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Synthesis of Elongated Esters from Alkenes

Tomoya Miura,* Yuuta Funakoshi, Junki Nakahashi, Daisuke Moriyama, and Masahiro Murakami*

Abstract: A convenient method for synthesizing elongated aliphatic esters from alkenes is reported. An (alkoxycarbonyl)methyl radical species is generated upon visible-light irradiation of an ester-stabilized phosphorus ylide in the presence of a photoredox catalyst. It adds onto the carbon–carbon double bond of an alkene to produce an elongated aliphatic ester.

The Wittig-type reaction of aldehydes with phosphorus ylides stabilized by an ester group and its related analogs present one of the most reliable synthetic methods to construct an elongated unsaturated carbon chain equipped with an alkoxycarbonyl functionality.^[1] A carbonyl group, *i.e.*, a carbon–oxygen double bond, joints the carbon chain to an ester group by making a carbon–carbon double bond in this protocol. From a strategic viewpoint in organic synthesis, it would make another strong protocol if an ester group would be installed onto a carbon–carbon double bond of an alkene with elongation of the carbon chain.^[2] We now report a convenient method to install an (alkoxycarbonyl)methyl group onto a carbon–carbon double bond of alkenes using phosphorus ylides stabilized by an ester group (Figure 1).



Figure 1. Synthesis of esters from alkenes with elongation of carbon chains.

Recent interest in visible-light photoredox-catalyzed reactions has led to numerous advances in the methods to generate radical species, allowing the use of various reagents as competent radical precursors.^[3] We envisaged that phosphorus ylides stabilized by an ester group could act as the precursor of an (alkoxycarbonyl)methyl radical species,^[4] which would possibly add onto a carbon-carbon double bond of alkenes.^[5-7] Thus, a mixture of 4-phenylbut-1-ene (1a, 0.20 mmol), ester-stabilized phosphorus ylide 2 (2.0 equiv), ascorbic acid (5.0 equiv),^[5b,8] fac-Ir(ppy)₃ (1.0 mol %, ppy = 2phenylpyridinato), and pentafluorobenzenethiol (20 mol %) in 1,2-dimethoxyethane (DME)/H₂O (1:1, 0.1 M) was irradiated with blue LEDs (470 nm, 23 W) at room temperature for 40 hours [Eq. (1)]. The 3-phenylpropyl 6-phenylhexanoate (3a) was obtained in 89% yield based on the alkene 1a after chromatographic isolation [see the supporting information for optimization of the reaction conditions (Table S1)].^[9] In a formal sense, the terminal carbon-carbon double bond of 1a underwent a regioselective hydro[(alkoxycarbonyl)-methylation] reaction. A hydrogen atom was attached to the internal

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carbon and an (alkoxycarbonyl)methyl group was attached to the terminal carbon. A similar photo-induced transformation of alkenes has been reported, in which α -bromo esters are used as the radical precursors.^[7a] However, this procedure requires the use of a large excess of alkene (10 equiv), a quartz apparatus, a low-pressure mercury lamp as the source of UV light, and low concentration (0.025 M),^[10] significantly limiting its utility as the alkene-based synthetic protocol.

The mechanistic scheme shown in Scheme 1 would possibly explain the production of 3a from 1a and 2. Initially, ester-stabilized phosphorus ylide 2 (p K_{aH} = ca. 8.0~9.0)^[11] reacts with ascorbic acid $(AscH_2: pK_a = 4.0)^{[12]}$ to generate phosphonium ascorbate $[Ph_3PCH_2CO_2R^1]^+[AscH]^-$ 4. Upon visible-light irradiation of fac-Ir(ppy)3 ([Ir(III)]), its excited species [lr(III)*] is generated to transfer a single electron to 4, which gives rise to (alkoxycarbonyl)methyl radical species 5 with liberation of PPh₃ along with [Ir(IV)]^{*}[AscH][−]. The carbon radical species 5 undergoes electrophilic addition onto the carboncarbon double bond of 1a to afford secondary carbon radical 6, then hydrogen which accepts а atom from pentafluorobenzenethiol to produce the ester 3a and a thiyl radical (ArS). $^{[13]}$ The $[Ir(IV)]^{\star}$ species and ArS are reduced back to the Ir(III) species and ArSH by the action of the ascorbate anion [AscH]^{-,[14]} which becomes dehydroascorbic acid (DHA).^[15]



