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Reaction of Phenyliodonium Ylides of β-Dicarbonyl Compounds with Allylic Sulfides and Selenides

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ABSTRACT

An efficient and mild reaction for introducing an allylic moiety and an alkylthio- or alkylseleno-group onto the α-carbon of β-dicarbonyl compounds in one step by tandem transylidation and [2,3]-sigmatropic rearrangement is described.

INTRODUCTION

Iodonium ylides constitute an interesting class of hypervalent iodine compounds, whose chemistry has recently been reviewed by Koser [1]. Various reactions of iodonium ylides have been developed for use in organic synthesis, such as reactions with electrophilic reagents [2] and reactions with alkenes and alkynes to form a new carbon–carbon bond [3]. Furthermore, the reaction with other heteroatom nucleophilic species transfers the iodonium ylides into other ylides [1,4]. In conjunction with the use of [2,3]-sigmatropic rearrangements of sulfonium and selenonium ylides, a one-pot carbon–carbon bond-constructing reaction of an iodonium ylide is proposed. Here, we report the results of the concomitant [2,3]-sigmatropic rearrangements of the transient allylic sulfonium and selenonium ylides which were obtained by reactions of iodonium ylides with allylic sulfides and allylic selenides.

TABLE 1 Reaction of Allyl Alkyl Sulfides with Iodonium Ylides[a]

Entry	*Ylide*	*R¹*	*R³*	*R²*	*R⁴*	*R⁵*	*Product*	*Yield*[b]
1	**1**	H	H	H	H	Bn	**6a**	85%
2	**1**	H	H	$(CH_2)_3$		Bn	**6b**	58%
3	**1**	H	Me	H	H	Bn	**6c**	48%
4	**1**	Me	H	H	H	Bn	**6d**	83%
5	**1**	H	H	H	H	*n*-hexyl	**6e**	91%
6	**1**	H	H	$(CH_2)_3$		*n*-hexyl	**6f**	61%
7	**1**	H	Me	H	H	*n*-hexyl	**6g**	44%
8	**1**	H	H	H	H	*i*-butyl	**6h**	66%
9	**2**[c]	H	H	H	H	Bn	**6i**	57%
10	**3**[d]	H	H	H	H	Bn	**6j**	43%

[a] Reaction time: 4 hours at room temperature.
[b] Isolated yield.
[c] Reaction time: 8 hours.
[d] Reaction time: 10 hours.

RESULTS AND DISCUSSION

The iodonium ylide of 2,2-dimethyl-1,3-dioxane-2,4-dione (Meldrum's acid) **1** was readily prepared by simple condensation of Meldrum's acid with diacetoxyiodobenzene [5]. In exploring the reaction of **1** with allylic sulfides, we found that allyl phenyl sulfide undergoes no reaction with **1** either directly or in the presence of TsOH, despite the fact that the reaction between diphenyl sulfide and the phenyl-iodonium ylide of a cyclopentadienyl derivative is known to proceed in good yield [6]. When allyl benzyl sulfide was used instead of the allyl phenyl sulfide, the reaction proceeded smoothly without the need of added catalyst, and 5-allyl-5-benzylthioisopropylidene malonate **6a** was obtained in 85% yield (entry 1 of Table 1). This demonstrated that the desired rearrangement hap-

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Dedicated to Prof. Yao-Zeng Huang on the occasion of his eightieth birthday.

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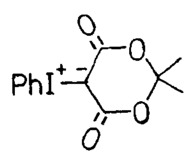
TABLE 2 Reaction of Allyl Alkyl Selenides with Iodonium Ylides[a]

Entry	Ylide	R^1	R^2	R^3	R^4	R^5	Product	Yield (%)[b]
1	**2**	H	H	CH_3	H	methallyl	**7a**	74%
2	**2**	CH_3	H	H	H	Bn	**7b**	90%
3	**2**	H	H	H	H	Bn	**7c**	75%
4	**3**	H	H	H	H	Bn	**7d**	70%
5	**3**	CH_3	H	H	H	E-crotonyl	**7e**	80%
6	**3**	H	H	CH_3	H	methallyl	**7f**	43%
7	**3**	CH_3	H	H	H	Bn	**7g**	72%
8	**4**	H	H	H	H	Bn	**7h**	45%
9	**4**	CH_3	H	H	H	Bn	**7i**	50%
10	**4**	CH_3	H	H	H	E-crotonyl	**7j**	52%

[a] Reaction time: 8 hours at room temperature.
[b] Isolated yield.



