N-(1-butenyl)morpholine, 15431-03-5; *N*-isobutenylmorpholine, 2403-55-6; *N*-(1-cyclohexenyl)morpholine, 670-80-4; methyl 3-amino-2-butenoate, 14205-39-1; methyl 3-(methylamino)-2-butenoate, 13412-12-9; methyl 3-(phenylamino)-2-butenoate, 40801-08-9; *tert*-butyl 3-amino-2-butenoate, 14205-43-7; 2-methoxyfuran, 25414-22-6; 2-(1,2-dihydro-2-oxo-1-pyridyl)ethanesulfonic acid, 71517-73-2; 2,2′-(4-hydroxyphenylimino)bis[ethanesulfonyl fluoride], 71517-74-3; 2-(1-naphthalenylamino)ethanesulfonyl fluoride, 60353-08-4; 2,2′-[(3-trifluoromethylphenyl)imino]bis[ethanesulfonyl fluoride], 71517-75-4; 2-[(3-(methoxycarbonyl)-5-phenylthiophen-2-yl)-amino]ethanesulfonyl fluoride, 71517-76-5; 2-[(5-acetamido-2-methylphenyl)amino]ethanesulfonyl fluoride, 71517-77-6; *N,N′*-bis[(2-fluorosulfonyl)ethyl]benzenediamine, 71549-36-5; 4-aminophenol, 123-30-8; 1-naphthalenamine, 134-32-7; 3-(trifluoromethyl)benzenamine, 98-16-8; 3-(methoxycarbonyl)-5-phenylthiophene-2-amine, 61325-02-8; 5-acetamido-2-methylbenzenamine, 6375-16-2; 1-[[2-(fluorosulfonyl)ethyl]amino]-4-(methylamino)anthraquinone, 59385-74-9; 1,4-bis[[2-(fluorosulfonyl)ethyl]amino]anthraquinone, 59385-80-7; 1,5-bis[[2-(fluorosulfonyl)ethyl]amino]anthraquinone, 59385-77-2; 1,4-bis[[2-(fluorosulfonyl)ethyl]amino]-2-methoxyanthraquinone, 59385-78-3; 1-benzamido-4-[[2-(fluorosulfonyl)-ethyl]amino]anthraquinone, 59385-79-4; 1-amino-4-(methylamino)anthraquinone, 1220-94-6; 1,4-diaminoanthraquinone, 128-95-0; 1,5-diaminoanthraquinone, 129-44-2; 1,4-diamino-2-methoxyanthraquinone, 2872-48-2; 1-amino-4-benzamidoanthraquinone, 81-46-9; 2-(ethylphenylamino)ethanesulfonyl fluoride, 60353-81-3; 2-[ethyl(3-methylphenyl)amino]ethanesulfonyl fluoride, 60353-04-0; 2-[(3-chlorophenyl)ethylamino]ethanesulfonyl fluoride, 60353-05-1; 2-[(5-acetamido-2-methoxyphenyl)ethylamino]ethanesulfonyl fluoride, 60353-06-2; 2-[(2,2,2-trifluoroethyl)phenylamino]ethanesulfonyl fluoride, 71517-78-7; *N*-ethylbenzenamine, 103-69-5; *N*-acetyl-*N′*-ethyl-*m*-phenylenediamine, 41378-27-2; *N*-ethyl-3-methylbenzenamine, 102-27-2; 3-chloro-*N*-ethylbenzenamine, 15258-44-3; 5-acetamido-*N*-ethyl-2-methoxybenzenamine, 57039-61-9; *N*-(2,2,2-trifluoroethyl)benzenamine, 351-61-1; 2-(2,3-dihydro-6-nitro-4*H*-1,4-benzoxazin-4-yl)ethanesulfonyl fluoride, 71517-79-8; 2-(6-acetamido-2,3-dihydro-4*H*-1,4-benzoxazin-4-yl)ethanesulfonyl fluoride, 71517-80-1; 2-indolin-1-ylethanesulfonyl fluoride, 71517-81-2; 2-1*H*-benzotriazol-1-ylethanesulfonyl fluoride, 71517-82-3; 2-1*H*-1,2,4-triazol-1-ylethanesulfonyl fluoride, 71517-83-4; 2-imidazol-1-ylethanesulfonyl fluoride, 71517-84-5; 3,4-dihydro-6-nitro-2*H*-1,4-benzoxazine, 28226-22-4; 6-acetamido-3,4-dihydro-1*H*-1,4-benzoxazine, 71517-85-6; 2,3-dihydro-1*H*-indole, 496-15-1; 1*H*-benzotriazole, 95-14-7; 1*H*-1,-2,4-triazole, 288-88-0; *N*-butyl-2-(methylphenylamino)ethanesulfonamide, 60353-13-1; 2-(benzylphenylamino)ethanesulfonamide, 60353-15-3; 2,2′-(phenylimino)bis[ethanesulfonamide], 60353-17-5; 2-[(3-acetamidophenyl)ethylamino]ethanesulfonamide, 60353-18-6; *N*-butyl-2-(ethylphenylamino)ethanesulfonamide, 