(M^+, 100%), 217 (14), 161 (60), 117 (75).

Anal. Calcd for $C_{29}H_{30}N_2O_3$: C, 76.63; H, 6.65; N, 6.16. Found: C, 76.87; H, 6.58; N, 5.99.

(b) With *C,N*-Diphenylnitrone (18b). A solution of 1 (243 mg, 1.0 mmol) and *C,N*-diphenylnitrone (**18b**) (200 mg, 1.02 mmol) in toluene (2 mL) was refluxed for 9 h. Similar workup gave the adduct **19b** (320 mg, 72%): mp 160–162 °C (dichloromethane–*n*-hexane); IR (KBr) 1682 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (9 H, s), 2.87 (1 H, t, J = 6.6 Hz; H-3a), 4.27 (1 H, br s; H-3), 4.59 (1 H, d, J = 6.6 Hz; H-9a), 5.25 (2 H, s; H-1 and H-7), 7.0–7.5 (14 H, m; ArH).

Anal. Calcd for $C_{28}H_{28}N_2O_3$: C, 76.34; H, 6.41; N, 6.36. Found: C, 76.38; H, 6.70; N, 6.16.

Cyclizations and Rearrangements of Propynylsulfamides: X-ray Crystal Structure of 2,3-Dihydro-2-acetyl-3,3-dimethyl-4-[(1*E*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadiazole 1,1-Dioxide

Ronald J. Baker, Sai-keung Chiu, Cheryl Klein, Jack W. Timberlake,* and Louis M. Trefonas

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122

Richard Majestē

Department of Chemistry, Southern University in New Orleans, New Orleans, Louisiana 70126

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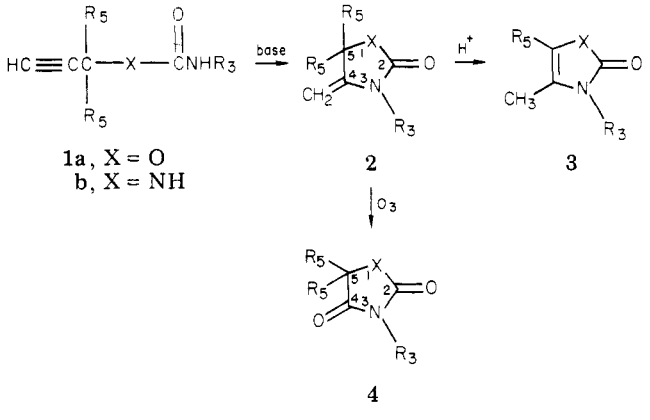
The base-catalyzed cyclization of 2-propynylsulfamides and the subsequent amino-Claisen rearrangement of one of these products are described. The X-ray structure of 2,3-dihydro-2-acetyl-3,3-dimethyl-4-[(1*E*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadiazole 1,1-dioxide has been determined.

Base-catalyzed cyclizations of 2-propynyl carbamates (**1a**) and 2-propynylureas (**1b**) produce five-membered rings (**2a,b**) with exocyclic double bonds. Acid-catalyzed



