JOC *Note*

1,2-Thio Group Migration in Rh(II) Carbene Reactions

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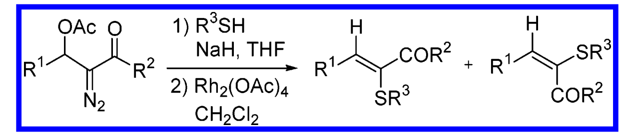
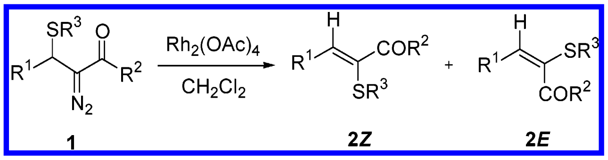


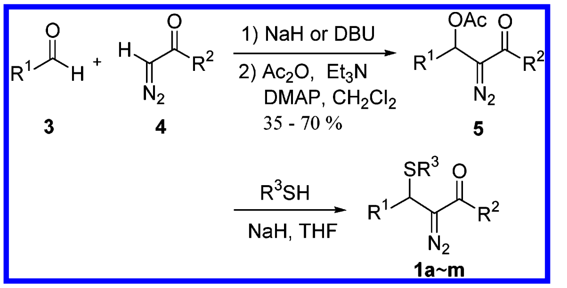
A series of β-thio group substituted α-diazo carbonyl compounds have been prepared by nucleophilic substitution reactions of thiophenol, thionaphthol, or benzyl mercaptan with β-acetoxy-α-diazo carbonyl compounds. The diazo decomposition of these diazo carbonyl compounds with various transition metal catalysts, including Rh(II) carboxylates and Cu(I) and Cu(II) complexes, has been investigated. It was found that the diazo decomposition of these compounds gave 1,2-thio group migration products. No 1,2-hydride or 1,2-aryl migration products were observed in all cases.

1,2-Migration is one of the fundamental reactions in transition metal-catalyzed reaction of α-diazo carbonyl compounds.[1,2] Although cyclopropanation, dimerization, and X−H (X = C, O, S, N, etc.) bond insertions are major reaction pathways, the 1,2-migration may become competitive in certain cases. Among the 1,2-migration reactions, the 1,2-hydride migration is generally predominant, but 1,2-alkyl, 1,2-aryl, 1,2-vinyl, and 1,2-acetylenyl migrations are also observed.[3] Recent study in our group has revealed that the migratory aptitude was dramatically affected by the nonmigratory substituents.[3e] In certain circumstances, 1,2-aryl migration can override 1,2-hydride migration. On the other hand, it has been reported that the acetoxy group has higher 1,2-migratory aptitude over hydride in the $Rh_2(OAc)_4$-mediated reaction of β-acetoxy α-diazo carbonyl compounds, presumably due to the interaction of the carbonyl oxygen lone pair with the carbene carbon p orbital to form a favorable five-membered-ring transition state.[4] In this paper we report 1,2-thio group migration in the $Rh_2(OAc)_4$-catalyzed reaction of the β-thio group-substituted α-diazo carbonyl compounds. To the best of our knowledge, this type of 1,2-migration has not been reported in Rh(II) carbene reactions.

SCHEME 1



SCHEME 2



Our recent study suggests that the β position of the α-diazo carbonyl compound is liable to nucleophilic substitution.[5] This observation makes it possible to prepare the diazo compounds with various β-substituents. Consequently, the β-thio group-substituted α-diazo carbonyl compounds **1** that have been used in this investigation can be prepared by nucleophilic substitution of the corresponding β-acetoxy-α-diazo carbonyl compounds **5** with the anion generated through the deprotonation of a suitable thio compound,[6] while the β-acetoxy-α-diazo carbonyl compound **5** can be easily prepared from aldehyde and acyldiazomethane in two steps (Scheme 2).[4c,7]

Thus, β-acetoxy-α-diazo carbonyl compounds **5** were prepared by the methods shown in Scheme 2 with the yields ranging from 35% to 70%. Then R^3SH was treated

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(1) For comprehensive reviews, see: (a) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley-Interscience: New York, 1998. (b) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1901.

