Allylic Carbonates. Efficient Allylating Agents of Carbonucleophiles in Palladium-Catalyzed Reactions under Neutral Conditions

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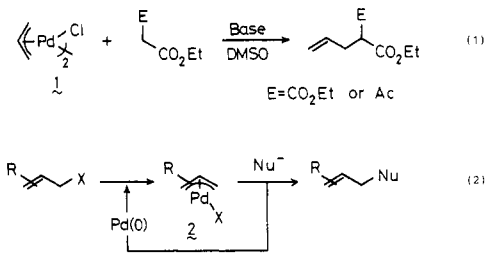
Allylation of β-keto esters or malonates was carried out in good yields under neutral conditions by using allylic carbonates in the presence of palladium–phosphine catalyst. Although simple ketones, esters, nitriles, and sulfones hardly react with allylic carbonates, α-alkenyl or α-aryl ketones, esters, nitriles, and sulfones were also allylated by using palladium–bis(diphenylphosphino)ethane catalyst under neutral conditions.

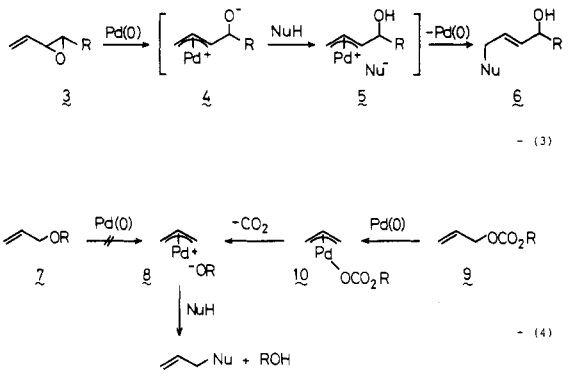
We have reported the reaction of (π-allyl)palladium chloride (**1**) with carbonucleophiles such as malonates, acetoacetates, and enamines as a new method for carbon–carbon bond formation[1] (Scheme I, eq 1). Later, in situ formation of (π-allyl)palladium complexes **2** as intermediates from various allylic compounds and Pd(0) complexes and subsequent reaction with nucleophiles have been discovered[2,3] (eq 2). Since then the catalytic allylation of nucleophiles has been studied extensively as a useful method for carbon–carbon bond formation.[4]

A number of allylic compounds such as allylic esters, ethers, alcohols, phosphates,[5] amines,[3] ammonium salts,[6] sulfones,[7] and nitro compounds[8] are used in the palladium-catalyzed allylation. Among these, allylic acetates are most widely used, giving allylated products in high yields. However, bases must be added to carry out the reaction smoothly with allyl acetates in order to generate carbanions and neutralize acetic acid formed by the reaction. Usually a stoichiometric amount of NaH is added. We have been interested in carrying out the palladium-catalyzed allylation under very mild conditions, particularly under neutral conditions without attacking base-sensitive functional groups present in the same molecule. As one example of neutral allylation, we have found that 1,3-diene monoepoxides react with nucleophiles under neutral conditions[9,10] (Scheme II, eq 3). By the oxidative addition of diene monoepoxides **3** to Pd(0), alkoxide is generated, which acts as a base and abstracts protons from the nucleophiles, and hence the reaction proceeds without addition of bases. This result suggested us that allylation of carbonuclephiles under neutral conditions may be possible with allyl alkyl ethers **7**, since alkoxides **8** are formed by oxidative addition, but the reaction of allyl alkyl ethers **7** with Pd(0) complexes is extremely slow. Then we have speculated that allyl alkyl carbonates **9** react with Pd(0) complex easily and undergo facile decarboxylation to form (π-allyl)palladium alkoxides **8**.[11] Thus we have found that the allylation of nucleophiles can be carried out under neutral conditions as expected by using allylic carbonates as the

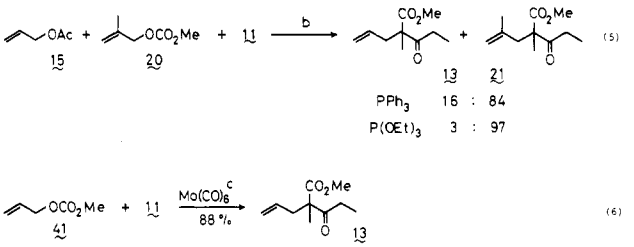
Scheme I



Scheme II



Scheme III[a]



[a] (a) $Pd_2(dba)_3 \cdot CHCl_3$–PPh_3, THF, room temperature 2 h; (b) $Pd_2(dba)_3 \cdot CHCl_3$–ligand, THF, room temperature 20 min; (c) $Mo(CO)_6$, toluene, reflux, 14 h.

(1) (a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, 4387–4388. (b) Tsuji, J.; Takahashi, H.; Morikawa, M. *Kogyo Kagaku Zasshi* **1966**, *69*, 920–924.

(2) Takahashi, K.; Miyake, A.; Hata, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230–236; *J. Chem. Soc., Chem. Commun.* **1970**, 1392–1393.

(3) Atkins, K. E.; Walker, W. E.; Manyik, R. M. *Tetrahedron Lett.* **1970**, 3821–3824.

(4) For reviews, see: (a) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: Berlin, 1981. (b) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615–2649. (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385–393.

(5) Tanigawa, Y.; Nishimura, K.; Kawasaki, A.; Murahashi, S. *Tetrahedron Lett.* **1982**, *23*, 5549–5552.

(6) Hirao, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1982**, *236*, 409–414.

