hydropyridine. Each of the reactants was dissolved or dispersed in acetonitrile (a total of 10 mL) and was added to the reaction vessel in the following order: palladium acetate (0.11 g, 0.50 mmol) in 1 mL of acetonitrile, tri-*o*-tolylphosphine (0.61 g, 2.0 mmol) in 1 mL of acetonitrile, 3-(benzyloxy)iodobenzene or 3-hydroxyiodobenzene (10 mmol) in 4 mL of acetonitrile, silver nitrate (1.7 g, 10 mmol) in 2 mL of acetonitrile, triethylamine (2.0 g, 20 mmol) in 1 mL of acetonitrile, and 1-propyl-1,2,3,6-tetrahydropyridine (5.0 g, 40 mmol) in 1 mL of acetonitrile. The reaction mixture was magnetically stirred and heated at 100 °C for 4 h. The reaction was allowed to cool and thereafter dispersed in diethyl ether. The tarry mixture was filtered by suction, and the ethereal solution was extracted with 0.5 M HCl. The combined water phases were neutralized (2 M NaOH) and extracted with diethyl ether. The organic portions were dried (Na_2SO_4) and evaporated thoroughly. The excess of 1-propyl-1,2,3,6-tetrahydropyridine was removed by Kugelrohr distillation (40 °C (1.3 mmHg)). The residual oil was submitted to flash chromatography. Dichloromethane/methanol (95/5) was used as eluent for purification of **2** and dichloromethane/methanol (90/10) for purification of 1-propyl-3-(3-hydroxyphenyl)-1,2,3,6-tetrahydropyridine. The crude product was dissolved in dichloromethane and evaporated on coarse gel before application to the column. A 2-fold excess of 1-propyl-1,2,3,6-tetrahydropyridine resulted in lower yields.

1-Propyl-3-(3-(benzyloxy)phenyl)-1,2,3,6-tetrahydropyridine (2): yellow oil 1.37 g (43%); ^{1}H NMR δ 0.90 (t, 3 H, $NCH_2CH_2CH_3$, J = 7.3 Hz), 1.55 (sext, 2 H, $NCH_2CH_2CH_3$), 2.24 (dd, 1 H, NCH_2CHAr, J = 11.2 and 8.9 Hz), 2.38 (m, 2 H, $NCH_2CH_2CH_3$), 2.85 (m, 1 H, NCH_2CH=), 3.00 (dd, 1 H, NCH_2CHAr, J = 11.2 and 5.4 Hz), 3.23 (m, 1 H, NCH_2CH=), 3.62 (m, 1 H, CHAr), 5.05 (s, 2 H), 5.77 (m 1 H, NCH_2CH=CH), 5.86 (m, 1 H, NCH_2CH=), 6.80–7.28 (m, 4 H), 7.30–7.48 (m, 5 H); MS m/z (relative intensity) 307 (M^+, 27), 278 (16), 236 (29), 210 (12), 145 (41), 122 (10), 117 (21), 91 (100), 80 (18), 77 (10); HRMS (m/z) for $C_{21}H_{25}NO$ calcd 307.1936, found 307.1927.

Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.9; H, 8.4; N, 4.5.

GC yields before workup were 73% of **2**, <5% of a saturated isomer of **2**, and 22% of (benzyloxy)benzene.

1-Propyl-3-(3-hydroxyphenyl)-1,2,3,6-tetrahydropyridine: yellow oil 0.61 g (28%); mp (oxalate) 189–190 °C (methanol/diethyl ether); ^{1}H NMR (liberated amine) δ 0.89 (t, 3 H, $NCH_2CH_2CH_3$, J = 7.3 Hz), 1.58 (sext, 2 H, $NCH_2CH_2CH_3$), 2.27 (dd, 1 H, NCH_2CHAr, J = 11.4 and 9.9 Hz), 2.44 (m, 2 H, $NCH_2CH_2CH_3$), 2.88 (m, 1 H, NCH_2CH=), 3.10 (dd, 1 H, NCH_2CHAr, J = 11.4 and 5.6 Hz), 3.34 (br d, 1 H, NCH_2CH=, J = 17.3 Hz), 3.66 (m, 1 H, CHAr), 5.75–5.90 (m, 2 H, CH=), 6.64–7.20 (m, 4 H), 7.63 (v br s, 1 H, OH); MS m/z (relative intensity) 217 (M^+, 27), 188 (17), 146 (100), 131 (23), 117 (16), 72 (33).

