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Thermal Decomposition of 2*H*-[1,2,4]Oxadiazolo[2,3-*a*]pyridine-2-thione and 2*H*-[1,2,4]Oxadiazolo[2,3-*b*]pyridazine-2-thiones: Generation of Aza-heteroaromatic α-Isocyanates and Their Utilization for the Synthesis of Unsymmetrical Disubstituted Ureas

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Thermal decomposition of 2*H*-[1,2,4]oxadiazolo[2,3-*a*]pyridine-2-thione afforded 3-(2-pyridyl)-2*H*-pyrido[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-dione and 1,3-di(2-pyridyl)urea, and similar decomposition of its pyridazine analog afforded 3-(3-pyridazinyl)-2*H*-pyridazino[1,6-*a*]-1,3,5-triazine-2,4(3*H*)-dione and 1,3-di(3-pyridazinyl)urea. Aza-heteroaromatic α-isocyanates, which are intermediates in the decomposition, were utilized for the synthesis of unsymmetrical 1,3-disubstituted ureas.

Keywords——pyrolysis; 2*H*-oxadiazolopyridine-2-thione; 2*H*-oxadiazolopyridazine-2-thione; 1,3-disubstituted ureas; unsymmetrical ureas; aza-heteroaromatic isocyanates; isocyanates; urea synthesis

It has been reported[2] that pyrolysis of 2*H*-[1,2,4]oxadiazolo[2,3-*a*]pyridin-2-one (**1**) leads to the elimination of carbon dioxide to form 2-pyridylnitrene as an intermediate, which isomerizes to afford cyanopyrroles and 1,3-dicyanopropene. On the other hand, the synthesis of 2*H*-[1,2,4]oxadiazolo[2,3-*a*]pyridine-2-thione (**2a**), a sulfur analog of compound **1**, was reported by Taurins *et al.*,[3] who described the explosive character of **2a** upon heating; the nature of the products formed during the explosion was not investigated.

In a previous communication,[4] we have reported that the thermal decomposition of **2a** and **2b** gave 3-(2-pyridyl)-2*H*-pyrido[1,2-*a*]-1,3,5-triazine-2,4(3*H*)-dione (**3a**) and its pyridazine analog (**3b**), together with the 1,3-disubstituted ureas (**4a** and **4b**), respectively (Chart 1).

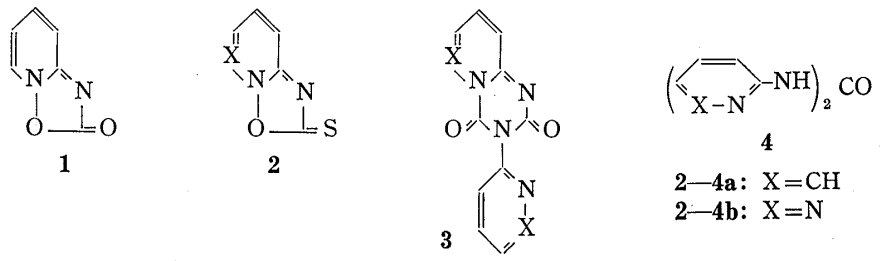

Chart 1

This paper presents further details and some additional data regarding this reaction and the utilization of **2** for the synthesis of unsymmetrical 1,3-disubstituted ureas.

Results and Discussion

Thermolysis of 2

The thermal decomposition of the compounds **2** with short contact times according to Brown's method[2] was not applicable because of their low volatilities (sublimation was not

1) Location: *Shinagawa-ku, Tokyo 142, Japan.*
2) R.F.C. Brown and R.J. Smith, *Aust. J. Chem.*, **25**, 607 (1972).
3) D. Rousseau and A. Taurins, *Can. J. Chem.*, **55**, 3736 (1977).
4) A. Ohsawa, H. Arai, and H. Igeta, *Heterocycles*, **12**, 917 (1979).

observed at bath temperatures below 80° at 0.01 mmHg); instead, explosion occurred, as described by Taurins *et al.*,[3] when **2** was heated at *ca.* 140°. As shown in Table I, the results of the decomposition of **2a** were essentially the same under various conditions; 3-(2-pyridyl)-2*H*-pyrido[1,2-*a*]-1,3,5-triazine-2,4(3*H*)dione (**3a**),[5] 1,3-di(2-pyridyl)urea (**4a**), and elemental sulfur were formed. Similarly, the pyrolysis of **2b** gave the corresponding **3** and **4**, and sulfur. No other characteristic compound was detected from the mixture by thin-layer chromatography and nuclear magnetic resonance (NMR) spectroscopy.

