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Rh(II)-catalyzed formation and rearrangement of trifluoroacetyl-containing sulfur ylides

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Abstract—A facile, convenient, efficient, and high yielding Rh(II)-catalyzed formation and rearrangement of trifluoroacetyl-containing sulfur ylides are reported. It is a $Rh_2(OAc)_4$-catalyzed [2,3]-sigmatropic rearrangement of sulfur ylide intermediates generated from α-diazo compounds.

1. Introduction

The unique properties of fluorine atom make the fluorinated and trifluoromethylated compounds extremely attractive in the area of theoretical chemistry, modern agrochemistry, material science, and medicinal chemistry.[1,2] The synthesis of trifluoromethylated materials is an ongoing area of research, in which, on one hand, the innovative methods for introducing a CF_3 group to aromatic compounds by direct trifluoromethylation have emerged and on the other hand, appropriate means for constructing CF_3-containing aliphatic compounds have not been well-documented.[3] Therefore, new approaches to trifluoromethylated aliphatic compounds under mild reaction conditions with a tolerance of functionalities are still highly desirable.

The generation of sulfur ylides and their chemical transformation have received much attention because of their utilities in synthesis and their possible involvement in biochemical processes.[4] For example, sulfur ylides are good reagents for preparation of oxiranes,[5] cyclopropanes,[6] and other natural products.[7] The [2,3]-sigmatropic rearrangement of sulfur ylide is widely recognized as a facile bond reorganization process, which has undergone a renaissance because of the discovery of metal complexes, rhodium(II) acetate in particular as high effective catalysts for the ylide generation.[8] Although sigmatropic sulfur ylide rearrangements catalyzed by $Rh_2(OAc)_4$ are well-documented,[9] there is still considerable interest in the development of effective catalytic systems for the rearrangement of ylides generated from reactions of diazo compounds with allylic substrates.[10]

α-Diazocarbonyl compounds are an important class of intermediates for the preparation of structurally complex and diverse natural product.[11] In general, these are often used as synthetic precursors for certain transition metal-catalyzed reactions, such as ylide formation, cyclopropanation, and C–H insertion.[12] As a part of our continuing effort on the synthesis of fluorine-containing compounds using fluorinated diazo compounds,[13] we have developed Rh(II)-catalyzed formation and rearrangement of trifluoroacetyl-containing sulfur ylides from the 1,1,1-trifluoro-3-diazoacetoacetate **1** and allyl sulfides **2**. Herein, we wish to report this facile, convenient, efficient, and high yielding method for the synthesis of trifluoroacetyl-containing aromatic and aliphatic compounds.

2. Results and discussion

Initially, we began our studies with the Rh(II)-catalyzed reaction of α-diazo-β-ketoester **1** in the presence of allyl sulfides **2**. The reaction of electrophilic carbenes and carbenoids with unsaturated divalent sulfur compounds to give sulfonium ylides, which then undergo a [2,3]-sigmatropic rearrangement, is a well-described process.[14] It is believed that the lone pair of the sulfide adds to the electrophilic carbenoid intermediate and subsequent dissociation of the catalyst produces the sulfonium ylide.[14b] The symmetry-allowed [2,3]-sigmatropic rearrangement is widely recognized as a facile bond reorganization process, especially for allylic sulfides.[15] Accordingly, diazo compound **1** (1 mmol) was treated with an equimolar quantity of sulfide **2a** in refluxing toluene in

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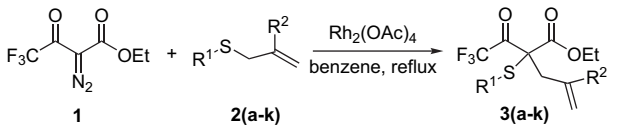
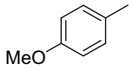
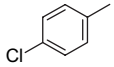
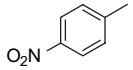
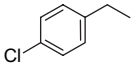
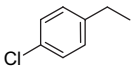
the presence of $Rh_2(OAc)_4$ (1 mol %) to give the corresponding product **3a** in 78% yield (Scheme 1). The structure of **3a** was determined by NMR, MS, and IR spectral data analysis. In order to investigate the scope of the sulfides, several sulfide derivatives were employed in this reaction. The results are summarized in Table 1.