Anal. Calcd for $C_{30}H_{40}N_2O_6$ (oxalate): C, 68.68; H, 7.68; N, 5.34. Found: C, 68.3; H, 7.8; N, 5.3.

1-Propyl-3-(3-hydroxyphenyl)piperidine (1). A mixture of **2** (0.41 g, 1.3 mmol), 5% Pd/C (0.28 g, 0.13 mmol Pd), and absolute ethanol (25 mL) was placed in a Parr shaking apparatus. The reaction was pressurized with H_2 to 50 psi and shaken vigorously at room temperature for 10 h. The catalyst was removed by filtration through Celite, and the solvent was evaporated. The reaction yielded 0.26 g (93%: total yield, 40% based on 3-(benzyloxy)iodobenzene) of the title compound **1** (100% pure according to GC analysis). Compound **1** exhibited spectroscopic data in agreement with the literature.[11]

1-(Methoxycarbonyl)-1,2,3,6-tetrahydropyridine. To a solution of 1,2,3,6-tetrahydropyridine (Aldrich; 25 g, 0.30 mmol), triethylamine (84 mL, 0.60 mmol), and dichloromethane (300 mL) was added methyl chloroformate (24 mL, 0.31 mmol) dropwise with stirring. After 3 h, the reaction was evaporated to dryness and the resulting semisolid mass was extracted with diethyl ether. The solvent was removed, and the crude product was distilled to give 1-(methoxycarbonyl)-1,2,3,6-tetrahydropyridine (36 g, 86%) as a colorless liquid, which exhibited ^{1}H NMR data in agreement with the literature.[12]

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Phenylation of 1-(Methoxycarbonyl)-1,2,3,6-tetrahydropyridine. A mixture of palladium acetate (0.11 g, 0.50 mmol), triethylamine (2.0 g, 20 mmol), iodobenzene (2.0 g, 10 mmol), 1-(methoxycarbonyl)-1,2,3,6-tetrahydropyridine (5.6 g, 40 mmol), and DMSO (8 mL) was stirred until homogenous and heated at 100 °C for 4 h. The cooled reaction mixture was diluted with diethyl ether, filtered, and washed with water. The aqueous layer was extracted with diethyl ether, and the combined organic phases were washed once with water, dried ($MgSO_4$), and evaporated. The excess of 1-(methoxycarbonyl)-1,2,3,6-tetrahydropyridine was thereupon removed by distillation (82–84 °C (9mmHg)). The resulting material was subjected to flash chromatography using pentane/diethyl ether (3/1) as eluent. The crude product was dissolved in diethyl ether and evaporated on coarse gel before application to the column. A yield of 1.56 g (72%) of a mixture of two regioisomers, in a ratio of 3:2, was obtained. The two isomers were separated by HPLC (a nucleosil silica gel column, 500 × 10 i.d., and eluation with heptane/ethyl acetate (95/5)).

Reactions in the presence of tri-*o*-tolylphosphine and silver nitrate resulted in a similar regioisomeric ratio but in a slower conversion. Structural assignment of the two isomers was confirmed by COSY, DEPT, and ^{13}C–^{1}H HETCOR experiments.

1-(Methoxycarbonyl)-3-phenyl-1,2,3,4-tetrahydropyridine: colorless crystals; mp 47–49 °C; ^{1}H NMR δ 2.30 (m, 2 H, $=CCH_2CHPh$), 2.99 (m, 1 H, CHPh), 3.16–3.32 (m, 1 H, NCH_2), 3.74, 3.78 (s, 3 H, CO_2CH_3), 4.10, 4.25 (br d, 1 H, NCH_2, J = 12.0 Hz), 5.01, 5.10 (m, 1 H, NCH=C*H*), 6.85, 6.99 (d, 1 H, N*CH*=CH, J = 8.1 Hz), 7.19–7.39 (m, 5 H); ^{13}C NMR δ 29.28 (CH_2), 38.52 (CH), 47.60, 47.93 (CH_2), 52.96 (CH_3), 106.10, 106.30 (CH), 124.87, 125.32 (CH), 126.88, 127.18, 127.34, 128.47 (CH), 142.91 (C), 153.76 (C); MS m/z (relative intensity) 217 (M^+, 20), 104 (100), 91 (15).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.7; H, 6.8; N, 6.5.

