# Reinvestigation of the Condensation of 2-Hydrazinobenzothiazole with Ethyl Acetoacetate



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The reaction of 2-hydrazinobenzothiazole (**1**) with ethyl acetoacetate has twice been reported to yield a fused triazepinobenzothiazolone, namely, 3-methyl[1,2,4]triazepino[3,4-*b*]benzothiazol-5(4*H*)-one (**4**). We have repeated this work and reassigned the reaction product as 2-(2-benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**5**) on the basis of X-ray crystallography.

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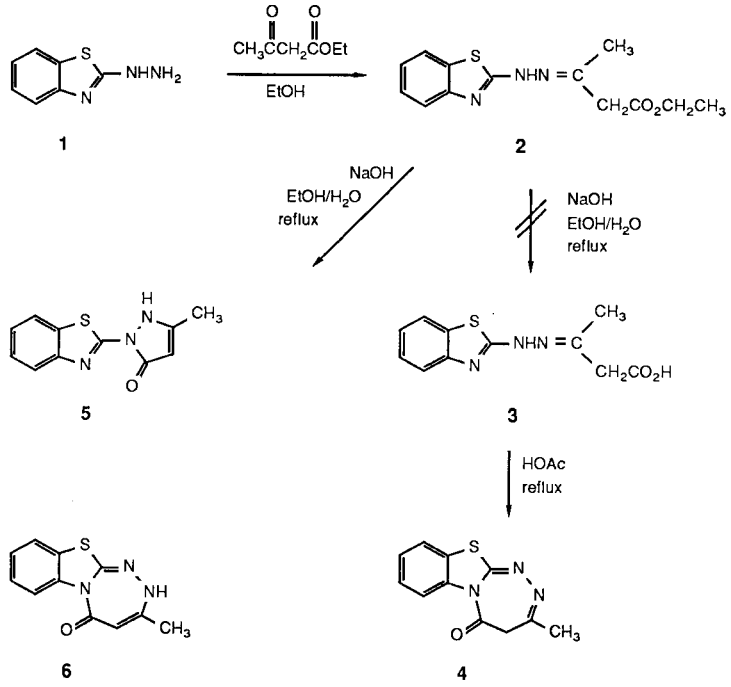
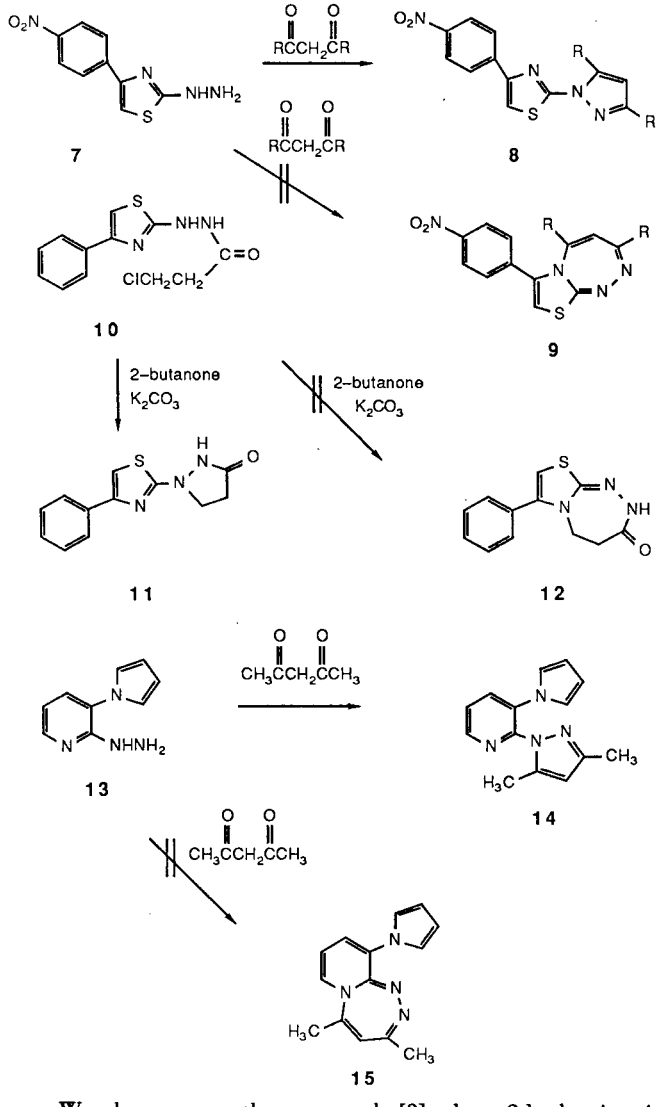
A recent report by Kulkarni and Deshpande [1] described the synthesis of 5-methyl-7*H*-1,3,4-triazepino[2,3-*a*]-benzothiazol-7-one (**4**) and benzosubstituted analogs. An earlier report by Dehuri, *et al.* [2], also described the synthesis of **4**, by the same route, as well as two related compounds. These two sets of authors reported that hydrazone **2**, made from 2-hydrazinobenzothiazole (**1**) and ethyl acetoacetate, could be hydrolyzed to the corresponding carboxylic acid **3**, and then cyclized to triazepinobenzothiazolone **4** in acetic acid at reflux as shown in Scheme I. We have repeated this work and found it to be in error.

