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Cobalt mediated alkene / diene coupling; documentation of scope, limitations, and regioselectivity

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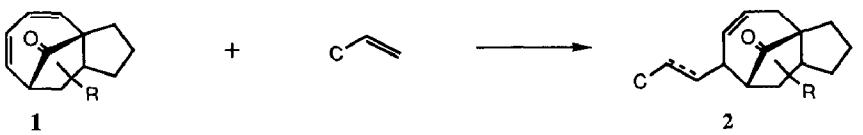
Abstract

The cobalt hydride catalyzed addition of alkenes bearing electron withdrawing groups to methylated 1,3-butadienes leads to functionalized hexadiene products. The reaction is limited to addends featuring at least one terminal alkene moiety.

Introduction

The ready availability of dienone **1** through [6π + 2π] intramolecular photocyclization of an alkenyltropone precursor provides an expeditious route to natural products which embody the bicyclo [6.3.0]undecane substructure [1,2]. One such project ongoing in our laboratory requires attachment of a three carbon unit to the diene portion of **1** to furnish an alkylated cyclooctenyl unit as shown in **2** (Eq. 1). Initial attempts to functionalize the diene moiety of **1** through classical electrophile or free radical-based protocols were not fruitful, leading either to recovery of starting material or to destruction of the substrate. Accordingly, we sought to exploit an alternative approach which might be both mild enough to preserve the structural integrity of the substrate, and regioselective in the sense shown in Eq. 1. The great wealth of catalytic cooligomerization and simple addition chemistry between 1,3-dienes and alkenes mediated by low valent late transition metals suggested that prospecting among these species might provide a solution [3,4]. Herein, we describe our efforts to define the scope, limitations, and applicability of one of these compounds, **5**, first reported by Wilke and Bonnemann [4], to the regioselective combination of functionalized alkenes with substituted 1,3-dienes (Eq. 2). This well characterized, stable organocobalt species [5] is thought to serve as a precursor to an active L_nCo–H catalyst.



1 **2** (1)

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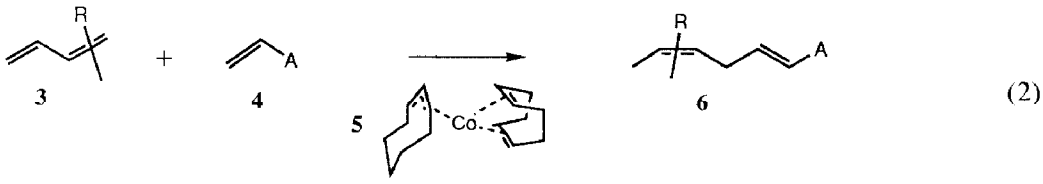
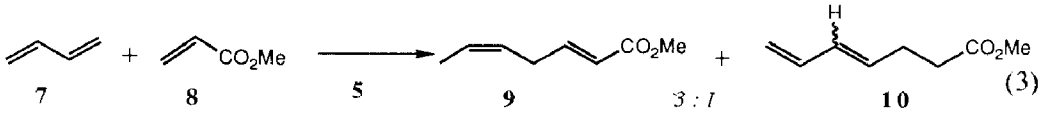


(2)

Initially, this cobalt mediated chemistry appeared to offer several advantages over related Pd^0 or Ni^0 catalyzed transformations. Competitive self condensation (oligomerization) of the 1,3-diene or alkene components is minimized, relative to desired 1 : 1 addition, with the cobalt system. Furthermore, tolerance to oxygenated addends, as is required for eventual applications in organic synthesis as mentioned above, differentiated the cobalt mediated chemistry from several of the Pd and Ni systems [3]. Wilke and Bonnemann's initial disclosure in this area related to the 1 : 1 coupling of butadiene (**7**) with methyl acrylate (**8**) to produce the skipped and conjugated hexadienoates **9** and **10**, respectively, in the ratio shown (Eq. 3) [4]. We have attempted to extend this work to include a variety of ester- and oxygen-substituted addends, paying particular attention to the relationship between the steric and electronic characteristics of substituents and the regiochemistry of product formation.