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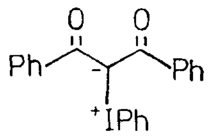

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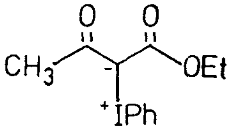

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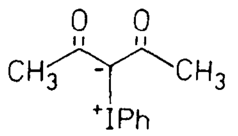

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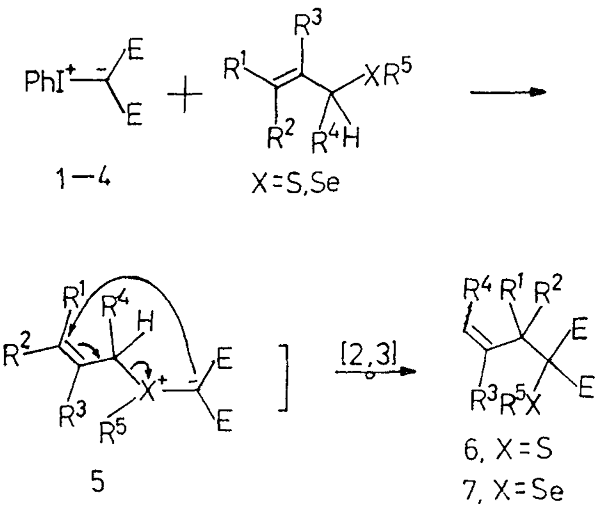

pened concomitantly with the transylidation reaction. Other alkyl allylic sulfides reacted similarly, the results being shown in Table 1. The allylic group may be acyclic or cyclic as well (entries 2 and 6). The product isolated, as shown in entry 4, reveals that the rearrangement is indeed a [2,3]-sigmatropic rearrangement and not a Stevens [1,2] rearrangement. The reaction course is thus depicted as shown in Equation 1—the formation of a sulfonium ylide intermediate **5** followed by rearrangement leading to product **6**. For these two consecutive reactions, the mildness of the reaction conditions (room temperature within 4 hours) [7,8] and the high yields are noteworthy. The reaction of iodonium ylides derived from other β-dicarbonyl compounds **2** and **3** also proceed similarly (entries 9 and 10).

To the best of our knowledge, there has been only one example of the transylidation of an iodonium ylide with diphenyl selenide documented in the literature [6]. We found that the reaction between ylides **2**, **3**, and **4** with alkyl allylic selenides occurred exactly in the same manner as shown in Equation 1, and the corresponding alkylseleno products were obtained. The results are listed in Table 2. The products isolated as shown in entries 2, 5, 7, and 10 again demonstrate the [2,3]-sigmatropic rearrangement pathway. The reaction between alkyl allylic selenides and the iodonium ylide **1** behaved differently, affording bicyclic products [9].

In conclusion, the reactions examplified here represent a general, simple, and mild procedure for introducing an allylic moiety and an alkylthio or alkylseleno group onto the α-carbon of β-dicarbonyl derivatives in a one-pot reaction. The resulting products could easily be transformed to 2-alkylthio-4-pentenoic acid derivatives as well as 3-alkylthio or 3-alkylseleno-2,5-pentadione derivatives. In addition, the seleno-product of **7** has been used in the synthesis of dihydrofuran derivatives [10]. All of these reactions introduce easily transformable functionalities and will certainly be useful in organic synthesis.

EXPERIMENTAL

Melting points were uncorrected. The ^1H NMR spectra were recorded on a Varian EM-60A spectrometer with $CDCl_3$ as solvent and TMS as internal standard. The IR spectra were taken on a Shimadzu 440-IR spectrometer, and mass spectra were determined on a Finnigan MAT 4201 spectrometer.