Hydrazone **2** was prepared by treatment of 2-hydrazinobenzothiazole (**1**) with ethyl acetoacetate in ethanol at 60° for 30 minutes. Longer reaction times or higher temperatures gave a cyclized product directly. Our sample of **2**, which was consistent with all spectral data and analyzed correctly for $C_{12}H_{13}N_3O_2S$, melted sharply at 109-110°. Kulkarni and Deshpande [1] report a melting point of 84° for **2**, while Dehuri, *et al.* [2] report a melting point for **2** of 215°. When hydrazone **2** was treated with sodium hydroxide in aqueous ethanol, a cyclized product was obtained instead of a hydrolysis product corresponding to **3**. We felt that this product of cyclization was 2-(2-benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**5**) rather than triazepinone **4**, on the basis of our previous work which is summarized in Scheme II.

Scheme I



Scheme II

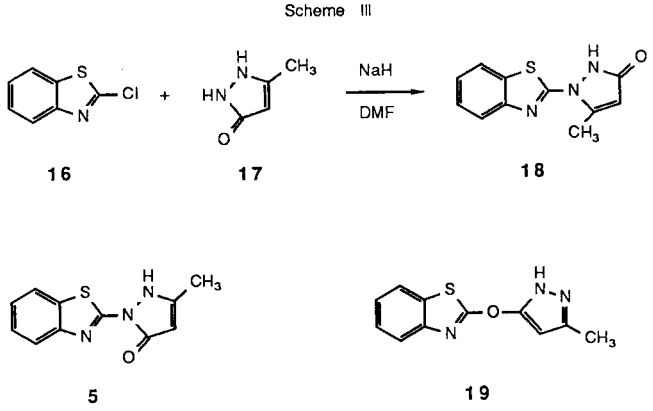


We have recently reported [3] that 2-hydrazino-4-(4-nitrophenyl)thiazole (**7**) condenses with 1,3-diketones to give 2-(1*H*-pyrazol-1-yl)-4-(4-nitrophenyl)thiazoles (**8**) rather than 3-(4-nitrophenyl)thiazolo[2,3-*c*][1,2,4]triazepines (**9**) as previously reported [4,5]. Likewise, we have shown that 3-chloropropanoic acid 2-(4-phenyl-2-thiazolyl)-hydrazide (**10**) cyclizes to give 1-(4-phenyl-2-thiazolyl)-3-pyrazolidinone (**11**) rather than 4,5-dihydro-7-phenylthiazolo[2,3-*c*][1,2,4]triazepin-3(2*H*)-one (**12**), on treatment with potassium carbonate in 2-butanone [7]. In addition, we have found that 2-hydrazino-3-(1*H*-pyrrol-1-yl)pyridine (**13**) condenses with acetylacetone to give the sterically congested 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-(1*H*-pyrrol-1-yl)pyridine (**14**) [8] rather than 3,5-dimethyl-10-(1*H*-pyrrol-1-yl)pyrido[2,1-*c*][1,2,4]triazepine (**15**) as was recently reported [9]. Thus, in competitive cyclizations where pyrazoles or fused triazepines can form, pyrazole formation prevails.

