20. ANHANG

20.1 Abkürzungen

abs. absolut/absolutiert
Ac Acetyl-
AIBN 2,2'-Azo-bis(isobuttersäurenitril)
Ar Aryl-/Aromat
Alox Aluminiumoxid

ber. berechnet
Bn Benzyl-
Brine gesättigte NaCl-Lösung
Bz Benzoyl-

c Konzentration
COSY Correlated Spectroscopy

DC Dünnschichtchromatographie/-gramm
DDQ 2,3-Dichlor-5,6-dicyano-benzochinon
dest. destilliert
DIBAH Diisobutylaluminiumhydrid
DMAP 4-N,N'-Dimethylaminopyridin
DMF N,N'-Dimethylformamid
DMSO Dimethylsulfoxid
ds Diastereomerenüberschuß

E entgegen (Doppelbindungsgeometrie)
EA Elementaranalyse
ee Enantiomerenüberschuß
EE Essigester (auch EtOAc)
EI Elektronenstoßionisation
äq. Äquivalent (auch äq.), äquatorial
EtOAc Essigester (auch EE)
Et_2O Diethylether

Gef. gefunden
gem. gemessen
ges. gesättigt

Hex. n-Hexan
HPLC
Hünig Base N-Ethyl-diisopropylamin

HV Hochvakuum
h Stunde

iPr Isopropanol
IR Infrarotspektrum

J Kopplungskonstante

LAH Lithiumaluminiumhydrid
LDA Lithium-diisopropyl-amid
Lsg. Lösung

Me Methyl-
MS Massenspekrum

NMR kernmagnetische Resonanz
NOE Nuclear Overhauser Effect

PG Schutzgruppe
Ph Phenyl
PMB para-Methoxybenzyl
ppm parts per million
PpTs Pyridinium-para-toluolsulfonsäure
Py Pyridin

RT Raumtemperatur (273 K)

Schmp. Schmelzpunkt
Smp. Schmelzpunkt

TBAF Tetran-butyl-ammonium-fluorid
TBDMS tert-Butyldimethylsilyl
TEA Triethylamin
tert/t tertiär
THF Tetrahydrofuran
TMS Trimethylsilyl
Ts p-Toluolsulfonyl-
TsOH p-Toluolsulfonsäure

Z zusammen (Doppelbindungsgeometrie)

20.2 Röntgenstrukturdaten des Carbinols (60)

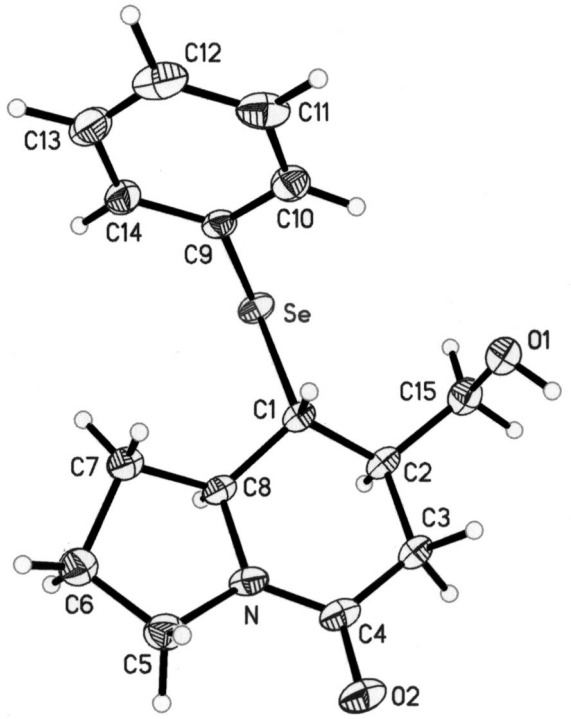

Abb. (7*R*, 8*R*, 8a*S*)-7-Hydroxymethyl-8-phenylselenyl-(8*H*)-indolizidin-5-on **60**[1, 2]

formula	$C_{15}H_{19}NO_2Se$
mol. weight	324.28
crystal color	colorless, transparent
crystal shape	thick plate
crystal dimensions	0.18 x 0.75 x 0.82 mm^3
crystal system	monoclinic
space group	P 21
space group number	4
a	5.3245 (9) Å
b	9.328 (2)
c	14.201 (3)
β	94.22 (1) °
V	703.4 (3) $Å^3$
Z	2
Dcalc	1.531 g/cm^3
linear absorption coeff.	26.4 cm^{-1}

---

[1] Die Röntgenstrukturanalysen wurden dankenswerterweise von Herrn Dr. Bats (Goethe-Universität in Frankfurt am Main) angefertigt