Table I. Thermal Decomposition of **2**

Compound	Solvent	Conditions	Products (%)		Sulfur
			3	**4**	
2a	Without solvent	140°[a] 0.1 mmHg	80	10	80
	DMSO[b]	80°[a] 1 hr	68	21	80
	Decalin[c]	80°[a] 2 hr	82	14	95
2b	DMSO[b]	80°[a] 1 hr	76	9	84
	Benzene[c]	Reflux 1 hr	77	tr	91

a) Bath temperature.
b) Although Taurins *et al.* carried out, the recrystallization of **2a** from DMSO, **2a** quickly decomposed at elevated temperature in DMSO. The same was true for **2b**.
c) Suspension.

The results led us to conclude that the aza-heteroaromatic α-isocyanate (**5**) might be formed as the intermediate of **3** although attempts to detect **5** directly were unsuccessful, as described later. The following mechanisms are proposed for the formation of these compounds (Chart 2).

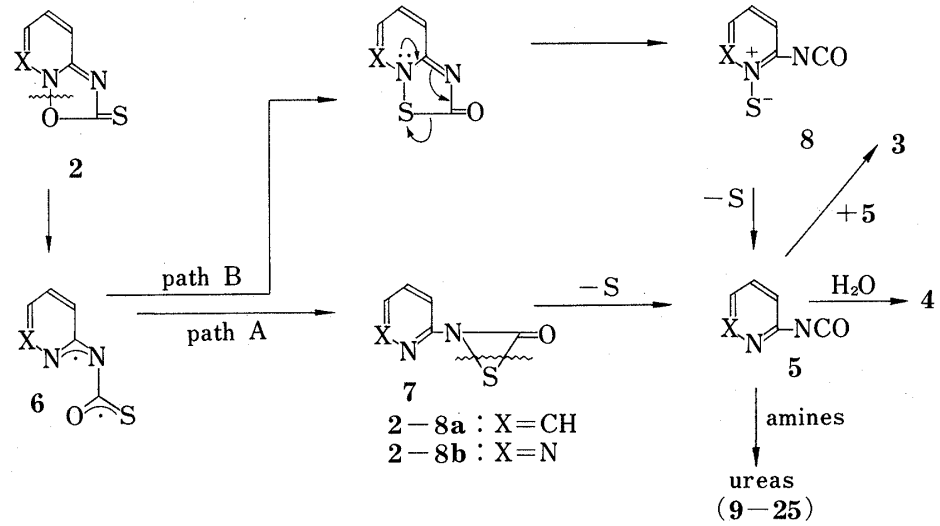

Chart 2

The N–O bonds of **2** are cleaved by thermolysis to form biradical intermediates (**6**), which are transformed *via* path A or path B into **7** or **8**, respectively, followed by elimination of the sulfur atoms to give the isocyanates **5**. It has been reported that ordinary azaheteroaromatic α-isocyanates readily undergo cyclodimerization and are too unstable to be isolated.[5] It is also possible that compounds **4** were derived from **5** and corresponding amines formed from **5** by the action of moisture.

5) U.v. Gizycki and G. Oertel, *Angew. Chem.*, **80**, 363 (1968).

Thus, it was found that the behavior of **2a** upon pyrolysis was quite different from that of **1**.[2)]

Reaction of 2 with Amines

The heteroaromatic α-isocyanates generated in this reaction were utilized for the synthesis of 1,3-disubstituted ureas. Katritzky reported[6)] that the reaction of **1** with morpholine afforded 2-(morpholinocarbonylamino) pyridine *N*-oxide (45%) while the reaction of **1** with aniline gave 1,3-diphenylurea, without formation of 1-phenyl-3-(1-oxido-2-pyridyl)urea, and Hoegerle reported[7)] that the reaction of **1** with ammonia gave 1-(1-oxido-2-pyridyl)urea (Chart 3). In these reactions, the *N*-oxide groups were retained on the pyridine rings of the ureas and there is some difference, in this respect, between their results and ours. We found that when compounds **2** were heated with amines in dimethylsulfoxide (DMSO) the corresponding ureas (**9**—**25**) were obtained in considerable yields. The results are shown in Table II.

