Reactions of Alkyl Isocyanates and Chlorosulfonyl Isocyanate with 1*H*-Tetrazol-5-amine and Conversion of Reaction Products to (1*H*-Tetrazol-5-yl)ureas

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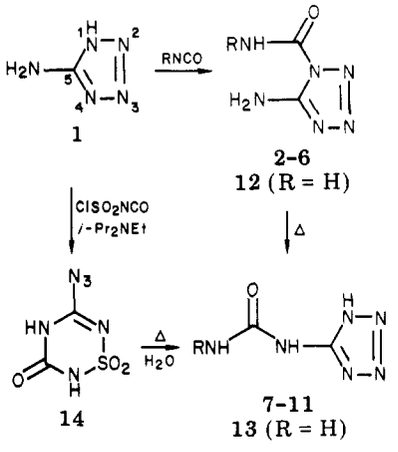
5-Amino-*N*-alkyl-1*H*-tetrazole-1-carboxamides **2–6** were prepared by reaction of alkyl isocyanates with 1*H*-tetrazol-5-amine (**1**) and thermally isomerized to (1*H*-tetrazol-5-yl)ureas **7–11**. The parent compound of the former series, 5-amino-1*H*-tetrazole-1-carboxamide (**12**), was prepared by treatment of **1** with aqueous isocyanic acid, and the parent compound of the latter series, (1*H*-tetrazol-5-yl)urea (**13**), was prepared either by heating **12** or by hydrolysis of 5-azido-2*H*-1,2,4,6-thiatriazin-3(4*H*)-one 1,1-dioxide (**14**). X-ray crystallographic studies were used to establish the structures of the octyl derivative **4** and the thiatriazine **14**.

1*H*-Tetrazol-5-amine (**1**) possesses three potentially reactive sites for initial electrophilic attack on the molecule. These are the two different ring nitrogens and the exocyclic amino group. Reactions of **1** involving each of these three possible positions have been reported, as well as descriptions of isomerizations of groups from the ring nitrogen at position 1 to the amino group and the reverse, depending upon the nature of the substituent.[1,2] Heating of **1** with carboxylic acids,[3] acid chlorides,[3,4] or phenyl isocyanate[5] has been reported to give 5-(acylamino)-1*H*-tetrazole derivatives. A recent publication[6] claims that such derivatives are also obtained under more mild conditions.

It has now been found that mild treatment of **1** in pyridine at room temperature with five homologous alkyl isocyanates results in the attachment of the alkylcarbamoyl groups to nitrogen at ring position 1, yielding compounds **2–6** (see Scheme I and Table I). The conversion of **1** to **4** by reaction with octyl isocyanate was performed in acetonitrile (93% yield) and tetramethylene sulfone (80% yield) as alternatives to pyridine (40% yield) in order to demonstrate the possibility of solvent involvement in the course of the reaction. The results indicate that the basicity of pyridine does not exert a controlling influence over the observed direction of substitution. The structures indicated for **2–6** are supported by IR, NMR, and mass spectra; but these methods do not discriminate between attachment at ring positions 1 and 2. Proof of the actual bond position in the octyl derivative **4** was obtained by X-ray crystallographic studies (Figure 1 and Table II), and the results are extended to the other members in this series in view of the close similarities in all physical properties. As indicated in Figure 1, the carbonyl group lies in the plane of the ring and within hydrogen-bonding distance of the amino group.

Heating **2–6** just above their melting points resulted in isomerization to the corresponding ureas **7–11** in high yield.[7] Differential thermal analysis (DTA) of compound **3** showed a melting endotherm above the capillary value (117 vs. 110 °C) followed immediately by a reaction exotherm, and finally by a second endotherm at 209 °C, corresponding to the melting point of **8**.

Scheme I



The UV spectra of **2–6** in ethanol showed typical tetrazole absorptions.[8] For example, the ring-substituted compound **2** showed a maximum at 241.5 nm which displayed instability in solution, experiencing a decay of the molecular extinction coefficient to 64% of its original value on standing overnight at room temperature. Infrared differences between the pairs of isomers are most strikingly shown in the positions of the solid-state carbonyl absorptions, the endocyclic series (**2–6**) showing ν(C=O) at $\sim$1730 cm^{-1} and those for the exocyclic group (**7–11**) shifting to $\sim$1670 cm^{-1}. The question as to whether compounds **7–11** might exist in a tautomeric imino form A rather than as structures of type B is addressed by con-

