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Efficient Highly Selective Synthesis of Methyl 2-(Ethynyl)alk-2(*E*)-enoates and 2-(1′-Chlorovinyl)alk-2(*Z*)-enoates from 2-(Methoxycarbonyl)-2,3-allenols

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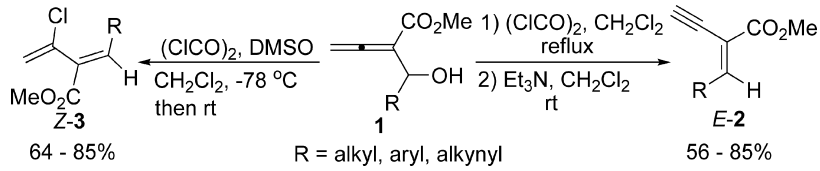
ABSTRACT



Highly regio- and stereoselective reactions of readily available 2-(methoxycarbonyl)-2,3-allenols 1 with oxalyl chloride in the presence of Et_3N or DMSO afforded methyl 2-(ethynyl)alk-2(*E*)-enoates (*E*)-2 and 2-(1′-chlorovinyl)alk-2(*Z*)-enoates (*Z*)-3, respectively, in moderate to good yields.

The efficient stereoselective syntheses of conjugated enynes[1] and conjugated 1,3-dienes[2] are of current interest since they are very important intermediates in organic synthesis.[3,4] Usually, the stereodefined enynes are prepared by Sonogashira-type coupling reactions between stereodefined alkenyl halides with terminal alkynes,[5]cross-metathesis of alkynes and alkenes with major (*Z*)-selectivity,[6] Wittig−Horner−Wadsworth−Emmons-type reactions usually with a poor stereoselectivity,[7] the reactions of alkenylborane derivatives with alkynyllithiums,[8] etc.[9] On the other hand, many efficient synthetic methods for the preparation of conjugated 1,3-dienes have also been developed.[2] In addition, conjugated 1,3-dienes may be synthesized from the reactions of 2,3-allenols or their derivatives, but always with a lower stereoselectivity.[10] Recently, Lee et al. have developed a DABCO-catalyzed method for the synthesis of ethyl 2-(ethynyl)alk-2(*E*)-enoates from 2,3-allenol acetates, prepared from the acetylation of 2-(ethoxycarbonyl)-2,3-allenols.[11] This prompted us to report here a one-pot highly stereoselective synthesis of methyl 2-(ethynyl)alk-2(*E*)-enoates and 2-(1′-chlorovinyl)alk-2(*Z*)-enoates from 2-(methoxycarbonyl)-2,3-allenols[12] in moderate to good yields, respectively.

Originally, we were conducting the Swern oxidation[13] reaction of 3-(methoxycarbonyl)-1,2-nonadien-4-ol **1a** (Scheme 1). Instead of forming the expected oxidation product, i.e., 1,2-allenic ketone, surprisingly, the reaction afforded methyl 2-(ethynyl)oct-2(*E*)-enoate (*E*)-**2a** and methyl 2-(1′-chlorovinyl)oct-2(*Z*)-enoate (*Z*)-**3a** in 2% and 54% yields, respectively, with a 16% recovery of **1a**; in the absence of Et_3N, the reaction afforded (*Z*)-**3a** as the only product in 48% yield, but also with a 15% recovery of **1a**. Interestingly, in the absence of DMSO, (*E*)-**2a** were formed as a major

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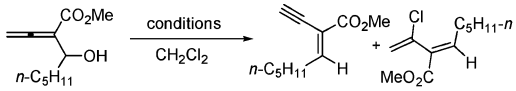
Scheme 1

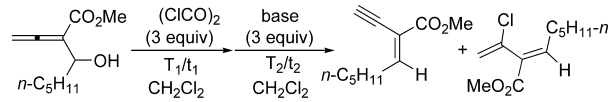


entry	conditions	*E*-**2a** (%)[a]	*Z*-**3a** (%)[a]
1	6 equiv $(ClCO)_2$, 6 equiv DMSO, -78 °C, 5 h; then 6 equiv Et_3N, -78 °C - rt, 13 h	2	54[b]
2	6 equiv $(ClCO)_2$, 6 equiv DMSO, -78 °C - rt, 23 h	0	48[c]
3	3 equiv $(ClCO)_2$, -78 °C - rt, 4 h; then 3 equiv Et_3N, rt, 1 h	68	7

