Intramolecular Asymmetric Amidations of Sulfonamides and Sulfamates Catalyzed by Chiral Dirhodium(II) Complexes

by **Corinne Fruit*** and **Paul Müller**

Department of Organic Chemistry, University of Geneva, 30 Quai Ernest Ansermet, CH-1211 Geneva 4

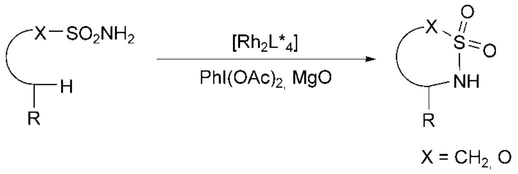
Dedicated to Dr. *Günther Ohloff* on the occasion of his 80th birthday

Enantioselective intramolecular amidation of aliphatic sulfonamides was achieved for the first time by means of chiral carboxylatodirhodium(II) catalysts in conjunction with PhI(OAc)$_2$ and MgO in high yields and with enantioselectivities of up to 66% (*Scheme 3*, *Table 1*). The best results were obtained with [Rh$_2${(*S*)-nttl)$_4$] and [Rh$_2${(*R*)-ntv)$_4$] as catalysts ((*S*)-nttl = (*αS*)-*α*-(*tert*-butyl)-1,3-dioxo-2*H*-benz[*de*]isoquinoline-2-acetato, (*R*)-nto = (*αR*)-*α*-isopropyl-1,3-dioxo-2*H*-benz[*de*] isoquinoline-2-acetato). In addition, these carboxylatodirhodium(II) catalysts were also efficient in intramolecular amidations of aliphatic sulfamates esters, although the enantioselectivity of these latter reactions was significantly lower (*Scheme 4*, *Table 3*).

Introduction. – Amidation of saturated C–H bonds and aziridination of olefins catalyzed by metal complexes based on Fe, Mn, Ru, Cu, or Rh are established methodologies for C–N bond-formation [1] and, consequently, for the synthesis of amine derivatives. Some years ago, the Rh^{II}-catalyzed aziridination [2] and sulfonamidation [3] with phenyliodinanes derived from aromatic sulfonamides has been investigated in our group. The reactions exhibited features analogous to the corresponding metal-catalyzed carbene-transfer reactions [4]. The aziridination was found to be stereospecific, except in the case of stilbene, and the amidation proceeded with retention of configuration at the reacting C-atom, indicating intervention of a metal-complexed nitrene, in analogy to the corresponding intermediate metallocarbenes resulting from decomposition of diazo compounds with Rh^{II} catalysts. Some preliminary experiments showed that the system was suitable for asymmetric nitrene transfer. However, it suffered several shortcomings. Owing to the requirement of aromatic sulfonamides as precursors for the phenyliodinanes [5], the possibilities of carrying out intramolecular aziridinations and/or amidations [6] appeared very limited. In addition, a large excess of substrate was necessary in the case of intermolecular reactions to achieve satisfactory yields, while reactions carried out with an excess of reagent over the substrate produced unsatisfactory results. Finally, some reactions, in particular intermolecular amidations, proceeded very sluggishly and resulted in decomposition of the phenyliodinanes to afford sulfonamides without generation of the expected products of nitrene insertion.

The transition-metal-catalyzed nitrene transfer has been further developed by other groups. *Dodd*, *Dauban*, and co-workers reported that, contrary to the traditional opinion [7], phenyliodinanes derived from aliphatic sulfonamides are isolable and may be used for nitrene-transfer reactions [8]. In addition, they found conditions allowing generation of phenyliodinanes from sulfamates and PhI=O, followed by Cu-catalyzed decomposition *in situ* to afford aziridines. At the same time, an analogous system for *in situ* generation of phenyliodinanes with $PhI(OAc)_2$ from sulfamates and carbamates, and their subsequent Rh^{II}-catalyzed nitrene transfer was designed by *Du Bois* and co-workers [9]. Rh^{II}-Catalyzed intramolecular asymmetric aziridinations with ee values of up to 76% have been reported [10]; however, so far, the highest inductions in catalytic intramolecular amidations have been achieved with porphyrinatoruthenium complexes [11]. In view of these recent developments, we carried out a series of Rh^{II}-catalyzed intramolecular amidations with *in situ* generated phenyliodinanes derived from sulfonamides and sulfamates (*Scheme 1*).

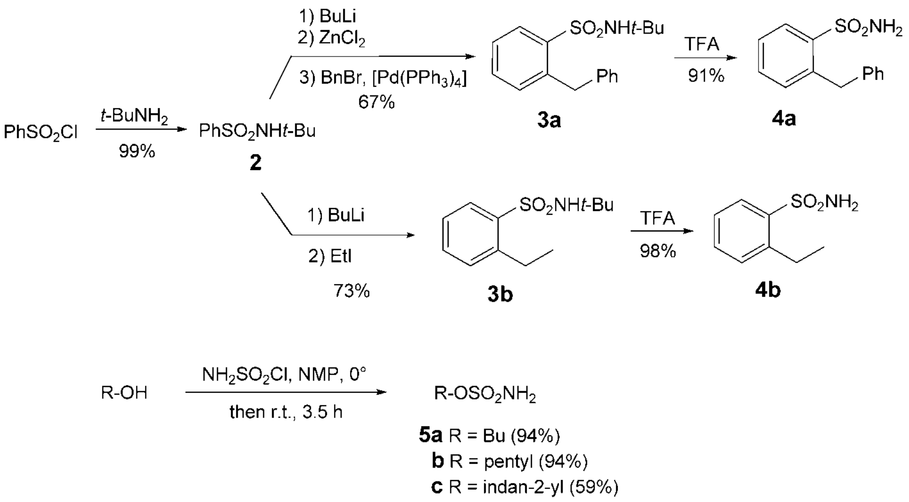
Scheme 1



Results and Discussion. – *Synthesis of Sulfonamides and Sulfamates.* The aliphatic sulfonamides **1a**–**d** ($R(CH_2)_4SO_2NH_2$) were prepared according to the literature from the corresponding bromo derivatives in a three-step procedure with overall yields of 44–63% [12]. Aromatic sulfonamides, in turn, were obtained in a three-step procedure starting from commercially available benzenesulfonyl chloride. Ethyl and benzyl groups were introduced in *ortho* position *via* metallation-alkylation [13] and *Negishi* cross-coupling [14], respectively, starting from *N*-(*tert*-butyl)benzenesulfonamide (**2**) [15] (→**3a** and **3b**, resp.; *Scheme 2*). Subsequent acid cleavage with CF_3COOH afforded sulfonamides **4a** and **4b** [12]. The synthesis of the aliphatic sulfamates **5a**–**c** was achieved starting from the corresponding alcohols and *in situ* generated sulfamoyl chloride [16] with good yields (*Scheme 2*).