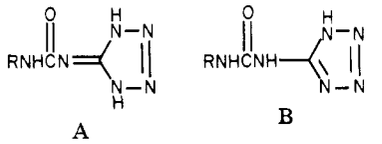


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Table I. Synthesis and Isomerization of 1-Alkylcarbamoyltetrazoles

2-6					7-11			
no.	R	yield, %	mp, °C[a]	CH_2NH, δ[b]	no.	yield, %	mp, °C[c]	CH_2NH, δ[b]
2[d]	butyl	53	119-121	8.85	7[e]	83[f]	208-209	6.63
3	hexyl	25	108-110	8.91	8	90	211-212	6.67
4	octyl	40	109-110	8.92	9	79	208-210	6.65
5	dodecyl	65	111-112	8.92	10	90	198-204	6.62
6	octadecyl	38	113-114	8.90	11	93	198-201	6.64

[a] Clear melt which resolidified prior to cooling. [b] In Me_2SO-d_6, triplets, J = 2 Hz. [c] With vigorous effervescence. [d] Originally prepared by J. Przytycki, E. E. Harris, and A. A. Patchett of these laboratories; UV (EtOH) 241.5 nm (ϵ 5870); IR (Nujol) 1730 (C=O) cm^{-1}; pK_a = 8.27, 10.30 (30% EtOH). [e] UV (EtOH) none; IR (Nujol) 1670 (C=O) cm^{-1}; pK_a = 4.85 (30% EtOH). [f] Yield given represents impure product; this urea alone required purification by crystallization from EtOH.

Table II. Crystal Data for 5-Amino-N-octyl-1H-tetrazole-1-carboxamide (4)[a]

molecular formula $C_{10}H_{20}N_6O$	ρ_{calcd} 1.19 g/cm³
molecular weight 240.30	Z 4
cell constants a 14.290 (3) Å	space group $P2_1/c$
b 7.659 (1) Å	λ (Cu Kα) 1.5418 Å
c 12.339 (2) Å	R (unweighted) 0.049
β 97.43 (1)°	
V 1339.1 Å	

[a] The following crystallographic programs were used: P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson "MULTAN 78, a System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data", University of York, York, England; J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, "The X-Ray System, Version of June, 1972", TR-192, University of Maryland, College Park, Maryland (1972); C. K. Johnson, "ORTEPII, A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", U. S. Atomic Energy Commission, Report ORNL-3794 (2nd Rev., with Supplemental Instructions), Oak Ridge National Laboratory, Oak Ridge, TN (1970).

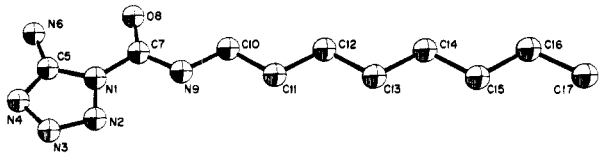

Figure 1. Computer-generated drawing of 4 with hydrogens omitted for clarity.

sidering the findings of Shchipanov et al.[9] who established that carbonyl absorptions for 5-(acyl*amino*) derivatives of tetrazole fall in the 1672–1750-cm^{-1} region and are higher than those of the 5-(acyl*imino*)tetrazoles (ν(C=O) 1620–1650 cm^{-1}). Thus the carbonyl frequencies for ureas 7–11 are more compatible with an amido, as opposed to an imido, functionality. Furthermore, UV spectra of tetrazoles having fixed imino structures (A) have been shown previously to have absorptions at 260 and 267 nm, peaks which are not seen in the spectra of the ureas.[10] ^1H NMR spectra are in accord with the proposed structures, with the most significant differences between isomers being in the chemical shifts of the NH signals where nitrogen is attached to methylene, as shown in Table I.

The parent carbamoyl compound **12** was prepared by adding aqueous potassium cyanate solution to either the hydrochloride of **1** in water[11] or to a solution of **1** in aqueous acetic acid. An attempted capillary melting point determination on **12** showed no apparent change up to 300 °C, but DTA revealed a broad exotherm beginning at 150 °C and rising to a sharp peak at 180–190 °C. This information was next utilized in the design of an experiment intended to bring about the thermal isomerization **12** → **13**. The choice of the temperature range 180–190 °C results in a nearly quantitative *solid-phase* conversion to **13**, identification being attained by analyses and spectroscopic measurements.