It is difficult to differentiate between pyrazolone **5** and the isomerization product of **4**, triazepinone **6** (Scheme I), on the basis of spectral data. Thus, we attempted to unequivocally establish the structure of the cyclization product which we obtained from hydrazone **2** through an alternative synthesis.

Treatment of 2-chlorobenzothiazole (**16**) with the anion of 1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**17**) [10], prepared from **17** and sodium hydride in dimethylformamide as shown in Scheme III yielded a single product which was isomeric with, but different from, the product obtained from the cyclization of hydrazine **2**. Possible products of this reaction were the desired pyrazolone **5**; the other *N*-alkylated product, namely, 1-(2-benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**18**); or the product resulting from *O*-alkylation, 2-[(5-methyl-1*H*-pyrazol-3-yl)-oxy]benzothiazole (**19**).

Scheme III



Since alkylation of **17** with **16** did not provide the product resulting from cyclization of **2**, we obtained single crystal x-ray data on the cyclization product. The ORTEP drawing of this structure is shown in Figure I, which clearly shows it to be 2-(benzothiazol-2-yl)-5-methylpyrazol-3(1*H*)-one (**5**).

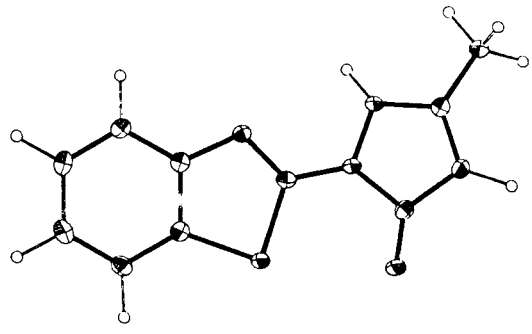


Figure I. ORTEP Drawing of 2-(2-Benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**5**).

While the $^1$H nmr spectrum for **5** is indeed consistent with structure, the $^{13}$C nmr spectrum clearly reveals only eight of the eleven expected signals. Intensities of some of

these signals are inconsistent with structure. However, under acidic conditions (1*M* hydrochloric acid, *ca.* 1 drop added to the sample), the $^{13}C$ nmr spectrum displays the expected eleven sharp signals. The $^{1}H$ nmr spectrum of **5** changes only slightly on addition of acid. We speculate that some signals in the initial spectrum are broadened due to tautomeric exchange in **5**. The $^{13}C$ and $^{1}H$ nmr spectral parameters for **5** are compiled in Tables I and II.

The $^{13}C$ nmr spectrum of **5** was also acquired using gated proton decoupling to allow for full carbon-proton coupling to occur during acquisition and maintain the nuclear Overhauser enhancement (NOE) effect. Not only are the large carbon-proton single bond couplings visible in the spectrum but also the smaller 2, 3, and 4 bond couplings [11]. Signals due to the non-protonated carbons C-3a', C-5, C-3, and C-2 give very different spectral patterns under these conditions and are unequivocally assigned on this basis.

The $^{13}C$-$^{1}H$ heteronuclear correlation (HETCOR) [12] spectrum for **5** (*ca.* 50 mg of **5** in 0.7 ml dimethylsulfoxide-$d_6$ with 1 drop of 1*M* hydrochloric acid) is shown in Figure II. All of the $^{13}C$ resonances for the benzo carbons bearing protons are readily correlated with the corresponding proton resonances. In addition, the carbon signal for C-4 (δ 91.2) correlates with the proton signal at (δ 5.28) as expected.

Table I

$^{1}H$ NMR Spectral Parameters for 2-(2-Benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**5**)

| Assignment | Chemical [a] Shift (DMSO-$d_6$) | Chemical [b] Shift (acid) | Coupling [c] Constants |
|---|---|---|---|
| NH | 12.85 | ---- | |
| H7' | 8.06 | 8.00 | $^{3}J_{H4'-H5'} = 8.1$ |
| H4' | 7.85 | 7.81 | $^{3}J_{H6'-H7'} = 7.9$ |
| H5' | 7.50 | 7.47 | $^{4}J_{H4'-H6'} = 1.2$ |
| H6' | 7.36 | 7.34 | $^{4}J_{H5'-H7'} = 1.4$ |
| H4 | 5.30 | 5.28 | $^{5}J_{H4'-H7'} = 0.8$ |
| $CH_3$ | 2.24 | 2.22 | |

[a] Sample in DMSO-$d_6$, shifts in ppm from TMS. [b] Sample in DMSO-$d_6$ with 1 drop of 1*M* hydrochloric acid added. [c] Proton-proton coupling in Hz.