(7) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979–5981.

(8) (a) Tamura, R.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 3727–3729. (b) Ono, N.; Hamamoto, I.; Kato, A. *J. Chem. Soc., Chem. Commun.* **1982**, 821–822.

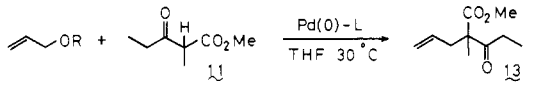
(9) Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575–2578.

(10) (a) Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969–5972. (b) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6112–6114; **1983**, *105*, 5940–5942.

(11) Guibe, F.; Saint M'Leux, Y. *Tetrahedron Lett.* **1981**, *22*, 3591–3594.

0022-3263/85/1950-1523$01.50/0

Table I. Palladium-Catalyzed Allylation of 2-Methyl-3-oxopentanoate[a]



11 13

run	allylic compound	base	ligand	time	yield,[b] %
1	$(CH_2{=}CHCH_2O)CO$ (12)		PPh_3	10 min	98
2[c]	12		PPh_3	30 min	90
3[d]	12		PPh_3	2 h	87
4	12		$P(OEt)_3$	3.5 h	94
5	12		#a	5 h	92
6[e]	12		$P(OPh)_3$	23 h	19
7	$CH_2{=}CHCH_2OCON(i\text{-}Pr)_2$ (14)		PPh_3	10 min	100
8	$CH_2{=}CHCH_2OAc$ (15)		PPh_3	22 h	24
9	15	NaH	PPh_3	30 min	95
10	15		$P(OEt)_3$	24 h	5
11	15	NaH	$P(OEt)_3$	7 h	95
12	$CH_2{=}CHCH_2OPh$ (16)		PPh_3	19 h	0
13[f]	16		PPh_3	7.5 h	62
14	16	NaH	PPh_3	4 h	5
15	$CH_2{=}CHCH_2OPO(OEt)_2$ (17)		PPh_3	24 h	6
16	17	NaH	PPh_3	1.5 h	96
17[f]	$CH_2{=}CHCH_2OH$ (18)		PPh_3	15 h	8
18[f]	$(CH_2{=}CHCH_2)_2O$ (19)		PPh_3	22 h	4

[a] See general procedure A or B in Experimental Section. [b] GLC analysis. [c] Reaction at 0 °C. [d] Reaction at −78 °C. [e] Reaction at 50 °C. [f] Reaction at 65 °C.

allylating agent[12] (eq 4). A part of studies on neutral allylation has been published as a communication,[13] and details of the related studies are presented in this paper.

Results

1. Allylation of β-Keto Esters and Malonates. At first allylation of methyl 2-methyl-3-oxopentanoate (11) with various allylic compounds was carried out in order to compare the reactivity of allylic compounds using palladium complexes combined with PPh_3 as the catalyst. As shown in Table I, reaction of diallyl carbonate (12) proceeded rapidly in 10 min without addition of a base at room temperature to give the allylated product 13 in nearly quantitative yield. The allylation of 11 with the carbonate 12 proceeded even at −78 °C. Allyl diisopropylcarbamate (14), which generates amide anion after decarboxylation, is similarly reactive and gave a good result. On the other hand, no reaction took place with allyl phenyl ether (16) at room temperature under neutral conditions, but the product 13 was obtained in 62% yield by the reaction at 65 °C for 7.5 h.[14] Allyl acetate (15) and allyl diethyl phosphate (17) showed poor reactivity in the absence of a base, but satisfactory results were obtained by the addition of a stoichiometric amount of NaH. Almost no reaction took place with allyl alcohol (18) and diallyl ether (19).

Reactivities of allylic carbonates and allylic acetates were compared by using phosphites as ligand which are less effective than PPh_3. When triethyl phosphite was used instead of PPh_3, allyl acetate (15) scarcely reacted without a base (Scheme III). On the other hand, the diallyl carbonate (12) reacted smoothly. Triphenyl phosphite gave a poor result even when the carbonate 12 was used. These results show that the higher the basicity of the ligand of palladium catalyst, the higher the catalytic reactivity. Big differences of reactivity between allyl carbonates and acetates under neutral conditions make the following chemoselective reaction possible. By the reaction of (*E*)- and (*Z*)-4-acetoxy-2-butenyl methyl carbonate (34 and 36) with the β-keto ester 11, only the allylic carbonate moiety reacted chemoselectivity to give 35 in 77% and 72% yields, respectively, and the allylic acetate moiety remained intact. (Table II, entries 8 and 9).

Also the competitive reaction of allyl acetate (15) and more crowded methallyl methyl carbonate (20) with the β-keto ester 11 was carried out. Reaction of a 1:1 mixture of 15 and 20 with the β-keto ester 11 using PPh_3 at room temperature proceeded chemoselectively to give 21 and 13 in a ratio of 84:16. Chemoselectivity was raised to 97:3 when triethyl phosphite was used as the ligand.