An alternative synthesis of **13** was accomplished by way of the interesting thiatriazine derivative **14**, formed from **1** by reaction with chlorosulfonyl isocyanate and subsequent treatment with the hindered base ethyldiisopropylamine.[12] This approach was undertaken in view of the recently demonstrated utility of the thiatriazine ring system in forming novel compounds upon ring opening with nucleophiles.[13] The solid-state infrared spectrum of **14** showed a characteristic azide absorption band at 2190 cm^{-1}, and the structure was confirmed by X-ray crystallography (see Figure 2 and Table III). The mode of formation of **14** is consistent with the known propensity

Table III. Crystal Data for 5-Azido-2H-1,2,4,6-thiatriazin-3(4H)-one 1,1-Dioxide (14)[a]

molecular formula $C_2H_2N_6O_3S$	Z 2
molecular weight 190.109	space group $P\bar{1}$
cell constants a 6.240 (3) Å	ρ_{calcd} 1.89 g/cm³
b 6.949 (5) Å	λ (Cu Kα) 1.5418 Å
c 9.665 (4) Å	R (unweighted) 0.053
α 94.00 (5)°	
β 119.53 (3)°	
γ 67.77 (5)°	
V 333.9 (3) Å³	

[a] See footnote *a*, Table II.

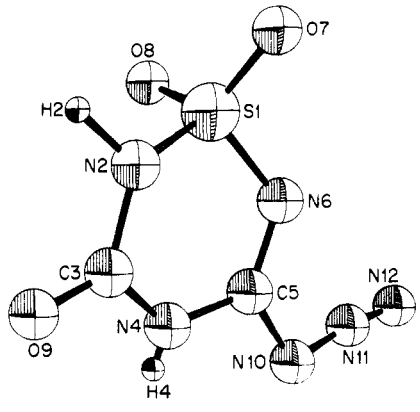

Figure 2. Computer-generated drawing of 14.

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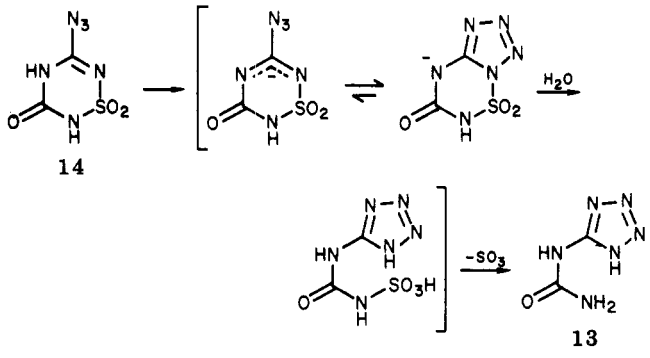
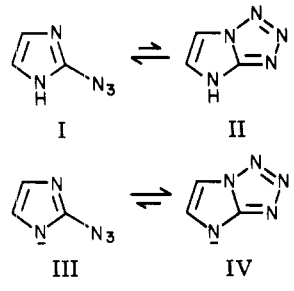
Scheme II



of 1 to form sulfonylguanyl azides when treated with sulfonyl chlorides.[14] Brief treatment of 14 with boiling water converted it to the urea 13 in which the tetrazole system was reconstituted, possibly in accordance with the following mechanistic pathway. Recent studies[15] of the



related compound 2-azidoimidazole (I) and its tetrazole tautomer (II) demonstrated that while I exists primarily in the azide form, the equilibrium is shifted to the tetrazole form when the corresponding anions III and IV are involved. These observations were considered to follow from the effect of more efficient delocalization of charge into the tetrazole ring when the anions were generated, thereby shifting the equilibrium in favor of species IV. In an analogous manner, one can propose a similar reaction mechanism for 14 to support the azide–tetrazole equilibrium shown in Scheme II. Subsequent hydrolytic scission of the sulfur to nitrogen bond could provide the sulfamic acid shown, in agreement with precedent,[13,14] which would extrude SO_3 to yield the urea 13, as illustrated.

The observed thermal isomerizations of 5-amino-1*H*-tetrazole-1-carboxamides to the corresponding ureas may proceed via a mechanism involving ring opening, then ring closure, as has been observed for acylamino- and alkylamino-1*H*-tetrazole derivatives. Furthermore, electronegative substituents on nitrogen are known to shift the equilibria in favor of the exocyclic isomers,[16] which is in harmony with the behavior observed in the present experiments with tetrazoles bearing an electronegative carboxamide function.

Experimental Section

^{1}H NMR spectra were measured on a Varian EM 390 spectrometer with tetramethylsilane as an internal reference. ^{13}C NMR spectra were determined on a Varian CFT-20 spectrometer. Other instruments were as follows: IR, Perkin-Elmer Models 137 and 621; UV, Cary Model 11 MS; melting point, Thomas-Hoover Uni-Melt (uncorrected); mass spectra, AEI MS 902; DTA, 990 thermal analyzer; X-ray, Syntex $P2_1$.