Scheme 1.

Table 1. Reaction results of diazo compound **1** with allylic sulfide derivatives **2** in the presence of $Rh_2(OAc)_4$

Entry	R1	R2	Product	Yield[a] (%)
1		H	**3a**	78
2		H	**3b**	53
3		H	**3c**	98
4		H	**3d**	69
5		H	**3e** **4e**	8 42
6		H	**3f**	N.R.[b]
7		H	**3g**	87
8		CH_3	**3h**	51
9	CH_3CH_2–	H	**3i**	84
10	Me_3C–	H	**3j**	91
11	CH_2=$CHCH_2$–	H	**3k**	66

[a] Yield determined by ^1H and ^{19}F NMR.
[b] No reaction.

As shown from Table 1, not only aliphatic sulfides (entries 9–11) but also the aromatic sulfides substituted with electron-rich groups (entries 2–3) are good substrates for this reaction. However, to our surprise, for those aromatic sulfides substituted with electron-withdrawing groups (entries 4–6), the reaction results varied depending on the strength of the electron-withdrawing substituent.

In our study, we found that the reactivity of the substrate was extremely sensitive to the electron effect of the substituted groups on the phenyl ring. The presence of electron-donating groups such as methyl and methoxy enhances the reactivity of the reaction. For example, when the substrate contained a strong electron-donating methoxy group, short reaction time and high yield were observed (entry 3). However, when a weak electron-withdrawing substituted group such as chloride was connected to the phenyl ring, longer reaction time was required and the yield was lower (entry 4). It was an interesting observation that when **2e** was employed under the same reaction condition, only 8% of the expected product **3e** was observed in NMR spectrum, while 42% of **4e**, a des-$CF_3C(O)$ by-product, was isolated (entry 5, Scheme 2). The mechanism of the by-product formation is not clear. On the other hand, strong electron-withdrawing substituent in the phenyl ring resulted in no reaction according to ^1H NMR and TLC analysis even with prolonged reaction time or increased reaction temperature (entry 6). Based on the experimental results, we think that electron-donating substitution would stabilize the sulfur ylide intermediates, therefore, favor this reaction, while the electron-withdrawing substitution would destabilize the sulfur ylide intermediates.

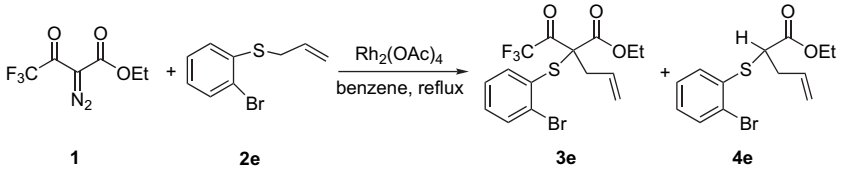
Comparing with the aromatic sulfide, we were delighted to find out that aliphatic sulfide was more reactive in catalytic ylide reaction. For example, in the case of **2j**, the reaction proceeded very well to give the desired product **3j** in 91% yield (entry 10). Similarly, when allyl(4-chlorobenzyl)-sulfane (**2g**) was used, it also gave the desired product in good yield (entry 9).

The reaction pathway for this conversion may involve formation of allylic sulfonium ylides derived from rhodium-catalyzed decomposition of **1** in the presence of allylic sulfides **2**, which could undergo sequentially the rhodium-catalyzed *carbenoid generation/sulfonium ylide formation/[2,3]-sigmatropic rearrangement* to produce the target product **3** (Scheme 3). As shown in Scheme 3, the aromatic R group bearing electron-withdrawing substituents may either reduce the electron density of the sulfide or destabilize the positive charge on sulfur ylide intermediates, therefore, may result in decreased yields or no reaction.

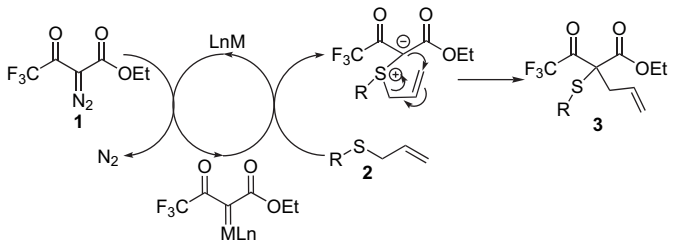
It is worthy to note that the reaction can be extended to a more interesting allylic substrate **2k**, which is a potentially useful intermediate in organic synthesis and may undergo many useful organic transformations, such as cyclization[9] (Table 1, entry 11; Scheme 4).

