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Tetrahedron Letters 44 (2003) 8733–8737

TETRAHEDRON LETTERS

Ruthenium(II) porphyrin catalyzed cyclopropanation of alkenes with tosylhydrazones

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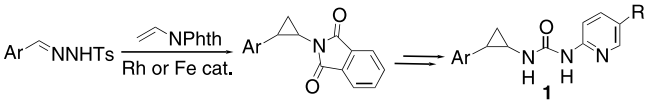
Received 30 June 2003; revised 29 August 2003; accepted 10 September 2003

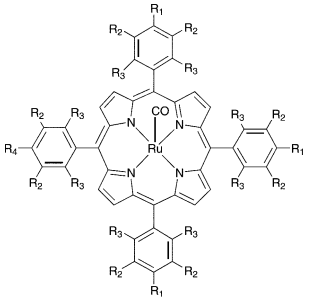
Abstract—The diastereoselective ruthenium(II) porphyrin catalyzed cyclopropanation of a variety of alkenes with aryl diazomethanes generated in situ from stable tosylhydrazone derivatives, was achieved in good to excellent yields (up to 92%) and product turnovers. The practical utility of [Ru^{II}(*p*-Cl-TPP)(CO)] (H_2(*p*-Cl-TPP) = *meso*-tetrakis(*p*-chlorophenyl)porphyrin) **3** was illustrated in the synthesis of the potent HIV-1 reverse transcriptase inhibitor **10**. Preferential formation of sulfone products for reactions involving *o*- and *m*-monosubstituted aryl tosylhydrazones demonstrated a hitherto unknown ruthenium(II) porphyrin catalyzed sulfonation reaction.

Transition metal-catalyzed carbenoid transfer reactions to C=C bonds and insertion to C–H bonds have demonstrated important applications in drug synthesis.[1,2] Aggarwal et al. recently reported one such strategy involving the Rh- or Fe-catalyzed cyclopropanation of *N*-vinylphthalimide with tosylhydrazone derivatives[2] in the synthesis of urea-PETT analogues **1**,[2a] a potent class of HIV-1 reverse transcriptase inhibitors (Scheme 1).[3]

Ruthenium(II) porphyrins catalyzed carbenoid transfer reactions using diazo compounds have received much attention in recent years (Fig. 1).[1,4–6] We and others recently demonstrated high product turnovers and reactivity exhibited by this class of catalysts in reactions involving C–C,[4] C–O[4i,5] and C–N[4i,6] bond formations. Work in our laboratory found that tosylhydrazone derivatives could be used as the carbene source in stereoselective Ru-catalyzed intramolecular carbenoid insertion to C–H bonds.[1i,4m] In light of this work, we wondered whether the same carbene source could be applied to the ruthenium(II) porphyrin catalyzed cyclopropanation of alkenes. Herein we describe the realization of a Ru-catalyzed protocol for effecting intermolecular alkene cyclopropanation with aryl tosylhydrazones. The competitive formation of aryl sulfones for reactions involving *o*- and *m*-monosubstituted aryl tosylhydrazones, a hitherto unknown ruthenium(II) porphyrin catalyzed sulfonation reaction, is also discussed.



Scheme 1. Rh- and Fe-catalyzed strategies to the synthesis of urea-PETT analogues **1**.



2: R_1 = R_4 = Me, R_2 = R_3 = H, [Ru^{II}(TTP)CO)];
3: R_1 = R_4 = Cl, R_2 = R_3 = H, [Ru^{II}(*p*-Cl-TPP)CO)];
4: R_1=R_2 = R_4 = H, R_3 = Cl, [Ru^{II}(2,6-Cl-TPP)CO)];
5: R_1=R_3 = R_4 = Me, R_2 = H, [Ru^{II}(TMP)CO)];
6: R_1 = R_2 = R_3 = R_4 = F, [Ru^{II}(F_{20}-TPP)CO];
7: R_1 = Cl, R_2 = R_3 = H, R_4 = Merrifield resin (loading = 0.1mmol/g);
8: R_1 = Me, R_2 = R_3 = H, R_4 = Merrifield resin (loading = 0.1mmol/g).