1-(Methoxycarbonyl)-4-phenyl-1,2,3,4-tetrahydropyridine: colorless oil; ^{1}H NMR δ 1.82 (m, 1 H, NCH_2CH_2CHPh), 2.14 (m, 1 H, NCH_2CH_2CHPh), 3.51 (m, 1 H, CHPh), 3.55–3.76 (m, 2 H, NCH_2), 3.79 (s, 3 H, CO_2CH_3), 4.93, 5.03 (m, 1 H, NCH=C*H*), 6.96, 7.10 (d, 1 H, N*CH*=CH, J = 8.2 Hz), 7.19–7.36 (m, 5 H); ^{13}C NMR δ 31.07 (CH_2), 38.11 (CH), 40.36 (CH_2), 53.04 (CH_3), 108.88, 109.08 (CH), 125.62, 125.99 (CH), 127.65, 128.31, 128.46, 128.56 (CH); MS m/z (relative intensity) 217 (M^+, 49), 202 (100), 158 (19), 140 (20), 130 (25), 115 (38), 103 (15), 91 (34), 77 (18); HRMS (m/z) for $C_{13}H_{15}NO_2$ calcd 217.1103, found 217.1104.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 70.6; H, 6.9; N, 6.5.

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Registry No. **1**, 83228-38-0; **2**, 141090-48-4; 3-(benzyloxy)iodobenzene, 107623-21-2; 3-hydroxyiodobenzene, 626-02-8; 1-propyl-1,2,3,6-tetrahydropyridine, 53385-78-7; 1-propyl-3-(3-hydroxyphenyl)-1,2,3,6-tetrahydropyridine, 141090-47-3; 1,2,3,6-tetrahydropyridine, 694-05-3; methyl chloroformate, 79-22-1; 1-(methoxycarbonyl)-1,2,3,6-tetrahydropyridine, 75250-59-8; 1-(methoxycarbonyl)-3-phenyl-1,2,3,4-tetrahydropyridine, 141090-49-5; 1-(methoxycarbonyl)-4-phenyl-1,2,3,4-tetrahydropyridine, 141090-50-8.

(*E*)-β,γ-Unsaturated Esters from 9-Alkenyl-9-BBN and Ethyl (Dimethylsulfuranylidene)acetate

Min-Zhi Deng,* Nan-Sheng Li, and Yao-Zeng Huang*

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

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Introduction

β,γ-Unsaturated esters and lactones, which are important functionalities in naturally occurring compounds,[1] can

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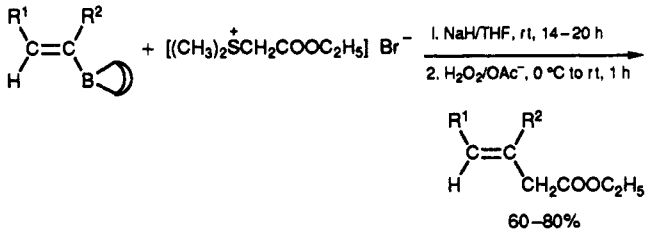
Scheme I



be readily transformed into γ-hydroxy- or γ-oxo-α,β-unsaturated carbonyl compounds,[2] also key functionalities of natural products, especially macrolides.[3] The usual method for preparing β,γ-unsaturated esters is the deprotonation and reprotonation of α,β-unsaturated esters;[4] however, this method usually affords a mixture of (*E*)- and (*Z*)-β,γ-unsaturated esters. Hooz et al. reported that (*E*)-β,γ-unsaturated esters could be prepared from (*E*)-9-alkenyl-9-BBN and diazoacetic ester in 21–25% yield,[5] and Brown et al. reported that (*E*)-β,γ-unsaturated esters 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*-butylphenolate. However, the reaction gave a 1:1 mixture of *E* and *Z* isomers in the case of internal alkenyl-9-BBN compounds.[6] In the literature, much attention has been paid to the 1,2-migration of trialkylboranes with nucleophiles possessing a leaving group,[7] but there are only a few reports on the reaction of alkenyldialkylborane with this kind of reagent.[5,6,8] In this paper, we describe the reaction of stereodefined 9-alkenyl-9-BBN with ethyl (dimethylsulfuranylidene)-acetate.