(2) 1,2-Hydrogen migration: (a) Frazen, V. *Liebigs Ann. Chem.* **1957**, *602*, 199. (b) Pellicciari, R.; Fringuelli, R.; Ceccherelli, P.; Sisani, E. *J. Chem. Soc., Chem. Commun.* **1979**, 959. (c) Pellicciari, R.; Fringuelli, R.; Sisani, E. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2566. (d) Hoffmann, K.-L.; Regitz, M. *Tetrahedron Lett.* **1983**, *24*, 5355. (e) Hudlicky, T.; Olivo, H. F.; Natchus, M. G.; Umpierrez, E. F.; Pandolfi, E.; Volonterio, C. *J. Org. Chem.* **1990**, *55*, 4767. (f) Taber, D. F.; Hoerrner, R. S. *J. Org. Chem.* **1992**, *57*, 441. (g) Taber, D. F.; Hennessy, M. J.; Louey, J. P. *J. Org. Chem.* **1992**, *57*, 436. (h) Taber, D. F.; Herr, R. J.; Pack, S. K.; Geremia, J. M. *J. Org. Chem.* **1996**, *61*, 2908. (i) Sarabia García, F.; Pedraza Cebrián, G. M.; Heras López, A.; López Herrera, F. J. *Tetrahedron*, **1998**, *54*, 6867. (j) Ye, T.; McKervey, M. A. *Tetrahedron* **1992**, *48*, 8007. (k) Ohno, M.; Itoh, M.; Umeda, M.; Furuta, R.; Knodo, K.; Eguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 7075.

(3) 1,2-Aryl and 1,2-alkyl migrations: (a) Nagao, K.; Chiba, M.; Kim, S.-W. *Synthesis* **1983**, 197. (b) Kanemasa, S.; Kanai, T.; Araki, T.; Wada, E. *Tetrahedron Lett.* **1999**, *40*, 5055. (c) Jiang, N.; Qu, Z.; Wang, J. *Org. Lett.* **2001**, *3*, 2989. (d) Shi, W.; Jiang, N.; Zhang, S.; Wu, W.; Du, D.; Wang, J. *Org. Lett.* **2003**, *5*, 2243. (e) Jiang, N.; Ma, Z.; Qu, Z.; Xing, X.; Xie, L.; Wang, J. *J. Org Chem.* **2003**, *68*, 893.(f) Aggarwal, V. K.; Sheldon, C. G.; Macdonald, G. J.; Martin, W. P. *J. Am. Chem. Soc.* **2002**, *124*, 10300.

(4) 1,2-Acetoxy migration: (a) Ikota, N.; Takamura, N.; Young, S. D.; Ganem, B. *Tetrahedron Lett.* **1981**, *22*, 4163. (b) Lopez-Herrera, F. J.; Sarabia-Garcia F. *Tetrahedron Lett.* **1994**, *35*, 6705. (c) Lopez-Herrera, F. J.; Sarabia-Garcia F. *Tetrahedron* **1997**, *53*, 3325.

(5) Shi, W.; Zhang, B.; Liu, B.; Xu, F.; Xiao, F.; Zhang, J.; Zhang, S.; Wang, J. *Tetrahedron Lett.* **2004**, *45*, 4563.

(6) As suggested by one of the referees, an alcohol can be transformed to a thioether under a mild condition with PhSSPh/Bu_3P in MeCN. See: (a) Wang, X.-Z.; Wu, Y.-L.; Jiang, S.; Singh, G. *J. Org. Chem.* **2000**, *65*, 8146. (b) Hanessian, S.; Tyler, P. C.; Demailly, G.; Chapleur, Y. *J. Am. Chem. Soc.* **1981**, *103*, 6243. We examined this procedure with the β-hydroxy α-diazo carbonyl compounds **5a** (R^1 = Et, R^2 = OEt) and **5j** (R^1 = Ph, R^2 = OEt). The expected thioethers **1a** and **1j** could be isolated after stirring the reaction mixture for 40 h. However, the yields were less than 10%, and most of the starting materials were recovered.

(7) Jiang, N.; Wang, J. *Tetrahedron Lett.* **2002**, *43*, 1285.

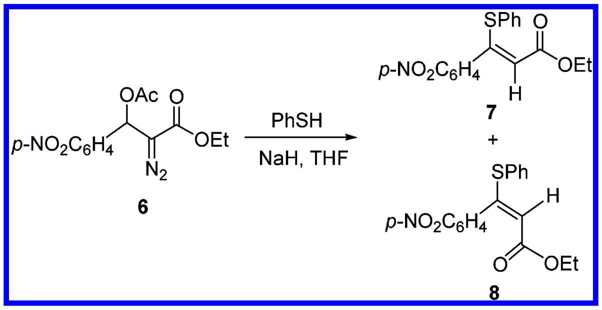
10.1021/jo050109v CCC: $30.25

TABLE 1. Nucleophilic Substitution of 5 with R^3SNa

entry	R^1	R^2	R^3	product	yield (%)[a]
1	Et	OEt	Ph	**1a**	66
2	Et	OEt	$PhCH_2$	**1b**	81
3	*n*-hexyl	OEt	Ph	**1c**	55
4	*n*-hexyl	OEt	$PhCH_2$	**1d**	65
5	Et	Me	Ph	**1e**	87
6	Et	Me	$PhCH_2$	**1f**	82
7	Et	Ph	Ph	**1g**	68
8	Et	Ph	$PhCH_2$	**1h**	65
9	Et	OEt	2-naphthyl	**1i**	57
10	Ph	OEt	Ph	**1j**	60
11	Ph	OEt	$PhCH_2$	**1k**	68
12	*p*-PhC_6H_4	OEt	Ph	***1l***	40
13	*p*-MeOPh	OEt	Ph	**1m**	47

[a] Yields after column chromatographic purification with silica gel.

SCHEME 3



with NaH in anhydrous THF at 0 °C, followed by the addition of a solution of *β*-acetoxy-α-diazo carbonyl compound **5** in anhydrous THF. The substitution reaction was completed within 8 h, and the *β*-thio group-substituted α-diazo carbonyl compounds **1a**–**m** were obtained in yields ranging from 40% to 87% as shown in Table 1. This reaction provides an effective method of bringing the thio group to the α position of the diazo group. It is demonstrated again that the adjacent position of a diazo group is liable to nucleophilic attack.

It is worthwhile to note that the substitution reaction can be quenched at 0 °C if R^1 is an alkyl group and the corresponding *β*-thio-substituted α-diazo carbonyl compounds **1** can be obtained after column chromatography. If R^1 is aryl group, however, the reaction must be quenched at −78 °C, otherwise the product will decompose to give a mixture of **1** and other byproducts. It is obvious that the diazo compounds with a thio group in the benzylic position are unstable. Besides, when trying to prepare the *β*-phenylthio α-diazo ester bearing a *β*-(*p*-nitro)phenyl substituent, only α,*β*-unsaturated ester **7** and **8** were isolated (Scheme 3).

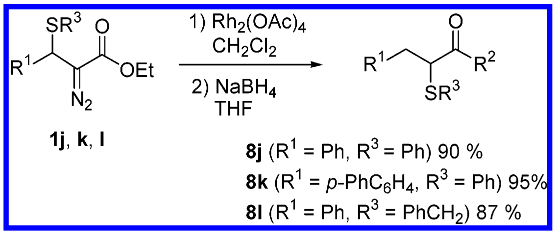
With *β*-thio group α-diazo carbonyl compounds **2a**–**m** in hand, we then proceeded to study their reaction with $Rh_2(OAc)_4$ catalyst. The diazo decomposition occurred smoothly at 0 °C in dichloromethane to give a stereoisomeric mixture of 1,2-thio group migration products **2*Z*** and **2*E*** (Scheme 1 and Table 2). The reactions were finished in 2 to 24 h and no 1,2-hydride migration products were detected in all the cases. When other commonly used catalysts, such as $Cu(CH_3CN)_4PF_6$ and $Cu(acac)_2$, were employed in this reaction, similar 1,2-thio group migration occurred, although with these catalysts the reaction needed to be carried out in refluxing benzene.

TABLE 2. $Rh_2(OAc)_4$-Catalyzed Reaction of Diazo Compounds 1a–m

entry	substrate **1**	reaction time (h)	products	yield (%)[a,b]	product ratio (**2*Z***:**2*E***)
1	**1a**	10	**2*Z*a** + **2*E*a**	78	>20:1
2	**1b**	12	**2*Z*b** + **2*E*b**	79	2.4:1
3	**1c**	10	**2*Z*c** + **2*E*c**	96	6.3:1
4	**1d**	19	**2*Z*d** + **2*E*d**	97	1.6:1
5	**1e**	2	**2*Z*e** + **2*E*e**	81	8.0:1
6	**1f**	11	**2*Z*f** + **2*E*f**	60	9.3:1
7	**1g**	24	**2*Z*g** + **2*E*g**	88	3.7:1
8	**1h**	24	**2*Z*h** + **2*E*h**	73	1:1.7
9	**1i**	3.5	**2*Z*i** + **2*E*i**	99	1.1:1
10	**1j**	10	**2*Z*j** + **2*E*j**	99	1.7:1[c]
11	**1k**	13	**2*Z*k** + **2*E*k**	93	2.0:1[c]
12	**1l**	6.5	**2*Z*l** + **2*E*l**	98	2.0:1[c]
13	**1m**	2	**2*Z*m** + **2*E*m**	71	1.2:1[c]

[a] Yields after column chromatographic purification with silica gel (entries 1–9). [b] Crude product yields (entries 10–13). [c] Ratio determined by ^1H NMR (300 MHz) of the crude product. The ratio could be either **2Z**:**2E** or **2E**:**2Z** for entries 10–13.

SCHEME 4



When R^1 was the alkyl group, it was easy to identify the products to be 1,2-thio group migration, rather than 1,2-hydrogen migration. In the ^1H NMR spectrum of the products, a triplet peak between *δ* 6.0 and 8.0 due to the proton attached to the double bond is coupled with the adjacent methylene protons.

When R^1 was the aryl group, however, the structure characterization was not straightforward. In these cases, 1,2-thio group, 1,2-aryl, or 1,2-hydrogen migrations all give a singlet for the corresponding proton. The ^1H NMR spectra of the products show the absorption of this proton appears in the aromatic region, thus excluding the 1,2-H migration products because the α proton of an α,*β*-unsaturated carbonyl compound is generally below *δ* 7.0. The 1,2-thio and 1,2-aryl migration products can be further differentiated by the reduction of the migration products with $NaBH_4$ [8] and then comparing the reduction products with known compounds (Scheme 4).[9] Reduction of the migration products from the $Rh_2(OAc)_4$-catalyzed reaction of **1j**–***l*** with $NaBH_4$ at 0 °C occurs smoothly to give single product **8j**–***l*** in each case, thus unambiguously confirming only 1,2-thio group migration occurs in $Rh_2(OAc)_4$-catalyzed reactions.

It was noted when R^1 was the alkyl group, in most cases the *Z* and *E* isomers of 1,2-thio group migration products could be separated by column chromatography and it was confirmed that *Z*, *E* isomerization did not

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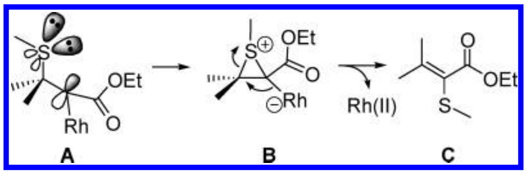
(8) The $NaBH_4$ reduction of a doubly activated unsaturated ester is known. For an example, see: Salomon, R. G.; Sachinvala, N. D.; Raychaudhuri, S. R.; Miller, D. B. *J. Am. Chem. Soc.* **1984**, *106*, 2211.

(9) Trost, B. M.; Salzmann T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1975**, *97*, 4887.

SCHEME 5



occur during the separation.[10] The exceptions were the reactions with **1g** and **1h** (entries 7 and 8), in which cases *Z*, *E* isomerization occurred on the silica gel column. On the other hand, when R^1 was the aryl group, the *Z* and *E* isomers of 1,2-thio group migration products could not be separated by silica gel column. The ratios were thus determined by the crude ^1H NMR spectra (entries 10−13). It was also noted in these cases that the *Z*, *E* selectivities were poor, ranging from 1.2:1 to 2.0:1.

The facile 1,2-thio group migration is presumably due to the easy overlap of the lone pair occupied sp^3 orbital of the sulfur with the p orbital of the Rh(II) carbene carbon, which is positively polarized (**A**, Scheme 5). A thiiranium intermediate (**B**) may be generated, followed by the extrusion of Rh(II) catalyst to give 1,2-migration product (**C**). This is comparable to the 1,2-acetoxy group migration, in which case the interaction between the lone pair of the carbonyl oxygen and the Rh(II) carbene carbon generates a five-membered-ring transition state.[4a]

In conclusion, we have reported an unprecedented 1,2-thio group migration in the Rh(II) carbene reaction. It demonstrates that the thio group has a higher migratory aptitude over hydrogen. The reaction sequence from aldehydes represents a two-carbon homologation to the α-thio unsaturated carbonyl compounds,[11] which may find application in organic synthesis.

Experimental Section

Caution: Diazo compounds are potentially explosive. They should be handled with care in a well-ventilated fumehood.