1a, X = O
b, X = NH

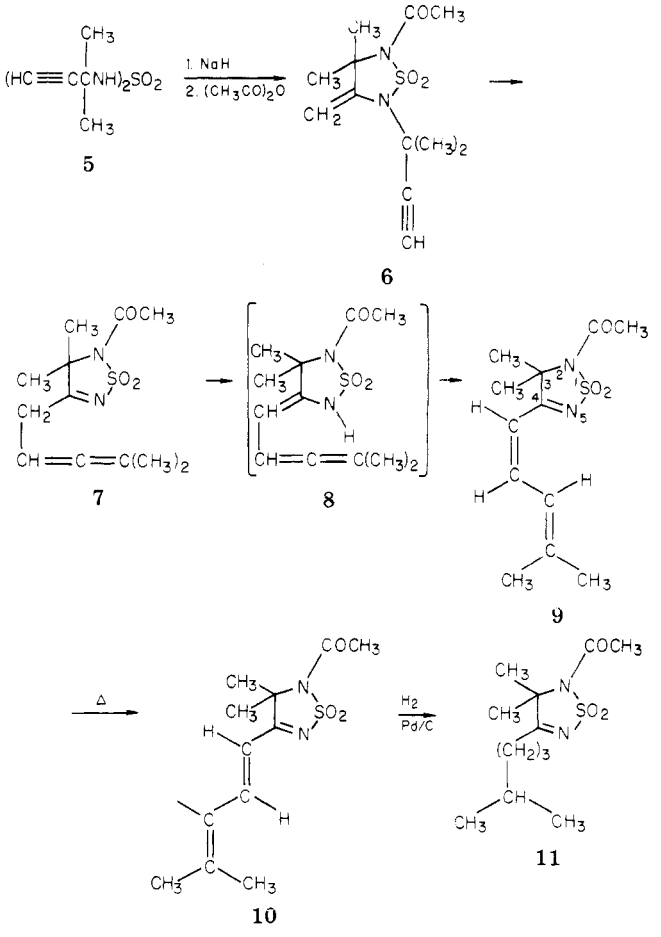
2 3

4

tautomerization to the endocyclic isomer **3** can occur if one or both groups at the 5-position are hydrogen.[2,3] Recently we reported the isolation of 5,5-disubstituted imidazolidinones (**2b**) and oxazolidines (**2a**)[4] where isomerization is blocked. Ozonolysis of these derivatives gave 2,4-imidazolidinediones (**4b**) and 2,4-oxazolidinediones (**4a**). These compounds are medicinally useful as anticonvulsants,[5,6] and this method appears to be the best way of introducing tertiary alkyl (hydrophobic) groups into the 3-position of the ring **4**.

This report deals with the similar cyclization of *N,N'*-bis(1,1-dimethyl-2-propynyl)sulfamide, the subsequent rearrangement of the cyclized product, **6**, and the X-ray structure determination of the final rearranged product, **10**.

Treatment of sulfamide **5** with sodium hydride and acetic anhydride, depending on the reaction conditions, led to the isolation of three products: 2-acetyl-3,3-dimethyl-4-methylene-5-(1,1-dimethyl-2-propynyl)-1,2,5-thiadiazolidine 1,1-dioxide (**6**), 2,3-dihydro-2-acetyl-3,3-



5 6 7 8 9 10 11

dimethyl-4-[(1*Z*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadia-

(1) N. Schachat and J. J. Bagnell, *J. Org. Chem.*, **28**, 991 (1963).
(2) Y. Yura, *Chem. Pharm. Bull.*, **10**, 1087 (1962).
(3) P. J. Stoffel and W. D. Dixon, *J. Org. Chem.*, **29**, 978 (1964).
(4) S. K. Chiu, M. Dube, L. Keifer, S. Szilagyi, and J. W. Timberlake, *J. Org. Chem.*, **43**, 61 (1978).
(5) J. A. Vida, Ed., "Anticonvulsants", Academic Press, New York, 1977.
(6) S. K. Chiu, L. Keifer, and J. W. Timberlake, *J. Med. Chem.*, **22**, 746 (1979).

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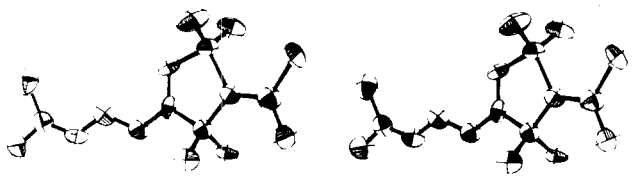
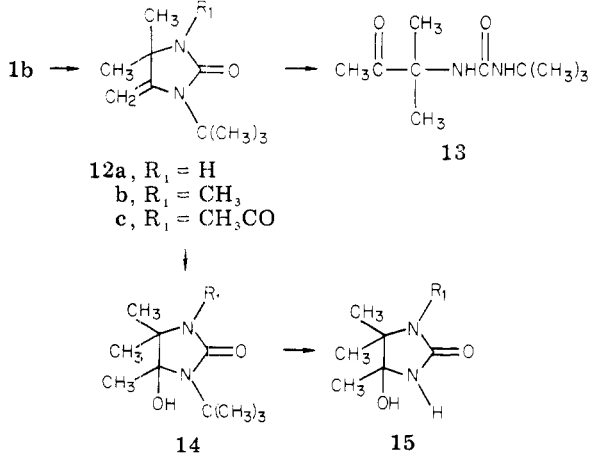


