Preparation and Properties of Some Isomeric *v*-Triazolopyridines. 1- and 3-Deaza-8-azapurines[1]

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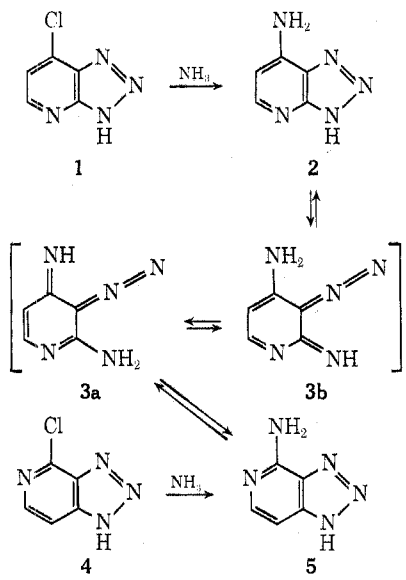
The preparation of both 1- and 3-deaza-8-azapurine (*v*-triazolopyridines) analogs of adenine, purine-6(1*H*)-thione, 6-(methylthio)purine, and hypoxanthine are reported. The Dimroth rearrangement of the 7-amino-3*H*-*v*-triazolo[4,5-*b*]pyridine (**2**)–4-amino-1*H*-*v*-triazolo[4,5-*c*]pyridine (**5**) system and the rearrangement of two *v*-triazolopyridinethione–amino[1,2,3]thiadiazolopyridine systems are described.

When the work herein reported was started, the synthesis of both 1- and 3-deaza-8-azapurines (*v*-triazolopyridines), analogs of 6-substituted purines, had not been reported. Recently a number of derivatives of these ring systems were prepared.[2] In this paper we report the preparation of the analogs of adenine, 6(1*H*)-purinethione, 6-(methylthio)purine, and hypoxanthine by more direct procedures. Also the reversible *v*-triazolopyridinethione–amino[1,2,3]thiadiazolopyridine rearrangement and the existence in the amino-*v*-triazolopyridines of a new type of Dimroth rearrangement are described.

The conversion of 4-amino-2-chloropyridine[3] to 4-amino-2-chloro-3-nitropyridine[3,4] and reduction of the latter with Raney nickel[5] gave 3,4-diamino-2-chloropyridine, which was nitrosated by the reported method to give **4**.[4] Similarly the nitrosation of 2,3-diamino-4-chloropyridine[6] gave **1**.[2]

The displacement of the chloro group of **1** to give **2** with ethanolic ammonia at 145° for 20 hr was reported to result in total decomposition.[2] We found that treatment of **1** with ethanolic ammonia at 150° for 19 hr gave a 55% yield of **2** and a 7% yield of about a 1:1 mixture of **2** and the rearrangement product **5**.



The latter was identified by tlc and by comparison of its pmr spectrum with that of an authentic sample of **5** (see below). Presumably this rearrangement involves diazo-type intermediates like **3a–b**, similar to the intermediates recently proposed for a new kind of Dimroth rearrangement observed in an 8-azapurine system.[7] Under essentially the same conditions treatment of **4** with ethanolic ammonia gave a 71% yield of **5** and a 22% yield of about a 1:1 mixture of **2** and **5** (tlc, pmr). Also treatment of pure **5** with ethanolic ammonia at 150° (65 hr) gave a mixture of **2** and **5** (tlc). The amount of **2** obtained in the mixtures suggested that the thermodynamic stability of **2** is greater than **5** in the presence of ammonia. In contrast the nitrosation of 2,3,4-triaminopyridine gave a mixture of **2** and **5** with that of **5** predominating.[2] The thermal rearrangement of **5** to **2** was unsuccessful as shown by heating a solution of **5** in either ethanol (150°, 65 hr) or tetramethylene sulfone (165°, 5 hr), heating solid **5** (200°, 18 hr) *in vacuo*, and refluxing a solution of **5** in 3,4-lutidine (18 hr). Although an 8-azapurine was rearranged in hot dimethylacetamide,[7] refluxing a solution of **5** in this solvent gave a mixture containing a minor amount of **5** and mainly an *N*-acetyl compound. The latter is presumably the corresponding 4-acetamido derivative of **5** based on elemental analyses, the presence of CH_3CO and broad NH (δ 2.2, 8–13) absorption in the pmr spectrum, and treatment of the mixture with dilute NaOH to again give **5** (tlc, pmr). The above results imply that the interconvertibility of **2** and **5** is catalyzed by ammonia.