Recently, the allylation of carbonucleophiles using allylic acetates catalyzed by $Mo(CO)_6$ has been reported.[15] Allylation of 11 was also carried out by using allyl methyl carbonate (41) with $Mo(CO)_6$ without addition of a base. But larger amounts of $Mo(CO)_6$ (10 mol %), higher reaction temperature (110 °C), and a longer reaction time (14 h) were necessary to achieve similar yields (88%).[16]

Reactions of various allylic carbonates and active methylene compounds were carried out to give the corresponding allylated compounds. As shown in Table II, the reaction proceeded smoothly without affecting carbonyl and nitrile groups. Olefin isomerization was observed in the reaction of allylic carbonates 31 and 36. (*Z*)-Olefin 36 was completely isomerized to the *E* form. The reaction of geranyl carbonate 28 (*E*/*Z* = 99/1) with methyl acetoacetate gave geranylacetone (29) with almost complete retention of configuration (*E*/*Z* = 92/8) after hydrolysis and decarboxylation. On the contrary, reaction of neryl carbonate 31 (*E*/*Z* 3/97) and methyl acetoacetate gave a 52:48 mixture of *E*/*Z*. The reaction of carbonate 32 derived from cyanohydrin of methacrolein was regioselective, and α,β-unsaturated nitriles 33 were obtained as a 4:1 mixture of *E*/*Z* stereoisomers.[17]

Allylation of Less Stabilized Carbonucleophiles. Carbonucleophiles commonly used for the palladium-catalyzed allylation with allyl acetates are soft nucleophiles with two electron-withdrawing groups. Malonates and β-keto esters are typical. Nitroalkanes are exceptional compounds which are allylated easily.[18] We wanted to broaden the scope of the neutral allylation with allyl carbonates and attempted allylation of some carbonucleophiles which have one electron-withdrawing group. We found that protected mandelonitrile can be allylated with allyl carbonates. The nitrile 39 is less reactive than malonates or β-keto esters, and hence the reaction was carried out in boiling THF by using dppe as the ligand, which shows higher catalytic activity than PPh_3. The results are shown in Table III. All allyl alkyl carbonates (12, 41–44) showed similar reactivity, but almost no reaction took place with allyl phenyl carbonate (45), showing that phenoxide anion is not a good proton abstractor of 39.

(12) As one precedented example of palladium-catalyzed allylation using allylic carbonates, allylation of a malonate anion using a cyclic carbonate has been mentioned. Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7550–7559.

(13) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, *23*, 4809–4812.

(14) Fiaud, J. C.; Hibon De Gournay, A.; Larcheveque, M.; Kagan, H. B. *J. Organomet. Chem.* **1978**, *154*, 175–185.

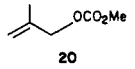
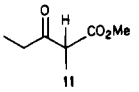
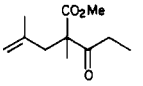
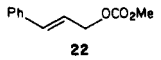
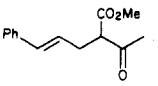
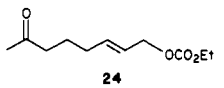
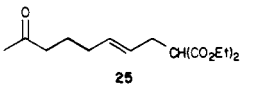
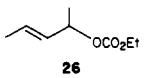
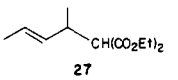
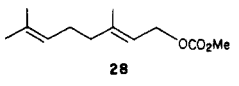
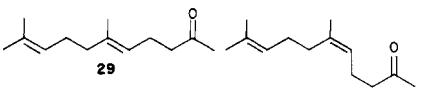
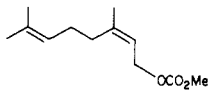
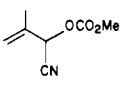
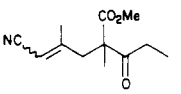
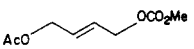
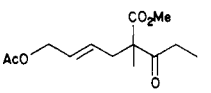
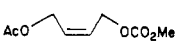
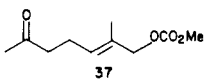
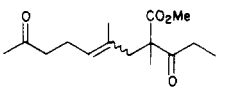
(15) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543–5545; **1983**, *105*, 3343–3344. A similar nucleophilic reaction using allylic carbonate or acetate catalyzed by tungsten compounds has been reported. Trost, B. M.; Hung, M. H. *J. Am. Chem. Soc.* **1983**, *105*, 7757–7759.

(16) When diallyl carbonate (12) (2 equiv of 11) was used, ester exchange reaction took place and allyl 2-methyl-2-allyl-3-oxopentanoate (50% GLC analysis) was obtained with the methyl ester 13.

(17) Tsuji, J.; Ueno, H.; Kobayashi, Y.; Okumoto, H. *Tetrahedron Lett.* **1981**, *22*, 2573–2574.

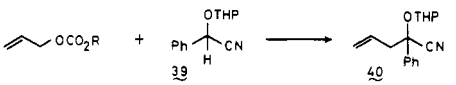
(18) Wade, P. A.; Morrow, S. D.; Hardinger, S. A. *J. Org. Chem.* **1982**, *47*, 365–367.

Table II. Reactions of Allylic Carbonates with β-Keto Esters and Malonates[a]

run	allylic carbonate	nucleophile	ligand	temp, °C	time, h	product	yield,[b] %
1	 20	 11	PPh_3	30	0.2	 21	92
2	 22	$CH_3COCH_2CO_2Me$	PPh_3	25	1	 23	90
3	 24	$CH_2(CO_2Et)_2$	dppe	30	0.5	 25	91
4	 26	$CH_2(CO_2Et)_2$	PPh_3	30	2	 27	86
5	 28	$CH_3COCH_2CO_2Me$	dppe	50	3	 29 30 (92:8)	74[c]
6	 31	$CH_3COCH_2CO_2Me$	dppe	50	3	**29 + 30** (52:48)	54[c]
7	 32	11	PPh_3	65	5	 33	93[d]
8	 34	11	PPh_3	65	2	 35	77
9	 36	11	PPh_3	25	2	**35**	72
10	 37	11	dppe	65	2	 38	99[e]

[a] General procedure C. [b] Isolated yield. [c] After decarboxylation. [d] E/Z = 4/1. [e] E,Z mixture.

