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(*E*)-β,γ-Unsaturated Esters from (*E*)-[2′-(Tributyltin)alkenyl]dialkylboranes and Ethyl (Dimethylsulfuranylidene)acetate

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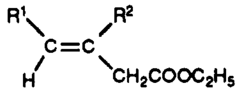
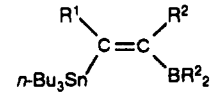
Introduction

β,γ-Unsaturated esters (I), which have been noted as important functionality in naturally occurring compounds,[1] can be readily transformed into γ-hydroxy or γ-oxo-α,β-unsaturated carbonyl compounds.[2] They are also the important starting materials for the syntheses of some natural products, especially macrolides.[3] Hence, the preparation of β,γ-unsaturated esters is attractive and interesting in organic synthesis. The usual method for preparing β,γ-unsaturated esters is the deprotonation and reprotonation of α,β-unsaturated esters; but this method usually affords a mixture of (*E*)- and (*Z*)-β,γ-unsaturated esters.[4] Pelter et al. reported that pure (*Z*)-β,γ-unsaturated esters (I) (R^1 and R^2 are alkyls, $R^1 = R^2$ or $R^1 \neq R^2$) could be prepared by the reaction of lithium trialkylalkynylborates with ethyl α-bromoacetate.[5] However, to the best of our knoweldge, no method for the preparation of corresponding pure (*E*)-β,γ-unsaturated esters (I) (R^1 and R^2 are alkyls; $R^1 = R^2$ or $R^1 \neq R^2$) has been appeared in literature.

Brown et al. reported that (*E*)-β,γ-unsaturated esters (I) (R^1 = alkyl, R^2 = H) could be prepared in 57–65% yield from *B-trans*-9-alkenyl-9-BBN and ethyl α-bromoacetate with the special hindered base, potassium 2,6-di-*tert*-butyl phenolate; but the reaction gave a mixture of *E* and *Z* isomers (I) (R^1 and R^2 are alkyls, *E*/*Z* = 50:50) in the case of internal 9-alkenyl-9-BBN compounds.[6] Recently, we found that (*E*)-β,γ-unsaturated esters (I) (R^1 and R^2 are alkyls, $R^1 = R^2$ or R^1 = alkyl, Ph, R^2 = H) could be prepared in 60–80% yield from stereodefined 9-alkenyl-9-BBN with ethyl (dimethylsulfuranylidene)acetate.[7] In this reaction, 9-alkenyl-9-BBN compounds were easily obtained by the hydroboration of terminal or symmetric internal alkynes with 9-BBN, but might not be easily obtained by the hydroboration of generally unsymmetric internal alkynes because of the low regioselectivity in the case of the generally unsymmetric internal alkynes. Thus, this reaction procedure is also not suited to prepare the (*E*)-β,γ-unsaturated esters (I) with two different alkyl groups ($R^1 \neq R^2$) on the carbon–carbon double bond.



(I)



(II)

(*E*)-[2′-(Tributyltin)alkenyl]dialkylboranes (II), which can be easily prepared by the reaction of lithium trialkylalkynylborates with tributyltin chloride,[8] are versatile synthetic intermediates. For example, they can react with (methylthio)methyllithium–TMEDA to give the 1,2-migrating products[8] and react with halohydrocarbons to give the coupling products[9] with high stereoselectivity. Additionally, the reaction of the intermediates containing two heteroatoms (II) has also been investigated by Wrackmeyer et al.[10] In this paper, we wich to report the results of the reaction of stereodefined (*E*)-[2′-(tributyltin)alkenyl]dialkylboranes with ethyl (dimethylsulfuranylidene)acetate. We found that (*E*)-β,γ-unsaturated esters (I) (R^1 and R^2 are alkyls; $R^1 = R^2$ or $R^1 \neq R^2$) could be easily prepared by this reaction with high stereoselectivity and good overall yield.