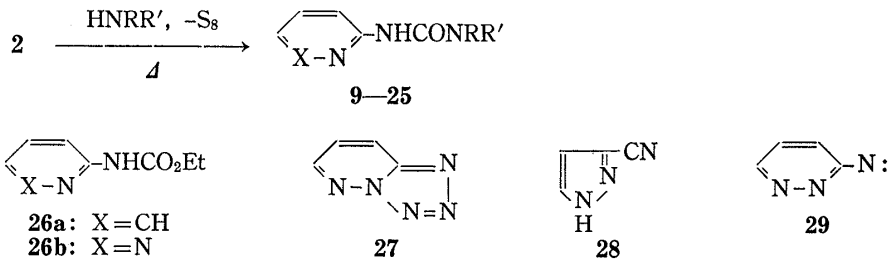

Chart 3

TABLE II. Preparation of Ureas from **2** by Treatment with Amines

2 —amines→ ureas (**9**—**25**)

Amine	Ureas (%)	
	From **2a**	From **2b**
Aniline	**9**(83)	**18**(74)
Methylaniline	**10**(87)	**19**(54)
2-Aminopyridine	**4a**(92)	**12**(69)
2-Aminopyrimidine	**11**(87)	**20**(78)
3-Aminopyridazine	**12**(20)	**4b**(82)
2-Aminopyridine 1-oxide	**13**(41)	**21**(20)
2-Aminopyrimidine 1-oxide	**14**(29)	**22**[a)](16)
3-aminopyridazine 2-oxide	**15**(tr)	**23**(18)
Piperidine	**16**(40)	**24**(59)
Morpholine	**17**(59)	**25**(18)

a) As the reaction gave a mixture of **22** and **4b** which could not be separated, the yield was estimated by NMR spectroscopy of the mixture.

Although it was expected that the reaction of carbamates **26a** and **26b** with amines would afford the disubstituted ureas, treatment of these compounds with aniline under the aforementioned conditions resulted in recovery of the starting materials, and only 1,3-diphenylurea was obtained under more severe conditions (*i.e.*, a solution of the carbamate was heated at 150—160° in aniline), disubstituted ureas such as **9** or **18** not being obtained. Treatment of **26a** or **26b** with other amines (shown in Table II) also failed to afford the expected ureas.

6) A.R. Katritzky, *J. Chem. Soc.*, **1956**, 2063.
7) K. Hoegerle, *Helv. Chim. Acta*, **41**, 548 (1958).

In addition, 1-(1-oxido-2-pyridyl)-3-(2-pyridyl)urea (**13**) has not been obtained by the oxidation of 1,3-di(2-pyridyl)urea (**4a**) with hydrogen peroxide in acetic acid; the *N*,*N*′-dioxide of **4a** was obtained instead.[6]

Thus, it was found that this reaction provides a method for the synthesis of unsymmetrical 1,3-disubstituted ureas, and in particular, for the synthesis of 1,3-di(α-heteroaromatic)-ureas.

Photolysis of 2b

The photolysis of tetrazolo[1,5-*b*]pyridazine (**27**) afforded 3-cyanopyrazole (**28**), probably *via* intermediate **29** by elimination of molecular nitrogen,[8] and similar photolysis of **2b** was expected to yield **29** by elimination of SCO. Meanwhile, the irradiation of **2b** in methylene chloride afforded **3b** and **4b** in 35 and 36% yields, respectively, the expected products such as **28** not being detected by NMR spectroscopy of the reaction mixture. These results suggest that the isocyanate **5b** occurs as an intermediate in this photolysis, as in the thermolysis of the compound.

The 1,3-disubstituted ureas described in Table II are of particular interest, because some pyridine- or pyrimidine-substituted ureas are known to show plant growth-regulating activity and microbiological activity.[9,10]

Experimental

All melting points are uncorrected. The NMR spectra were run on Hitachi R-20 and R-22 spectrometers. Infrared (IR) spectra were measured with a JASCO IRA-1 instrument.