[2] M. Diederich, U. Nubbemeyer *Synthesis* **1999**, No.2, 286-289

radiation	Mo-K_α
scan range	sphere
(2 theta)max	61°
resolution	0.70 Å
number of reflections measured	11432
number of independent reflections	3700
reflections used with I > 0	3689
number of variables	248
R(F)	0.021
wR(F)	0.027
S	1.23

A single crystal was measured on a SIEMENS SMART diffractometer at a temperature of about -140 °C. Repeatedly measured reflections remained stable. A numerical absorption correction was performed based on six crystal faces. The transmission factor ranged from 0.178 to 0.622 . Äquivalent reflections were averaged. The h k l and h -k l reflections which have different anomalous scattering contributions were not averaged. R(F)internal = 0.023 . The structure was determined by Patterson and subsequent Fourier syntheses. The H atoms were taken from a difference synthesis and were refined with isotropic thermal parameters. The non-H atoms were refined with anisotropic thermal parameters. The structure was refined on F values using weighting scheme:

$w(F) = 4 * F^2 / [sigma^2(F^2) + (0.03 * F^2)^2]$

A refinement of the Flack x - parameter gave x = -0.002(6) and confirmed the absolute configuration of the structure. The final difference density was between -0.36 and +0.44 e/ Å. The calculations were performed with the SMART, SHELX and MolEN program systems.

Table of positional Parameters and their estimated standard deviations

Atom	**x**	**y**	**z**	**B(A2)**
Se	-0.15085(2)	0.00004(0)	0.29913(1)	1.881(2)
O1	0.3502(2)	0.2038(1)	0.17202(8)	2.39(2)
O2	0.4541(2)	-0.2675(2)	0.00319(9)	2.94(2)
N	0.2026(2)	-0.2872(1)	0.12221(9)	1.97(2)
C1	0.0875(3)	-0.0724(1)	0.20999(9)	1.61(2)
C2	0.0653(2)	0.0102(2)	0.11631(8)	1.78(2)

C3	0.2536(3)	-0.0534(2)	0.0506(1)	2.13(2)
C4	0.3085(3)	-0.2111(2)	0.0564(1)	2.06(2)
C5	0.2661(3)	-0.4388(2)	0.1417(1)	2.39(3)
C6	0.1006(3)	-0.4779(2)	0.2207(1)	2.47(3)
C7	0.0723(3)	-0.3349(2)	0.2723(1)	2.37(3)
C8	0.0316(3)	-0.2294(2)	0.19063(9)	1.74(2)
C9	0.0674(2)	-0.0202(1)	0.41239(9)	1.78(2)
C10	0.2822(3)	0.0650(2)	0.4259(1)	2.20(2)
C11	0.4337(3)	0.0536(2)	0.5090(1)	2.80(3)
C12	0.3718(4)	-0.0422(2)	0.5785(1)	3.02(3)
C13	0.1578(4)	-0.1266(2)	0.5650(1)	2.82(3)
C14	0.0045(3)	-0.1163(2)	0.4818(1)	2.25(2)
C15	0.1094(3)	0.1714(2)	0.1270(1)	2.17(2)
H1	0.286(4)	-0.067(2)	0.247(2)	3.3(5)*
H01	0.458(5)	0.221(3)	0.128(2)	4.0(5)*
H2	-0.107(3)	0.001(3)	0.085(1)	2.0(3)*
H3B	0.199(4)	-0.030(2)	-0.016(1)	2.8(4)*
H3A	0.437(4)	-0.001(4)	0.065(2)	4.1(5)*
H5A	0.447(4)	-0.444(3)	0.158(2)	3.2(4)*
H5B	0.240(3)	-0.497(3)	0.085(1)	2.3(3)*
H6B	-0.071(3)	-0.511(3)	0.199(1)	2.5(4)*
H6A	0.164(4)	-0.552(2)	0.259(2)	2.7(4)*
H7B	0.239(5)	-0.309(3)	0.308(2)	3.2(5)*
H7A	-0.062(5)	-0.339(3)	0.314(2)	3.2(4)*
H8	-0.152(3)	-0.238(2)	0.169(1)	2.1(4)*
H10	0.337(5)	0.123(3)	0.376(2)	5.0(6)*
H11	0.601(4)	0.110(3)	0.517(2)	4.3(6)*
H12	0.459(5)	-0.051(2)	0.645(2)	3.8(5)*
H13	0.112(3)	-0.195(2)	0.615(1)	2.4(4)*
H14	-0.154(4)	-0.172(3)	0.472(2)	3.7(5)*
H15B	-0.027(4)	0.222(2)	0.164(2)	2.7(4)*
H15A	0.096(3)	0.218(2)	0.065(1)	1.9(3)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic äquivalent displacement parameter defined as:

