Organic Letters
Letter
pubs.acs.org/OrgLett

$Bi(OTf)_3$ Mediated *exo*-Olefin Isomerization of α-Benzoyl β-Styrylsulfones

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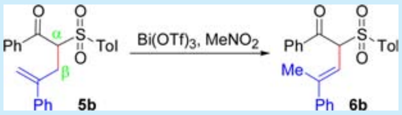
Ⓢ *Supporting Information*

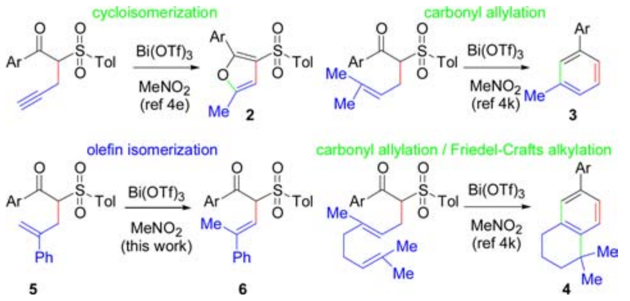
ABSTRACT: $Bi(OTf)_3$-mediated stereoselective *exo*-olefin isomerization of α-benzoyl β-styrylsulfones **5** in $MeNO_2$ afforded α-benzoyl α-cinnamylsulfones **6** in moderate to good yields.



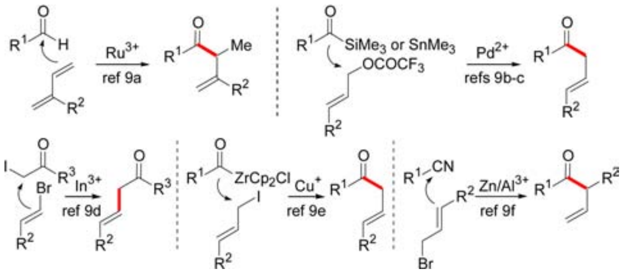
Functionalized organosulfones serve as versatile building blocks in numerous biologically active molecules, pharmaceuticals, intermediates, and natural products owing to the diverse reactivity of the α-methylene or arene position and the facile removal of the sulfonyl group.[1,2] Among the functionalized skeletons with a unique sulfonyl group, α-substituted β-ketosulfones (**1**) are important starting materials in a variety of organic transformations,[3] owing to them being easily converted into diversified cyclic structural frameworks that include the following: (i) monocyclic vinylcyclopropanes,[4a] cyclopentanones,[4b] pyrroles,[4c] dihydrofurans,[4d] furans,[4e,f] pyrazoles,[4g,h] oxazoles,[4i] tetrahydropyrans,[4j] arenes,[4k,l] and cycloheptanes;[4m] (ii) bicyclic hexahydroquinolinones[5a] and [3.2.1]octanones;[5b] and (iii) tricyclic phenanthrenes[6] through a direct transition-metal-catalyzed, oxidant-mediated, or organobase-promoted facile procedure. Recently, we have developed a $Bi(OTf)_3$-mediated one-pot conversion of β-ketosulfones (**1**) with an α-propargyl, α-prenyl, or α-geranyl substituent to furans (**2**), biphenyls (**3**), or tetralins (**4**) in good to moderate yields under mild conditions.[4e,k] $Bi(OTf)_3$, with nontoxic and environmental friendly properties, has been reported for a wide variety of organic reactions.[7,8]

In continuation of our investigations into the synthetic applications of β-ketosulfones (**1**), a novel and efficient $Bi(OTf)_3$-mediated intramolecular *exo*-olefin isomerization of α-benzoyl β-styrylsulfones **5** with a γ,δ-unsaturated ketone motif (derived from α-allylation of β-ketosulfones **1**) in $MeNO_2$ has been employed to construct the framework of α-benzoyl α-cinnamylsulfones **6** with a β,γ-unsaturated ketone motif, as shown in Scheme 1. Many synthetic approaches to β,γ-unsaturated ketones have been reported, such as Ru^{3+}-mediated diene hydroacylation of isoprenes with aldehydes,[9a] Pd^{2+}-catalyzed cross-coupling of allylic trifluoroacetates with acylsilanes[9b] or acylstannanes,[9c] In^{3+}-promoted α-vinylation of α-halocarbonyls,[9d] Cu^+-assisted coupling of acylzirconocenes with allylic halides,[9e] and Al^{3+}-promoted Barbier-type addition of allylzinc bromide with nitriles,[9f] as shown in Scheme 2. Recently, Tofimov reported a *t*-BuOK/DMSO-promoted synthetic approach to β,γ-enones via transition-metal free stereoselective α-vinylation of ketones with arylacetylenes.[10] To the best of our knowledge, no literature on the bismuth-mediated olefin isomerization has been reported. Therefore, further investigation into such a novel olefin migration remains of interest.

