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.

Acknowledgments.—The authors are indebted to Dr. W. C. Coburn, Jr., and members of the Molecular Spectroscopy Section of Southern Research Institute, who performed most of the microanalytical and spectral determinations reported.

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

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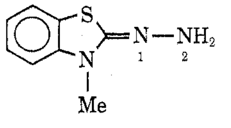
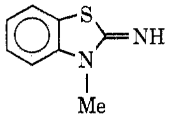
The syntheses of 3-methyl-2-benzothiazolinone hydrazone-*1*-^{15}N (**1a**) and -*2*-^{15}N (**1b**), 2-imino-^{15}N-3-methylbenzothiazoline (**2a**), *N*-(3-methyl-2-benzothiazolinylidene)benzamide-^{15}N (**6a**), 3-methyl-2-(nitrosimino-*imino*-^{15}N)benzothiazoline (**7a**), and 3-methyl-2-(nitrosimino-*nitroso*-^{15}N)benzothiazoline (**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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(1) NATO Postdoctoral Fellow, 1967–1968.

(2) Address correspondence to Department of Chemistry, Washington State University, Pullman, Wash. 99163.

(3) R. A. Bartsch, S. Hünig, and H. Quast, *J. Amer. Chem. Soc.*, **92**, 6007 (1970).

(4) R. Riemschneider, *Monatsh. Chem.*, **89**, 683 (1958).

TABLE I

REACTION OF 2-X-3-METHYLBENZOTHIAZOLIUM FLUOROBORATE WITH AMMONIUM NITRATE AND SODIUM METHOXIDE IN METHANOL

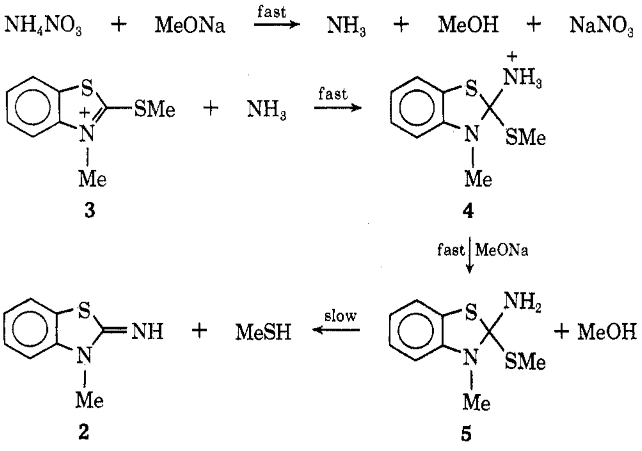
Run	X	NH_4NO_3, mmol	MeONa, mmol	Solvent	Reaction time, days	Yield of imine 1, %[a,b]
1	SMe	1.05	1.0	MeOH	0.1	0[c]
2	SMe	1.03	2.0	MeOH	2	22[d]
3	SMe	1.05	2.0	MeOH	5	57–68
4	SMe	1.01	2.0	MeOH–MeCN	5.5	15
5	SMe	1.03	3.0	MeOH	1	0
6	SMe	1.00	4.0	MeOH	6	0
7	Cl	1.00	2.0	MeOH–MeCN	3	0[c]
8	OEt	1.01	2.0	MeOH–MeCN	5	0

[a] Isolated as the benzoylated derivative, *N*-(3-methyl-2-benzothiazolinylidene)benzamide. [b] Yield based upon ammonium nitrate. [c] Apparent formation of 3-methyl-2-benzothiazolinone monoazamonomethinecyanine fluoroborate by reaction of **2** with **3**: H. Quast and S. Hunig, *Justus Liebigs Ann. Chem.*, **711**, 157 (1968). [d] Incomplete reaction.

benzothiazoline (**2a**), since this step has been employed in the preparation of similar imino compounds.[5]

