SUPPLEMENTARY MATERIAL

for
the full article
entitled

**Tetronamides as Latent Acyclic Vinylogous Amides in Formal *Aza*-[3 + 3]
Cycloaddition Reactions with
[α,β]-Unsaturated Iminium Salts. An Unexpected Rearrangement and An
Approach to Synthesis of Substituted Piperidines.**

authored by

Nadiya Sydorenko, Richard P. Hsung*, Ossama Saleh Darwish, Juliet M. Hahn, and Jia Liu

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

X-ray Structural Report For Hydrogenated **16.**

hydrogenated **16**

REFERENCE NUMBER: 04079

CRYSTAL STRUCTURE REPORT

$C_{18}H_{21}NO_2$

Report prepared for:

N. Sydorenko, Prof. R. Hsung

May 07, 2004

Derek Fox

X-Ray Crystallographic Laboratory

Department of Chemistry

University of Minnesota

207 Pleasant St. S.E.

Minneapolis, MN 55455

Data collection

A crystal (approximate dimensions 0.32 x 0.12 x 0.08 mm³) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 33 reflections. The data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 4.89 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Two major sections of frames were collected with 0.30° steps in ω at two different ϕ settings and a detector position of -28° in 2θ . The intensity data were corrected for absorption and decay (SADABS).¹ Final cell constants were calculated from the xyz centroids of 2348 strong reflections from the actual data collection after integration (SAINT).² Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97³ and refined using SHELXL-97.³ The space group *Pbcn* was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0652$ and $wR2 = 0.1689$ (F^2 , all data).

Structure description

The structure is the one suggested.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 160 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1)include Derek Fox as a coauthor or 2)acknowledge Derek Fox, Victor G. Young, Jr., and the X-Ray Crystallographic Laboratory.

¹ An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38 (1995).

² SAINT V6.2, Bruker Analytical X-Ray Systems, Madison, WI (2001).

³ SHELXTL V6.10, Bruker Analytical X-Ray Systems, Madison, WI (2000).

Some equations of interest:

$$R_{\text{int}} = \frac{\sum |F_o|^2 - \langle F_o^2 \rangle}{\sum |F_o|^2}$$

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR2 = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}$$

$$\text{where } w = \frac{q}{\sum^2 (F_o^2) + (a^*P)^2 + b^*P + d + e^*\sin(\theta)}$$

$$\text{GooF} = S = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{(n-p)} \right]^{1/2}$$

Table 1. Crystal data and structure refinement for 04079.

Identification code	04079	
Empirical formula	C ₁₈ H ₂₁ N O ₂	
Formula weight	283.36	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pbcn</i>	
Unit cell dimensions	$a = 18.708(4)$ Å	$\alpha = 90^\circ$
	$b = 9.979(2)$ Å	$\beta = 90^\circ$
	$c = 15.617(3)$ Å	$\gamma = 90^\circ$
Volume	2915.3(11) Å ³	
<i>Z</i>	8	
Density (calculated)	1.291 Mg/m ³	
Absorption coefficient	0.084 mm ⁻¹	
<i>F</i> (000)	1216	
Crystal color, morphology	colorless, needle	
Crystal size	0.32 x 0.12 x 0.08 mm ³	
Theta range for data collection	2.18 to 25.07°	
Index ranges	-22 ≤ <i>h</i> ≤ 22, -11 ≤ <i>k</i> ≤ 10, -16 ≤ <i>l</i> ≤ 18	
Reflections collected	13332	
Independent reflections	2584 [<i>R</i> (int) = 0.0566]	
Observed reflections	1574	
Completeness to theta = 25.07°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000000 and 0.642796	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	2584 / 0 / 191	
Goodness-of-fit on <i>F</i> ²	1.031	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0652, <i>wR</i> 2 = 0.1498	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1018, <i>wR</i> 2 = 0.1689	
Extinction coefficient	0.0025(8)	
Largest diff. peak and hole	0.272 and -0.219 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 04079. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	zU_{eq}	
O1	4126(1)	3039(2)	7981(1)	56(1)
O2	3954(1)	1938(2)	9221(1)	59(1)
N1	3790(1)	560(2)	6327(1)	46(1)
C1	3948(2)	1903(3)	8439(2)	51(1)
C2	3790(2)	832(3)	7857(2)	46(1)
C3	3524(2)	-544(3)	8053(2)	52(1)
C4	3176(2)	-1124(3)	7238(2)	50(1)
C5	3017(2)	-2623(3)	7317(2)	62(1)
C6	3687(2)	-3466(3)	7326(2)	65(1)
C7	4150(2)	-3199(3)	6543(2)	68(1)
C8	4324(2)	-1713(3)	6460(2)	55(1)
C9	3647(2)	-884(3)	6443(2)	46(1)
C10	3891(2)	1285(3)	7049(2)	46(1)
C11	4092(2)	2739(3)	7079(2)	53(1)
C12	4110(2)	984(3)	5507(2)	49(1)
C13	3818(2)	2278(3)	5166(2)	45(1)
C14	4281(2)	3305(3)	4928(2)	48(1)
C15	4030(2)	4488(3)	4578(2)	55(1)
C16	3305(2)	4661(3)	4467(2)	57(1)
C17	2831(2)	3671(3)	4706(2)	58(1)
C18	3086(2)	2477(3)	5052(2)	51(1)