Treatment of **4** with hydrated NaSH in propanol gave an 84% yield of the thione **10**. In contrast to the report that reaction of **4** with thiourea in ethanol for 1 hr gave **10** directly,[2] we found that treatment of **4** with thiourea in propanol for 3.5 hr gave an 18% yield of the propylthio compound **8** and a 30% yield of the thiadiazolopyridine rearrangement product **12**. Presumably **8** results from addition of propanol to the intermediate 2-thiopseudourea **6** to give **7** followed by an O → S propyl group migration with concomitant elimination of urea.[8] The structure of **8** was confirmed by comparison of its spectral properties with those of **9**, prepared by methylation of **10** with MeI. The thiadiazolopyridine **12** must result from an intermediate in which the *v*-triazole ring is opened, and this intermediate might be formed from **6**, **7**, or **10**. Support for a diazo-type intermediate like **11** was shown by refluxing a solution of **10** in propanol (18 hr) to give

(1) This investigation was supported by funds from the C. F. Kettering Foundation, and Chemotherapy, National Cancer Institute, National Institutes of Health, Contract NIH-71-2021.

(2) K. B. deRoos and C. A. Salemink, *Recl. Trav. Chim. Pays-Bas*, **90**, 1166 (1971).

(3) P. C. Jain, S. K. Chatterjee, and N. Anand, *Indian J. Chem.*, **4**, 403 (1966).

(4) Z. Talik and E. Plazek, *Rocz. Chem.*, **30**, 1139 (1956); *Chem. Abstr.*, **51**, 12089*f* (1957).

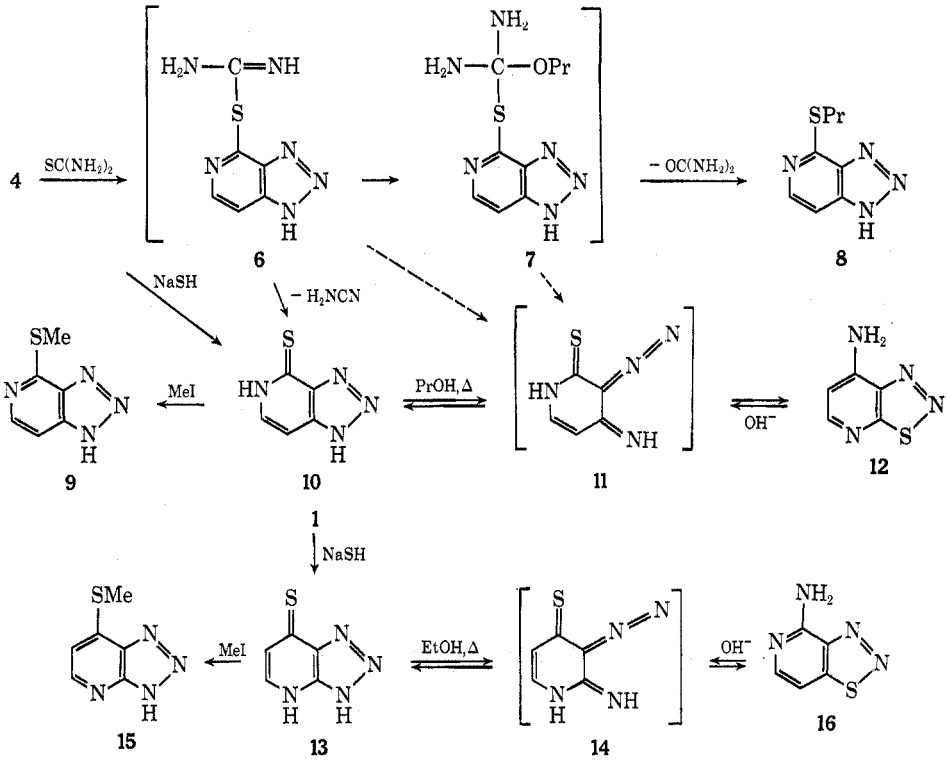
(5) J. A. Montgomery and K. Hewson, *J. Med. Chem.* **9**, 105 (1966).

(6) K. B. deRoos and C. A. Salemink, *Recl. Trav. Chim. Pays-Bas*, **88**, 1263 (1969).

(7) C. Temple, Jr., B. H. Smith, Jr., and J. A. Montgomery, *Chem. Commun.*, 52 (1972).