Table II

$^{13}C$ NMR Spectral Parameters for 2-(2-Benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**5**)

| Assignment | Chemical Shifts [a] | Coupling Constants [b] | |
|---|---|---|---|
| C3 | 162.0 | $^{1}J_{H4'-C4'}$ | = 161.6 |
| C5 | 153.8 | $^{1}J_{H5'-C5'}$ | = 160.5 |
| C2' | 152.6 | $^{1}J_{H6'-C6'}$ | = 162.3 |
| C3'a | 148.3 | $^{1}J_{H7'-C7'}$ | = 165.2 |
| C7'a | 131.6 | $^{1}J_{H4-C4}$ | = 181.0 |
| C5' | 126.4 | $^{1}J_{H-C(Me)}$ | = 129.6 |
| C6' | 124.0 | $^{2}J_{H4-C3}$ | = 7.0 |
| C7' | 122.0 | $^{2}J_{H4-C5}$ | = 6.5 |
| C4' | 120.6 | $^{2}J_{CH3-C5}$ | = 6.5 |
| C4 | 91.2 | $^{3}J_{H4'-C6'}$ | = 7.7 |
| $CH_3$ | 12.3 | $^{3}J_{H4'-C7'a}$ | = 6.8 |
| | | $^{3}J_{H5'-C3'a}$ | = 9.5 |
| | | $^{3}J_{H5'-C7'}$ | = 9.0 |
| | | $^{3}J_{H6'-C4'}$ | = 7.7 |
| | | $^{3}J_{H6'-C7'a}$ | = 10.2 |
| | | $^{3}J_{H7'-C5'}$ | = 7.8 |
| | | $^{3}J_{H7'-C3'a}$ | = 7.2 |
| | | $^{3}J_{CH3-C4}$ | = 3.7 |
| | | $^{3}J_{H4-C(CH3)}$ | = 1.8 |

[a] Sample in DMSO-$d_6$ with 1 drop of 1*M* hydrochloric acid added. [b] Proton-carbon coupling in Hz.

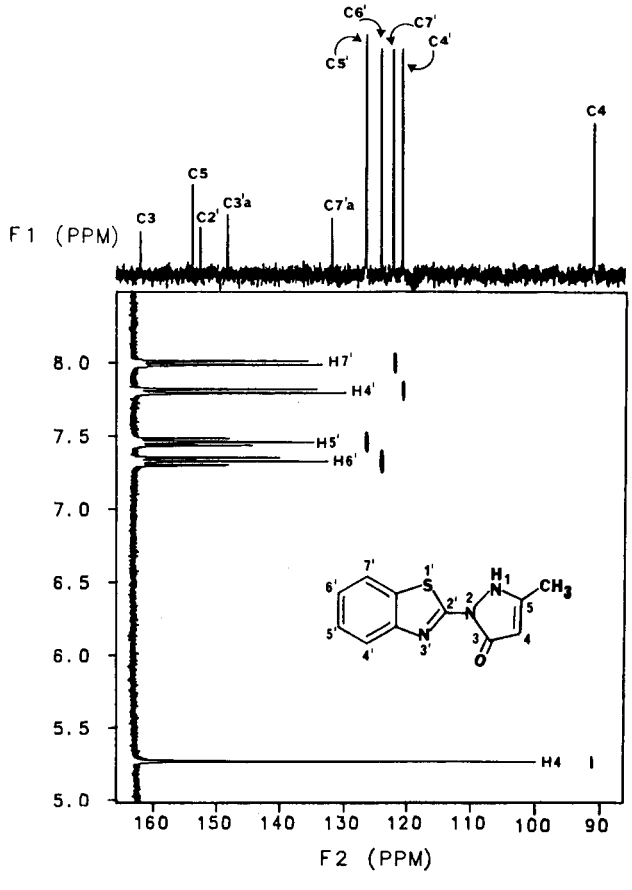



Figure II. $^{13}C$-Proton Heteronuclear Correlation Spectrum for 2-(2-Benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**5**).