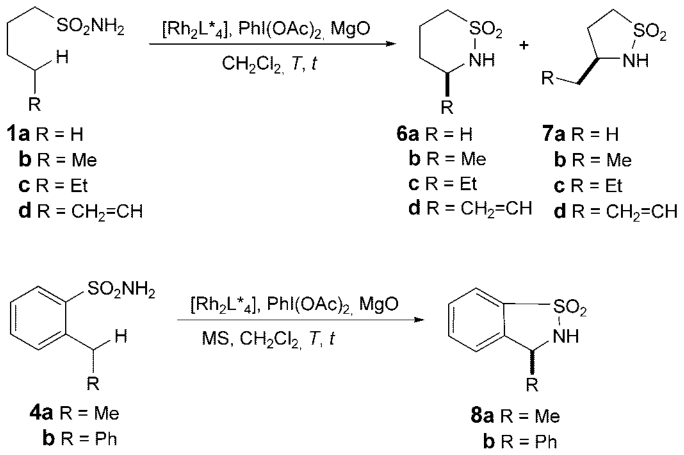
Intramolecular Amidations with Sulfonamides. The amidations with **1** were carried out under *in situ* conditions with $PhI(OAc)_2$ in the presence of MgO with 2–5% of catalyst (see *Fig.*), generally at 40°, and afforded cyclization products in quite variable yield (*Scheme 3*, *Table 1*). Formation of six-membered sultams (see **6**) was preferred over the five-membered ones (see **7**). This trend is opposite to the one found in carbenoid insertion where cyclopentanones or γ-lactones usually are formed preferentially over cyclohexanones or δ-lactones, respectively. No insertion products could be isolated upon decomposition of butanesulfonamide (**1a**). In this case, formation of the five-membered sultam **7a** is disfavored; however, the six-membered isomer **6a** is not formed either, presumably owing to the low tendency of the Me group to undergo nitrene insertion [3b]. No five-membered sultam **7d** was observed in any reaction of **1d**, where the presence of the C=C bond activates the allylic position and contributes further to the selective formation of the six-membered-ring compound **6d**. As previously reported [3b], the carboxamidatodirhodium(II) catalysts were insufficiently effective and gave only poor yields of insertion products. Among the carboxylatodi-

Scheme 2



TFA = CF$_3$COOH, NMP = 1-methylpyrrolidin-2-one

Scheme 3



rhodium(II)-catalysts, [Rh$_2${(S)-nttl}$_4$] ((*S*)-nttl = (α*S*)-α-(*tert*-butyl)-1,3-dioxo-2*H*-benz[*de*]isoquinoline-2-acetato; see *Fig.*) was most selective and gave 57% ee at 40° and 66% ee at −20°, respectively, followed by [Rh$_2${(R)-ntv}$_4$] ((*R*)-ntv = (α*R*)-α-isopropyl-1,3-dioxo-2*H*-benz[*de*]isoquinoline-2-acetato; see *Fig.*). The selectivity of the other catalysts was disappointing, however.

The enantioselectivity of the aromatic sulfonamides **4a**,**b** was investigated with the same catalysts. These reactions proceeded with respectable yields to five-membered sultams **8a**,**b**. However the enantioselectivity never exeeded 20% (*Table 2*).

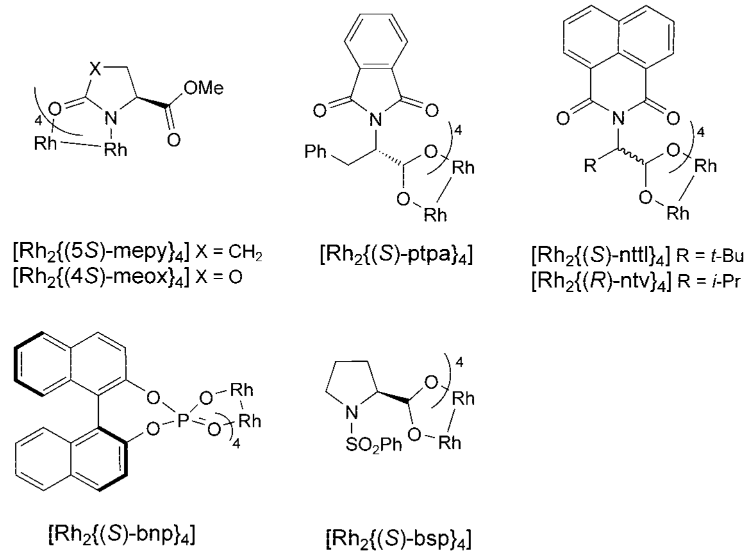


Figure. *Rh^{II} Catalysts used in the intramolecular amidation*

Table 1. *Intramolecular Amidation of Aliphatic Sulfonamides* **1a**–**d** ($R(CH_2)_4SO_2NH_2$)[a])