60353-14-2; *N*-*tert*-butyl-2-(methylphenylamino)ethanesulfonamide, 71517-86-7; 2-[(ethyl(3-methylphenyl)amino]ethanesulfonamide, 71517-87-8; 2-[(3-acetamidophenyl)ethylamino]-*N*-ethylethanesulfonamide, 71517-88-9; 2-(benzylphenylamino)ethanesulfonyl fluoride, 71517-89-0; 2-[(5-acetamido-2-methylphenyl)amino]ethanesulfonamide, 71517-90-3; *N*-ethyl-2-[(5-acetamido-2-methylphenyl)amino]ethanesulfonamide, 71517-91-4; *N,N*-diethyl-2-[(5-acetamido-2-methylphenyl)amino]-ethanesulfonamide, 71517-92-5; 2-[ethyl[4-[(4-sulfamoylphenyl)-azo]phenyl]amino]ethanesulfonyl fluoride, 60353-19-7; 2-[[4-[[2,4-bis(methylsulfonyl)-3-methylphenyl]azo]phenyl]ethylamino]-ethanesulfonyl fluoride, 60353-22-2; 2-[[3-acetamido-4-[(2,4-bis-(methylsulfonyl)phenyl]azo]phenyl]ethylamino]ethanesulfonyl fluoride, 71517-93-6; 2-[[5-acetamido-2-methoxy-4-[[3-(methoxycarbonyl)-4-methyl-5-nitro-2-thienyl]azo]phenyl]ethylamino]-ethanesulfonyl fluoride, 60353-32-4; 2,2′-[[4-[(2-chloro-4-sulfamoylphenyl)azo]phenyl]imino]bis[*N*-*tert*-butylethanesulfonamide], 66756-25-0; *N*-butyl-2-[[4-[(2-chloro-5-sulfamoylphenyl)azo]-phenyl]methylamino]ethanesulfonamide, 66756-16-9; 2-[[4-[(2-methoxy-5-sulfamoylphenyl)azo]phenyl]methylamino]ethanesulfonamide, 66756-26-1; 2-[[4-[[2-chloro-5-(methylsulfonyl)-phenyl]azo]phenyl]amino]ethanesulfonamide, 71517-94-7; 2-[[4-[(2-chloro-5-sulfamoylphenyl)azo]phenyl](2,2,2-trifluoroethyl)-amino]ethanesulfonamide, 71517-95-8; 4-sulfamoylaniline, 63-74-1; 5-nitro-2-thiazolamine, 121-66-4; methyl 2-amino-4-methyl-5-nitro-3-thiophenecarboxylate, 71517-96-9; 2-chloro-4-sulfamoylaniline, 53297-68-0; 2-chloro-5-sulfamoylaniline, 29092-34-0; 2-methoxy-5-sulfamoylaniline, 6973-08-6; 2,1-benzisothiazol-3-amine, 2400-12-6; phenyliminobis[*N*-*tert*-butylethanesulfonamide], 71517-97-0; 2-[phenyl(2,2,2-trifluoroethyl)amino]ethanesulfonamide, 71517-98-1; 3,4-dihydro-9-methylpyrido[2,1-*c*][1,2,4]thiadiazine 2,2-dioxide, 71517-99-2; 3,4-dihydropyrimido[2,1-*c*][1,2,4]thiadiazine 2,2-dioxide, 71518-00-8; 3,4-dihydro-6-methylpyrimido[2,1-*c*][1,2,4]thiadiazin-8(9*H*)-one 2,2-dioxide, 71518-01-9; 3,4-dihydro-6-methylthiazolo-[2,3-*c*][1,2,4]thiadiazine-7-sulfonyl fluoride 2,2-dioxide, 71518-02-0; 3,4-dihydro-7-[(4-methoxyphenyl)azo]-6-methylthiazolo[2,3-*c*][1,-2,4]thiadiazine 2,2-dioxide, 71518-03-1; 3,4-dihydro-8-(methylsulfonyl)[1,2,4]thiadiazino[3,4-*b*]benzothiazole 2,2-dioxide, 71518-04-2; 3,4-dihydro[1,2,4]thiadiazino[3,4-*b*]benzothiazole 2,2-dioxide, 71518-05-3; 3-methyl-2-pyridinamine, 1603-40-3; 2-pyrimidinamine, 109-12-6; 2-amino-6-methyl-4-pyrimidinol, 3977-29-5; 5-(fluorosulfonyl)-4-methyl-2-thiazolamine, 2196-72-7; 5-[(4-methoxyphenyl)azo]-4-methyl-2-thiazolamine, 71549-34-3; 2-benzothiazolamine, 136-95-8; 6-(methylsulfonyl)-2-benzothiazolamine, 17557-67-4; 7-cyclohexyl-3,4-dihydro[1,3,4]thiadiazolo[2,3-*c*][1,2,4]thiadiazine 2,2-dioxide, 71518-06-4; 3,4-dihydro[1,3,4]thiadiazolo[2,3-*c*][1,2,4]-thiadiazin-7-amine 2,2-dioxide, 71518-07-5; 5-cyclohexyl-1,3,4-thiadiazol-2-amine, 56882-77-0; 1,3,4-thiadiazole-2,5-diamine, 2937-81-7.

