81. Rhodium(II)-Catalyzed CH Insertions with {[(4-Nitrophenyl)sulfonyl]imino}phenyl-λ^3-iodane

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Dedicated to Prof. *Dieter Seebach* on the occasion of his 60th birthday

(13.II.97)

The $[Rh_2(OAc)_4]$-catalyzed decomposition of {[(4-nitrophenyl)sulfonyl]imino}phenyl-λ^3-iodane (NsN=IPh) resulted in formal insertions into CH bonds, activated by phenyl or vinyl groups, or by O-substituents. Scope and limitations of the reaction were investigated. Yields of up to 84% were achieved in the most favorable cases. Yields were enhanced by electron-releasing substituents and decreased by steric hindrance. Aziridination competed with allylic insertion with olefinic substrates. The insertion reaction proceeded with retention of configuration. With chiral Rh^{II} catalysts, a modest asymmetric induction was observed. A mechanism involving direct insertion by a Rh-complexed nitrene into the CH bond is proposed.

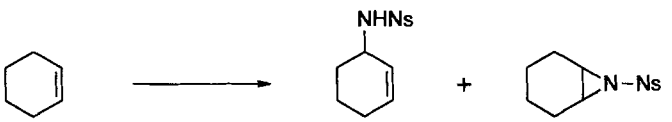
1. Introduction. – The transition-metal-catalyzed transfer of carbenes to organic compounds is a well-established synthetic method, and several systems for enantioselective cyclopropanation [1], cyclopropenation [2], and CH insertion [3] have been developed. The corresponding reactions of carbene analogs are, however, much less known. An exception to this is the transfer of sulfonylnitrene from TsN=IPh (phenyl[(tosylsulfonyl)imino]-λ^3-iodane = [4-methylbenzenesulfonamidato(2−)-*N*]phenyliodide) [4]. *Mansuy et al.* reported the aziridination of olefins with TsN=IPh in the presence of Fe^{III} and Mn^{III} porphyrinates [5], and subsequently, *Evans et al.* described an enantioselective aziridination of olefins using TsN=IPh and chiral Cu^{I} catalysts [6]. *Jacobsen*'s *Schiff*-base ligands exhibited particular efficiency in Cu-catalyzed aziridinations [7].

Prior to this, however, *Breslow* and *Gellman* had reported the low-yield (3.1–6.5%, based on λ^3-iodane) *p*-toluenesulfonamidation of cyclohexane with TsN=IPh under catalysis with Mn^{III} or Fe^{III} porphyrinates [8], while the phenyl-λ^3-iodane derived from 2,5-diisopropylbenzenesulfonamide underwent intramolecular CH insertion in 86% yield when exposed to $[Rh_2(OAc)_4]$ [9]. Insertion products have been repeatedly observed upon aziridination of olefins with TsN=IPh under catalysis with Mn^{III} or, less efficiently, Fe^{III} porphyrinates [6]. Cyclohexane and adamantane (at the bridgehead) were amidated with TsN=IPh in 15 and 56% yield, respectively, in the presence of [Mn(tdcpp)] (tdcpp = tetrakis(2,6-dichlorophenyl)porphyrinato). A radical mechanism, initiated by H-abstraction by a high-valent Mn-nitrene intermediate was proposed for the Mn-catalyzed insertions [10]. However, the catalyzed amidation with TsN=IPh has so far not been exploited for synthetic applications.

[1]) Part of the planned Ph. D. Thesis.

We have recently reported the Rh^{II}-catalyzed aziridination of olefins using NsN=IPh ({[(4-nitrophenyl)sulfonyl]imino}phenyl-λ^3-iodane = [4-nitrobenzenesulfonamidato-(2–)-*N*]phenyliodine) as source of the nitrene [11]. In this context, we observed a high yield (70%) of allylic 4-nitrobenzenesulfonamide **2b** upon exposure of cyclohexene (**1b**) to NsN=IPh/$[Rh_2(OAc)_4]$, while the aziridine **3b** was formed in only 5% yield. We have now investigated this formal insertion reaction with the objective of developing a synthetic procedure for metal-catalyzed nitrene insertions. Some of our results have been published in preliminary form [12].

Scheme 1



1b **2b** **3b**

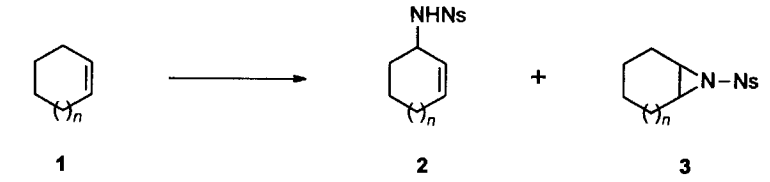
Ns = (4-nitrophenyl)sulfonyl

2. Results and Discussion. – 2.1. *Scope and Limitations.* A series of model compounds was investigated to establish the scope of the amidation. Reactions were run in CH_2Cl_2 at room temperature in the presence of 0.02 equiv. of $[Rh_2(OAc)_4]$ relative to NsN=IPh (see *Exper. Part*). Since NsN=IPh decomposes slowly in the presence of $[Rh_2(OAc)_4]$, the reactions were carried out with a 20-fold excess of substrate. Yields are expressed relative to NsN=IPh (*Schemes 2* and *3*).

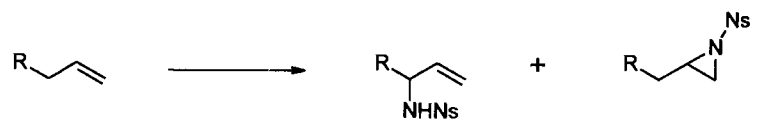
In the cycloalkene series, the ratio of amidation/aziridination (*i.e.*, **2**/**3**) varied with ring size from 83:17 for cyclopentene (**1a**) to 95:5 for cyclohexene (**1b**) and 41:59 for cycloheptene (**1c**), while aziridination occurred exclusively with cyclooctene (**1d**) (see *Scheme 2*). A parallel trend has been reported for the Pd-catalyzed allylic acetoxylation/epoxidation of cycloalkenes with hydrogen peroxide [13]. In general, however, olefins reacted *via* aziridination, rather than insertion. Even penta-1,4-diene (**4a**) and 3-phenylpropene (**4b**), where the CH_2 groups are activated by two C=C bonds or by one C=C bond and a Ph group, reacted preferentially, if not exclusively, *via* attack at the C=C bond (**5a**/**6a** 0:100, **5b**/**6b** 9:91).

Reactions with arylalkanes gave the most satisfactory results; insertion into benzylic CH_2 groups occurred in 50–69% yield for ethylbenzene (**7b**), indan (**9a**), and tetralin (**9b**) (→ **8a**, **10a**, and **10b**, resp.; see *Scheme 2*). The reaction showed a marked sensitivity with respect to substituents: While toluene (**7a**) was almost totally inert (3% of **8a**), ethylbenzene (**7b**) reacted with 50% yield, but the yield decreased to 8% with isopropylbenzene (**7c**). The presence of a second Ph group in the α-position of the reacting CH bonds was detrimental, and only 13% of substitution product **8d** was obtained from diphenylmethane (**7d**). The higher reactivity of Et *vs.* Me groups points out the necessity for electronic stabilization in the transition state of the reaction. However, the fact that **7c** and **7d** are again less reactive than ethylbenzene (**7b**) contradicts the expected trend and is best attributed to steric hindrance. When the reactions of the unreactive arylalkanes were repeated at 83° (refluxing dichloroethane), the product yields increased significantly, and **8a**, **8c**, and **8d** were isolated in yields of 16, 18, and 50%, respectively.

Scheme 2



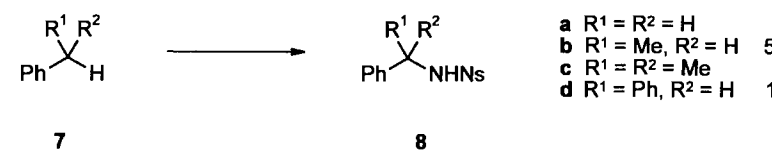
a $n = 0$	44%	9%
b $n = 1$	70%	4%
c $n = 2$	17%	24%
d $n = 3$	0%	54%



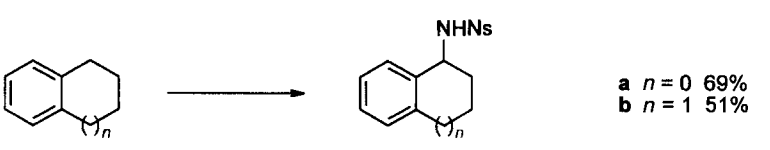
4a R = $CH{=}CH_2$
b R = Ph

5a R = $CH{=}CH_2$ (0%)
b R = Ph (3%)

6a R = $CH{=}CH_2$ (40%)
b R = Ph (32%)



a $R^1 = R^2 = H$ 3%
b R^1 = Me, $R^2 = H$ 50%
c $R^1 = R^2$ = Me 8%
d R^1 = Ph, $R^2 = H$ 13%



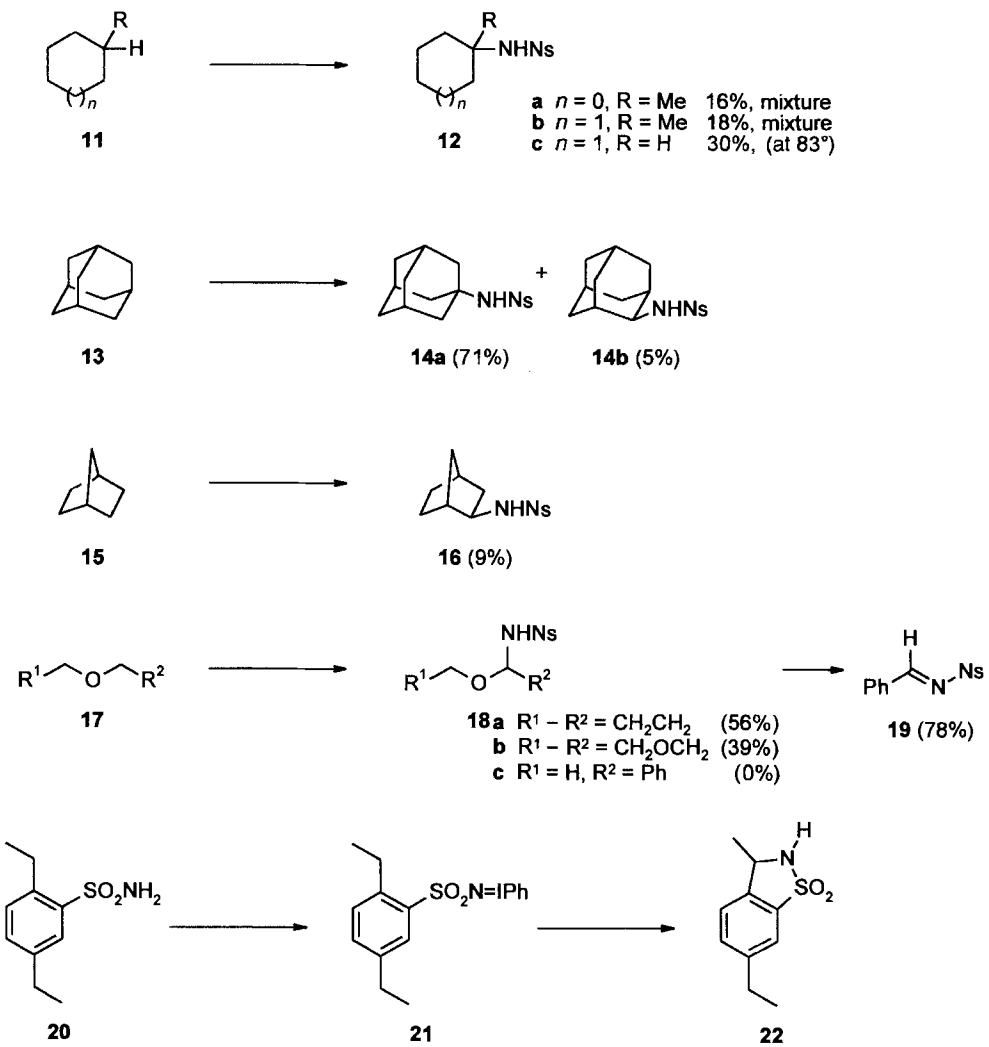
a $n = 0$ 69%
b $n = 1$ 51%

Ns = (4-nitrophenyl)sulfonyl

Hydrocarbons reacted only sluggishly and unselectively with NsN=IPh/$[Rh_2(OAc)_4]$. Typically, methylcyclopentane (**11a**) and methylcyclohexane (**11b**) afforded a 16 and 18% yield of amidation products **12a** and **12b**, respectively, as an untractable mixture of isomers (*Scheme 3*). Cyclohexane (**11c**) was unreactive at room temperature, but reacted in refluxing dichloroethane to afford a 30% yield of **12c**. Adamantane (**13**) underwent reaction almost exclusively at the bridgehead position to afford **14a** in 71% yield, while only a trace (5%) of insertion into the CH_2 group to **14b** occurred. In

contrast, trinorbornane **15** gave no bridgehead derivative, but reacted at C(2) to afford **16** in moderate yield (9%). The structure of **16** was unambiguously established by comparison of its spectral data with those of the sulfonamide prepared independently from commercial 8,9,10-trinorbornane-2-*exo*-amine (= 2-aminonorbornane). The tendencies for nitrene insertion into CH bonds upon photochemical decomposition of ethyl azidoformate ($N_3C(=O)OEt$), which is believed to proceed from the singlet state [14] are somewhat different [15]: The bridgehead reactivity (per H-atom) of adamantane (**13**) is 6.3, while that at the secondary position is 0.94. This would result in a **14a**/**14b** product ratio of *ca.* 2:1. The bridgehead and 7-positions of trinorbornane **15** are very unreactive

Scheme 3



Ns = (4-nitrophenyl)sulfonyl

(0.44 and 0.19), and attack occurs preferentially at the *exo* bond at C(2). The trend observed with NsN=IPh may be attributed to a stronger electrophilic character of the sulfonylnitrene in comparison to the (ethoxycarbonyl)nitrene. However, a steric effect owing to complexation of the nitrene by Rh^{II} may also intervene.

