Platinum and Palladium Complex-Catalyzed Regioselective Nucleophilic Substitutions with Two Different Nucleophiles at the Central and Terminal Carbon Atoms of the π-Allyl Ligand

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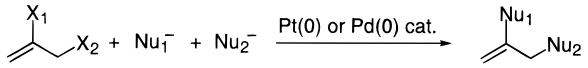
The reaction of 2-chloroallyl acetate with a mixture of sodium diethyl methylmalonate and sodium phenoxide in the presence of a platinum(0) complex as a catalyst gave a product having the carbon nucleophile at the central carbon atom of the π-allyl ligand and the oxygen nucleophile at the terminal carbon atom. The key process of this reaction is the nucleophilic substitution at the central carbon atom of the π-allyl ligand. Further examples of nucleophilic substitution at the central and terminal carbon atoms of a π-allyl ligand were demonstrated for the case of a palladium(0) complex as the catalyst.

Introduction

In the reaction of π-allyl transition metal complexes with nucleophiles, nucleophilic attack is possible at either of two sites, namely the central and terminal carbon atoms of the π-allyl ligand. Nucleophilic attack at the terminal carbon atom of the π-allyl ligand leads to the usual allylation product,[1] while nucleophilic attack at the central carbon atom, although rare, leads to metallacyclobutane formation,[2] cyclopropanation,[3] via reductive elimination from the metallacyclobutane, and nucleophilic substitution[4−7] in the case of π-allyl complexes that contain an appropriate leaving group at the central carbon atom. In the latter case, a π-allyl complex is re-formed after nucleophilic substitution at the central carbon atom and is subjected to further nucleophilic attack at the terminal carbon atom. The fact that certain types of π-allyl complexes can have two different sites that are susceptible to nucleophiles holds considerable promise for the multifunctionalization of allylic compounds. In this context, it would be very interesting and useful if two different nucleophiles could be introduced regioselectively into two different positions, i.e., at both the central and terminal carbon atoms (Scheme 1).

Scheme 1



We recently reported on the nucleophilic substitution at the central carbon atom of a π-allyl ligand.[4] For example, in the presence of a platinum(0) complex, the reaction of 2-chloroallyl acetate with 2 equiv of sodium diethyl methylmalonate gave the doubly alkylated product.[4a] The catalytic reaction with sodium ethyl acetoacetate resulted in the formation of furan derivatives. With this knowledge, efforts to carry out the new reaction shown in Scheme 1 have been made. In this paper, we describe the regioselective nucleophilic substitution at both the central and terminal carbon atoms of a π-allyl ligand by two different nucleophiles.

Results and Discussion

We earlier reported that the platinum(0)-catalyzed reaction of 2-chloroallyl acetate with sodium ethyl

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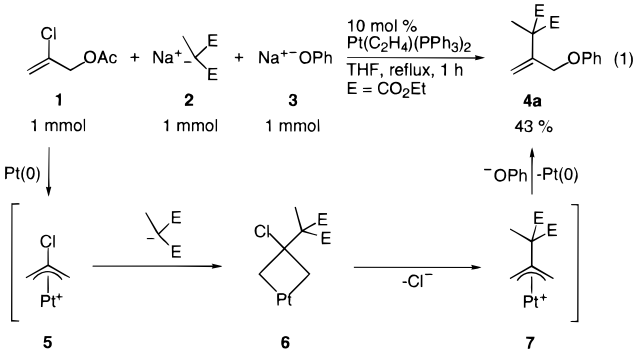
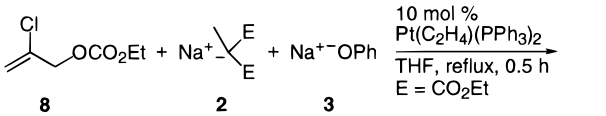
acetoacetate gave furan derivatives.[4] In this reaction, the central carbon atom was substituted by a carbanion and the terminal carbon was substituted by an oxygen anion, although this reaction is intramolecular. Therefore, the use of a combination of a stabilized carbanion and a phenoxide anion, which serve as two different nucleophiles, seems promising in achieving an intermolecular version of this type of reaction. In the presence of $Pt(C_2H_4)(PPh_3)_2$ (0.1 mmol) as catalyst, the reaction of 2-chloroallyl acetate (**1**) (1.0 mmol) with sodium diethyl methylmalonate (**2**) (1.0 mmol) and sodium phenoxide **3** (1.0 mmol) in THF at reflux temperature gave the expected product **4a**. Compound **4a** was alkylated at the central carbon atom and substituted by phenoxide at the terminal and represents one of the four possible products that are possible for this reaction (eq 1). This represents the first example of the introduction of two different groups into the central and terminal carbon atom of a π-allylic ligand.