$R(CH_2)_4SO_2NH_2$[b])	[$Rh_2L^*_4$][c])	mol-%	T [°]	t [h]	Yield [%]	**6**/**7**[d])	ee [%]
1a	[$Rh_2(OAc)_4$]	2.0	40	4.5	0	–	–
1b	[$Rh_2(OAc)_4$]	5.0	40	4	70	93 : 7	–
1c	[$Rh_2(OAc)_4$]	5.0	40	2	77	77 : 23	–
1d	[$Rh_2(OAc)_4$]	2.0	40	3	51	99 : 1	–
1b	[Rh_2{(*S*)-ptpa}$_4$]	3.5	40	4	100	95 : 5	15
1d	[Rh_2{(*S*)-ptpa}$_4$]	5.0	– 20	4	31	99 : 1	10
1b	[Rh_2{(*S*)-nttl}$_4$]	3.5	40	4	83	98 : 2	57
1b	[Rh_2{(*S*)-nttl}$_4$]	3.5	– 20	6.5	94	99 : 1	66
1c	[Rh_2{(*S*)-nttl}$_4$]	3.5	40	2	98	98 : 2	13
1d	[Rh_2{(*S*)-nttl}$_4$]	2.0	40	3	23	99 : 1	8
1b	[Rh_2{(*R*)-ntv}$_4$]	2.0	40	3	90	97 : 3	54
1c	[Rh_2{(*R*)-ntv}$_4$]	3.5	40	2	90	97 : 3	22
1b	[Rh_2{(5*S*)-mepy}$_4$]	2.5	40	4	6	n.d.[e])	n.d.[e])
1d	[Rh_2{(5*S*)-mepy}$_4$]	5.0	40	3	23	99 : 1	8
1d	[Rh_2{(5*S*)-mepy}$_4$]	5.0	– 20	48	6	99 : 1	n.d.[e])
1d	[Rh_2{(4*S*)-meox}$_4$]	2.0	40	51	22	99 : 1	6
1d	[Rh_2{(*S*)-bsp}$_4$]	2.5	40	72	54	92 : 8	6
1d	[Rh_2{(*S*)-bsp}$_4$]	5.0	– 20	4	50	99.1	7
1b	[Rh_2{(*S*)-bnp}$_4$]	2.0	40	32	–	–	–
1d	[Rh_2{(*S*)-bnp}$_4$]	4.0	20	24	–	–	–

a) Conditions: all reactions were performed in CH_2Cl_2 at 40° or – 20° with a **1**/$PhI(OAc)_2$/MgO molar ratio of 1 : 1.5 : 2.5. [b]) **a**, R = H; **b**, R = Me; **c**, R = Et; **d**, R = CH_2=CH. [c]) For the catalysts, see *Figure*. [d]) Ratio determined by GC. [e]) n.d. = not determined.

Table 2. *Intramolecular Amidation of Aromatic Sulfonamides* **4a**,**b**[a])

	$[Rh_2L^*_4]$[b])	mol-%	*t* [h]	Yield [%]	ee [%]
4a	$[Rh_2(OAc)_4]$	5	2.5	65	–
4b	$[Rh_2(OAc)_4]$	5	2.5	45	–
4a	$[Rh_2\{(S)\text{-nttl}\}_4]$	3.5	2.5	31	20
4b	$[Rh_2\{(S)\text{-nttl}\}_4]$	3.5	2.5	44	n.d.[c])
4a	$[Rh_2\{(S)\text{-ptpa}\}_4]$	3.5	2.5	[d])	–
4b	$[Rh_2\{(R)\text{-ntv}\}_4]$	3.5	5.5	33	n.d.[c])

[a]) Conditions: all reactions were performed at 40° in CH_2Cl_2 for 2.5 or 5.5 h with a **4**/$PhI(OAc)_2$/MgO molar ratio of 1 : 1.5 : 2.5. [b]) For the catalysts, see *Figure*. [c]) n.d. = not determined. [d]) Degradation of **4a**.

Intramolecular Amidation with Sulfamate Esters. The decomposition of phenyliodonium ylides derived from sulfamates in the presence of dirhodium catalysts results in cyclic sulfamidates that are versatile reagents for organic synthesis [17]. This class of compounds is of interest for the synthesis of various products possessing heteroatomic functional groups. For example, they are useful precursors for the preparation of amino acid derivatives [18], amino alcohols [19], piperazines or thiomorpholines [20], oligosaccharides [21], glycopeptides [22], or indolizidine derivatives [23].

Following the pioneering work of *Du Bois* and co-workers, we explored the *in situ* generation and chiral Rh^{II}-catalyzed decomposition of phenyliodonium ylides derived from aliphatic sulfamate esters **5a** – **c** (*Scheme 4*, *Table 3*). The reaction conditions were optimized with $[Rh_2(OAc)_4]$, and PhI(OAc) in conjunction with MgO was superior to PhI=O for the generation of the phenyliodinane. CH_2Cl_2 was the most suitable solvent for this reaction. Screening of chiral Rh^{II} catalysts showed that $[Rh_2\{(S)\text{-nttl}\}_4]$ [24] and $[Rh_2\{(R)\text{-ntv}\}_4]$ [25] gave the highest ee values, although the enantioselectivity was significantly below that obtained in the intramolecular amidation of sulfonamides. This contrasts with the intramolecular amidation of aromatic sulfamates, where ee values of up to 52% have been reported with these catalysts [26].

Scheme 4

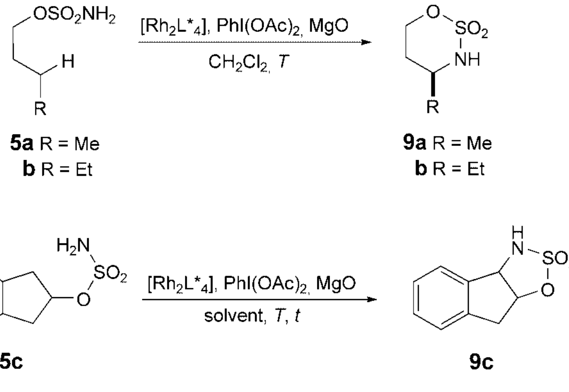


Table 3. *Intramolecular Amidation of Sulfamates* **5a**–**c**a)