Preparation of 2b——Compound **2b** was prepared by a method similar to that reported for the synthesis of **2a** by Taurins *et al.*,[3] and recrystallization was carried out as follows: ether–benzene (2: 1) was added dropwise to a solution of **2b** in a minimum amount of DMSO, and the deposited crystals were collected. Compound **2b** was obtained in 46% yield; yellow powder, mp 118° (explosion). IR ν_{max}^{KBr} cm^{-1}: 3090, 1603, 1490, 1390, 1365, 1270, 1140, 1015. NMR (DMSO-d_6) δ: 8.05 (1H, dd, 7-H, $J_{6,7}=4.5$, $J_{7,8}=9.0$ Hz), 8.33 (1H, d, 8-H), 8.68 (1H, d, 6-H). *Anal.* Calcd for $C_5H_3N_3OS$: C, 39.22; H, 1.98; N, 27.45. Found: C, 38.77; H, 1.99; N, 26.85. This compound is considerably unstable and repeated elemental analyses of samples obtained from individual recrystallizations did not give satisfactory values.

Thermolysis of 2a——1) Without Solvent: Compound **2a** (500 mg) was placed in a flask (50 ml) which was connected to a glass tube (liq. N_2 trap). The vessel was evacuated (0.1 mmHg) through the trap and heated on an oil bath. When the bath temperature reached *ca.* 140°, the material exploded and sublimed material solidified on the wall of the trap. The solid was collected and washed with hexane. The hexane extract gave 85 mg of elemental sulfur. The hexane-insoluble solid was then extracted with hot benzene, and the extract gave 35 mg of **4a**:[11] colorless needles from benzene, mp 173.5—174°. IR ν_{max}^{KBr} cm^{-1}: 3240—3000, 1710. NMR ($CDCl_3$) δ: 6.88—7.05 (2H, m), 7.60—7.80 (4H, m), 8.30—8.45 (2H, d), 10.80 (2H, brs). The benzene-insoluble solid was recrystallized from $CHCl_3$–DMSO (9: 1) to give 315 mg of **3a**:[5] colorless needles, mp 239—242°. IR ν_{max}^{KBr} cm^{-1}: 1680, 1645, 1550. NMR (DMSO-d_6) δ: 7.00 (1H, dd, $J=7.3$ and 7.9 Hz), 7.12 (1H, d, $J=9.0$ Hz), 7.40—7.62 (2H, m), 7.78—7.14 (2H, m), 8.44 (1H, d, $J=7.0$ Hz), 8.57 (1H, brd).

2) In DMSO: A solution of **2a** (500 mg) in 5 ml of DMSO was heated at 80° for 1 hr. The DMSO was distilled off *in vacuo* and the residue was subjected to separation as described above.

3) In Decalin: A suspension of **2a** (500 mg) in 5 ml of decalin was heated at 80° for 2 hr. The mixture was then treated in the manner noted above.

4) With Nujol: A mull of **2a** with Nujol was heated at *ca.* 160° in a KBr cell. Immediate measurement of the IR spectrum did not show –N=C=O stretching vibration, although complete decomposition of **2a** into **4a** was observed.

8) T. Tsuchiya, H. Arai, and H. Igeta, *J. Chem. Soc. Chem. Commun.*, **1972**, 1059.

9) For details of such plant growth regulators, see *e.g.*, Y. Isogai, K. Shudo, and T. Okamoto, *Plant Cell Physiol.*, **17**, 591 (1976); S. Takahashi, T. Yatsunami, K. Shudo, T. Okamoto, K. Yamada, and Y. Isogai, *Chem. Pharm. Bull.*, **26**, 2286 and 3250 (1978); and references therein.

10) For details of compounds with microbiological activity, see *e.g.*, P.E. Thompson, D.F. Walker, and M.C. Dunn, *J. Amer. Pharm. Assoc.*, **42**, 647 (1953) [*Chem. Abstr.*, **48**, 1581*h* (1954)]; A.E. Bundeally, B.W. Kulkarni, B.S. Rathore, and R.A. Bellare, *Indian J. Microbiol.*, **5**, 33 (1965) [*Chem. Abstr.*, **65**, 9381*h* (1966)]; L. Benes, B. Rada, and A. Borovansky, *Cesk. Farm.*, **26**, 154 (1977) [*Chem. Abstr.*, **88**, 950*b* (1978)].