 $[Ir(IV)]^+[AscH]^- + ArS^- \longrightarrow [Ir(III)] + ArSH + DHA$

Scheme 1. Plausible mechanism for the formation of 3a from alkene 1a and phosphorus ylide 2.

A variety of mono-substituted alkenes 1 were subjected to the reaction with 2 (Table 1). The hydro[(alkoxycarbonyl)methylation] reaction occurred with an excellent regioselectivity and no other isomer was observed in all cases. A wide range of functional groups were well tolerated to afford the corresponding aliphatic esters 3b-3j in yields ranging from 60% to 87% (entries 1-9). In particular, vinyl acetate (1k), vinyltriethylsilane (1l), and vinylboronic acid pinacol ester (1m) were eligible for the reaction (entries 10–12). Although the reaction of styrene (1n) in DME/H₂O (1:1) gave a mixture of unidentified products, the desired product 3n was

formed in 43% yield when the solvent was changed to CH_3CN/H_2O (1:1) (entry 13).

Table 2: Scope of multiply-substituted alkenes 7.[a]



Table 1: Scope of mono-substituted alkenes 1.[a]

Entry	Alkene 1	Product 3	Yield [%] ^[b]
1	Me (15) 1b	Me CO ₂ R ¹ 3b	74
2	<i>n</i> -BuO 1 c	<i>n</i> -BuO CO ₂ R ¹ 3c	61
3	BocHN 1d	BocHN CO ₂ R ¹ 3d	87
4	Ac y 1e	Ac CO_2R^1 3e	85 ^[c]
5	HO ₂ C H3 1f	$HO_2C_{V_3} CO_2R^1$ 3f	60 ^[c]
6	NC (13) 1g	NC CO ₂ R ¹ 3g	84
7	HO HO 1h	$HO_{HO_{4}} CO_{2}R^{1}$ 3h	84
8	AcO Har 1i	AcO	82
9	Cl v 1j	Cl CO ₂ R ¹ 3j	76 ^[c]
10	AcO 🔨 1k	AcO CO ₂ R ¹ 3k	45
11	Et₃Si ∕∕∕ 1I	Et ₃ Si CO ₂ R ¹ 3I	67
12	(pin)B 🔨 1m	(pin)BCCO ₂ R ¹ 3m	64
13	Ph 🔨 1n	PhCO ₂ R ¹ 3n	43 ^[d]

[a] On a 0.20 mmol scale. See Eq. (1) for reaction conditions. R¹ = (CH₂)₃Ph. [b] Yield of isolated product after chromatographic purification. [c] 4-Cl-C₆H₄SH (20 mol %, 0.04 mmol) was used. [d] CH₃CN/H₂O (1 mL/1 mL).