Results and Discussions

The reaction was simple. (Carbethoxymethyl)dimethylsulfonium bromide could be easily prepared by direct reaction of dimethyl sulfide with ethyl α-bromoacetate.[11] The stereodefined (*E*)-[2′-(tributyltin)alkenyl]dialkylborane, in situ generated from lithium trialkylalkynylborate and tributyltin chloride,[8] readily reacted with ethyl (dimethylsulfuranylidene)acetate, which was prepared from (carbethoxymethyl)dimethylsulfonium bromide and sodium hydride at 0 °C in THF. The reaction mixture was then oxidized by H_2O_2/OAc^-, giving (*E*)-β,γ-unsaturated ester with 57–64% overall yield, as shown in Scheme I.

The protonation under basic conditions seems to be important. We found that the reaction intermediate (tributylalkenyltin) of (*E*)-[2′-(tributyltin)alkenyl]dialkylboranes with ethyl (dimethylsulfuranylidene)acetate was more easily protonated by H_2O_2/base than by HCOOH, AcOH, CH_3OH, etc. to give (*E*)-β,γ-unsaturated esters. Eaborn et al. also found that trimethylaryltin was protonated to give substituted benzene more easily by base than by acid.[12] In addition, we found that the product (*E*)-β,γ-unsaturated ester was much easily isolated by silica gel column chromatography if the reaction mixture was oxidized by H_2O_2 in the presence of base.

The results of the reactions of various (*E*)-[2′-(tributyltin)alkenyl]dialkylboranes with ethyl (dimethylsulfuranylidene)acetate are shown in Table I.

The configurations of (*E*)-β,γ-unsaturated esters were confirmed by ^1H NMR ($CDCl_3$/TMS, 200 MHz). In the

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[1] (a) Millar, J. G.; Oehlschlager, A. C.; Wong, J. W. *J. Org. Chem.* **1983**, *48*, 4404. (b) Oehlschlager, A. C.; Wong, J. W.; Verigin, V. G.; Pierce, H. D., Jr. *J. Org. Chem.* **1983**, *48*, 5009.

[2] (a) Mali, R. S.; Pohmakotr, M.; Weidmann, B.; Seebach, D. *Liebigs Ann. Chem.* **1981**, 2272. (b) Fujisawa, T.; Takeuchi, M.; Sato, T. *Chem. Lett.* **1982**, 1795.

[3] Hirao, T.; Fujihara, Y.; Kurokawa, K.; Ohshiro, Y.; Agawa, T. *J. Org. Chem.* **1986**, *51*, 2830 and refs cited therein.

[4] (a) Krebs, E.-P. *Helv. Chim. Acta* **1981**, *64*, 1023. (b) Kende, A. S.; Toder, B. H. *J. Org. Chem.* **1982**, *47*, 163. (c) Ikeda, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. *Tetrahedron* **1987**, *43*, 743.

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[7] Deng, M.-Z.; Li, N.-S.; Huang, Y.-Z. *J. Org. Chem.* **1992**, *57*, 4017.

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[9] Chu, K. H.; Wang, K. K. *J. Org. Chem.* **1986**, *51*, 767.

[10] Wrackmeyer, B.; Horcher, K. Z. *Naturforsch B Chem. Sci.* **1990**, *45*, 437 and refs cited therein.

[11] Speziale, A. S.; Tung, C. C.; Ratts, K. W.; Yao, A. *J. Am. Chem. Soc.* **1965**, *87*, 3460.

[12] Eaborn, C., Hornfeld, H. L., Walton, D. R. M. *J. Chem. Soc. (B)* **1967**, 1036. Eaborn et al. demonstrated that the dominating driving force was provided by the nucleophile attack of the base on the tin atom, electrophilic attack by the solvent on the carbon being of secondary importance and probably occurring only as a subsequent fast step.