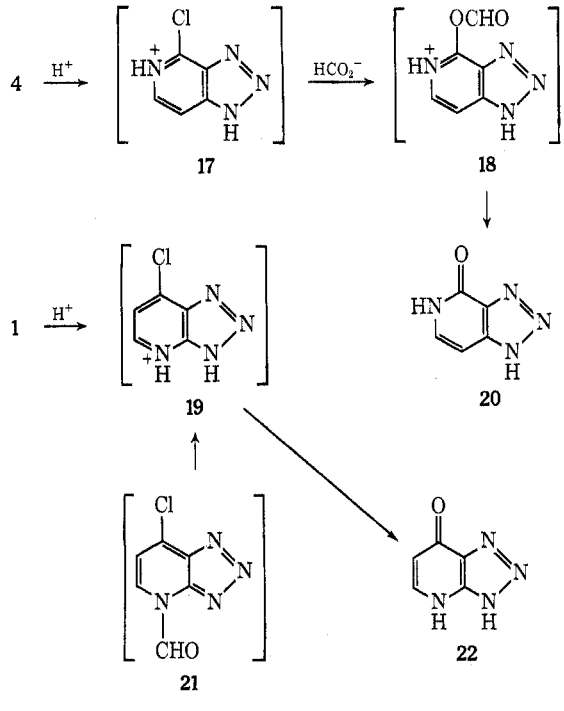
(8) C. Temple, Jr., and J. A. Montgomery, *J. Org. Chem.*, **31**, 1417 (1966).

SCHEME I



a mixture of **10** and **12** (tlc). The rearrangement of **10** to **12** and not **5** to **2** in alcohol suggested that triazole ring opening is controlled at least in part by the electron-withdrawing inductive effect of the substituent in the pyridine ring (–HNCS– or –NCSH > –NCNH$_2$–). The rearrangement of a thiadiazolopyrimidine to a 8-azapurinethione[9] and of related thiazolopyrimidines to purinethiones[10] with base has been demonstrated, and the conversion of **12** to **10** was also effected under these conditions. Presumably, opening of the thiadiazolo ring of **12** with base gave the electron-donating anion of the pyridinethione intermediate **11**, which favored triazole ring formation. Reaction of **1** with hydrated NaSH gave a 75% yield of **13**. This material was alkylated with MeI to give **15** and refluxed in propanol (141 hr) to give a 72% yield of **16** presumably formed *via* **14**. The anomalous low decomposition point (~176°) of **13** was attributed to rearrangement of **13** to **16** by heat (tlc). Treatment of **16** with aqueous NaOH in ethanol reversed the rearrangement to give **13**. (See Scheme I.)

Treatment of **4** with anhydrous formic acid at reflux for 4 hr gave a 91% yield of **20**. Apparently this reaction involves the attack of the formyloxy anion on the protonated chloro compound **17** to give **18**, which undergoes hydrolysis to give **20**. In contrast treatment of **1** with formic acid gave a low yield of **22**, presumably formed from **19**. Another sample obtained from this reaction was shown by its pmr spectrum to contain a minor amount of **22** and mainly two unidentified compounds. Elemental analyses and the pmr spectrum suggested that these compounds are N-formylated derivatives of **1** and **22**. Practically complete conversion to **22** was effected by heating the mixture with formic acid (42 hr). These results suggest that the slow rate of formation of **22**, when compared with that of **20**, is because of N-formylation of **1** to give presumably **21**, which undergoes deformylation to give **19** before conversion to **22**. In contrast to the conversion of **13** into **16** refluxing a solution of **22** in propanol (140 hr) gave no detectable rearrangement to 4-amino[1,2,3]oxodiazolo[4,5-*c*]pyridine.



The ultraviolet, infrared, and pmr spectral properties of these compounds are listed in Table I.

(9) A. Albert and K. Tratt, *Angew. Chem., Int. Ed. Engl.*, **5**, 587 (1966).

(10) G. B. Brown, G. Levin, S. Murphy, A. Sele, H. C. Reilly, G. S. Tarnowski, F. A. Schmidt, M. N. Teller, and C. C. Stock, *J. Med. Chem.*, **8**, 190 (1965); D. J. Brown and S. F. Mason, *J. Chem. Soc.*, 682 (1957).