Not only mono-substituted alkenes 1 but also a diverse array of multiply-substituted alkenes 7 were eligible to the reaction with the ester-stabilized phosphorus ylide 2 (Table 2). Five- to eight-membered cyclic di-substituted alkenes 7a-7d afforded the corresponding products 8a-8d in moderate to high yields (entries 1-4). Bicyclo[2.2.1]-hept-2-enes 7e and 7f gave a single stereoisomer 8e and 8f, respectively (entries 5 and 6). The (alkoxycarbonyl)methyl radical species added onto the carbon-carbon double bond from the exo face. In the case of 2,3-dihydrofuran (7g), the addition of the (alkoxycarbonyl)methyl radical species occurred in a direction to form a stable α-oxy radical (entry 7). Acyclic 1,2-di-substituted alkenes [(Z)- and (E)-7h] gave the product 8h in moderate yields with the alkenes remaining unreacted (entries 8 and 9). Geminally di-substituted and tri-substituted alkenes 7i-7m also furnished the products 8i-8m (entries 10-14). In the reaction of 1-methylcyclopent-1ene (71), a diastereomeric mixture was formed, being in suggestive of non-stereoselective hydrogen transfer to an intermediate tertiary radical species. Notably, even tetrasubstituted alkene 7n underwent the elongation reaction to give the product 8n in 73% yield (entry 15).

A competitive reaction among the mono-substituted alkene **1a**, the geminally di-substituted alkene **7i**, and the tri-substituted alkene **7m** was carried out to compare their reactivities [Eq. (2)].

[a] On a 0.20 mmol scale. See Eq. (1) for reaction conditions. R¹ = $(CH_2)_3Ph$. [b] Yield of isolated product after chromatographic purification. [c] **2** (5.0 equiv, 1.0 mmol) and *fac*-Ir(ppy)₃ (2.0 mol %, 4 µmol) were used for 64 h. [d] 4-CI-C₆H₄SH (20 mol %, 0.04 mmol) was used.

The products **3a**, **8i**, and **8m** were formed in 83%, 4%, and <1% GC yields, respectively. Thus, the mono-substituted alkene **1a** was far more reactive than the geminally di-substituted **1a** was far more reactive than the geminally di-substituted alkene **7i** and the tri-substituted alkene **7m**, suggesting that sterics rather than electronics were the dominant factor operating during the electrophilic addition step of an (alkoxycarbonyl)-methyl radical species onto a carbon–carbon double bond.

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The late-stage functionalization of biologically active compounds was conducted (Table 3). Eugenol (1o) and vinclozolin (1p, fungicide) successfully participated in the reaction (entries 1 and 2). *d*-Limonene (7o) and rotenone (7p) were converted into the elongated esters 8o and 8p as a 1:1 mixture of diastereomers (entries 3 and 4). In the reaction of *d*-limonene (7o), the geminally di-substituted alkene moiety reacted in preference to the tri-substituted alkene moiety, being in agreement with the result of the competitive experiment mentioned above.

Table 3: Late-stage functionalization of biologically active compounds.^[a]





In the reaction of β -pinene (**7q**), the ring-opening product **8q**' was formed in 7% yield in addition to the simple adduct **8q** (51%) [Eq. (3)]. This result is in accordance with the proposed reaction mechanism involving a more-substituted alkyl radical species and also indicates that a hydrogen atom transfer (HAT) to the alkyl radical species is fast relative to the ring-opening of the four-membered ring.^[16]



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In the case of benzofuran (**7r**), the addition occurred with dearomatization in a direction to form a benzylic radical rather than an α -oxy radical.^[17] Then, HAT occurred in preference to re-aromatization to give the 2,3-dihydrobenzofuran **8r** [Eq. (4)]. 1-Methylindole (**7s**) also gave the indoline **8s** [Eq. (5)].



Variation in stabilized phosphorus ylides **9** was examined using **1a** as the alkene (Table 4). Benzyl and ethyl esters **9a** and **9b** were suitable ylides (entries 1 and 2). An experiment using 793 mg of **1a** (6.0 mmol) and 4.09 g of **9b** (12 mmol) gave a comparable result to yield 1.13 g of **10b**, indicating the scalability of the present reaction (entry 3). It should be noted

Table 4: Scope of stabilized phosphorus ylides 9.[a]