To clearly establish the spectral assignments on the phenyl ring, the HETCOR experiment was adjusted to highlight smaller long range couplings (*ca.* 10 Hz). Under these conditions only two prominent cross peaks are observed. The cross peaks link the proton due to H-4′ (δ 7.34) with the carbon signal due to C-7a′ (δ 131.66) and the proton signal due to H-5′ (δ 7.47) with the carbon signal due to C-3a′ (δ 148.3).

The HETCOR spectrum for pyrazolone **18** (*ca.* 50 mg of **18** in 0.7 ml of dimethylsulfoxide-$d_6$), the structure we tentatively assigned to the alkylation product of **17** with **16**, is shown in Figure III. In addition to the resonance correlations in the benzo portion of the molecule, the correlation of C-4′ with C-4′-H is also observed. Substantial literature data is available on the $^{13}C$ nmr of benzothiazoles (including 2-aminobenzothiazoles) [13,14] and pyrazolones and their hydroxypyrazole tautomers [15-19]. In spite of this data, we were unable to definitively assign the structure of our alkylation product on the basis of the nmr studies, even with spectra of authentic **5** for comparison.

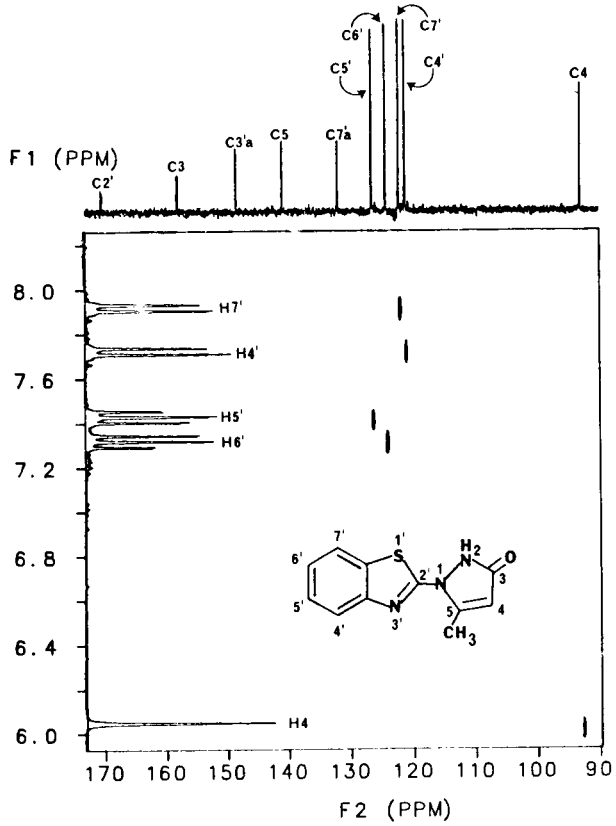



Figure III. $^{13}C$-Proton Heteronuclear Correlation Spectrum for 1-(2-Benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**18**).

High resolution mass spectral data allowed us to assign the structure of the product from the alkylation of **17** with **16**. We observed a fragment of m/e 203 (relative intensity 20%) which represented a loss of 28 mass units from the parent and base peak of m/e 231. This loss was CO and not $N_2$, which confirmed **18** as our alkylation product. Compound **19** should suffer loss of $N_2$ and not CO in the mass spectrometer, while **18** would predictably undergo decarbonylation.

1-Substituted 3-hydroxypyrazoles have been extensively studied and shown to predominantly exist in the hydroxypyrazole form [20-23]. We feel that **18** exists in the hydroxypyrazole form in the solid state, since the infrared spectrum (potassium bromide) showed a lack of carbonyl absorption. The carbonyl band for 1-substituted 3-pyrazolones occurs as low as 1580 $cm^{-1}$ [23]. Although we observed bands for **18** at 1590 and 1570 $cm^{-1}$, they were sharp and of medium intensity, and we ascribed them to C=N stretching. The $^1H$ nmr spectrum for **18** also suggests a strong contribution from the hydroxypyrazole tautomer in dimethylsulfoxide-$d_6$ solution. The pyrazole C4-H proton in **18** (Figure III) appears at δ 6.05, while the corresponding field position for the C4-H proton of **5** is δ 5.30. The relatively deshielded position of C4-H in **18** would coincide with the aromatic hydroxypyrazole structure.