[a] NMR yield. [b] 16% of **1a** was recovered. [c] 15% of **1a** was recovered.

product in 68% yield together with 7% yield of (*Z*)-**3a** (Scheme 1). In order to further optimize the reaction conditions for the selective formation of (*E*)-**2a** or (*Z*)-**3a**, temperature and base effects were tested. Some of the most typical results are summarized in Table 1. 3-(Methoxycarbonyl)-1,2-nonadien-4-ol **1a** was first treated with oxalyl chloride under reflux, which was followed by the elimination at rt using Et_3N as the base to afford the product (*E*)-**2a** in the highest yield with the best selectivity (compare entries 1−4, Table 1). Among the bases screened, $EtN(Pr\text{-}i)_2$ demonstrated a poor selectivity affording (*E*)-**2a** and (*Z*)-**3a** in 71% and 8% yields, respectively (entry 5, Table 1); when

Table 1. Temperature and Base Effects of the Reaction of **1a**



entry	T_1 (°C)/t_1(h)	base	T_2 (°C)/t_2(h)	(*E*)-**2a**[a] (%)	(*Z*)-**3a**[a] (%)
1	−78 °C−rt/4	Et_3N	rt/1	68	7
2	rt/2	Et_3N	rt/3	66	5
3	reflux/2	Et_3N	reflux/3	64	6
4	reflux/2	Et_3N	rt/5	87	<0.5
5	reflux/2	$EtN(Pr\text{-}i)_2$	rt/3	71	8
6	reflux/2	pyridine	rt/21	0	25

[a] NMR yield using 1,3,5-trimethylbenzene as the internal standard.

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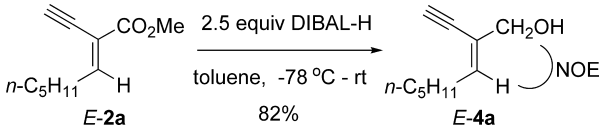
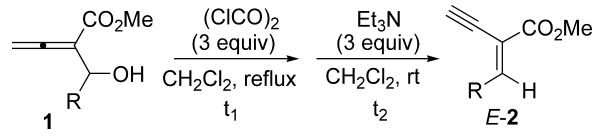
Scheme 2



pyridine was used as the base, the reaction afforded (*Z*)-**3a** as the only product in 25% yield (entry 6, Table 1). In conclusion, the reaction afforded methyl 2-ethynyloct-2(*E*)-enoate (*E*)-**2a** in 87% yield when conducted with 3 equiv each of oxalyl chloride and Et_3N (entry 4, Table 1). ^1H NMR analysis of the crude product indicated the exclusive formation of the (*E*)-stereoisomer. The stereochemistry was established by the NOESY analysis of (*E*)-**4a**, which was prepared by the reduction of (*E*)-**2a** with DIBAL-H in toluene in 82% yield (Scheme 2).

Table 2. Synthesis of Methyl 2-(Ethynyl)alk-2(*E*)-enoates (*E*)-**2**[a]



entry	R	t_1 (h)	t_2 (h)	yield of (*E*)-**2** (%)
1	n-C_5H_{11} (**1a**)	2	5	83 ((*E*)-**2a**)
2	C_2H_5 (**1b**)	2.5	4.5	62 ((*E*)-**2b**)
3	n-C_3H_7 (**1c**)	2	4	65 ((*E*)-**2c**)
4	i-C_3H_7 (**1d**)	2	3.5	67 ((*E*)-**2d**)
5	Ph (**1e**)	7	10.5	83 ((*E*)-**2e**)
6[b]	Ph (**1e**)	7	15	85 ((*E*)-**2e**)
7	p-$CH_3C_6H_4$ (**1f**)	4	7	69 ((*E*)-**2f**)
8[c]	p-BrC_6H_4 (**1g**)	7	10.5	83 ((*E*)-**2g**)
9[c,d]	n-$C_4H_9C{\equiv}C$ (**1h**)	9	12	56 ((*E*)-**2h**)

[a] Allenol **1** (0.4 mmol) was used. [b] Allenol **1e** (4 mmol) was used. [c] 5 equiv each of oxalyl chloride and Et_3N were used. [d] (*Z*)-**3h** was also afforded in 12% NMR yield.

