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Catalytic Thia-Sommelet−Hauser Rearrangement: Application to the Synthesis of Oxindoles

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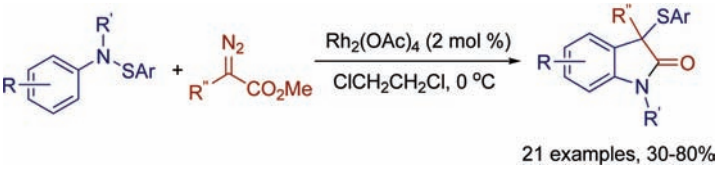
ABSTRACT



A series of 3-arylthio-1,3-disubstituted-oxindoles were prepared in good yields by the reaction of α-diazocarbonyl compounds and sulfenamides. The reaction involves a Rh-catalyzed thia-Sommelet−Hauser-type rearrangement.

Oxindole and its derivatives are frequently occurring structure units in medicinally active compounds of both natural and synthetic origin.[1] Recently, a plethora of new methods for the synthesis of oxindoles bearing quaternary carbon centers in the 3-position have been developed through transition-metal-catalyzed coupling reactions[2] or various cyclization methods.[3] In particular, the derivatives with a thio group at the 3-position have been widely investigated.[4,5] Among various approaches toward this

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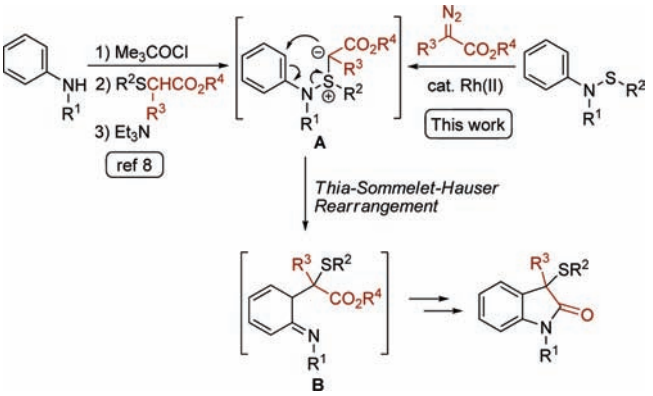
Scheme 1. Indolin-2-one Synthesis via Thia-Sommelet−Hauser Rearrangement



type of oxindoles,[4−9] we noticed that Gassman and co-workers developed a useful method to synthesize (3-methylthio)oxindoles by the reaction of α-carboalkoxy sulfides and aniline derivatives through a thia-Sommelet−Hauser rearrangement (Scheme 1).[8] The synthesis needs several steps, which include (a) formation of mono-*N*-chloroaniline; (b) generatation of azasulfonium salt; (c) the formation of sulfonium ylide **A** by treatment of the salt with base; (d) thia-Sommelet−Hauser-type rearrangement leading to imine **B**; and (e) acid-promoted intramolecular attack of the amino group on the carbonyl group. Later, Wierenga further optimized this procedure.[9a]

In Gassman's synthesis, thia-Sommelet−Hauser rearrangement is the key step, which is a unique process involving a [2,3]-sigmatropic dearomatization with subsequent [1,3]-shift rearomatization. This unique rearrangement is a useful way for constructing a cyclic quaternary carbon center from aromatic rings[8,9] or making *ortho*-substituted aromatic compounds.[10,11] It is noteworthy that in classic thia-Sommelet−Hauser rearrangement, the formation of sulfonium ylides is achieved by the treatment of the corresponding sulfonium salts with stoichiomeric amount of base.[8−10]

On the other hand, the reaction of sulfide with the in situ generated metal carbene, which can be easily achieved by transition-metal-catalyzed reaction of diazo compounds, is another reliable way to form sulfonium ylide.[12] This method has been proved to be highly efficient and operationally simple and can avoid the introduction of stoichiometric base. Various [2,3]-sigmatropic and 1,2-shift rearrangements of sulfonium ylides based on this method have been previously reported.[13,14] However, application of this approach to catalytic thia-Sommelet−Hauser rearrangement has been so far rather limited. Aggarwal and co-workers reported the first catalytic thia-Sommelet−Hauser rearrangement that was observed as side reaction.[11a] We have recently developed a Rh(II)-catalyzed thia-Sommelet−Hauser rearrangement that can be used as an efficient way to introduce a substituent to the *ortho* position of arylacetates efficiently.[11b] As an extension of this work, we further conceived that the sulfonium ylide intermediate **A** in Gassman's oxindole synthesis should be accessed through a catalytic carbene transformation by invoking a sulfenamide as substrate to react with metal carbene (Scheme 1). If this is indeed the case, then a catalytic version of Gassmen's oxindole synthesis will be achieved. Herein, we report the results of the study along this line.