Table 3. Bond lengths [Å] and angles [°] for 04079.

O(1)-C(1)	1.381(3)	C(13)-C(14)	1.393(4)
O(1)-C(11)	1.442(3)	C(13)-C(18)	1.395(4)
O(2)-C(1)	1.222(3)	C(14)-C(15)	1.384(4)
N(1)-C(10)	1.353(3)	C(14)-H(14A)	0.9500
N(1)-C(12)	1.475(3)	C(15)-C(16)	1.378(4)
N(1)-C(9)	1.477(3)	C(15)-H(15A)	0.9500
C(1)-C(2)	1.434(4)	C(16)-C(17)	1.380(4)
C(2)-C(10)	1.353(4)	C(16)-H(16A)	0.9500
C(2)-C(3)	1.491(4)	C(17)-C(18)	1.392(4)
C(3)-C(4)	1.543(4)	C(17)-H(17A)	0.9500
C(3)-H(3A)	0.9900	C(18)-H(18A)	0.9500
C(3)-H(3B)	0.9900	C(1)-O(1)-C(11)	109.0(2)
C(4)-C(5)	1.529(4)	C(10)-N(1)-C(12)	120.9(2)
C(4)-C(9)	1.541(4)	C(10)-N(1)-C(9)	116.4(2)
C(4)-H(4A)	1.0000	C(12)-N(1)-C(9)	117.4(2)
C(5)-C(6)	1.511(4)	O(2)-C(1)-O(1)	119.5(3)
C(5)-H(5A)	0.9900	O(2)-C(1)-C(2)	131.0(3)
C(5)-H(5B)	0.9900	O(1)-C(1)-C(2)	109.5(2)
C(6)-C(7)	1.523(5)	C(10)-C(2)-C(1)	108.2(2)
C(6)-H(6A)	0.9900	C(10)-C(2)-C(3)	123.0(2)
C(6)-H(6B)	0.9900	C(1)-C(2)-C(3)	128.7(3)
C(7)-C(8)	1.523(4)	C(2)-C(3)-C(4)	108.5(2)
C(7)-H(7A)	0.9900	C(2)-C(3)-H(3A)	110.0
C(7)-H(7B)	0.9900	C(4)-C(3)-H(3A)	110.0
C(8)-C(9)	1.513(4)	C(2)-C(3)-H(3B)	110.0
C(8)-H(8A)	0.9900	C(4)-C(3)-H(3B)	110.0
C(8)-H(8B)	0.9900	H(3A)-C(3)-H(3B)	108.4
C(9)-H(9A)	1.0000	C(5)-C(4)-C(9)	109.2(2)
C(10)-C(11)	1.500(4)	C(5)-C(4)-C(3)	112.5(2)
C(11)-H(11A)	0.9900	C(9)-C(4)-C(3)	111.4(2)
C(11)-H(11B)	0.9900	C(5)-C(4)-H(4A)	107.9
C(12)-C(13)	1.500(4)	C(9)-C(4)-H(4A)	107.9
C(12)-H(12A)	0.9900	C(3)-C(4)-H(4A)	107.9
C(12)-H(12B)	0.9900	C(6)-C(5)-C(4)	112.6(3)