Supplementary Material Available: Further examples of reactions covered in Tables I–IV and toxicological data on compounds **3**, **4**, and **1** (12 pages). Ordering information is given on any current masthead page.

Reactions of Isocyanates with 1-Cyanothioformanilide

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The triethylamine-catalyzed reaction of 1-cyanothioformanilide (**2**) with isocyanates forms 1-substituted 5-imino-3-phenyl-4-thioxo-2-imidazolidinones **5** in excellent yield. Compounds **5** are converted by aqueous acid into 3-phenyl-4-thioxo-2,5-imidazolidinediones **6** and are oxidized by H_2O_2 in HOAc to 3-phenylimidazolidinetriones **4**. Condensation of **5** with *o*-phenylenediamine yields 1*H*-imidazo[4,5-*b*]quinoxalin-2(3*H*)-ones **8**. Upon being heated **2** reacts with 2 equiv of isocyanate to form 5-carbamoylimino-3-phenyl-4-thioxo-2-imidazolidinones **7**.

Nitriles containing an appropriately located nucleophilic group have been reported to undergo cyclization reactions with isocyanates to form imino or (if the possibility for tautomerism exists) amino heterocycles. Typical examples are the formation of aminooxazoles from α-aminonitriles,[1] iminotetrahydroquinazolines from anthranilonitrile,[2] iminooxazolidinones from cyanohydrins,[3] and iminoimidazolidinones from iminodiacetonitrile.[4] The work described in this paper was undertaken to investigate the expected analogous behavior toward isocyanates of 1-

(1) A. H. Cook and G. D. Hunter, *J. Chem. Soc.*, 3789 (1952).

(2) E. C. Taylor and R. V. Ravindranathan, *J. Org. Chem.*, **27**, 2622 (1962).

(3) T. L. Patton, *J. Org. Chem.*, **32**, 383 (1967).

(4) J. Perronnet and J.-P. Demoute, *Bull. Soc. Chim. Fr.*, 1168 (1970).