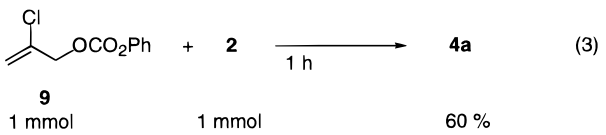
(1)

1 **2** **3** **4a** **5** **6** **7**

The central attack by carbanion **2** on the 2-chloro(π-allyl)Pt(II) complex **5** would give platinacyclobutane **6**. The elimination of a chloride anion from **6** would give 2-substituted (π-allyl)Pt(II) complex **7**. The phenoxide anion then attacks the terminal carbon of the (π-allyl)-Pt(II) complex **7** to give **4a** with regeneration of the initial Pt(0) catalyst. Whether the attack takes place externally (from the opposite face of the Pt metal) or internally (first onto the Pt metal, followed by migration to the carbon from the same side of the metal) is not known at present. The use of 2-chloroallyl carbonate **8** gave a similar result (eq 2). Phenyl cabonate **9**, which can generate a phenoxide anion by decarboxylation after the (π-allyl) complex formation, afforded **4a** in a better yield (60%) (eq 3).



(2)

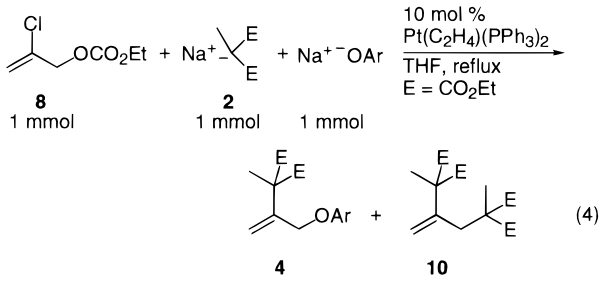


(3)

Several substituted phenoxides were examined in the reaction of 2-chloroallyl carbonate **8** (eq 4), and the results are summarized in Table 1.

Table 1. Platinum-Catalyzed Reactions of 2-Chloroallyl Carbonate with Phenoxide Anions

entry	phenoxide	time (h)	yield (%) of **4**	yield (%) of **10**
1	$C_6H_5O^-$	0.5	**4a** 53	trace
2	p-$MeC_6H_4O^-$	1	**4b** 53	trace
3	p-$MeOC_6H_4O^-$	3	**4c** 46	trace
4	p-$ClC_6H_4O^-$	14	**4d** 20	21
5	p-$CNC_6H_4O^-$	6	**4e** 6	19
6	p-$NO_2C_6H_4O^-$	6	**4f** 0	29
7	o-$MeC_6H_4O^-$	2	**4g** 51	trace



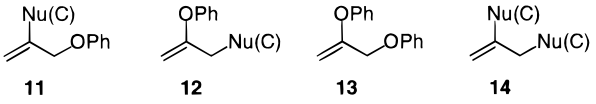
(4)

Phenoxide anions with electron-donating substituents, such as methyl and methoxy groups, gave results that were similar to that for the nonsubstituted phenoxide anion (entries 2 and 3). The chloro-substituted phenoxide gave the doubly alkylated product **10** along with **4d** (entry 4), and the nitro-substituted phenoxide gave only **10** (entry 6). These selectivities (between **4** and **10**) are consistent with the tendency of substituted phenoxide anions to be stabilized. Thus, groups that are strongly electron withdrawing in character stabilize phenoxide anions and diminish their nucleophilicity. In addition, even once formed, **4**, which has an electron-withdrawing group, will easily return to a π-allyl complex, because of the high tendency for such phenoxides to function as a leaving group.