	$[Rh_2L_4^*]$b)	mol-%	Solvent	T [°]	t [h]	Yield [%]	ee [%]
5a	$[Rh_2(OAc)_4]$	5	CH_2Cl_2	40	10	87	–
5b	$[Rh_2(OAc)_4]$	5	CH_2Cl_2	40	10	67	–
5b	$[Rh_2(OAc)_4]$	5	MeCN	40	24	31	–
5b	$[Rh_2(OAc)_4]$	5c)	CH_2Cl_2	40	10	29	–
5b	$[Rh_2(OAc)_4]$	5c)	MeCN	40	32	20	–
5c	$[Rh_2(OAc)_4]$	5	CH_2Cl_2	40	3.5	55	–
5c	$[Rh_2(OAc)_4]$	5	PhMe	80	3.5	43	–
5a	$[Rh_2\{(S)\text{-ptpa}\}_4]$	2.5	CH_2Cl_2	40	6	97	9
5b	$[Rh_2\{(S)\text{-ptpa}\}_4]$	3.5	CH_2Cl_2	40	10	82	< 5
5c	$[Rh_2\{(S)\text{-ptpa}\}_4]$	3.5	CH_2Cl_2	40	3.5	71	18
5a	$[Rh_2\{(S)\text{-nttl}\}_4]$	3.5	CH_2Cl_2	40	4	97	19
5a	$[Rh_2\{(S)\text{-nttl}\}_4]$	3.5	CH_2Cl_2	– 20	10	97	21
5b	$[Rh_2\{(S)\text{-nttl}\}_4]$	3.5	CH_2Cl_2	40	10	60	< 5
5c	$[Rh_2\{(S)\text{-nttl}\}_4]$	3.5	CH_2Cl_2	40	3.5	62	22
5a	$[Rh_2\{(R)\text{-ntv}\}_4]$	2.0	CH_2Cl_2	40	4	80	17
5b	$[Rh_2\{(R)\text{-ntv}\}_4]$	3.5	CH_2Cl_2	40	10	91	< 5
5c	$[Rh_2\{(R)\text{-ntv}\}_4]$	3.5	CH_2Cl_2	40	3.5	52	30
5a	$[Rh_2\{(4S)\text{meox}\}_4]$	2.0	CH_2Cl_2	40	29	42	< 5
5b	$[Rh_2\{(4S)\text{-meox}\}_4]$	2.0	CH_2Cl_2	40	22	16	< 5
5c	$[Rh_2\{(4S)\text{-meox}\}_4]$	3.5	CH_2Cl_2	40	3.5	34	< 5
5a	$[Rh_2\{(S)\text{-bsp}\}_4]$	2.0	CH_2Cl_2	40	17	42	< 5

a) Standard conditions: see *Exper. Part.* b) For the catalysts, see *Figure.* c) Iodosylbenzene was used instead of $PhI(OAc)_2$.

Conclusions. – In summary, we reported the first enantioselective intramolecular amidation reactions by using aliphatic sulfonamides and chiral dirhodium catalysts. We demonstrated that $[Rh_2\{(S)\text{-nttl}\}_4]$, developed in our group, is the most effective catalyst for enantioselective amidation of C–H bonds (ee up to 66%). Intramolecular nitrene insertion into C–H bonds was also achieved by using aliphatic sulfamate esters and chiral dirhodium complexes. These amidations proceed with up to 30% ee in the presence of $[Rh_2\{(R)\text{-ntv}\}_4]$.

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Experimental Part

1. *General.* All reactions were carried out under Ar. CH_2Cl_2, MeCN, and toluene were dried (CaH_2) and distilled. The other solvents were purchased from *Fluka* or *Acros* and used without purification. Flash chromatography (FC): silica gel *32-63 60 Å (Merck 9385)*. CC = column chromatography. TLC: *Macherey-Nagel Polygram Sil/UV$_{254}$*; detection by UV light or with $KMnO_4$. The enantiomeric excess (ee) of the products was determined by GC (*β-Dex* column) or by HPLC (*Chiracel OD H*); retention times t_R in min. IR Spectra: *Mattson-Instruments Polaris* FT-IR instrument; NaCl cells; in cm^{-1}. NMR Spectra: *Bruker AV-300*, *Bruker DRX-500*; chemical shifts δ in ppm with respect to $SiMe_4$ (= 0 ppm), coupling constants J in Hz. MS: *Varian-CH4* or *-SM1* spectrometer with electron impact or electrospray; in *m/z* (rel. %). High-resolution (HR) MS: anal. *VG-7070* spectrometer (data system 11 250, resolution 7000).

2. *Aliphatic Sulfonamides: General Procedure.* A soln. of bromoalkane or bromoalkene and sodium sulfite (1.2 equiv.) in H_2O (5 ml) was refluxed overnight. After cooling to r.t., the aq. soln. was washed with Et_2O and

evaporated. The resulting white solid was dried under vacuum at 130° and then treated with $POCl_3$ (10 equiv.) for 4 h at 130°. After evaporation, the residue was taken up in MeCN, and a soln. of aq. ammonia in MeCN was slowly added at 0°. The mixture was stirred at 0° for 1 h, then diluted with CH_2Cl_2, and washed with H_2O. The org. phase was dried (Na_2SO_4) and evaporated: white solid.

Butane-1-sulfonamide (**1a**): Yield 44%. M.p. 57°.

Pentane-1-sulfonamide (**1b**): Yield 63%. M.p. 76°.

Hexane-1-sulfonamide (**1c**): Yield 55%. M.p. 114°.

Hex-5-ene-1-sulfonamide (**1d**) [12]: Yield 50%. M.p. 52°.

*2-Benzyl-*N*-(*tert*-butyl)benzenesulfonamide* (**3a**). A mixture of *N*-(*tert*-butyl)benzenesulfonamide (**2**) [15] (1.066 g, 5 mmol) and THF (10 ml) was purged with Ar and cooled at −78°. Then 1.6M BuLi in hexane (6.6 ml, 10.5 mmol) was added dropwise. The mixture was stirred for 30 min at 0° and then cooled to −78°. $ZnCl_2$ (1.70 g, 12.5 mmol) in THF (5 ml) was added, and the mixture was stirred for another 15 min and allowed to reach 0°. Then benzyl bromide (0.71 ml, 6 mmol) and $[Pd(PPh_3)_4]$ (0.310 g, 5 mol-%) were added. The mixture was warmed to 50°, stirred for 21 h, then poured into 2N HCl (20 ml), and extracted with CH_2Cl_2. The org. phase was dried ($MgSO_4$) and evaporated and the residue purified by FC (silica gel, pentane/AcOEt 5 : 1): **3a** (1.02 g, 67%). White solid. TLC: R_f 0.58. M.p. 126°. IR (neat): 3288, 2973, 1494, 1474, 1419, 1390, 1305, 1145, 1122, 1065, 997, 765. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.06 (*s*, Me_3C); 4.34 (br., NH); 4.51 (*s*, CH_2); 7.25 (*m*, 4 CH); 7.37 (*m*, 3 CH); 7.49 (*m*, 1 CH); 8.12 (*d*, $J = 7.9$, 1 CH). ^{13}C-NMR ($CDCl_3$, 75 MHz): 29.9 (*Me*$_3$C); 38.4 (CH_2); 54.7 (C); 126.7 (CH); 128.9 (CH); 129.2 (CH); 129.5 (CH); 132.3 (CH); 132.7 (CH); 138.9 (C); 139.7 (C); 141.4 (C). HR-MS: 303.12924 ($C_{17}H_{21}NO_2S^+$; calc. 303.12930).