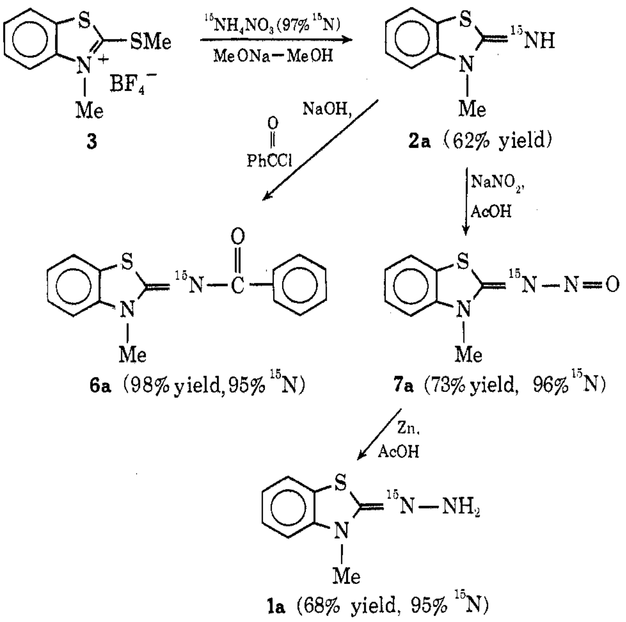
With the goal of establishing appropriate conditions for the reaction of 2-substituted 3-methylbenzothiazolium salts with ammonia, which was to be generated *in situ* from ammonium nitrate and sodium methoxide, the experiments summarized in Table I were performed. The course of the reactions was followed with ultraviolet spectroscopy by observing the appearance of absorption at λ_{max} 292 nm for the imine **2**. Reaction of 3-methyl-2-methylmercaptobenzothiazolium fluoroborate with 1 equiv of ammonium nitrate and 2 equiv of sodium methoxide in methanol gave reasonable yields of 2-imino-3-methylbenzothiazoline (**2**). Other ratios of sodium methoxide to ammonium nitrate and other 2-substituted 3-methylbenzothiazolium fluoroborates failed to produce **2**. In runs 2–4, the ultraviolet spectrum of the reaction solution exhibited a maximum at 301 nm soon after mixing of the reagents. During the span of several days, the absorption at 301 nm decreased and was replaced by an absorption with λ_{max} 292 nm for the imine **2**. A mechanism which is consistent with the observed stoichiometry and the spectral changes[6–8] is presented in Scheme I.

SCHEME I



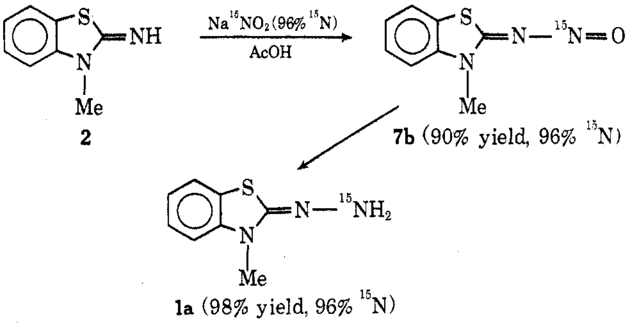
The synthetic route to 3-methyl-2-benzothiazolinone hydrazone-*1*-^{15}N is outlined in Scheme II. The reported yields are yields for each step. Conversion of the imine **2a** into the hydrazone **1a** was accomplished by modification of the procedure of Besthorn.[9] The ^{15}N content of **1a**, **6a**, and **7a**, as determined by mass spectrometry, demonstrates complete incorporation of the isotopic nitrogen label.

SCHEME II



3-Methyl-2-benzothiazolinone Hydrazone-*2*-^{15}N.—The synthesis of hydrazone **1b** from 2-imino-3-methylbenzothiazoline is depicted in Scheme III. The procedure of Besthorn for this conversion[9] was modified to achieve the highest yield of **7b** from reaction of limited labeled ammonium nitrite. Again complete incorporation of the ^{15}N label was observed.

SCHEME III



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[5] H. Quast and S. Hünig, *Chem. Ber.*, **101**, 435 (1968).

[6] The ultraviolet spectra of 3-methylbenzothiazolium iodide in ethanol exhibits λ_{max} at 276 nm.[7]

[7] J. Metzger, H. Larivé, R. Dennilauler, R. Baralle, and C. Gaurat, *Bull. Soc. Chim. Fr.*, 2868 (1964).

[8] The ultraviolet spectrum of 2-ethoxy-3-methylbenzothiazoline in ethanol exhibits λ_{max} at 308 nm.[7]

[9] E. Besthorn, *Chem. Ber.*, **43**, 1519 (1910).

Infrared Spectral Investigations.—The availability of ^{15}N labeled derivatives of **1**, **2**, **6**, and **7** encouraged careful study of the infrared spectra of corresponding labeled and unlabeled compounds.[10] The results of this investigation, which are presented in Tables II–V, further support the specificity of the synthetic routes to **1a** and **1b** and allow for the identification of several absorption bands in the complex spectra of **1**, **2**, **6**, and **7**.