Results and Discussion

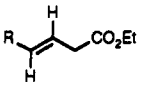
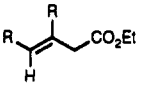
The reaction, shown in Scheme I, is very simple. (Carbethoxymethyl)dimethylsulfonium bromide is easily generated from dimethyl sulfide and ethyl α-bromoacetate,[9] and the stereodefined 9-alkenyl-9-BBN compounds are easily obtained by the hydroboration of various alkynes with 9-BBN in THF.[10] The 9-alkenyl-9-BBN derivative generated in situ readily reacts with (carbethoxymethyl)dimethylsulfonium bromide and sodium hydride in THF. The reaction mixture is then oxidized with H_2O_2/OAc^-, giving (*E*)-β,γ-unsaturated esters in 60–80% yields. The reactions of various 9-alkenyl-9-BBN compounds with ethyl (dimethylsulfuranylidene)acetate were studied, and the results are shown in Table I.

The oxidation conditions seem to be very important for the preparation of pure (*E*)-β,γ-unsaturated esters. When the reaction mixture was oxidized with H_2O_2/OAc^- at 0 °C, no *Z* isomer was found in the product. However, when the reaction mixture was oxidized with H_2O_2/OH^- at 0 °C or with H_2O_2/OAc^- at rt, small amounts of the *Z* isomer were found in the product. For example, when the product of the reaction of 9(*E*)-1′-decenyl-9-BBN and ethyl (dimethylsulfuranylidene)acetate (Table I, entry 5) was oxidized with H_2O_2/OH^- at 0 °C, a 97:3 mixture of the *E* and *Z* isomers was obtained. [^{1}H NMR ($CDCl_3$/TMS): *E* isomer δ 3.01 ppm (d, CH_2COO);[6] *Z* isomer δ 3.08 ppm (d, CH_2COO).] When the product of the reaction of 9(*Z*)-4′-octenyl-9-BBN and ethyl (dimethylsulfuranylidene)-acetate (Table I, entry 7) was oxidized with H_2O_2/OH^- at 0 °C, an approximately 70:30 mixture of *E* and *Z* isomers was obtained. [^{1}H NMR ($CDCl_3$/TMS): *E* isomer δ 2.97 ppm (s, CH_2COO); [11] *Z* isomer δ 3.03 ppm (s, CH_2COO).[11]] The product of the reaction of 9(*Z*)-4′-octenyl-9-BBN with ethyl (dimethylsulfuranylidene)acetate was oxidized with H_2O_2/OAc^- at rt to give an approximately 96:4 mixture of *E* and *Z* isomers. [^{1}H NMR ($CDCl_3$/TMS): *E* isomer δ 2.97 ppm (s, CH_2COO);[11] *Z* isomer δ 3.03 ppm (s, CH_2COO).[11]]

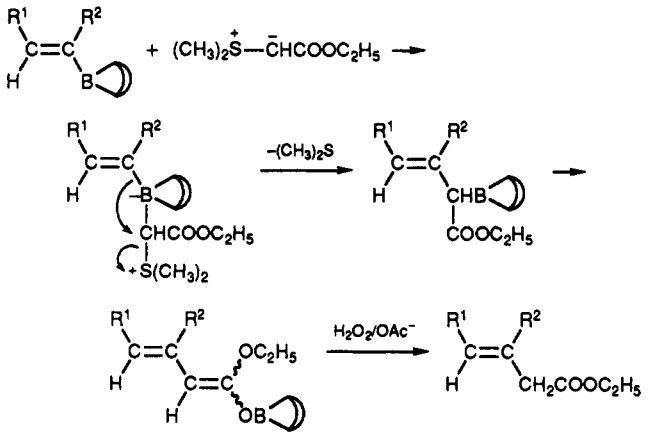
The stereospecific formation of (*E*)-β,γ-unsaturated esters in good yields indicates that the preferential migration of the alkenyl moiety from boron to the carbon of ethyl (dimethylsulfuranyldiene)acetate occurs with complete retention of configuration. The reaction mechanism is depicted in Scheme II.