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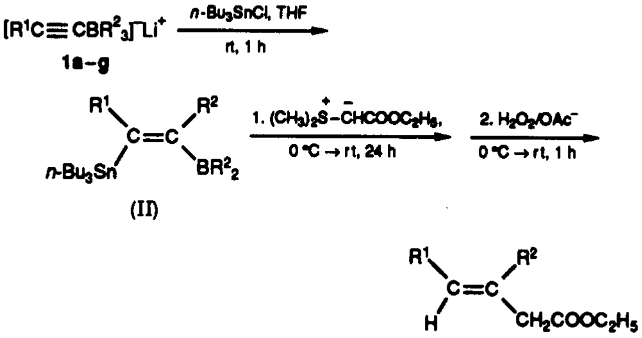
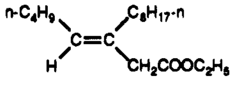
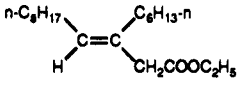
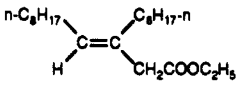
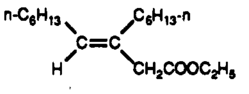
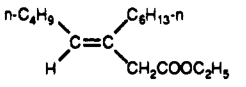
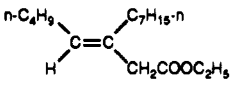
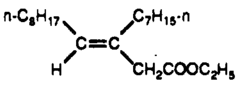
Scheme I



2a–g

seven examples, overall yield: 57–64%

Table I. (*E*)-β,γ-Unsaturated Esters Prepared

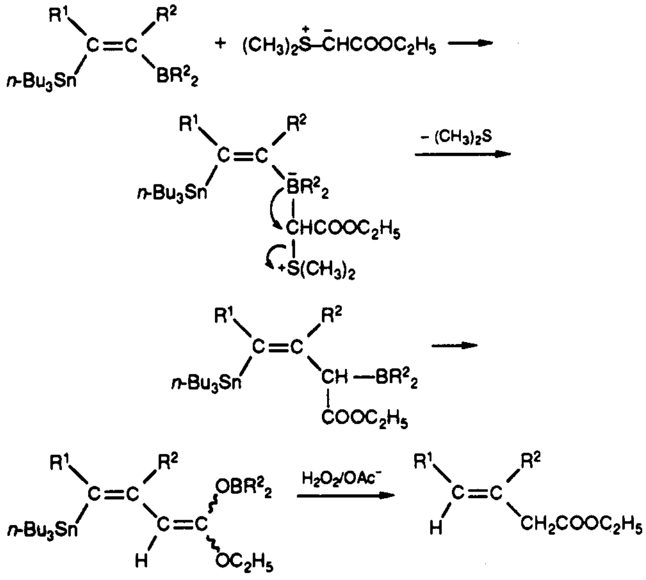
entry	R¹	R²	product[a]	yield (%)[b]
1	n-C_4H_9	n-C_8H_{17}	 (2a)	57
2	n-C_8H_{17}	n-C_6H_{13}	 (2b)	60
3	n-C_8H_{17}	n-C_8H_{17}	 (2c)	57
4	n-C_6H_{13}	n-C_6H_{13}	 (2d)	58
5	n-C_4H_9	n-C_6H_{13}	 (2e)	64
6	n-C_4H_9	n-C_7H_{15}	 (2f)	58
7	n-C_8H_{17}	n-C_7H_{15}	 (2g)	60

[a] All products were characterized by ¹H NMR, IR, MS, and elemental analysis. [b] Isolated yield.

¹H NMR spectra of all products (**2a–g**), there were peaks at $\delta \sim 2.97$ (s, CH_2COO) ppm[5,7] for the *E*-isomers, but no peak at $\delta \sim 3.03$ (s, CH_2COO) ppm[5,7] for *Z*-isomers was observed. The ¹H NMR of **2d** was also confirmed by comparison with the authentic sample of ethyl (*E*)-3-hexyl-3-decenoate, prepared by the procedure in the literature.[7]

The high stereoselective formation of (*E*)-β,γ-unsaturated esters in good overall yields (three steps) indicated that the preferential migration of (*E*)-2′-(tributyltin)-alkenyl moiety from boron to the carbon of ethyl (dimethylsulfuranylidene)acetate and the protolysis of the reaction intermediate (alkenyltin compound) occurred with complete retention of configuration. The reaction mechanism was proposed as depicted in Scheme II.

Scheme II



This method, which is suited to not only in the case of R¹ = R² but also in the case of R¹ ≠ R², may be attractive for the synthesis of (*E*)-β,γ-unsaturated esters (I) (R¹ and R² are alkyls) because both (*E*)-[2′-(tributyltin)alkenyl]-dialkylboranes and ethyl (dimethylsulfuranylidene)acetate are readily avaible, the reaction affords (*E*)-β,γ-unsaturated ester under mild conditions, and the overall yields (three steps) are usually high.