TABLE II

INFRARED ABSORPTION BAND SHIFTS[a,b] FOR 2-IMINO-3-METHYLBENZOTHIAZOLINE (**2**) AND 2-IMINO-^{15}*N*-3-METHYLBENZOTHIAZOLINE (**2a**) IN THE REGIONS 3200–3400 AND 800–1700 CM^{-1}

Absorption maxima, cm^{-1}		Strength of absorption[c]	$\Delta\nu$(2–2a), cm^{-1}	Assignment
2	**2a**			
3344	3338	w	6	NH stretch
1610	1602.5	s	7.5	C=N stretch
1590	1586	s	4	NH bend
1584	1579.5	s	4.5	NH bend

[a] Measured in CH_2Cl_2 solution. [b] Shifts of 2 cm^{-1} or less are not reported. [c] w, weak; s, strong.

TABLE V

INFRARED ABSORPTION BAND SHIFTS[a,b] FOR *N*-(3-METHYL-2-BENZOTHIAZOLINYLIDENE)BENZAMIDE (**6**) AND *N*-(3-METHYL-2-BENZOTHIAZOLINYLIDENE)BENZAMIDE-^{15}*N* (**6a**) IN THE REGION 800–1700 CM^{-1}

Absorption maxima, cm^{-1}		Strength of absorption[c]	$\Delta\nu$(6–6a), cm^{-1}	Assignment
6	**6a**			
1510	1505	s	5	C=N stretch
1456.5	1462	s	−3.5	
1367	1350	s	17	OC—N stretch
905	900	m	5	

[a] Measured in CH_2Cl_2. [b] Shifts of 2 cm^{-1} or less are not reported. [c] m, medium; s, strong.

For 2-imino-3-methylbenzothiazoline (**2**), characteristic ketimine absorptions in the regions 3200–3260 (NH stretch) and 1600–1650 cm^{-1} (C=N stretch) might be anticipated.[11,12] For **2**, the absorptions at 3344 (NH stretch) and 1610 cm^{-1} (C=N stretch) shift by 6 and 7.5 cm^{-1}, respectively, when a ^{15}N-labeled imino nitrogen is incorporated (Table II). For the gas-phase spectrum of ethyleneimine, the N–H stretch at 3346 cm^{-1} is displaced by 9 cm^{-1} in ^{15}*N*-ethyleneimine.[13] The bands at 1590 and 1584 cm^{-1}, which both shift by 4 cm^{-1} in **2a**, are in the region (1500–1590 cm^{-1}) of N–H bending vibrations for imines.[14]

The absorption bands of 3-methyl-2-benzothiazolinone hydrazone **1** at 3358 and 1645 cm^{-1} may be assigned to N–H stretch and C=N stretch, respectively, on the basis of the frequency shifts observed for **1a** and **1b** (Table III). Although both symmetrical and asymmetrical N–H stretching vibrations might be anticipated, hydrazones only exhibit one absorption in the region.[15] The shifts noted in the absorption band at 1082.5 cm^{-1} of **1** for both **1a** and **1b** suggest that this band is an N–N stretching vibration. The N–N stretching mode of nitrosoamines occurs in this region.[16]

TABLE III

INFRARED ABSORPTION BAND SHIFTS[a,b] FOR 3-METHYL-2-BENZOTHIAZOLINONE HYDRAZONE (**1**) 3-METHYL-2-BENZOTHIAZOLINONE HYDRAZONE-*1*-^{15}*N* (**1a**) AND 3-METHYL-2-BENZOTHIAZOLINONE HYDRAZONE-*2*-^{15}*N* (**1b**) IN THE REGIONS 3100–3550 AND 800–1700 CM^{-1}

Absorption maxima, cm^{-1}			Strength of absorption[c]	$\Delta\nu$(1–1a), cm^{-1}	$\Delta\nu$(1–1b), cm^{-1}	Assignment
1	**1a**	**1b**				
3358	3358	3348	vw	0	10	NH stretch
1645	1631	1646	s	14	−1	C=N stretch
1568	1565	1567	m	3	1	
1082.5	1077.5	1077	w	5	5.5	NN stretch
1021	1018	1020	w	3	1	

[a] Measured in CH_2Cl_2 solution. [b] Shifts of 2 cm^{-1} or less are not reported. [c] vw, very weak; w, weak; m, medium; s, strong.