Entry	Phosphorus ylide 9	Product 10	Yield [%] ^{[i}
	Ph ₃ P=CHCO ₂ R ²	Ph_{ψ_2} CO_2R^2	
1	9a R ² = Bn	10a	86
2	9b R ² = Et	10b	80
3	9b R ² = Et	10b	85 ^[c]
	Ph ₃ P=CR ³ CO ₂ Et	Ph H2 CO ₂ Et	
4	9c R ³ = Me	10c	65
5	9d R ³ = <i>n</i> -Bu	10d	73
6	Ph ₃ P O 9e	$Ph_{\frac{1}{10}}$	51 ^[d]
7	Ph ₃ P=CHCONEt ₂ 9f	Ph	47 ^[e]

[a] On a 0.20 mmol scale. See Eq. (1) for reaction conditions. [b] Isolated yield after chromatographic purification. [c] On a 6.0 mmol scale. For 64 h. [d] **9e** (5.0 equiv, 1.0 mmol) and *fac*-lr(ppy)₃ (2.0 mol %, 4 µmol) were used for 64 h. [e] **9f** (5.0 equiv, 1.0 mmol) were used for 64 h.

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that di-substituted phosphorus ylides **9c** and **9d** successfully participated in the reaction (entries 4 and 5). The reaction with γ -butyrolactone phosphorus ylide **9e** was slower, and required more forcing conditions (entry 6). Amide-stabilized phosphorus ylide **9f** was also amenable to the reaction (entry 7).

It was possible to convert the (alkoxycarbonyl)methyl group into a methyl group and a benzyl group *via* an *N*hydroxyphthalimide ester^[18] (Scheme 2). After the reaction of **1a** with **2**, the crude product **3a** was directly hydrolyzed to 6phenylhexanoic acid (**11**). Carbodiimide-mediated condensation with *N*-hydroxyphthal-imide (NHPI) afforded the ester **12**. The following reductive photodecarboxylation^[19] afforded 1phenylpentane (**13**). On the other hand, nickel-catalyzed decarboxylative cross-coupling of **12** with iodobenzene gave 1,5-diphenylpentane (**14**).^[20] These sequential procedures allow formal 1,2-hydromethylation^[21] and 1,2-hydrobenzylation of unactivated alkenes in an *anti*-Markovnikov manner.



Scheme 2. Formal 1,2-hydromethylation and 1,2-hydrobenzylation of unactivated alkenes.

In summary, we have developed the hydro[(alkoxycarbonyl)methylation] reaction of alkenes. The substrate scope is broad and the reaction conditions allow a variety of functional groups. These features will make this reaction extremely useful for synthesizing elongated aliphatic esters from alkenes.

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Keywords: alkenes • ascorbic acid • photocatalysis • phosphorus ylides • radical reactions

 For a seminal report, see: a) G. Wittig, W. Haag, *Chem. Ber.* 1955, *88*, 1654. For reviews, see: b) B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, 89, 863; c) P. R. Blakemore, *Comprehensive Organic Synthesis*, 2nd ed.; Vol. 1; G. A. Molander, P. Knochel, Eds.; Elsevier: Oxford, 2014, 516.