Figure 1. ORTEP drawing of **10**.

zole 1,1-dioxide (**9**), and 2,3-dihydro-2-acetyl-3,3-dimethyl-4-[(1*E*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadiazole 1,1-dioxide (**10**). The structure of the trans product **10** was established by single-crystal X-ray methods as described below. Both **9** and **10** have nearly identical mass spectra and similar ^{13}C NMR spectra (except that the cis CH=CH is characteristically upfield from the trans)[7] but different melting points and ^1H NMR and IR spectra. The 200-MHz ^1H NMR of *cis*-**9** shows a clear ABX pattern for the olefinic protons while that of *trans*-**10** displays an ABC pattern. Both **9** and **10** are catalytically hydrogenated to a common product identified as 2,3-dihydro-2-acetyl-3,3-dimethyl-4-(4-methylpentyl)-1,2,5-thiadiazole 1,1-dioxide (**11**). Control experiments show that **9** and **10** are not isomerized in the presence of Pd/C alone.

Compound **9** was thermally isomerized to **10** in refluxing hexane or chloroform, and when the cyclization of **5** was conducted at elevated temperature, only **10** was produced. It thus appears that the rearrangement of **6** kinetically favors **9**, with the thermodynamically favored product being **10**. In an attempt to obtain some evidence for the rearrangement as illustrated, a sample of **6** was heated slowly to 60 °C in the NMR probe. Decoupling the terminal allenic methyl signals shows a clear triplet at 5.10 ppm for the single allenic proton. An IR band at 1975 cm^{-1} helps confirm **7** as the likely [3,3] sigmatropic intermediate from the amino-Claisen rearrangement of **6**.[8-10] No experimental evidence for the tautomerization of **7** to **8** and the subsequent 1,5 hydrogen shift from **8** to **9** has been obtained.

It is interesting to contrast this sequence of reactions with the cyclization of **5** in the absence of acetic anhydride. Here the cyclized product without the *N*-acetyl group undergoes hydrolysis to the monoketo sulfamide [CH_3CO $C(CH_3)_2NHSO_2NHC(CH_3)_2C{\equiv}CH$] in the aqueous work-up.[4] We have no explanation for the N-1 substituent effect, but a similar result is observed for cyclized 2,4-imidazolidinones; for example, for compound **12a** facile



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(10) J. Corbier and P. Cresson, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **270**, 2077 (1977).

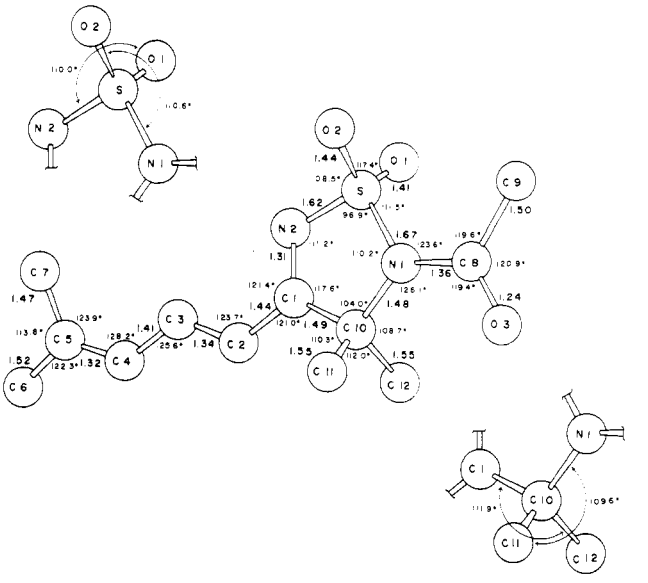

Figure 2. Schematic drawing of **10** with distances and angles indicated.

hydrolysis leads to keto urea **13**. When **1b** is cyclized in the presence of methyl iodide or acetic anhydride, **12b** and **12c** are respectively obtained. Aqueous hydrolysis of **12b** and **12c** gives 4-hydroxyimidazolidinones **14b** and **14c**. Under more vigorous conditions **12b** gives only the "de-*tert*-butylated" product **15b**.