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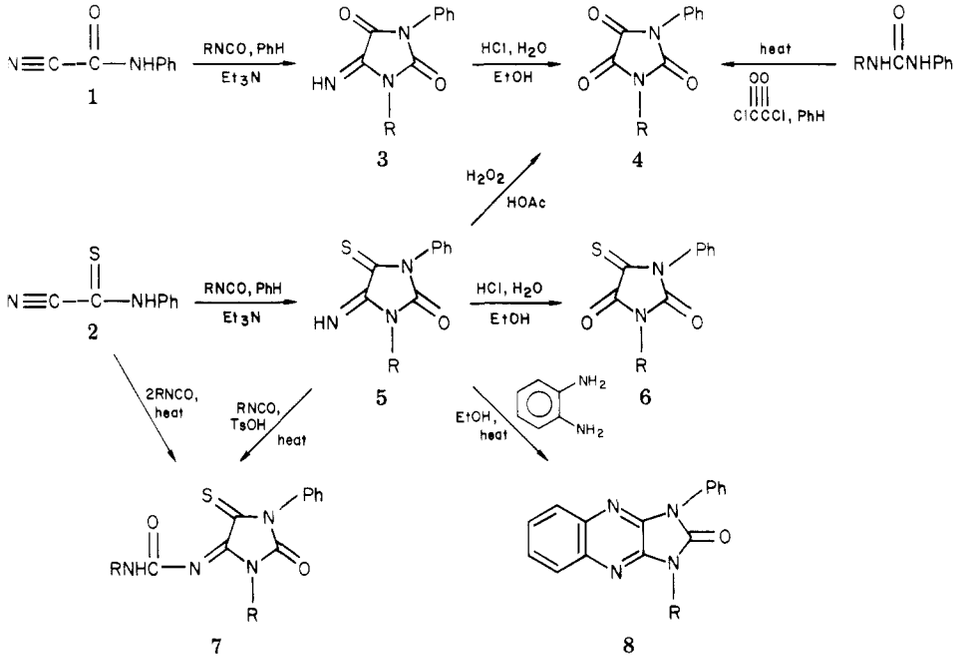
Table I[a]

	3		4		5	
compd	yield,[b] %	mp, °C	yield,[b,c] %	mp, °C	yield,[b] %	mp, °C
a	94	135-137[d,e]	95	201-203[d,h]	93	122-122.5[d]
b	82	115-117[d]	100	159-160.5[i,j]	95	162-164[d]
c	86	132-133[f]	97	170-171[d]	88	108-110[d]
d	93	158-161.5[d]	97	201-202[d,j]	98	148-150[d]
e	60	89-90[g]	92	75-76[h,l]	95	102-104[h]
f	69	96-97[g]	92	64-65[m]	87	109.5-111[d]

[a] Satisfactory analytical data (±0.30% for C, H, N) were submitted for all new compounds listed in this table. [b] Crude or recrystallized product with melting point lower than that of the analytically pure compound by not more than 10 °C. [c] Method B. [d] Recrystallized from ethanol. [e] Literature[7] mp 137 °C. [f] Recrystallized from methanol-water. [g] Sublimed. [h] Literature[9] mp 202 °C. [i] Recrystallized from benzene-petroleum ether (bp 63-75 °C). [j] K. A. Kraft and J. Reese, German Patent 1 916 932 (Cl. C 07d); *Chem. Abstr.* 74, P53798a (1971). Melting point not given. [k] Recrystallized from petroleum ether (bp 63-75 °C). [l] Literature mp 97 °C [R. Andreasch, *Chem. Ber.*, 31, 137 (1898)]. [m] Recrystallized from ethyl acetate-petroleum ether (bp 35-60 °C).



3-8a, R = Ph; b, R = 4-MeC$_6$H$_4$; c, R = 2-MeC$_6$H$_4$; d, R = 4-ClC$_6$H$_4$; e, R = Et; f, R = *n*-Bu

cyanothioformanilide (**2**),[5] which contains a potentially nucleophilic nitrogen atom α to a cyano group. This expectation was corroborated by the known reaction of **2** with *N*-(1,2,2,2-tetrachloroethyl)carboxamides to form 5-imino-2-(trichloromethyl)-4-imidazolidinethiones.[6]

As anticipated, **2** was found to react readily with isocyanates, in the presence of a catalytic amount of triethylamine, to form 1-substituted 5-imino-3-phenyl-4-thioxo-2-imidazolidinones **5** in excellent yield (Table I). As in no case was an open-chain adduct isolated, it may be concluded that, if the reaction occurs in two steps, ring formation occurs very rapidly, at least for the isocyanates used. Some degree of steric limitation is indicated by the fact that the reaction fails with *tert*-butyl isocyanate, although it still gives good results with *o*-tolyl isocyanate. Structure **5** is supported by the IR spectra of the products, which exhibit sharp N-H stretching bands at 3200-3250 cm^{-1}, carbonyl bands at relatively high wavenumbers (1760-1780 cm^{-1}), and strong C=N bands at 1650-1670 cm^{-1} but contain no C≡N bands. The NMR spectra of the products are entirely consistent with their proposed structures. A close analogy for this reaction exists in the formation of 5-imino-1,3-diphenyl-2,4-imidazolidinedione (**3a**) by the alkali-catalyzed reaction of phenyl isocyanate with hydrogen cyanide, presumably through the intermediacy of 1-cyanoformanilide (**1**).[7]