- [2] For recent examples of hydrofunctionalization of unactivated alkenes under visible-light irradiation, see: a) D. J. Wilger, N. J. Gesmundo, D. A. Nicewicz, *Chem. Sci.* 2013, 4, 3160; b) S. Mizuta, S. Verhoog, K. M. Engle, T. Khotavivattana, M. O'Duill, K. Wheelhouse, G. Rassias, M. Médebielle, V. Gouverneur, *J. Am. Chem. Soc.* 2013, 135, 2505; c) A. J. Musacchio, B. C. Lainhart, X. Zhang, S. G. Naguib, T. C. Sherwood, R. R. Knowles, *Science* 2017, 355, 727; d) A. J. Boyington, M.-L. Y. Riu, N. T. Jui, *J. Am. Chem. Soc.* 2017, 139, 6582; e) H. Wang, N. T. Jui, *J. Am. Chem. Soc.* 2018, 140, 163; f) Q. Zhu, D. E. Graff, R. R. Knowles, *J. Am. Chem. Soc.* 2018, 140, 741. For a review, see: g) K. A. Margrey, D. A. Nicewicz, *Acc. Chem. Res.* 2016, 49, 1997.
- [3] For reviews, see: a) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* 2011, 40, 102; b) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* 2016, 116, 10035; c) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* 2016, 116, 10075; d) J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan, *Nat. Rev. Chem.* 2017, 1, 52; e) L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* 2018, 57, 10034; *Angew. Chem.* 2018, 130, 10188.
- [4] For photocatalytic reactions using *gem*-difluorinated phosphonium salts as the precursors of (alkoxycarbonyl)difluoromethyl radical species, see: a) Q.-Y. Lin, X.-H. Xu, K. Zhang, F.-L. Qing, *Angew. Chem. Int. Ed.* **2016**, 55, 1479; *Angew. Chem.* **2016**, *128*, 1501; b) L. I. Panferova, A. V. Tsymbal, V. V. Levin, M. I. Struchkova, A. D. Dilman, *Org. Lett.* **2016**, *18*, 996; c) Q.-Y. Lin, Y. Ran, X.-H. Xu, F.-L. Qing, *Org. Lett.* **2016**, *18*, 2419; d) Y. Ran, Q.-Y. Lin, X.-H. Xu, F.-L. Qing, *Org. Lett.* **2016**, *81*, 7001. See also: e) W. Yu, X.-H. Xu, F.-L. Qing, *Org. Lett.* **2016**, *18*, 5130.
- [5] For examples of photocatalytic atom transfer radical addition (ATRA) reactions using an (alkoxycarbonyl)methyl radical species, see: a) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska, C. R. J. Stephenson, J. Am. Chem. Soc. 2011, 133, 4160; b) C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner, C. R. J. Stephenson, J. Am. Chem. Soc. 2012, 134, 8875; c) E. Arceo, E. Montroni, P. Melchiorre, Angew. Chem. Int. Ed. 2014, 53, 12064; Angew. Chem. 2014, 126, 12260; d) X.-J. Tang, W. R. Dolbier, Jr. Angew. Chem. Int. Ed. 2015, 54, 4246; Angew. Chem. 2015, 127, 4320; e) G. Magagnano, A. Gualandi, M. Marchini, L. Mengozzi, P. Ceroni, P. G. Cozzi, Chem. Commun. 2017, 53, 1591; f) J. Cheng, Y. Cheng, J. Xie, C. Zhu, Org. Lett. 2017, 19, 6452. For a recent review, see: g) T. Courant, G. Masson, J. Org. Chem. 2016, 81, 6945.
- [6] For examples of photocatalytic ATRA-type reactions, see: a) H. Yi, X. Zhang, C. Qin, Z. Liao, J. Liu, A. Lei, Adv. Synth. Catal. 2014, 356, 2873; b) N. Esumi, K. Suzuki, Y. Nishimoto, M. Yasuda, Org. Lett. 2016, 18, 5704; c) M. Silvi, C. Sandford, V. K. Aggarwal, J. Am. Chem. Soc. 2017, 139, 5736; d) Y.-Y. Liu, X.-Y. Yu, J.-R. Chen, M.-M. Qiao, X. Qi, D.-Q. Shi, W.-J. Xiao, Angew. Chem. Int. Ed. 2017, 56, 9527; Angew. Chem. 2017, 129, 9655; e) I. Triandafillidi, M. G. Kokotou, C. G. Kokotos, Ora. Lett. 2018, 20, 36.
- [7] For examples of reductive ATRA-type reactions, see: a) S. Sumino, A. Fusano, I. Ryu, Org. Lett. 2013, 15, 2826. See also: b) M. Nakajima, Q. Lefebvre, M. Rueping, Chem. Commun. 2014, 50, 3619; c) C. Yu, N. Iqbal, S. Park, E. J. Cho, Chem. Commun. 2014, 50, 12884; d) S. Sumino, M. Uno, T. Fukuyama, I. Ryu, M. Matsuura, A. Yamamoto, Y. Kishikawa, J. Org. Chem. 2017, 82, 5469.
- [8] a) T. Hamada, A. Nishida, O. Yonemitsu, J. Am. Chem. Soc. 1986, 108, 140; b) G. Pandey, S. Hajra, M. K. Ghorai, K. R. Kumar, J. Am. Chem. Soc. 1997, 119, 8777; c) T. Maji, A. Karmakar, O. Reiser, J. Org. Chem. 2011, 76, 736; d) V. I. Supranovich, V. V. Levin, M. I. Struchkova, A. D. Dilman, Org. Lett. 2018, 20, 840; e) X. Guo, O. S. Wenger, Angew. Chem. Int. Ed. 2018, 57, 2469; Angew. Chem. 2018, 130, 2494.
- [9] When 3-phenylpropyl 2-bromoacetate was used instead of the ylide 2 under the same conditions as Eq. (1), the bromo-adduct was mainly formed (67% NMR yield). See the supporting information (Table S1).