With the optimized conditions in hand, the scope of this reaction was explored. Some of the typical results are summarized in Table 2. It is concluded that R may be a primary (entries 1−3, Table 2) or secondary (entry 4, Table 2) alkyl group and a phenyl- or methyl/bromo-substituted phenyl group (entries 5−8, Table 2); in addition, even an alkynyl group may be introduced to this position (entry 9, Table 2). The structure of the product (*E*)-**2** was further established by the X-ray diffraction studies of (*E*)-**2e** (Figure 1).[14]

On the other hand, we further optimized the reaction conditions for the highly selective formation of (*Z*)-**3a** from the reaction of 3-(methoxycarbonyl)-1,2-nonadien-4-ol **1a** with oxalyl chloride in the presence of DMSO (Scheme 1). After being stirred at −78 °C for about 18 min and then rt for another 5 h, the reaction afforded (*Z*)-**3a** in 83% yield without the recovery of **1a** (entry 1, Table 3). Some of the

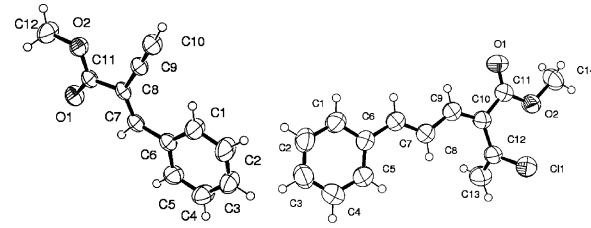
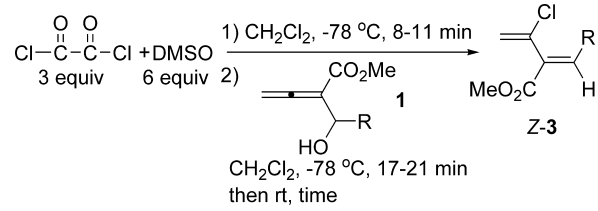


Figure 1. ORTEP representation of (*E*)-**2e** and (*Z*)-**3i** (right).

typical results are summarized in Table 3. Alkyl groups (entries 1−4, Table 3), aryl groups (entries 5−6, Table 3), and alkynyl group-substituted secondary alcohols (entry 7, Table 3) all afforded the conjugated 1,3-diene products (*Z*)-**3** in good yields.

Table 3. Synthesis of Methyl 2-(1′-Chlorovinyl)alk-2(*Z*)-enoates (*Z*)-**3**



entry	R	time (h)	yield of (*Z*)-**3** (%)
1	n-C_5H_{11} (**1a**)	5	83 ((*Z*)-**3a**)
2	C_2H_5 (**1b**)	5	76 ((*Z*)-**3b**)
3	n-C_3H_7 (**1c**)	5	85 ((*Z*)-**3c**)
4	i-C_3H_7 (**1d**)	5	76 ((*Z*)-**3d**)
5	Ph (**1e**)	5	78 ((*Z*)-**3e**)
6	p-BrC_6H_4 (**1g**)	6	80 ((*Z*)-**3g**)
7	n-$C_4H_9C{\equiv}C$ (**1h**)	6	64 ((*Z*)-**3h**)

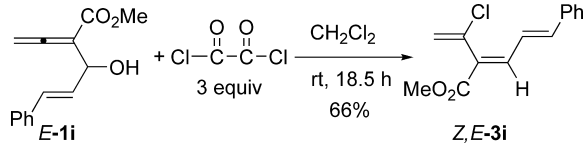
When R is cinnamyl group, the reaction of 4-(methoxycarbonyl)-1(*E*)-phenyl-1,4,5-hexatrien-3-ol *E*-**1i** and oxalyl chloride occurred directly to afford methyl 2-(1′-chlorovinyl)-5-phenylpenta-(2*Z*,4*E*)-dienoate (*Z*,*E*)-**3i** in 66% yield, which was also established by the X-ray diffraction studies (Figure 1)[15] (Scheme 3).

However, the reaction of the substrate with an alkyl substituent at the 4-position, i.e., 1-(4′-chlorophenyl)-2-

(14) Crystal data for (*E*)-**2e**: $C_{12}H_{10}O_2$, MW = 186.20, triclinic, space group *P*-1, final *R* indices [$I > 2\sigma(I)$], R1 = 0.0731, wR2 = 0.1959, *R* indices (all data) R1 = 0.0829, wR2 = 0.2063, a = 9.4588(14) Å, b = 9.6985(14) Å, c = 11.9322(17) Å, α = 74.013(2)°, β = 88.980(3)°, γ = 70.029(2)°, V = 985.5(2) Å^3, T = 293(2) K, Z = 4, reflections collected/unique: 5435/3807 (R_{int} = 0.1539), number of observations [$>2\sigma(I)$] 2929, parameters: 271. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre: CCDC 722253.