Insertion occurred also into CH_2 groups in α-position of ethers, as exemplified by the reaction of tetrahydrofuran (**17a**; 56%) and 1,4-dioxane (**17b**: 39%; *Scheme 3*), but no products derived from insertion into methine groups activated by ether O-atoms (*i.e.*, 2,5-dimethyltetrahydrofuran, *sec*-butyl methyl ether (= 2-methoxybutane), *cis*-2,5-dimethyl-1,4-dioxane-3,6-dione) could be isolated. The insertion products of benzyl methyl ether (**17c**) underwent elimination of MeOH and was isolated as the benzenemethanimine **19** in 78% yield. An analogous imine has been isolated upon attempted tosylaziridination of cinnamyl methyl ether [6]. No reaction occurred, however, at the α-position of amines and amides.

The intramolecular version of the benzylic amidation was investigated with the ylide **21** which was synthesized from 1,4-diethylbenzene *via* the sulfonamide **20** [16] (*Scheme 3*). The insertion product **22** was formed in 35% yield when **21** was exposed to $[Rh_2(OAc)_4]$ under standard conditions.

2.2. *Optimization of Reaction Conditions.* A series of experiments were performed with cyclohexene (**1b**) and indan (**9a**) to establish optimal conditions with respect to yield and chemoselectivity of the reaction. The rhodium(II) carboxylates were clearly more efficient than the carboxamidates, *i.e.*, $[Rh_2\{(S)\text{-mepy}\}_4]$ ((*S*)-mepy = methyl (2*S*)-5-oxopyrrolidine-2-carboxylato) [2] [3] (see *Table 1, Entry 2*). This latter catalyst produced equally low yields with cyclopentene (**1a**), cycloheptene (**1c**), and cyclooctene (**1d**). The reaction of **1a** or **11c** with $[Rh_2(pfb)_4]$ (pfb = perfluorobutanoato) [17] resulted in a very low overall yield (< 10% in refluxing dichloroethane) of amidation and aziridination products. Chemoselectivity and yields changed only little with solvent or temperature, but were strongly influenced by the bulk of the carboxylato ligands. The amidation/aziridination ratio **2b**/**3b** changed from 95:5 with $[Rh_2(OAc)_4]$ to 48:52 with *Ikegami*'s highly crowded tetrakis(*N*-phthaloylphenylalaninato)dirhodium(II) ($[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$) (see *Table 1, Entry 3*). Cu-Catalysts reportedly afford only minor amounts of allylic insertion products with **1b** [6]. The highest yields of **2b** were obtained at 20° in CH_2Cl_2 containing 5% of sulfolane (= tetrahydrothiophene 1,1-dioxide) (see *Table 1, Entry 16*). Other effective solvents are acetone (total yield 48%), chlorobenzene (57%), methyl acetate (55%), dimethyl carbonate (69%), and nitromethane containing 5% of DMPU (49%) (DMPU = 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one). Particularly poor results were recorded with dimethylformamide, nitromethane, and *t*-BuOMe (*tert*-butyl methyl ether). No reaction, except decomposition of NsN=IPh to $NsNH_2$ occurred in pure DMPU and pyridine.

The beneficial effect of the adjonction of sulfolane to CH_2Cl_2 was further investigated with ethylbenzene (**7b**). Neat CH_2Cl_2 afforded the amidation product **8b** in 50% yield. With 2.5% of added sulfolane, the yield decreased to 44%, but it increased to 70% in the presence of 5% of sulfolane (*Table 2*). Further addition of sulfolane (10 and 50%) resulted in decreasing yields of 50 and 25%, respectively. The same trend was observed with indan (**9a**). The effect of small amounts of sulfolane in the solvent resulted in

Table 1. *Effects of Catalyst and Reaction Conditions on Amidation of Cyclohexene* (**1b**)[a])

Entry	Catalyst	Solvent	T [°C]	Yield (**2b** + **3b**)	Ratio **2b**/**3**
1	$[Rh_2(OAc)_4]$	CH_2Cl_2	20	58	91:9
2	$[Rh_2\{(S)\text{-mepy}\}_4]$	CH_2Cl_2	20	5	91:9
3	$[Rh_2\{(S)\text{-ptpa}\}_4]$	CH_2Cl_2	20	72	48:52
4	$[Rh_2(OAc)_4]$	$ClCH_2CH_2Cl$	83	55	92:8
5	$[Rh_2(OAc)_4]$	CH_2Cl_2	40	55	88:12
6	$[Rh_2(OAc)_4]$	C_6H_6	80	41	85:15
7	$[Rh_2(OAc)_4]$	$MeNO_2$	20	23	91:9
8	$[Rh_2(OAc)_4]$	MeC(O)Me	20	48	94:6
9	$[Rh_2(OAc)_4]$	MeC(O)Me	56	26	93:7
10	$[Rh_2(OAc)_4]$	$PhNO_2$	20	48	97:3
11	$[Rh_2(OAc)_4]$	$PhNO_2$	80	52	92:8
12	$[Rh_2(OAc)_4]$	PhCl	20	57	87:13
13	$[Rh_2(OAc)_4]$	*t*-BuOMe	20	32	87:13
14	$[Rh_2(OAc)_4]$	AcOMe	20	55	91:9
15	$[Rh_2(OAc)_4]$	$(MeO)_2CO$	20	69	89:11
16	$[Rh_2(OAc)_4]$	$CH_2Cl_2/(CH_2)_4SO_2$[b])	20	78	92:8
17	$[Rh_2(OAc)_4]$	CH_2Cl_2/DMPU[b])	20	16	95:5
18	$[Rh_2(OAc)_4]$	$MeNO_2$/DMPU[b])	20	49	89:11
19	$[Rh_2(OAc)_4]$	*t*-BuOMe/$(CH_2)_4SO_2$[b])	20	40	94:6

[a]) Conditions: 20 mmol of **1b**, 1 mmol of NsN=IPh, 0.02 mmol of catalyst, 5.0 g of molecular sieves, 15 ml of solvent.

[b]) 5% of cosolvent.

significantly higher yields of amidation products in all other cases studied, except with adamantane (**13**) where the yield is lower (see *Table 2*).

When the ratio of substrate to NsN=IPh was lowered, the yields decreased. For example, tetralin (**9b**) afforded a 51% yield (with respect to NsN=IPh) of amidation product **10b** under standard conditions (in CH_2Cl_2), when used in 20-fold excess. The yield decreased to 10% when the **9b**/ylide ratio was 1:1 and to 12% (with respect to **9b**) with a ratio **9b**/ylide of 1:0.5. This is ascribed to the previously mentioned competitive decomposition of NsN=IPh by $[Rh_2(OAc)_4]$.

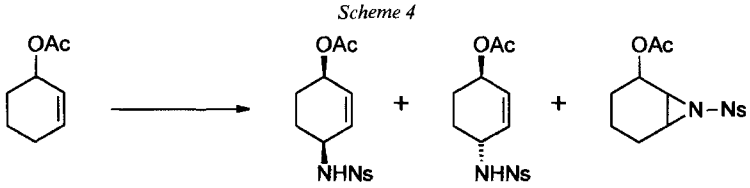
2.3 *Mechanistic Aspects.* The allylic amination of cyclohexene (**1b**) could occur either by an insertion mechanism, by an ene reaction, or by ring opening of an intermediate aziridine **3b**. In order to distinguish between these mechanisms, the amidation of cyclohex-2-en-1-yl acetate (**23**) with NsN=IPh/$[Rh_2(OAc)_4]$ was investigated. The reaction afforded a 43% yield of insertion products as a 1:1 mixture of the *cis*- and *trans*-isomers **24** and **25**, respectively, together with a small amount (4%) of aziridine **26**, the relative configuration of which was not determined. The isomers were separated by prep. HPLC. An attempt was made to determine the structure of isomer **25**, which has the longer retention time on the *Lichrosorb Si 60* column, by X-ray crystallography. However, the crystals were disordered to such a degree that only the *trans*-configuration of the acetoxy and sulfonamido substituents could be determined with certainty.

Table 2. *Yields of Amidation Products in 5% Sulfolan/CH_2Cl_2*[a])

Reactant	Solvent	Yield [%]	Yield [%] in CH_2Cl_2
1a	5% $(CH_2)_4SO_2/CH_2Cl_2$	61[b])	44
13	5% $(CH_2)_4SO_2/CH_2Cl_2$	51	71
15	5% $(CH_2)_4SO_2/CH_2Cl_2$	14.4	9.3
7b	50% $(CH_2)_4SO_2/CH_2Cl_2$	25	50
	10% $(CH_2)_4SO_2/CH_2Cl_2$	50	50
	5% $(CH_2)_4SO_2/CH_2Cl_2$	70	50
	2.5% $(CH_2)_4SO_2/CH_2Cl_2$	44	50
7c	5% $(CH_2)_4SO_2/CH_2Cl_2$	13	8
7d	5% $(CH_2)_4SO_2/CH_2Cl_2$	16	13
9a	5% DMPU/CH_2Cl_2	8	69
	1% $(CH_2)_4SO_2/CH_2ClCH_2Cl$	63	69
	5% $(CH_2)_4SO_2/CH_2ClCH_2Cl$	72	69
	PhCl	52	69
	$(MeO)_2CO$	71	69
9b	5% $(CH_2)_4SO_2/CH_2Cl_2$	75	51

[a]) Conditions: see *Table 1*; room temperature.
[b]) + 10% of **3a**.

Scheme 4



23 **24** (22%) **25** (21%) **26** (4%)

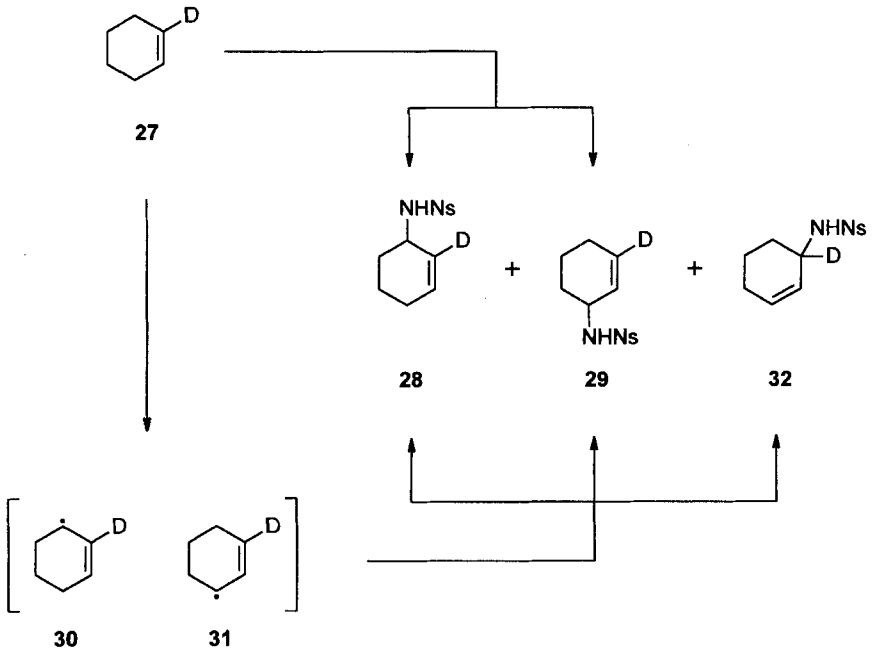
Ns = (4-nitrophenyl)sulfonyl

The 1,4-substitution pattern of **24** and **25** rules out the intermediacy of the aziridine **26** as a reactive intermediate, since ring-opening of **26** would afford a 1,2- or 1,3-disubstituted cyclohexene. It is also inconsistent with the ene mechanism.