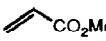
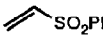
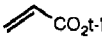
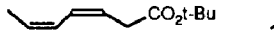
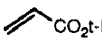
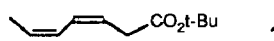
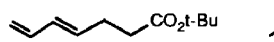
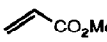
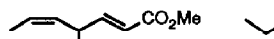
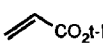
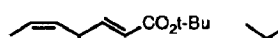
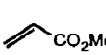
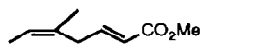
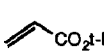
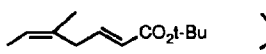
(3)

Results and discussion

Numerous dienes, featuring alkyl, aryl, and ether substituents, and representative alkenes containing ester, sulfone and aryl residues, were subjected to reaction mediated by the cobalt precatalyst **5** (hexane solvent, 55°C, 5 mol% catalyst). Successful coupling was achieved for the addends shown in Table 1. Thus, the prototypical reaction between butadiene and methyl acrylate afforded the expected dienes **9** and **10**, but the preference for the skipped diene **9** is enhanced eight-fold in hexane as solvent relative to the reaction without solvent (cf. Eq. 3). The sulfonyl and t-butyl ester-substituted alkenes **11** and **14** respectively, are effective addends as well, and both exhibit a strong preference for the desired skipped diene products. Interestingly, the ratio of diene to acrylate (compare entries *c* and *d*) has a significant effect on the product distribution, with the selectivity for the 1,4-diene product **17** enhanced at higher butadiene concentrations. Resubmission of the purified product mixtures from entry *c*, and independently, entry *d*, to reaction conditions did not lead to any alteration in isomer ratios.

Both 1,3-pentadiene (**19**) and isoprene (**24**) engage in successful coupling with methyl and t-butyl acrylate, entries *e–h*. In all cases, complete regiochemical control for the skipped diene products was observed. However, the methyl substituent on the diene had only rather modest influence on the regioselectivity of C–C bond formation. For example, replacing the sterically bulky t-butyl acrylate with methyl acrylate in the coupling reaction with 1,3-pentadiene led to only an incremental improvement (1.2/1 vs. 1/1) in selectivity for alkene attachment at the more substituted terminus of the diene (entries *e* and *f*). In the isoprene case (entries *g*

Table 1

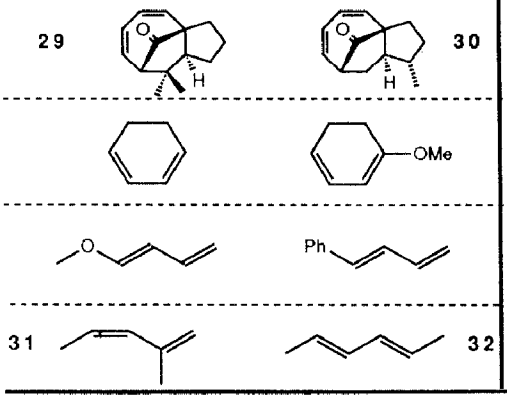
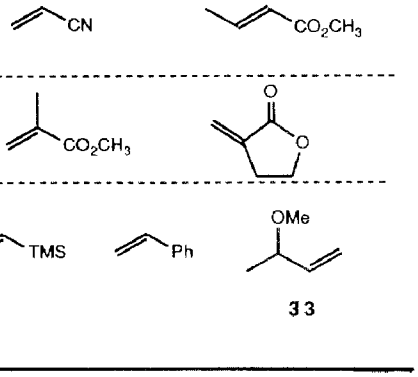
	diene [a] (eq.)	alkene (eq.)	product dienes [c] (eq.)	yield [b]
(a)	 7 (1)	 8 (1)	 10 (1) 9 (24)	53 %
(b)	 7 (1)	 11 (1)	 12 (1.4) 13 (1)	48 %
(c)	 7 (2.7)	 14 (1)	 15 (1) 16 (2)  17 (23)	50 %
(d)	 7 (1)	 14 (1)	 15 (1) 16 (2)  18 (4.5) 17 (6)	55 %
(e)	 19 (1)	 8 (1)	 20 (1) 21 (1)	50 %
(f)	 19 (1)	 14 (1)	 22 (1.2) 23 (1)	52 %
(g)	 24 (1)	 8 (1)	 25 (3.5) 26 (1)	48 %
(h)	 24 (1)	 14 (1)	 27 (2.5) 28 (1)	53 %

[a] All reactions were run in hexane at 55 °C for 30 min using 0.05 eq. 5. Inferior yields resulted when other temperatures were utilized. [b] Yields are based on isolated, chromatographically pure material. [c] Products were fully characterized by spectroscopic techniques (^{1}H NMR, ^{13}C NMR, IR, MS, and HRMS). Olefin geometry was assigned based on coupling constants and/or DNOE measurements (see experimental).

and *h*), t-butyl acrylate actually proved marginally less selective than methyl acrylate (2.5/1 vs. 3.5/1) for addition at the disubstituted alkene portion of the diene. In every case examined, however, the product olefin that originated from the butadiene addend was formed with strictly (*Z*) geometry.

Unfortunately, the limited scope of this particular process is underscored by the entries in Table 2. A survey of dienes which do not undergo successful coupling to

Table 2

dienes unreactive with methyl acrylate	*alkenes unreactive with butadiene*
	

methyl acrylate under the standard reaction conditions is shown in Column 1. Thus, cyclic dienes, including photocyclization adducts **29** and **30**, related to **1**, do not participate in the reaction. Furthermore, 1-methoxy or 1-phenyl substituents on butadiene are not permissible. Lastly, simple dimethyl substituted butadienes **31** and **32** lead to no characterizable products. Column 2 illustrates representative alkenes which do not form hexadiene products upon Co–H mediated reaction with butadiene. Simple acrylate congeners, such as acrylonitrile, methyl crotonate, methyl methacrylate or α-methylene butyrolactone are unreactive under standard coupling conditions. In a similar manner, no coupled products could be detected from butadiene and vinyltrimethylsilane, styrene, or the allylic ether **33**.

Attempts to improve the scope and selectivity of this transformation centered on solvent variation and the effects of (potentially) activating or ligating additives. Unfortunately, examination of the butadiene/methyl acrylate coupling in various solvents (PhH, THF, Et_2O, CH_3CN, CH_3OH) led either to inferior yields or attenuated regioselectivity relative to hexane. Lewis acid additives ($AlMe_3$, $BF_3 \cdot Et_2O$) suppressed the butadiene/methyl acrylate combination, while incorporation of phosphorous ligands (PPh_3, $P(OEt)_3$) led to diminished yields. For example, inclusion of 2 eq. PPh_3 (per cobalt precatalyst) in the reaction medium led to isolation of the expected dienes in 25% yield as a 1.3/1 ratio of **9** to **10**.

A mechanistic hypothesis, which encompasses divergent pathways featuring either initial Co–H (formed by β-hydride elimination from the precatalyst **5**) insertion into the diene component leading eventually to the major skipped diene regioisomer, or initial Co–H insertion into the alkene partner leading eventually to the minor conjugated diene regioisomer, has been proposed [4]. In hexane solvent, our experimental results are consistent with expression of product formation through the former channel with the almost complete supression of the latter option. The failure of the variously substituted dienes and alkenes to engage in productive coupling is suggestive of very strict structural requirements for reaction of the addend with the active cobalt catalyst. The limited data, however, do not permit a distinction to be made between potentially offending electronic or steric factors that may be responsible for inhibition of reaction. The obtention of the product **20**

derived from bond formation at a methylated carbon indicates that substitution per se is not sufficient to suppress coupling—rather, the problem may lie in interference with the obligatory complexation of the unsaturated substrate with the cobalt catalyst.

Conclusion

The L_nCo–H catalyzed coupling of 1,3-butadiene (and monomethylated analogs) with acrylate and vinyl sulfone derivatives proceeds in fair yield to afford regioisomeric hexadiene products. In most cases, an overiding preference for skipped (*E*,*Z*) diene products is observed. However, the limitations of this reaction become apparent when more complicated or highly functionalized addends are utilized. Thus, each addend must have an unsubstituted terminal carbon to engage in bond formation. Furthermore, 1,1-disubstituted alkenes are not reactive, nor are dienes bearing substituents other than methyl. These limitations, taken together, clearly render this transformation unsuitable for functionalizing photoadducts of the type **1** within the context of natural products synthesis. Nevertheless, for those few systems where selectivity for the skipped (*E*,*Z*) diene product is high, for example **9**, **17** and **25**, this methodology may provide an efficient and economical alternative to classical multistep approaches.

Experimental

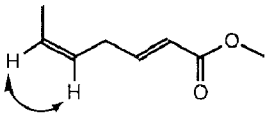
Infrared (IR) spectra were recorded on a Perkin Elmer 281B infrared spectrophotometer. Magnetic resonance spectra (^{1}H NMR, ^{13}C NMR) were recorded on either Bruker WP-200, AM-300 or WM-360 spectrometers. Chemical shifts are reported in δ units, with tetramethylsilane (TMS) as internal standard. Low- and high-resolution mass spectra (MS, HRMS) were obtained on a Kratos MS9/50 hexapole focusing mass spectrometer. Gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 5890A instrument equipped with a capillary cross-linked methyl silicone column (25 m, i.d. 0.20 mm; film thickness 0.33 mm) and a flame-ionization detector. Helium was used as the carrier gas, and the chromatograms were recorded on a HP 3390A integrator. Liquid (flash) chromatography was carried out with 32-63-μm silica gel (Woelm-Pharma) and the indicated solvent. Analytical thin-layer chromatography (TLC) was performed using precoated silica gel (60 F_{254}) plates (E. Merck). High-pressure liquid chromatography (HPLC) was performed on a Waters 6000A semipreparative instrument equipped with an R-400 refractometer and 440 UV detector, using a ZORBAX-SIL ® silica gel column (Dupont). Moisture- and oxygen-sensitive reactions were carried out in predried glassware and under an inert atmosphere (N_2, Ar).

Catalytic coupling of olefin and 1,3-diene substrates. General procedure.

In an inert atmosphere glove box, π-cyclooctenyl-π-cycloocta-1,5-diene cobalt (**5**) [5] (30 mg, 0.08 mmol, 5 mol%) was dissolved in 7 ml of HPLC grade hexane in a 25 ml resealable reaction tube. Olefin and 1,3-diene substrates (1.73 mmol each, unless otherwise indicated (Table 1)) were introduced in the inert atmosphere glove box or, where possible, via vacuum transfer to give a final reaction solution 0.25 *M* in substrate. The reaction solution was degassed using 3 freeze-vacuum-thaw cycles

and promptly placed into a 55°C oil bath with stirring for 0.5 h. At this time, the reaction solution was filtered through a 5 gm portion of silica gel using 15% Et_2O in hexane as eluent, carefully concentrated in vacuo, and the residue was purified by flash chromatography using 3% Et_2O in hexane as eluent. In all cases, HPLC was required to obtain pure samples of the products. The yields, based on isolated material, are given in Table 1.

Methyl (E,Z)-hepta-2,5-dienoate (9). IR(CCl_4) 1715 cm^{-1} (C=O), 1640 cm^{-1} (C=C); ^1H NMR (360 MHz, $CDCl_3$) δ 6.96 (dt, J 15.7, 6.3 Hz, 1H, HC=$CHCO_2CH_3$), 5.84 (dt, J 15.7, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 5.71–5.55 (m, 1H, CH_3CH=CH), 5.48–5.35 (m, 1H, CH_3CH=CH), 3.73 (s, 3H, CO_2CH_3), 2.95 (dd, J 6.6, 6.4 Hz, 2H, CH=CHCH_2), 1.63 (d, J 6.7 Hz, 3H, CH_3CH=CH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.1, 147.3, 126.9, 124.9, 120.9, 51.3, 29.5, 12.7; MS m/z (relative intensity) 140 (10%, M^+), 81 (95%, $M^+ - CO_2CH_3$), 41 (100%, $M^+ - C_5H_7O_2$); HRMS. Calcd. for $C_8H_{12}O_2$: 140.0837. Found: 140.0831.

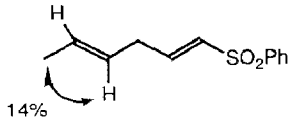


12%

DNOE

Methyl (E)-hepta-4,6-dienoate (10). IR(CCl_4) 1730 cm^{-1} (C=O), 1600 cm^{-1} (C=C); ^1H NMR (360 MHz, $CDCl_3$) δ 6.27 (dt, J 17.0, 10.3 Hz, 1H, H_2C=CH), 6.07 (dd, J 15.2, 10.3 Hz, 1H, CH_2=CHCH=CH), 5.71–5.65 (m, 1H, CH_2=CH-CH=CH), 5.10 (d, J 17.0 Hz, 1H, (H)HC=CH), 4.98 (d, J 10.3 Hz, 1H, (H)HC=CH), 3.66 (s, 3H, CO_2CH_3), 2.38 (t, J 6.8 Hz, 2H, $CH_2CO_2CH_3$), 1.53 (t, J 7.0 Hz, 2H, $CH_2CH_2CO_2CH_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 171.3, 135.8, 130.6, 123.2, 119.6, 50.2, 35.8, 24.32; MS m/z (relative intensity) 140 (25%, M^+), 81 (100%, $M^+ - CO_2CH_3$), 67 (50%, $M^+ - C_3H_5O_2$); HRMS. Calcd. for $C_8H_{12}O_2$: 140.0838. Found: 140.0830.

(E,E)-1-Phenylsulfonylhexa-1,4-diene (12). IR (CCl_4) 1635 cm^{-1} (C=C), 1445, 1145 cm^{-1} (SO_2); ^1H NMR (360 MHz, $CDCl_3$) δ 7.91–7.86 (m, 2H, ArH), 7.67–7.49 (m, 3H, ArH), 7.00 (dt, J 15.1, 6.2 Hz, 1H, CH=$CHSO_2$), 6.32 (dt, J 15.1, 1.8 Hz, 1H, CH=$CHSO_2$), 5.59–5.46 (m, 1H, CH_3CH=CH), 5.43–5.28 (m, 1H, CH_3CH=CH), 2.95–2.88 (m, 2H, CH=CHCH_2), 1.67 (d, J 6.1 Hz, 3H, CH_3CH=CH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 146.3, 142.3, 133.4, 130.8, 129.56, 129.1, 127.4, 124.4, 34.0, 17.9; MS m/z (relative intensity) 222 (88%, M^+), 80 (100%, $M^+ - SO_2Ph$), 41 (26%, $M^+ - C_9H_9SO_2$); HRMS. Calcd. for $C_{12}H_{14}SO_2$: 222.0715. Found: 222.0723.

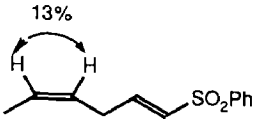


14%

DNOE

(E,Z)-1-Phenylsulfonylhexa-1,4-diene (13). IR (CCl_4) 1635 cm^{-1} (C=C), 1445, 1145 cm^{-1} (SO_2); ^1H NMR (360 MHz, $CDCl_3$) δ 7.90–7.85 (m, 2H, ArH), 7.66–7.26 (m, 3H, ArH), 7.00 (dt, J 15.0, 5.9 Hz, 1H, CH=$CHSO_2$), 6.33 (dt, J

15.0, 1.8 Hz, 1H, CH=C*H*SO_2), 5.70–5.58 (m, 1H, CH_3CH=C*H*), 5.42–5.29 (m, 1H, CH_3CH=CH), 3.00 (dd, *J* 6.7, 6.5 Hz, CH=CHCH_2), 1.59 (d, *J* 7.6 Hz, 3H, CH_3CH=CH); ^{13}C NMR (90 MHz, $CDCl_3$) δ 145.1, 140.6, 133.2, 130.6, 129.2, 128.1, 127.5, 123.5, 28.8, 12.8; MS *m/z* (relative intensity) 222 (77%, M^+), 81 (100%, $M^+ - SO_2Ph$), 41 (36%, $M^+ - C_9H_9SO_2$); HRMS. Calcd. for $C_{12}H_{14}SO_2$: 222.0715. Found: 222.0716.

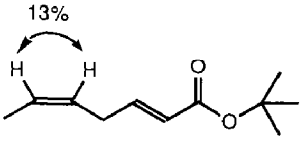


DNOE

*1,1-Dimethylethyl (Z,Z)-hepta-3,5-dienoate (**15**).* IR (CCl_4) 1730 cm^{-1} (C=O), 1600 cm^{-1} (C=C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.43 (dd, *J* 11.3, 11.1 Hz, 1H, CH_3CH=CHC*H*=CH), 6.21 (dd, *J* 11.3, 9.8 Hz, 1H, CH_3CH=C*H*), 5.64–5.58 (m, 2H, CH_3C*H*=CHCH=C*H*), 3.14 (dd, *J* 7.1, 1.6 Hz, 2H, CH=CHCH_2), 1.76 (dd, *J* 6.8, 1.6 Hz, 3H, CH_3CH=CH), 1.45 (s, 9H, $CO_2C(CH_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 170.9, 127.8, 125.7, 123.9, 122.5, 80.6, 34.4, 28.0, 13.2; MS *m/z* (relative intensity) 182 (0.4%, M^+), 57 (100%, $M^+ - C_7H_9O_2$), 41 (10%, $M^+ - C_8H_{13}O_2$); HRMS. Calcd. for $C_{11}H_{18}O_2$: 182.1307. Found: 182.1311.

*1,1-Dimethylethyl (E,Z)-hepta-3,5-dienoate (**16**).* IR (CCl_4) 1730 cm^{-1} (C=O), 1600 cm^{-1} (C=C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.42 (dd, *J* 15.2, 11.0 Hz, 1H, CH_3CH=CHC*H*=CH), 6.03 (dd, *J* 11.0 10.7 Hz, 1H, CH_3CH=C*H*CH=CH), 5.72 (dd, *J* 15.2, 7.4 Hz, 1H, CH_3CH=CHCH=C*H*), 5.49–5.44 (m, 1H, CH_3C*H*=CH), 3.06 (d, *J* 7.4 Hz, 2H, CH=CHC$H_2CO_2C(CH_3)_3$), 1.74 (dd, *J* 7.1, 1.6 Hz, 3H, CH_3CH=CH), 1.45 (s, 9H, $CO_2C(CH_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 171.0, 128.8, 128.4, 125.8, 125.2, 80.6, 39.5, 28.1, 13.3; MS *m/z* (relative intensity) 182 (2%, M^+), 57 (100%, $M^+ - C_7H_9O_2$), 41 (19%, $M^+ - C_8H_{13}O_2$); HRMS. Calcd. for $C_{11}H_{18}O_2$: 182.1307. Found: 182.1306.

*1,1-Dimethylethyl (E,Z)-hepta-2,5-dienoate (**17**).* IR (CCl_4) 1705 cm^{-1} (C=O), 1645 cm^{-1} (C=C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.86 (dt, *J* 15.6, 6.3 Hz, 1H, C*H*=CH$CO_2C(CH_3)_3$), 5.76 (dd, *J* 15.6, 1.8 Hz, 1H, CH=C*H*$CO_2C(CH_3)_3$), 5.64–5.59 (m, 1H, CH_3C*H*=CH), 5.43–5.40 (m, 1H, CH_3CH=C*H*), 2.95–2.90 (m, 2H, CH=CHCH_2), 1.60 (d, *J* 9.8 Hz, 3H, CH_3CH=CH), 1.48 (s, 9H, $CO_2C(CH_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 166.1, 145.7, 126.6, 125.3, 123.0, 80.8, 29.4, 28.1, 12.7; MS *m/z* (relative intensity) 182 (1%, M^+), 57 (100%, $M^+ - C_7H_9O_2$), 41 (18%, $M^+ - C_8H_{13}O_2$); HRMS. Calcd. for $C_{11}H_{18}O_2$: 182.1307. Found: 182.1304.



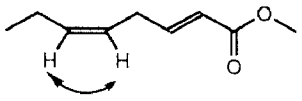
DNOE

*1,1 Dimethylethyl (E)-hepta-4,6-dienoate (**18**).* IR (CCl_4) 1730 cm^{-1} (C=O), 1600 cm^{-1} (C=C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.30 (dt, *J* 17.0, 10.4 Hz, 1H, CH_2=C*H*), 6.08 (dd, *J* 15.2, 10.4 Hz, 1H, CH_2=CHC*H*=CH), 5.69 (dt, *J* 15.2, 6.3 Hz, 1H, CH_2=CHCH=C*H*), 5.11 (d, *J* 17.0 Hz, 1H, H(*H*)C=CH), 4.99 (d, *J* 10.4

Hz, 1H, *H*(H)C=CH), 2.38–2.28 (m, 4H, CH=CHCH_2CH_2), 1.44 (s, 9H, $CO_2C(CH_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 172.3, 136.9, 132.9, 131.7, 115.5, 80.3, 35.0, 28.1, 28.0; MS *m/z* (relative intensity) 182 (2%, M^+), 57 (100%, $M^+ - C_8H_{12}O_2$), 67 (31%, $M^+ - C_6H_{11}O_2$); HRMS. Calcd. for $C_8H_{13}O_2$: 141.0916. Found: 141.0882.

Methyl (E,Z)-4-methylhepta-2,5-dienoate (20). IR(CCl_4) 1715 cm^{-1} (C=O), 1640 cm^{-1} (C=C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.90 (dd, *J* 15.7, 6.4 Hz, 1H, C*H*=CHCO$_2$CH$_3$), 5.77 (dd, *J* 15.7, 1.6 Hz, 1H, CH=C*H*CO$_2$CH$_3$), 5.53 (dq, *J* 10.7, 6.8 Hz, 1H, (CH$_3$)(*H*)CC(H)(CH$_3$)), 5.22 (dd, *J* 10.7, 7.8 Hz, 1H, CH$_3$CH=C*H*), 3.73 (s, 3H, CO$_2$CH_3), 3.35–3.33 (m, 1H, =CHC(*H*)(CH$_3$)), 1.63 (dd, *J* 6.8, 1.8 Hz, 3H, =CHC(H)(CH_3)), 1.13 (d, *J* 6.9 Hz, 3H, CH_3CH=Ch); ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.2, 152.5, 132.0, 124.9, 118.9, 51.3, 33.8, 17.9, 13.0; MS *m/z* (relative intensity) 154 (11%, M^+), 95 (100%, $M^+ - CO_2CH_3$), 41 (43%, $M^+ - C_6H_9O_2$); HRMS. Calcd. for $C_9H_{14}O_2$: 154.0994. Found: 154.0985.

Methyl (E,Z)-octa-2,5-dienoate (21). IR (CCl_4) 1715 cm^{-1} (C=O), 1640 cm^{-1} (C=C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.96 (dt, *J* 15.6, 6.3 Hz, 1H, C*H*=CH-CO$_2$CH$_3$), 5.84 (dt, *J* 15.6, 1.8 Hz, 1H, CH=C*H*CO$_2$CH$_3$), 5.56–5.23 (m, 1H, CH$_3$CH$_2$C*H*=CH), 5.38–5.33 (m, 1H, CH$_3$CH$_2$CH=C*H*), 3.72 (s, 3H, CO$_2$CH_3), 2.96–2.92 (m, 2H, CH_2CH=CH) 2.06–2.02 (m, 2H, CH$_2$CH_2), 0.97 (t, *J* 7.6 Hz, 3H, CH_3CH$_2$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.1, 147.5, 134.5, 123.3, 120.9, 50.4, 29.8, 20.5, 14.0; MS *m/z* (relative intensity) 154 (33%, M^+), 95 (90%, $M^+ - CO_2CH_3$) 79 (100%, $M^+ - C_3H_7O_2$); HRMS. Calcd. for $C_9H_{14}O_2$: 154.0994. Found: 154.0993.

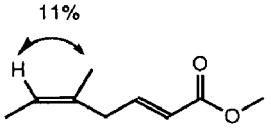


DNOE

1,1-Dimethylethyl (E,Z)-4-methylhepta-2,5-dienoate (22). IR (CCl_4) 1705 cm^{-1} (C=O), 1645 cm^{-1} (C=C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.78 (dd, *J* 15.6, 6.3 Hz, 1H, C*H*=CHCO$_2$C(CH$_3$)$_3$), 5.76 (dd, *J* 15.6, 1.5 Hz, 1H, CH=C*H*CO$_2$C(CH$_3$)$_3$), 5.50 (dq, *J* 10.6, 6.8 Hz, 1H, CH$_3$C*H*=CH), 5.20 (ddd, *J* 10.6, 6.3, 1.7 Hz, 1H, CH$_3$CH=C*H*), 3.31–3.28 (m, 1H, CH=CH C(CH$_3$)*H*), 1.62 (dd, *J* 6.8, 1.7 Hz, 3H, CH_3CH=CH), 1.46 (s, 9H, $CO_2C(CH_3)_3$), 1.10 (d, *J* 6.8 Hz, 3H, CH=CHC(CH_3)); ^{13}C NMR (90 MHz, $CDCl_3$) δ 166.3, 151.1, 132.2, 124.6, 121.0, 80.0, 33.9, 28.1, 19.9, 12.9; MS *m/z* (relative intensity) 180 (58%, $M^+ - CH_4$), 57 (100%, $M^+ - C_8H_{11}O_2$), 41 (46%, $M^+ - C_{10}H_{15}O_2$); HRMS. Calcd for $C_{12}H_{20}O_2$: 196.1464. Found: 196.1454.

1,1-Dimethylethyl (E,Z)-octa-2,5-dienoate (23). IR (CCl_4) 1705 cm^{-1} (C=O), 1645 cm^{-1} (C=C); ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.83 (dt, *J* 15.6, 6.3 Hz, 1H, C*H*=CHCO$_2$C(CH$_3$)$_3$), 5.74 (dt, *J* 15.6, 1.8 Hz, 1H, CH=C*H*CO$_2$C(CH$_3$)$_3$), 5.57 (dt, *J* 10.7, 6.8 Hz, CH$_3$CH$_2$C*H*=CH), 5.33 (dt, *J* 10.7, 5.0 Hz, 1H, CH$_3$CH$_2$-CH=C*H*), 2.90 (dd, *J* 6.3, 5.0 Hz, 2H, CH=CHCH_2), 2.03 (dq, *J* 6.8, 7.3 Hz, 2H, CH$_3$CH_2CH=CH), 1.46 (s, 9H, $CO_2C(CH_3)_3$), 0.96 (t, *J* 7.3 Hz, 3H, CH_3CH$_2$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 166.1, 146.0, 132.2, 123.7, 123.0, 80.0, 29.6, 28.1, 20.4, 14.1; MS *m/z* (relative intensity) 196 (2%, M^+), 57 (100%, $M^+ - C_8H_{11}O_2$), 69 (1%, $M^+ - C_7H_{11}O_2$); HRMS. Calcd. for $C_{12}H_{20}O_2$: 196.1464. Found: 196.1476.

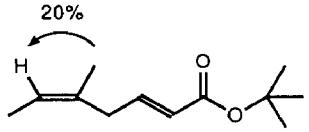
*Methyl (E,Z)-5-methylhepta-2,5-dienoate (**25**).* IR (CCl_4) 1715 cm^{-1} (C=O), 1640 cm^{-1} (C=C); ^1H NMR (360 MHz, $CDCl_3$) δ 6.91 (dt, *J* 15.6, 6.7 Hz, 1H, C*H*-$CHCO_2CH_3$), 5.83 (dt, *J* 15.6, 1.7 Hz, 1H, $CH{=}CHCO_2CH_3$), 5.40–5.33 (m, 1H, $CH_3CH{=}C(CH_3)$), 3.72 (s, 3H, CO_2CH_3), 2.90 (d, *J* 6.7 Hz, 1H, $CH{=}C(CH_3)$-CH_2), 1.73–1.64 (m, 3H, $CH_3CH{=}C(CH_3)$), 1.58–1.55 (m, 3H, $CH{=}C(CH_3)$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.0, 152.7, 146.2, 131.5, 130.0, 51.3, 39.1, 23.3, 13.0; MS *m/z* (relative intensity) 154 (17%, M^+), 95 (100%, $M^+ - CO_2CH_3$), 69 (10%, $M^+ - C_4H_5O_2$); HRMS. Calcd. for $C_9H_{14}O_2$: 154.0994. Found: 154.0974.