This method, which is suited to not only terminal but also internal 9-alkenyl-9-BBN compounds, is attractive for the synthesis of (*E*)-β,γ-unsaturated esters because both the 9-alkenyl-9-BBN compounds and ethyl (dimethylsulfuranylidene)acetate are readily available, the reaction affords (*E*)-β,γ-unsaturated esters under mild conditions, and the yields are usually high.

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

entry	R	product	yield (%)
1	n-C_3H_7		76
2	n-C_4H_9		63
3	n-C_5H_{11}		64
4	n-C_6H_{13}		62
5	n-C_8H_{17}		80
6	Ph		60
7	n-C_3H_7		65
8	n-C_4H_9		73
9	n-C_5H_{11}		80
10	n-C_6H_{13}		71

Scheme II



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Experimental Section

^{1}H NMR spectra were recorded at 200 MHz in $CDCl_3$. A 9-BBN solution (0.42 M) in THF was prepared according to Brown's method.[12] 5-Decyne, 6-dodecyne, and 7-tetradecyne were prepared according to the literature.[13] Hexane and THF were dried by standard methods. All reactions were carried out under argon.

Ethyl (*E*)-3-Dodecenoate (Table I, Entry 5). To a solution of 1-decyne (1.38 g, 0.01 mol) in THF (10 mL) at 0 °C under argon was added 9-BBN in THF (11.9 mL, 0.42 M, 0.005 mol) dropwise. The reaction mixture was stirred at rt for 3 h. (When an internal alkyne in excess of 10% was used to prepare 9-alkenyl-9-BBN, the reaction was maintained at rt for at least 10 h.) In another dry flask, NaH (0.18 g, 80%, 0.006 mol) was washed with dry hexane (2 mL), and then THF (15 mL) was added under argon. The mixture of NaH and THF was cooled to 0 °C, (carbethoxymethyl)dimethylsulfonium bromide (1.37 g, 0.006 mol) was added, and the reaction mixture was stirred at 0 °C for 2 h. Then the THF solution of 9(*E*)-1′-decenyl-9-BBN was transferred into the THF solution of ethyl (dimethylsulfuranylidene)acetate at 0 °C. The reaction was allowed to continue at rt for 18 h, and then the mixture was oxidized with H_2O_2 (3 mL, 30%) and NaOAc (3 mL, 3 N) at 0 °C for 1 h. The reaction mixture was neutralized with aqueous HCl and extracted with ether, and the ethereal solution was dried over $MgSO_4$. Ethyl (*E*)-3-dodecenoate (0.9 g, 80%) was isolated by silica gel (200–300 mesh) chromatography with 9:1 petroleum:ether. The peak at 970 cm^{-1} in the IR spectrum and the coupling constant of the two vinyl protons in the ^{1}H NMR (C_6D_6, J = 15.2 Hz) spectrum of this compound clearly indicated that the compound was the *E* isomer: ^{1}H NMR ($CDCl_3$/TMS) δ 0.88 (t, 3 H, J = 6.8, CH_3), 1.28 (m, 15 H, $(CH_2)_6$, CH_3), 2.02 (br, 2 H, CH_2C=), 3.01 (d, 2 H, J = 4, *trans*-CH_2COO),[6] 4.13 (q, 2 H, J = 7.5 Hz, CH_2O), 5.53 (m, 2 H, CH=CH); ^{1}H NMR (C_6D_6/TMS) δ 0.90 (t, 3 H, J = 7.0, CH_3), 1.23 (m, 15 H, $(CH_2)_6$, CH_3), 1.94 (br, 2 H, CH_2C=), 2.91 (d, 2 H, J = 7.1, CH_2COO), 3.95 (q, 2 H, J = 7.0, CH_2O), 5.43 (dt, 1 H, J = 7.1, J = 15.2, *trans*-CH=CCOO), 5.65 (dt, 1 H, J = 7.1, J = 15.2, *trans*-C=CHCCOO), MS m/e 227 (M + 1, 100), 226 (M$^+$, 2), 180 (28), 138 (44), 55 (90), 43 (82); IR (neat) ν 1740, 1250, 970 cm^{-1}. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.21; H, 11.58. Found: C, 73.76; H, 11.60.