Table III. Palladium-Catalyzed Allylation of 2-[(2-Tetrahydropyanyl)oxy]-2-phenylacetonitrile (39) with Various Allyl Carbonates[a]

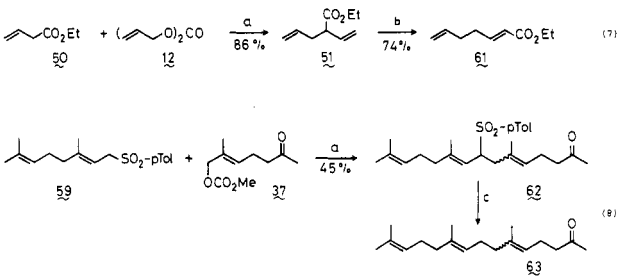

39 40

run	allyl carbonate	solvent	temp, °C	time, h	yield, %
1	CH_2=$CHCH_2OCO_2Me$ (**41**)	THF	65	1	75
2	CH_2=$CHCH_2OCO$-*n*-Bu (**42**)	THF	65	1	70
3	CH_2=$CHCH_2OCO_2$-*i*-Pr (**43**)	THF	65	1	51
4	CH_2=$CHCH_2OCO_2$-*t*-Bu (**44**)	THF	65	1	78
5	CH_2=$CHCH_2OCO_2Ph$ (**45**)	THF	65	1	trace
6	$(CH_2$=$CHCH_2O)_2CO$ (**12**)	THF	65	1	65
7[b]	**12**	THF	65	1	88
8	**12**	PhH	80	2	16
9	**12**	DMF	25	2	60

[a] See General procedure D in Experimental Section. PPh_3 was used as a ligand. [b] Dppe (0.2 mmol) was used as a ligand instead of PPh_3.

Then the possibility of allylation of ketones, nitriles, estes, and sulfones with allyl carbonates was examined in boiling THF with dppe as the ligand, and the results are shown in Table IV. Esters, ketones, nitriles, sulfones, and protected cyanohydrins were allylated in satisfactory yields when the phenyl or vinyl group is present at the α-position.[19] On the other hand, no allylation was possible with simple ketones, esters, and cyanohydrins under the same conditions. Allylation of β,γ-unsaturated esters, nitriles, ketones, and sulfones offers interesting synthetic application, because it gives 1,5-dienes with functional group at C-3 position. These 1,5-dienes undergo facile [3.3] sigmatropic rearrangement to give 1-substituted 1,5-dienes.[20] For example, ethyl 2-vinyl-4-pentenoate (**51**) obtained by the allylation of ethyl 3-butenoate (**50**) was

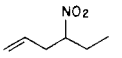
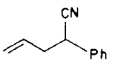
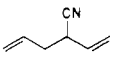
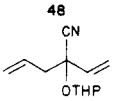
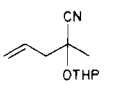
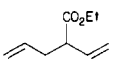
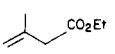
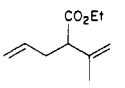
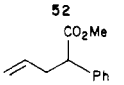
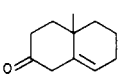
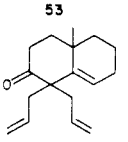
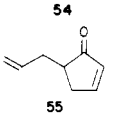
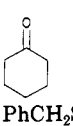
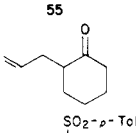
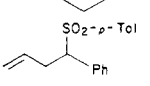
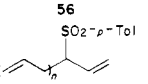
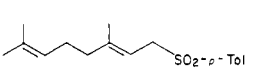
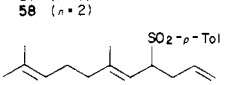
Scheme IV[a]


50 12 51 61 59 37 62 63

[a] (a) $Pd_2(dba)_3 \cdot CHCl_3$-dppe, THF, 65 °C; (b) 160 °C; (c) Na(Hg), Na_2HPO_4, MeOH.

(19) A stoichiometric nucleophilic reaction of allylic sulfones with (π-allyl)palladium complexes has been reported. Manchand, P. S.; Wong, H. S.; Blount, J. F. *J. Org. Chem.* **1978**, *43*, 4769–4774.
(20) Rhoads, S. J.; Raulins, N. R. *Org. React. (N.Y.)* **1975**, *22*, 1–252.

Table IV. Palladium-Catalyzed Allylation of Nitro, Cyano, Sulfonyl, and Carbonyl Compounds with Diallyl Carbonate[a]

run	nucleophile	product	yield,[b] %
1[c]	$CH_3CH_2CH_2NO_2$	 46	76[d]
2	$PhCH_2CN$	 47	91
3	$CH_2{=}CHCH_2CN$	 48	73
4		 49	66
5			0
6	$CH_2{=}CHCH_2CO_2Et$	 51	86
7		 52	31
8	$PhCH_2CO_2Me$	 53	91
9		 54	70
10		 55	29
11			trace
12	$PhCH_2SO_2$-*p*-Tol	 56	92
13	$CH_2{=}CHCH_2SO_2$-*p*-Tol	 57 (n = 1) 58 (n = 2)	**57**, 57; **58**, 12
14	 59	 60	72

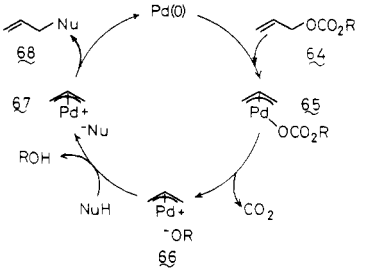
[a] Procedure D in Experimental Section. [b] Isolated yield. [c] Nitro compound (4 mmol) and diallyl carbonate (1 mmol) were used. [d] Based on diallyl carbonate.

converted to ethyl 2,6-heptadienoate (**61**) in 74% yield (Scheme IV). Also, these allylations of allylic compounds offer a useful preparative mehtod of unsymmetrical 1,5-dienes for terpene synthesis. For example, the sulfone **62** was obtained from geranyl sulfone **59** and the carbonate **37** in 45% yield. Desulfonylation of **62** with Na–Hg gave farnesyl acetone as a 5:1 mixture of E/Z isomers.