3. Conclusion

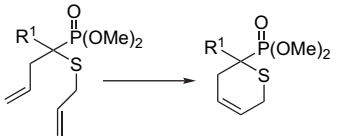
In summary, we have studied the [2,3]-sigmatropic rearrangement of sulfur ylide intermediates derived from catalytic decomposition of trifluoroacetyl-containing diazo compound **1** in the presence of allylic sulfides, which



Scheme 2.



Scheme 3.



Scheme 4.

afforded a variety of functionalized trifluoroacetyl-containing sulfides. Aliphatic sulfides are more reactive substrates for this reaction. It is a facile, convenient, efficient, and high yielding method for the synthesis of trifluoroacetyl-containing sulfide compounds.

4. Experimental

4.1. General

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on either a Bruker AM-300 or AM-400 spectrometer with Me_4Si and $CFCl_3$ (with upfield negative) as the internal and external standards, respectively. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low-resolution mass spectra or high-resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 or a Finnigan MAR-8430 instrument using the electron impact ionization technique (70 eV), respectively.

4.2. Typical procedure for the formation and rearrangement of sulfur ylides

Under a nitrogen atmosphere, a solution of diazo compound **1** (210 mg, 1 mmol) in 2 mL of benzene was added to a dry Schlenk tube containing $Rh_2(OAc)_4$ (4 mg, 1 mol %), sulfide (1 mmol), and benzene (2 mL) over 2 h with a syringe pump. After addition, the reaction mixture was stirred at reflux until completion, monitored by TLC. The solvent was removed in vacuum and the residue was purified on silica gel using ethyl acetate–hexane as eluant to afford the corresponding products.

4.3. Spectral data

4.3.1. Ethyl 2-(phenylthio)-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3a). Colorless liquid. IR (KBr): 2985, 1735, 1440, 1300, 1205, 1163, 1097, 924, 750 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.47–7.33 (m, 5H), 5.95–5.81 (m, 1H), 5.21–5.10 (m, 2H), 4.34–4.18 (m, 2H), 2.62–2.45 (m, 2H), 1.27 (t, J=7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.94 (q, J_{CF}=26 Hz), 165.84, 137.59, 130.77, 130.38, 129.42, 126.64, 120.07, 115.89 (q, J_{CF}=233 Hz), 65.25, 63.11, 36.40, 13.79. ^{19}F NMR (282 MHz, $CDCl_3$): δ=–70.47 (s, 3F). MS: m/z (%)=332 (M^+, 5), 291 (2), 161 (39), 135 (49), 123 (44), 110 (51), 109 (100), 85 (28), 77 (22), 73 (4), 69 (30), 45 (27), 41 (22). HRMS m/z calcd for $C_{15}H_{15}F_3O_3S$: 332.0694; found: 332.0700.

4.3.2. Ethyl 2-(*o*-tolylthio)-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3b). Colorless liquid. IR (KBr): 2985, 1736, 1470, 1299, 1202, 1163, 1095, 923, 755 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.27–7.05 (m, 4H), 5.76–5.62 (m, 1H), 5.07–4.98 (m, 2H), 4.13 (q, J=7 Hz, 2H), 2.44 (s, 3H), 1.17 (t, J=7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=182.91 (q, J_{CF}=33 Hz), 166.29, 144.65, 138.32, 131.07, 130.71, 130.67, 126.73, 126.52, 119.99, 115.91 (q, J_{CF}=291 Hz), 65.17, 62.91, 36.87, 21.18, 13.68. ^{19}F NMR (282 MHz, $CDCl_3$): δ=–70.54 (s, 3F). MS: m/z (%)=346 (M^+, 5), 175 (22), 149 (35), 123 (36), 97 (3), 91 (26), 77 (28), 73 (4), 69 (9), 45 (100), 41 (12). HRMS m/z calcd for $C_{16}H_{17}F_3O_3S$: 346.0851; found: 346.0836.