Initially, we observed that when a 3:1 mixture of diazoacetate **2a**[15] and sulfenamide **1a**[16] in toluene was catalyzed by 0.5 mol % of $Rh_2(OAc)_4$, 1,3-dimethyl-3-(phenylthio)oxindole **3a** was isolated in 42% yield (Table 1, entry 1). A series of Rh(II) catalysts were then examined in order to optimize the reaction conditions. $Rh_2(O_2CCF_3)_4$ only gave trace amount of product (entry 2); $Rh_2(O_2CC_3F_7)_4$ and $Rh_2(acam)_4$ also led to lower yields (entries 3 and 4). Chiral dirhodium catalysts Rh_2(*S*-DOSP)$_4$ and Rh_2(*S*-TBSP)$_4$ afforded oxindole **3a** with relatively high yields (entries 5 and 6). It was noted that the reaction

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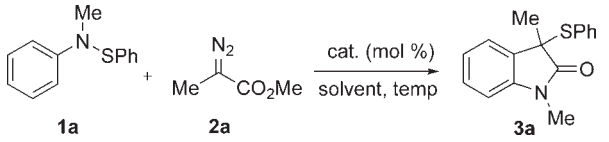
Table 1. Conditions on the Reaction of Sulfenamide **1a** and Diazoester **2a**[a]



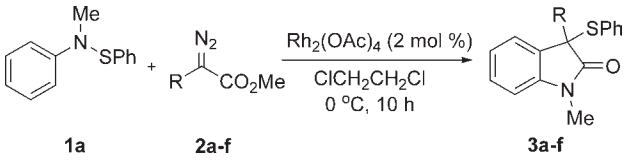
entry	cat. (mol %)	solvent	temp (°C)	time (h)	yield[b] (%)
1	$Rh_2(OAc)_4$ (0.5)	toluene	60	10	42
2	$Rh_2(O_2CCF_3)_4$ (0.5)	toluene	60	10	trace
3	$Rh_2(O_2CC_3F_7)_4$ (0.5)	toluene	60	10	24
4	$Rh_2(acam)_4$ (0.5)	toluene	60	10	22
5[c]	Rh_2(*S*-DOSP)$_4$ (0.5)	toluene	0	2	51
6[c]	Rh_2(*S*-TBSP)$_4$ (0.5)	toluene	0	2	49
7	$Cu(CH_3CN)_4PF_6$ (10)	DCE	60	2	7
8	CuI (10)	toluene	60	2	10
9	$Rh_2(OAc)_4$ (1)	toluene	0	10	45
10	$Rh_2(OAc)_4$ (2)	toluene	0	10	68
11	$Rh_2(OAc)_4$ (3)	toluene	0	10	68
12	$Rh_2(OAc)_4$ (2)	toluene	rt	10	61
13	$Rh_2(OAc)_4$ (2)	toluene	−20	10	58
14	$Rh_2(OAc)_4$ (2)	toluene	−40	10	43
15	$Rh_2(OAc)_4$ (2)	toluene	−78	10	44
16	**$Rh_2(OAc)_4$(2)**	**DCE**	**0**	**10**	**70**
17	$Rh_2(OAc)_4$ (2)	CH_2Cl_2	0	10	67
18	$Rh_2(OAc)_4$ (2)	DMF	rt	10	NR[d]
19	$Rh_2(OAc)_4$ (2)	CH_3CN	rt	10	30
20	$Rh_2(OAc)_4$ (2)	THF	0	10	48
21	$Rh_2(OAc)_4$ (2)	dioxane	15	10	64
22	$Rh_2(OAc)_4$ (2)	*n*-hexane	15	10	37

[a] The reaction was carried out with 1.0 equiv of **1a** and 3.0 equiv of **2a**. [b] Isolated yields after column chromatography. [c] The reaction gave a racemic product, as determined by HPLC with chiral OD-chromatography column. [d] NR: no reaction occurred.

could be carried out efficiently at 0 °C. However, the reaction did not show any enantioselectivity. Copper(I) catalysts were also investigated but neither of them was as effective as Rh(II) salt for the reaction (entries 7 and 8).