TABLE I

Compd	Uv absorption[a] spectra at pH 7, λ_{max}, nm ($\epsilon \times 10^{-3}$)	Ir absorption[b] spectra in KBr, selected bands, cm^{-1}	Pmr spectral assignments,[c] chemical shift, δ (rel area)
1	285 (10.6)	1575	7.66 (1, 6 H), 8.66 d (1, 5 H, J_{56} = 5.0 Hz), ~10–12(1, NH)
4	257 sh (3.76), 263 (4.30), 286 (6.20)	1610, 1580	7.87 d (1, 7 H), 8.31 d (1, 6 H, J_{67} = 5.8 Hz)[d]
2	214 (15.1), 265 (9.15), 302 (14.8), 330 sh (1.24)	1620, 1515	6.39 d (1, 6 H), 7.50 (2, NH_2), 8.01 d (1, 5 H, J_{56} = 5.8 Hz), 10.9 br (NH)
5	286 (6.68), 326 (1.81)[e]	1690, 1650, 1625	6.89 d (1, 7 H), 7.36 br, 7.58 d (4, NH, 6 H, J_{67} = 6.0 Hz)
8	262 (3.27), 305 (10.7)	1600, 1575	1.03 t (3, CH_3), 1.78 m (2, CH_2), 3.39 t (2, CH_2), 7.53 d (1, 7 H), 8.33 d (1, 6 H, J_{67} = 6.0 Hz), ~13–16 (NH)
9	261 (3.12), 303 (10.7)[f]	1600, 1575	2.70 (3, CH_3), 7.53 d (1, 7 H), 8.35 (1, 6 H, J_{67} = 5.8 Hz), ~10–13 (NH)
15	212 (15.9), 286 (13.6), 302 (13.6)[f]	1595, 1570	2.71 (CH_3),[g] 7.27 d (1, 6 H), 8.52 d (1, 5 H, J_{56} = 4.8 Hz), ~12–16 (NH)
10	253 (5.20), 334 (16.8)	1585, 1530	7.18 d (1, 7 H), 7.52 t (1, 6 H, J_{56} = 6.0 Hz, J_{67} = 7.0 Hz), 13.2 br, ~15–18 (NH)
13	230 (10.9), 278 sh (4.73), 281 (6.42), 292 sh (5.69), 354 (17.8)[f]	1610, 1590	7.11 d (1, 6 H), 7.83 d (1, 5 H, J_{56} = 6.2 Hz), ~13–16(2, NH)
12	233 (13.1), 243 (13.2), 269 (4.46), 342 (5.47)	3365, 3320, 1655	6.73 d (1, 6 H), 7.76 (2, NH_2), 8.27d (1, 5 H, J_{56} = 5.2 Hz)
16	249 (5.92), 284 (4.38), 338 (4.44)[e]	3375, 3300, 1640	7.37 d (1, 7 H), 7.62 (2, NH_2), 8.71 d (1, 6 H, J_{67} = 5.2 Hz)
20	263 (6.62), 273 (6.80)	1660, 1610, 1570	6.64 d (1, 7 H), 7.31 d (1, 6 H, J_{67} = 7.0 Hz), ~10.4 br, 14–17 (1, 1, NH)
22	209 (15.7), 258 (8.50), 296 (14.7), 304 (11.9)[f]	1620, 1525	6.14 d (1, 6 H), 7.91 d (1, 5 H, J_{56} = 6.8 Hz), ~12.3 br (2, NH)

[a] Cary Model 17 spectrophotometer. [b] Perkin-Elmer Model 521 and 621 spectrophotometers. [c] Pmr spectra of samples were determined in DMSO-d_6 solutions (4–10% w/v) with Varian A-60A and XL-100-15 spectrometers with TMS as an internal reference; peak positions quoted in the case of multiplets are measured from the approximate center, and the relative peak areas are given to the nearest whole number. [d] Position of the NH peaks was not determined. [e] Solvent contains 0.8% DMSO, 9.2% MeOH, and 90% pH 7 buffer. [f] Solvent contains 10% 0.1 *N* NaOH and 90% pH 7 buffer. [g] This peak overlapped the DMSO-d_5 multiple.

Experimental Section[11]

7-Chloro-1*H*-*v*-triazolo[4,5-*b*]pyridine (1)[2] was prepared by a procedure similar to that reported from 2,3-diamino 4-chloropyridine (3.4 g)[6] and solid sodium nitrite (1.8 g) in 0.4 *N* HCl, yield 2.3 g (63%). A sample was recrystallized from aqueous EtOH and dried *in vacuo* over P_2O_5 at 78° for analyses, mp >300°.

Anal. Calcd for $C_5H_3ClN_4$: C, 38.87; H, 1.95; Cl, 22.93; N, 36.24. Found: C, 38.68; H, 1.84; Cl, 23.18; N, 36.07.

7-Amino-3*H*-*v*-triazolo[4,5-*b*]pyridine (2).—A suspension of 1 (0.50 g) in 12% w/w ethanolic ammonia (20 ml) was heated in a Parr bomb for 19 hr at 150°. The reaction mixture was evaporated to dryness, and the resulting residue was dissolved in 0.4 *N* NaOH. Acidification (pH 5, paper) of this solution with HOAc deposited the product, which was dried *in vacuo* over P_2O_5 at 110°, yield 0.24 g (55%), mp 250° dec (lit.[2] mp 270° with sublimation).

Anal. Calcd for $C_5H_5N_5$: C, 44.45; H, 3.73; N, 51.83. Found: C, 44.20; H, 3.66; N, 51.60.

The filtrate from above was evaporated to dryness, and the residue was washed with H_2O to give a solid, yield 0.03 g (7%). This sample was identified as an approximately 1:1 mixture of 2 and 5 by tlc and by its pmr spectrum.

4-Chloro-1*H*-*v*-triazolo[4,5-*c*]pyridine (4).[4]—Solid sodium nitrite (4.8 g) was added with stirring to a cooled solution (10°) of 3,4-diamino-2-chloropyridine (9.0 g)[4,5] in 0.4 *N* HCl (350 ml). After the solution was stirred at ice bath and room temperatures for 1 hr each, the tan solid was collected by filtration and dried *in vacuo* over P_2O_5, yield 8.8 g (91%). A sample was recrystallized from EtOH for analyses, mp >325°.

Anal. Calcd for $C_5H_3ClN_4$: C, 38.87; H, 1.95; N, 36.24. Found: C, 39.02; H, 1.96; N, 36.42.

4-Amino-1*H*-*v*-triazolo[4,5-*c*]pyridine (5).[2]—A suspension of 4 (1.5 g) in 12% w/w ethanolic ammonia (60 ml) was heated in a Parr bomb for 19 hr at 150–152°. The reaction mixture was evaporated to dryness, and the resulting solid was suspended with stirring in H_2O (15 ml) containing 1 *N* NaOH (10 ml). After 15 min the product was collected by filtration, yield 0.93 g (71%). A sample was precipitated from a NaOH solution with HOAc and dried *in vacuo* over P_2O_5 at 78° for analyses, mp >325°.

Anal. Calcd for $C_5H_5N_5$: C, 44.45; H, 3.73; N, 51.83. Found: C, 44.34; H, 3.75; N, 51.73.

The basic wash from above was acidified with HOAc to deposit a solid, yield 0.29 g (22%). This sample was shown to be an approximately 1:1 mixture of 2 and 5 by tlc and by its pmr spectrum.

7-(Propylthio)-1*H*-*v*-triazolo[4,5-*c*]pyridine (8) **and 7-Amino-[1,2,3]thiadiazolo[5,4-*b*]pyridine** (12).—A solution of 4 (5.0 g) and thiourea (2.7 g) in PrOH (150 ml) was refluxed for 3.5 hr and evaporated to dryness *in vacuo*. The residue was stirred in 1 *N* NaOH (50 ml) for 15 min, and 12 was collected by filtration, washed with H_2O, and dried *in vacuo* over P_2O_5, yield 1.5 g (30%), mp 190–191° dec.

Anal. Calcd for $C_5H_4N_4S$: C, 39.46; H, 2.65; N, 36.82. Found: C, 39.60; H, 2.72; N, 36.58.

Tlc indicated that a mixture of 10 and 12 resulted from refluxing a suspension of 10 in PrOH for 18 hr.

The combined filtrate and wash from above was acidified to pH 6 (paper) with dilute HCl to deposit 8, yield 1.1 g (18%), mp 158–160°.

Anal. Calcd for $C_8H_{10}N_4S$: C, 49.46; H, 5.19; N, 28.84. Found: C, 49.32; H, 5.16; N, 28.31.

4-(Methylthio)-1*H*-*v*-triazolo[4,5-*c*]pyridine (9).—A solution of 10 (2.40 g) in DMF (50 ml) containing anhydrous K_2CO_3 (2.18 g) and CH_3I (2.24 g) was stirred at room temperature for 18 hr and evaporated to dryness *in vacuo*. The residue was dissolved in H_2O (70 ml), and the solution was acidified to pH 5 (paper) with dilute HCl. After being chilled for 20 hr the product was collected by filtration and dried *in vacuo* over P_2O_5 at 78°, yield 0.72 g (27%), mp 170°.

Anal. Calcd for $C_6H_6N_4S$: C, 43.35; H, 3.64; N, 33.71; S, 19.29. Found: C, 43.52; H, 3.54; N, 33.62; S, 19.28.

Tlc indicated that the aqueous filtrate was a complex mixture of 9 and four other components.

1,5-Dihydro-4*H*-*v*-triazolo[4,5-*c*]pyridine-4-thione (10). **A.**—A suspension of 4 (4.0 g) and hydrated NaSH (20 g) in PrOH was refluxed for 20 hr. After filtration the filtrate was evaporated to dryness, and the resulting solid was dissolved in H_2O (100 ml). This solution was acidified with HOAc to deposit 10, which was collected by filtration, washed with C_6H_6, and dried *in vacuo* over P_2O_5 at 110°, yield 3.3 g (84%), mp ~234° dec (lit.[2] dec > 230°).

Anal. Calcd for $C_5H_4N_4S$: C, 39.46; H, 2.65; N, 36.82. Found: C, 39.22; H, 2.57; N, 36.98.

B.—A solution of 12 (0.20 g) in EtOH (25 ml) and 1 *N* NaOH (3 ml) was refluxed for 2 hr and evaporated to dryness. The resi-

(11) Melting points were determined on a Mel-Temp apparatus, and thin layer chromatograms (silica gel G) were developed with mixtures of $CHCl_3$ and MeOH.

due was dissolved in H_2O and acidified with dilute HCl to deposit **10**, which was identified by tlc with an authentic sample, yield 0.14 g (70%), mp ~227 dec.

1,4-Dihydro-7*H*-*v*-triazolo[4,5-*b*]pyridine-7-thione (13). A.—Treatment of **1** (2.7 g) and hydrated NaSH (13 g) under conditions similar to that described above for the preparation of **10** gave **13**, yield 2.0 g (75%), mp 176–177° dec with sublimation (lit.[2] dec > 200°).

Anal. Calcd for $C_5H_4N_4S$: C, 39.46; H, 2.65; N, 36.82. Found: C, 39.41; H, 2.56; N, 36.60.

B.—A solution of **16** (0.10 g) in EtOH (12 ml) and 1 *N* NaOH (3 ml) was refluxed for 16 hr and acidified to pH 1 (paper) with concentrated HCl to deposit **13**, yield 0.04 g, mp 176–177° dec with sublimation.

7-(Methylthio)-1*H*-*v*-triazolo[4,5-*b*]pyridine (15) was prepared by a procedure similar to that of **9** from **13** (0.89 g), anhydrous K_2CO_3 (0.81 g), and CH_3I (0.83 g) in DMF (18 ml), yield 0.50 g (51%), mp 208–209°.

Anal. Calcd for $C_6H_6N_4S$: C, 43.35; H, 3.64; N, 33.71; S, 19.29. Found: C, 43.42; H, 3.54; N, 33.88; S, 19.15.

4-Amino[1,2,3]thiadiazolo[4,5-*c*]pyridine (16). A.—A suspension of **13** (1.55 g) in EtOH (160 ml) was refluxed for 141 hr and evaporated to dryness *in vacuo*. The residue was extracted with hot CH_3CN (250 ml), and the extract was evaporated to dryness. Recrystallization of the resulting solid from EtOAc–petroleum ether (bp 80–105°) gave the product, which was dried *in vacuo* over P_2O_5 at 78°, yield 1.11 g (72%), mp 185–187°.

Anal. Calcd for $C_5H_4N_4S$: C, 39.46; H, 2.65; N, 36.82; S, 21.07. Found: C, 39.67; H, 2.65; N, 36.62; S, 20.85.

B.—A sample of **13** was heated to 190° in a capillary tube. Tlc indicated that the resulting dark, gummy residue and white sublimate contained only **16**.