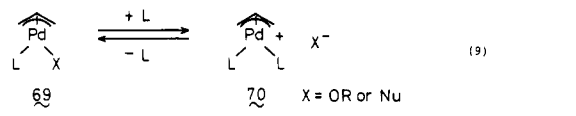
Discussion

The reaction of carbonucleophiles with allyl carbonates without addition of bases can be explained in the following mechanism (Scheme V). Oxidative addition of Pd(0)–phosphine complex to allylic carbonates **64** gives (π-allyl)palladium carbonates **65**. The carbonate anion of **65** undergoes decarboxylation to give the (π-allyl)palladium alkoxide **66**. The alkoxide anion generated in situ picks up the active hydrogen of nucleophiles to produce carbanion **67**. Nucleophilic attack of carbanion on (π-al-

Scheme V

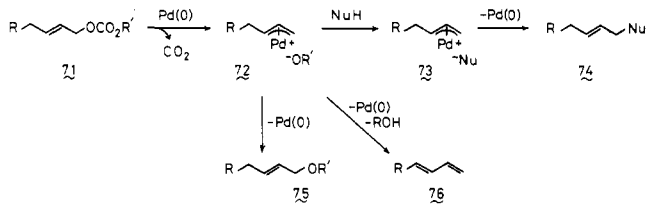


Scheme VI



69 70 X = OR or Nu

Scheme VII



71 72 73 74 75 76

lyl)palladium gives the allylated compound **68**, and Pd(0)–phosphine complex is regenerated.

Carbonucleophiles mentioned in this paper are classified into three groups, reactive, less reactive, and unreactive nucleophiles, from their reactivity with allylic carbonates. Malonates and β-keto esters are the reactive nucleophiles which react easily with diallyl carbonate at room temperature, using Pd(0)–PPh_3 catalyst. β,γ-Unsaturated ketones, estes, nitriles, and sulfones are less reactive nucleophiles, which do not react at room temperature with Pd(0)–PPh_3 catalyst but react smoothly in refluxing THF with Pd(0)–dppe catalyst. Simple ketones, esters, nitriles, and sulfones are unreactive. Even in boiling THF with the Pd(0)–dppe catalyst, no allylation takes place. Considering pK_a values (pK_a = 16–18) of conjugated acids of alkoxides generated by decarboxylation of carbonate anion, concentration of anion of these unreactive substrates (pK_a of conjugated acid is higher than 20) is not enough to undergo the allylation.

In the reaction of the reactive nucleophiles **11** with diallyl carbonate (**12**), the rate of allylation decreased when weakly basic ligands were used. This indicates that in the reaction with reactive nucleophiles oxidative addition of Pd(0) to allylic carbonates (**64** → **65**) is rate determining, since abstraction of active hydrogen (**66** → **67**) and nucleophilic attack of stabilized carbanion to (π-allyl)palladium complex (**67** → **68**) is very fast. But in the reaction with less reactive nucleophiles, the rate of the reaction is determined by the nucleophilic attack to the (π-allyl)palladium complex (**67** → **68**). For the reaction with less reactive nucleophiles, the bidentate ligand dppe is more effective than PPh_3, probably because the cationic (π-allyl)palladium complex **70**, known as the active species for the nucleophilic reaction, is much more preferential to the neutral ones (**69**) when the bidentate ligand is used[21,22] (Scheme VI).

When the reaction of the carbonate **71** was carried out in the absence of the active methylene compounds, 1,3-dienes **76** or allyl alkyl ethers **75** are obtained at 65 °C (Scheme VII). 1,3-Diene **76** is formed by β-elimination of Pd–H from (π-allyl)palladium complex **72**.[23,24] Generation of allyl alkyl ethers from allylic carbonates by nucleophillic attack of alkoxide anion to (π-allyl)palladium complex is known.[11] However, in the presence of active methylene compounds, the β-elimination or ether formation was negligible.

In addition to the reaction of active methylene compounds described here, we have demonstrated before other advantages of using allylic carbonates in the palladium-catalyzed reactions with carbon monoxide, silyl enol ethers, ketene silyl acetals, or enol acetates.[25-28]

Experimental Section

General Methods. THF, ether, benzene, and toluene was distilled from benzophenone ketyl. DMF was distilled from CaH_2 under reduced pressure. ^1H NMR spectra were measured with either a Hitachi R-24A (60 MHz) or a JEOL FX-90Q (90 MHz) instrument. Chemical shifts are given in δ units (parts per million) relative to tetramethylsilane as an internal standard. Spliting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). ^{13}C NMR spectra were recorded on a JEOL FX-90Q (22.5 MHz) instrument. Infrared spectra were recorded on a JASCO IRA-2 spectrophotometer. GLC analyses were performed on a Shimadzu GC-4C chromatograph using a column packed with Silicone DC 550 (3 mm × 3 m), and the peak areas were calculated on a Shimadzu chromatopack C-E1B. TLC analyses were carried out with Merk Kieselgel $60F_{254}$ sheet. Column chromatography was performed on a Wako gel C-200 in a weight ratio of 10/1–15/1 silica gel/crude product.