General Procedure for the Reactions of Iodonium Ylides

With Alkyl Allylic Sulfides. The iodonium ylide (2.0 mmol) was added to a stirred solution of a given alkyl allylic sulfide (2.0 mmol) in CH_2Cl_2 (15 mL). The resultant mixture was stirred at room temperature for the time given in the Tables. Then the solvent was removed, and the residue was purified by chromatography on silica gel.

6a: mp 68–69°C. ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 3H), 1.88 (s, 3H), 3.03 (d, J = 6 Hz, 2H), 3.99 (s, 2H), 4.97–5.95 (m, 3H), 7.20 (s, 5H). IR (KBr): 1775, 1730, 1645, 1280 cm^{-1}. MS m/z 306 (M, 0.06%), 248 (2.51), 91 (100). Anal.: Calcd for $C_{16}H_{18}O_4S$: C, 62.75; H, 5.88. Found: C, 62.64; H, 5.64.

6b: mp 109.5–110.5°C. ^{1}H NMR ($CDCl_3$) δ 1.05–2.25 (m, 12H), 3.00–3.50 (m, 1H), 3.97 (s, 2H), 5.91 (s, 2H), 7.23 (s, 5H). IR (KBr): 1775, 1725, 1650, 1280 cm^{-1}. MS m/z 346 (M, 0.08%), 288 (14.34), 91 (87.24), 81 (100). Anal.: Calcd for $C_{19}H_{22}O_4S$: C, 65.90; H, 6.36. Found: C, 65.70; H, 6.24.

6c: mp 75–76°C. ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 6H), 1.92 (s, 3H), 3.10 (s, 2H), 4.03 (s, 2H), 4.70 (s, 1H), 4.87 (s, 1H), 7.25 (s, 5H). IR (KBr); 1775, 1730, 1650, 1290 cm^{-1}. MS m/z 320 (M, 0.29%), 262 (6.43), 91 (100). Anal.: Calcd for $C_{17}H_{20}O_4S$: C, 63.75; H, 6.25. Found: C, 63.55; H, 6.28.

6d: mp 35–37°C. ^{1}H NMR ($CDCl_3$) δ 1.32 (d, J = 6 Hz, 3H), 1.71 (s, 3H), 1.88 (s, 3H), 3.04–3.60 (m, 1H), 3.98 (s, 2H), 4.94–5.51 (m, 3H), 7.31 (s, 5H). IR (KBr): 1775, 1740, 1650, 1280 cm^{-1}. MS m/z 320 (M, 1.22%), 262 (21.54), 91 (100). Anal.: Calcd for $C_{17}H_{20}O_4S$: C, 63.75; H, 6.25. Found: C, 63.60; H, 6.21.

6e: ^{1}H NMR ($CDCl_3$) δ 0.55–1.65 (m, 11H), 1.68 (s, 3H), 1.93 (s, 3H), 2.84 (t, J = 6 Hz, 2H), 3.03 (d, J = 6 Hz, 2H), 4.85–5.85 (m, 3H). IR (film); 1785, 1745, 1645, 1275 cm^{-1}. MS m/z 300 (M, 4.27%), 242 (4.41), 85 (100). Anal.: Calcd for $C_{15}H_{24}O_4S$: C, 60.00; H, 8.00. Found: C, 59.83; H, 7.77.

6f: ^{1}H NMR ($CDCl_3$) δ 0.60–2.30 (m, 23H), 2.77 (t, J = 6 Hz, 2H), 2.96–3.40 (m, 1H), 5.88 (s, 2H). IR (film) 1785, 1748, 1645, 1277 cm^{-1}. MS m/z 340 (M, 0.06%), 282 (7.94), 81 (100). Anal.: Calcd for $C_{18}H_{28}O_4S$: C, 63.53; H, 8.24. Found: C, 63.28; H, 7.96.