4.3.3. Ethyl 2-(*p*-tolylthio)-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3c). Colorless liquid. IR (KBr): 2984, 1733, 1592, 1495, 1291, 1203, 1161, 1096, 1029, 832, 740 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.33 (d, J=9 Hz, 2H), 6.87 (d, J=9 Hz, 2H), 5.95–5.81 (m, 1H), 5.20–5.11 (m, 2H), 4.32–4.21 (m, 2H), 3.81 (s, 3H), 2.59–2.44 (m, 2H), 1.27 (t, J=9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.64 (q, J_{CF}=33 Hz), 165.93, 161.77, 139.20, 130.51, 119.90, 116.92, 115.90 (q, J_{CF}=291 Hz), 114.99, 65.35, 62.99, 55.30, 36.21, 13.68. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−70.50 (s, 3F). MS: m/z (%)=362 (M^+, 6), 141 (5), 139 (100), 107(1), 97 (2), 77 (5), 69 (4), 45 (4), 41 (4). HRMS m/z calcd for $C_{16}H_{17}F_3O_4S$: 362.0800; found: 362.0804.

4.3.4. Ethyl 2-(4-chlorophenylthio)-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3d). Colorless liquid. IR (KBr): 2985, 1736, 1574, 1477, 1300, 1208, 1165, 1095, 1014, 927, 826, 719 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.27 (s, 4H), 5.91–5.78 (m, 1H), 5.22–5.12 (m, 2H), 4.19 (q, J=7 Hz, 2H), 2.64–2.45 (m, 2H), 1.20 (t, J=7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.96 (q, J_{CF}=33 Hz), 165.61, 138.73, 137.59, 130.02, 129.73, 125.14, 120.34, 115.80 (q, J_{CF}=292 Hz), 65.34, 63.23, 36.31, 13.77. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−70.55 (s, 3F). MS: m/z (%)=366 (M^+, 13), 269 (15), 223 (27), 195 (37), 177 (14), 143 (90), 108 (100), 69 (36), 45 (34), 41 (31). HRMS m/z calcd for $C_{15}H_{14}F_3O_4SCl$: 366.0304; found: 366.0312.

4.3.5. Ethyl 2-(2-bromophenylthio)pent-4-enoate (4e). Colorless liquid. IR (KBr): 2984, 1737, 1447, 1204, 1164,

1094, 1021, 925, 755 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.48 (d, J=8 Hz, 1H), 7.43 (d, J=8 Hz, 1H), 7.16 (t, J=8 Hz, 1H), 7.01 (t, J=8 Hz, 1H), 5.81–5.68 (m, 1H), 5.10–5.00 (m, 2H), 4.03 (q, J=7 Hz, 2H), 3.77 (t, J=7 Hz, 1H), 1.05 (t, J=7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=171.01, 134.94, 133.42, 133.11, 128.71, 127.66, 126.82, 118.10, 61.11, 49.13, 35.50, 13.92. MS: m/z (%)=314 or 316 (M^+, 55), 275 (41), 227 (41), 201 (53), 188 (23), 162 (88), 127 (52), 108 (100), 45 (8), 41 (5). HRMS m/z calcd for $C_{13}H_{15}O_2BrS$: 313.9976; found: 313.9981.

4.3.6. Ethyl 2-(4-chlorobenzylthio)-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3g). Colorless liquid. IR (KBr): 2985, 1732, 1492, 1301, 1257, 1207, 1163, 1095, 1016 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.30–7.16 (m, 4H), 5.82–5.71 (m, 1H), 5.23–5.14 (m, 2H), 4.28–4.22 (m, 2H), 3.60–3.54 (m, 1H), 3.39–3.33 (m, 1H), 2.87–2.82 (m, 2H), 1.27 (t, J=7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.50 (q, J_{CF}=33 Hz), 165.77, 133.79, 130.66, 129.82, 128.96, 120.33, 115.85 (q, J_{CF}=291 Hz), 63.53, 63.18, 35.95, 32.79, 13.81. ^{19}F NMR (282 MHz, $CDCl_3$): δ=–70.89 (s, 3F). MSI: 381 (M^+). HRMS m/z calcd for $C_{16}H_{16}F_3O_3SCl$: 380.0416; found: 380.0467.