N*-(*tert*-Butyl)-2-ethylbenzenesulfonamide* (**3b**). A soln. of **2** [15] (2.133 g, 10 mmol) in THF (25 ml), precooled to 0° under Ar, was treated dropwise with 1.6M BuLi in hexane (13 ml, 20.1 mmol). The resulting bright yellow soln. was stirred at 0° for 30 min, prior to quenching with iodoethane (0.96 ml, 12 mmol) in THF (5 ml). After stirring for 1 h, the mixture (white suspension) was quenched with sat. NH_4Cl soln. (50 ml), and the mixture was extracted with CH_2Cl_2 (3 × 50 ml). The org. phase was dried ($MgSO_4$) and evaporated and the residue purified by FC (silica gel, pentane/AcOEt 7 : 1): **3b** (2.28 g, 73%). White solid. TLC: R_f 0.50. IR (neat): 3277, 2981, 1446, 1426, 1392, 1309, 1142, 1097, 1009, 995, 865, 754. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.24 (*s*, Me_3C); 1.34 (*t*, $J = 7.4$, *Me*CH_2); 3.10 (*q*, $J = 7.4$, MeC*H*$_2$); 5.21 (br., NH); 7.29 (*m*, 1 CH); 7.38 (*d*, $J = 7.4$, 1 CH); 7.49 (*m*, 1 CH); 8.04 (*d*, $J = 8.1$, 1 CH). ^{13}C-NMR ($CDCl_3$, 75 MHz): 15.0 (Me); 25.5 (CH_2); 30.1 (*Me*$_3$C); 54.9 (C); 125.8 (CH); 129.1 (CH); 130.3 (CH); 132.4 (CH); 140.8 (C); 142.9 (C).

2-Benzylbenzenesulfonamide (**4a**). A soln. of **3a** (0.910 g, 3.0 mmol) in anisole (= methoxybenzene; 9.7 ml, 3 equiv.) and neat CF_3COOH (33 ml) was stirred for 24 h at 0°. After dilution with AcOEt (40 ml), the soln. was neutralized at 0° with aq. Na_2CO_3 soln. The org. phase was dried (Na_2SO_4) and evaporated: **4a** (0.679 g, 91%). White solid. M.p. 142°. IR (neat): 3327, 1662, 1453, 1300, 1221, 1132, 910. ^{1}H-NMR ((D_6)DMSO, 300 MHz): 4.38 (*s*, CH_2); 7.09 (*d*, $J = 7.0$, 1 CH); 7.20 – 7.45 (*m*, 7 H); 7.52 (br., NH_2); 7.90 (*d*, $J = 7.9$, 1 H). ^{13}C-NMR ((D_6)DMSO, 75 MHz): 37.6 (CH_2); 126.6 (CH); 126.7 (CH); 127.6 (CH); 128.8 (CH); 129.8 (CH); 132.0 (CH); 132.2 (CH); 139.6 (C); 140.7 (C); 142.5 (C). HR-MS: 230.03985 ($C_{13}H_{11}O_2S^+$; calc. 230.04015).

2-Ethylbenzenesulfonamide (**4b**). As described for **4a**, with **3b** (0.600 g, 2.48 mmol), anisole (8 ml, 3 equiv.), CF_3COOH (27 ml), and AcOEt (30 ml): **4b** (0.450 g, 98%). Creamy solid. M.p. 124°. IR (neat): 3342, 3240, 1309, 1295, 1137. ^{1}H-NMR ((D_6)DMSO, 300 MHz): 1.21 (*t*, $J = 7.4$, *Me*CH_2); 2.99 (*q*, $J = 7.4$, MeC*H*$_2$); 7.31 – 7.39 (*m*, 2 CH); 7.41 (br., NH_2); 7.49 (*m*, 1 CH); 7.83 (*d*, $J = 6.8$, 1 CH). ^{13}C-NMR ((D_6)DMSO, 75 MHz): 15.9 (Me); 25.7 (CH_2); 126.3 (CH); 127.5 (CH); 131.0 (CH); 132.4 (CH); 142.4 (C); 142.9 (C). HR-MS 185.05029 ($C_8H_{11}NO_2S^+$; calc. 185.05105).

3. *Sulfamates: General Procedure.* To chlorosulfonyl isocyanate (= sulfuryl chloride isocyanate; 3.5 ml, 40 mmol, 2.0 equiv.) at 0° under Ar, anh. formic acid (1.5 ml, 40 mmol, 2.0 equiv.) was added dropwise with rapid stirring. The mixture was stirred at r.t. until gas evolution ceased (from 1 to 4 h). To the resulting sulfamoyl chloride, a soln. of alcohol (20 mmol) in 1-methylpyrrolidin-2-one (30 ml) was added dropwise with ice-cooling over 30 – 60 min. The mixture was stirred at r.t. for 3 h (yellow-orange soln.) and was then poured into cold brine (100 ml) and washed twice with AcOEt (150 ml). The combined org. extract was dried ($MgSO_4$) and evaporated. Purification of the residue by FC (silica gel, pentane/AcOEt) afforded the desired sulfamate ester.