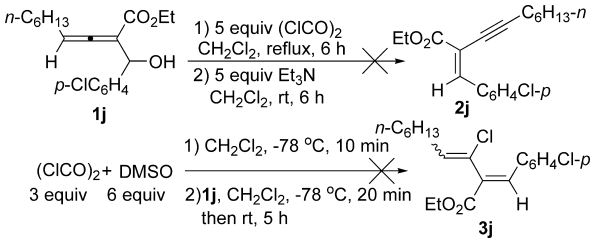
(15) Crystal data for (*Z*)-**3i**: $C_{14}H_{13}ClO_2$, MW = 248.69, monoclinic, space group *P*2(1)/*c*, final *R* indices [$I > 2\sigma(I)$], R1 = 0.0425, wR2 = 0.1163, *R* indices (all data) R1 = 0.0477, wR2 = 0.1240, a = 7.9734(5) Å, b = 16.9107(10) Å, c = 9.8279(6) Å, α = 90.00°, β = 99.353(2)°, γ = 90.00°, V = 1307.54(14) Å^3, T = 296(2) K, Z = 4, reflections collected/unique: 14705/2303 (R_{int} = 0.0222), number of observations [$>2\sigma(I)$] 2005, parameters: 163. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre: CCDC 722252.

Scheme 3



(ethoxycarbonyl)deca-2,3-dien-1-ol **1j**,[16] failed to afford the corresponding products **2j** or **3j** under the standard conditions (Scheme 4).

Scheme 4

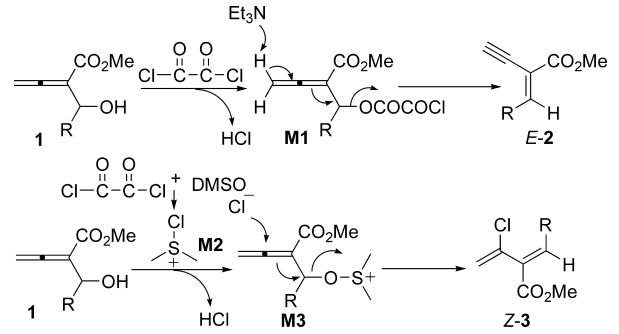


A possible mechanism for these two types of reactions is shown in Scheme 5. First, the reaction of **1** with oxalyl chloride yields the intermediate **M1**; deprotonation of allenyl proton with Et_3N[17] followed by the elimination reaction would afford (*E*)-**2** directly. Similarly, the reaction of **1** with **M2** generated in situ from the reaction of oxalyl chloride with DMSO[13a] affords the intermediate **M3**. Subsequent S_N2'-type reaction of **M3** with chloride anion would afford (*Z*)-**3**.

(16) The substrate **1j** was prepared according to the literature procedure: Xu, B.; Hammond, G. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 689.

(17) (a) Hoff, S.; Steenstra, B. H.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1284. (b) Bridges, A. J.; Fischer, J. W. *J. Chem. Soc., Chem. Commun.* **1982**, 665. (c) Back, T. G.; Lai, E. K. Y.; Muralidharan, K. R. *J. Org. Chem.* **1990**, *55*, 4595. (d) Padwa, A.; Yeske, P. E. *J. Org. Chem.* **1991**, *56*, 6386. (e) Kitagaki, S.; Teramoto, S.; Mukai, C. *Org. Lett.* **2007**, *9*, 2549.

Scheme 5



In conclusion, we have developed a one-pot highly selective synthesis of methyl 2-(ethynyl)alk-2(*E*)-enoates (*E*)-**2** and 2-(1′-chlorovinyl)alk-2(*Z*)-enoates (*Z*)-**3**, which are useful building blocks in organic synthesis, from the readily available 2-(methoxycarbonyl)-2,3-allenols[12] in moderate to good yields, respectively. Due to the easy availability of the starting materials and the potentials of these two types of products, this method will be useful in organic synthesis. Further studies including the scope and synthetic application of this type of reaction are being carried out in our laboratory.

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Supporting Information Available: Experimental procedures and copies of ^1H and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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