Recently, palladium-promoted nucleophilic substitution at the central carbon atom of a π-allyl ligand has been reported.[5−7] Bäckvall has reported that the site of nucleophilic attack (central or terminal) in the reaction of a 2-chloro(π-allyl) palladium complex with sodium diethyl methylmalonate (**2**) changes with the type of the ligand on the metal.[5] Central attack was observed when bipyridyl or TMEDA was used as the ligand, but terminal attack occurred when phosphine ligands were used. Organ has reported that in the presence of Pd-$(PPh_3)_4$ as catalyst the reaction of 2,3-dibromopropene with sodium phenoxide gave a product that is substituted by two phenoxides, one of which had been introduced as a result of central attack.[7] However, when $Pd_2(dba)_3{\cdot}CHCl_3$ and TMEDA were used, an allylated product by terminal attack, in the usual manner, was observed. It appears that, in the presence of $Pd(PPh_3)_4$, the carbon nucleophile attacks the terminal carbon atom, and the phenoxide anion attacks the central. Inversely, in the presence of Pd−TMEDA, the carbon nucleophile attacks the central carbon atom, and the phenoxide anion attacks the terminal. We concluded that, on the basis of these results, palladium would be able to catalyze regioselective nucleophilic substitution by two different nucleophiles at the central and terminal carbon atoms of a π-allyl ligand.

We initially examined Pd−TMEDA for use as a catalyst. In the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025

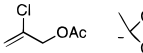
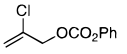
Scheme 2



11 **12** **13** **14**

Nu(C) represents carbon nucleophiles

Table 2. Palladium-Catalyzed Reactions of 2-Chloroallyl Compounds with Carbon Nucleophiles and Phenoxide[d]

entry	allyl substrate	Nucleophiles	time(h)	yields(%) of 11	12	13
1	 **1**	 **15** + $^-$OPh **3**	0.5	22[a]	44[a]	11
2	**1**	 **16** + **3**	1	27[b]	37[b]	19
3	 **9**	**15**	2	25[a]	31[a]	10
4	**9**	**16**	1	30[b] (36)[c]	28[b] (41)[c]	trace

[a] Nu(C) = ethyl methyl acetoacetate. [b] Nu(C) = methyl acetylacetonate. [c] At room temperature. [d] Reactions were performed in the presence of $Pd(PPh_3)_4$ (0.05 mmol) in THF at reflux. Allyl compounds (1.0 mmol), carbon nucleophiles (1.0 mmol), and phenoxide (1.0 mmol) were used in entries 1 and 2. Carbon nucleophiles (1.0 mmol) were used in entries 3 and 4.

mmol) and TMEDA (0.05 mmol), the reaction of 2-chloroallyl acetate (**1**) (1.0 mmol) with a mixture of sodium diethyl methylmalonate (**2**) (1.0 mmol) and sodium phenoxide **3** (1.0 mmol) resulted in almost no reaction. In a subsequent attempt using $Pd(PPh_3)_4$ (0.05 mmol) instead of Pd−TMEDA, the reaction was complicated, but the expected products (**11**−**14** in Scheme 2) appeared to be obtained in the product mixture, though they were not absolutely identified.

Similar reactions using other substrates such as allyl ethyl carbonate **8** and allyl phenyl carbonate **9** with a mixture of **2** and **3** were sluggish. The use of other carbon nucleophiles such as **15** and **16** resulted in the formation of the three products, **11**−**13** (Table 2, entries 1 and 2).

Although the selectivities was low, the formation of **11** or **12** represents the first example of the Pd-catalyzed introduction of two different groups into the central and terminal carbon atoms of a single allylic system. These products were also formed in the reaction of phenyl carbonate **9**, but the selectivity was even lower (Table 2, entries 3 and 4).

We undertook an extensive search for a palladium complex that is capable of catalyzing nucleophilic substitution at the central carbon atom in allylic compounds. When an active methylene compound **17**, which contains no methyl group at the reacting center, was used as a carbon nucleophile, the reaction involving the attack at the central carbon in the allylic moiety took place. In the presence of $Pd(PPh_3)_4$ (0.05 mmol), the reaction of phenyl carbonate **9** (1.0 mmol) with sodium ethyl acetoacetate (**17**) (1.0 mmol) gave a furan derivative **18** (eq 5).