Butyl Sulfamate (**5a**): From butan-1-ol (1.8 ml), after FC (pentane/AcOEt 3 : 2): colorless oil (2.87 g, 94%). TLC: R_f 0.63. IR (neat): 3374, 3282, 2963, 1558, 1467, 1351, 1172, 920, 792. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.93 (*t*, $J = 7.4$, Me); 1.42 (*m*, 1 CH_2); 1.71 (*m*, 1 CH_2); 4.19 (*t*, $J = 6.6$, 1 CH_2); 5.36 (br., NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.4 (Me); 18.6 (CH_2); 30.6 (CH_2); 71.3 (CH_2O). HR-MS: 125.01121 ($C_2H_7NO_3S^+$; calc. 125.01185).

Pentyl Sulfamate (**5b**): From pentan-1-ol (2.2 ml), after FC (pentane/AcOEt 3 : 2): white solid (3.13 g, 94%). M.p. 59°. TLC: R_f 0.63. IR (neat): 3385, 3277, 2959, 2927, 2868, 1770, 1556, 1467, 1354, 1178, 965. ^{1}H-NMR

($CDCl_3$, 300 MHz): 0.93 (*t*, $J=7.0$, Me); 1.39 (*m*, 2 CH_2); 1.76 (*m*, 1 CH_2); 4.21 (*t*, $J=6.6$, 1 CH_2); 5.22 (br., NH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.9 (Me); 22.1 (CH_2); 27.5 (CH_2); 28.4 (CH_2); 71.6 (CH_2O). HR-MS: 138.02367 ($C_3H_8NO_3S^+$; calc138.02249).

Indan-2-yl Sulfamate (=*1,3-Dihydro-2*H*-inden-2-yl Sulfamate*; **5c**) [9a][11]: From indan-2-ol (2.68 g), after FC (pentane/AcOEt 1:1): white solid (2.52 g, 59%). M.p. 89°. TLC: R_f 0.56. IR (neat): 3347, 2938, 1750, 1731, 1349, 1207, 892. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.35 (*m*, 2 CH_2); 4.95 (br., NH_2); 5.46 (*m*, 1 CH); 7.22–7.30 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 39.8 (CH_2); 83.6 (CH); 124.7 (CH); 127.2 (CH); 139.3 (C).

4. *Cyclic Sulfonamides or Oxathiazinanes by Dirhodium(II) Complex Catalysis: General Procedure.* CH_2Cl_2 (3–5 ml) was added by syringe to the sulfonamide or sulfamate (0.3–0.5 mmol), $PhI(OAc)_2$ (1.5 equiv.), MgO (2.5 equiv.), activated 4-Å molecular sieves, and the rhodium catalyst (0.5–5 mol-%) under Ar at r.t. The resulting suspension was stirred vigorously under reflux until complete consumption of starting material was indicated by TLC. The mixture was diluted with CH_2Cl_2 (5 ml) and filtered through a pad of *Celite*. The filter cake was washed with CH_2Cl_2, the filtrate evaporated, and the residue purified by CC (silica gel, pentane/AcOEt): cyclic sulfonamide, or oxathiazinane or oxathiazole product.

3-Methyl-1,2-thiazinane 1,1-Dioxide (= *Tetrahydro-3-methyl-2*H*-1,2-thiazine 1,1-Dioxide*; **6b**): From **1b** (0.076 g, 0.50 mmol) and [$Rh_2(OAc)_4$] (5 mol-%), after FC (pentane/AcOEt 1:1): white solid (0.052 g, 70%). M.p. 113°. TLC ($KMnO_4$): R_f 0.30. GC (*β-Dex-120*, 145°, 2 min, then 0.25°/min): t_R 18.9, 19.9. IR (neat): 3271, 2930, 1726, 1287, 1132. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.21 (*d*, $J=8.4$, Me); 1.29 (*m*, 1 CH); 1.76 (*m*, 1 CH); 2.18 (*m*, 1 CH_2); 2.86 (*m*, 1 CH); 3.16 (*m*, 1 CH); 3.56 (*m*, 1 CH); 4.31 (br., NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): 21.4 (Me); 23.1 (CH_2); 31.9 (CH_2); 48.8 (CH_2); 52.6 (CH). HR-MS: 149.05042 ($C_4H_9NO_2S^+$; calc. 149.05105).

3-Ethyl-1,2-thiazinane 1,1-Dioxide (=*3-Ethyl-tetrahydro-2*H*-1,2-thiazine 1,1-Dioxide*; **6c**): From **1c** (0.082 g, 0.50 mmol) and [$Rh_2(OAc)_4$] (5 mol-%), after FC (pentane/AcOEt 1:1): colorless oil (0.063 g, 77%). TLC ($KMnO_4$) R_f 0.37. GC (*β-Dex-120*, 135°): t_R 48.5, 50.6. IR (neat): 3213, 2961, 2929, 1739, 1706, 1667, 1587, 1378, 1339, 1239, 1130, 779. ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.95 (*t*, $J=7.5$, Me); 1.51 (*m*, 1 CH_2); 1.77 (*m*, 1 CH); 2.17 (*m*, 1 CH_2); 2.87 (*m*, 1 CH); 3.16 (*m*, 1 CH_2); 3.36 (*m*, 1 CH); 4.32 (*d*, $J=9.2$, NH). ^{13}C-NMR ($CDCl_3$, 125 MHz): 10.1 (Me); 23.0 (CH_2); 28.6 (CH_2); 29.7 (CH_2); 49.2 (CH_2); 58.3 (CH). HR-MS: 163.06755 ($C_6H_{13}NO_2S^+$; calc. 163.06670).