Scheme 1. $Bi(OTf)_3$-Mediated Transformations



Scheme 2. Transition-Metal-Promoted Synthesis of β,γ-Enones

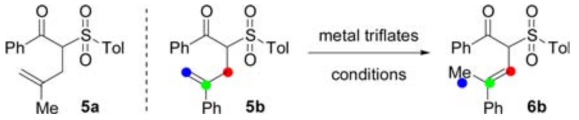


After further comparison of literature reports and our previous studies on bismuth triggered useful reactions; first, substrate **5a** was examined. Complex results were observed when **5a** was treated with the $Bi(OTf)_3/MeNO_2$ system. However, upon changing the methyl to a phenyl group, we found that this $Bi(OTf)_3/MeNO_2$ system could catalyze the transformation from germinal-disubstituted *exo*-alkene **5b** to trisubstituted *endo*-olefin **6b** with the (*E*)-stereoisomer emerging as the sole product at rt for 10 h in a 76% yield, as shown in Table 1 and entry 1. When the reaction mixture was conducted with other metal triflates, including $Zn(OTf)_2$, $Ni(OTf)_2$, $Cu(OTf)_2$, $In(OTf)_3$,

Received: October 19, 2015
Published: November 4, 2015

DOI: 10.1021/acs.orglett.5b03020
Org. Lett. 2015, 17, 5702−5705

Table 1. Conditions for the Olefin Isomerization of 5b[a]



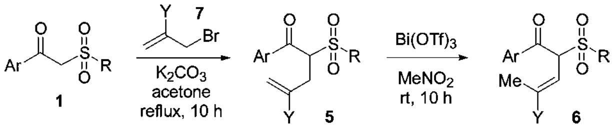
entry	$M(OTf)_n$ (mol %)	solvent (mL)	temp (°C)	yield (%)[b]
1	$Bi(OTf)_3$ (10)	$MeNO_2$ (5)	25	76
2	$Zn(OTf)_2$ (10)	$MeNO_2$ (5)	25	–[c]
3	$Ni(OTf)_2$ (10)	$MeNO_2$ (5)	25	–[c]
4	$Cu(OTf)_2$ (10)	$MeNO_2$ (5)	25	–[c]
5	$In(OTf)_3$ (10)	$MeNO_2$ (5)	25	30[c] (41)[d–e]
6	$Sc(OTf)_3$ (10)	$MeNO_2$ (5)	25	10[c,e]
7	$La(OTf)_3$ (10)	$MeNO_2$ (5)	25	–[c]
8	$Sm(OTf)_3$ (10)	$MeNO_2$ (5)	25	–[c]
9	$Yb(OTf)_3$ (10)	$MeNO_2$ (5)	25	–[c]
10	$Ga(OTf)_3$ (10)	$MeNO_2$ (5)	25	–[c]
11	$BiCl_3$ (10)	$MeNO_2$ (5)	25	–[c]
12	$BiBr_3$ (10)	$MeNO_2$ (5)	25	–[c]
13	$Bi(OTf)_3$ (5)	$MeNO_2$ (5)	25	60
14	$Bi(OTf)_3$ (20)	$MeNO_2$ (5)	25	75
15	$Bi(OTf)_3$ (10)	$MeNO_2$ (10)	25	70
16	$Bi(OTf)_3$ (10)	$MeNO_2$ (5)	101	58[f]
17	$Bi(OTf)_3$ (10)	$MeNO_2$ (5)	25	72[e]
18	$Bi(OTf)_3$ (10)	$PhNO_2$ (5)	25	52
19	$Bi(OTf)_3$ (10)	MeCN (5)	25	38[c]
20	$Bi(OTf)_3$ (10)	DMF (5)	25	51
21	$Bi(OTf)_3$ (10)	$(CH_2Cl)_2$ (5)	25	28[c]
22	$Bi(OTf)_3$ (10)	acetone (5)	25	–[c]
23	$Bi(OTf)_3$ (10)	$MeNO_2$ (5)	25	77[g]

[a] The reactions were run on a 0.2 mmol scale with **5b** at rt for 10 h. [b] Isolated yields. [c] Major **5b** was recovered. [d] 30% yield of **5b** was recovered. [e] 40 h. [f] The mixture of *E*/*Z* isomers was isolated. [g] TfOH (10 mmol %) was added.