This reaction proceeds via the nucleophilic substitution at the central carbon atom of a π-allyl ligand, followed by enolate oxygen cyclization and exo to endo

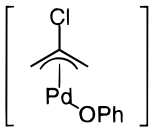
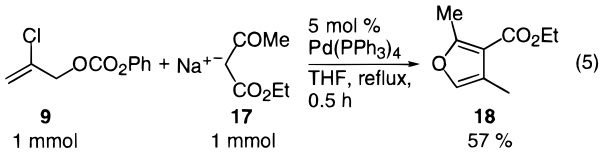
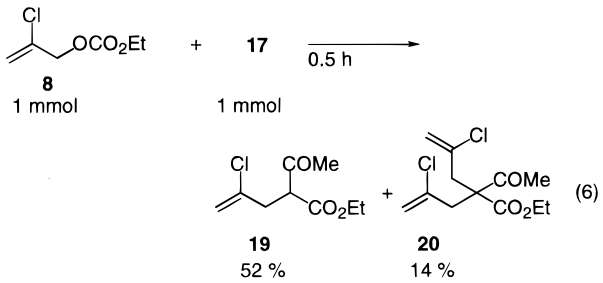


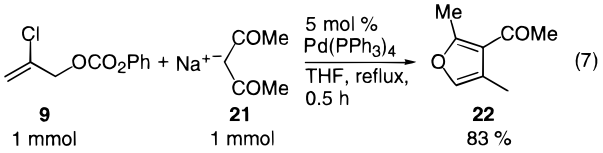
Figure 1.

double-bond isomerization. The reaction is similar to that observed in the case of a platinum catalyst.[4] We initially expected the product that is alkylated at the central carbon atom and substituted by phenoxide at the terminal, but in fact, the furan derivative **18** was obtained. This suggests that enolate oxygen cyclization is faster than the attack of the phenoxide anion. The use of ethyl carbonate **8** instead of phenyl carbonate **9** led to the usual allylation to **19** and a double allylation to **20** (eq 6). These two results indicate that the





phenoxide anion is important, in that it brings about the central attack of the nucleophile, even though it is not incorporated into the product. An intermediate such as a neutral (π-allyl) palladium complex coordinated by phenoxide (Figure 1) may be important, but this issue remains to be elucidated.[8]A similar result was obtained in the case of sodium acetyl acetonate (**21**) (eq 7).



Conclusion

The platinum-catalyzed nucleophilic substitution by two different nucleophiles, one at the central and the other at the terminal carbon atoms of a π-allyl ligand, has clearly been demonstrated. Furthermore, the first example of a palladium(0) complex-catalyzed reaction of a similar type using two different nucleophiles has also been achieved, although the reaction is not highly selective.

Experimental Section

Materials. Protonated nucleophiles diethyl methylmalonate (**2**), ethyl methylacetoacetate (**15**), methyl acetyl acetone (**16**),

(8) In this intermediate, phenoxide shares its electron density with palladium, which becomes electron rich. Therefore, the partial positive charge of the terminal carbon atom of π-allyl ligand is reduced, and nucleophilic attack at the central carbon atom will be dominant.[5]

ethyl acetoacetate (**17**), and acetyl acetone (**21**) were purified by distillation. THF was distilled over Na−benzophenone prior to use. $Pt(C_2H_4)(PPh_3)_2$ was prepared according to published procedures.[9]

Preparation of 2-Chloroallyl Phenyl Carbonate (9). A mixture of 2,3-dichloro-1-propene (11.1 g, 100 mmol) and K_2CO_3 (15.2 g, 110 mmol) in water (100 mL) was stirred at reflux for 12 h. After cooling to room temperature, the mixture was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give a yellow oil. The residue was distilled under atmospheric pressure to give 2-chloro-2-propen-1-ol (8.51 g, 92 mmol, 92% yield, bp 127−129 °C). To a mixture of this alcohol (2.78 g, 30 mmol) and pyridine (30 mL) at 0 °C was added dropwise phenyl chloroformate (4.14 mL, 33 mmol), and the resulting solution was stirred at room temperature for 1 h. After adding 1 N HCl (50 mL) to the reaction mixture, it was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give a yellow oil. The residue was purified by column chromatography on silica gel (eluent: 10:1 hexane/ethyl acetate) to give 2-chloroallyl phenyl carbonate **9** (5.07 g, 23.8 mmol, 79% yield), a colorless liquid. R_f: 0.29 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 4.80 (s, 2H), 5.49 (d, J = 1.9 Hz, 1H), 5.59 (m, 1H), 7.18−7.28 (m, 3H), 7.37−7.43 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 69.7, 115.9, 120.9, 126.2, 129.5, 134.8, 151.0, 153.0. IR (neat): 1768 s, 1239 bs, 1210 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 212 (M^+, 4), 133 (100), 105 (31), 77 (34), 75 (53). Found: C 56.66; H 4.28; Cl 16.51. Anal. Calcd for $C_{10}H_9O_3Cl$: C 56.49; H 4.27; O 22.57; Cl 16.67.

Typical Procedure. Ethyl acetoacetate (130 mg, 1.0 mmol) and phenol (94 mg, 1.0 mmol) were added to a suspension of NaH (60 wt % in mineral oil, 80 mg, 2.0 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature for 30 min, at which time $Pt(C_2H_4)(PPh_3)_2$ (74.7 mg, 0.1 mmol) was added. 2-Chloroallyl acetate (**1**) (134.5 mg, 1.0 mmol) was then added, and the flask was immersed in an oil bath at 80 °C. The reaction was monitored by analytical GC, and after 1 h the substrate had been completely consumed. After the reaction mixture was cooled to room temperature, water (10 mL) was added. The resulting solution was extracted with diethyl ether, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give a yellow oil. The residue was subjected to column chromatography on silica gel (eluent: 10:1 hexane/ethyl acetate) to give diethyl 2-methyl-2-[2′-(3′-phenoxy)-1′-propenyl] malonate (**4a**) (132 mg, 43% yield) as a colorless liquid. R_f: 0.17 (15:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 7.2 Hz, 6H), 1.70 (s, 3H), 4.20 (m, 4H), 4.69 (s, 2H), 5.30 (s, 1H), 5.53 (t, J = 1.4 Hz, 1H), 6.91−6.96 (m, 3H), 7.24−7.30 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.9, 20.8, 58.1, 61.7, 68.7, 114.7, 116.2, 120.9, 129.4, 141.7, 158.5, 170.7. IR (neat): 2988 m, 1734 bs cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 306 (M^+, 1.8), 213 (21), 139 (26), 113 (30), 111 (100). Found: C 66.45; H 7.17. Anal. Calcd for $C_{17}H_{22}O_5$: C 66.65; H 7.24; O 26.11.

Diethyl 2-[2′-(3′-*p*-Tolyloxy)-1′-propenyl]-2-methyl Malonate (4b): a colorless liquid. R_f: 0.20 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 7.0 Hz, 6H), 1.69 (s, 3H), 2.28 (s, 3H), 4.20 (m, 4H), 4.65 (s, 2H), 5.28 (s, 1H), 5.51 (s, 1H), 6.83 (m, 2H), 7.06 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.9, 20.4, 20.8, 58.2, 61.7, 68.9, 114.6, 116.0, 129.8, 130.1, 141.9, 156.5, 170.7. IR (neat): 2988 m, 1733 s, 1514 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 320 (M^+, 4.6), 213 (40), 139 (34), 113 (41), 111 (100). HRMS Found: 320.1625. Calcd for $C_{18}H_{24}O_5$: 320.1624.

Diethyl 2-[2′-(3′-*p*-Methoxyphenoxy)-1′-propenyl]-2-methyl Malonate (4c): a colorless liquid. R_f: 0.09 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 7.0 Hz, 6H), 1.69 (s, 3H), 3.76 (s, 3H), 4.20 (m, 4H), 4.63 (s, 2H), 5.28 (s, 1H), 5.51 (t, J = 1.2 Hz, 1H), 6.79−6.89 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 13.9, 20.8, 55.7, 58.1, 61.7, 69.5, 114.5, 115.7, 116.0, 141.9, 152.7, 153.9, 170.7. IR (neat): 2990 m, 1732 s, 1512 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 337 (M^+ + 1, 0.5), 336 (M^+, 3.1), 213 (44), 139 (30), 113 (33), 111 (100). Found: C 64.14; H 7.18. Anal. Calcd for $C_{18}H_{24}O_6$: C64.27; H 7.19; O 23.54.

Diethyl 2-[2′-(3′-*p*-Chlorophenoxy)-1′-propenyl]-2-methyl Malonate (4d): a colorless liquid. R_f: 0.20 (20:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 7.0 Hz, 6H), 1.69 (s, 3H), 4.20 (m, 4H), 4.66 (s, 2H), 5.30 (s, 1H), 5.49 (s, 1H), 6.87 (m, 2H), 7.22 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.9, 20.7, 58.0, 61.7, 69.0, 116.0, 116.3, 125.7, 129.2, 141.3, 157.1, 170.6. IR (neat): 2988 m, 1732 s, 1107 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 340 (M^+, 1.4), 213 (31), 139 (26), 113 (34), 111 (100). Found: C 59.95; H 6.15; Cl 10.46. Anal. Calcd for $C_{17}H_{21}O_5Cl$: C 59.91; H 6.21; O 23.47; Cl 10.40.

Diethyl 2-[2′-(3′-*p*-Cyanophenoxy)-1′-propenyl]-2-methyl Malonate (4e): a colorless liquid. R_f: 0.13 (5:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, J = 7.0 Hz, 6H), 1.70 (s, 3H), 4.21 (m, 4H), 4.76 (s, 2H), 5.33 (s, 1H), 5.47 (s, 1H), 7.02 (m, 2H), 7.58 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.9, 20.7, 57.9, 61.9, 68.9, 104.2, 115.5, 116.6, 119.2, 133.9, 140.5, 161.7, 170.5. IR (neat): 2986 w, 1732 s, 1607 s, 1511 s, 1108 bs cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 331 (M^+, 2.1), 213 (37), 139 (34), 113 (39), 111 (100). Found: C 64.94; H 6.28; N 4.16. Anal. Calcd for $C_{18}H_{21}O_5N$: C 65.24; H 6.39; N 4.23; O 24.14.

Diethyl 2-Methyl-2-[2′-(3′-*o*-tolyloxy)-1′-propenyl] Malonate (4f): a colorless liquid. R_f: 0.07 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 7.2 Hz, 6H), 1.71 (s, 3H), 2.23 (s, 3H), 4.20 (m, 4H), 4.68 (s, 2H), 5.28 (s, 1H), 5.55 (s, 1H), 6.84−6.88 (m, 2H), 7.12−7.16 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.9, 16.3, 20.8, 58.2, 61.7, 68.4, 111.1, 115.8, 120.4, 126.7, 130.6, 141.8, 156.6, 170.7. IR (neat): 2986 m, 1733 s, 1107 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 321 (M^+ + 1, 1.0), 320 (M^+, 4.7), 213 (100), 139 (45), 113 (47), 115 (90). Found: C 67.29; H 7.38. Anal. Calcd for $C_{18}H_{24}O_5$: C 67.48; H 7.55; O 24.97.

Ethyl 2-Acetyl-2-methyl-3-phenoxymethyl But-3-enoate (11a): a colorless liquid. R_f: 0.14 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, J = 7.0 Hz, 3H), 1.61 (s, 3H), 2.29 (s, 3H), 4.19 (q, J = 7.0 Hz, 2H), 4.61 (s, 2H), 5.25 (s, 1H), 5.55 (s, 1H), 6.87−6.98 (m, 3H), 7.24−7.30 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.9, 19.8, 27.0, 61.7, 63.9, 69.0, 114.6, 117.3, 121.1, 129.4, 142.6, 158.3, 171.4, 204.5. IR (neat): 2986 w, 1716 s, 1499 s, 1241 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 276 (M^+, 1.4), 183 (100), 113 (70), 112 (64), 110 (86), 109 (80). Found: C 69.37; H 7.19. Anal. Calcd for $C_{16}H_{20}O_4$: C 69.55; H 7.30; O 23.16.

3-Methyl-3-[2′-(3′-phenoxymethyl)-1′-propenyl) Pentane-2,4-dione (11b): a colorless liquid. R_f: 0.08 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.59 (s, 3H), 2.24 (s, 6H), 4.53 (s, 2H), 5.22 (s, 1H), 5.60 (s, 1H), 6.85−6.88 (m, 2H), 6.93−6.98 (m, 1H), 7.24−7.30 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 18.5, 27.3, 69.1, 69.5, 114.5, 118.3, 121.3, 129.5, 142.9, 158.1, 207.0. IR (neat): 2998 w, 1719 s, 1703 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 246 (M^+, 4.0), 153 (100), 111 (94), 110 (43), 109 (75), 95 (83). Found: C 72.86; H 7.23. Anal. Calcd for $C_{15}H_{18}O_3$: C 73.15; H 7.37; O 19.49.

Ethyl 2-Acetyl-2-methyl-4-phenoxy Pent-4-enoate (12a): a colorless liquid. R_f: 0.21 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.23 (t, J = 7.1 Hz, 3H), 1.47 (s, 3H), 2.21 (s, 3H), 2.88 (m, 2H), 3.91 (d, J = 2.0 Hz, 1H), 4.12 (d, J = 2.0 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 6.97−7.00 (m, 2H), 7.10−7.16 (m, 1H), 7.30−7.36 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 14.0, 18.7, 26.0, 39.3, 58.5, 61.5, 90.9, 121.3, 124.5, 129.6, 154.5, 159.2, 172.4, 204.5. IR (neat): 2998 w, 1716 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 276 (M^+, 5), 233 (30), 159 (53), 111 (100), 109 (65). Found: C 69.48; H 7.32. Anal. Calcd for $C_{16}H_{20}O_4$: C 69.55; H 7.30; O 23.16.

3-Methyl-3-[1′-(2′-phenoxy)-2′-propenyl] Pentane-2,4-

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dione (12b): a colorless liquid. R_f: 0.13 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.46 (s, 3H), 2.18 (s, 6H), 2.91 (s, 2H), 3.90 (d, J = 2.0 Hz, 1H), 4.11 (d, J = 2.0 Hz, 1H), 6.93−6.97 (m, 2H), 7.11−7.17 (m, 1H), 7.30−7.36 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 17.8, 26.6, 39.0, 65.8, 90.7, 121.3, 124.7, 129.6, 154.3, 159.3, 206.2. IR (neat): 2986 w, 1701 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 246 (M^+, 2.4), 153 (10), 111 (75), 110 (100), 109 (60). Found: C 73.04; H 7.52. Anal. Calcd for $C_{15}H_{18}O_3$: C 73.15; H 7.37; O 19.49.

Ethyl 2-Acetyl-4-chloro Pent-4-enoate (19): a colorless liquid. R_f: 0.15 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.28 (t, J = 7.1 Hz, 3H), 2.29 (s, 3H), 2.89 (m, 2H), 3.90 (t, J = 7.3 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 5.23 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 14.0, 29.7, 37.7, 57.1, 61.7, 115.1, 138.6, 168.4, 201.4. IR (neat): 1742 bs, 1642 s, 1362 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 204 (M^+, 4.7), 169 (100), 134 (43), 133 (41), 123 (49). Found: C 52.64; H 6.18; Cl 17.33. Anal. Calcd for $C_9H_{13}O_3Cl$: C 52.82; H 6.40; O 23.45; Cl 17.32.

Ethyl 2-Acetyl-4-chloro-2-[1′-(2′-chloro-2′-propenyl)] Pent-4-enoate (20): a colorless liquid. R_f: 0.17 (10:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.28 (t, J = 7.1 Hz, 3H), 2.25 (s, 3H), 3.17 (d, J = 2.4 Hz, 4H), 4.22 (q, J = 7.1 Hz, 2H), 5.27 (s, 2H), 5.34 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.8, 26.7, 40.3, 61.5, 62.2, 117.8, 137.1, 170.3, 202.3. IR (neat): 1720 bs, 1634 s, 1360 s cm^{-1}. MS (70 eV): *m*/*z* (relative intensity, %) 278 (M^+, 1.5), 169 (39), 137 (48), 129 (51), 91 (100). Found: C 51.73; H 5.54; Cl 25.27. Anal. Calcd for $C_{12}H_{16}O_3Cl_2$: C 51.63; H 5.78; O 17.19; Cl 25.40.

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