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

Ethyl (*E*)-3-heptenoate (Table I, entry 1): from 1-pentyne (1.02 g, 0.015 mol), yield 0.59 g (76%); ^{1}H NMR δ 0.89 (t, 3 H, J = 6.8), 1.26 (t, 3 H, J = 7.5), 1.34–1.48 (m, 2 H), 2.03 (br, 2 H), 3.02 (d, 2 H, J = 4), 4.14 (q, 2 H, J = 7.5), 5.54 (m, 2 H); MS m/e 157 (M + 1, 100), 156 (M$^+$, 17); IR (neat) ν 1740, 1250, 970 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.80; H, 10.37.

Ethyl (*E*)-3-octenoate (Table I, entry 2): from 1-hexyne (1.23 g, 0.015 mol), yield 0.54 g (63%); n^{20}_D = 1.4356 (lit.[6] n^{20}_D = 1.4362); ^{1}H NMR δ 0.88 (t, 3 H, J = 6.8), 1.20–1.48 (m, 7 H), 2.03 (m, 2 H), 3.01 (d, 2 H, J = 4), 4.14 (q, 2 H, J = 7.5 Hz), 5.54 (m, 2 H); MS m/e 171 (M + 1, 100), 170 (M$^+$, 20); IR (neat) ν 1740, 1250, 970 cm^{-1}.

Ethyl (*E*)-3-nonenoate (Table I, entry 3): from 1-heptyne (0.96 g, 0.01 mol), yield 0.59 g (64%); ^{1}H NMR δ 0.89 (t, 3 H, J = 6.8), 1.20–1.40 (m, 9 H), 2.05 (m, 2 H), 3.01 (d, 2 H, J = 4), 4.15 (q, 2 H, J = 7.5), 5.53 (m, 2 H); MS m/e 185 (M + 1, 100), 184 (M$^+$, 18); IR (neat) ν 1740, 1250, 970 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.71; H, 10.94. Found: C, 71.61; H, 11.06.

Ethyl (*E*)-3-decenoate (Table I, entry 4): from 1-octyne (1.1 g, 0.01 mol), yield 0.61 g (62%); n^{20}_D = 1.4370 (lit.[6] n^{20}_D = 1.4372); ^{1}H NMR δ 0.88 (t, 3 H, J = 6.8), 1.20–1.40 (m, 11 H), 2.05 (m, 2 H), 3.02 (d, 2 H, J = 4), 4.15 (q, 2 H, J = 7.5 Hz), 5.51 (m, 2 H); MS m/e 199 (M + 1, 100), 198 (M$^+$, 20); IR (neat) ν 1740, 1250, 970 cm^{-1}.

Ethyl (*E*)-4-phenyl-3-butenoate (Table I, entry 6): from phenylacetylene (1.02 g, 0.01 mol), yield 0.57 g (60%); ^{1}H NMR δ 1.22 (t, 3 H, J = 7.5), 3.10 (d, 2 H, J = 5), 4.15 (q, 2 H, J = 7.5), 6.25 (m, 2 H), 7.20 (m, 5 H); MS m/e 190 (M$^+$, 43), 117 (100), 91 (23); IR neat ν 3050, 3020, 1735, 1650, 1600, 1580, 1500, 970 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37. Found: C, 75.53; H, 7.32.

Ethyl (*E*)-3-propyl-3-heptenoate (Table I, entry 7): from 4-octyne (0.61 g, 0.0055 mol), yield 0.64 g (65%); ^{1}H NMR δ 0.87 (m, 6 H), 1.20–1.42 (m, 7 H), 2.03 (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); MS m/e 198 (M$^+$, 30), 55 (100); IR (neat) ν 1740, 1250 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.74; H, 11.30.

Ethyl (*E*)-3-butyl-3-octenoate (Table I, entry 8): from 5-decyne (0.78 g, 0.0055 mol), yield 0.82 g (73%); ^{1}H NMR δ 0.86 (m, 6 H), 1.20–1.40 (m, 11 H), 2.04 (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); MS m/e 227 (M + 1, 100), 226 (M$^+$, 19); IR (neat) ν 1740, 1250 cm^{-1}. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 73.83; H, 11.80.