$Sc(OTf)_3$, $La(OTf)_3$, $Sm(OTf)_3$, $Yb(OTf)_3$, and $Ga(OTf)_3$ (see entries 2–10), unexpectedly, we did not obtain better yields for the desired *α*-sulfonyl *β*,*γ*-enones **6b** regardless of which catalyst was used. Under thermodynamic conditions, the use of other Bi(III) salts was examined for the synthesis of **6b**. When **5b** was treated with $BiCl_3$ or $BiBr_3$, recovery of **5b** was observed (entries 11–12). In comparison with these Bi(III) salts, $Bi(OTf)_3$ was a better catalyst for the generation of **6b**. Using $Bi(OTf)_3$ as the catalyst, variations of the equivalents, reaction concentrations, solvents, and temperatures were studied next. When 5 mol % of $Bi(OTf)_3$ was used (entry 13), **6b** was isolated in a 60% yield along with 15% of **5b**. When 20 mol % of $Bi(OTf)_3$ was used (entry 14), the yield for **6b** was similar to when 10 mol % was used. After decreasing the reaction concentration (5 mL → 10 mL, entry 15), the yield was decreased slightly. Obvious changes in the isolation of *E*/*Z* isomers occurred at elevated temperatures (25 °C → reflux, entry 16). Elongating the reaction time (10 h → 40 h, entry 17) provided similar results. After changing the solvents (from $MeNO_2$ to $PhNO_2$, MeCN, DMF, $(CH_2Cl)_2$), a sluggish conversion was achieved (entries 18–21). Entry 22 shows that the addition of acetone could not afford **6b**. By the involvement of catalytic amounts of TfOH (entry 23), the yield of **6b** was maintained (77%).

With optimized conditions in hand (see Table 1, entry 1), we further explored the substrate scope of the reaction, and the results are shown in Table 2. First, *α*-benzoyl *β*-styrylsulfones **5a–p** were generated with yields in the range 85%–95% (after recrystallization from hexanes and EtOAc) by a facile K_2CO_3-mediated mono-*α*-allylation of *β*-ketosulfones **1a–j** (Ar = Ph, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$, 4-PhC_6H_4, 2-naphthalene; R = Tol, 4-FC_6H_4, 4-$MeOC_6H_4$, Ph, Me) with *α*-styryl bromides **7a–i** (Y = Ph, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-$CF_3C_6H_4$, 4-$NO_2C_6H_4$, 4-PhC_6H_4, 2-naphthalene) in the presence of boiling acetone providing **5a–p**, as shown in Table 2. The stereoselective *exo*-olefin isomerization of **5a–p** with the $Bi(OTf)_3$/$MeNO_2$ system was further examined. All entries showed that Ar and R groups, with both electron-withdrawing and -donating substituents, were well tolerated, providing the desired *α*-benzoyl *α*-cinnamylsulfones **6** in moderate to good yields (56–92%) except for **6a** (Y = Me), **6d** (Y = 4-$MeOC_6H_4$), and **6g** (Y = 4-$MeOC_6H_4$). From the above results, we found that the Y group of skeleton **5** could better affect the efficiency of the intramolecular olefin isomerization than the Ar and R groups (substituent effect: Y > Ar ≈ R). Y, with a methyl group, provided complex results due to intramolecular carbonyl allylation of **5a** occurring (entry 1).[4k] In addition, Y, with a 4-methoxyphenyl or 4-nitrophenyl group, could inhibit the isomerization procedure, and the starting materials were recovered (entries 4 and 7). In contrast, when the Ar group of skeleton **5** was an electron-withdrawing group (**5n**, 4-FC_6H_4; **5p**, 4-$NO_2C_6H_4$), the desired product provided excellent yields (92% and 90%, entries 14 and 16). However, after the Ar group was changed to a donating group (**5o**, Ar = 4-$MeOC_6H_4$), a lower yield (65%, entry 11) was observed. Furthermore, the R group (**5j**, R = 4-FC_6H_4; **5k**, R = 4-$MeOC_6H_4$) performed with similar results, as shown in entries 10–11. The structural frameworks of **6h**, **6n**, and **6q** were determined by single-crystal X-ray crystallography.[11]

Table 2. Synthesis of 5 and 6[a–b]