6g: ^{1}H NMR ($CDCl_3$) δ 0.66–2.20 (m, 20H), 2.76 (t, J = 6 Hz, 2H), 3.00 (s, 2H), 4.63 (s, 1H), 4.80 (s, 1H). IR (film): 1785, 1745, 1645, 1290 cm^{-1}. MS m/z 314 (M, 2.34%), 256 (17.64), 55 (100). Anal.: Calcd for $C_{16}H_{26}O_4S$: C, 61.15; H, 8.28. Found: C, 60.78; H, 7.94.

6h: ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 6 Hz, 6H), 1.50–2.20 (m, 7H), 2.73 (d, J = 6 Hz, 2H), 3.00 (d, J = 5 Hz, 2H), 4.94–5.53 (m, 3H). IR (film): 1785, 1750, 1645, 1275 cm^{-1}. MS m/z 272 (M, 4.74%), 214 (7.72), 57 (100). Anal.: Calcd for $C_{13}H_{22}O_2S$: C, 57.35; H, 7.35. Found: C, 57.16; H, 7.48.

6i: mp 108–110°C. ^{1}H NMR ($CDCl_3$) δ 3.20 (d, J = 8 Hz, 2H), 3.55 (s, 2H), 4.55–5.35 (m, 2H), 5.72–6.25 (m, 1H), 7.05–7.78 (m, 15H). IR (KBr): 1660, 1642 cm^{-1}. MS m/z 386 (M, 4.72%), 263 (39.41), 105 (100), 91 (52.52), 77 (43.37). Anal.: Calcd for $C_{25}H_{22}O_2S$: C, 77.72; H, 5.70. Found: C, 77.46; H, 5.38.

6j: ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J = 7 Hz, 3H), 2.29 (s, 3H), 2.83 (d, J = 7 Hz, 2H), 3.63 (s, 2H), 4.27 (q, J = 7 Hz, 2H), 4.88–5.44 (m, 2H), 5.55–6.14 (m, 1H), 7.25 (s, 5H). IR (film): 1730, 1708, 1639 cm^{-1}. MS m/z 293 (M + 1, 3.32%), 250 (10.51), 170 (33.49), 123 (8.11), 91 (100). Anal.: Calcd for $C_{16}H_{20}O_3S$: C, 65.75; H, 6.85. Found: C, 65.39; H, 6.72.

7a: ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 6H), 2.01 (s, 2H), 2.16 (s, 2H), 4.41–5.30 (m, 4H), 7.27–7.97 (m, 10H). IR (film): 1650, 1600, 1230 cm^{-1}. MS m/z 412 (M, 0.26%), 357 (9.16), 277 (12.88), 135 (6.31), 105 (100), 77 (24.51). Anal.: Calcd for $C_{23}H_{24}O_2Se$: C, 67.15; H, 5.84. Found: C, 66.88; H, 5.62.

7b: mp 77°C. ^{1}H NMR ($CDCl_3$) δ 1.12 (d, J = 7 Hz, 3H), 2.84–3.26 (m, 1H), 3.33 (s, 2H), 4.36–6.17 (m, 3H), 6.71–8.13 (m, 15H). IR (KBr): 1660, 1600, 1230 cm^{-1}. MS m/z 449 (M + 1, 0.12%), 357 (2.45), 277 (6.6), 105 (100), 91 (32.47), 77 (43.00). Anal.: Calcd for $C_{26}H_{24}O_2Se$: C, 69.80; H, 5.37. Found: C, 69.47; H, 5.20.

7c: mp 107–109°C. ^{1}H NMR ($CDCl_3$) δ 3.01 (d, J = 7 Hz, 2H), 3.41 (s, 2H), 4.43–6.18 (m, 3H), 7.08–7.83 (m, 15H). IR (KBr): 1650, 1600, 1240 cm^{-1}. MS m/z 435 (M + 1, 0.58%), 343 (6.30), 263 (50.62), 105 (100), 91 (36.48), 77 (32.97). Anal.: Calcd for $C_{25}H_{22}O_2Se$: C, 69.28; H, 5.08. Found: C, 69.01; H, 4.94.