It was thought desirable to establish fully this analogy in the behavior of reagents **1** and **2** toward isocyanates by running a series of reactions between isocyanates and **1** corresponding to the reactions of **2**. Reagent **1** was prepared by the treatment of phenyl isocyanate with aqueous potassium cyanide and acidification of the resulting solution, thus avoiding the use of anhydrous hydrogen cyanide which is prescribed in the literature method.[7] The reaction of **1** with aromatic isocyanates was found to occur exactly as for its thio analogue and to yield 1-aryl-5-imino-3-phenyl-2,4-imidazolidinediones (**3a-d**) in excellent yield (Table I). In the case of the less electrophilic aliphatic isocyanates, competition arises from phenyl isocyanate generated by dissociation of **1** in the basic reaction medium. As a result, a mixture of some 1-alkyl-5-imino-3-phenyl- and, mostly, 5-imino-1,3-diphenyl-2,4-imidazolidinedione (**3a**) is obtained when equal molar amounts of reactants are used. A large excess of the alkyl isocyanate, however, suppresses the competing reaction[8]

(5) A. Reissert and K. Brüggemann, *Chem. Ber.*, 57, 981 (1924).
(6) M. S. Singer, U. S. Patent 3,721,679 (1973); *Chem. Abstr.*, 79, 5340 (1973).
(7) W. Dieckmann and H. Kämmerer, *Chem. Ber.*, 38, 2977 (1905); 40, 3737 (1907).

Table II[a]

	6			7		8	
compd	yield,[b] %	mp, °C	color	yield,[b,h] %	mp, °C	yield,[b] %	mp, °C
a	90	156-158[c]	purple	80	217.5-218.5 dec[i]	69	277-278.5[o,p]
b	100	116-118[d]	beige-yellow	71	232-233[j]	67	259.5-260.5[o]
c	100	129-130[e]	carmine	63	215-216[k]	56	242-243[o]
d	100	149.5-151[f]	red-brown	77	220-221[l]	56	260.5-261.5[q]
e	90	80-82[g]	pink-orange	87	158.5-160.5[m]	71	190-191[j]
f	90	67-69[g]	brown-red	67	118.5-120.5[n]	75	149-150[j]

[a] Satisfactory analytical data (±0.30% for C, H, N) were submitted for all new compounds listed in this table. [b] Crude or recrystallized product with melting point lower than that of the analytically pure compound by not more than 10 °C. [c] Recrystallized from benzene-petroleum ether (bp 63-75 °C). [d] Recrystallized from carbon tetrachloride-petroleum (bp 63-75 °C). [e] Recrystallized from cyclohexane. [f] Recrystallized from methanol. [g] Recrystallized from petroleum ether (bp 63-75 °C). [h] Method A. [i] Recrystallized from acetone-water. [j] Recrystallized from ethanol. [k] Recrystallized from dimethylformamide-ethanol. [l] Recrystallized from benzene. [m] Recrystallized from ethyl acetate-petroleum ether (bp 63-75 °C). [n] Recrystallized from carbon tetrachloride. [o] Recrystallized from 1-butanol. [p] Literature[10] mp 275-276 °C. [q] Recrystallized from 1-propanol.

and leads to the 1-alkyl derivatives **3e,f** (Table I). Like those of **5**, the IR spectra of **3** contain N-H bands at 3250–3270 cm^{-1}, C=O bands at 1730–1750 and 1780–1800 cm^{-1}, and C=N bands at 1670–1680 cm^{-1} but no C≡N bands. The NMR spectra of **3** are closely similar to those of **5**, except that the signal of the NH proton appears consistently about 0.2 ppm further downfield for **3** than for **5**, possibly because of intramolecular hydrogen bonding in **3**.