General Procedure for the Preparation of β-Thio-Substituted α-Diazo Carbonyl Compounds 1a−i. To a solution of thio alcohol (1.2 mmol) in anhydrous THF (20 mL) at 0 °C was added sodium hydride (1.44 mmol) under N_2. The mixture was stirred for 5 min, then a solution of β-acetoxy-α-diazo carbonyl compound **5** (1.0 mmol) in anhydrous THF (5 mL) was added dropwise during a period of 30 min. The mixture was then stirred until TLC analysis indicated the complete disappearance of the starting material. The reaction mixture was then quenched with saturated aqueous NaCl (10 mL). The mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure, and the crude yellow product was purified by column chromatography to yield β-thio α-diazo carbonyl compounds **1a**−**i**.

Ethyl 2-diazo-3-(phenylthio)pentanoate (1a): TLC petroleum ether:ethyl acetate = 30:1; R_f 0.30; 8 h, 66%; IR (film) 2086, 1691, 1286, 1118, 743, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.05 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H), 1.67−1.88 (m, 2H), 4.02−4.16 (m, 3H), 7.26−7.31 (m, 3H), 7.44−7.47 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.8, 14.3, 26.5, 45.2, 60.7, 127.7, 128.8, 133.0, 133.3, 166.0; EI-MS (*m/z*, rel intensity) 264 (M^+, 1), 236 [$(M - 28)^+$, 11], 190 (16), 155 (33), 127 (31), 110 (62), 99 (60), 55 (33), 29 (100). Anal. Calcd for $C_{13}H_{16}N_2O_2S$: C, 59.07; H, 6.10; N, 10.60. Found: C, 59.26; H, 6.06; N, 10.53.

General Procedure for the Preparation of β-Thio-Substituted α-Diazo Carbonyl Compounds 1j−m. To a solution of mercaptan (1.2 mmol) in anhydrous THF (20 mL) at 0 °C was added sodium hydride (1.44 mmol) under N_2. The mixture was stirred for 5 min, and was then cooled to −78 °C with dry ice−acetone. Then the solution of β-acetoxy-α-diazo carbonyl compounds **5** (1.0 mmol) in anhydrous THF (5 mL) was added dropwise during a period of 30 min. The mixture was then stirred for 8 h until TLC analysis indicated the complete disappearance of the starting material, during which the temperature of the reaction mixture rose to 0 °C. The reaction mixture was cooled to −78 °C again and quenched with dropwise addition of the saturated aqueous NaCl (10 mL). The usual workup gave a crude yellow product, which was purified by column chromatography to yield β-thio α-diazo carbonyl compounds **1j**−**m**.

Ethyl 2-diazo-3-phenyl-3-(phenylthio)propionate (1j): 60%; TLC petroleum ether:ethyl acetate = 30:1 R_f 0.33; IR (film) 2094, 1676, 1368, 1296, 1097, 711 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.13 (t, J = 7.2 Hz, 3H), 4.11 (q, J = 7.2 Hz, 2H), 5.38 (s, 1H), 7.21−7.46 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.2, 47.0, 60.9, 127.1, 127.7, 128.0, 128.8, 128.9, 132.1, 133.5, 138.0, 165.4; EI-MS (*m/z*, rel intensity) 284 [$(M - 28)^+$, 40], 211 (54), 203 (39), 175 (54), 147 (75), 129 (18), 109 (47), 103 (93), 91 (37), 77 (50). Anal. Calcd for $C_{17}H_{16}N_2O_2S$: C, 65.36; H, 5.16; N, 8.97. Found: C, 65.49; H, 5.24; N, 8.61.

General Procedure for $Rh_2(OAc)_4$-Catalyzed Reaction of β-Thio-Substituted α-Diazo Carbonyl Compounds 1a−m. A solution of diazo compound **1a**−**m** (0.5 mmol) in CH_2Cl_2 (20 mL) was stirred with $Rh_2(OAc)_4$ (1 mg) at 0 °C under N_2 until TLC analysis indicated the complete disappearance of the starting material (2−24 h). The solvent was then removed under reduced pressure and the crude residue was purified by column chromatography to give the corresponding 1,2-thio group migration products.