Figure 1. Ruthenium(II) porphyrin catalysts **2**–**8** used in this work. H_2(TTP) = *meso*-tetrakis(tolyl)porphyrin, H_2(2,6-Cl_2TPP) = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin, H_2-(TMP) = *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrin, H_2-(F_{20}-TPP) = *meso*-tetrakis(pentafluorophenyl)porphyrin.

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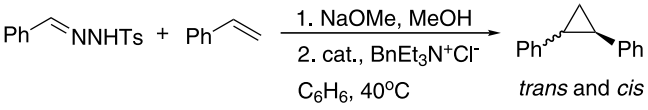
0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2003.09.157

The cyclopropanation of styrene with benzaldehyde tosylhydrazone was chosen as the model system to establish the reaction conditions. This revealed treatment of the benzaldehyde tosylhydrazone sodium salt with [Ru^{II}(TTP)(CO)] **2** (0.1 mol%) and $BnEt_3N^+Cl^-$ (phase transfer catalyst, 5.0 mol%) in C_6H_6 giving the best result. Under these conditions the *trans*-product was preferentially furnished (*trans*:*cis* = 95:5) in excellent yield (91%) and with a product turnover of 910 (Table 1, entry 1). The analogous Rh- and Fe-catalyzed reactions gave slightly lower *trans*-selectivity.[2a] Examination of other different ruthenium(II) porphyrins revealed the performance of **3** was similar to that observed for **2** in terms of yield, stereoselectivity and product turnover (entry 2). In contrast, ruthenium(II) porphyrins **4**–**6** containing either electron-withdrawing or electron-donating groups substituted at the *o*-position were found to exhibit lower reactivity and selectivity (entries 3–5). In every case, the main product was identified as stilbene. The use of Merrifield resin supported ruthenium porphyrins **7** and **8**[5i] gave product yields and selectivity lower than that of their homogenous counterparts **2** and **3** (entries 6 and 7).

Under similar conditions, the reactions of a variety of alkenes with either benzaldehyde- or naphthalene-2-carbaldehyde tosylhydrazone were examined (Table 2). These reactions gave the corresponding *trans*-cyclopropanes in good to excellent yields (up to 90%) and turnovers (up to 800) (entries 1–2, 4–6 and 8). Even in one instance where it was envisaged that the use of the sterically hindered alkene *trans*-β-methyl styrene would not be favorable under the present conditions, moderate product yield and selectivity was still obtained (entry 3). Notably, cyclopropanation of buta-1,3-dienyl-benzene occurred at the terminal C=C bond, suggested the present protocol to be regioselective (entry 7). Furthermore, the reaction of styrene with

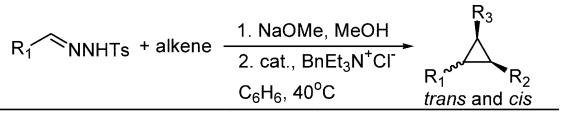
Table 1. Cyclopropanation of styrene with benzaldehyde tosylhydrazone catalyzed by ruthenium porphyrins **2**–**8**[a]



Entry	Catalyst	Yield (%)[b] (TON)	*trans*:*cis*[c]
1	**2**	91 (910)	95:5
2	**3**	92 (920)	96:4
3	**4**	42 (420)	34:66
4	**5**	36 (360)	70:30
5	**6**	25 (250)	74:26
6	**7**	68 (680)	72:28
7	**8**	66 (660)	75:25

[a] All reactions were performed in C_6H_6 at 40°C for 24 h with catalyst: $BnEt_3N^+Cl^-$: benzaldehyde tosylhydrazone:styrene ratio of 1:50:1000:5000.
[b] Isolated yield based on benzaldehyde tosylhydrazone consumed.
[c] Determined by GC compared with authentic sample.