Treatment with hydrochloric acid cleaves the imino group of **3** and yields the corresponding imidazolidinetriones **4** (Table I), the structures of which were confirmed by their syntheses from the appropriate ureas and oxalyl chloride.[9] In the same manner, cleavage of the imino group of **5** by aqueous acid gives brilliantly colored 1-substituted 3-phenyl-4-thioxo-2,5-imidazolidinediones **6** (Table II). The conversion of **3** into **4** and **5** into **6** is indicated very clearly by the absence in the IR spectra of the products of the N-H and C=N bands which are prominent in the spectra of the starting materials. On the other hand, oxidation of the thiocarbonyl group in **5** by hydrogen peroxide in acetic acid proceeds with simultaneous cleavage of the imino group and leads to the imidazolidinetriones **4**.

When **2** is heated with 2 equiv of an isocyanate, the initial cyclization is accompanied by reaction with isocyanate at the imino nitrogen atom of the original adduct, and a carbamoylimino derivative (**7**, Table II) is formed as product. Analogies exist in the formation of 5-(*N*-phenylcarbamoyl)imino-1,3-diphenyl-2,4-imidazolidinedione from **1**,[7] carbamoyliminooxazolidinones from cyanohydrins,[3] and carbamoyliminoimidazolidinones from iminodiacetonitrile.[4] The structure proposed for compounds **7** is consistent with their IR (N-H bands at 3200–3300 cm^{-1}, C=O bands at 1690–1700 and 1770–1780 cm^{-1}, and C=N bands at 1640–1650 cm^{-1}) and NMR spectra. It is further confirmed by the fact that compounds **5** react with isocyanates upon heating to form the corresponding **7**. This reaction was generally found to give better results when run in the presence of a catalytic amount of *p*-toluenesulfonic acid.

Compounds **5** are suitably functionalized at ring positions 4 and 5 to undergo condensation–cyclization reactions with 1,2-diamines. Indeed, they react with *o*-phenylenediamine in refluxing ethanol to yield 1,3-disubstituted 1*H*-imidazo[4,5-*b*]quinoxalin-2(3*H*)-ones **8** (Table II) with loss of H_2S and NH_3. The structures of these products are supported by their IR (C=O bands at 1730–1750 cm^{-1}, no N-H bands) and NMR spectra, as well as by the fact that the melting point of one of them (**8a**) agrees with that reported in the literature.[10] In contrast, the attempted reactions of **5** with aliphatic diamines, e.g., ethylenediamine, were found to yield tarry products, very likely as a result of ring-opening reactions caused by the greater basicity of the reagents. It is interesting to note that an attempted preparation of **8a** from 1,3-diphenylimidazolidinetrione and *o*-phenylenediamine resulted in ring opening and formation of 1,4-dihydro-2,3-quinoxalinedione together with *N,N'*-diphenylurea.[11]

Experimental Section[12]

5-Imino-3-phenyl-4-thioxo-2-imidazolidinones 5. Addition of 2 or 3 drops of triethylamine to a mixture of 0.01 mol of **2**,[5] 0.01 mol of isocyanate, and 5 mL of benzene caused an exothermic reaction to occur followed in many cases by immediate crystallization of the product. The resulting mixture was allowed to stand for about 1 h and was then mixed with petroleum ether (bp 63–75 °C for **5a–d**, bp 35–60 °C for **5e,f**) and filtered to yield the product.

1-Cyanoformanilide (1). Into a vigorously stirred, ice-cooled solution of 19.5 g (0.30 mol) of potassium cyanide in 150 mL of water was allowed to flow 24 g (0.20 mol) of phenyl isocyanate over a period of 10 min. After the reaction mixture had been stirred for an additional 10 min, it was suction filtered directly into a mixture of ice and dilute hydrochloric acid (*Caution*: to be performed in a well-ventilated hood).[13] A new filtration, followed by air drying of the precipitate, yielded 20.5 g (70%) of **1**, mp 130–133 °C dec,[14] pure enough for most further uses.

5-Imino-3-phenyl-2,4-imidazolidinediones 3. Compounds **3a–d** were prepared from **1** exactly as their thio analogues **5** were

(8) A very similar competition was proposed to account for the formation of iminoimidazolidinediones, instead of the expected iminooxazolidinones, by the reaction of acetone cyanohydrin with isocyanates.[3]

(9) H. Biltz and E. Topp, *Chem. Ber.*, **46**, 1387 (1913).

(10) C. Iijima, *Yakugaku Zasshi*, **87**, 164 (1967); *Chem. Abstr.*, **67**, 3066 (1967).