(*Z*)-Ethyl 2-(phenylthio)-2-pentenoate (2Za):[12] 10 h, 74%; TLC petroleum ether:ethyl acetate = 30:1; R_f 0.51; IR (film) 2927, 2361, 1713, 1236, 1044, 740, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.06−1.12 (m, 6H), 2.48−2.58 (m, 2H), 4.10 (q, J = 7.2 Hz, 2H), 7.15−7.28 (m, 5H), 7.39 (t, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 13.7, 24.0, 61.3, 125.8, 126.0, 127.9, 128.7, 135.8, 154.3, 165.2; EI-MS (*m/z*, rel intensity) 236 (M^+, 66), 190 (100), 161 (59), 147 (24), 129 (89), 109 (26), 105 (84), 91 (21), 85 (62), 65 (18), 45 (24), 29 (24). Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 65.83; H, 6.82.

(*E*)-Ethyl 2-(naphthylthio)-2-pentenoate (2*E*i): 3.5 h, 47%; TLC petroleum ether:ethyl acetate = 30:1; R_f 0.50; IR (film) 1712, 1213, 1133, 1030, 813, 745 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.05 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.5 Hz, 3H), 2.51−2.61 (m, 2H), 4.10 (q, J = 7.5 Hz, 2H), 6.52 (t, J = 7.5 Hz, 1H), 7.39−7.50 (m, 3H), 7.74−7.79 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 13.9, 24.2, 61.1, 125.7, 125.9, 126.4, 127.2, 127.3, 127.6, 128.2, 128.5, 132.0, 132.4, 133.6, 151.0, 165.3; EI-MS (*m/z*, rel intensity) 286 (M^+, 68), 257 (3), 240 (64), 213 (19), 197 (12), 179 (29), 171 (11), 155 (100), 128 (54), 115 (42), 99 (5), 85 (12), 63 (3), 45 (6), 29 (6). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.14; H, 6.42.

General Procedure for $Rh_2(OAc)_4$-Catalyzed Reaction of 1j−*l* Followed by Reduction with $NaBH_4$. The crude product obtained from $Rh_2(OAc)_4$-catalyzed reaction of **1i**−**j** was dissolved in anhydrous THF (10 mL), then $NaBH_4$ (1.0 equiv) was added at 0 °C under N_2. The reaction mixture was stirred until TLC analysis indicated the complete disappearance of the starting material (24 h). The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ (10 mL). The usual workup

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(10) The major isomer is assigned to have the *Z* configuration by comparing the ^1H NMR spectral data with the corresponding simulated spectra.

(11) For the examples of two-carbon homologation of an aldehyde to the α-thio unsaturated ester or ketone, see: (a) Babin, D.; Demassey, J.; Demoute, J. P.; Dutheil, P.; Terrie, I.; Tessier, J. *J. Org. Chem.* **1992**, *57*, 585. (b) Marcantoni, E.; Massaccesi, M.; Petrini, M.; Bartoli, G.; Bellucci, M. C.; Bosco, M.; Sambri, L. *J. Org. Chem.* **1992**, *57*, 4553. (c) Zhdankin, V. V.; Maydanovych, O.; Herschbach, J.; Bruno, J.; Matveeva, E. D.; Zefirov, N. S. *Tetrahedron Lett.* **2002**, *43*, 2359. (d) Deng, G. S.; Zhi Huang, Z.; Huang, X. *Chin. Chem. Lett.* **2003**, *14*, 3. (e) Deng, G. *Chin. J. Org. Chem.* **2004**, *24*, 286.

(12) Miller, R. D.; Hassig, R. *Tetrahedron Lett.* **1985**, *26*, 2395.

gave a crude product, which was purified by column chromatography to yield **8j**−***l***.

Ethyl 3-phenyl-2-(phenylthio)propionate (8j):[9] 90%; TLC petroleum ether:ethyl acetate = 30:1; R_f 0.45; IR (film) 1687, 1592, 1478, 1356, 1224, 1209, 1024, 740, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (t, J = 7.2 Hz, 3H), 3.03−3.24 (AB part of ABX, J_{AB} = 13.8 Hz, 2H), 3.88−3.93 (X part of ABX, J_{AX} = 6.3 Hz, J_{BX} = 9.3 Hz, 1H), 3.99−4.08 (m, 2H), 7.18−7.31 (m, 8H), 7.43−7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 37.8, 52.1, 61.0, 126.7, 127.9, 128.3, 128.8, 128.9, 133.0, 137.6, 171.5; EI-MS (*m*/*z*, rel intensity) 286 (M$^+$, 67), 195 (27), 177 (100), 149 (70), 135 (73), 121 (64), 109 (29), 103 (27), 91 (55).

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Supporting Information Available: Characterization data for **1b**−**i**, **1k**−**m**, **1zb**−**i**, **8k**,***l***, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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