Preparation of Allylic Carbonates. Diallyl Carbonate (12). To a solution of allyl alcohol (23.2 g, 0.4 mol) and pyridine (31.6 g, 0.4 mol) in dry ether (250 mL) was added trichloromethyl chloroformate (19.8 g, 0.1 mol) dropwise with stirring for 1 h at 0 °C under nitrogen. The resulting mixture was stirred at 25 °C for 5 h. The suspension was filtered through Celite, and the filtrate was washed with saturated $CuSO_4$ solution and dried over $MgSO_4$. Fractional distillation gave diallyl carbonate (24.3 g, 85%): bp 67 °C (17 torr); IR (film) 1750, 970, 935 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 4.55 (d, J = 6 Hz, 4 H), 5.00–5.50 (m, 4 H), 5.58–6.25 (m, 2 H). Other allylic carbonates and the carbamate **14** were prepared from the corresponding allylic alcohols or diisopropylamine and chloroformates with pyridine in essentially the same manner as described in the previous paper.[25] Physical and spectral data of the carbonates are as follows.

Allyl diisopropylcarbamate (14): bp 145 °C (93 torr); IR (film) 1690, 995, 925 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) 1.21 (d, J = 7 Hz, 12 H), 3.83 (q, J = 7 Hz, 1 H), 3.95 (q, J = 7 Hz, 1 H), 4.52 (d, J = 6 Hz, 2 H), 5.00–5.45 (m, 2 H), 5.67–6.30 (m, 1 H).

Methallyl methyl carbonate (20): bp 48 °C (28 torr); IR (film) 1750, 910 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.72 (s, 3 H, 3.68 (s, 3 H), 4.46 (s, 2 H), 4.87 (br s, 1 H), 4.95 (br s, 1 H); MS, m/e 130 (M^+).

(*E*)-Cinnamyl methyl carbonate (22): bp 113–115 °C (2 torr); IR (film) 1750, 970 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 3.64 (s, 3H), 4.64 (d, J = 6 Hz, 2 H), 6.18 (dt, J = 16 and 6 Hz, 1 H), 6.53 (d, J = 16 Hz, 1 H), 7.19 (bs, 5 H); MS, m/e 192 (M^+).

Ethyl (*E*)-7-oxo-2-octenyl carbonate (24): bp 130–134 °C (8 torr); IR (film) 1745, 1710, 970 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.26 (t, J = 7 Hz, 3 H), 1.63 (tt, J = 7 and 7 Hz, 2 H), 1.75–2.52 (m, 4 H), 2.04 (s, 3 H), 4.08 (q, J = 7 Hz, 2 H), 4.43 (d, J = 5 Hz, 2 H), 5.48–5.74 (m, 2 H). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.76; H, 8.45.

Ethyl (*E*)-1-methyl-2-butenyl carbonate (26): bp 70 °C (17 torr); IR (film) 1745, 965 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.26 (t, J = 7 Hz, 3 H), 1.32 (d, J = 6 Hz, 3 H), 1.66 (d, J = 5 Hz, 3 H), 4.11 (q, J = 7 Hz, 2 H), 5.07 (dq, J = 6 and 6 Hz, 1 H), 5.33–6.04 (m, 2 H); MS, m/e 158 (M^+).

Geranyl methyl carbonate (28): bp 112 °C (8 torr); IR (film) 1750, 795 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.57 (s, 3 H), 1.63 (s, 3 H), 1.69 (s, 3 H), 2.00 (br, 4 H), 3.65 (s, 3 H), 4.51 (d, J = 7 Hz, 2 H), 4.80–5.43 (m, 2 H); MS, m/e 212 (M^+).

Methyl neryl carbonate (31): bp 78 °C (4 torr); IR (film) 1750, 795 cm^{-1}; ^1H NMR (CCl4, 60 MHz) δ 1.57 (s, 3 H), 1.63 (s,

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(22) See: Jeffrey, P. D.; McCombie, S. W. *J. Org. Chem.* **1982**, *47*, 587–590, footnote 4.
(23) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075–2078.
(24) Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301–2304.
(25) Tsuji, J.; Sato, K.; Okumoto, H. *Tetrahedron Lett.* **1982**, *23*, 5189–5190; *J. Org. Chem.* **1984**, *49*, 1341–1344.
(26) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 1793–1796.
(27) Tsuji, J.; Minami, I.; Shimizu, I. *Chem. Lett.* **1983**, 1325–1326.
(28) Tsuji, J.; Takahashi, K.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 4783–4786.

3 H), 1.74 (s, 3 H), 2.10 (br, 4 H), 3.65 (s, 3 H), 4.51 (d, J = 7 Hz, 2 H), 4.85–5.50 (m, 2 H); MS, m/e 212 (M^+).

1-Cyano-2-methyl-2-propenyl methyl carbonate (32): IR (film) 1760, 880 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.90 (s, 3 H), 3.90 (s), 5.18 (br, 1 H), 5.34 (br, 1 H), 5.58 (s, 1 H); MS, m/e 155 (M^+).