In summary, single crystal x-ray crystallography confirmed pyrazolone **5** as the cyclization product of **2**, which was misassigned as triazepinobenzothiazolone **4** by both Kulkarni and Deshpande [1] and Dehuri, *et al.* [2]. Four additional homologous compounds reported by Kulkarni and Deshpande [1] are also undoubtedly misassigned, as are two additional compounds related to **4** which were reported by Dehuri, *et al.* [2]. The structure of pyrazolone **18**, the reaction product of **16** with the anion of **17**, was established by high resolution mass spectrometry.

## EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded with a Perkin-Elmer Model 710B spectrophotometer and mass spectra with a Finnigan Model 4500 (electron impact and chemical ionization) mass spectrometer. Combustion analyses for C, H and N were performed by Merrell Dow Analytical Department, Cincinnati, Ohio.

NMR Parameters.

All nmr spectra recorded on the Varian XL-300 spectrometer utilized standard Varian software (version 6.1D). The $^1H$ nmr spectra were acquired using 30,000 data points over a 4000 Hz spectral width (digital resolution 0.26 Hz/pt). Sixteen scans were averaged using 14° rf pulses and a relaxation delay of 10 seconds. The $^{13}C$ nmr spectra were acquired using 60° rf pulses with WALTZ [24] proton decoupling ($\gamma H2/2\pi$ = 2165 Hz). A total of 30,000 points were used to define a 16,500 Hz spectral width (digital resolution = 1.1 Hz), and 1024 scans were acquired. For the fully coupled carbon spectrum with NOE, full proton decoupling was utilized during a 5 second preparation period, allowing the NOE to build. The decoupler was then gated off during the acquisition period.

Normal heteronuclear correlation (HETCOR) experiments were carried out using a spectral width of 6000 Hz in the first domain (F2, carbon, *ca.* δ 100 - 180) and 2000 Hz in the second domain (F1, proton, *ca.* δ 4 - 9), a 1024 x 512 data matrix, 128 time increments, and 128 transients per FID. Long range heteronuclear correlation experiments used the same spectral parameters as above with the exception that J1XH was set to the expected size of the coupling constant (*ca.* 10 Hz). J1HX is used in-

ternally in the Varian HETCOR sequence to set optimum delays to highlight the coupling interactions of interest.

Crystal Data.

$C_{11}H_9N_3OS$, monoclinic space group $P2_1/c$, a = 6.035 (2), b = 18.486 (15), c = 9.073 (4), $\beta$ = 102.83 (2); U = 986.97 A'^3, Z = 4, $D_c$ = 1.556 gm/cc³. There were 2011 reflections (out of 2264 unique) with $F \geq 3$ (I) collected with a Picker goniostat using graphite-monochromatized molybdenum radiation. The diffractometer, data-handling techniques, and general procedure have been described previously [25]. The structure was solved by direct methods and refined by full-matrix least squares. Final residuals are R = 0.0349 and $R_w$ = 0.0406. Atomic coordinates for this work are available on request from the Director of Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EN, England. Any request should be accompanied by the full literature citation of this article. Complete crystallographic details are also available in microfiche form from the Chemistry Library, Indiana University, Bloomington, Indiana 47405. Request MSC Report No. 86707.

2-Hydrazinobenzothiazole (**1**).

A solution of 8.48 g (50.0 mmoles) of 2-chlorobenzothiazole and 8.00 g (0.160 mole) of hydrazine monohydrate in 40 ml of ethanol was heated at reflux for 40 minutes. A precipitate was present at the end of the reflux period. The mixture was cooled and the solid was collected, washed with water and air-dried to give 8.26 g (100%) of **1**, mp 196-199°. Recrystallization from ethanol gave **1** as white needles, mp 197-199° [lit (26) mp 199.5°]; ir (Nujol): 3300, 3190, and 3120 ($NHNH_2$), 1645 (C=N) $cm^{-1}$; nmr (dimethylsulfoxide-$d_6$): $\delta$ 9.00 (s, 1H, NH), 7.67 (dd, 1H, aromatic), 7.22 (dd, 1H, aromatic), 6.99 (ddd, 1H, aromatic), 5:02 (s, 2H, $NH_2$); ms: (70 eV, electron impact) m/e 165 (molecular ion).