Ethyl (*E*)-3-pentyl-3-nonenoate (Table I, entry 9): from 6-dodecyne (0.91 g, 0.0055 mol), yield 1.0 g (80%); ^{1}H NMR δ 0.87 (m, 6 H), 1.20–1.40 (m, 15 H), 2.04 (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); MS m/e 254 (M$^+$, 23), 166 (97), 55 (100); IR neat ν 1740, 1250 cm^{-1}. Anal. Calcd for $C_{16}H_{32}O_2$: C, 75.53; H, 11.89. Found: C, 75.44; H, 12.00.

Ethyl (*E*)-3-hexyl-3-decenoate (Table I, entry 10): from 7-tetradecyne (1.07 g, 0.0055 mol), yield 1.0 g (71%); ^{1}H NMR δ 0.87 (m, 6 H), 1.20–1.42 (m, 19 H), 2.04 (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); MS m/e 283 (M + 1, 100), 282 (M$^+$, 18); IR (neat) ν 1740, 1250 cm^{-1}. Anal. Calcd for $C_{18}H_{34}O_2$: C, 76.59; H, 12.13. Found: C, 76.18; H, 12.48.

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Registry No. 9(*E*)-1′-Pentenyl-9-BBN, 69322-44-7; 9(*E*)-1′-hexenyl-9-BBN, 69322-45-8; 9(*E*)-1′-heptenyl-9-BBN, 74676-16-7; 9(*E*)-1′-octenyl-9-BBN, 73062-42-7; 9(*E*)-1′-decenyl-9-BBN, 69322-46-9; 9(*E*)-1′-(2-phenylethenyl)-9-BBN, 69322-49-2; 9-(*E*)-4′-octenyl-9-BBN, 140929-39-1; 9(*Z*)-4′-octenyl-9-BBN, 105090-63-9; 9(*E*)-5′-decenyl-9-BBN, 140929-40-4; 9(*E*)-6′-dodecenyl-9-BBN, 140929-41-5; 9(*E*)-7′-tetradecenyl-9-BBN, 140929-42-6; 9-BBN, 280-64-8; $(CH_3)_2{}^+S^-CHCOOC_2H_5$, 7380-81-6; $[(CH_3)_2SCH_2COOC_2H_5]^+Br^-$, 5187-82-6; ethyl (*E*)-3-heptenoate, 54340-71-5; ethyl (*E*)-3-octenoate, 26553-47-9; ethyl (*E*)-3-nonenoate, 54211-36-8; ethyl (*E*)-3-decanoate, 82561-67-9; ethyl (*E*)-3-dodecenoate, 82561-69-1; ethyl (*Z*)-3-dodecenoate, 79837-93-7; ethyl (*E*)-4-phenyl-3-butenoate, 1205-84-1; ethyl (*E*)-3-propyl-3-heptenoate, 140929-43-7; ethyl (*Z*)-3-propyl-3-heptenoate, 141017-55-2; ethyl (*E*)-3-butyl-3-octenoate, 140929-44-8; ethyl (*E*)-3-pentyl-3-nonenoate, 140929-45-9; ethyl (*E*)-3-hexyl-3-decenoate, 51916-59-7; 1-decyne, 764-93-2; 1-pentyne, 627-19-0; 1-hexyne, 693-02-7; 1-heptyne, 628-71-7; 1-octyne, 629-05-0; phenylacetylene, 536-74-3; 4-octyne, 1942-45-6; 5-decyne, 1942-46-7; 6-dodecyne, 6975-99-1; 7-tetradecyne, 35216-11-6.

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In Situ Generation and Utilization of Electrophilic Selenium Species ($PhSe^+$) by Photooxidative (Single Electron Transfer) Cleavage of Diphenyl Diselenide (PhSeSePh)[†,‡,1]

Ganesh Pandey* and B. B. V. Soma Sekhar

Division of Organic Chemistry (Synthesis), National Chemical Laboratory, Pune 411 008, India

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Photochemical processes operating via a single electron transfer (SET) mechanism have been attracting considerable attention owing to their mechanistic interest[2] and

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[‡] Major part of the work was carried out at IICT, Hyderabad 500 007, India.

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