(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of General Displacement Parameter Expressions - U's

Name	**U(1,1)**	**U(2,2)**	**U(3,3)**	**U(1,2)**	**U(1,3)**	**U(2,3)**
Se	0.01991(5)	0.03045(5)	0.02166(5)	0.00395(5)	0.00528(4)	-0.00215(6)
O1	0.0320(5)	0.0304(5)	0.0284(5)	-0.0026(4)	0.0035(4)	0.0015(4)
O2	0.0398(6)	0.0412(6)	0.0325(5)	0.0053(5)	0.0160(5)	-0.0061(5)
N	0.0272(5)	0.0275(5)	0.0207(5)	0.0037(4)	0.0039(4)	-0.0043(4)
C1	0.0196(5)	0.0247(6)	0.0172(5)	0.0023(5)	0.0043(4)	-0.0010(5)
C2	0.0200(4)	0.0285(5)	0.0195(4)	0.0030(6)	0.0030(4)	0.0023(6)
C3	0.0281(6)	0.0325(6)	0.0215(6)	-0.0013(5)	0.0088(5)	0.0003(5)
C4	0.0228(6)	0.0344(6)	0.0214(6)	0.0011(5)	0.0028(5)	-0.0042(5)
C5	0.0333(7)	0.0275(6)	0.0304(7)	0.0049(6)	0.0037(6)	-0.0034(6)
C6	0.0394(7)	0.0261(8)	0.0283(6)	0.0012(5)	0.0017(6)	-0.0009(5)
C7	0.0417(8)	0.0258(6)	0.0228(6)	0.0017(6)	0.0048(6)	-0.0001(5)
C8	0.0222(5)	0.0259(5)	0.0184(5)	0.0003(5)	0.0038(5)	-0.0024(5)
C9	0.0241(5)	0.0240(6)	0.0202(5)	0.0024(4)	0.0050(4)	-0.0042(4)
C10	0.0251(6)	0.0308(6)	0.0284(6)	0.0001(6)	0.0075(5)	-0.0040(6)
C11	0.0268(7)	0.0432(7)	0.0362(7)	0.0042(6)	0.0004(6)	-0.0139(7)
C12	0.0410(8)	0.0461(8)	0.0270(7)	0.0122(6)	-0.0030(6)	-0.0074(6)
C13	0.0503(9)	0.0338(7)	0.0234(6)	0.0104(6)	0.0066(6)	0.0021(6)
C14	0.0342(7)	0.0266(6)	0.0253(6)	0.0015(5)	0.0074(5)	-0.0016(5)
C15	0.0267(6)	0.0288(6)	0.0272(6)	0.0039(5)	0.0049(5)	0.0051(5)

The form of the anisotropic displacement parameter is:

exp [-2PI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}]

where a,b, and c are reciprocal lattice constants.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Se	C1	1.977(1)	C3	C4	1.501(2)
Se	C9	1.923(1)	C5	C6	1.522(2)
O1	C15	1.422(2)	C6	C7	1.534(2)
O2	C4	1.239(2)	C7	C8	1.524(2)
N	C4	1.331(2)	C9	C10	1.395(2)
N	C5	1.475(2)	C9	C14	1.391(2)
N	C8	1.481(2)	C10	C11	1.384(2)
C1	C2	1.535(2)	C11	C12	1.388(3)
C1	C8	1.515(2)	C12	C13	1.387(3)
C2	C3	1.538(2)	C13	C14	1.390(2)
C2	C15	1.528(2)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Se	C9	97.18(5)	C5	C6	C7	103.1(1)
C4	N	C5	122.6(1)	C6	C7	C8	102.2(1)
C4	N	C8	125.4(1)	N	C8	C1	110.4(1)
C5	N	C8	111.7(1)	N	C8	C7	101.8(1)
Se	C1	C2	111.79(9)	C1	C8	C7	118.1(1)
Se	C1	C8	108.65(9)	Se	C9	C10	119.9(1)
C2	C1	C8	109.1(1)	Se	C9	C14	119.6(1)
C1	C2	C3	108.7(1)	C10	C9	C14	120.5(1)
C1	C2	C15	114.0(1)	C9	C10	C11	119.6(1)
C3	C2	C15	109.7(1)	C10	C11	C12	120.1(2)
C2	C3	C4	118.5(1)	C11	C12	C13	120.2(2)
O2	C4	N	121.2(1)	C12	C13	C14	120.2(2)
O2	C4	C3	120.7(1)	C9	C14	C13	119.4(1)
N	C4	C3	118.1(1)	O1	C15	C2	112.4(1)
N	C5	C6	103.3(1)				

Numbers in parentheses are estimated standard deviations in the least significant digits:

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
C9	Se	C1	C2	-142.55	(0.10)
C9	Se	C1	C8	97.05	(0.09)
C1	Se	C9	C10	66.88	(0.12)
C1	Se	C9	C14	-115.48	(0.11)
C5	N	C4	O2	5.19	(0.22)
C5	N	C4	C3	-172.70	(0.13)
C8	N	C4	O2	178.39	(0.13)
C8	N	C4	C3	0.50	(0.20)
C4	N	C5	C6	180.00	(0.56)
C8	N	C5	C6	5.96	(0.16)
C4	N	C8	C1	-27.59	(0.18)
C4	N	C8	C7	-153.80	(0.14)
C5	N	C8	C1	146.25	(0.12)
C5	N	C8	C7	20.04	(0.15)
Se	C1	C2	C3	-179.31	(0.10)
Se	C1	C2	C15	57.96	(0.13)
C8	C1	C2	C3	-59.14	(0.14)
C8	C1	C2	C15	178.12	(0.11)
Se	C1	C8	N	178.67	(0.09)
Se	C1	C8	C7	-64.87	(0.14)
C2	C1	C8	N	56.59	(0.14)
C2	C1	C8	C7	173.05	(0.12)
C1	C2	C3	C4	33.33	(0.17)
C15	C2	C3	C4	158.59	(0.12)
C1	C2	C15	O1	58.07	(0.15)
C3	C2	C15	O1	-64.09	(0.15)
C2	C3	C4	O2	178.22	(0.13)
C2	C3	C4	N	-3.88	(0.20)
N	C5	C6	C7	-29.47	(0.15)
C5	C6	C7	C8	42.12	(0.15)
C6	C7	C8	N	-37.48	(0.14)

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
C6	C7	C8	C1	-158.48	(0.13)
Se	C9	C10	C11	177.70	(0.12)
C14	C9	C10	C11	0.09	(0.22)
Se	C9	C14	C13	-177.59	(0.12)
C10	C9	C14	C13	0.03	(0.21)
C9	C10	C11	C12	-0.05	(0.28)
C10	C11	C12	C13	-0.11	(0.28)
C11	C12	C13	C14	0.23	(0.27)
C12	C13	C14	C9	-0.20	(0.25)

Table of Least-Squares Planes

Orthonormal Äquation of Plane 1

-0.7289 X +	-0.2060 Y +	-0.6529 Z -	-1.2823	=	0
0.0005	0.0005	0.0005	0.0012		

Crystallographic Äquation of Plane

-3.8811 X +	-1.9216 Y +	-8.4847 Z-	-1.2823 = 0
0.0025	0.0049	0.0236	0.0012

Atom	X	Y	Z	Distance		Esd
C2	0.2263	0.0953	1.6472	0.0223	+	-0.0012
C3	1.2973	-0.4978	0.7161	-0.0283	+-	0.0015
C4	1.5835	-1.9693	0.7988	0.0123	+-	0.0015
N	0.9512	-2.6788	1.7308	0.0109	+-	0.0012
C8	-0.0308	-2.1397	2.6998	-0.0171	+-	0.0013

Chi Squared = 1023.9

Other Atoms

C1	0.2467	-0.6757	2.9739	-0.7000	+	-0.0014
Se	-1.1158	0.0004	4.2363	-0.6703	+	-0.0001
C15	0.4499	1.5988	1.7993	-0.5497	+	-0.0015

O2	2.4144	-2.4951	0.0452	0.0069	+	-0.0012
C5	1.2690	-4.0928	2.0062	-0.1094	+	-0.0016
C6	0.3047	-4.4575	3.1263	-0.0626	+	-0.0016
C7	0.1006	-3.1237	3.8568	-0.6656	+	-0.0016

Orthonormal Äquation of Plane 2

-0.7193 X +	-0.2416 Y +	-0.6514 Z -	-1.1981	=	0
0.0007	0.0007	0.0008	0.0031		

Crystallographic Äquation of Plane

-3.8297 X +	-2.2541 Y +	-8.4731 Z -	-1.1981	=	0
0.0037	0.0068	0.0298	0.0031		

Atom	**X**	**Y**	**Z**	**Distance**		**Esd**
C8	-0.0308	-2.1397	2.6998	-0.0212	+	-0.0013
N	0.9512	-2.6788	1.7308	0.0339	+	-0.0012
C5	1.2690	-4.0928	2.0062	-0.0324	+	-0.0016
C6	0.3047	-4.4575	3.1263	0.0197	+	-0.0016