TABLE IV

INFRARED ABSORPTION BAND SHIFTS[a,b] FOR 3-METHYL-2-NITROSIMINOBENZOTHIAZOLINE (**7**), 3-METHYL-2-(NITROSIMINO-*imino*-^{15}*N*)BENZOTHIAZOLINE (**7a**), AND 3-METHYL-2-(NITROSIMINO-*nitroso*-^{15}*N*)BENZOTHIAZOLINE (**7b**) IN THE REGION 800–1700 CM^{-1}

Absorption maxima, cm^{-1}			Strength of absorption[c]	$\Delta\nu$(7–7a), cm^{-1}	$\Delta\nu$(7–7b), cm^{-1}	Assignment
7	**7a**	**7b**				
1556, 1548	1554	1548	w, b			
1436	1436	1429	s	0	7	N=O stretch
1405	1403	1396	s	2	6	N=O stretch
1063.5	1059	1060	m	4.5	3.5	NN stretch
1020.5	1015	1018	m	4.5	2.5	NN stretch
861.5	857.5	857	s	4	4.5	

[a] Measured in CH_2Cl_2. [b] Shifts of 2 cm^{-1} or less are not reported. [c] w, weak; m, medium; s, strong; b, broad.

In the monomeric state, nitrosoamines exhibit infrared absorptions in the regions 1430–1530 (N=O stretch) and 925–1150 cm^{-1} (N–N stretch).[16] The infrared spectra of 2-nitrosoimino-3-methylbenzothiazoline (**7**) and its ^{15}N-labeled drivative (**7a** and **7b**) (Table IV) indicate the presence of the two geometrical isomeric forms **8** and **9** for **7**. The presence of two iso-

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(10) For a recent summary of infrared spectra of ^{15}N-labeled compounds see S. Pinchas and J. Laulicht, "Infrared Spectra of Labelled Compounds," Academic Press, New York, N. Y., 1971, pp 216–237.

(11) P. L. Pickard and G. W. Polly, *J. Amer. Chem. Soc.*, **76**, 5169 (1954).

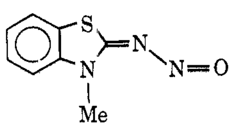
(12) C. J. Thoman and I. M. Hunsberger, *J. Org. Chem.*, **33**, 2852 (1968).

(13) R. W. Mitchell, J. C. Burr, Jr., and J. A. Merritt, *Spectrochim. Acta*, **23A**, 195 (1967).

(14) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 135.

(15) L. A. Jones, J. C. Holmes, and R. B. Seligman, *Anal. Chem.*, **28**, 191 (1956).

(16) C. N. R. Rao and K. R. Bhaskar in "The Chemistry of the Nitro and Nitroso Group," Part 1, H. Feuer, Ed., Interscience, New York, N. Y., 1969, pp 144–147.



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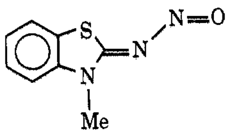

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mers is inferred from the similar frequency shifts in the absorptions at 1436 and 1405 cm^{-1} (N=O stretch) when the nitroso nitrogen is labeled with ^{15}N and at 1063.5 and 1020.5 cm^{-1} (N–N stretch) when either the imino or the nitroso nitrogen of **7** is labeled. In the spectrum of *N*-methyl-*p*-nitrophenylnitrosoamine, single absorptions at 1466 (N=O stretch) and 942 cm^{-1} (N–N stretch) have been identified by ^{15}N labeling.[17] Evidence for geometrical isomerism of imino compounds[18] and alkoxydiazenium salts[19] has been obtained by pmr spectroscopy. However, the pmr spectrum of **7** in deuteriochloroform shows only a singlet for the 3-methyl group. The presence of only a single absorption indicates either that the distance between the anisotropic nitrosimino function and the *N*-methyl group is too great or that **8** and **9** are in rapid equilibrium relative to the pmr time scale so that an averaged signal is obtained. No infrared absorption which could be attributed to a C=N stretching vibration was evident in the spectrum of **7**.

On the basis of the observed shifts in the spectrum of *N*-(3-methyl-2-benzothiazolinylidene)benzamide (**6**), when the imino nitrogen is labeled with ^{15}N, the 1510- and 1367-cm^{-1} bands are assigned to C=N stretching and OC–N stretching modes, respectively. The OC–N stretching band of dimethylformamide is displaced from 1383 to 1370 cm^{-1} in ^{15}*N*-dimethylformamide.[20]

Experimental Section

General.—Melting points are uncorrected. Infrared spectra were measured in methylene chloride solution (0.12–0.17 g/ml) with a Beckman IR-12 infrared spectrophotometer. Mass spectrometric analysis was performed using low ionization voltages (8–18 eV).