Experimental Section

IR spectra were measured with an IR-440 spectrometer. ¹H NMR spectra were recorded on a Varian XL-200 (200 MHz) spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were taken on a Finnigan 4021 spectrometer. Lithium trialkylalkynylborates were prepared from alkynyllithium and trialkylboranes according to Pelter's procedure.[13] Hexane and THF were dried by standard methods. All reactions were carried out under argon.

Ethyl (*E*)-3-Hexyl-3-octanoate (2e). Typical procedure: Under argon, to the solution of lithium trialkylalkynylborate (5 mmol) in THF (20 mL) was added tributyltin chloride (1.63 g, 5 mmol) at 0 °C. The reaction mixture was stirred at rt for 1 h. In another dry flask, NaH (0.18 g, 80%, 6 mmol) was washed by dry hexane (2 mL) to remove the paraffin and then THF (15 mL) was added to it under argon. Into the mixture of NaH in THF was added (carbethoxymethyl)dimethylsulfonium bromide (1.37 g, 6 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and then the solution of (*E*)-[2′-(tributyltin)-1′-hexylhexenyl]-dihexylborane in THF was transferred and dropped into the solution of ethyl (dimethylsulfuranylidene)acetate in THF at 0 °C. After the reaction was continued at rt for 24 h, the mixture was oxidized by H_2O_2 (3 mL, 30%) and NaOAc (3 mL, 3 N) at 0 °C for 1 h, neutralized with aqueous HCl, and extracted with ether, and the etheral solution was dried by $MgSO_4$. **Ethyl (*E*)-3-hexyl-3-octenoate (2e)** (0.81 g, 64% yield) was isolated by silica gel (200–300 mesh) column chromatography with petroleum/ether (9:1, v/v) as eluent: ¹H NMR δ 0.85–1.00 (m, 6 H, 2 CH_3), 1.20–1.45 (m, 15 H, 6 CH_2, CH_3), 1.94–2.17 (m, 4 H, $CH_2C{=}CCH_2$), 2.96 (s, 2 H, CH_2COO),[5,7] 4.12 (q, 2 H, J = 7.5, OCH_2), 5.28 (t, 1 H, J = 7.2 Hz, $CH{=}C$) ppm; MS *m/e* 254 (M^+, 2.25), 185 ($M + 1 - C_5H_{10}$, 47.95), 113 ($M - C_6H_{13} - C_4H_8$, 59.68), 85 (C_6H_{13}, 57.20), 71 (C_5H_{11}, 88.59), 58 (C_4H_{10}, 95.78), 43 (C_3H_7, 100.00); IR (neat, film) ν_{max} 1740 (s), 1660 (w), 1250 (s), 1155 (s), 1035 (m), 720 (m) cm⁻¹. Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.53; H, 11.89. Found: C, 75.25; H, 12.19.

The following β,γ-unsaturated esters were prepared from the indicated lithium trialkylalkynylborates by the procedure described above.

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(13) Pelter, A.; Bentley, T. W.; Harrison, C. R.; Subrahmanyam, C.; Laub, R. J. *J. Chem. Soc., Perkin Trans. I* **1976**, 2419.

Ethyl (*E*)-3-Octyl-3-octenoate (2a): from lithium trioctylhexynylborate (5 mmol), yield 0.80 g (57%); ^{1}H NMR δ 0.84–0.98 (m, 6 H), 1.20–1.46 (m, 19 H), 1.95–2.18 (m, 4 H), 2.97 (s, 2 H), 4.12 (q, 2 H, *J* = 7.5), 5.28 (t, 1 H, *J* = 7.2 Hz) ppm; MS *m/e* 283 (M + 1, 100.00), 282 (M$^+$, 29.83), 213 (76.58), 211 (21.59), 194 (86.76), 88 (12.62), 71 (63.87), 57 (36.50), 43 (46.06); IR (neat, film) ν_{max} 1740 (s), 1660 (w), 1250 (s), 1155 (s), 1035 (m), 720 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13. Found: C, 76.46; H, 12.19.