4.3.7. Ethyl 2-(4-chlorobenzylthio)-4-methyl-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3h). Colorless liquid. IR (KBr): 2983, 1730, 1491, 1201, 1161, 1094, 1016, 903, 836 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=7.28 (d, J=8 Hz, 2H), 7.19 (d, J=8 Hz, 2H), 4.95 (s, 1H), 4.87 (s, 1H), 4.30–4.19 (m, 2H), 3.63 (d, J=11 Hz, 1H), 3.33 (d, J=11 Hz, 1H), 2.96 (d, J=15 Hz, 1H), 2.84 (d, J=15 Hz, 1H), 1.80 (s, 3H), 1.28 (t, J=7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=180.56 (q, J_{CF}=33 Hz), 165.88, 139.02, 133.79, 132.99, 130.70, 128.95, 117.09, 116.04 (q, J_{CF}=291 Hz), 63.55, 63.05, 39.49, 33.22, 23.09, 13.68. ^{19}F NMR (282 MHz, $CDCl_3$): δ=–70.47 (s, 3F). TOF MS EI^+4.86e4: 394 (M^+), 297, 269, 195, 171, 157, 139, 125, 99. HRMS m/z calcd for $C_{17}H_{18}F_3O_3SCl$: 394.0617; found: 394.0632.

4.3.8. Ethyl 2-(*tert*-butylthio)-4-methyl-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3i). Colorless liquid. IR (KBr): 2970, 1737, 1464, 1369, 1298, 1202, 1161, 1094, 719 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=5.89–5.75 (m, 1H), 5.09 (d, J=12 Hz, 2H), 4.23–4.07 (m, 2H), 2.96 (d, J=8 Hz, 2H), 1.31 (s, 9H), 1.19 (t, J=7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=184.74 (q, J_{CF}=32 Hz), 166.16, 130.95, 119.79, 115.97 (q, J_{CF}=292 Hz), 64.10, 62.85, 48.43, 38.01, 31.97, 13.70. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−69.88 (s, 3F). MS: m/z (%)=313 (M^++1, 3), 297 (9), 257 (57), 239(1), 85 (7), 73 (1), 69 (3), 57 (100), 45 (3), 41 (29). HRMS m/z calcd for $C_{13}H_{19}F_3O_3S$: 312.1007; found: 312.0998.

4.3.9. Ethyl 2-(ethylthio)-4-methyl-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3j). Colorless liquid. IR (KBr): 2984, 1732, 1447, 1301, 1205, 1162, 1018, 719 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=5.87–5.72 (m, 1H), 5.21–5.15 (m, 2H), 4.35–4.17 (m, 2H), 2.81 (d, J=9 Hz, 2H), 2.50–2.38 (m, 1H), 1.31–1.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.33 (q, J_{CF}=33 Hz), 165.98, 130.12, 119.92, 115.86 (q, J_{CF}=291 Hz), 62.92, 62.73, 35.80, 22.31, 13.72, 12.92. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−70.89 (s, 3F). MS: m/z (%)=285 (M^++1, 5), 211 (12), 109 (15), 97 (6), 85 (100), 81 (31), 75 (98), 73 (21), 69 (24), 61 (490), 55 (37), 53 (29), 45 (51), 41 (40). HRMS m/z calcd for $C_{11}H_{15}F_3O_3S$: 284.0694; found: 284.0695.

4.3.10. Ethyl 2-(allylthio)-4-methyl-2-(2,2,2-trifluoroacetyl)pent-4-enoate (3k). Colorless liquid. IR (KBr): 2985, 1732, 1301, 1260, 1206, 1163, 1097, 1018, 926, 804, 717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ=5.86–5.65 (m, 2H), 5.26–5.13 (m, 4H), 4.31–4.13 (m, 2H), 3.31–2.80 (m, 4H), 1.27 (t, J=7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=181.65 (q, J_{CF}=33 Hz), 165.89, 131.34, 130.05, 120.14, 119.64, 115.82 (q, J_{CF}=291 Hz), 63.05, 61.04, 35.98, 31.73, 13.79. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−70.89 (s, 3F). TOF MS EI^+1.15e3: 296 (M^+), 250, 223, 199, 178, 153, 125, 109, 85, 73, 45, 41. HRMS m/z calcd for $C_{12}H_{15}F_3O_3S$: 296.0694; found: 296.0705.

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