(*E*)-4-Acetoxy-2-butenyl methyl carbonate (34): IR (film) 1750, 1740, 970 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.00 (s, 3 H), 3.70 (s, 3 H), 4.51 (br, 4 H), 5.82 (br, 2 H); MS, m/e 188 (M^+).

(*Z*)-4-Acetoxy-2-butenyl methyl carbonate (36): IR (film) 1755, 1735, 735 cm^{-1}, ^1H NMR (CCl_4, 60 MHz) δ 2.10 (s, 3 H), 3.72 (s, 3 H), 4.61 (br d, J = 5 Hz, 2 H), 4.67 (br d, J = 5 Hz, 2 H), 5.71 (br t, J = 5 Hz, 2 H); MS, m/e 188 (M^+).

Methyl (*E*)-2-methyl-6-oxo-2-heptenyl carbonate (37): IR (film) 1740, 1710, 970 cm^{-1}; ^1H NMR 1.64 (s, 3 H), 2.03 (s, 3 H), 1.90–2.70 (m, 4 H), 3.60 (s, 3 H), 4.30 (s, 2 H), 5.25 (t, J = 7 Hz, 1 H); MS, m/e 201 (M^+).

General Procedure A for the Allylation without Addition of a Base (Table I). Methyl 2-Allyl-2-methyl-3-oxopentanoate (13). A solution of $Pd_2(dba)_3{\cdot}CHCl_3$[29] (26 mg, 0.025 mmol) and PPh_3 (52 mg, 0.2 mmol) in dry THF (2 mL) was stirred for 10 min at 30 °C under argon. A solution of diallyl carbonate (**12**, 284 mg, 2 mmol) and methyl 2-methyl-3-oxopentanoate (**11**, 144 mg, 1 mmol) in dry THF (1 mL) was added to the solution. Then the mixture was stirred for 10 min at 30 °C or appropriate temperature under argon, and the reaction was monitored by GLC analysis (yield 98%). An analytically pure sample of **13** was obtained according to general procedure C after purification by chromatography on SiO_2 with hexane–ether followed by Kugelrohr distillation at 65 °C (4 torr).

13: IR (film) 1740, 1710, 990, 930 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.05 (t, J = 7 Hz, 3 H), 1.34 (s, 3 H), 2.47 (q, J = 7 Hz, 2 H), 2.55 (dd, J = 7 and 14 Hz, 1 H), 2.61 (dd, J = 7 and 14 Hz, 1 H), 3.72 (s, 3 H), 4.99–5.14 (m, 2 H), 5.33–5.89 (m, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 8.0 (q), 19.1 (q), 31.8 (t), 39.6 (t), 52.3 (q), 59.3 (s), 118.9 (t), 132.8 (d), 173.2 (s), 207.6 (s). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.27; H, 8.83.

General Procedure B for the Allylation Using NaH (Table I). Reaction of 11 with 15. The β-keto ester **11** (114 mg, 1 mmol) was added to a suspension of NaH (36 mg, 50% in mineral oil, 1.5 mmol, prewashed with hexane) in dry THF (1 mL), and the mixture was stirred for 1 h. The resultant mixture and allyl acetate (**15**, 200 mg, 2 mmol) in dry THF (1 mL) were added to a solution of Pd(0)–PPh_3 catalyst prepared by the same manner as above, and the reaction mixture was stirred for 30 min at 30 °C under argon. The reaction was monitored by GLC analysis (yield 95%).

Allylation of 11 with Allyl Methyl Carbonate (41) Using $Mo(CO)_6$ Catalyst. A solution of $Mo(CO)_6$ (26 mg, 0.1 mmol), allyl methyl carbonate (**41**, 174 mg, 1.5 mmol), and **11** (144 mg, 1 mmol) in toluene (5 mL) was stirred at 110 °C for 12 h under argon. The usual workup and purification by column chromatography on SiO_2 gave **13** (162 mg, 88%).

General Procedure C for the Reaction of Allylic Carbonates and Malonates or β-Keto Esters (Table II, Preparative Procedures). Methyl 2,4-Dimethyl-2-(1-oxopropyl)-4-pentanoate (21). A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (25 mg, 0.025 mmol) and PPh_3 (52 mg, 0.2 mmol) in dry THF (2 mL) was stirred for 10 min at room temperature under argon. A solution of methallyl methyl carbonate (**20**, 130 mg, 1 mmol) and the β-keto ester **11** (288 mg, 2 mmol) in dry THF (1 mL) was added dropwise to the solution. The reaction mixture was stirred at 30 °C for 0.2 h under argon and filtered through Florisil. The filtrate was condensed in vacuo. The residue was chromatographed on SiO_2 with hexane–ether (10:1) to give methyl 2,4-dimethyl-2-(1-oxopropyl)-4-pentanoate (**21**, 183 mg, 92 %). Analytically pure sample of **21** was obtained by Kugelrohr distillation at 70 °C (4 torr).

21: IR (film), 1740, 1710, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ u.06 (t, J = 7 Hz, 3 H), 1.35 (s, 3 H), 1.63 (s, 3 H), 2.48 (q, 2 H), 2.59 (d, J = 14 Hz, 1 H), 2.69 (d, J = 14 Hz, 1 H), 3.72 (s, 3 H), 4.68 (br s, 1 H), 4.84 (br s, 1 H); ^{13} C NMR ($CDCl_3$, 22.5 MHz) δ 8.2 (q), 19.1 (q), 23.6 (q), 31.6 (t), 42.6 (t), 52.3 (q), 59.1 (s), 115.3 (t), 141.0 (s), 173.6 (s), 208.0 (s). Anal. Calcd for $C_{11}H_{16}O_3$: C, 66.64; H, 9.15. Found: C, 66.60; H, 9.17.