Ethyl (*E*)-3-Hexyl-3-dodecenoate (2b): from lithium trihexyldecynylborate (5 mmol), yield 0.93 g (60%); ^{1}H NMR δ 0.85–1.00 (m, 6 H), 1.20–1.46 (m, 23 H), 1.95–2.20 (m, 4 H), 2.96 (s, 2 H), 4.12 (q, 2 H, *J* = 7.5), 5.27 (t, 1 H, *J* = 7.2 Hz) ppm; MS *m/e* 311 (M + 1, 100.00), 310 (M$^+$, 25.96), 264 (22.05), 222 (85.08), 166 (25.57), 152 (22.51), 137 (19.24), 124 (31.72), 110 (34.86), 95 (40.62), 88 (14.14); IR (neat, film) ν_{max} 1740 (s), 1660 (w), 1250 (s), 1155 (s), 1040 (m), 720 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{38}O_2$: C, 77.36; H, 12.33. Found: C, 77.69; H, 12.71.

Ethyl (*E*)-3-Octyl-3-dodecenoate (2c): from lithium trioctyldecynylborate (5 mmol), yield 0.96 g (57%); ^{1}H NMR δ 0.85–1.00 (m, 6 H), 1.20–1.46 (m, 27 H), 1.96–2.19 (m, 4 H), 2.97 (s, 2 H), 4.12 (q, 2 H, *J* = 7.5), 5.28 (t, 1 H, *J* = 7.2 Hz) ppm; MS *m/e* 339 (M + 1, 100.00), 338 (M$^+$, 20.32), 292 (16.58), 251 (46.18), 225 (13.37), 88 (5.89); IR (neat, film) ν_{max} 1740 (s), 1660 (w), 1250 (s), 1155 (s), 1035 (m), 720 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{42}O_2$: C, 78.04; H, 12.51. Found: C, 78.03; H, 12.81.

Ethyl (*E*)-Hexyl-3-decenoate (2d): from lithium trihexyloctylnylborate (5 mmol), yield 0.82 g (58%); ^{1}H NMR δ 0.84–0.98 (m, 6 H), 1.20–1.44 (m, 19 H), 1.94–2.18 (m, 4 H), 2.96 (s, 2 H), 4.12 (q, 2 H, *J* = 7.5), 5.27 (t, 1 H, *J* = 7.2) ppm; MS *m/e* 283 (M + 1, 100.00), 282 (M$^+$, 14.03), 214 (88.06); IR (neat, film) ν_{max} 1740 (s), 1660 (w), 1250 (s), 1155 (s), 1040 (m), 720 (m) cm^{-1}.

Ethyl (*E*)-3-Heptyl-3-octenoate (2f): from lithium triheptylhexynylborate (5 mmol), yield 0.78 g (58%); ^{1}H NMR δ 0.85–1.00 (m, 6 H), 1.20–1.45 (m, 17 H), 1.94–2.18 (m, 4 H), 2.97 (s, 2 H), 4.12 (q, 2 H, *J* = 7.5), 5.27 (t, 1 H, *J* = 7.2 Hz) ppm; MS *m/e* 269 (M + 1, 100.00), 268 (M$^+$, 6.25), 223 (12.15), 71 (13.04), 57 (15.19), 43 (23.03); IR (neat, film) ν_{max} 1740 (s), 1660 (w), 1250 (s), 1155 (s), 1035 (m), 720 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 76.01; H, 12.03.

Ethyl (*E*)-3-Heptyl-3-dodecenoate (2g): from lithium triheptyldecynylborate (5 mmol), yield 0.97 g (60%); ^{1}H NMR δ 0.85–1.00 (m, 6 H), 1.20–1.46 (m, 25 H), 1.96–2.19 (m, 4 H), 2.97 (s, 2 H), 4.12 (q, 2 H, *J* = 7.5), 5.28 (t, 1 H, *J* = 7.2 Hz) ppm; MS *m/e* 325 (M + 1, 100.00), 324 (M$^+$, 10.28), 236 (19.12); IR (neat, film) ν_{max} 1740 (s), 1660 (w), 1250 (s), 1150 (s), 1035 (m), 720 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42. Found: C, 77.46; H, 12.42.

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