The structure of **10** was confirmed by X-ray crystallographic analysis. The least-squares coordinates, anisotropic temperature factors for nonhydrogen atoms, and isotropic temperature factors for hydrogens together with the estimated standard deviation (esd) for each parameter are summarized in the table available as supplementary material. Figure 1 shows an ORTEP stereodrawing of the molecule while Figure 2 gives a schematic drawing with the various bond distances and angles indicated.

A least-squares fit defining the plane through the five-membered ring (S, N-1, N-2, C-1, C-10) and the sp^2-hybridized C-8 and O-3 is planar within an esd value of ±0.009 Å. A second plane in this molecule was found which consisted of the conjugated double bond system in the tail end of the molecule. A least-squares fit of these four atoms (C-2, C-3, C-4, C-5) gave a plane within an esd of 0.015 Å. These two planes can be readily seen from the ORTEP stereoplot in Figure 1. The angle between them is 21.5°.

Considering the heterocycle first, all of the bond distances and bond angles are chemically reasonable. The S–N bond distances (1.67 and 1.62 Å) compare favorably with those found for 2-thia-1,3,5-triaza-7-phosphaadamantane 2,2-dioxide.[11] The S–O (1.41 and 1.44 Å) and N–C (1.48 Å) bond distances were also in good agreement with the analogous bond distances in the adamantane molecule. The NSN bond angle of 96.9° compares favorably with the NSN angle in 3,4-diphenyl-1,2,5-thiadiazole.[12] The difference between the N1–C10–C1 angle of 104.0° and N2–C1–C10 angle of 117.6° reflects the fact that C-1 is an sp^2-hydridized carbon atom whereas C-10 is an sp^3-hybridized carbon atom.

The average carbon to methyl bond distance is 1.52 ± 0.017 Å which compares favorably with accepted C–C bond distances.[13] The C2–C3 and C4–C5 bond lengths are also

(11) J. R. Delerno, R. J. Majesté, and L. M. Trefonas, *J. Heterocycl. Chem.*, **13**, 757 (1976).
(12) M. Mellini and S. Merlino, *Acta Crystallogr., Sect. B*, **32**, 1074–8 (1976).

in good agreement with accepted olefinic bond distances.[13] However, the C1–C2, C3–C4, and N1–C8 bond distances are shortened due to sp^2 hydridization and, therefore, π-electron delocalization and hence assume double bond character. The molecule has a trans configuration around the C2–C3 bond.

Experimental Section

Crystallography. A single platelike crystal of 2,3-dihydro-2-acetyl-3,3-dimethyl-4-[(1*E*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadiazole 1,1-dioxide having its longest dimension no greater than 0.3 mm was selected for analysis. Extinctions of k odd for ($0k0$) and l odd for ($h0l$) uniquely characterized the space group as $P2_1/c$. Lattice constants were determined by a least-squares fit of 31 carefully measured reflections at high 2θ values under fine conditions (2° takeoff angle and a 0.05° slit). The resultant lattice constants and their estimated standard deviations together with other pertinent cell data are as follows: a = 12.189 (2) Å, b = 7.777 (1) Å, c = 14.695 (2) Å, β = 94.04 (2)°, V = 1390.7 Å^3, mol wt 270.1.

Three-dimensional intensity data were collected on a GE XRD-490 by the stationary-counter, stationary-crystal method using balanced nickel and cobalt filters. A total of 2338 independent reflections were measured (to a 2θ maximum of 120°), and of this total 982 were considered statistically significant. After correction for $K\alpha_1$–$K\alpha_2$ splitting, absorption as a function of ϕ, decay, and Lorentz–polarization effects, the intensities were reduced to structure amplitudes in the usual manner.