(11) P. K. De and A. C. Sircar, *Q. J. Indian Chem. Soc.*, **4**, 531 (1927); *Chem. Abstr.*, **22**, 2552 (1928).

(12) Melting points were determined in capillaries with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer using mineral oil mulls. NMR spectra were obtained on a Varian EM 360 spectrometer using solutions in hexadeuteriodimethyl sulfoxide and tetramethylsilane as internal standard. Cross-identification of compounds was accomplished by comparison of IR and NMR spectra, as well as by determination of mixture melting points.

(13) Slow precipitation of *N,N'*-diphenylurea is observed upon standing of the alkaline solution as a result of dissociation of the anion of **1** to form phenyl isocyanate.[7]

(14) A variety of melting points have been reported for **1**: 120 °C dec,[7] 128 °C dec,[15] 122–125 °C,[16] 125–135 °C,[17] 129–132 °C.[18]

(15) G. Schultz, G. Rohde, and G. Herzog, *J. Prakt. Chem.*, [II] **74**, 88 (1906).

(16) R. Malachowski and J. Jankiewicz-Wasowska, *Rocz. Chem.*, **25**, 35 (1951).

(17) F. Piozzi, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.*, **22**, 629 (1957); *Chem. Abstr.*, **52**, 7278e (1958).

(18) J. H. Sellstedt, C. J. Guinosso, A. J. Begany, S. C. Bell, and M. Rosenthale, *J. Med. Chem.*, **18**, 926 (1975).

prepared from **2**. For compounds **3e,f**, the reaction was run in the same manner, except that a 7:1 ratio of isocyanate to **1** was used.

3-Phenylimidazolidinetriones 4. A. By Hydrolysis of 3. Addition of 3 mL of concentrated hydrochloric acid to a mixture of 0.5 g of **3** and 5 mL of ethanol caused an exothermic reaction to occur. The resulting mixture was allowed to stand for 10–120 min and was then diluted with water and filtered to yield the product.

B. From Ureas.[9] A mixture of benzene (25–50 mL) and equal weights (5–10 g) of oxalyl chloride and the urea was refluxed for 1–6 h and then cooled, diluted with petroleum ether (bp 63–75 °C), and filtered to yield the product.

C. By Oxidation of 5. To an ice-cold mixture of 0.5 g of **5** and 3–5 mL of acetic acid was added 3 mL of 30% hydrogen peroxide, and the resulting mixture was allowed to stand at room temperature until its yellow color had essentially been discharged (1–48 h). For the slower reactions (**5c,e,f**), a further 2–3 mL of H_2O_2 was added in portions, whereas for the faster reactions the mixture was occasionally cooled to prevent overheating. The product was isolated by dilution with water and filtration.

3-Phenyl-4-thioxo-2,5-imidazolidinediones 6. Addition of 3–5 mL of concentrated hydrochloric acid to a mixture of 1 g of **5** and 10–15 mL of ethanol caused an exothermic reaction to occur. The resulting mixture was allowed to stand for about 1 h and was then diluted with water and filtered to yield the product.

5-Carbamoylimino-3-phenyl-4-thioxo-2-imidazolidinones 7. A. A mixture of 0.010 mol of **2** and 0.020 mol of isocyanate was heated on the steam bath (closed flask for **7e**) until it had essentially completely solidified. The length of the heating period seemed to affect the quality of the product. Satisfactory results were obtained after 30 min for **7a**, 2 h for **7b,c**, 1.5 h for **7e**, and 5 h for **7f**. The crude product was triturated and washed with ethanol for **7b–c** and with petroleum ether (bp 63–75 °C) for **7a,e,f**. To prepare **7d**, we refluxed a solution of 0.80 g (0.0050 mol) of **2** and 1.5 g (0.010 mol) of 4-ClC_6H_4NCO in 10 mL of benzene for 45 h and then cooled and filtered the resulting solution to yield the product.

B. A mixture of 0.50 g of **5**, 1.0 g of isocyanate, and 0.050 g of *p*-toluenesulfonic acid was heated on the steam bath (closed flask for **7e**) until it had essentially solidified (15 min for **7a,b**; 1 h for **7c,f**; 2 h for **7e**). The crude product was triturated and washed with ethanol for **7a–c** and with petroleum ether (bp 63–75 °C) for **7f**. In the case of **7e**, the crude product was dissolved in ethanol and, after filtration of the solution, reprecipitated by addition of water. For **7d**, the mixture of **5d**, isocyanate, and *p*-TsOH was heated briefly on a Bunsen flame to obtain a melt, which was allowed to solidify, and then treated with EtOH.