2-Imino-^{15}*N*-3-methylbenzothiazoline (2a).—To 0.34 g (4.2 mmol, 97% ^{15}N, Isocommerz, Berlin, DDR) of $^{15}NH_4NO_3$ dissolved in 40 ml of MeOH was added 8.0 ml of 1.04 *M* MeONa–MeOH. During 2 hr, a solution of 1.13 g (4.0 mmol) of 2-methylmercapto-3-methylbenzothiazolium fluoroborate[4] (**3**) in 160 ml of MeOH was added. After 5 days the reaction solution was evaporated *in vacuo*. Recrystallization of the residue from cyclohexane gave 0.38 g (56%) of crude **2a**, mp 105–115° (reported[9] mp 123°), which was used without further purification.

***N*-(3-Methyl-2-benzothiazolinylidene)benzamide-^{15}*N* (6a).**—As in the synthesis of **2a**, 0.085 g (1.05 mmol) of $^{15}NH_4NO_3$ in 10 ml of MeOH, 2.0 ml of 1.04 *M* MeONa–MeOH, and 0.28 g (1.00 mmol) of **3** were combined. After 4 days, the reaction solution was evaporated *in vacuo*. To the residue was added 50 ml of H_2O, 2 g of NaOH, and 0.5 ml of benzoyl chloride. After vigorous shaking, the mixture was placed in a refrigerator overnight. The precipitate was filtered, washed with H_2O, dissolved in hot AcOH, and slowly reprecipitated with H_2O. Filtration, washing with H_2O, and drying the resulting **6a** *in vacuo* yielded 0.18 g (62%), mp 149–150° (reported[21] mp 155°).

3-Methyl-2-(nitrosimino-*imino*-^{15}*N*)benzothiazoline (7a).—During 15 min, a solution of 0.17 g (2.5 mmol) of $NaNO_2$ in 1.5 ml of H_2O was added dropwise to a stirred solution of 0.24 g (1.5 mmol) of **2a** in 2 ml of AcOH at room temperature. After 1.5 hr, 20 ml of H_2O was added and the mixture was stirred for several hours. The orange precipitate was filtered, washed with H_2O, and dried *in vacuo*, producing 0.20 g (73%) of **7a**, mp 149° dec (reported[9] mp 147° dec).

3-Methyl-2-benzothiazolinone Hydrazone-*1*-^{15}*N* (1a).—To a stirred mixture of 0.18 g (0.93 mmol) of **7a** and 5 ml of 90% AcOH cooled to 0° was added 0.41 g (6.2 mg-atoms) of zinc dust in small portions during 1 hr. After an additional 1 hr, the excess zinc dust was removed by filtration. The filtrate was cooled to 0° and the hydrazone **1a** was precipitated by addition of concentrated NH_4OH. The precipitate was filtered and dried *in vacuo*, yielding 0.11 g (68%) of crude **1a**, with mp 133–135°. Three recrystallizations from benzene gave **1a**, mp 142–143° (reported[9] mp 143°).

3-Methyl-2(nitrosimino-*nitroso*-^{15}*N*)benzothiazoline (7b).—Using the procedure described for **7a**, 0.36 g (5.2 mmol) of $Na^{15}NO_2$ (96% ^{15}N, Isocommerz, Berlin, DDR) in 5 ml of H_2O and 1.08 g (6.6 mmol) of **1** in 4 ml of AcOH were combined. The orange **7b** weighed 0.90 g (90%) and had mp 147.5° dec (reported[9] mp 147° dec).

3-Methyl-2-benzothiazolinone Hydrazone-*2*-^{15}*N* (1b).—The synthetic method reported for **1a** was used to treat 0.48 g (2.5 mmol) of **7b** in 15 ml of 90% AcOH with 1.22 g (18.7 mg-atoms) of zinc dust. The crude **1b** (0.36 g, 80% yield) had mp 140–141° (reported[9] mp 143°).

Registry No.—**1a**, 35667-05-1; **1b**, 35667-06-2; **2a**, 35667-07-3; **6a**, 35667-08-4; **7a**, 35667-09-5; **7b**, 35667-10-8.

Acknowledgment.—We wish to thank Dr. Seidl of BASF-Ludwishafen for performing the mass spectrometric analysis. Use of the facilities of the department of Chemistry of Washington State University, in which this manuscript was composed, is acknowledged by R. A. B.

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[17] R. Kuebler, and W. Luettke, *Ber. Bunsenges. Phys. Chem.* **67**, 2 (1963).

[18] M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971), and references cited therein.

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[21] S. Hünig, and H. Quast, *Justus Liebigs Ann. Chem.*, **711**, 139 (1968).