The structure was solved by direct methods using the program FAZC.[14] Normalized structure factor magnitudes, scaled with a K curve,[15] led to an E map which contained 7 of the 18 nonhydrogen atoms. Subsequent cycles of Fourier synthesis alternating with least-squares refinement led to the 18 nonhydrogen atom positions with a value of R = 0.124.[16] Hydrogen positions were located on a subsequent difference map, and the structure was refined, isotropically, to a value of R = 0.081. After conversion of the anisotropic temperature factors to unit weights and an anomalous dispersion correction for the sulfur, the structure was refined to its final value of R = 0.077.

***N,N'*-Bis(1,1-dimethyl-2-propynyl)sulfamide (5)** was prepared by the method of Engle and Bishop in 55% yield: mp 121.5–123 °C (lit.[18] mp 121.8–123.4 °C).

2-Acetyl-3,3-dimethyl-4-methylene-5-(1,1-dimethyl-2-propynyl)-1,2,5-thiadiazolidine 1,1-Dioxide (6). A solution of 5.0 g (21.9 mmol) of sulfamide **5** and 1.25 g (2.6 mmol) of sodium hydride dispersion in 60 mL of THF was heated at reflux for 2 h. After the mixture was cooled to room temperature, acetic anhydride (2.5 g, 26.5 mmol) was added dropwise to the mixture which was stirred for 2 h. Water (30 mL) was added, and THF was removed in vacuo. The residue was extracted with two 100-mL portions of ether. The ether extracts were dried ($MgSO_4$) and concentrated, and the residual reddish brown oil was washed with three 50-mL portions of pentane. The pentane washings were cooled in a dry ice/acetone bath, and the yellow solid which formed was recombined with the red oil after filtration. The filtrate was cooled again in the dry ice/acetone bath, and 1.2 g (20%) of **6** as white crystals was obtained: mp 45–46 °C; NMR ($CDCl_3$) δ 1.72 (s, 6 H), 1.92 (s, 6 H), 2.48 (s, 3 H), 2.55 (s, 1 H), 4.53 (d, 1 H, J = 4 Hz), 4.99 (d, 1 H, J = 4 Hz); IR ($CHCl_3$) 3300, 1700, 1640 cm^{-1}. This compound was somewhat unstable and was not further characterized.

2,3-Dihydro-2-acetyl-3,3-dimethyl-4-[(1*Z*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadiazole 1,1-Dioxide (9). A solution of 1.0 g (3.7 mmol) of **6** in 50 mL of $CHCl_3$ was heated to reflux for 2 h to give the intermediate compound 2,3-dihydro-2-acetyl-3,3-dimethyl-4-(4-methyl-2,3-pentadienyl)-1,2,5-thiadiazole 1,1-dioxide (**7**): IR (warm $CHCl_3$) 1975, 1700, 1620 cm^{-1}; NMR (hot CCl_4) δ 1.18 (s, 9 H), 1.22 (s, 3 H), 2.43 (s, 3 H), 3.20 (d, 2 H, J = 7 Hz), 5.10 (m, 1 H, J = 3 Hz). The multiplet at δ 5.10 changed to a triplet (J = 7 Hz) when the center of the two signals at δ 1.18 and 1.22 was irradiated. The doublet at δ 3.20 and the two signals at δ 1.18 and 1.22 both collapsed to two broad singlets when the multiplet at δ 5.10 was irradiated.