Chi Squared = 1553.3

Other Atoms

C7	0.1006	-3.1237	3.8568	-0.6316	+	-0.0016
C1	0.2467	-0.6757	2.9739	-0.7532	+	-0.0014
C4	1.5835	-1.9693	0.7988	0.0147 +	-	0.0015

Orthonormal Äquation of Plane 3

0.5695 X	+	-0.7112 Y	+	-0.4121 Z	-	-2.3139	=	0
0.0006		0.0005		0.0006		0.0044		

Crystallographic Äquation of Plane

3.0326 X	+	-6.6342 Y	+	-6.4312 Z	-	-2.3139	=	0
0.0030		0.0045		0.0262		0.0044		

Atom	X	Y	Z	Distance		Esd
C9	-0.0720	-0.1888	5.8405	0.0004	+	-0.0013
C10	1.0576	0.6065	6.0321	-0.0008	+	-0.0015
C11	1.7774	0.4999	7.2089	0.0001	+	-0.0018
C12	1.3753	-0.3934	8.1928	0.0009	+	-0.0018
C13	0.2499	-1.1812	8.0023	-0.0013	+	-0.0018
C14	-0.4793	-1.0846	6.8234	0.0006	+	-0.0016

Chi Squared = 1.3

Other Atoms

Se	-1.1158	0.0004	4.2363	-0.0675	+	-0.0001

Dihedral Angles Between Planes:

Plane No.	Plane No.	Dihedral Angle		
1	2	2.12	+	-1.34
1	3	89.98	+	-0.04
2	3	88.25	+	-0.05

20.3 *Abstract:* The Diastereoselective Zwitterionic Aza-Claisen Rearrangement

A novel type of ketene-Claisen rearrangement was developed. Allyl amines have been used in ketene-Claisen reactions rarely. The rearrangement was restricted to activated ketenes like dichloroketene, since alkyl ketenes are apparently not electrophilic enough to attack the allyl amine. Since acetyl chloride is a synthetic equivalent for ketene, special conditions were developed for the Claisen-rearrangement of allyl amines with the easier applicable acetyl chloride. The zwitterionic aza-Claisen rearrangement is not restricted to activated ketenes. Complete 1,3-chirality transfer and a high simple diastereoselectivity was observed in the reaction of various carboxylic acid chlorides with *N*-allyl amines. A range of optically active nine-membered ring lactams have been generated in 5-7 steps under very mild reaction conditions.

The obtained optically active nine-membered ring lactame were treated with electrophiles that induced regio- and diastereoselective transanular ring contractions. The resulting chiral indolizidinone can be used as key intermediate in an efficient asymmetric synthesis of (-)-8a-*epi*-denroprimine, a naturally occurring 5,7-dimethylindolizidine alkaloide.

20.4 Lebenslauf von Michel Diederich

Geburtstag	12. Januar 1962 in Berlin
1969	Zinnowald-Grundschule in Berlin-Zehlendorf
1974, Aug.	Droste-Hülshoff Gymnasium in Berlin-Zehlendorf
1981, Dez.	Abitur am Droste-Hülshoff-Gymnasium
1982	Aufnahmeprüfung für ein Instrumentalstudium an der HdK-Berlin
1983	Studium an der HdK, Hauptfach Gitarre
1984	Studienfachwechsel : Ab Sommer-Semester Studium der Chemie an der Freien-Universität-Berlin
1987, Mai.	Vordiplom
1990, April	Arbeitsvertrag mit der FU-Berlin als studentische Hilfskraft im Chemiepraktikum für Mediziner
1992, Jan. bis Dez.	Diplomarbeit im Arbeitskreis von Herrn Dr. Udo Nubbemeyer an der FU-Berlin. Thema: Synthese von chiralen Neunring-Lactamen via Keten-Claisen-Reaktion
1993, Jan	Beginn meiner Forschungsarbeit für die Promotion. Thema:
Synthese	von (-)-Dendroprimin via Aza-Claisen-Reaktion
1993, Juni	Privatdienstvertrag als wissenschaftlicher Mitarbeiter im
Rahmen eines	DFG-Projekts an der FU-Berlin
1994, Mai-1997, Mai	Angestellter der FU-Berlin als Assistent im Grund- und Fortgeschrittenenpraktikum für organische Chemie
seit April 1999	Angestellter der Firma Chiratec GmbH in Luckenwalde