The CH insertion of singlet nitrenes proceeds with retention of configuration [18] in analogy to that of singlet carbenes, while triplet nitrenes react *via* H-abstraction/radical recombination [19]. The amidation of the labeled (1-D)cyclohexene (**27**) by direct insertion is expected to afford a 1:1 mixture of two isomeric products **28** and **29**, while for the stepwise mechanism, two isomeric radicals **30** and **31** should be formed, resulting in a 2:1:1 ratio of sulfonamides **28**, **29**, and **32**, respectively.

(1-D)Cyclohexene (**27**) was synthesized by reduction of cyclohexanone with $LiAlD_4$ to (1-D)cyclohexanol, which underwent elimination *via* the tosylate [20]. Amidation of **27** with NsN=IPh/$[Rh_2(OAc)_4]$ afforded **28** and **29** in a 1:1 ratio, as expected for the insertion mechanism, although a trace of contamination tentatively ascribed to **32** was also present. Although this result is consistent with the insertion mechanism, the two-step pathway cannot be definitely ruled out, since a fast radical recombination leading to *ipso* attack could occur faster than reorientation of the radicals which is required for the formation of **32**.

Scheme 5



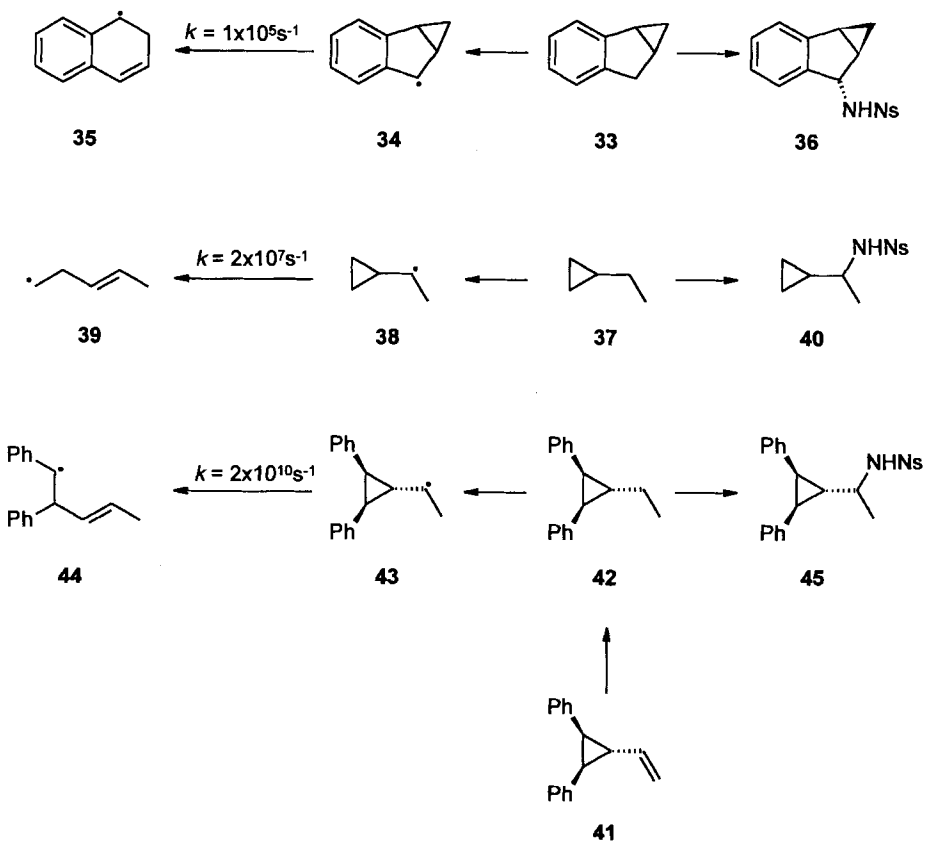
Ns = (4-nitrophenyl)sulfonyl

The possible intervention of radicals in the amidation was further tested by the use of radical clocks [21]. The secondary radical **34** derived from tetrahydrocyclopprop[*a*]indene **33** undergoes ring-opening to **35** with a rate constant of $1 \cdot 10^5\ s^{-1}$ [22] (see *Scheme 6*). The amidation of **33**, which is readily available *via* cyclopropanation of indene [23], proceeded to **36** with a yield of 84%. The *trans*-orientation of the sulfonamido substituent relative to the cyclopropane ring in **36** was determined by X-ray crystal-structure analysis (see *Exper. Part*).

Other radical clocks with higher rate constants for ring-opening produced substitution products without rearrangements, although the product yields were much lower. The rate constants for ring-opening of the secondary 1-cyclopropylethyl radical (**38**) to **39**, and for its diphenyl derivative **43** to **44** are $2 \cdot 10^7\ s^{-1}$ and $2 \cdot 10^{10}\ s^{-1}$, respectively [24]. Ethylcyclopropane (**37**) was synthesized *via Wolff-Kishner* reduction of 1-cyclopropylethanone [25]. It reacted in 21% yield to afford **40**; only unreacted **37**, but no products derived from **39** were detected in the reaction mixture. Pt-Catalyzed [26] hydrogenation of (*t*-3-ethenylcyclopropane-*r*-1,*c*-2-diyl)bis(benzene) (**41**) [27] afforded **42** which underwent amidation in low yield (5%) to **45**, again without formation of ring-opened products.

The significance of the results with **37** and **42** suffers seriously from the poor product yields. Nevertheless, it may be concluded that the reactions must proceed either *via* a direct insertion mechanism, or by H-abstraction/radical recombination where the second step is extremely fast.

Scheme 6



Ns = (4-nitrophenyl)sulfonyl

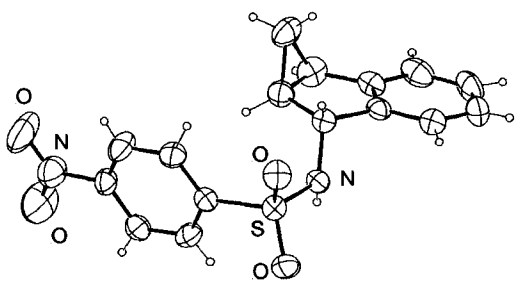


Fig. 1. *Perspective view of the crystal structure of 4-nitro-*N*-[(1a*RS,*6*RS,*6a*SR*)-1,1α,6,6α-tetrahydrocyclo-prop[a]inden-6-yl]benzenesulfonamide* (**36**). Ellipsoids are represented at 50% probability level.

The polar substituent effect of the reaction was investigated by competition experiments using pairs of substituted ethylbenzenes **7b** and **7e–i** (see *Table 3*). Relative rate constants were determined from the product ratios of the sulfonamides **8b** and **8e–i** as

Table 3. Hammett *Plot for Sulfonamidation of 4-Substituted Ethylbenzenes* 7 (see *Scheme 2*, R^1 = Me, R^2 = H) *with NsN=IPh/[Rh$_2$(OAc)$_4$]*

	Substituent at Ph	σ^+	log (k/k_0)	Yield [%] of **8**[a])	M.p. [°] of **8**[a])
7e	4-MeO	−0.78	0.62	58	148
7f	4-Me	−0.31	0.36	61	108–110
7g	4-Ph	−0.18	0.28	68	165–170
7b	H	0	0	51	124–125
7h	4-Br	0.15	−0.16	68	161–164
7i	4-NO_2	0.79	−0.73	55	153–155

[a]) For *Formulae*, see **8** in *Scheme 2* (R^1 = Me, R^2 = H).

determined by ^{1}H-NMR and GLC (see *Exper. Part*). The plot of log k_{rel} *vs.* σ^+ is shown in *Fig. 2*. The *Hammett* ρ constant is −0.90, somewhat higher than that of −0.60 measured for aziridination of styrenes with NsN=IPh/[Rh$_2$(OAc)$_4$] [12].

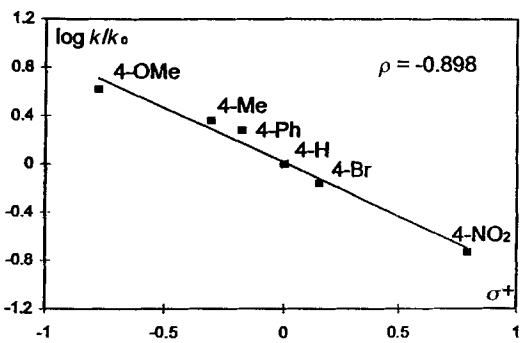
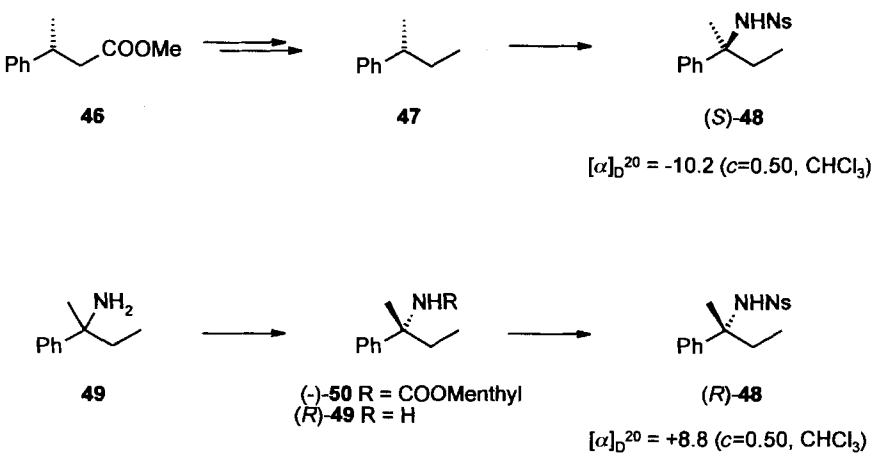


Fig. 2. Hammett *plot for amidation of ethylbenzenes* **7b** *and* **7e**–**i** *with NsN=IPh/[Rh$_2$(OAc)$_4$]*. ρ = −0.90; r = 0.988; σ = 0.083.

(1,3-D_2)Adamantane (1,3-D_2-**13**) was chosen for the determination of the intramolecular kinetic isotope effect of the reaction, because **13** is the only hydrocarbon reacting in high yields at a tertiary CH bond. This allows the determination of the primary isotope effect without the intervention of secondary effects. The compound was synthesized with 98.2% deuterium content by reduction of 1,3-dibromoadamantane with $LiAlD_4$ in the presence of Bu_3SnCl [28]. After the amidation, the 2-isomer D_2-**14** was separated by chromatography and the ratio of mono- and dideuterated D_1- and D_2-**14a** was determined by MS. After correction for 100% D-content in 1,3-D_2-**13**, the isotope effect was calculated to 3.5 ± 0.2 by means of the equations given by *Meunier et al.* [28]. The interpretation of this value is unfortunately not straightforward, since there are no data available for isotope effects in intermolecular nitrene insertions for comparison. *Meunier et al.* [28] reported isotope effects of H-abstraction from D_2-adamantane by metalloporphyrins. The values varied from 2.83 to 8.71, depending on the metal, the solvent, and the O-donor. In the light of these enormous variations, our single value is of limited significance and could accommodate an insertion as well as a H-abstraction mechanism.

The stereochemical course of the amidation was investigated using (*R*)-2-phenylbutane (**47**) as substrate which was obtained by reduction of commercially available optically active methyl (*R*)-3-phenylbutanoate (**46**) (*Scheme 7*). As with other tertiary CH bonds, the yield of amidation product **48** obtained from **47** was very low (3%), even when the reaction was carried out at elevated temperature. Nevertheless, **48** was optically active ($[\alpha]_D^{20} = -10.2$ ($CHCl_3$, $c = 0.50$)). Its absolute configuration was determined to be (*S*) by comparison with the optical rotation of an independently prepared sample of (*R*)-**48**: Racemic 2-phenylbutan-2-amine (**49**) was synthesized according to literature procedures [29]. The resolution of the racemate *via* the tartrate, which is described in [30] failed in our hands. The amine **49** was, therefore, converted to the carbamate **50** by reaction with (1*R*)-menthyl chloroformate. A portion of the more polar diastereoisomer (–)-**50** was separated by MPLC and cleaved with KOH in diethylene glycol (100°, 20 h) to afford (*R*)-**49** of known absolute configuration [31] (see *Exper. Part*). Reaction of (*R*)-**49** with 4-nitrobenzenesulfonyl chloride afforded the sulfonamide (*R*)-**48** with $[\alpha]_D^{20} = +8.8$ ($CHCl_3$, $c = 0.34$). The sulfonamide **48** obtained in the insertion reaction has, therefore, (*S*)-configuration. Since replacement of the H-atom of **47** by the sulfonamide group results in a change of the substituent priorities in the CIP system, the formation of (*S*)-**48** from (*R*)-configurated **47** corresponds to retention of configuration.

Scheme 7

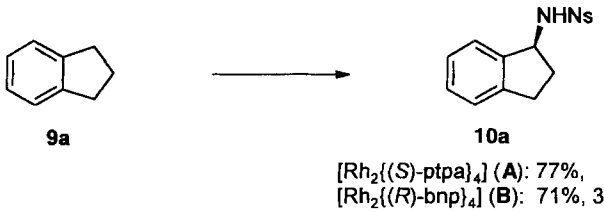


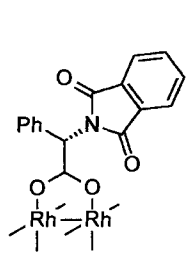
Ns = (4-nitrophenyl)sulfonyl

Preliminary experiments show that the Rh^{II}-catalyzed amidation with NsN=Ph can be enantioselective. Indan (**9a**) reacted in the presence of *Ikegami*'s tetrakis[μ-(*S*)-*N*-phthaloylphenylalaninato-O^1,O^1]dirhodium(II)(*Rh–Rh*) (**A**) [32] to **10a** with 77% yield and 7% ee. With *Pirrung*'s {μ-(*R*)-[1,1'-bi(naphthalene)]-2,2'-diyl phosphato-*O*,*O*}-dirhodium(II)(*Rh–Rh*) (**B**) [33], the yield was 71% with 31% ee.

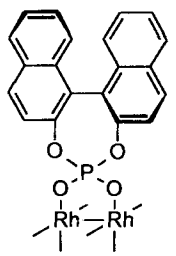
Conclusion. – The Rh^{II}-catalyzed decomposition of NsN=IPh results in intermolecular nitrene insertion into activated CH bonds with appreciable yields. The reaction is remarkable because the analogous intermolecular carbenoid insertions are practically

Scheme 8





A



B

not observed. The results obtained this far for the Rh^{II}-catalyzed CH insertion with NsN=IPh are consistent with a direct nitrene insertion mechanism, and no evidence for a two-step radical process was found. This contrasts with the corresponding TsN=IPh/[Mn(tpp)Cl] (tpp = tetraphenylporphyrinato) system, where CH insertions proceed *via* a radical pathway. The recently developed system for cleavage of 4-nitrobenzenesulfonamide under mild S_NAr conditions [34] adds further attractiveness to this method for hydrocarbon functionalization.

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Experimental Part

1. *General.* See [35].

2. *{[(4-Nitrophenyl)sulfonyl]imino}phenyl-λ³-iodane* (NsN=IPh). NsN=IPh was prepared in 98% yield according to the procedure described for TsN=IPh [4]. IR (KBr): 3100*m*, 1525*vs*, 1346*s*, 1274*s*, 1125*s*, 1080*s*, 878*m*, 853*s*, 736*s*. ^{1}H-NMR (400 MHz, (D_7)DMF): 7.40 (*m*, 2 H); 7.51 (*m*, 1 H); 7.92 (*m*, 4 H); 8.18 (*d*, J = 8.7, 2 H). ^{13}C-NMR ((D_7)DMF): 128.1 (*d*); 132.2 (*d*); 134.9 (*d*); 135.3 (*d*); 137.9 (*d*); 149.2 (*s*); 152.4 (*s*). MS: 404 (0.4, M^+), 204(62), 186(60), 122(62), 77(100). HR-MS: 403.9288 ($C_{12}H_9IN_2O_4S^+$; calc. 403.9328).

3. *General Procedure for [Rh₂(OAc)₄]-Catalyzed CH Insertion with NsN=IPh.* The substrate (20 mmol) in CH_2Cl_2 (5.0 ml) was added at r.t., by means of a syringe and with stirring, to 4 Å molecular sieves (5.0 g) suspended in dry CH_2Cl_2 (5.0 ml) containing $[Rh_2(OAc)_4]$ (0.02 mmol) under N_2. After 10 min, NsN=IPh (404 mg, 1.0 mmol) was added and the mixture was stirred at r.t. for 15 h. The soln. was then filtered with CH_2Cl_2 through silica gel (3 g), and the products were separated and purified by column chromatography (SiO_2).

4. *Characterization of Insertion and Aziridination Products.* N-*(Cyclopent-2-en-1-yl)-4-nitrobenzenesulfonamide* (**2a**): M.p. 140–141°. IR ($CHCl_3$): 3376*m*, 3030*m*, 2857*w*, 1607*w*, 1534*s*, 1417*w*, 1351*s*, 1312*w*, 1166*s*, 1094*m*, 1061*w*, 909*w*, 855*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.50–1.57 (*m*, 1 H); 2.16–2.29 (*m*, 2 H); 2.37–2.44 (*m*, 1 H); 4.48–4.52 (*m*, 1 H); 4.55 (*d*, *J* = 9.2, 1 H); 5.46–5.49 (*m*, 1 H); 5.92–5.95 (*m*, 1 H); 8.08 (*d*, *J* = 8.8, 2 H); 8.38 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 30.9 (*t*); 31.8 (*t*); 60.3 (*d*); 124.4 (*d*); 128.3 (*d*); 129.8 (*d*); 136.0 (*d*); 147.3 (*s*); 150.2 (*s*). MS: 268 (5, M^+), 204 (9), 187 (5), 122 (11), 82 (100), 67 (56), 55 (45). HR-MS: 268.0491 ($C_{11}H_{12}N_2O_4S^+$; calc. 268.0518).

6-[(4-Nitrophenyl)sulfonyl]-6-azabicyclo[3.1.0]hexane (**3a**): M.p. 93–94°. IR ($CHCl_3$): 3028*w*, 2962*w*, 1608*w*, 1594*s*, 1351*s*, 1333*m*, 1223*w*, 1162*m*, 1094*w*, 979*m*, 878*m*, 856*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.35–1.42 (*m*, 1 H); 1.59–1.73 (*m*, 3 H); 1.95–2.00 (*m*, 2 H); 3.48 (*s*, 2 H); 8.14 (*d*, *J* = 8.8, 2 H); 8.38 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 19.4 (*t*); 27.0 (*t*); 47.8 (*d*); 124.2 (*d*); 128.8 (*d*); 145.1 (*s*); 150.6 (*s*). MS: 186 (0.3), 122 (2), 82 (77), 55 (100).

N-*(Cyclohex-2-en-1-yl)-4-nitrobenzenesulfonamide* (**2b**) *and 7-[(4-Nitrophenyl)sulfonyl]-7-azabicyclo[4.1.0]heptane* (**3b**): See [11].

N-*(Cyclohept-2-en-1-yl)-4-nitrobenzenesulfonamide* (**2c**): M.p. 140–141°. IR ($CHCl_3$): 3382*w*, 3034*w*, 2925*w*, 1607*w*, 1533*s*, 1411*w*, 1350*s*, 1308*w*, 1226*w*, 1164*s*, 1090*w*, 856*m*, 614*m*, 561*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.27–1.40 (*m*, 1 H); 1.43–1.66 (*m*, 3 H); 1.72–1.90 (*m*, 2 H); 2.00–2.15 (*m*, 2 H); 4.02–4.09 (*m*, 1 H); 4.60–4.65 (*m*, 1 H); 5.32–5.36 (*m*, 1 H); 5.70–5.80 (*m*, 1 H); 8.06 (*d*, *J* = 8.8, 2 H); 8.36 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 26.3 (*t*); 26.9 (*t*); 28.3 (*t*); 34.8 (*t*); 54.9 (*d*); 124.4 (*d*); 128.2 (*d*); 133.0 (*d*); 133.7 (*d*); 145.0 (*s*); 150.3 (*s*). MS: 296 (11, M^+), 267 (5), 241 (10), 215 (6), 186 (12), 122 (23), 110 (100), 94 (42), 80 (30), 67 (33). HR-MS: 296.0829 ($C_{13}H_{16}N_2O_4S^+$; calc. 296.0831).

8-[(4-Nitrophenyl)sulfonyl]-8-azabicyclo[5.1.0]octane (**3c**): M.p. 118°. IR ($CHCl_3$): 3030*w*, 2932*w*, 2848*w*, 1608*w*, 1534*s*, 1423*w*, 1350*s*, 1331*w*, 1226*w*, 1162*s*, 1089*m*, 964*m*, 935*m*, 855*m*, 627*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.10–1.22 (*m*, 1 H); 1.32–1.63 (*m*, 5 H); 1.73–1.88 (*m*, 4 H); 3.12 (*t*, *J* = 2.6, 2 H); 8.15 (*d*, *J* = 8.8, 2 H); 8.38 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 25.1 (*t*); 28.0 (*t*); 30.8 (*t*); 45.4 (*d*); 124.2 (*d*); 128.8 (*d*); 145.0 (*s*); 150.4 (*s*). MS: 296 (0.3, M^+), 241 (11), 186 (4), 10 (100), 94 (7), 83 (39), 67 (7), 55 (89). Anal. calc. for $C_{13}H_{16}N_2O_4S$: C 52.69, H 5.44, N 9.45, S 10.82; found: C 52.58, H 5.43, N 9.46, S 10.94.

9-[(4-Nitrophenyl)sulfonyl]-9-azabicyclo[6.1.0]nonane (**3d**): M.p. 154–155°. IR ($CHCl_3$): 3030*w*, 2933*m*, 2856*w*, 1605*w*, 1535*s*, 1469*w*, 1350*s*, 1161*s*, 1091*m*, 1013*w*, 934*m*, 854*m*, 824*m*, 669*m*, 628*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.25–1.38 (*m*, 2 H); 1.39–1.52 (*m*, 3 H); 1.53–1.68 (*m*, 5 H); 2.04 (*d*, *J* = 13.6, 2 H); 2.90–2.94 (*m*, 2 H); 8.15 (*d*, *J* = 8.8, 2 H); 8.39 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 25.2 (*t*); 26.1 (*t*); 26.3 (*t*); 45.0 (*d*); 124.3 (*d*); 128.9 (*d*); 144.9 (*d*); 150.5 (*s*). MS: 124 (64), 97 (6), 55 (100). Anal. calc. for $C_{14}H_{18}N_2O_4S$: C 54.18, H 5.85, N 9.03, S 10.33; found: C 54.18, H 5.92, N 8.95, S 10.26.

4-Nitro-N-*(1-phenylprop-2-enyl)benzenesulfonamide* (**5b**): IR ($CHCl_3$): 3380*w*, 3029*w*, 1607*w*, 1533*s*, 1494*w*, 1455*w*, 1406*w*, 1350*s*, 1312*w*, 1229*w*, 1164*s*, 1092*w*, 855*w*, 701*w*, 664*w*, 615*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.99 (*d*, *J* = 7.5, 1 H); 5.06–5.15 (*m*, 1 H); 5.16–5.24 (*m*, 2 H); 5.85–5.95 (*m*, 1 H); 7.06–7.12 (*m*, 2 H); 7.18–7.25 (*m*, 3 H); 7.84 (*d*, *J* = 8.8, 2 H); 8.18 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 60.3 (*d*); 117.6 (*t*); 123.9 (*d*); 127.2 (*d*); 128.2 (*d*); 128.8 (*d*); 136.5 (*d*); 138.4 (*s*); 146.6 (*s*); 149.8 (*s*). MS: 318 (1, M^+), 291 (21), 241 (5), 186 (18), 132 (100), 105 (83), 77 (36). HR-MS: 318.0641 ($C_{15}H_{14}N_2O_4S^+$; calc. 318.0674).

1-[(4-Nitrophenyl)sulfonyl]-2-(prop-2-enyl)aziridine (**6a**): M.p. 61–62°. IR ($CHCl_3$): 3105*w*, 1644*w*, 1608*w*, 1535*s*, 1402*w*, 1350*s*, 1311*m*, 1226*w*, 1168*s*, 1092*m*, 964*m*, 924*m*, 856*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.15–2.24 (*m*, 2 H); 2.32–2.39 (*m*, 1 H); 5.09 (*d*, *J* = 7.0, 1 H); 2.94–3.00 (*m*, 1 H); 5.02 (*dd*, *J* = 10.3, 1.0, 1 H); 5.09 (*dd*, *J* = 17.3, 1.0, 1 H); 5.56–5.66 (*m*, 1 H); 8.15 (*d*, *J* = 8.8, 2 H); 8.41 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 33.8 (*t*); 35.1 (*t*); 40.2 (*d*); 118.2 (*t*); 124.2 (*d*); 129.3 (*d*); 132.3 (*d*); 144.1 (*s*); 150.6 (*s*). MS: 267 (1, [M – 1]), 186 (15), 122 (28), 82 (83), 55 (100). HR-MS: 267.0440 ($C_{11}H_{10}N_2O_4S^+$, [M – 1]$^+$; calc. 267.0399).

1-[(4-Nitrophenyl)sulfonyl]-2-(phenylmethyl)aziridine (**6b**): IR ($CHCl_3$): 3105*w*, 3030*w*, 2920*w*, 1608*w*, 1534*s*, 1497*w*, 1455*w*, 1403*w*, 1349*m*, 1312*w*, 1232*w*, 1166*s*, 1092*w*, 1015*w*, 943*w*, 855*m*, 700*m*, 626*w*, 546*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.32 (*d*, *J* = 4.4, 1 H); 2.48 (*dd*, *J* = 8.4, 13.7, 1 H); 2.90 (*d*, *J* = 6.6, 1 H); 2.96–3.07 (*m*, 2 H); 6.98 (*d*, *J* = 7.7, 2 H); 7.70–7.16 (*m*, 3 H); 7.88 (*d*, *J* = 8.8, 2 H); 8.17 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 33.4 (*t*); 37.5 (*t*); 42.8 (*d*); 124.0 (*d*); 126.8 (*d*); 128.5 (*d*); 128.7 (*d*); 129.0 (*d*); 136.9 (*s*); 143.5 (*s*); 150.4 (*s*). MS: 318 (13, M^+), 186 (4), 132 (100), 105 (93), 105 (93), 77 (24). HR-MS: 318.0686 ($C_{15}H_{14}N_2O_4S_2^+$; calc. 318.0674).

4-Nitro-N-*(phenylmethyl)benzenesulfonamide* (**8a**): M.p. 111–113° ([36]: 126.6–127°). IR (CH_2Cl_2): 3943*w*, 3692*w*, 3054*s*, 2986*m*, 1451*m*, 1269*s*, 896*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.24 (*d*, *J* = 6.0, 2 H); 4.96 (*m*, 1 H); 7.18 (*m*, 2 H); 7.27 (*m*, 3 H); 7.99 (*d*, *J* = 8.8, 2 H); 8.31 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 47.4 (*t*); 124.3 (*d*); 127.9 (*d*); 128.3 (*d*); 135.5 (*s*); 146.1 (*s*); 150 (*s*). MS: 292 (1.25, M^+), 122 (12), 106 (100), 91 (39), 77 (28).

4-Nitro-N-*(1-phenylethyl)benzenesulfonamide* (**8b**): M.p. 124–125° ([37]: 125–125.5°). IR (CH_2Cl_2): 3943*w*, 3691*w*, 3370*m*, 3054*s*, 2986*m*, 1606*w*, 1533*m*, 1422*m*, 1350*s*, 1256*s*, 1165*w*, 896*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.48 (*d*, *J* = 7.2, 3 H); 4.60 (*quint.*, *J* = 6.8, 1 H); 5.42 (*d*, *J* = 6.4, 1 H); 7.04 (*m*, 2 H); 7.13 (*m*, 3 H); 7.78 (*d*, *J* = 9.2, 2 H); 8.12 (*d*, *J* = 9.2, 2 H). ^{13}C-NMR ($CDCl_3$): 23.6(*q*); 54.2(*d*); 123.9(*d*); 126.2(*d*); 127.8(*d*); 128.2(*d*); 128.6(*d*); 141.0(*s*); 146.6(*s*); 149.6(*s*). MS: 306 (0.3, M^+), 291(100), 186(35), 120(59), 105(43), 77(37).

N-*(1-Methyl-1-phenylethyl)-4-nitrobenzenesulfonamide* (**8c**): M.p. 161–162°. IR (CH_2Cl_2): 3943*w*, 3691*w*, 3054*s*, 2984*m*, 1422*s*, 1260*s*, 1150*w*, 896*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.71 (*s*, 6 H); 5.24 (*s*, 1 H); 7.13 (*m*, 3 H); 7.20 (*m*, 2 H); 7.68 (*d*, *J* = 8.8, 2 H); 8.12 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 30.1(*q*); 58.6(*s*); 123.8(*d*); 125.9(*d*); 127.5(*d*); 128.1(*d*); 128.2(*d*); 143.2(*s*); 147.9(*s*); 149.3(*s*). MS: 320 (0.4, M^+), 305(100), 243(8), 186(41), 119(83), 104(42), 91(73), 77(65).

N-*(Diphenylmethyl)-4-nitrobenzenesulfonamide* (**8d**): M.p. 220–222° ([38]: 180–182°). IR (CH_2Cl_2): 3944*w*, 3691*w*, 3053*m*, 2968*m*, 1422*m*, 1260*s*, 896*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.52 (*d*, *J* = 6.6, 1 H); 5.72 (*d*, *J* = 6.6, 1 H); 7.10 (*m*, 6 H); 7.73 (*m*, 2 H); 8.08 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 61.7(*d*); 123.8(*d*); 127.3(*d*); 128.0(*d*); 128.3(*d*); 128.7(*d*); 139.4(*s*); 146.2(*s*); 149.6(*s*). MS: 291(18), 182(100), 167(46), 152(17), 104(65), 77(48).

N-*(2,3-Dihydro-1*H*-inden-1-yl)-4-nitrobenzenesulfonamide* (**10a**): M.p. 168°. IR ($CHCl_3$): 3377*w*, 3030*w*, 1607*w*, 1534*s*, 1478*w*, 1430*w*, 1350*s*, 1311*w*, 1165*s*, 1093*m*, 985*w*, 854*m*, 686*w*, 553*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.75–1.81 (*m*, 1 H); 2.35–2.41 (*m*, 1 H); 2.78 (*quint.*, *J* = 8.0, 1 H); 2.90–2.97 (*m*, 1 H); 4.89–4.93 (*m*, 2 H); 7.09 (*d*, *J* = 7.2, 1 H); 7.15–7.26 (*m*, 3 H); 8.12 (*d*, *J* = 8.8, 2 H); 8.39 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 29.9(*t*); 34.7(*t*); 59.1(*d*); 124.0(*d*); 124.5(*d*); 125.1(*d*); 127.1(*d*); 128.3(*d*); 128.7(*d*); 141.1(*s*); 142.9(*s*); 147.2(*s*); 150.1(*s*). MS: 318 (1, M^+), 186(1), 132(60), 116(100), 91(21), 77(14). HR-MS: 318.0655 ($C_{15}H_{14}N_2O_4S^+$; calc. 318.0674).

4-Nitro-N-*(1,2,3,4-tetrahydronaphthalen-1-yl)benzenesulfonamide* (**10b**): M.p. 156–157°. IR ($CHCl_3$): 3381*w*, 3029*w*, 2935*w*, 1607*w*, 1533*s*, 1491*w*, 1452*w*, 1404*w*, 1350*s*, 1313*w*, 1165*s*, 1094*m*, 1076*m*, 984*w*, 836*w*, 856*m*, 686*w*, 611*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.68–1.88 (*m*, 4 H); 2.64–2.82 (*m*, 2 H); 4.55–4.59 (*m*, 1 H); 4.87 (*d*, *J* = 8.0, 2 H); 6.96 (*d*, *J* = 8.0, 1 H); 7.06–7.10 (*m*, 2 H); 7.15–7.19 (*m*, 1 H); 8.12 (*d*, *J* = 8.8, 2 H); 8.39 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 19.0(*t*); 28.7(*t*); 30.9(*t*); 52.5(*d*); 124.5(*d*); 126.5(*d*); 128.1(*d*); 128.3(*d*); 128.6(*d*); 129.5(*d*); 134.8(*s*); 137.6(*s*); 147.2(*s*); 150.1(*s*). MS: 332 (1, M^+), 186(2), 146(37), 130(100), 117(47), 91(31), 76(15), 63(5).

N-*Cyclohexyl-4-nitrobenzenesulfonamide* (**12c**): M.p. 137° ([39]: 135–137°). IR ($CHCl_3$): 3378*m*, 3030*m*, 2938*s*, 2855*m*, 1605*w*, 1533*vs*, 1452*m*, 1414*m*, 1350*vs*, 1310*m*, 1220*vs*, 1163*vs*, 1093*m*, 1071*m*, 989*w*, 918*w*, 855*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.07–1.32 (*m*, 5 H); 1.52–1.80 (*m*, 5 H); 3.18–3.28 (*m*, 1 H); 4.60 (br. *d*, *J* = 8.1, 1 H); 8.07, 8.36 (apparent *AA'XX'*, *d*, *J* = 8.8, 4 H). ^{13}C-NMR ($CDCl_3$): 24.6(*t*); 25.0(*t*); 34.0(*t*); 53.1(*d*); 124.4(*d*); 128.1(*d*); 147.4(*s*); 149.9(*s*). MS: 284 (18, M^+), 255(4), 241(100), 186(64), 170(2), 122(67), 98(50), 92(16), 82(56), 76(42), 67(23), 55(51), 50(30). Anal. calc. for $C_{12}H_{16}N_2O_4S$: C 50.69, H 5.68, N 9.86; found: C 50.63, H 5.64, N 9.96.

4-Nitro-N-*(tricyclo[3.3.1.1^{3,7}]dec-1-yl)benzenesulfonamide* (**14a**): M.p. 220–222° ([40]: > 280°). IR (CH_2Cl_2): 3684*w*, 3345*w*, 2915*m*, 1610*w*, 1532*s*, 1350*s*, 1162*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.59 (*m*, 6 H); 1.80 (*m*, 6 H); 2.04 (*m*, 3 H); 4.73 (*s*, 1 H); 8.10 (*m*, 2 H); 8.35 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 29.4(*d*); 35.7(*t*); 43.2(*t*); 55.9(*s*); 124.2(*d*); 128.2(*d*); 149.7(*s*). MS: 336 (16, M^+), 279(25), 150(7), 135(21), 122(12), 93(100).

4-Nitro-N-*(tricyclo[3.3.1.1^{3,7}]dec-2-yl)benzenesulfonamide* (**14b**): IR (CH_2Cl_2): 3686*w*, 3383*w*, 2915*m*, 1616*w*, 1533*m*, 1351*m*, 1165*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.25–1.82 (*m*, 14 H); 3.50 (*d*, *J* = 7.7, 1 H); 5.08 (*d*, *J* = 7.4, 1 H); 8.08 (*m*, 2 H); 8.36 (*m*, 2 H). ^{13}H-NMR ($CDCl_3$): 26.6(*d*); 26.8(*d*); 31.2(*t*); 32.8(*d*); 37.1(*t*); 37.2(*t*); 58.3(*d*); 124.3(*d*); 128.1(*d*); 147.3(*s*). MS: 336 (7, M^+), 280(2), 150(65), 122(32), 106(20), 92(100), 79(87).

N-*(Bicyclo[2.2.1]hept-2-*exo*-yl)-4-nitrobenzenesulfonamide* (**16**): M.p. 125–127°. IR (CH_2Cl_2): 3371*s*, 2961*m*, 1522*s*, 1273*s*, 1166*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.00–1.70 (*m*, 8 H); 2.10 (*m*, 1 H); 2.24 (*m*, 1 H); 3.22 (*dt*, *J* = 7.4, 1 H); 4.82 (*d*, *J* = 7.4, 1 H); 8.08 (*d*, *J* = 8.8, 2 H); 8.38 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 25.2(*t*); 26.9(*t*); 34.2(*t*); 34.6(*d*); 39.9(*t*); 41.7(*d*); 56.0(*d*); 123.4(*d*); 127.3(*d*); 146.9(*s*); 150.0(*s*). MS: 296 (0.9, M^+), 215(11), 186(18), 122(30), 110(100), 94(61), 81(98), 76(37), 67(91), 55(58).

4-Nitro-N-*(tetrahydrofuran-2-yl)benzenesulfonamide* (**18a**): M.p. 105–106°. IR ($CHCl_3$): 3377*w*, 3030*w*, 1608*w*, 1533*s*, 1431*w*, 1350*s*, 1313*w*, 1224*w*, 1167*s*, 1094*w*, 854*m*, 618*m*, 558*w*. ^{1}H-NMR (400 MHz, DMSO): 1.68–1.73 (*m*, 2 H); 1.79–1.92 (*m*, 1 H); 2.01–2.15 (*m*, 1 H); 3.41–3.52 (*m*, 2 H); 5.20–5.22 (*m*, 1 H); 8.04 (*d*, *J* = 8.8, 2 H); 8.38 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR (DMSO): 23.6(*t*); 31.2(*t*); 66.3(*t*); 84.5(*d*); 124.2(*d*); 127.9(*d*); 148.2(*s*); 149.3(*s*). MS: 231(1), 202(1), 186(5), 122(11), 71(100).

N-*(1,4-Dioxan-2-yl)-4-nitrobenzenesulfonamide* (**18b**): M.p. 158–187°. IR ($CHCl_3$): 3378*w*, 3027*w*, 2931*w*, 1608*w*, 1533*s*, 1350*m*, 1313*w*, 1208*w*, 1166*m*, 1094*w*, 1044*w*, 991*w*, 909*w*, 855*w*, 620*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.75–1.84 (*m*, 1 H); 1.86–1.95 (*m*, 2 H); 2.23–2.33 (*m*, 1 H); 3.62–3.74 (*m*, 2 H); 5.14 (*d*, *J* = 9.3, 1 H); 5.42–5.49 (*m*, 1 H); 8.13 (*d*, *J* = 8.8, 2 H); 8.35 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 24.1 (*t*); 32.8 (*t*); 67.4 (*t*); 85.1 (*d*); 124.1 (*d*); 128.5 (*d*); 147.2 (*s*); 150.0 (*s*). MS: 288 (5), 231 (41), 202 (16), 186 (29), 139 (92), 122 (72), 86 (78), 75 (100), 50 (87).

4-Nitro-N-*(phenylmethylidene)benzenesulfonamide* (**19**): M.p. 164–167°. IR ($CHCl_3$): 3106*w*, 3030*w*, 1600*m*, 1572*m*, 1567*m*, 1534*s*, 1350*s*, 1168*s*, 1088*m*, 853*w*, 798*s*, 646*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.53 (*t*, *J* = 8.0, 2 H); 7.68 (*t*, *J* = 8.0, 1 H); 7.96 (*d*, *J* = 8.0, 2 H); 8.22 (*d*, *J* = 8.8, 2 H); 8.40 (*d*, *J* = 8.8, 2 H); 9.13 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 124.3 (*d*); 129.3 (*d*); 129.4 (*d*); 131.7 (*d*); 132.0 (*s*); 135.8 (*d*); 144.2 (*s*); 150.6 (*s*); 172.3 (*d*). MS: 290 (10, M^+), 226 (3), 186 (19), 122 (56), 104 (100), 77 (81), 64 (10), 51 (36). HR-MS: 290.0362 ($C_{13}H_{10}N_2O_4S^+$; calc. 290.0361).

5. *Intramolecular Insertion. 6-Ethyl-2,3-dihydro-3-methyl-1,2-benzisothiazole 1,1-Dioxide* (**22**). The *2,5-diethylbenzenesulfonamide* (**20**) was synthesized according to literature procedures *via* sulfonation of 1,4-diethylbenzene and reaction with $POCl_3$ followed by NH_3 [16]. Reaction of **20** with (diacetoxyiodo)benzene [4] (= diacetoxy-(phenyl)-λ^3-iodane) gave *{[(2,5-diethylphenyl)sulfonyl]imino}phenyl-λ^3-iodane* (**21**) in 58% yield. The insertion was carried out by stirring a suspension of crude **21** (1.0 mmol) in CH_2Cl_2 (10 ml) containing [Rh(OAc)$_4$] (0.02 mmol) and activated molecular sieves (6.0 g) under N_2 at r.t. The ylide dissolved almost immediately. The mixture was stirred for 40 min and then filtered through *Celite*, and the filtrate evaporated. Purification of the crude product by flash chromatography (SiO_2, hexane/Et_2O 1:1) afforded 36% of **22** as an oil. When *Pirrung*'s catalyst [Rh_2{(*R*)-bnp}$_4$] was used, **22** was formed in 22% yield and with 10% ee. IR ($CHCl_3$): 3360*w*, 3026*m*, 2972*m*, 1372*w*, 1296*s*, 1156*vs*, 1020*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.28 (*t*, *J* = 7.6, 3 H); 1.60 (*d*, *J* = 6.4, 3 H); 2.75 (*q*, *J* = 7.6, 2 H); 4.74–4.79 (*m*, 2 H); 7.29 (*d*, *J* = 8.0, 1 H); 7.46 (*dd*, *J* = 8.0, 1.2, 1 H); 7.59 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 15.3 (*q*); 21.6 (*q*); 28.6 (*t*); 53.2 (*d*); 120.0 (*d*); 123.7 (*d*); 133.3 (*d*); 135.6 (*s*); 139.1 (*s*); 146.1 (*s*). HR-MS: 211.0667 ($C_{10}H_{13}O_2NS^+$, calc. 211.0666).

6. *Reaction with Cyclohex-2-en-1-yl Acetate* (**23**). The *General Procedure* afforded, after workup and column chromatography (SiO_2, hexane/AcOEt 3:1), a 1:1 mixture of **24** and **25** (43%) and of pure **26** (4%). The stereoisomers were separated by HPLC (*Lichrosorb Si 60* (7 μm) column, 200 × 12 mm, (*i*-Pr)$_2$O (3 ml/min)).

N-*(*cis*-4-Acetoxycyclohex-2-en-1-yl)-4-nitrobenzenesulfonamide* (**24**): HPLC: t_R 19 min. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.60–1.90 (*m*, 4 H); 2.04 (*s*, 3 H); 2.04 (*s*, 3 H); 3.90–3.92 (*m*, 1 H); 4.85 (*d*, *J* = 8.8, 1 H); 5.14 (*d*, *J* = 3.7, 1 H); 5.63 (*dd*, *J* = 9.9, 2.6, 1 H); 5.83 (*ddd*, *J* = 9.9, 3.7, 1.8, 1 H); 8.09, 8.36 (*AA'XX'*,'*d*', *J* = 8.8, 4 H). ^{13}C-NMR ($CDCl_3$): 21.2 (*q*); 25.4 (*t*); 26.6 (*t*); 49.4 (*d*); 66.1 (*d*); 124.5 (*d*); 128.2 (*d*); 130.0 (*d*); 131.4 (*d*); 147.0 (*s*); 150.1 (*s*); 170.4 (*s*).

N-*(*trans*-4-Acetoxycyclohex-2-en-1-yl)-4-nitrobenzenesulfonamide* (**25**): HPLC: t_R 29 min. M.p. 175–176°. IR: 3300*w*, 3016*m*, 2929*w*, 1725*s*, 1534*s*, 1349*s*, 1245*s*, 1164*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.50–1.63 (*m*, 2 H); 2.01–2.04 (*m*, 2 H); 2.04 (*s*, 3 H); 3.98–4.00 (*m*, 1 H); 4.87 (*d*, *J* = 8.8, 1 H); 5.21–5.23 (*m*, 1 H); 5.57 (*d*, *J* = 10.3, 1 H); 5.78 (*ddd*, *J* = 10.3, 2.6, 2.2, 1 H); 8.08, 8.36 (*AA'XX'*, '*d*', *J* = 8.8, 4 H). ^{13}C-NMR ($CDCl_3$): 21.2 (*q*); 26.4 (*t*); 28.3 (*t*); 49.5 (*d*); 67.3 (*d*); 124.5 (*d*); 130.7 (*d*); 130.8 (*d*); 147.1 (*s*); 150.1 (*s*); 170.6 (*s*). MS: 312 (2), 280 (26), 202 (19), 186 (16), 154 (18), 139 (15), 122 (31), 112 (40), 96 (100), 94 (92), 84 (33), 77 (32), 76 (88), 69 (78), 50 (33), 45 (18). Anal. calc. for $C_{14}H_{16}N_2O_6S$: C 49.41, H 4.74, N 8.23; found: C 49.58, H 4.87, N 7.98.

2-Acetoxy-7-[(4-nitrophenyl)sulfonyl]-7-azabicyclo[4.1.0]heptane (**26**): IR ($CHCl_3$): 3106*w*, 3028*m*, 2953*m*, 2877*w*, 1730*s*, 1607*m*, 1534*vs*, 1403*m*, 1368*s*, 1349*vs*, 1310*s*, 1241*vs*, 1164*vs*, 1091*s*, 1037*m*, 982*s*, 855*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.20–1.35 (*m*, 4 H); 1.73–2.00 (*m*, 2 H); 2.08 (*s*, 3 H); 3.05 (*d*, *J* = 6.6, 1 H); 3.28–3.30 (*m*, 1 H); 4.75 (*dd*, *J* = 8.1, 5.5, 1 H); 8.19, 8.41 (*AA'XX'*, app. *d*, *J* = 8.8, 4 H). ^{13}C-NMR ($CDCl_3$): 14.9 (*t*); 21.0 (*q*); 22.5 (*t*); 25.9 (*t*); 40.1 (*d*); 43.3 (*d*); 67.2 (*d*); 124.3 (*d*); 129.2 (*d*); 144.2 (*s*); 150.7 (*s*); 170.1 (*s*). MS: no M^+, 297 (0.2), 281 (0.4), 254 (1), 218 (1), 202 (1), 186 (1), 154 (11), 122 (2), 112 (100), 94 (8), 84 (19), 67 (7).

7. *Synthesis and Amidation of (1-D)Cyclohexene* (**27**). *Synthesis.* (1-D)Cyclohexyl *p*-toluenesulfonate (10.2 g, 40 mmol) [20] was heated in DMSO to 95°, and **27** was distilled out of the reaction flask continuously at 160 Torr. Purification by bulb-to-bulb distillation gave **27** in 79% yield. B.p. 82°. IR ($CHCl_3$): 3028*w*, 2925*s*, 2859*m*, 2838*m*, 1438*m*, 1136*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.60–1.64 (*m*, 4 H); 1.99–2.00 (*m*, 4 H); 5.67–5.68 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 22.58 (*t*); 22.61 (*t*); 25.00 (*t*); 25.08 (*t*); 127.09 (*d*). MS: 83 (53, M^+), 68 (100), 55 (69), 54 (40).

Amidation. The General Procedure with NsN=IPh (2 mmol), **27** (2 mmol), and [$Rh_2(OAc)_4$] (0.04 mmol) in CH_2Cl_2/sulfolane 95:5 afforded, after chromatography (SiO_2, hexane/AcOEt 5:1), **28**/**29** 1:1 (21%) and deuterated aziridine D_2-**3b** (2%). **28**/**29**: ^{1}H-NMR (400 MHz, $CDCl_3$): 1.57–1.62 (*m*, 3 H); 1.75–1.90 (*m*, 1 H); 1.95–1.97 (*m*, 2 H); 3.87–3.98 (*m*, 1 H); 4.85 (*d*, *J* = 8.5, 1 H); 5.35–5.37 (*m*, 0.5 H); 5.81–5.84 (*m*, 0.5 H); 8.08 (*d*, *J* = 8.8, 2 H); 8.37 (*d*, *J* = 8.8, 2 H). ^{2}D-NMR (400 MHz, $CHCl_3$): 3.90 (*s*, trace); 5.40 (*s*, 1 D); 5.86 (*s*, 1 D).

8. *Amidation of Cyclopropane Derivatives. 4-Nitro-*N-*[(1a*RS,*6*RS,*6a*SR*)-1,1a,6,6a-tetrahydrocycloprop[*a*]-inden-6-yl]benzenesulfonamide* (**36**). The *General Procedure* using **33** [23] (20 mmol) afforded **36** in 84% yield. M.p. 219° (from acetone). IR (KBr): 3286*s*, 3128*w*, 3036*w*, 2997*w*, 1608*w*, 1526*s*, 1476*m*, 1462*m*, 1434*m*, 1349*s*, 1311*s*, 1159*s*, 1077*m*, 1053*m*, 856*m*, 763*m*, 741*m*, 626*m*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO): −0.06, −0.03 (*m*, 1 H); 1.02–1.07 (*m*, 1 H); 1.60–1.64 (*m*, 1 H); 2.41–2.43 (*m*, 1 H); 4.58 (*s*, 1 H); 6.93 (*d*, *J* = 7.3, 1 H); 7.06 (*t*, *J* = 7.3, 1 H); 7.16 (*t*, *J* = 7.3, 1 H); 7.30 (*d*, *J* = 7.3, 1 H); 8.14 (*d*, *J* = 8.8, 2 H); 8.45 (*d*, *J* = 8.8, 2 H); 8.65 (*s*, 1 H). ^{13}C-NMR (DMSO): 19.4(*t*); 22.8(*d*); 24.5(*d*); 58.6(*d*); 123.2(*d*); 124.7(*d*); 125.9(*d*); 126.0(*d*); 127.9(*d*); 128.0(*d*); 140.7(*s*); 146.3(*s*); 147.8(*s*); 149.5(*s*). MS: 330 (5, M^+), 215(5), 186(2), 144(74), 128(100), 76(7). HR-MS: 330.0627 ($C_{16}H_{14}N_2O_4S^+$; calc. 330.0674).

Crystal Structure Determination of **36**: $C_{16}H_{14}N_2O_4S$, M_r 330.4; $\mu = 2.130\ mm^{-1}$, $F(000) = 688$, $d_x = 1.46\ g \cdot cm^{-3}$, monoclinic, *Cc*, $Z = 4$, $a = 12.609(1)$, $b = 5.2626(2)$, $c = 22.751(1)$ Å, $\beta = 97.002(3)$, $V = 1498.4(1)$ Å^3, from 25 reflections ($64° < 2\theta < 81°$). Cell dimensions and intensities were measured at r.t. on a *Nonius-CAD4* diffractometer with graphite-monochromated CuK_α radiation (λ 1.5418 Å), ω-2θ scans, scan width 1.5° + 0.14 tg θ, and scan speed 0.092°/s. $-13 < h < 13$; $0 < k < 5$; $0 < l < 24$ and all *Friedel* pairs; 1939 measured reflections, 1880 unique reflections of which 1865 were observables ($|F_o| > 4\sigma(F_o)$); R_{int} for equivalent reflections 0.008. Data were corrected for *Lorentz* and polarization effects and for absorption [41] ($A^*_{min,max} = 1.436, 1.661$). The structure was solved by direct methods using MULTAN 87 [42], all other calculations used XTAL [43] program. The polarity of the structure was refined, and the absolute structure parameter [44] converges to $x = -0.03(2)$. Full-matrix least-squares refinement based on *F* using weight of $1/\sigma^2(F_o)$ gave final values $R = 0.028$, $\omega R = 0.026$ for 250 variables and 1865 contributing reflections. All H-atoms were observed and refined with a fixed value of isotropic displacement parameters ($U = 0.04$ Å^2). The final difference electron density map showed a maximum of + 0.13 and a minimum of −0.13 e Å^{-3}. In the crystal packing, the molecules are associated in chains by H-bonds along the *b* axis involving the amino group and an O-atom of the sulfonyl: N…O(x, $y-1$, z) = 3.024(5) Å, N–H…O = 162(4)°. Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Center* as supplementary publication No. CCDC-10/48. Copies of the data can be obtained free of charge on application to The Director, *CCDC*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).

N-*(1-Cyclopropylethyl)-4-nitrobenzenesulfonamide* (**40**). The *General Procedure* with **37** [25] (20 mmol) afforded, after purification (SiO_2, CH_2Cl_2), **40** in 21% yield. M.p. 87°. IR ($CHCl_3$): 3382*w*, 3104*w*, 3030*w*, 2916*w*, 1607*w*, 1533*s*, 1409*w*, 1350*s*, 1310*w*, 1163*m*, 1091*m*, 974*m*, 856*m*, 614*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.04–0.08 (*m*, 1 H); 0.15–0.18 (*m*, 1 H); 0.33–0.36 (*m*, 1 H); 0.47–0.51 (*m*, 1 H); 0.77–0.79 (*m*, 1 H); 1.18 (*d*, *J* = 6.6, 3 H); 2.75–2.85 (*m*, 1 H); 4.86 (*d*, *J* = 7.1, 1 H); 8.09 (*d*, *J* = 8.8, 2 H); 8.36 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 3.4(*t*); 4.1(*t*); 17.9(*d*); 21.2(*q*); 55.4(*d*); 124.3(*d*); 128.2(*d*); 147.4(*s*); 149.9(*s*). MS: 270 (1, M^+), 255(100), 229(40), 186(42), 122(71). HR-MS: 270.0675 ($C_{11}H_{14}N_2O_4S^+$; calc. 270.0674).

*Synthesis and Amidation of (*t*-3-Ethylcyclopropane-*π*-1,*c*-2-diyl)bis(benzene)* (**42**). *Synthesis.* (*t*-3-ethenylcyclopropane-*π*-1,*c*-2-diyl)bis(benzene) (**41**; 1.91 g, 8.7 mmol) [27] was hydrogenated with 10% Pt/C (30 mg) in MeOH under H_2 at normal pressure. Filtration through *Celite* and evaporation of the filtrate gave **42** in 71% yield. Yellow oil. IR ($CHCl_3$): 3062*m*, 3026*m*, 3010*s*, 2962*s*, 2871*m*, 1945*w*, 1882*w*, 1805*w*, 1750*w*, 1602*m*, 1497*m*, 1456*m*, 1074*w*, 1028*w*, 700*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.21 (*t*, *J* = 7.2, 3 H); 1.60–1.69 (*m*, 3 H); 2.28 (*d*, *J* = 5.1, 2 H); 6.94–7.02 (*m*, 4 H); 7.07–7.20 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 13.5(*q*); 27.4(*t*); 27.8(*d*); 31.8(*d*); 125.4(*d*); 127.8(*d*); 128.7(*d*); 138.7(*s*). MS: 222 (30, M^+), 193(100), 178(22), 115(82), 91(42). HR-MS: 222.1404 ($C_{17}H_{18}^+$; calc. 222.1409)

Amidation: N-*[1-(*t*-2,*t*-3-Diphenylcycloprop-r-1-yl)ethyl]-4-nitrobenzenesulfonamide* (**45**). The *General Procedure* with **42** (5 mmol) afforded, after chromatography (SiO_2, hexane/AcOEt 5:1), 5% of **45**. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.47 (*d*, *J* = 6.6, 3 H); 1.69–1.71 (*m*, 1 H); 2.17–2.20 (*m*, 1 H); 2.30–2.35 (*m*, 1 H); 3.30–3.36 (*m*, 1 H); 4.85 (*d*, *J* = 7.1, 1 H); 6.53–6.58 (*m*, 2 H); 6.82–6.87 (*m*, 2 H); 6.95–6.97 (*m*, 3 H); 7.04–7.10 (*m*, 3 H); 7.97 (*d*, *J* = 8.8, 2 H); 8.08 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 21.7(*q*); 30.5(*d*); 30.9(*d*); 31.7(*d*); 55.0(*d*); 124.3(*d*); 126.1(*d*); 126.3(*d*); 127.7(*d*); 127.9(*d*); 128.0(*d*); 128.1(*d*); 129.1(*d*); 136.1(*s*); 136.3(*s*); 147.1(*s*); 149.6(*s*). MS: 422 (0.3, M^+), 229(100), 186(24), 122(21), 115(33).

9. Hammett *Plot for Amidation of 4-Substituted Ethylbenzenes.* The reactivities of a series of 4-substituted ethylbenzenes were determined by competition experiments relative to the unsubstituted compound, using ethylbenzene (**7b**) (10 mmol), the 4-substituted ethylbenzene (10 mmol), NsN=IPh (1 mmol), and [Rh_2(OAc)$_4$] (0.02 mmol) in CH_2Cl_2 (10.0 ml) at 25°. Relative yields were determined by NMR and GLC. The log(k/k_0) values in *Table 3* refer to average values from 2 to 4 determinations with an average error of 5%. The yields of products **8** (*Table 3*) were obtained from separate runs of the individual ethylbenzenes.

10. *Isotope Effect for Amidation of (1,3-D_2)Tricyclo[3.3.1.1^{3,7}]decane* (1,3-D_2-**13**). As described [28], 1,3-D_2-**13** was synthesized from the 1,3-dibromo derivative with $LiAlD_4$/Bu_3SnCl. MS Analysis using slow-scan integration in the region of *m/z* 138–137 revealed a composition of 98.2% of dideuterated and 1.8% of monodeuterated material. HR-MS: 138.1381 ($C_{10}H_{14}D_2^+$; calc. 138.1378). The amidation was carried out according to the *General Procedure* in dichloroethane at r.t. The 1-isomer D-**14a** (51%) was separated by column chromatography (SiO_2, CH_2Cl_2) and purified by repeated dissolution in MeOH. The composition of D-**14a**, determined by MS at *m/z* 338–337 was 76% D_2 and 24% D_1.

11. *Synthesis and Amidation of (*R*)-2-Butylbenzene* (**47**). Compound **47** was synthesized from methyl (*R*)-3-phenylbutanoate (**46**) *via* reduction with $LiAlH_4$, tosylation of the resulting alcohol, and subsequent reduction with $LiAlH_4$ [45]. $[\alpha]_D^{20} = -25.8$ (*c* = 1.0, $CHCl_3$). ([46]: $[\alpha]_D^{20} = -24.3$ (neat)).

Treatment of **47** with NsN=IPh according to the *General Procedure* afforded (*S*)-**48** in 3% yield. $[\alpha]_D^{20} = -10.2$ ($CHCl_3$, *c* = 0.50). IR ($CHCl_3$): 3375*w*, 3029*w*, 2962*w*, 1716*w*, 1609*w*, 1532*s*, 1406*w*, 1350*m*, 1313*w*, 1262*s*, 1163*m*, 1092*s*, 1014*s*, 854*w*, 808*s*, 611*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.76 (*t*, *J* = 7.1, 3 H); 1.73 (*s*, 3 H); 1.87–2.07 (*m*, 2 H); 5.30 (*s*, 1 H); 7.06–7.19 (*m*, 5 H); 7.66 (*d*, *J* = 8.8, 2 H); 8.10 (*d*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 8.3(*q*); 24.8(*q*); 36.1(*t*); 62.2(*s*); 123.8(*d*); 125.9(*d*); 126.4(*d*); 127.3(*d*); 128.1(*d*); 141.9(*d*); 148.0(*s*); 149.4(*s*). MS: 305(100), 259(6), 186(39), 132(10), 122(79), 77(46).

(–)-Menthyl N-*(1-Methyl-1-phenylpropyl)carbamate* ((–)-**50**). To racemic 2-phenyl-2-amine (**49**; 1.49 g, 10.0 mmol) in Et_2O containing Et_3N (15 mmol), (–)-(1*R*)-menthyl chloroformate (2.84 g, 13 mmol) was added within 15 min at 0°. The suspension was stirred at 0° during 10 min and then at r.t. overnight. It was filtered and the filtrate washed with 3 successive portions of NaOH (5%), HCl (5%), and sat. $NaHCO_3$ soln. The org. layer was dried ($MgSO_4$) and evaporated to afford 4.0 g of the carbamate as a viscous, colorless liquid. A portion of the carbamate (2.0 g) was separated partially on a MPLC column (30 g of SiO_2 (40 μm), hexane/Et_2O 10:1, *p* = 8 bar). The more polar component (–)-**50** (100 mg) was obtained as colorless crystals. M.p. 62°. $[\alpha]_D^{20} = -40.4$ ($CHCl_3$, *c* = 1.38). IR ($CHCl_3$): 3443*m*, 3010*w*, 2958*s*, 2928*s*, 2870*m*, 1719*s*, 1684*s*, 1496*s*, 1456*m*, 1400*w*, 1373*w*, 1319*w*, 1243*m*, 1181*w*, 1084*m*, 700*m*, 670*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.68–2.05 (*m*, 26 H); 4.48 (*dt*, *J* = 4.4, 10.6, 1 H); 4.93 (*s*, 1 H); 7.18–7.43 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 8.2(*q*); 20.8(*q*); 22.3(*t*); 23.7(*t*); 25.6(*q*); 29.6(*q*); 31.5(*d*); 34.5(*t*); 41.6(*t*); 47.6(*d*); 58.3(*s*); 74.5(*d*); 124.9(*d*); 125.4(*d*); 126.4(*d*); 128.2(*d*); 146.5(*s*); 155.1(*s*). MS: 302(50), 258(7), 164(37), 146(15), 139(21), 133(23), 120(100), 95(18), 91(29), 83(86), 69(32), 55(40). Anal. calc. for $C_{21}H_{33}NO_2$: C 76.09, H 10.03, N 4.22; found: C 76.07, H 10.17, N 4.18.

*(+)-(*R*)-2-Phenylbutan-2-amine* ((*R*)-**49**). Carbamate (–)-**50** (155 mg, 0.47 mmol) was heated with aq. 50% KOH soln. (1.0 ml) and diethylene glycol (1.0 ml) at 100° during 20 h. After cooling to 20°, H_2O (30 ml) and CH_2Cl_2 (30 ml) was added to the black soln. The free amine was isolated *via* extraction of the acidified aq. soln. Yield 71%. $[\alpha]_D^{20} = +16.2$ ($CHCl_3$, *c* = 1.07) ([47]: $[\alpha]_D^{20} = +18$ ($CHCl_3$, *c* = 0.8); [48]: $[\alpha]_D^{20} = +15.8$ (neat) for (*R*)-**49**; [49]: $[\alpha]_D^{20} = -15.7$ (neat) for (*S*)-**49**). IR ($CHCl_3$): 3087*w*, 3081*w*, 2968*m*, 2935*m*, 2879*w*, 1583*w*, 1495*w*, 1459*w*, 1445*w*, 1380*w*, 1003*w*, 885*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.74 (*t*, *J* = 7.4, 3 H); 1.45 (*s*, 3 H); 1.59 (br. *s*, 2 H); 1.64 (*m*, 2 H); 7.15–7.54 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 8.7(*q*); 30.6(*q*); 37.7(*t*); 55.2(*s*); 124.6(*s*); 125.3(*d*); 126.0(*d*); 128.1(*d*). MS: 148 (0.2, [*M* – 1]), 134(18), 120(100), 104(7), 91(6), 77(9), 72(6), 60(4), 51(6).

*(+)-(*R*)-N-(1-Methyl-1-phenylpropyl)-4-nitrobenzenesulfonamide* ((*R*)-**48**). Amine (*R*)-**49** (26 mg, 0.17 mmol) was stirred with NsCl (39.9 mg, 0.17 mmol) in pyridine (1.0 ml) at 50° during 15 h. After addition of CH_2Cl_2 (20 ml) and 20% HCl soln. (20 ml), the org. phase was washed with 20% HCl soln. (3 times), 2N NaOH, and sat. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated to afford 34 mg of crude product having $[\alpha]_D^{20} = +6.8$ ($CHCl_3$, *c* = 1.85). Pure (*R*)-**48** (23 mg, 26%) was obtained after chromatography (SiO_2, CH_2Cl_2). M.p. 143°. $[\alpha]_D^{20} = +8.8$ ($CHCl_3$, *c* = 0.34). Spectral data: see (–)-(*S*)-**48**. Anal. calc. for $C_{16}H_{18}N_2O_4S$: C 57.47, H 5.43, N 8.38; found: C 57.24, H 5.31, N 8.29.

12. *Asymmetric Induction in Rh^{II}-Catalyzed Amidation of 2,3-Dihydro-1*H*-indene* (**9a**). The reactions were carried out according to the *General Procedure*. The enantiomeric excess was determined by ^{1}H-NMR using [Eu(hfc)$_3$]. Catalyst [Rh_2(bnp)$_4$]: $[\alpha]_D^{20} = +9.5$ for 31% ee; catalyst [Rh_2(ppa)$_4$]: $[\alpha]_D^{20} = -3.5$ for 7% ee.

REFERENCES

[1] M. P. Doyle, in 'Catalytic Asymmetric Synthesis', Ed. I. Ojima, VCH, Weinheim, 1993, pp. 63–99.

[2] M. P. Doyle, M. Protopopova, P. Müller, D. Ene, E. A. Shapiro, *J. Am. Chem. Soc.* **1994**, *116*, 8492; M. N. Protopopova, M. P. Doyle, P. Müller, D. Ene, *ibid.* **1992**, *114*, 2755.

[3] P. Müller, P. Polleux, *Helv. Chim. Acta* **1994**, *77*, 645; M. P. Doyle, A. B. Dyatkin, G. H. P. Roos, F. Cañas, D. A. Pierson, A. van Basten, P. Müller, P. Polleux, *J. Am. Chem. Soc.* **1994**, *116*, 4507.

[4] Y. Yamada, T. Yamamoto, M. Okawara, *Chem. Lett.* **1975**, 361.
[5] J.-P. Mahy, P. Battioni, D. Mansuy, J. Fisher, R. Weiss, J. Mispelter, I. Morgenstern-Badarau, P. Gans, *J. Am. Chem. Soc.* **1984**, *106*, 1699; D. Mansuy, J.-P. Mahy, A. Dureault, G. Bedi, P. Battioni, *J. Chem. Soc., Chem. Commun.* **1984**, 1161; J.-P. Mahy, G. Bedi, P. Battioni, D. Mansuy, *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517.
[6] D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Org. Chem.* **1991**, *56*, 6744; D. A. Evans, M. M. Faul, M. T. Bilodeau, B. A. Anderson, D. M. Barnes, *J. Am. Chem. Soc.* **1993**, *115*, 5328; D. A. Evans, M. M. Faul, M. T. Bilodeau, *ibid.* **1994**, *116*, 2742.
[7] Z. Li, K. R. Conser, E. N. Jacobsen, *J. Am. Chem. Soc.* **1993**, *115*, 5326; W. Zhang, N. H. Lee, E. N. Jacobsen, *ibid.* **1994**, *116*, 425; Z. Li, R. W. Quan, E. N. Jacobsen, *ibid.* **1995**, *117*, 5889.
[8] R. Breslow, S. H. Gellman, *J. Chem. Soc., Chem. Commun.* **1982**, 1400.
[9] R. Breslow, S. H. Gellman, *J. Am. Chem. Soc.* **1983**, *105*, 6728.
[10] J.-P. Mahy, G. Bedi, P. Battioni, D. Mansuy, *New J. Chem.* **1989**, *13*, 651; J.-P. Mahy, G. Bedi, P. Battioni, D. Mansuy, *Tetrahedron Lett.* **1988**, *29*, 1927.
[11] P. Müller, C. Baud, Y. Jacquier, *Tetrahedron* **1996**, *52*, 1543.
[12] P. Müller, C. Baud, Y. Jacquier, M. Moran, I. Nägeli, *J. Phys. Org. Chem.* **1996**, *9*, 341.
[13] C. Jia, P. Müller, H. Mimoun, *J. Mol. Catal., A: Chem.* **1995**, *101*, 127.
[14] J. M. Simson, W. Lwowski, *J. Am. Chem. Soc.* **1969**, *91*, 5107.
[15] D. S. Breslow, E. I. Edwards, R. Leone, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1968**, *90*, 7097.
[16] E. H. White, H. M. Lim, *J. Org. Chem.* **1987**, *52*, 2162; W. F. Erman, H. C. Kretschmar, *ibid.* **1961**, *26*, 4841.
[17] R. S. Drago, J. R. Long, R. Cosmano, *Inorg. Chem.* **1982**, *21*, 2196.
[18] G. Smolinski, B. I. Feuer, *J. Am. Chem. Soc.* **1964**, *86*, 3085.
[19] C. J. Moody, G. H. Whitham, 'Reactive Intermediates', Oxford University Press, Oxford, 1992.
[20] T. Hashimoto, G. K. Surya Prakash, J. G. Shih, G. A. Olah, *J. Org. Chem.* **1987**, *52*, 931; H. R. Nace, *J. Am. Chem. Soc.* **1959**, *81*, 5428.
[21] D. Griller, K. U. Ingold, *Acc. Chem. Res.* **1980**, *13*, 317.
[22] A. L. J. Beckwith, V. W. Bowry, *J. Org. Chem.* **1988**, *53*, 1632; A. L. J. Beckwith, in 'Radical Reactions Rates in Liquids', Landolt-Boernstein, New Series, Ed. H. Fischer, Springer, Berlin, 1984, Vol. 13a.
[23] E. C. Friedrich, E. J. Lewis, *J. Org. Chem.* **1990**, *55*, 2491; E. C. Friedrich, R. L. Holmstead, *ibid.* **1971**, *36*, 971.
[24] G.-X. He, T. C. Bruice, *J. Am. Chem. Soc.* **1991**, *113*, 2747; A. J. Castellino, T. C. Bruice, *ibid.* **1988**, *110*, 1313; A. J. Castellino, T. C. Bruce, *ibid.* **1988**, *110*, 7512.
[25] R. van Volkenburgh, K. W. Greenlee, J. M. Derfer, C. E. Boord, *J. Am. Chem. Soc.* **1949**, *71*, 172; C. H. Herr, F. C. Whitmore, R. W. Schiessler, *ibid.* **1945**, *67*, 2061.
[26] P. N. Rylander, *Aldrichim. Acta* **1979**, *12*, 53; W. Cocker, P. V. R. Shannon, P. A. Staniland, *J. Chem. Soc. (C)* **1966**, 41.
[27] R. Breslow, R. Winter, M. Battiste, *J. Org. Chem.* **1959**, *24*, 415; R. Breslow, J. Lockhart, A. Small, *J. Am. Chem. Soc.* **1962**, *84*, 2793; S. Hibino, E. Sugino, Y. Adachi, K. Nomi, *Heterocycles* **1989**, 275.
[28] A. Sorokin, A. Robert, B. Meunier, *J. Am. Chem. Soc.* **1993**, *115*, 7293.
[29] F. A. Davis, W. A. R. Slegeir, S. Evans, A. Schwartz, D. L. Goff, R. Palmer, *J. Org. Chem.* **1973**, *38*, 2809; F. A. Davis, P. A. Mancinelli, *ibid.* **1977**, *42*, 398.
[30] J. A. Garbarino, J. Sierra, R. Tapia, *J. Chem. Soc., Perkin Trans. 1* **1973**, 1866.
[31] W. Klyne, J. Buckingham, 'Atlas of Stereochemistry', 2nd edn., Chapman and Hall, London, 1977, Vol. 1, p. 44; D. J. Cram, *J. Am. Chem. Soc.* **1952**, *74*, 2149; D. J. Cram, N. L. Allinger, *ibid.* **1954**, *76*, 4516; D. J. Cram, *ibid.* **1952**, *74*, 2137.
[32] S. Hashimoto, N. Watanabe, S. Ikegami, *Synlett* **1994**, 353; S. Hashimoto, N. Watanabe, K. Kawano, S. Ikegami, *Synth. Commun.* **1994**, 3277; N. Watanabe, M. Anada, S. Hashimoto, S. Ikegami, *Synlett* **1994**, 1031.
[33] M. C. Pirrung, J. Zhang, A. T. McPhail, *J. Org. Chem.* **1991**, *56*, 6269; M. C. Pirrung, J. Zhang, A. T. Morehead, *Tetrahedron Lett.* **1994**, *35*, 6229; M. C. Pirrung, Y. R. Lee, *ibid.* **1994**, *34*, 6231.
[34] T. Fukuyama, C.-K. Jow, M. Cheung, *Tetrahedron Lett.* **1995**, *36*, 6373.
[35] M. P. Doyle, W. R. Winchester, M. N. Protopopova, P. Müller, G. Bernardinelli, D. Ene, S. Motallebi, *Helv. Chim. Acta* **1993**, *76*, 2227.
[36] B. Nyasse, L. Grehn, U. Ragnarsson, H. L. S. Maia, L. S. Monteiro, I. Leito, J. Koppel, *J. Chem. Soc., Perkin Trans. 1* **1995**, 2025.
[37] F. Nerdel, H. Goetz, E. Fabienk, *Liebigs Ann. Chem.* **1961**, *643*, 6.

[38] M. M. Kremlev, S. A. Boiko, *J. Org. Chem. USSR (Engl. Transl.)* **1971**, *7*, 1528.
[39] P. J. de Christopher, J. P. Adamek, G. D. Lyon, S. A. Klein, R. J. Baumgarten, *J. Org. Chem.* **1974**, *39*, 3525.
[40] V. L. Narayanan, to *Squibb & Sons*, US Patent 3501511, 1970 (*CA*: **1970**, *72*, 111090).
[41] E. Blanc, D. Schwarzenbach, H. D. Flack, *J. Appl. Crystallogr.* **1991**, *24*, 1035.
[42] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M. M. Woolfson, 'A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data', Universities of York, England, and Louvain-la-Neuve, Belgium, 1987.
[43] 'XTAL 3.2 User's Manual', Eds. S. R. Hall, H. D. Flack, and J. M. Stewart, Universities of Western Australia and Maryland, 1992.
[44] G. Bernardinelli, H. D. Flack, *Acta Crystallogr., Sect. A* **1985**, *41*, 500.
[45] W. A. Bonner, C. E. Stehr, J. R. Do Amaral, *J. Am. Chem. Soc.* **1958**, *80*, 4732; T. Hayashi, M. Konishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika, M. Kumada, *ibid.* **1982**, *104*, 180.
[46] D. J. Cram, *J. Am. Chem. Soc.* **1952**, *74*, 2137.
[47] D. H. Hua, S. W. Miao, J. S. Chen, S. Iguchi, *J. Org. Chem.* **1991**, *56*, 4.
[48] D. Cram, *J. Am. Chem. Soc.* **1963**, *85*, 1108.
[49] K. R. Kopecky, T. W. Mojelsky, T. Gillan, J. A. Barry, J. A. L. Sastre, *Can. J. Chem.* **1977**, *55*, 1001.