With $Rh_2(OAc)_4$ as catalyst, we set out to further optimize other reaction parameters. First, the yield was improved when the loading of catalyst was increased to 2 mol % (entries 9 and 10). However, no further improvement of yield was observed when the catalyst was increased to 3 mol % (entry 11). The effect of temperature was then studied (entries 12−15). The yields diminished, the reaction was then carried out at low temperature, and it was concluded that the reaction at 0 °C provided optimal results in terms of reaction time and yield. Finally, the effect of solvent was investigated, and dichloroethane (DCE), dichloromethane (DCM), and toluene afforded the products in approximately same yields (entries 10, 16, and 17). DCE led to a slightly cleaner reaction system. It was observed that polar solvent was disfavored for this reaction (entries 18−21). The reaction also proceeded inefficiently in solvent such as *n*-hexane as the sulfenamide **1a** became poorly soluble under such conditions (entry 22).

Table 2. Reaction of **1a** with **2a**−**f**[a]



entry	**2**, R =	**3**, yield[b] (%)
1	**2a**, CH_3	**3a**, 70
2	**2b**, $CH_3CH_2CH_2$	**3b**, 55
3	**2c**, $C_6H_5CH_2$	**3c**, 51
4	**2d**, CF_3	**3d**, 44
5	**2e**, $(CH_3)_2CH$	**3e**, −[c]
6	**2f**, *c*-hexyl	**3f**, −[c]

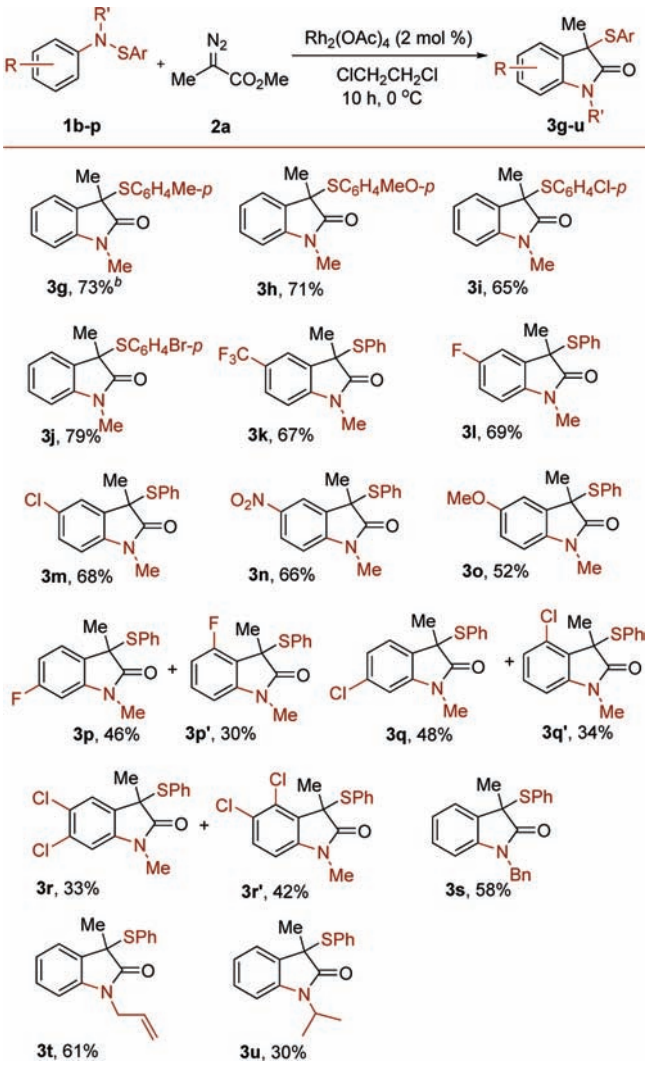
[a] Reaction conditions: to a solution of sulfenamide **1a** (0.5 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (0.01 mmol, 2 mol %) in 2 mL of DCE were added diazo compounds **2a**−**f** (1.5 mmol, 3.0 equiv) in 1 mL of DCE over 5 h with a syringe pump. The solution was further stirred for 10 h at 0 °C. [b] Isolated yields after column chromatography. [c] No expected products could be identified.