Table 2. Cyclopropanation of alkenes with tosylhydrazone derivatives catalyzed by **2** and **3**[a]



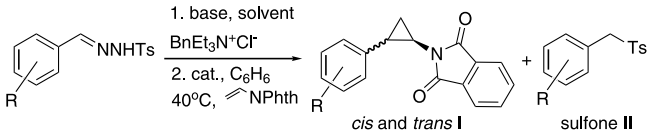
Entry	R_1	Alkene	Catalyst	Yield/% (TON)[b]	*trans* :*cis*
1	Ph		**2**	78 (780)	86: 14[c]
2			**3**	86 (860)	92: 8[c]
3	Ph		**3**	23 (230)	50: 50[d]
4	Ph		**3**	90 (800)	94: 6[d]
5	Ph		**3**	50 (500)	88: 12[d]
6	Ph		**3**	54 (540)	74: 26[d]
7	Ph		**3**	42 (420)	75: 25[c]
8			**3**	70 (700)	95: 5
9			**2**	68 (680)	63: 37[c]
10			**3**	78 (780)	79: 22

[a] All reactions were performed in C_6H_6 at 40°C for 24 h with catalyst: $BnEt_3N^+Cl^-$: tosylhydrazone: alkene ratio of 1:50:1000:5000.
[b] Isolated yield based on tosylhydrazone consumed.
[c] Determined by GC comparison with authentic sample.
[d] Determined by ^1H NMR compared with known compounds.[1h,8]

trans-cinnamaldehyde tosylhydrazone giving [2-(2-phenyl-cyclopropyl)-vinyl]-benzene as the sole product in 68% yield implied the present procedure was also chemioselective. No byproducts that could be attributed to competitive dimerization were detected (entry 9). *It is worth mentioning that the analogous [$Rh_2(CH_3CO_2)_4$]-catalyzed reaction gave both the cyclopropane and 2-(6-phenyl-hexa-1,3,5-trienyl)-benzene as an inseparable mixture of products in 38% yield.*[7] The chemioselectivity of the present procedure was further highlighted by the cyclopropanation of styrene with 3-phenyl-but-2-enal tosylhydrazone which afforded the corresponding cyclopropane as the sole product in 78% yield (entry 10). Albeit not unexpected, 3,4-dihydro-2*H*-pyran and tosylhydrazones derived from aryl ketones were the only examples found not to undergo reaction.[2a]

The cyclopropanation of *N*-vinylphthlimide with a variety of substituted tosylhydrazones was found to be somewhat intriguing (Table 3). Reaction of *N*-vinylphthlimide with benzaldehyde tosylhydrazone gave the desired product with preferential *cis*-selectivity in yields up to 72% (entries 1 and 2). However, with *o*-fluorobenzaldehyde tosylhydrazone the corresponding *cis*-cyclopropane was obtained as the minor product in moderate yields and turnovers (up to 350). The major isolated product was the corresponding arylsulfone (entries 3 and 4).[9] In this work, the analogous [Fe(TPP)Cl]-(H_2TPP = *meso*-tetrakis(phenyl)porphyrin) and [$Rh_2(CH_3CO_2)_4$]-catalyzed reactions afforded either the desired *cis*-cyclopropane adduct in yields up to 35% (entries 5 and 6). Similarly, the reactions of both *o*-bromo- and *o*-chlorobenzaldehyde tosylhydrazone gave

Table 3. Cyclopropanation of *N*-vinylphthalimide with arylaldehyde tosylhydrazones catalyzed by **2** and **3**[a]



Entry	R	Catalyst	Yield of I (%)[d] (TON)	*cis*:*trans*[e]	Yield of II (%)[d]
1	H	**2**	66 (660)	60:40	–
2	H	**3**	72 (720)	66:34	–
3	2-F	**2**	20 (100)	*cis* only	65
4	2-F	**3**	35 (350)	*cis* only	50
5	2-F	[b]	20 (10)	*cis* only	–
6	2-F	[c]	35 (18)	*cis* only	–
7	2-Cl	**3**	–	–	83
8	2-Br	**3**	–	–	86
9	3-OMe	**3**	70 (700)	*cis* only	20
10[f]	4-OMe	**3**	43 (430)	75:25	–
11	2-Cl,6-F	**3**	46 (460)	65:35	–
12	2-Cl,6-F	[b]	30 (30)	65:35	–
13	2-Cl,6-F	[c]	40 (40)	90:10	–