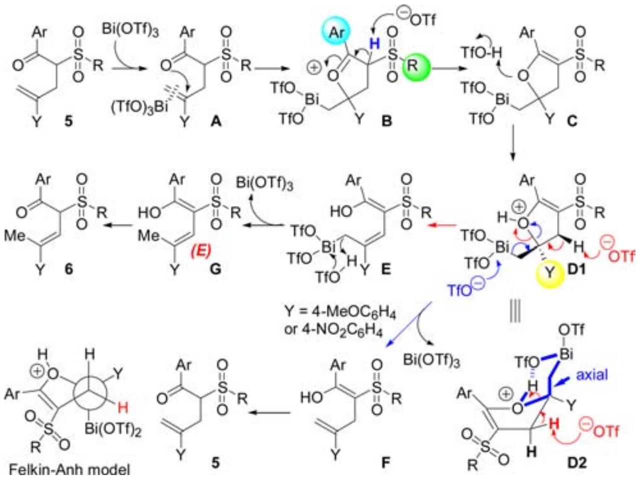


entry	**1**, Ar = , R = ; **7**, Y =	**5** (%)[c]	**6** (%)[c]
1	**1a**, Ph, Tol; **7a**, Me	**5a**, 92	**6a**, –[d]
2	**1a**, Ph, Tol; **7b**, Ph	**5b**, 90	**6b**, 76
3	**1a**, Ph, Tol; **7c**, 4-FC_6H_4	**5c**, 86	**6c**, 85
4	**1a**, Ph, Tol; **7d**, 4-$MeOC_6H_4$	**5d**, 84	**6d**, –[e]
5	**1a**, Ph, Tol; **7e**, 4-MeC_6H_4	**5e**, 86	**6e**, 75
6	**1a**, Ph, Tol; **7f**, 4-$CF_3C_6H_4$	**5f**, 86	**6f**, 89
7	**1a**, Ph, Tol; **7g**, 4-$NO_2C_6H_4$	**5g**, 85	**6g**, –[e]
8	**1a**, Ph, Tol; **7h**, 4-PhC_6H_4	**5h**, 84	**6h**, 80
9	**1a**, Ph, Tol; **7i**, 2-naphthalene	**5i**, 86	**6i**, 78
10	**1b**, Ph, 4-FC_6H_4; **7a**, Ph	**5j**, 86	**6j**, 82
11	**1c**, Ph, 4-$MeOC_6H_4$; **7a**, Ph	**5k**, 88	**6k**, 56
12	**1d**, Ph, Ph; **7a**, Ph	**5l**, 86	**6l**, 70
13	**1e**, Ph, Me; **7a**, Ph	**5m**, 83	**6m**, 72
14	**1f**, 4-FC_6H_4, Tol; **7a**, Ph	**5n**, 85	**6n**, 92
15	**1g**, 4-$MeOC_6H_4$, Tol; **7a**, Ph	**5o**, 85	**6o**, 65
16	**1h**, 4-$NO_2C_6H_4$, Tol; **7a**, Ph	**5p**, 84	**6p**, 90
17	**1i**, 4-PhC_6H_4, Tol; **7a**, Ph	**5q**, 86	**6q**, 76
18	**1j**, 2-naphthalene, Tol; **7a**, Ph	**5r**, 88	**6r**, 82

[a] The *α*-allylation was run on a 1.0 mmol scale with **1**, K_2CO_3 (2.0 mmol), **7** (1.05 mmol), acetone (15 mL), reflux, 10 h. [b] The olefin isomerization was run on a 0.2 mmol scale with **4**, $Bi(OTf)_3$ (10 mol %), $MeNO_2$ (5 mL), 25 °C, 10 h. [c] Isolated yields. [d] Complex results were observed. [e] No reactions.

Based on the substituent effect, we provide a possible reaction mechanism, as shown in Scheme 3. How is the conversion from **5** to **6** explained? Initially, complexation of $Bi(OTf)_3$ with a