11) R. Camps, *Arch. Pharm.*, **240**, 351 (1902).

Thermolysis of 2b——1) In DMSO: A solution of **2b** (500 mg) in 5 ml of DMSO was heated in the manner described above. Ether (*ca.* 10 ml) was added to the mixture and deposited crystals were collected and recrystallized from DMSO to give 1,3-di(3-pyridazinyl)urea (**4b**): 30 mg, colorless powder, mp 297—298°. IR ν_{max}^{KBr} cm^{-1}: 3220—2880, 1720. NMR (DMSO-d_6) δ: 7.72 (2H, dd, 5- and 5′-H, $J_{5,6}$=5.0, $J_{4,5}$=9.0 Hz), 8.18 (2H, dd, 4- and 4′-H, $J_{4,6}$=1.0, $J_{4,5}$=9.0 Hz), 8.98 (2H, dd, 6- and 6′-H), 11.0 (2H, brs, NH). *Anal.* Calcd for $C_9H_8N_6O$: C, 50.00; H, 3.73; N, 38.88. Found: C, 49.71; H, 3.50; N, 38.59. The filtrate was distilled to dryness and the residue was washed with benzene. The benzene extract was evaporated to dryness *in vacuo* to give 88 mg of sulfur. The benzene-insoluble solid was recrystallized from methanol to give 300 mg of **3b**: yellow fine needles, mp 254° (dec.). IR ν_{max}^{KBr} cm^{-1}: 1760, 1680, 1630, 1540. NMR (DMSO-d_6) δ: 7.55—8.12 (4H, m), 8.55—8.66 (1H, m), 9.32 (1H, dd, 7-H, $J_{7,8}$=5.0, $J_{7,9}$=1.0 Hz). *Anal.* Calcd for $C_{10}H_6N_6O_2$: C, 49.59; H, 2.50; N, 34.70. Found: C, 49.91; H, 2.53; N, 34.48.

2) In Benzene: A suspension of **2b** (200 mg) in 10 ml of benzene was refluxed for 1 hr. The mixture was cooled in an ice bath and precipitated crystals were collected and recrystallized from DMSO to give 122 mg of **3b**. A trace amount of **4b** was obtained from the mother liquor. The benzene layer was evaporated to dryness *in vacuo* to give sulfur.

3) With Nujol: A suspension of **2b** in Nujol was heated at *ca.* 160° in a KBr cell, and the IR spectrum was measured. No –N=C=O absorption was observed, although complete decomposition of **2b** into **4b** occurred.

Reaction of 2 with Amines——General Procedure: A solution of **2** (300—500 mg) and an amine (1.2—1.3 mol eq.) in 5—7 ml of DMSO was heated at 80—90° for 1—2 hr. The solvent was distilled off *in vacuo*. The residue was washed with hexane. Compounds **9**—**15** and **18**—**23** were obtained by recrystallization of the hexane-insoluble materials from appropriate solvents. Compounds **16**, **17**, **24**, and **25** were obtained by aluminum oxide column chromatography of the hexane-insoluble residue. The results are listed in Table II.

1-Phenyl-3-(2-pyridyl)urea (**9**):[12] Colorless needles from benzene, mp 182—184°. This compound was identical with the urea prepared from phenyl isocyanate and 2-aminopyridine.

1-Methyl-1-phenyl-3-(2-pyridyl)urea (**10**): Yellow prisms (hexane–ether), mp 78—79°. IR ν_{max}^{KBr} cm^{-1}: 3410, 1685. NMR ($CDCl_3$) δ: 3.35 (3H, s), 6.80—7.00 (1H, m), 7.02 (1H, brs), 7.20—7.75 (6H, m), 8.01—8.22 (2H, m). *Anal.* Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.77; N, 18.49. Found: C, 68.60; H, 5.81; N, 18.92.

1,3-Di(2-pyridyl)urea: This compound was identical with **4a**.