1,5-Dihydro-4*H*-*v*-triazolo[4,5-*c*]pyridin-4-one (20).—A solution of **4** (2.0 g) in formic acid (40 ml) was refluxed for 4 hr and evaporated to dryness *in vacuo*. The residue was dissolved in dilute aqueous NaOH, and after filtration the filtrate was acidified with concentrated HCl to deposit **20**, which was dried *in vacuo* over P_2O_5 at 78°, yield 1.6 g (91%). A sample was recrystallized from H_2O for analyses, mp >360°.

Anal. Calcd for $C_5H_4N_4O$: C, 44.12; H, 2.96; N, 41.16. Found: C, 43.92; H, 2.83; N, 40.99.

1,4-Dihydro-7*H*-*v*-triazolo[4,5-*b*]pyridin-7-one (22).—A solution of **1** (2.0 g) in formic acid (40 ml) was refluxed for 4 hr and evaporated to dryness; the resulting residue was dissolved in dilute NaOH. After filtration the filtrate was neutralized with dilute HCl to deposit a solid, which was again reprecipitated from a NaOH solution with dilute HCl, yield 1.0 g. This material was dissolved in hot H_2O (400 ml), and the solution was cooled for about 60 hr to deposit a tan precipitate, yield 0.30 g. Elemental analysis of this solid showed the presence of chlorine, and the pmr spectrum indicated that the sample contained a minor amount of **22** and mainly two unidentified components, presumably N-formylated intermediates. A sample (0.13 g) was refluxed in formic acid for 42 hr, and the resulting solid was recrystallized from H_2O to give a trace amount of the unidentified component and **22** (see below), yield 0.08 g, mp 290° dec.

The aqueous filtrate from the mixture of components described above was concentrated to a low volume to deposit pure **22**, which was dried *in vacuo* over P_2O_5 at 78°, yield 0.51 g (29%), mp 290° dec.

Anal. Calcd for $C_5H_4N_4O$: C, 44.12; H, 2.96; N, 41.16. Found: C, 43.96; H, 3.11; N, 40.94.

Registry No.—**1**, 34550-49-7; **2**, 34550-46-4; **4**, 36258-82-9; **5**, 34550-62-4; **8**, 36258-84-1; **9**, 36258-85-2; **10**, 36258-86-3; **12**, 36258-87-4; **13**, 36258-88-5; **15**, 36258-89-6; **16**, 36258-90-9; **20**, 36286-97-2; **22**, 36286-98-3.

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Synthesis and Infrared Spectra of Nitrogen-15 Labeled 3-Methyl-2-benzothiazolinone Hydrazones and Related Compounds

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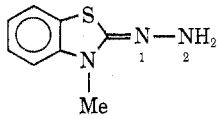
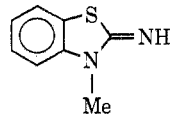
The syntheses of 3-methyl-2-benzothiazolinone hydrazone-*1*-^{15}N (**1a**) and -*2*-^{15}N (**1b**), 2-imino-^{15}N-3-methylbenzothiazoline (**2a**), *N*-(3-methyl-2-benzothiazolinylidene)benzamide-^{15}N (**6a**), 3-methyl-2-(nitrosimino-*imino*-^{15}N)benzothiazoline (**7a**), and 3-methyl-2-(nitrosimino-*nitroso*-^{15}N)benzothiazoline (**7b**) are reported. Infrared spectral studies of **1a**, **1b**, **2a**, **6a**, **7a**, and **7b** and the corresponding unlabeled compounds allow for the assignment of several absorption bands.

Mechanistic studies of the oxidation of 3-methyl-2-benzothiazolinone hydrazone (**1**) with potassium ferricyanide[3] required the preparation of 3-methyl-2-benzothiazolinone hydrazone-*1*-^{15}N (**1a**) and -*2*-^{15}N (**1b**). We wish to report viable synthetic routes to **1a** and **1b** which employ $Na^{15}NO_2$ and $^{15}NH_4NO_3$ as the sources of the isotopic nitrogen label.



1a, 1-^{15}N
b, 2-^{15}N



2a, 1-^{15}N

Results and Discussion

Stepwise introduction of the two hydrazone nitrogen atoms was deemed necessary in view of the isotopic scrambling that would attend reactions in which both nitrogen atoms become incorporated in one step.[4]

3-Methyl-2-benzothiazolinone Hydrazone-*1*-^{15}N.—It appeared that an attractive method for introduction of labeled nitrogen into the imino nitrogen position of **1a** might include the reaction of $^{15}NH_3$ with an appropriate benzothiazolium salt to form 2-imino-^{15}N-3-methyl-

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