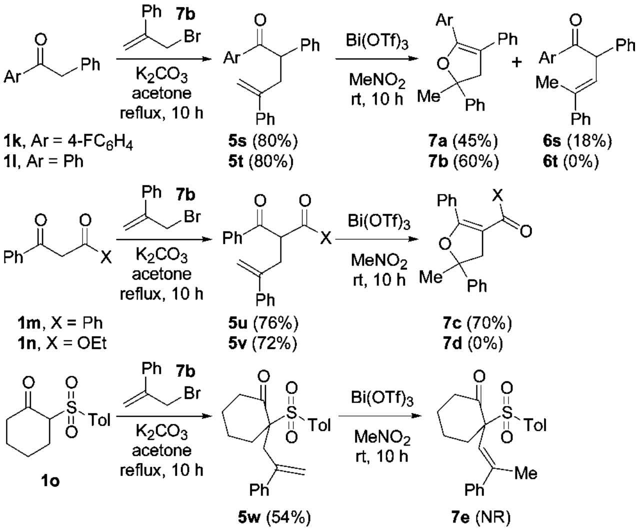
Scheme 3. Possible Mechanism



terminal olefin of **5** may yield intermediate **A**. Participation of a carbonyl group could lead to a cyclic intermediate **B** with a methylene bismuth arm. When Ar or R is a withdrawing group, the α-proton (blue H) with a higher acidity should be easy to abstract by an *in situ* generated triflate anion and it could promote transformation from **B** to **C**. Protonation of **C** with *in situ* HOTf gives **D1**. The resulting triflate ion could deprotonate the allylic proton (red arrow) to form **E**. The ring opening is suggested to be mediated by the released HOTf. Following the formation of an intramolecular hydrogen bond between the oxonium ion and the triflate ligand of the bismuth complex, the bismuth arm of **D2** should be orientated in an axial position due to the occurrence of a stable chair conformation. By the six-membered chair conformation on **D2**, the triflate anion could trap the equatorial proton (red H, not black H) regioselectively to force an *anti*-eliminated ring opening of the five-membered ring (E2 process) based on the Felkin–Anh model. However, when the Y group with an equatorial position is a stronger electron-donating or -withdrawing group, the debismuthation of **D1** (blue arrow) by the triflate anion may be preferred to generate **F**. Following by tautomerization of **F**, **5** is recovered. Finally, after the above-mentioned debismuthation pathway is finished, tautomerization of the corresponding **G** with an (*E*)-configured conformation gives **6**. According to the above-mentioned experimental conditions and results (Table 2), triflate anion-promoted intramolecular olefin isomerization from **5** to **6** suggests the proposed mechanism.

To examine the limitations of this Bi(OTf)$_3$-mediated route (see Scheme 4), K_2CO_3-mediated mono-C-allylation of deoxybenzoins **1k–l** (Ar = 4-FC_6H_4, and Ph), 1,3-diketone **1m**, β-ketoester **1n**, and cyclic β-keosulfone **1o** were first investigated. Under the standard protocol, **5s–t** were isolated in 54%–80% yields. When **5s** was treated with the Bi(OTf)$_3$/$MeNO_2$ system, cyclic dihydrofurans **7a** and an isomerized product **6s** were generated in a ratio of 7:3. However, treatment of **5t** afforded only isomer **7b** in a 60% yield and no **6t** was observed. A change in the substituent from an aryl to a benzoyl group gave a 70% yield of **7c** with a cyclic skeleton via the intramolecular annulation of **1m**. The structure of **7c** was determined by single-crystal X-ray crystallography.[11] However, attempts to react with **5v** failed to afford **7d** due to the decarboxylation of **5v** that occurred. The above-mentioned results show that debismuthation of **C** (see Scheme 3) by the triflate anion produced skeleton 7. Furthermore, only the starting material **5w** was recovered when cyclic **5w** was treated with the Bi(OTf)$_3$/$MeNO_2$ system.

Scheme 4. Bi(OTf)$_3$-Mediated Reactions of 1k–o



In summary, a Bi(OTf)$_3$-mediated stereoselective *exo*-olefin isomerization of α-benzoyl β-styrylsulfones **5** in $MeNO_2$ afforded α-benzoyl α-cinnamylsulfones **6** in moderate to good yields at 25 °C for 10 h. **5** was also provided in good yields via the K_2CO_3-mediated α-allylation of **1**. A plausible mechanism has been proposed for these isomerization reactions. The structures of the key products were confirmed by X-ray crystallography. Further investigations regarding the synthetic applications of β-ketosulfones will be conducted and published.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03020.

Detailed experimental procedures and spectroscopic data for all new compounds (PDF)
X-ray analysis data of **6h** (CIF)
X-ray analysis data of **6n** (CIF)
X-ray analysis data of **6q** (CIF)
X-ray analysis data of **7c** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the Ministry of Science and Technology of the Republic of China for financial support (MOST 104-2113-M-037-012).

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