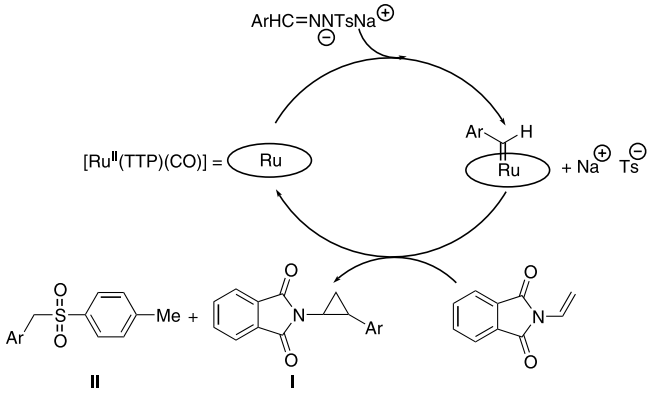
[a] All reactions were performed in C_6H_6 at 40°C for 48 h with catalyst: $BnEt_3N^+Cl^-$: tosylhydrazone: *N*-vinylthphalimide ratio of 1:50:1000:5000.
[b] [Fe(TPP)Cl], base: LiHMDS, in $PhCH_3$ at 40°C for 48 h with catalyst: $BnEt_3N^+Cl^-$: tosylhydrazone: *N*-vinylthphalimide ratio of 1:5:100:500.
[c] $[Rh_2(CH_3CO_2)_4]$, base: LiHMDS, in dioxane at 40°C for 48 h with catalyst: $BnEt_3N^+Cl^-$: tosylhydrazone: *N*-vinylthphalimide ratio of 1:10:100:500.
[d] Isolated yield based on tosylhydrazone consumed.
[e] Determined by ^1H NMR analysis compared with known literature.[1h,8]
[f] Base: LiHMDS.[10]

the corresponding arylsulfones as the sole products (entries 7 and 8).[9] Reactions with *m*- and *p*-methoxybenzaldehyde tosylhydrazones, on the other hand, afforded the desired cyclopropanes in moderate to good yields (up to 70%).[10] Note that for *m*-methoxybenzaldehyde tosylhydrazone, cyclopropanation was observed to occur with exclusive *cis*-selectivity (entries 9 and 10).[8] Furthermore, cyclopropanation with 2-chloro-6-fluorobenzaldehyde tosylhydrazone gave 2-[2-(6-chloro-2-fluoro-phenyl)-cyclopropyl]-1,3-isoindoledione in 46% yield (entry 11). This compared favorably to the analogous reactions catalyzed by $[Rh_2(CH_3CO_2)_4]$ or [Fe(TPP)Cl] (entries 12 and 13). In this work, the moderate turnover number achieved for the Ru-catalyzed reaction (460) has not been attained for the same reaction catalyzed by the latter two catalysts studied in this laboratory (entries 11–13).

Whilst it is currently unclear as to why the formation of the sulfone byproduct is preferentially favored, the mechanistics of this reaction is speculated to involve initial formation of a ruthenium-carbene intermediate.[11] Nucleophilic attack of this reactive species by the tosylate anion generated in situ, a hitherto unknown competitive reaction pathway in ruthenium-carbene chemistry, is subsequently reasoned to be responsible for the formation of the sulfone product (Scheme 2).

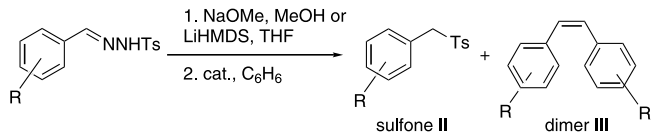
This is supported by studies examining the effect of metal-catalyzed decomposition of tosylhydrazones in the absence of alkene substrate (Table 4). These reactions furnished sulfone adduct in a number of cases as the major product in excellent yields (up to 88%) and product turnovers (up to 880) (entries 5 and 6). In other instances, the sulfone was furnished as the minor product in moderate yields along with the corresponding *cis*-stilbene[12] (entries 1, 2 and 8). The analogous Rh- and Fe-catalyzed reactions of *o*-fluorobenzaldehyde tosylhydrazone, in comparison, gave only the corresponding *cis*-stilbene (entries 3 and 4).