DNOE

*Methyl (E)-6-methylhepta-2,5-dienoate (**26**).* IR (CCl_4) 1715 cm^{-1} (C=O), 1640 cm^{-1} (C=C); ^1H NMR (360 MHz, $CDCl_3$) δ 6.95 (dt, *J* 15.6, 6.3 Hz, 1H, C*H*=CH-CO_2CH_3), 5.82 (dt, *J* 15.6, 1.7 Hz, 1H, $CH{=}CHCO_2CH_3$), 5.17–5.12 (m, 1H, $CH_3(CH_3)C{=}CH$), 3.72 (s, 3H, CO_2CH_3), 2.90–2.86 (m, 2H, $CH_3(CH_3)C{=}CH$-CH_2), 1.73 (s, 1H, $CH_3(CH_3)C{=}CH$), 1.61 (s, 3H, $CH_3(CH_3)C{=}CH$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.1, 148.0, 120.5, 118.9, 51.3, 38.1, 30.8, 25.6, 17.6; MS *m/z* (relative intensity) 154 (49%, M^+), 95 (100%, $M^+ - CO_2CH_3$), 69 (14%, $M^+ - C_4H_5O_2$); HRMS. Calcd. for $C_9H_{14}O_2$: 154.0994. Found: 154.0949.

*1,1-Dimethylethyl (E,Z)-5-methylhepta-2,5-dienoate (**27**).* IR (CCl_4) 1705 cm^{-1} (C=O), 1645 cm^{-1} (C=C); ^1H NMR (360 MHz, $CDCl_3$) δ 6.78 (dt, *J* 15.5, 6.6 Hz, 1H, $CH{=}CHCO_2C(CH_3)_3$), 5.72 (dt, *J* 15.5, 1.6 Hz, 1H, $CH{=}CHCO_2C(CH_3)_3$), 5.35–5.31 (m, 1H, $CH_3CH{=}CH$), 2.86 (d, *J* 6.6 Hz, 2H, $CH{=}C(CH_3)CH_2$), 1.67 (d, *J* 2.7 Hz, 3H, $CH_3CH{=}C(CH_3)$), 1.57 (dt, *J* 6.7, 1.4 Hz, 3H, $CH_3CH{=}C(CH_3)$), 1.47 (s, 9H, $CO_2C(CH_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 166.0, 144.8, 132.1, 123.3, 121.4, 80.0, 34.3, 28.1, 23.5, 13.3; MS *m/z* (relative intensity) 196 (1%, M^+), 95 (37%, $M^+ - CO_2C(CH_3)_3$), 57 (100% $M^+ - C_8H_{11}O_2$), 69 (2%, $M^+ - C_7H_{11}O_2$); HRMS. Calcd. for $C_{11}H_{17}O_2$: 181.1229. Found: 181.1213.



DNOE

*1,1-Dimethylethyl (E)-6-methylhepta-2,5-dienoate (**28**).* IR (CCl_4) 1705 cm^{-1} (C=O), 1645 cm^{-1} (C=C); ^1H NMR (360 MHz, $CDCl_3$) δ 6.82 (dt, *J* 15.5, 6.3 Hz, 1H, $CH{=}CHCO_2C(CH_3)_3$), 5.71 (dt, *J* 15.5, 1.8 Hz, 1H, $CH{=}CHCO_2C(CH_3)_3$), 5.15–5.10 (m, 1H, $CH_3(CH_3)C{=}CH$), 2.97 (dd, *J* 7.0, 6.4 Hz, 2H, $(CH_3)_2C{=}CH$-CH_2), 1.72 (s, 3H, $CH_3(CH_3)C{=}CH$), 1.60 (s, 3H, $CH_3(CH_3)C{=}CH$), 1.46 (s, 9H, $CO_2C(CH_3)_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 166.2, 146.4, 134.5, 122.7, 119.3, 80.0, 30.6, 28.1, 25.6, 17.6; MS *m/z* (relative intensity) 196 (1%, M^+), 57 (100%, $M^+ - C_8H_{12}O_2$), 69 (4%, $M^+ - C_7H_{11}O_2$); HRMS. Calcd. for $C_{12}H_{20}O_2$: 196.1464. Found: 196.1467

Acknowledgment

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