7d: ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J = 8 Hz, 3H), 2.21 (s, 3H), 2.70 (d, J = 7 Hz, 2H), 3.54 (s, 2H), 4.17 (q, J = 8 Hz, 2H), 4.80–5.61 (m, 3H), 7.15 (s, 5H). IR (film): 1720, 1695, 1640, 1210 cm^{-1}. MS m/z 341 (M + 1, 84.72%), 295 (24.77), 261 (19.23), 249 (55.52), 170 (35.67), 91 (100), 43 (10.36). Anal.: Calcd for $C_{16}H_{20}O_3Se$: C, 56.64; H, 5.90. Found: C, 56.48; H, 5.65.

7e: ^{1}H NMR ($CDCl_3$) δ 1.00–1.50 (m, 6H), 1.65 (s, 3H), 2.23 (s, 3H), 2.70–3.23 (m, 3H), 4.19 (q, J = 7 Hz, 2H), 4.76–6.35 (m, 5H). IR (film): 1730, 1695, 1640, 1220 cm^{-1}. MS m/z 319 (M + 1, 35.32%), 263 (100), 135 (29.83), 43 (36.06). Anal.: Calcd for $C_{14}H_{22}O_3Se$: C, 53.00; H, 6.94. Found: C, 52.82; H, 6.83.

7f: ^{1}H NMR ($CDCl_3$) δ 1.29 (t, J = 7 Hz, 3H), 1.70 (s, 3H), 1.78 (s, 3H), 2.29 (s, 3H), 2.76 (s, 2H), 3.01 (d, J = 6 Hz, 2H), 4.30 (q, J = 7 Hz, 2H), 4.78 (s, 4H). IR (film): 1720, 1700, 1640, 1220 cm^{-1}. MS m/z 318 (M, 0.10%), 263 (7.56), 189 (14.54), 135 (12.59), 55 (26.24), 43 (100). Anal.: Calcd for $C_{14}H_{22}O_3Se$: C, 53.00; H, 6.94. Found: C, 52.76; H, 6.88.

7g: ^{1}H NMR ($CDCl_3$) δ 1.11 (d, J = 7 Hz, 3H), 2.19 (s, 3H), 2.66–3.10 (m, 1H), 3.66 (s, 2H), 4.69–6.24 (m, 3H), 7.21 (s, 5H). IR (film): 1720, 1690, 1640, 1220 cm^{-1}. MS m/z 355 (M + 1, 49.93%), 263 (52.93), 91 (100). Anal.: Calcd for $C_{17}H_{22}O_3Se$: C, 57.79; H, 6.23. Found: C, 57.61; H, 5.99.

7h: ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 6H), 2.72 (d, J = 7 Hz, 2H), 3.47 (s, 2H), 4.80–6.13 (m, 3H), 7.13 (s, 5H). IR (film): 1690, 1640, 1190 cm^{-1}. MS m/z 311 (M + 1, 3.76), 195 (11.28), 177 (100), 91 (16.60). Anal.:

Calcd for $C_{15}H_{18}O_2Se$: C, 58.25; H, 5.83. Found: C, 58.12; H, 5.74.

7i: ^1H NMR ($CDCl_3$) δ 0.98 (d, J = 7 Hz, 3H), 2.10 (s, 6H), 2.73–3.20 (m, 1H), 3.48 (s, 2H), 4.66–6.33 (m, 3H), 7.08 (s, 5H). IR (film): 1690, 1640, 1190 cm^{-1}. MS m/z 325 (M + 1, 73.35%), 233 (100), 91 (57.17), 43 (25.82). Anal.: Calcd for $C_{16}H_{20}O_2Se$: C, 59.44; H, 6.16. Found: C, 59.12; H, 5.94.

7j: ^1H NMR ($CDCl_3$) δ 0.99 (d, J = 6 Hz, 3H), 1.65 (s, 3H), 2.11 (s, 6H), 2.69–3.28 (m, 3H), 4.78–6.38 (m, 5H). IR (film): 1690, 1640, 1190 cm^{-1}. MS m/z 289 (M + 1, 0.27%), 233 (16.32), 135 (27.93), 55 (55.63), 43 (100). Anal.: Calcd for $C_{13}H_{20}O_2Se$: C, 54.36; H, 6.97. Found: C, 54.22; H, 6.69.

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