To highlight the practical applicability of the present procedure, attention was turned to its deployment in the synthesis of the potent HIV-1 reverse transcriptase inhibitor precursor **10** previously studied by Aggarwal[2a] and Doyle[1h] using $[Rh_2(CH_3CO_2)_4]$ catalyst. Aryl tosylhydrazone **9** was prepared from commercially available 4-chloro-2-fluorophenol in three steps in 78% overall yield.[2] Deprotonation of **9** with NaOMe (1 M) and



Scheme 2. Proposed mechanism for aryl sulfone **II** formation.

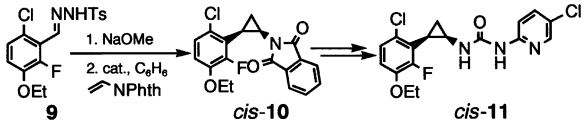
Table 4. Sulfonation of aryl tosylhydrazones catalyzed by ruthenium(II) porphyrins **2** and **3**[a]



Entry	R	Catalyst	Yield of II (%) (TON)[d]	Yield of III (%) (TON)[d]
1	2-F	**2**	30 (300)	60 (600)
2	2-F	**3**	32 (320)	61 (610)
3	2-F	[b]	–	90 (90)
4	2-F	[c]	–	90 (90)
5	2-Cl	**3**	84 (840)	10 (100)
6	2-Br	**3**	88 (880)	9 (90)
7	3-Br	**3**	–	80 (800)
8	3-MeO	**3**	22 (220)	74 (740)
9	4-MeO	**3**	–	90 (900)
10	2-Cl,6-F	**3**	–	82 (820)

[a] All reactions were performed in C_6H_6 at 40°C for 24 h with catalyst: $BnEt_3N^+Cl^-$: sodium tosylhydrazone salt ratio of 1:50:1000.
[b] [Fe(TPP)Cl] with catalyst: $BnEt_3N^+Cl^-$: lithium tosylhydrazone salt ratio of 1:50:100.
[c] $[Rh_2(CH_3CO_2)_4]$ with catalyst: $BnEt_3N^+Cl^-$: lithium tosylhydrazone salt ratio of 1:50:100.
[d] Isolated yield based on aryl tosylhydrazone consumed.

Table 5. Cyclopropanation of *N*-vinylphthalimide with tosylhydrazone **9** catalyzed by **2**, **3** and **8**[a]



Entry	Catalyst	Yield (%)[b] (TON)	*cis*:*trans*[c]
1	**2**	48 (480)	60:40
2	**3**	69 (690)	65:35
3	**8**	24 (240)	53:47

[a] Reactions were performed in C_6H_6 at 40°C for 48 h with catalyst: $BnEt_3N^+Cl^-$: tosylhydrazone: *N*-vinylthphalimide ratio of 1:50:1000:5000.
[b] Isolated yield based on tosylhydrazone consumed.
[c] Determined by ^1H NMR analysis.

treatment with *N*-vinylphthalimide, $BnEt_3N^+Cl^-$ and either **2** or **3** in C_6H_6 at 40°C for 24 h gave *cis*-**10** in good yields (up to 69%) and stereoselectivity (*cis*:*trans* ratio up to 65:35) (Table 5, entries 1 and 2). Moreover, this was accomplished with turnover numbers up to 690.[1h,2a] In comparison, the Merrifield resin polymer supported ruthenium(II) porphyrin **8** gave lower product yield and selectivity (entry 3). The use of this catalytic system did, however, allow for ease of recyclization and reuse for a further two times without loss of reactivity. Conversion of **10** to the *cis*-urea **11** that was spectroscopically identical with that reported,[1h] was subsequently achieved following literature procedures.[1h,2a]

Acknowledgements

This work is supported by the Area of Excellence Scheme (AoE/P-10-01) established under the University Grants Council (HKSAR), the Hong Kong Research Grants Council (No. 7077/01P) and the University Development Fund of the University of Hong Kong.

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