All new compounds gave satisfactory (±0.4%) elemental analyses for C, H, and N (and for S in 14). Spectral data were consistent with the proposed structures, with only diagnostic data being reported. ^{13}C NMR spectra for the isomeric pairs 4, 9 and 5, 10 were obtained, and while differences were observed, they were not amenable to interpretation.

General Procedure. 5-Amino-*N*-octyl-1*H*-tetrazole-1-carboxamide (4). Anhydrous 1 (2.3 g, 0.027 mol) in pyridine (50 mL) was combined with octyl isocyanate (4.9 g, 0.032 mol), and the solution was stirred for 3 h at room temperature under nitrogen. Concentration to a volume of 15 mL and dilution with 200 mL of ether gave 2.6 g (40%) of 4, mp 109–110 °C (clear melt, resolidified at 114 °C). Ethanol may be used as a crystallization solvent for 2–6 but is clearly not the ideal choice as subsequent experiments showed that the ultraviolet maxima of solutions in this solvent were significantly lowered on overnight standing.

General Procedure. *N*-Octyl-*N'*-(1*H*-tetrazol-5-yl)urea (9). 4 (0.30 g) was placed in a 50-mL round-bottomed flask, blanketed with nitrogen, and protected with a drying tube. The flask was placed in an oil bath at 110–115 °C for 15 min. Liquification of the solid was followed immediately by resolidification during this period. The cooled solid cake was ground in a mortar to give 235 mg (79%) of pure 9, mp 208–210 °C dec.

5-Amino-1*H*-tetrazole-1-carboxamide (12). Method A. From 1 and Isocyanic Acid. The monohydrate of 1 (2.47 g, 0.024 mol) was dissolved in 60 mL of HOAc and the solution diluted with 60 mL of H_2O. Addition of potassium cyanate (3.24 g, 0.040 mol) in 40 mL of H_2O caused the precipitation of 1.2 g (39%) of 12 after 0.5 h at room temperature. Capillary melting point showed no apparent phase change up to 300 °C; IR (Nujol) 1730 (C=O) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 7.40 (s, 2 H), 8.30 (s, 2 H); mass spectrum, *m/e* 128 (M^+).

Method B. From the Monohydrochloride Monohydrate of 1 and Potassium Cyanate. The crystalline monohydrochloride monohydrate of 1 (2.78 g, 0.02 mol), prepared according to the method of Thiele and Ingle,[10] was dissolved in 20 mL of H_2O by warming to 37 °C. Potassium cyanate (1.62 g, 0.02 mol) in 3.5 mL of H_2O was added to the hydrochloride solution at 25 °C over a 1-min period. Stirring for 10 min gave a solid which was collected and washed with H_2O and Et_2O to yield 1.5 g (59%) of pure 12. The product was converted to 1 when dissolved in hot H_2O.

(1*H*-Tetrazol-5-yl)urea (13). A 50-mL round-bottomed flask was charged with 0.30 g of 12, protected from moisture, blanketed with nitrogen, and kept in an oil bath at 180–190 °C for 0.5 h. Fusion of the solid was not observed. The product was cooled and ground in a mortar to give 0.29 g (97%) of 13: mp >300 °C; IR (Nujol) 1690 (C=O) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 6.60 (s, NH_2), 9.8–11.0 (br, CONH), 11.5–14.5 (br, ring NH); mass spectrum, *m/e* 128 (M^+).

5-Azido-2*H*-1,2,4,6-thiatriazin-3(4*H*)-one 1,1-Dioxide (14). A slurry was prepared from 4.25 g (0.05 mol) of anhydrous 1 and 300 mL of dry acetonitrile. This was cooled to 0 °C and 7.1 g (0.05 mol) of chlorosulfonyl isocyanate was added dropwise over a 15-min period. A clear solution was obtained, and after an additional 15-min period the mixture was brought to room temperature. Turbidity appeared and stirring was continued for 0.5 h, whereupon ethyldiisopropylamine (6.45 g, 0.05 mol) was added rapidly. Following a 2-day stirring period at room temperature, the slightly turbid reaction mixture was filtered, concentrated to a semisolid residue, and stirred with 100 mL of chloroform. The white powder obtained amounted to 7.83 g (83%), mp 204–210 °C dec. Purification was accomplished by dissolving the crude material in acetonitrile (60 mL/g) and reducing the volume to one-third by vacuum evaporation. Three such operations gave pure, rhomboid crystals of 14, mp 227 °C dec. Purified samples decomposed with a sudden release of gas at the melting point. The Beilstein test for halogen was negative. IR (Nujol) 2190 (N_3) cm^{-1}, (KBr) 2185 (N_3) cm^{-1}, (acetone) 2165 cm^{-1}; UV (H_2O) 217 nm (ε 11 400); mass spectrum, *m/e* 189.9905 (*m/e* calcd for $C_2H_2N_6O_3S$ 189.99087); NMR (Me_2SO-d_6) δ 10.4 (s, NH), 14.0–15.5 (br s, NH); pK_a (H_2O) = 3.33 and 8.30. When a sample of 14 (200 mg) was dissolved in 4 mL of H_2O and heated at 100 °C for 0.5 h, crystals of 13 (52% yield) were deposited on cooling.