C(6)-C(5)-H(5A)	109.1	C(2)-C(10)-C(11)	109.2(2)
C(4)-C(5)-H(5A)	109.1	O(1)-C(11)-C(10)	104.0(2)
C(6)-C(5)-H(5B)	109.1	O(1)-C(11)-H(11A)	111.0
C(4)-C(5)-H(5B)	109.1	C(10)-C(11)-H(11A)	111.0
H(5A)-C(5)-H(5B)	107.8	O(1)-C(11)-H(11B)	111.0
C(5)-C(6)-C(7)	111.5(3)	C(10)-C(11)-H(11B)	111.0
C(5)-C(6)-H(6A)	109.3	H(11A)-C(11)-H(11B)	109.0
C(7)-C(6)-H(6A)	109.3	N(1)-C(12)-C(13)	114.1(2)
C(5)-C(6)-H(6B)	109.3	N(1)-C(12)-H(12A)	108.7
C(7)-C(6)-H(6B)	109.3	C(13)-C(12)-H(12A)	108.7
H(6A)-C(6)-H(6B)	108.0	N(1)-C(12)-H(12B)	108.7
C(6)-C(7)-C(8)	111.1(3)	C(13)-C(12)-H(12B)	108.7
C(6)-C(7)-H(7A)	109.4	H(12A)-C(12)-H(12B)	107.6
C(8)-C(7)-H(7A)	109.4	C(14)-C(13)-C(18)	118.2(3)
C(6)-C(7)-H(7B)	109.4	C(14)-C(13)-C(12)	120.1(3)
C(8)-C(7)-H(7B)	109.4	C(18)-C(13)-C(12)	121.7(3)
H(7A)-C(7)-H(7B)	108.0	C(15)-C(14)-C(13)	121.4(3)
C(9)-C(8)-C(7)	110.8(3)	C(15)-C(14)-H(14A)	119.3
C(9)-C(8)-H(8A)	109.5	C(13)-C(14)-H(14A)	119.3
C(7)-C(8)-H(8A)	109.5	C(16)-C(15)-C(14)	119.4(3)
C(9)-C(8)-H(8B)	109.5	C(16)-C(15)-H(15A)	120.3
C(7)-C(8)-H(8B)	109.5	C(14)-C(15)-H(15A)	120.3
H(8A)-C(8)-H(8B)	108.1	C(17)-C(16)-C(15)	120.6(3)
N(1)-C(9)-C(8)	112.6(2)	C(17)-C(16)-H(16A)	119.7
N(1)-C(9)-C(4)	110.8(2)	C(15)-C(16)-H(16A)	119.7
C(8)-C(9)-C(4)	112.3(2)	C(16)-C(17)-C(18)	119.8(3)
N(1)-C(9)-H(9A)	106.9	C(16)-C(17)-H(17A)	120.1
C(8)-C(9)-H(9A)	106.9	C(18)-C(17)-H(17A)	120.1
C(4)-C(9)-H(9A)	106.9	C(17)-C(18)-C(13)	120.5(3)
N(1)-C(10)-C(2)	125.4(3)	C(17)-C(18)-H(18A)	119.8
N(1)-C(10)-C(11)	125.3(2)	C(13)-C(18)-H(18A)	119.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 04079. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	77(2)	44(1)	47(1)	-6(1)	3(1)	-6(1)
O2	77(2)	56(1)	44(1)	-6(1)	-1(1)	-2(1)
N1	62(2)	37(1)	40(1)	-1(1)	1(1)	-1(1)
C1	55(2)	50(2)	47(2)	-4(1)	-3(1)	4(1)
C2	55(2)	43(2)	41(2)	-1(1)	1(1)	2(1)
C3	64(2)	46(2)	46(2)	-1(1)	7(1)	-1(1)
C4	54(2)	45(2)	52(2)	0(1)	-1(1)	-2(1)
C5	74(2)	49(2)	62(2)	1(2)	0(2)	-15(2)
C6	100(3)	43(2)	53(2)	3(1)	7(2)	4(2)
C7	94(3)	48(2)	62(2)	1(2)	8(2)	13(2)
C8	67(2)	51(2)	48(2)	-1(1)	5(2)	8(1)
C9	60(2)	37(2)	40(2)	1(1)	-4(1)	-2(1)
C10	53(2)	39(2)	46(2)	-4(1)	0(1)	1(1)
C11	70(2)	46(2)	42(2)	-4(1)	2(1)	-5(1)
C12	61(2)	45(2)	40(2)	1(1)	3(1)	1(1)
C13	53(2)	44(2)	38(2)	-1(1)	1(1)	-1(1)
C14	53(2)	48(2)	43(2)	-3(1)	3(1)	-3(1)
C15	69(2)	46(2)	49(2)	1(1)	5(2)	-5(2)
C16	76(2)	51(2)	44(2)	6(1)	3(2)	4(2)
C17	56(2)	68(2)	49(2)	5(2)	2(2)	11(2)
C18	55(2)	56(2)	43(2)	1(1)	0(1)	-4(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 04079.