With the optimized reaction conditions in hand, we then explored the scope of the diazo compounds[15] in the reaction (Table 2). The reaction with the diazoacetates bearing primary alkyl substituents worked well to afford the corresponding oxindole products in moderate yields (entries 1 and 2). Diazoacetates bearing a benzyl or CF_3 substituent also worked, although the yields were slightly diminished (entries 3 and 4). It was observed that the reaction of diazoacetates bearing secondary alkyl substituents failed to afford the corresponding oxindole products (entries 5 and 6). The failure in these cases might be attributed to the increase of the steric hindrance of the diazo substrates, which poses a negative effect on the reaction of Rh(II) carbene intermediate with sulfenamide and also on the subsequent rearrangement step.

Next, the scope of sulfenamide substrates **1b**−**p**[16] was examined (Scheme 2). First, the electronic effect of substituents on the aromatic ring of SAr group was investigated. To our delight, the sulfenaminde substrates bearing either electron-rich or electron-deficient substituents on the aromatic ring of SAr all underwent the reaction smoothly to afford the corresponding oxindole products **3g**−**j** in good yields, which indicates that the electronic effect of SAr has no significant influence on the reaction.

Subsequently, we studied the effect of the substituents on the aromatic ring attached to nitrogen. A series of substituents were investigated, including *p*-CF_3, *p*-F, *p*-Cl, *p*-NO_2, and *p*-OMe. The reactions afforded the corresponding oxindole products **3k**−**o** in moderate to high yields, which indicate that the thia-Sommelet−Hauser rearrangement is not subjected to significant electronic effects of the aromatic ring. When a *meta* substituent is introduced to the aromatic ring attached to the nitrogen, the thia-Sommelet−Hauser rearrangement encounters

Scheme 2. Reaction of Sulfenamides **1b**−**p** with Diazo Compound **2a**[a]



[a] Reaction conditions: To a solution of sulfenamides **1b**−**q** (0.5 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (0.01 mmol, 2 mol %) in 2 mL of dichloroethane was added diazo compound **2a** (1.5 mmol, 3.0 equiv) in 1 mL of DCE over 5 h with a syringe pump. The solution was stirred for 10 h at 0 °C. [b] Isolated yields after column chromatography.

regioselectivity problem. In Gassman's synthesis of oxindole, generally low regioselectivity has been observed in the thia-Sommelet−Hauser rearrangement.[8b,9] We also observed low regioselectivities in our catalytic reaction system for the reaction with *m*-F-, *m*-Cl-, and *m,p*-Cl_2-substituted sulfenamides (**1k**, **1l** and **1m**, respectively), affording a mixture of (**3p** + **3p′**), (**3q** + **3q′**), and (**3r** + **3r′**), respectively.

At last, we varied another substituent on nitrogen (R′). The reaction with *N*-benzyl or *N*-allyl substituents afforded similar results (for **3s** and **3t**). However, the yield was significantly diminished when bulkier substituent, such as isopropyl, was introduced (**3u**).

The oxindole products obtained above were characterized by ^1H and ^{13}C NMR spectra. For one of the products, **3a**, the structure was determined by X-ray crystallography as show in Figure 1.

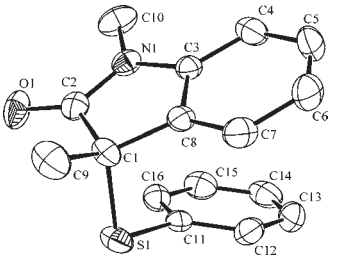


Figure 1. X-ray structures of **3a**.

In summary, we have achieved a catalytic version of Gassman's oxindole synthesis. With this $Rh_2(OAc)_4$-catalyzed transformation, a series of 3-arylthio-1,3-disubstituted oxindoles can be synthesized in one-step from easily available sulfenamides and diazoacetates. The catalytic reaction occurs under neutral conditions and can be carried out at low temperature, affording the products in moderately high yields. The reaction also shows excellent functional group tolerance. This reaction further demonstrates the efficacy of metal carbene-based catalytic thia-Sommelet-Hauser rearrangement in organic synthesis.

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Supporting Information Available. Experimental procedure, characterization data, ^1H and ^{13}C NMR spectra, and X-ray data (CIF) for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.