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(NMR), E. L. Cresson (UV), and R. E. Rhodes (mass spectra) for spectral data, and to T. H. Brunner for clerical assistance. Thanks are due to B. M. Trost, S. Danishefsky, and S. Karady for helpful discussions.

Registry No. 1, 4418-61-5; 2, 73079-15-9; 3, 73079-16-0; 4, 73079-17-1; 5, 73079-18-2; 6, 73079-19-3; 7, 73079-20-6; 8, 73079-21-7; 9, 73079-22-8; 10, 73079-23-9; 11, 73079-24-0; 12, 73079-25-1; 13, 6973-21-3; 14, 73079-26-2; butyl isocyanate, 111-36-4; hexyl isocyanate, 2525-62-4; octyl isocyanate, 3158-26-7; dodecyl isocyanate, 4202-38-4; octadecyl isocyanate, 112-96-9; chlorosulfonyl isocyanate, 1189-71-5.

Supplementary Material Available: X-ray data for 4 and 14 consisting of fractional atomic coordinates, temperature factors, and bond distances and bond angles, ^{13}C NMR spectra of 1, 4, 5, 9, 10, 14, and the reference compound *N*-octylurea (7 pages). Ordering information is given on any current masthead page.

Reactions of Primary and Secondary Amines with Fluoronitrene Generated from Isopropyl *N,N*-Difluorocarbamate[1]

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Isopropyl *N,N*-difluorocarbamate deaminates primary amines, RNH_2, affording RH, N_2, $RNHCO_2$-*i*-C_3H_7, and RNH_2·HF. With secondary amines, dibenzylamine gives bibenzyl, whereas pyrrolidine yields a ring-expansion product, 2,3,4,5-tetrahydropyridazine. The reactions are consistent with the generation of fluoronitrene and subsequent production of the intermediates RN=NH from RNH_2 and R_2N=N from R_2NH. The advantages of using isopropyl *N,N*-difluorocarbamate as a source of fluoronitrene are discussed.

Several studies have been done on reactions of primary and secondary amines with HNF_2[3-6] to yield deaminated and other products in which fluoronitrene has been implicated.[3] We report herein the use of isopropyl *N,N*-difluorocarbamate[7] as a convenient source of fluoronitrene,[8] the products obtained from the reaction of *i*-$C_3H_7OCONF_2$ with primary and secondary amines via NF as a postulated intermediate, and comparison with pertinent prior literature.

Fluoronitrene has previously been formed from a variety of sources, including FN_3,[9,10] NF_3,[11-13] N_2F_4,[14-17] HNF_2,[3-6,17-26] and F_2NCONH_2.[27] The first four of these precursors are gaseous, often explosive, and require vacuum-line techniques not suitable for preparative-scale work. *N,N*-Difluorourea is a sensitive explosive,[28] and one of its crystalline forms is hygroscopic.[28] In contrast, *i*-$C_3H_7OCONF_2$ is found to be a safe, convenient source of NF under a variety of conditions in quantities up to 0.3 mol.

Table I. Products from Primary Amines (RNH_2) and *i*-$C_3H_7OCONF_2$

	products, % yield			
R	RH	*i*-C_3H_7-OCONHR	N_2	$RNH_3^+F^-$
c-C_6H_{11}	14	87	63	88
n-C_8H_{17}	30	69	73	97
$C_6H_5CH_2$	42	71	75	91
o-$CH_3OC_6H_4$	60	74	69	
o-$CH_3C_6H_4$	37	66	54	81
C_6H_5	19[a]	80	60	88
C_6H_5	20[b]			
o-ClC_6H_4	3	62	50	

[a] Cf. ref 8. [b] With NHF_2, ref 3.

The feasibility of producing NF via reaction of *i*-

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