1*H*-Imidazo[4,5-*b*]quinoxalin-2(3*H*)-ones 8. A stirred mixture of 0.050 mol of **5**, 0.060–0.080 mol of *o*-phenylenediamine, and 10 mL of ethanol was refluxed until no more H_2S or NH_3 was evolved (24 h for **8b,c,e,f**; 48 h for **8a,d**). The product was isolated by cooling and filtration of the reaction mixture followed by washing of the precipitate with ethanol.

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Registry No. **1**, 6784-22-1; **2**, 4955-82-2; **3a**, 10319-52-5; **3b**, 71342-18-2; **3c**, 71342-19-3; **3d**, 71342-20-6; **3e**, 54095-14-6; **3f**, 71342-21-7; **4a**, 6488-59-1; **4b**, 30592-91-7; **4c**, 71342-22-8; **4d**, 30592-92-8; **4e**, 71342-23-9; **4f**, 71342-24-0; **5a**, 71342-25-1; **5b**, 71342-26-2; **5c**, 71342-27-3; **5d**, 71342-28-4; **5e**, 71342-29-5; **5f**, 71342-30-8; **6a**, 71342-31-9; **6b**, 71342-32-0; **6c**, 71342-33-1; **6d**, 71342-34-2; **6e**, 71342-35-3; **6f**, 71342-36-4; **7a**, 71342-37-5; **7b**, 71342-38-6; **7c**, 71342-39-7; **7d**, 71342-40-0; **7e**, 71342-41-1; **7f**, 71342-42-2; **8a**, 15051-50-0; **8b**, 71342-43-3; **8c**, 71342-44-4; **8d**, 71342-45-5; **8e**, 71342-46-6; **8f**, 71342-47-7; phenyl isocyanate, 103-71-9; *p*-tolyl isocyanate, 622-58-2; *o*-tolyl isocyanate, 614-68-6; *p*-chlorophenyl isocyanate, 104-12-1; ethyl isocyanate, 109-90-0; butyl isocyanate, 111-36-4; *N,N'*-diphenylurea, 102-07-8; *N*-phenyl-*N'*-*p*-tolylurea, 4300-33-8; *N*-phenyl-*N'*-*o*-tolylurea, 13140-49-3; *N*-phenyl-*N'*-*p*-chlorophenylurea, 1967-26-6; *N*-phenyl-*N'*-ethylurea, 621-04-5; *N*-phenyl-*N'*-butylurea, 3083-88-3; *o*-phenylenediamine, 95-54-5; oxalyl chloride, 79-37-8.

Synthesis of Some 1-Azirines from α-Bromo Ketoximes via Oxazaphospholines[1]

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A useful route from α-bromo ketoximes **1** to azirines is described which involves protection of **1** followed by phosphine substitution and deprotection via oxazaphospholine intermediates. The mild deprotection of the oxime ethers involves intramolecular assistance by a phosphonium group. New azirines, including a ring-deuterated species, have been synthesized.

Oxazaphospholines from Protected Oxime Ethers

α-Bromo ketoximes **1** undergo a Beckmann rearrangement[2] instead of halogen substitution when treated with triphenylphosphine. However, the phosphonium products **2** can be obtained by addition of base[2] or by employing α-chloro ketoximes.[3] We now find that protection of readily available α-bromo oximes **1** in the form of ketals **3** permits clean S_N2 substitution by triphenylphosphine to produce **4** which can be deprotected under very mild conditions (trace of aqueous acid in $CHCl_3$ for 20 min at 25 °C) to generate the salts **2** (see Scheme I). These phosphonium salts **2** are readily converted to oxazaphospholines **5**,[3] which in turn can be thermolyzed to 1-azirines.[4]

Some examples of the conversion of α-bromo ketones to oxazaphospholines **5** via Scheme I are summarized in Table I. The overall sequence **1** → **5** can be carried out in one flask without isolation of intermediates (see Experimental Section). Although the yields of **5** via this route do not differ substantially from those of previous routes, the advantage of this procedure over those reported[2,3] lies

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