3-Ethenyl-1,2-thiazinane 1,1-Dioxide (=*3-Ethenyl-tetrahydro-2*H*-thiazine 1,1-Dioxide*; **6d**) [12]: From **1d** (0.076 g, 0.50 mmol) and [$Rh_2(OAc)_4$] (5 mol-%), after FC (pentane/AcOEt 1:1): white solid (0.052 g, 70%). TLC ($KMnO_4$): R_f 0.30. GC (*Betadex-120*, 150°, 10 min, then 5.0°/min): t_R 18.8, 19.7. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.42 (*m*, 1 H, CH_2); 1.91 (*qd*, $J=3.1$, 14, 1 H, CH_2); 2.22–2.30 (*m*, 1 CH_2); 2.89–2.99 (*m*, 1 CH_2); 3.22 (*dt*, $J=3.6$, 13.4, 1 CH_2); 4.08 (*m*, 1 CH); 4.36 (*d*, $J=8.4$, NH); 5.21 (*d*, $J=10$, 1 H, CH_2); 5.28 (*d*, $J=18$, 1 H, CH_2); 5.82 (*ddd*, $J=5$, 10, 18, 1 CH). ^{13}C-NMR ($CDCl_3$, 125 MHz): 22.9 (CH_2); 29.7 (CH_2); 49.1 (CH_2); 57.9 (CH); 116.4 (CH_2); 136.4 (CH). HR-MS: 161.05184 ($C_6H_{11}NO_2S^+$; calc. 161.05105).

2,3-Dihydro-3-methyl-1,2-benzisothiazole 1,1-Dioxide (**8a**): From **4a** (0.092 g, 0.50 mmol) and [$Rh_2(OAc)_4$] (5 mol-%), after FC (pentane/AcOEt 1:2): brown oil (0.059 g, 65%). TLC: R_f 0.30. GC (*β-Dex-120*, 160°, 2 min, then 0.25°/min): t_R 57.0, 59.3. IR (neat): 3247, 2979, 1736, 1373, 1278, 1155, 1128, 756. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.62 (*d*, $J=6.8$, Me); 4.81 (*m*, 1 CH); 5.16 (br., NH); 7.40 (*d*, $J=7.7$, 1 CH); 7.53 (*m*, 1 CH); 7.64 (*m*, 1 CH); 7.77 (*d*, $J=7.7$, 1 CH). ^{13}C-NMR ($CDCl_3$, 75 MHz): 21.4 (Me); 53.4 (CH); 121.1 (CH); 124.0 (CH); 129.2 (CH); 133.2 (CH); 135.5 (C); 141.8 (C). HR-MS: 183.03358 ($C_8H_9NO_2S^+$; calc. 183.03540).

2,3-Dihydro-3-phenyl-1,2-benzisothiazole 1,1-Dioxide (**8b**): From **4b** (0.076 g, 0.50 mmol) and [$Rh_2(OAc)_4$] (5 mol-%), after FC (pentane/AcOEt 1:2): white solid (0.038 g, 45%). M.p. 130°. TLC: R_f 0.30. IR (neat): 3460, 3018, 2948, 1738, 1366, 1217. ^{1}H-NMR ($CDCl_3$, 500 MHz): 5.30 (br., NH); 5.73 (*d*, $J=3.6$, 1 CH); 7.15 (*m*, 1 CH); 7.39 (*m*, 2 CH); 7.58 (*m*, 2 CH); 7.70–7.78 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 61.4 (CH); 121.1 (CH); 123.1 (CH); 125.3 (CH); 126.6 (CH); 127.5 (CH); 130.4 (CH); 133.3 (C); 133.6 (C); 141.0 (C). HR-MS: 245.05366 ($C_{13}H_{11}NO_2S^+$; calc. 245.05105).

4-Methyl-1,2,3-oxathiazinane 2,2-Dioxide (= *Tetrahydro-4-methyl-1,2,3-oxathiazine 1,1-Dioxide*; **9a**): From **5a** (0.080 g, 0.52 mmol) and [$Rh_2(OAc)_4$] (5 mol-%), after FC (pentane/AcOEt 3.5:1): orange oil (0.070 g, 87%). TLC ($KMnO_4$): R_f 0.20. GC (*β-Dex-120*, 130°): t_R 39.64, 41.47. IR (neat): 3234, 1419, 1341, 1304, 1169, 1134, 1078, 1011, 960, 933, 868, 777, 715. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.30 (*d*, $J=6.6$, Me); 1.75 (*m*, 1 CH_2); 3.83 (*m*, CH); 4.27 (br., NH); 4.55 (*m*, 1 CH_2); 4.73 (*m*, 1 CH_2). ^{13}C-NMR ($CDCl_3$, 300 MHz): 20.9 (Me); 31.3 (CH_2); 52.0 (CH); 72.1 (CH_2O). EI-MS: 151 (10), 136 (62), 124 (100), 106 (9), 56 (19).

4-Ethyl-1,2,3-oxathiazinane 2,2-Dioxide (=*4-Ethyl-tetrahydro-1,2,3-oxathiazine 1,1-Dioxide*; **9b**): From **5b** (0.080 g, 0.52 mmol) and [$Rh_2(OAc)_4$] (5 mol-%), after FC (pentane/AcOEt 2:1): colorless oil (0.055 g, 67%). TLC ($KMnO_4$): R_f 0.30. GC (*β-Dex-120*, 135°): t_R 46.83, 47.99. IR (neat): 3262, 1419, 1349, 1179, 1014, 997, 861, 774. ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.02 (*t*, $J=7.5$, Me); 1.61 (*m*, 1 CH_2); 1.77 (*m*, 1 CH_2); 3.65 (*m*, 1 CH); 4.20

(br., NH); 4.57 (*m*, 1 H, CH_2); 4.74 (*m*, 1 H, CH_2). ^{13}C-NMR ($CDCl_3$, 75 MHz): 9.8 (Me); 28.3 (CH_2); 29.6 (CH_2); 57.6 (CH); 72.1 (CH_2O). HR-MS: 165.04506 ($C_5H_{11}NO_3S^+$; calc. 165.04597).

*3,3a,8,8a-Tetrahydroindeno[1,2-*d*]-1,2,3-oxathiazole 2,2-Dioxide* (**9c**) [9a][11]: From **5c** (0.085 g, 0.40 mmol) and [$Rh_2(OAc)_4$] (5 mol-%), after FC (CH_2Cl_2): white solid (0.046 g, 55%). M.p. 174°. TLC: R_f 0.34. HPLC (*OD-H*, 23°, hexane/^{i}PrOH 90 : 10, 0.5 ml/min): t_R 52.3, 59.3. IR (neat): 3008, 2970, 1739, 1438, 1366, 1217. ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.50 (*m*, 1 CH_2); 4.64 (br., NH); 5.33 (*t*, 1 CH); 5.55 (*m*, 1 CH); 7.30–7.42 (*m*, 4 CH). ^{13}C-NMR ($CDCl_3$, 75 MHz): 37.6 (CH_2); 64.4 (CH); 84.8 (CH); 125.4 (CH); 125.6 (CH); 128.4 (CH); 130.3 (CH); 137.4(C); 139.6 (C). HR-MS: 211.03161 ($C_9H_9NO_3S^+$; calc. 211.03032).