This result showed the advantage of using ${\bf 2}$ together with ascorbic acid.

- [10] The low concentration is required to suppress the formation of a bromo-adduct. Still 4% of the bromo-adduct is accompanied.
- [11] X.-M. Zhang, F. G. Bordwell, J. Am. Chem. Soc. 1994, 116, 968.
- [12] C. Creutz, Inorg. Chem. 1981, 20, 4449.
- [13] a) F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, A. V. Satish, X. Zhang, J. Am. Chem. Soc. 1991, 113, 9790. For a review, see: b) B. P. Roberts, Chem. Soc. Rev. 1999, 28, 25.
- [14] J. J. Warren, J. M. Mayer, J. Am. Chem. Soc. 2010, 132, 7784.
- [15] R. C. Kerber, J. Chem. Educ. 2008, 85, 1237.
- [16] a) G. Povie, L. Ford, D. Pozzi, V. Soulard, G. Villa, P. Renaud, *Angew. Chem. Int. Ed.* 2016, *55*, 11221; *Angew. Chem.* 2016, *128*, 11387. For a review, see: b) F. Dénès, M. Pichowicz, G. Povie, P. Renaud, *Chem. Rev.* 2014, *114*, 2587.
- [17] a) A. Nakatani, K. Hirano, T. Satoh, M. Miura, *Chem. Eur. J.* **2013**, *19*, 7691; b) E. C. Swift, T. M. Williams, C. R. J. Stephenson, *Synlett*, **2016**, 754.
- [18] For examples of recent studies using NHP esters, see: a) W. Zhao, R. P. Wurz, J. C. Peters, G. C. Fu, *J. Am. Chem. Soc.* 2017, *139*, 12153; b) C. Li, J. Wang, L. M. Barton, S. Yu, M. Tian, D. S. Peters, M. Kumar, A. W. Yu, K. A. Johnson, A. K. Chatterjee, M. Yan, P. S. Baran, *Science* 2017, *356*, eaam7355; c) A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers, V. K. Aggarwal, *Science* 2017, *357*, 283.
- [19] K. Okada, K. Okubo, N. Morita, M. Oda, *Tetrahedron Lett.* **1992**, *33*, 7377.
- [20] K. M. M. Huihui, J. A. Caputo, Z. Melchor, A. M. Olivares, A. M. Spiewak, K. A. Johnson, T. A. DiBenedetto, S. Kim, L. K. G. Ackerman, D. J. Weix, J. Am. Chem. Soc. 2016, 138, 5016.
- [21] H. T. Dao, C. Li, Q. Michaudel, B. D. Maxwell, P. S. Baran, J. Am. Chem. Soc. 2015, 137, 8046.

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