	x	y	z	U(eq)
H3A	3169	-508	8522	62
H3B	3926	-1121	8237	62
H4A	2712	-648	7145	60
H5A	2745	-2784	7851	74
H5B	2712	-2904	6830	74
H6A	3554	-4427	7341	78
H6B	3965	-3266	7851	78
H7A	3895	-3503	6022	81
H7B	4600	-3716	6590	81
H8A	4625	-1430	6950	66
H8B	4598	-1559	5927	66
H9A	3365	-1186	5934	55
H11A	4561	2891	6801	63
H11B	3728	3298	6790	63
H12A	4029	272	5077	59
H12B	4633	1079	5585	59
H14A	4781	3190	5008	58
H15A	4354	5176	4416	66
H16A	3130	5470	4224	68
H17A	2332	3802	4634	69
H18A	2759	1793	5212	62

Table 6. Torsion angles [°] for 04079.

C11-O1-C1-O2	178.9(3)	C3-C4-C9-C8	69.5(3)
C11-O1-C1-C2	-0.4(3)	C12-N1-C10-C2	-161.7(3)
O2-C1-C2-C10	-177.1(3)	C9-N1-C10-C2	-8.1(4)
O1-C1-C2-C10	2.0(3)	C12-N1-C10-C11	21.9(4)
O2-C1-C2-C3	5.6(5)	C9-N1-C10-C11	175.5(3)
O1-C1-C2-C3	-175.3(3)	C1-C2-C10-N1	-179.7(3)
C10-C2-C3-C4	-17.7(4)	C3-C2-C10-N1	-2.2(5)
C1-C2-C3-C4	159.2(3)	C1-C2-C10-C11	-2.8(3)
C2-C3-C4-C5	168.9(2)	C3-C2-C10-C11	174.7(3)
C2-C3-C4-C9	45.9(3)	C1-O1-C11-C10	-1.2(3)
C9-C4-C5-C6	54.5(3)	N1-C10-C11-O1	179.4(3)
C3-C4-C5-C6	-69.7(3)	C2-C10-C11-O1	2.5(3)
C4-C5-C6-C7	-55.4(4)	C10-N1-C12-C13	-65.6(3)
C5-C6-C7-C8	55.0(4)	C9-N1-C12-C13	141.0(3)
C6-C7-C8-C9	-55.5(4)	N1-C12-C13-C14	128.4(3)
C10-N1-C9-C8	-89.4(3)	N1-C12-C13-C18	-53.7(4)
C12-N1-C9-C8	65.2(3)	C18-C13-C14-C15	-0.7(4)
C10-N1-C9-C4	37.3(3)	C12-C13-C14-C15	177.3(3)
C12-N1-C9-C4	-168.1(2)	C13-C14-C15-C16	0.4(4)
C7-C8-C9-N1	-177.6(2)	C14-C15-C16-C17	0.4(4)
C7-C8-C9-C4	56.6(3)	C15-C16-C17-C18	-0.8(4)
C5-C4-C9-N1	177.9(2)	C16-C17-C18-C13	0.5(4)
C3-C4-C9-N1	-57.3(3)	C14-C13-C18-C17	0.3(4)
C5-C4-C9-C8	-55.3(3)	C12-C13-C18-C17	-177.7(3)

Symmetry transformations used to generate equivalent atoms: