Heterocycle Synthesis

Rhodium-Catalyzed Intramolecular C—H Bond Activation with Triazoles: Preparation of Stereodefined Pyrrolidines and Other Related Cyclic Compounds

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Abstract: On treatment of triazoles having an *N*-sulfonylprotected benzylamine moiety with $[Rh_2(C_7H_{15}CO_2)_4]$, intramolecular C–H bond insertion takes place at the benzylic position to give *cis-N*-sulfonyl-2-aryl-3-[(sulfonylimino)methyl]pyrrolidines in good yields and with highly stereoselectivities. Analogously, the similar treatment of triazoles having an ether or even an alkyl moiety affords 2-alkyl- or 2-aryl-3-[(sulfonylimino)methyl]tetrahydrofurans or a 2alkyl-3-[(sulfonylimino)methyl]cyclopentane in good yields.

Intramolecular C–H bond activation followed by carboncarbon bond formation is a convenient way to prepare cyclic compounds.^[1] The use of carbene species generated by Rh-catalyzed diazo decomposition is one of the most fundamental methods to achieve this,^[2] and this method has recently been extended to triazoles as a functionalized carbene precursor.^[3–5] In conjunction with our study on Rh-catalyzed cyclization through C–H bond activation to give functionalized dihydropyrans,^[6,7] we were interested in the preparation of heterocyclic compounds starting from triazoles under Rh catalysis (Scheme 1).^[8] We found this transformation particularly useful for the stereoselective synthesis of functionalized pyrrolidines,^[9] in addition to the preparation of tetrahydrofurans^[10] and even a cyclopentane, which is described herein.



Scheme 1. Rh-catalyzed cyclization of triazoles through C-H activation.

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Some preliminary results of the above reaction, taking *N*-sulfonyl-protected benzylamine **1** as the substrate and several rhodium complexes of the type $[Rh_2(RCO_2)_4]$ as the catalyst under a range of reaction conditions, are shown in Table 1. The

Table 1. Fundamental data for the cyclization of 1. ^[a]						
	N=N NTs	Rh cat.			NTs	
	└ _Ŋ ́∕₽h	solvent, T, 2 h		< <mark>∖</mark> Ņ́∕►Ph		
	⊤s 1			ל: 2 cis	selective	
Entry	Rh cat. (mol%)	Solvent	<i>T</i> [°C]	2	Yield [%] ^[b]	1
		_			cis/trans	-
1	[Rh ₂ (tfa) ₄] (1)	DCE	80	0	-	100
2	[Rh ₂ (OAc) ₄] (1)	DCE	80	95	95:5	0
3	[Rh ₂ (oct) ₄] (1)	DCE	80	quant.	97:3	0
4	[Rh ₂ (oct) ₄] (1)	CHCl₃	reflux	8	n.d.	92
5	[Rh ₂ (oct) ₄] (1)	PhCl	80	59	n.d.	41
6	[Rh ₂ (oct) ₄] (1)	toluene	80	31	n.d.	69
7	[Rh ₂ (oct) ₄] (1)	dioxane	80	15	n.d.	85
8	[Rh ₂ (oct) ₄] (1)	DCE	60	13	n.d.	86
9	[Rh ₂ (oct) ₄] (0.5)	DCE	80	57	n.d.	43
[a] $Ts = p$ -MeC ₆ H ₄ SO ₂ , tfa = CF ₂ CO ₂ , Ac = CH ₂ CO, oct = C ₇ H ₁₅ CO ₂ , DCE = 1.2-						

 $[a] IS = p-MeC_6 n_4 SO_2$; $IIa = Cr_3 CO_2$, $RC = Cr_3 CO_2$, $RC = Cr_3 CO_2$, $BC = Cr_3 CO_2$, $BC = 1,2^-$ dichloroethane, n.d. = not determined. [b] Yields and *cis/trans* ratios were determined by ¹H NMR spectroscopy with an internal standard before purification.

choice of catalyst appears important: whereas $[Rh_2(tfa)_4]$, which was the most effective catalyst in our previous study on C–H bond activation,^[6] did not catalyze the reaction at all (Table 1, entry 1), catalysis by $[Rh_2(OAc)_4]$ or, particularly, $[Rh_2(oct)_4]$ afforded the desired products in high yields (entries 2 and 3), indicating that a more electron-rich Rh center gives higher catalytic activity. Further optimization of the reac-



Scheme 2. Variation of *N*-protecting groups. Yields and *cis/trans* ratio were determined by ¹H NMR spectroscopy.

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Scheme 3. Purification and characterization of products. Yield of crude 2 was determined by ¹H NMR spectroscopy. Other yields refer to isolated products.



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tion conditions was performed with respect to solvent (Table 1, entries 4–7), temperature (entry 8), and catalyst loading (entry 9), which determined the use of 1 mol% of $[Rh_2(oct)_4]$ under heating in 1,2-dichloroethane (DCE) at 80°C (Table 1, entry 3) to be optimum.

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Moreover, the nature of the *N*-protecting group of the benzylamines was also found to be crucial (Scheme 2). It should be emphasized that the *N*-sulfonyl protecting group adopted in 1 is key to the success in obtaining pyrrolidine 2, as other amine derivatives, such as *N*-alkyl- or *N*-acyl-protected substrates 3-5, did not give the desired products 6-8 at all.

As can be seen from Table 1 and Scheme 2, another important feature of this transformation is the high stereoselectivity imparted to the product. Under the optimum conditions, representative starting material 1 gave crude sulfonylimine 2 in quantitative yield and with an isomeric ratio of 97:3 (judged by ¹H NMR spectroscopy). As sulfonylimines are unstable to moisture and could not be purified by routine flash chromatography, this crude product was immediately reduced with LiAlH₄ to give, after chromatography on silica gel, bis-sulfonylamine 9 in 74% overall yield from 1 and with the same isomeric composition as above (Scheme 3, method a). The cis and trans structures were unambiguously assigned to the major and minor isomers of 9, respectively, in comparison with authentic samples of both isomers of **9**,^[11] which in turn determined that the stereochemistry of the major isomer of parent sulfonylimine 2 was cis, as depicted. In certain cases where recrystallization of the products was operative, pure samples of sulfonylimines were available (Scheme 3, method b).^[12] For example, crude 2 was successfully recrystallized from hexane/ethyl acetate to give chemically and isomerically pure 2 in 54% overall yield from 1. When this pure sample of 2 was treated with LiAlH₄, as in the method a, pure **9** was produced in 98% yield, confirming that no cis/trans isomerization took place during the reduction. Therefore, when sulfonylimines such as 2 are required for the subsequent transformations, either their crude samples of high isomeric purities or isomerically pure samples after recrystallization could be used.

Other pyrrolidines prepared by this method are shown in Table 2. The products were isolated in one or both of the following two ways (Scheme 3): method a) When the crude products are reduced to sulfonylamines, the cis/trans ratios of the sulfonylamines most likely reflect those of the parent sulfonylimines; method b) when the products solidify, recrystallization to pure sulfonylimines can be undertaken, even though the yields are somewhat decreased. A variety of aryl groups in the benzylamine moiety, including electron-rich or -deficient ones, participated in the reaction to give pure cis-2-aryl-3-[(arenesulfonylimino)methyl]pyrrolidines 2 and 26 or their amine derivatives 9 and 18-22 with high cis-selectivities (Table 2, entries 1-6). Although several N-(arenesulfonyl) protecting groups were acceptable in this reaction, the naphthalenesulfonyl group, as in 16, could enhance the crystallization of products (Table 2, entry 8). Another sulfonyl group on the imino group could also be changed (Table 2, entry 9). The stereodefined pyrrolidines obtained by this method are useful for subsequent stereoselective transformations.

The mechanism of this reaction should involve the insertion of the in situ-generated Rh–carbenoid into the benzylic C–H bond. In fact, when bis-deuterated benzylamine $[D_2]1$ was submitted to the reaction [Eq. (1)], the two deuterium atoms were



preserved at the specified positions of product $[D_2]$ **9**, consistent with the above process. Based on this mechanism, the high *cis*-stereoselectivity of the product could be rationalized as in Scheme 4. In the six-membered transition state **31** following the generation of **30**, the sterically demanding [Rh] portion occupies the equatorial position, while the Ph group is located at the axial position to minimize the steric repulsion against the neighboring bulky *N*-sulfonyl group shown in another transition state **32**. From preferred structure **31**, observed [D₂]**2** was produced, releasing the Rh catalyst to make the catalytic cycle continue.



Scheme 4. Proposed stereochemical course of the reaction.

The above cyclization is also applicable to benzyl ethers (Scheme 5), with the reaction conditions given in Table 2. Benzyl ether **33** afforded crude tetrahydrofuran **34** with a 1:1 isomeric ratio in quantitative yield by ¹H NMR analysis. As **34** was an oil and a mixture of isomers, it was reduced to sulfonylamine **35**, the structure of which was unambiguously determined to be a 52:48 mixture of the *trans* and *cis* isomers by comparison with authentic samples of **35**. If necessary, crude sulfonylimines could be converted into the corresponding aldehydes by basic hydrolysis. For example, crude **34** (*trans/cis* = 47:53) afforded aldehyde **36** of a higher *trans* purity (*trans/cis* = 89:11) in excellent yield, apparently through concomitant

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Scheme 5. Preparation of tetrahydrofurans. Yield of 34 was determined by ¹H NMR spectroscopy with an internal standard. Other yields refer to isolated products.

equilibrium leading to the thermodynamically more stable isomer.

More results relating to Scheme 5 are summarized in Table 3. As the primary products, sulfonylimines, were all oils, they were purified after the aforementioned reduction. Although the diastereoselectivity remains unsatisfactory (Table 3, entries 1 and 2), high yields were uniformly observed even for a sterically congested starting material such as 37, giving spirocyclic product 42 (Table 3, entry 2). More importantly, this reaction is not limited to benzyl ethers and is applicable to allyl or even saturated alkyl ethers (38-41; Table 3, entries 3-6), affording the expected products 43-45 and spiro-fused 46. In light of these results, we suspected that a heteroatom within the tether was not essential to this reaction. To address this issue, we prepared the simplest substrate 47, which lacks a heteroatom in its methylene tether, and subjected it to the standard cyclization conditions (Scheme 6). Gratifyingly, the desired reaction took place cleanly to give crude cyclopentane 48 in good yield, which was subsequently reduced to 49 for characterization. Therefore, the present reaction proved to be a potential method to prepare a variety of [(sulfonylimino)methyl]-substituted cyclic products via C-H bond activation.

In conclusion, the Rh-catalyzed intramolecular cyclization of triazoles through C–H bond activation afforded various functionalized cyclic products, such as pyrrolidines, tetrahydrofurans, and a cyclopentane. In the synthesis of pyrrolidines, the

Table 3. Preparation of various tetrahydrofurans.							
Entry	N=N NTs O R Substrate	[Rh₂(oct)₄ DCE, 80] (1 mol%) C, 2 h crude sul Sulfonylimine ratio ^[a]	^{(∼} NTs R Ifonylimine Product	iv) min sulfor Sulfonyla	∼NHTs R nylamine amine yield [%] ^(b)	ratio ^(c)
1	N=N NTs O Ph	33	53:47	NHTs O Ph	35	97	52:48 ^(d) (52:48 ^(d))
2	N=N NTs O Ph	37	78:22	NHTs O Ph	42	92	70:30 (73:27)
3	N=N NTs OC ₃ H ₇	38	55:45	NHTs OC ₃ H ₇	43	84	57:43 (54:46)
4	N=N NTs O-CH ₃	39	-	O NHTs	44	62	-
5	N = N NTs C_5H_{11}	40	64:36	NHTs OC ₅ H ₁₁	45	84	64:36 (64:36)
6	N≥N NTs 0	41	_	O NHTs	46	91	-
[a] trans/cis Patio	or vice verse of the crude	producto	[h] Overall violds of	icolated triazolos [c] trans/	cic Patio or v	ico vorca hoforo n	rification, those after

[a] *trans/cis* Ratio or vice versa of the crude products. [b] Overall yields of isolated triazoles. [c] *trans/cis* Ratio or vice versa before purification; those after purification are shown in parentheses. [d] This refers to *trans/cis* ratio.



Scheme 6. Preparation of a cyclopentane. Yields of 48 and 49 were determined by 1 H NMR spectroscopy and isolation, respectively.

highly stereoselective cyclization was applied to the preparation of pure *cis*-2-aryl-3-[(arenesulfonylimino)methyl]pyrrolidines.

Experimental Section

cis-2-phenyl-1-(p-toluenesulfonyl)-3-{[(p-toluenesulfonyl)-Pure imino]methyl}pyrrolidine (2): A mixture of N-benzyl-N-{2-[1-(p-toluenesulfonyl)-1,2,3-triazol-4-yl]ethyl}-p-toluenesulfonamide (1; 0.495 g, 0.969 mmol) and rhodium octanoate dimer ([Rh₂(oct)₄]; 7.5 mg, 0.0097 mmol) in 1,2-dichloroethane (4.85 mL) was stirred in an oil bath maintained at 80 °C for 2 h. After the mixture had cooled to room temperature, the solvent was removed under reduced pressure to give the crude product as an oil, ¹H NMR spectroscopy of which showed that the cis/trans ratio was 97:3. The crude sample that solidified was dissolved in ethyl acetate (2 mL) in an oil bath maintained at 70 °C and then allowed to stand at room temperature for a few hours. After the crystallization was completed at room temperature, the supernatant was removed by syringe and the residue was washed with hexane/ethyl acetate (4:1) until the washings were colorless (3×0.5 mL). The crystals were dried under vacuum to give a pure sample of the title compound (0.253 g, 54% from the starting triazole) as white crystals and as a single isomer.

A 97:3 mixture of cis- and trans-2-phenyl-1-(p-toluenesulfonyl)-3-{[(p-toluenesulfonyl)amino]methyl}pyrrolidine (9): A mixture of N-benzyl-N-{2-[1-(p-toluenesulfonyl)-1,2,3-triazol-4-yl]ethyl}-p-toluenesulfonamide (1) (0.129 g, 0.252 mmol) and $[Rh_2(oct)_4]$ (2.0 mg, 0.0025 mmol) in 1,2-dichloroethane (1.25 mL) was stirred in an oil bath maintained at 80 °C for 2 h. After the mixture had cooled to room temperature, the solvent was removed under reduced pressure to give crude 2 as an oil, ¹H NMR spectroscopy of which showed the presence of a 97:3 mixture of cis- and trans-2. To a solution of this crude product in THF (1.25 mL) was added LiAlH₄ (11.9 mg, 0.314 mmol) at -78 °C. After being stirred at this temperature for 10 min and at room temperature for 20 min, the mixture was quenched with methanol (0.3 mL) at $-78\,^\circ\text{C}$ and allowed to warm to room temperature. After ethyl acetate and aqueous 1 N HCl solution (2 mL each) were added, the organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 mL×3). The combined organic layers were washed with brine (2 mL), dried over Na₂SO₄, and concentrated under vacuum to give crude 9 as an oil, ¹H NMR analysis of which showed that the *cis/* trans ratio was again 97:3. The crude product was purified by chromatography on silica gel (30% ethyl acetate in hexane) to afford the title compound (89.7 mg, 74%) as a white solid of the same diastereomeric composition observed prior to purification.

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