The reaction mixture was allowed to stand at room temperature for 2 days, and $CHCl_3$ was removed in vacuo. The white solid obtained was recrystallized from pentane–CH_2Cl_2 to yield 0.87 g (87%) of 2,3-dihydro-2-acetyl-3,3-dimethyl-4-[(1*Z*)-4-methyl-1,3-pentadienyl]-1,2,5-thiadiazole 1,1-dioxide (**9**): mp 125.5–126.5 °C; 200-MHz NMR ($CDCl_3$) δ 1.72 (s, 6 H), 1.98 (d, 3 H, J = 0.5 Hz), 2.03 (d, 3 H, J = 0.5 Hz), 2.56 (s, 3 H), 5.81 (d, 1 H, J = 10.8 Hz), 7.28 (m, 1 H), 7.47 (br d, 1 H, J = 12.2 Hz); IR ($CHCl_3$) 1700, 1620, 1550 cm^{-1}; mass spectrum m/e 270; ^{13}C NMR ($CDCl_3$ relative to Me_4Si; see X-ray structure for numbering) δ 18.9 (CH_3 trans to H), 23.1 (C-11, 12), 23.9 (C-9), 27.6 (CH_3 cis to H), 72.1 (C-10), 109.4 (C-3), 124.2 (C-2), 146.5 (C-4), 155.5 (C-5), 166.9 (C-1), 179.7 (C-8).

Anal. Calcd for $C_{12}H_{18}N_2O_3S$: C, 53.37; H, 6.57; N, 10.46. Found: C, 52.96; H, 6.28; N, 10.27.

2,3-Dihydro-2-acetyl-3,3-dimethyl-4-[(1*E*)-4-methyl-1,3-pentadienyl)-1,2,5-thiadiazole 1,1-Dioxide (10). The red oil remaining from the preparation of **6** was chromatographed on silica gel with benzene. Removal of the benzene and recrystallization of the residual solid from pentane–CH_2Cl_2 gave 1.1 g (18.6%) of **10**: mp 145.5–146.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 6 H), 2.00 (br s, 6 H), 2.52 (s, 3 H), 6.05 (d, 1 H, J = 14 Hz), 6.18 (br s, 1 H, J = 12 Hz), 8.00 (d, 0.5 H, J = 14 Hz), 8.18 (d, 0.5 H, J = 14 Hz); IR ($CHCl_3$) 1700, 1640, 1605, 1550 cm^{-1}; mass spectrum m/e 270; ^{13}C NMR ($CDCl_3$ relative to Me_4Si; see X-ray structure for numbering) δ 19.5 (C-7), 22.8 (C-11, 12), 23.7 (C-9), 27.0 (C-6), 71.0 (C-10), 113.8 (C-3), 124.8 (C-2), 145.6 (C-4), 153.8 (C-5), 166.6 (C-1), 181.2 (C-8).

Anal. Calcd for $C_{12}H_{18}N_2O_3S$: C, 53.37; H, 6.57; N, 10.46. Found: C, 53.31; H, 6.71; N, 10.36.

A mixture of 5.0 g (21.9 mmol) of sulfamide **5**, 1.25 g (~26.0 mmol) of NaH dispersion, and 60 mL of THF was heated at reflux for 2 h. After the mixture was cooled to room temperature, 2.5 g (26.5 mmol) of acetic anhydride was added, and the mixture was heated to reflux again for 2 h. Water (30 mL) was added with stirring at room temperature. The THF was removed in vacuo, and the residue was extracted with two 100-mL portions of ether. The ether was dried ($MgSO_4$) and concentrated to a red oil which was chromatographed on silica gel with benzene to give a yellow solid. The solid was recrystallized from pentane–CH_2Cl_2 to yield 2.32 g (39.2%) of pure **10**.

A solution of 0.3 g (1.11 mmol) of **9** in 10 mL of hexane was heated to reflux for 3 h. After the mixture was cooled to room temperature and the hexane removed, the residue was chromatographed on silica gel with benzene to yield first a small amount of **9** and then the major product, **10**. The major product was recrystallized from pentane–CH_2Cl_2 to yield 0.18 g (60%) of **10**.

2,3-Dihydro-2-acetyl-3,3-dimethyl-4-(4-methylpentyl)-1,2,5-thiadiazole 1,1-Dioxide (11). A mixture of 1.0 g (3.7 mmol) of **10**, 0.75 g of 10% Pd/C, and 25 mL of ethanol was hydrogenated at room temperature for 4 h at 50 psi of H_2. The solvent was removed after filtration, and the residue was recrystallized from pentane to give 0.86 g (85%) of **11**: mp 68–69 °C; IR ($CHCl_3$) 1700, 1620, 1460, 1340, 1285, 1180 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (d, 6 H, J = 6 Hz), 1.68 (s, 6 H), 2.50 (s, 3 H), the other 7 H gave two sets of multiplets between δ 1.00 and 2.00 and between δ 2.25 and 2.80; mass spectrum m/e 274.

