide **6** in one case analogously to formation of isothiocyanates from **1** and carbon disulfide.[1] The product distribution summarized in Table I seems to be delicately affected by rearrangement among the isomers **3–5**, which would be dependent on the substituents, and by reaction conditions.



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Experimental Section

Melting points (uncorrected), IR, and mass spectra (70 eV) were obtained as reported earlier.[7] NMR spectra were taken on JEOL JNM PMX-60 and FX-90Q spectrometers in $CDCl_3$ solutions using tetramethylsilane as internal standard. Reactions were carried out under nitrogen.

Materials. Phenyl isothiocyanate was obtained commercially. Preparation and determination of purity of the oxaziridine **1b** were done by described procedures.[7]

Reaction of Oxaziridine 1b with Isothiocyanate (2). To a solution of **2** (10.9 g, 81 mmol) in benzene (10 mL) was added **1b** (6.35 g, 40 mmol, active oxygen content 94%) in benzene (10 mL) dropwise with stirring, and the solution was allowed to stand at 80 °C for 5 h. Distillation of the reaction mixture gave 4.1 g (97%) of benzaldehyde and addition of a mixture of ether–hexane to the residue afforded crystalline sulfur (140 mg) and a large amount of viscous oil. The oil was chromatographed (SiO_2–benzene–hexane) to give 2.66 g (21%) of 4-ethyl-3,5-bis(phenylimino)-1,2,4-dithiazolidine (**3b**), 218 mg (2%) of 3-(ethylimino)-4-phenyl-5-(phenylimino)-1,2,4-dithiazolidine (**4b**), 436 mg (4%) of 2-ethyl-4-phenyl-5-(phenylimino)-1,2,4-thiadiazolidine-3-thione (**5b**), and 357 mg of sulfur (total yield 39%) after repeated crystallization of the eluted fractions.

Dithiazolidine **3b** was recrystallized from EtOH–benzene as colorless needles: mp 156.5–157.5 °C; IR (Nujol) 1580 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 1.43 (t, 3 H, J = 7.0 Hz, Me), 4.31 (q, 2 H, J = 7.0 Hz, CH_2), 6.8–7.6 (m, 10 H, 2 Ph); ^{13}C NMR (see, Table II); MS, m/e 313 (M^+).

Anal. Calcd for $C_{16}H_{15}N_3S_2$: C, 61.31; H, 4.82; N, 13.41. Found: C, 61.35; H, 4.74; N, 13.23.

Dithiazolidine **4b** was obtained as pale yellow needles from EtOH–benzene: mp 169–170 °C; IR (Nujol) 1615 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 1.16 (t, 3 H, J = 7.3 Hz, Me), 3.33 (q, 2 H, J = 7.3 Hz, CH_2), 6.7–7.6 (m, 10 H, 2 Ph); ^{13}C NMR (see, Table II); MS, m/e 313 (M^+).

Anal. Calcd for $C_{16}H_{15}N_3S_2$: C, 61.31; H, 4.82; N, 13.41. Found: C, 61.31; H, 4.98; N, 13.08.

Thiadiazolidinethione **5b** was obtained as colorless needles from CH_2Cl_2–hexane: mp 153–154 °C; IR (Nujol) 1625 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 1.29 (t, 3 H, J = 6.8 Hz, Me), 4.07 (q, 2 H, J = 6.8 Hz, CH_2), 6.7–7.5 (m, 10 H, 2 Ph); ^{13}C NMR (see, Table II); MS, m/e 313 (M^+).

Anal. Calcd for $C_{16}H_{15}N_3S_2$: C, 61.31; H, 4.82; N, 13.41. Found: C, 61.29; H, 4.83; N, 13.41.

Acknowledgment. We are very grateful to Prof. Gerrit L'abbé and Dr. Suzanne Toppet of University of Louvain, Belgium for helpful discussions and ^{13}C NMR measurements of some of the products. Thanks are also due to Miss Nobuko Kanehisa who helped us with ORTEP drawings.

Registry No. **1b**, 7771-15-5; **2**, 103-72-0; **3a**, 61249-39-6; **3b**, 99642-85-0; **3c**, 55210-96-3; **3d**, 55000-06-1; **4b**, 99642-86-1; **4e**, 99642-87-2; **5b**, 99642-88-3; **5c**, 99642-89-4; **5e**, 99642-90-7; **5f**, 99642-91-8; benzaldehyde, 100-52-7; sulfur, 7704-34-9.

(6) L'abbé, G.; Timmerman, A.; Martens, C.; Toppet, S. *J. Org. Chem.* **1978**, *43*, 4951.
(7) Komatsu, M.; Ohshiro, Y.; Hotta, H.; Sato, M.; Agawa, T. *J. Org. Chem.* **1974**, *39*, 948.

The Proton Sponge as Nucleophile

François Terrier,* Jean-Claude Halle, Marie-José Pouet, and Marie-Paule Simonnin

Laboratoire de Physicochimie des Solutions, U.A. CNRS 403, Ecole Nationale Supérieure de Chimie de Paris, 11, Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

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4,6-Dinitrobenzofuroxan (DNBF) and 4,6-dinitrobenzofurazan (DNBZ) are very strong aromatic electrophiles, which is reflected in their high ability to react with weak bases,[1-3] including very weak carbon bases like enols or II-excessive aromatic or heteroaromatic derivatives.[4,5] In these last cases, the reactions lead to the formation of

(1) (a) Terrier, F.; Millot, F.; Norris, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 5883. (b) Terrier, F. *Chem. Rev.* **1982**, *82*, 77. (c) Terrier, F.; Chatrousse, A. P.; Soudais, Y.; Hlaibi, M. *J. Org. Chem.* **1984**, *49*, 4176.
(2) Strauss, M. J.; Renfrow, R. A.; Buncel, E. *J. Am. Chem. Soc.* **1983**, *105*, 2473.
(3) (a) Spear, R. J.; Norris, W. P.; Read, R. W. *Tetrahedron Lett.* **1983**, *24*, 1555. (b) Read, R. W.; Spear, R. J.; Norris, W. P. *Aust. J. Chem.* **1983**, *36*, 1227.
(4) Terrier, F.; Simonnin, M. P.; Pouet, M. J.; Strauss, M. J. *J. Org. Chem.* **1981**, *46*, 3537.
(5) (a) Halle, J. C.; Simonnin, M. P.; Pouet, M. J.; Terrier, F. *Tetrahedron Lett.* **1983**, *24*, 2255. (b) Terrier, F.; Halle, J. C.; Simonnin, M. P.; Pouet, M. J. *J. Org. Chem.* **1984**, *49*, 4363. (c) Halle, J. C.; Pouet, M. J.; Simonnin, M. P.; Terrier, F. *Tetrahedron Lett.* **1985**, *26*, 1307.

0022-3263/86/1951-0409$01.50/0