1-(2-Pyridyl)-3-(2-pyrimidinyl)urea (**11**): Colorless needles (C_6H_6–$CHCl_3$); mp 233.5—234.5°. IR ν_{max}^{KBr} cm^{-1}: 3220—3000, 1730. NMR ($CDCl_3$) δ: 6.95—7.12 (2H, m), 7.60—7.85 (1H, m), 8.23 (1H, d, J=8.0 Hz), 8.45—8.56 (1H, m), 8.72 (2H, d, J=5.0 Hz), 9.0 (1H, brs), 10.75 (1H, brs). *Anal.* Calcd for $C_{10}H_9N_5O$: C, 55.81; H, 4.22; N, 32.54. Found: C. 55.58; H, 4.19; N, 32.46.

1-(3-Pyridazinyl)-3-(2-pyridyl)urea (**12**): Colorless needles (MeOH), mp 263°. IR ν_{max}^{KBr} cm^{-1}: 3250, 3230, 1720. NMR (DMSO-d_6) δ: 7.00—7.15 (1H, m), 7.60—7.96 (3H, m), 8.21 (1H, dd, J=1.5 and 9.0 Hz), 8.37 (1H, brd), 8.98 (1H, brd), 10.22 (1H, brs), 11.18 (1H, brs). *Anal.* Calcd for $C_{10}H_9N_5O$: C, 55.81; H, 4.22; N, 32.54. Found: C, 55.86; H, 4.19; N, 32.63.

1-(1-Oxido-2-pyridyl)-3-(2-pyridyl)urea (**13**): Colorless needles (DMSO), mp 218—219° (dec.). IR ν_{max}^{KBr} cm^{-1}: 3195, 1720. NMR (DMSO-d_6) δ: 7.00—7.28 (2H, m), 7.30—7.95 (3H, m), 8.28—8.98 (3H, m), 10.30 (1H, brs), 12.02 (1H, brs). *Anal.* Calcd for $C_{11}H_{10}N_4O_2$: C, 57.38; H, 4.38; N, 24.34. Found: C, 57.33; H, 4.35; N, 24.15.

1-(1-Oxido-2-pyrimidinyl)-3-(2-pyridyl)urea (**14**): Fine needles (DMSO), mp 226—227°. IR ν_{max}^{KBr} cm^{-1}: 3220—3000, 1735. NMR (DMSO-d_6) δ: 7.00—7.20 (2H, m), 7.65—7.90 (1H, m), 8.07 (1H, brd), 8.22—8.35 (1H, m), 8.69 (2H, d), 10.28 (1H, brs), 11.70 (1H, brs). *Anal.* Calcd for $C_{10}H_9N_5O_2$: C, 51.95; H, 3.90; N, 30.30. Found: C, 52.09; H, 3.95; N, 30.00.

1-(2-Oxido-3-pyridazinyl)-3-(2-pyridyl)urea (**15**): The reaction of **2a** with 3-aminopyridazine 2-oxide afforded **3a** (32%) and **4a** (21%), which were identical with corresponding authentic samples, along with a trace amount of **15** which was contaminated with a small amount of impurity; **15**: IR ν_{max}^{KBr} cm^{-1}: 3200, 1705. NMR (DMSO-d_6) δ: 6.95—7.15 (1H, m), 7.20—7.90 (3H, m), 8.22—8.37 (2H, m), 8.69 (1H, dd), 11.26 (1H, brs), 12.07 (1H, brs).

2-(Piperidinocarbonylamino)pyridine (**16**): Colorless needles (hexane–ether), mp 84—85°. IR ν_{max}^{KBr} cm^{-1}: 3280, 1645. NMR ($CDCl_3$) δ: 1.55—1.78 (6H, m), 3.35—3.60 (4H, m), 6.90 (1H, m), 7.44 (1H, brs), 7.60 (1H, m), 8.07 (1H, d, J=8.0 Hz), 8.18 (1H, d, J=5.2 Hz). *Anal.* Calcd for $C_{11}H_{15}N_3O$: C, 64.36; H, 7.37; N, 20.47. Found: C, 64.42; H, 7.54; N, 20.46.

2-(Morpholinocarbonylamino)pyridine (**17**): Colorless plates (isoPr$_2$O), mp 92°. IR ν_{max}^{KBr} cm^{-1}: 3280, 1665. NMR ($CDCl_3$) δ: 3.40—3.83 (8H, m), 6.95 (1H, m), 7.69 (1H, m), 8.07 (1H, d), 8.22 (1H, m), 7.40—7.80 (1H, brs). *Anal.* Calcd for $C_{10}H_{13}N_3O_2$: C, 57.96; H, 6.32; N, 20.28. Found: C, 57.80; H, 6.42; N, 20.55.