Anal. Calcd for $C_{12}H_{22}N_2O_3S$: C, 52.53; H, 8.08; N, 10.21. Found: C, 52.39; H, 8.24; N, 10.03.

Compound **9** (1.0 g, 3.7 mmol), 0.75 g of 10% Pd/C, and 25 mL of ethanol were stirred at room temperature for 4 h. A small portion of the solution was filtered and concentrated. The NMR spectrum indicated no change. The mixture was then hydrogenated as described above to yield 0.74 g (75%) of **11** as shown by a nondepressed mixture melting point and IR and NMR spectra.

(13) *Chem. Soc., Spec. Publ.*, **No.** 18, S165 (1965).

(14) J. N. Brown, L. M. Trefonas, and R. J. Majesté, part of the crystallographic computer package for the PDP-10 system (1968).

(15) J. Karle, H. Haptman, and C. L. Christ, *Acta Crystallogr.*, 11, 757 (1958).

(16) The conventional reliability index, $R = \sum w||kF_o| - |F_c||/\sum w|kF_o|$, is cited throughout the paper.

(17) The atomic scattering factors used were taken from the following sources: "International Tables for X-Ray Crystallography", 3rd ed., Kynoch Press, Birmingham, England, 1962, pp 202–3; D. Cromer and J. Waber, *Acta Crystallogr.*, 18, 104 (1965) (oxygen, nitrogen, carbon, sulfur).

(18) P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.*, **97**, 6754 (1975).

1,5,5-Trimethyl-3-*tert*-butyl-4-methylene-2-imidazolidinone (12b). To 0.3 g (~6.0 mmol) of NaH dispersion in 50 mL of THF was added 1.0 g (5.5 mmol) of *N*-*tert*-butyl-*N'*-(1,1-dimethyl-2-propynyl)urea.[4] The solution was heated to reflux for 2 h and cooled to room temperature, and 0.8 g (5.5 mmol) of iodomethane was added. After the mixture was stirred for 1 h, 50 mL of water was added cautiously, and the THF was removed in vacuo. The residue was distilled to give a liquid which solidified on standing. After recrystallization from $CHCl_3$–hexane, 0.65 g (60%) of **12b** was obtained: bp 137 °C (35 mm); mp 40–41 °C; NMR ($CDCl_3$) δ 1.25 (s, 6 H), 1.57 (s, 9 H), 2.72 (s, 3 H), 4.04 (d, 1 H, J = 3 Hz), 4.32 (d, 1 H, J = 3 Hz); mass spectrum m/e 196. The compound was hygroscopic and was analyzed as the hydantoin derivative, mp 81–82 °C, obtained by ozonolysis of **12b**.

Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.49; H, 9.04; N, 13.95.

1,4,5,5-Tetramethyl-3-*tert*-butyl-4-hydroxy-2-imidazolidinone (14b). The solid imidazolidinone **12b** (1.0 g, 5.1 mmol) was allowed to stand in an open 50-mL Erlenmeyer flask for 3 days, during which it liquefied and then resolidified. The solid was recrystallized from hexane–$CHCl_3$ to yield 0.8 g (73%) of **14b**: mp 86–87 °C; NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.17 (s, 3 H), 1.55 (s, 12 H), 2.35 (br s, 1 H), 2.63 (s, 3 H); IR ($CHCl_3$) 3400, 1705 cm^{-1}.

Anal. Calcd for $C_{11}H_{22}N_2O_2$: C, 61.65; H, 10.35; N, 13.07. Found: C, 61.71; H, 10.44; N, 12.88.