REFERENCES

[1] P. Dauban, R. H. Dodd, *Synlett* **2003**, 1571; P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905; I. D. G. Watson, A. K. Yudin, *Curr. Opin. Drug. Discov. Dev.* **2002**, *5*, 906; E. N. Jacobsen, in 'Comprehensive Asymmetric Catalysis', Eds. E. N. Jacobsen, A. Pfaltz, H. Zamamoto, Springer-Verlag, Berlin, 1999; Vol. 2, p. 607; P. Müller, in 'Advances in Catalytic Processes', Ed. M. P. Doyle, JAI Press, Greenwich, CT, 1997, Vol. 2, p. 113.

[2] P. Müller, C. Baud, Y. Jacquier, *Tetrahedron* **1996**, *52*, 1543; P. Müller, C. Baud, Y. Jacquier, *Can. J. Chem.* **1998**, *76*, 738; C. Baud, Ph.D. Thesis No. 2939, University of Geneva, 1997.

[3] P. Müller, C. Baud, Y. Jacquier, M. Moran, I. Nägeli, *J. Phys. Org. Chem.* **1996**, *9*, 341; I. Nägeli, C. Baud, G. Bernardelli, Y. Jacquier, M. Moran, P. Müller, *Helv. Chim. Acta* **1997**, *80*, 1087; I. Nägeli, Ph.D. Thesis No. 3018, University of Geneva, 1998.

[4] M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911.

[5] R. A. Abramovitch, T. D. Bailey, T. Takaya, V. Uma, *J. Org. Chem.* **1974**, *39,* 340; Y. Yamada, T. Yamamoto, M. Okawara, *Chem. Lett.* **1975**, 361.

[6] R. Breslow, S. H. Gellman, *J. Am. Chem. Soc.* **1983**, *105*, 6728; P. Müller, C. Baud, I. Nägeli, *J. Phys. Org. Chem.* **1998**, *11*, 597.

[7] P. Dauban, R. H. Dodd, *J. Org. Chem.* **1999**, *64*, 5304; P. H. Di Chenna, P. Dauban, A. Ghini, G. Burton, R. H. Dodd, *Tetrahedron Lett.* **2000**, *41*, 7041; P. H. Di. Chenna, P. Dauban, A. Ghini, R. Baggio, M. T. Garland, G. Burton, R. H. Dodd, *Tetrahedron* **2003**, *59*, 1009.

[8] F. Duran, L. Leman, A. Ghini, G. Burton, P. Dauban, R. H. Dodd, *Org. Lett.* **2002**, *4*, 2481.

[9] C. G. Espino, P. M. When, J. Chow, J. Du Bois, *J. Am. Chem. Soc.* **2001**, *123*, 6935; C. G. Espino, J. Du Bois, *Angew. Chem., Int. Ed.* **2001**, *40*, 598; A. Padwa, T. Stengel, *Org. Lett.* **2002**, *4*, 2137; E. Levites-Agababa, E. Menhaji, L. N. Perlson, C. M. Rojas, *Org. Lett.* **2002**, *4*, 863; P. M. When, J. Lee, J. Du Bois, *Org. Lett.* **2003**, *5*, 4823.

[10] S.-L. Liang, S.-X. Yuan, P. W. H. Chan, C.-M. Che, *Org. Lett.* **2002**, *4*, 4507; J.-L. Liang, S.-X. Yuan, P. W. H. Chan, C.-M. Che, *Tetrahedron Lett.* **2003**, *44*, 5917.

[11] J.-L. Liang, S.-X. Yuan, J.-S. Huang, W.-Y. Yu, C.-M. Che, *Angew. Chem., Int. Ed.* **2002**, *41*, 3465.

[12] P. Dauban, R. H. Dodd, *Org. Lett.* **2000**, *2,* 2327.

[13] S. L. Mac Neil, O. B. Familoni, V. Snieckus, *J. Org. Chem.* **2001**, *66*, 3662.

[14] R.-J. De Lang, M. J. C. M. Van Hooijdonk, L. Brandsma, *Tetrahedron* **1998**, 2953.

[15] J. G. Lombardino, *J. Org. Chem.* **1971**, *36*, 1843.

[16] M. Okada, S. Iwashita, N. Koizumi, *Tetrahedron Lett.* **2000**, *41*, 7047.

[17] R. E. Meléndez, W. D. Lubell, *Tetrahedron* **2003**, *59*, 2581.

[18] K. C. Nicolaou, X. Huang, S. A. Snyder, P. B. Rao, M. Bella, M. V. Reddy, *Angew. Chem., Int. Ed.* **2002**, *41*, 834.

[19] M. Atfani, L. Wei, W. D. Lubell, *Org. Lett.* **2001**, *3*, 2965.

[20] A. J. Williams, S. Chakthong, D. Gray, R. M. Lawrence, T. Gallagher, *Org. Lett.* **2003**, *5*, 811.

[21] B. Aguilera, A. Fernández-Mayoralas, *J. Chem. Soc., Chem. Commun.* **1996**, 127.

[22] S. B. Cohen, R. L. Halcomb, *J. Am. Chem. Soc.* **2002**, *124*, 2534.

[23] J. J. Fleming, K. W. Fiori, J. Du Bois, *J. Am. Chem. Soc.* **2003**, *125*, 2028.

[24] P. Müller, Y. Allenbach, E. Robert, *Tetrahedron Asymmetry* **2003**, *14*, 779.

[25] Y. F. Allenbach, Ph. D. Thesis, University of Geneva, 2003.

[26] C. Fruit, P. Müller, *Tetrahedron: Asymmetry* **2004**, *15*, 1019.

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