Ethyl 2-Oxobutyrate (2-Benzothiazolyl)hydrazone (**2**).

A mixture of 1.32 g (7.99 mmoles) of 2-hydrazinobenzothiazole (**1**), 1.04 g (8.00 mmoles) of ethyl acetoacetate and 20 ml of ethanol was heated in a waterbath at 60° for 30 minutes. The mixture was cooled and the precipitate was collected to give 1.10 g (50%) of **2**, mp 105-106°: mp 109-110° (ethanol); ir (Nujol): 1725 (ester C=O), 1600 (C=N) $cm^{-1}$; nmr (deuteriochloroform): $\delta$ 7.66 (d, 1H, aromatic), 7.50 (d, 1H, aromatic), 7.33 (dd, 1H, aromatic), 7.15 (dd, 1H, aromatic), 4.21 (q, J = 7 Hz, 2H, $CH_2$), 3.40 (s, 1H, NH), 2.01 (s, 3H, $CH_3C$=N), 1.30 (t, J = 7 Hz, 3H, $CH_2CH_3$); ms: (100 eV, chemical ionization, methane) 278 ($M^+ + 1$), 306 ($M^+ + 29$), 318 ($M^+ + 41$).

*Anal.* Calcd. for $C_{12}H_{13}N_3O_2S$: C, 56.31; H, 5.45; N, 15.16. Found: C, 56.21; H, 5.56; N, 15.26.

2-(2-Benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**5**).

A mixture of 1.66 g (5.99 mmoles) of hydrazone **2**, 0.48 g (12.0 mmoles) of sodium hydroxide and 50 ml of 50% aqueous ethanol was heated at reflux for 4 hours. The mixture was acidified with hydrochloric acid and the precipitate was collected, washed with water and dried to give 1.27 g (92%) of **5**, mp 216° (ethanol); ir (Nujol): 3250-2100 (NH), 1645 (C=O) $cm^{-1}$; nmr (see Figure II and Tables I and II); ms: (70 eV, electron impact) m/e 231 (molecular ion).

*Anal.* Calcd. for $C_{11}H_9N_3OS$: C, 57.14; H, 3.92; N, 18.18. Found: C, 57.02; H, 4.12; N, 18.33.

For single crystal x-ray crystallography, a concentrated solution of **5** in ethyl acetate was allowed to crystallize slowly to give long, clear prisms with flat faces.

1-(2-Benzothiazolyl)-1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**18**).

To a mixture of 1.68 g (70.0 mmoles) of dry sodium hydride and 50 ml of dimethylformamide was added 4.91 g (50.0 mmoles) of **17** (Pfaltz and Bauer, Inc.). After 10 minutes of stirring, 8.48 g (50.0 mmoles) of 2-chlorobenzothiazole (**16**) (Aldrich) was added and the mixture was heated at 120° for 15 hours. After cooling, the mixture was diluted with water and a gum precipitated. The supernatant was decanted and the gum was triturated with water. The resulting solid was collected and dried to give 2.60 g (22%) of **18**, mp 149-150° (ethanol); ir (potassium bromide): 3190, 3145, 3110, 1590, 1570 $cm^{-1}$; nmr (see Figure III); ms: (70 eV) m/e 231 (molecular ion).

*Anal.* Calcd. for $C_{11}H_9N_3OS$: C, 57.14; H, 3.92; N, 18.18. Found: C, 56.94; H, 3.96; N, 18.42.

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[5] The work of Alaka, *et al.* [4] was simultaneously reinvestigated by Singh, *et al.* [6], who employed an alternate synthesis of pyrazolothiazole **8** ( R = $CH_3$) which was different from ours.

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[10] The name proffered by the supplier (Pfaltz and Bauer, Inc.) of this material was 3-methyl-2-pyrazoline-5-one. However, the nmr (dimethylsulfoxide-$d_6$) spectrum which we recorded for this material displayed a singlet (1H) at $\delta$ 5.20 and a singlet (3H) at $\delta$ 2.10, which suggested that 1,2-dihydro-5-methyl-3*H*-pyrazol-3-one (**17**) or its hydroxyimino tautomer was the correct structure, at least in dimethylsulfoxide solution.

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