1-Acetyl-3-*tert*-butyl-4,5,5-trimethyl-4-hydroxy-2-imidazolidinone (14c). The imidazolidinone **12c** (3.0 g, 13.2 mmol) was allowed to stand in an open Erlenmeyer flask for 2 weeks. The solid obtained was recrystallized from hexane–$CHCl_3$ to yield 2.9 g (89%) of **14c**: mp 109.5–110.5 °C; NMR ($CDCl_3$) δ 1.40 (s, 3 H), 1.45 (s, 3 H), 1.55 (s, 3 H), 1.58 (s, 9 H), 2.30 (br s, 1 H), 1.49 (s, 3 H); IR ($CHCl_3$) 3418, 1725, 1686 cm^{-1}.

Anal. Calcd for $C_{12}H_{22}N_2O_3$: C, 59.48; H, 9.15; N, 11.56. Found: C, 59.49; H, 9.14; N, 11.40.

1,4,4,5-Tetramethyl-4-hydroxy-2-imidazolidinone (15b). Imidazolidinone **14b** (1.0 g, 4.67 mmol) was heated at 40 °C for 2 days in a solution of 10 mL of concentrated HCl, 95 mL of H_2O, and 100 mL of THF. The mixture was cooled to room temperature, neutralized with $NaHCO_3$, and extracted with three 75-mL portions of $CHCl_3$. The $CHCl_3$ extracts were dried ($MgSO_4$) and concentrated to a yellow oil. After chromatography on silica gel with dichloromethane, a white solid was obtained. This solid was recrystallized from pentane to give 0.4 g (54%) of **15b**: mp 93–94 °C; NMR ($CDCl_3$) δ 1.32 (s, 6 H), 2.15 (br s, 1 H), 2.30 (s, 3 H), 2.75 (br s, 1 H), 2.89 (s, 3 H); IR ($CHCl_3$) 3325, 1720, 1610 cm^{-1}.

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.34; H, 9.01; N, 17.75. Found: C, 53.15; H, 8.92; N, 17.71.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Louisiana Heart Association for partial support of this research.

Registry No. 1b (R_3 = *t*-Bu, R_5 = Me), 59863-61-5; **5**, 57542-27-5; **6**, 72331-02-3; **7**, 72331-03-4; **9**, 72331-04-5; **10**, 72331-05-6; **11**, 72331-06-7; **12b**, 62989-65-1; **12b**, hydantoin derivative, 70540-22-6; **12c**, 63989-66-2; **14b**, 72331-07-8; **14c**, 72331-08-9; **15b**, 72331-09-0.

Supplementary Material Available: Final atomic parameters and anisotropic thermal parameters are available (1 page). Ordering information is given on any current masthead page.

1,3-Diazepinones. 1. Synthesis of 5-Hydroxyperhydro-1,3-diazepin-2-one

Victor E. Marquez,* Paul S. Liu, James A. Kelley, and John S. Driscoll

Drug Design and Chemistry Section, Laboratory of Medicinal Chemistry and Biology, Developmental Therapeutics Program, National Cancer Institute, National Institutes of Health, Bethesda, Maryland 20205

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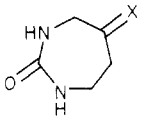
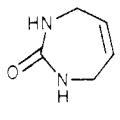
The synthesis of 5-hydroxyperhydro-1,3-diazepin-2-one (**3**) is accomplished by two different routes. The first route involves the reduction of the precursor ketone **2**, which is synthesized in seven steps from levulinic acid (**5**). The second approach makes use of the hydration of the symmetrically unsaturated precursor **4** via the hydroboration–oxidation procedure. This precursor in turn is obtained by direct cyclization of *cis*-1,4-diamino-2-butene (**12**).

As a result of our continued interest in novel cytidine deaminase inhibitors,[1] pyrimidine nucleosides where the base has been both reduced and ring-expanded appeared as interesting target compounds.

The few 1,3-diazepine nucleosides reported in the literature have been prepared by methylene insertion reactions into uridine derivatives followed by ring expansion.[2-4] Our approach, however, consisted in developing independent syntheses of the seven-member-ring heterocycles (**1**–**4**) in order to convert them to the ribofuranosyl analogues via the silyl ether modification of the Hilbert–Johnson reaction.[5-11]



1, X = H_2
2, X = O
3, X = H, OH



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