1-Phenyl-3-(3-pyridazinyl)urea (**18**): Colorless needles (MeOH), mp 230°. IR ν_{max}^{KBr} cm^{-1}: 3360—3000, 1720. NMR (DMSO-d_6) δ: 7.00—7.68 (6H, m), 8.10 (1H, dd, J=1.0 and 9.0 Hz), 8.92 (1H, dd, J=1.0 and 4.0 Hz), 9.88 (1H, brs), 9.44 (1H, brs). *Anal.* Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.16. Found:

12) D.G. Crosby and C. Niemann, *J. Amer. Chem. Soc.*, **76**, 4458 (1954).

C, 61.88; H, 4.63; N, 26.42. This compound was identical with the urea prepared from phenyl isocyanate and 3-aminopyridazine.

1-Methyl-1-phenyl-3-(3-pyridazinyl)urea (**19**): Yellow prisms (AcOEt–isoPr$_2$O), mp 95—96°. IR ν_{max}^{KBr} cm^{-1}: 3200—2880, 1670. NMR ($CDCl_3$) δ: 3.36 (3H, s), 7.30—7.70 (7H, m), 8.41 (1H, dd, J=1.2 and 9.0 Hz), 8.78 (1H, dd, J=1.2 and 4.8 Hz). *Anal.* Calcd for $C_{12}H_{12}N_4O$: C, 63.14; H, 5.30; N, 24.55. Found: C, 63.00; H, 5.15; N, 24.77.

1-(3-Pyridazinyl)-3-(2-pyrimidinyl)urea (**20**): Colorless powder (MeOH), mp 285—289° (dec.); IR ν_{max}^{KBr} cm^{-1}: 3200—2920, 1720. NMR (DMSO-d_6–CF_3COOH) δ: 7.82 (1H, dd, J=6.0 and 6.0 Hz), 8.63 (1H, dd, J=5.4 and 9.0 Hz), 9.17 (2H, d, J=6.0 Hz), 9.23 (1H, d, J=9.0 Hz), 9.45 (1H, d, J=5.4 Hz). *Anal.* Calcd for $C_9H_8N_6O$: C, 50.00; H, 3.73; N, 38.88. Found: C, 50.04; H, 3.61; N, 39.16.

1-(1-Oxido-2-pyridyl)-3-(3-pyridazinyl)urea (**21**): Yellow powder (DMSO), mp 230° (dec.). IR ν_{max}^{KBr} cm^{-1}: 3180, 1720. NMR (DMSO-d_6) δ: 7.00—7.22 (1H, m), 7.25—7.50 (1H, m), 7.64 (1H, dd, J=4.0 and 10.0 Hz), 8.12 (1H, d, J=10.0 Hz), 8.33 (2H, m), 8.88 (1H, brd), 10.31 (1H, brs), 12.02 (1H, brs). *Anal.* Calcd for $C_{10}H_9N_5O_2$: C, 51.94; H, 3.92; N, 30.29. Found: C, 51.81; H, 3.80; N, 30.50.

1-(1-Oxido-2-pyrimidinyl)-3-(3-pyridazinyl)urea (**22**): The reaction of **2b** (400 mg) with 2-aminopyridine 1-oxide (500 mg) gave pure **4b** (74 mg) along with a mixture (380 mg) of **4b** and **22**. The ratio of **4b** to **22** in the mixture was found to be *ca.* 5.5 to 1 by NMR spectroscopy. NMR (DMSO-d_6) δ: 7.22 (1H, dd, 5-H, J=5.0 and 9.0 Hz), 7.70 (1H, dd, 5′-H, J=4.5 and 9.0 Hz), 8.14 (1H, dd, 4′-H, J=1.6 and 9.0 Hz), 8.35 (1H, d, 6-H, J=9.0 Hz), 8.74 (1H, d, 4-H, J=5.0 Hz), 8.93 (1H, dd, 6′-H, J=1.6 and 4.5 Hz), 10.45 (1H, brs, NH), 12.23 (1H, brs, NH). Overlapping signals due to the protons at the 4-, 5-, and 6-positions of the pyridazine rings of **4b** and **22** appeared at δ 7.72, 8.18, and 8.98, respectively.

1-(2-Oxido-3-pyridazinyl)-3-(3-pyridazinyl)urea (**23**): Yellow powder (DMSO), mp 268°. IR ν_{max}^{KBr} cm^{-1}: 3210—2760, 1720. NMR (DMSO-d_6) δ 7.37 (1H, dd, J=5.0 and 8.4 Hz), 7.70 (1H, dd, J=4.9 and 9.5 Hz), 8.10 (1H, dd, J=10.0 and 9.5 Hz), 8.33 (1H, dd, J=2.4 and 5.0 Hz), 8.68 (1H, dd, J=2.4 and 8.4 Hz), 8.98 (1H, dd, J=4.9 and 10.0 Hz), 10.77 (1H, brs), 11.23 (1H, brs). *Anal.* Calcd for $C_9H_8N_6O_2$: C, 46.55; H, 3.47; N, 36.20. Found: C, 46.95; H, 3.84; N, 36.11.

3-(Piperidinocarbonylamino)pyridazine (**24**): Colorless plates (isoPr$_2$O), mp 103—104°. IR ν_{max}^{KBr} cm^{-1}: 3190, 1650. NMR ($CDCl_3$) δ: 1.50—1.70 (6H, m), 3.40—3.70 (4H, m), 7.38 (1H, dd, J=4.8 and 9.5 Hz), 8.28 (1H, dd, J=1.5 and 9.5 Hz), 8.50 (1H, brs), 8.82 (1H, dd, J=1.5 and 4.8 Hz). *Anal.* Calcd for $C_{10}H_{14}N_4O$: C, 58.23; H, 6.84; N, 27.17. Found: C, 58.68; H, 6.93; N, 27.28.

3-(Morpholinocarbonylamino)pyridazine (**25**): Yellow fine needles (AcOEt), mp 178°. IR ν_{max}^{KBr} cm^{-1}: 3240, 1660. NMR ($CDCl_3$) δ: 3.55—3.90 (8H, m), 7.46 (1H, dd, J=4.6 and 10.0 Hz), 8.30 (1H, d, J=10.0 Hz), 8.84 (1H, d, J=4.6 Hz), 9.10 (1H, brs). *Anal.* Calcd for $C_9H_{12}N_4O_2$: C, 51.91; H, 5.81; N, 26.91. Found: C, 51.88; H, 6.01; N, 26.73.

Reaction of 26a[13] **and 26b with Aniline**——1) In DMSO: A solution of **26a** or **26b** (500 mg) in 1 ml of aniline and 2 ml of DMSO was heated at 80° for 1 hr. The mixture was treated in the usual way to give the starting material (**26a** or **26b**, *ca.* 95% recovery).

2) In Aniline: A solution of **26a** (200 mg) in 1 ml of aniline was heated for 2 hr at 150—160°. The aniline was evaporated off *in vacuo* and the residue was washed with cold methanol. The methanol extract was evaporated to dryness and the residue was recrystallized from benzene to give a trace of **26a**. The solid insoluble in the cold methanol was recrystallized from methanol to give 125 mg of 1,3-diphenylurea. Similarly, a solution of **26b** (200 mg) in 1 ml of aniline was heated at 150—160° for 2 hr. The reaction mixture was then treated in the manner noted above to give 90 mg of **26b** and 125 mg of 1,3-diphenylurea. The compounds **9** and **18** were not obtained.

Photolysis of 2b——A solution of **2b** (400 mg) in 200 ml of CH_2Cl_2 was irradiated at room temperature (100 W, high-pressure Hg lamp). After 1 hr, the mixture was evaporated to dryness *in vacuo* and the residue was washed with benzene. The benzene extract gave 70 mg of sulfur. The benzene-insoluble solid was recrystallized from DMSO to give 100 mg of **4b**. The mother liquor was distilled off and the residue was recrystallized from MeOH to give 110 mg of **3b**.

13) R. Camps, *Arch. Pharm.*, **240**, 345 (1902); R.L. Shriner and R.G. Child, *J. Amer. Chem. Soc.*, **74**, 549 (1952).