Methyl 2-(1-oxoethyl)-5-phenyl-4-pentenoate (23): Kugelrohr distillation, 135 °C (2 torr); IR (film) 1740, 1710, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.19 (s, 3 H), 2.70 (dd, J = 7 and 7 Hz, 2 H), 3.58 (t, J = 7 Hz, 1 H), 3.67 (s, 3 H), 6.12 (dt, J = 16 and 7 Hz, 1 H), 6.39 (d, J = 16 Hz, 1 H), 7.24 (br s, 5 H), 12.83 (s, enol); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 29.1 (g), 31.5 (t), 52.3 (q), 59.2 (d), 125.7 (d), 126.1 (d), 127.4 (d), 128.5 (d), 132.6 (d), 137.0 (s), 169.5 (s), 202.0 (s). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.34; H, 6.97.

Diethyl [(*E*)-7-oxo-2-octenyl]malonate (25): Kugelrohr distillation, 100 °C (1 torr); IR (film) 1745, 1715, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.26 (t, J = 7 Hz, 6 H), 1.60 (tt, J = 7 and 7 Hz, 2 H), 1.82–2.12 (m, 2 H), 2.12 (s, 3 H), 2.41 (t, J = 7 Hz, 2 H), 2.56 (dd, J = 5 and 7 Hz, 2 H), 3.36 (t, J = 7 Hz, 1 H), 4.18 (q, J = 7 Hz, 4 H), 5.42 (dt, J = 5 and 15 Hz, 1 H), 5.44 (dt, J = 5 and 15 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.2 (q), 23.3 (t), 29.8 (q), 31.8 (t), 42.7 (t), 52.3 (d), 61.2 (t), 126.5 (d), 132.8 (d), 168.9 (s), 208.4 (s). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.34; H, 8.43.

Diethyl [(*E*)-1-methyl-2-butenyl]malonate (27): IR (film) 1740, 1150, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.07 (d, J = 7 Hz, 3 H), 1.24 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 1.63 (d, J = 5 Hz, 3 H), 2.69–3.01 (m, 1 H), 3.17–3.36 (m, 1 H), 4.16 (q, J = 7 Hz, 2 H), 4.19 (q, J = 7 Hz, 2 H), 5.21–5.73 (m, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.2, 17.8, 18.6, 37.3, 58.3, 61.1, 61.2, 126.0, 132.7, 168.4.

Methyl (*E*)- and (*Z*)-5-cyano-2,4-dimethyl-2-(1-oxopropyl)-4-pentenoate (33): E/Z = 4/1; IR (film) 2260, 1750, 1725, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.06 (t, J = 7 Hz), 1.35 (from E) and 1.40 (Z) (s, 3 H), 1.80 (E) and 1.97 (Z), (s, 3 H from E), 2.48 (q, J = 7 Hz, 2 H), 2.65 (E) (d, J = 14 Hz), 2.94 (E) (d, J = 14 Hz), 3.76 (s, 3 H), 5.16 (E) and 5.33 (Z) (d, J = 1 Hz, 1 H). Anal. Calcd for $C_{12}H_{17}NO$: C, 64.55; H, 7.67; N, 6.27. Found: C, 64.61; H, 7.64; N, 6.52.

Methyl (*E*)-6-acetoxy-2-methyl-2-(1-oxopropyl)-4-hexenoate (35): Kugelkohr distillation 100 °C (1 torr); IR (film) 1740, 1710, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.05 (t, J = 7 Hz, 3 H), 1.33 (s, 3 H), 2.05 (s, 3 H), 2.45 (q, J = 7 Hz, 2 H), 2.57 (br, 2 H), 3.72 (s, 3 H), 4.48 (br d, J = 4 Hz, 2 H), 5.56–5.67 (m, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 8.0 (q), 19.2 (q), 20.8 (q), 31.8 (t), 38.1 (t), 52.3 (q), 59.3 (s), 64.5 (t), 128.5 (d), 129.8 (d), 170.4 (s), 173.0 (s), 207.4 (s). Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.86. Found: C, 61.05; H, 7.89.

Methyl 2,4-dimethyl-2-(1-oxopropyl)-8-oxo-4-nonenoate (38): IR (film) 1740, 1710, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.00 (t, J = 7 Hz), 1.30 (s, 3 H), 1.52 (s, 3 H), 2.10 (s, 3 H), 2.10–2.60 (m, 8 H), 3.75 (s, 3 H), 5.06 (t, J = 7 Hz, 1 H). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.16; H, 9.01. Found: C, 67.23; H, 8.99.

(*E*)-6,10-Dimethyl-5,9-undecadien-2-one (Geranylacetone, 29). To a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (52 mg, 0.05 mmol) and dppe (78 mg, 0.2 mmol) in dry THF (4 mL) was added a solution of methyl geranyl carbonate (**28**, 427 mg, 2.0 mmol). Then methyl acetoacetate (929 mg, 8.0 mmol) in dry THF (2 mL) was added dropwise with stirring. The mixture was stirred at 50 °C for 3 h under argon. After mixture of the solvent under reduced pressure, 10% aqueous NaOH solution (10 mL) and methanol (10 mL) were added to the crude product, and the mixture was stirred overnight at room temperature. After neutralization with 3 N HCl, the resultant solution was extracted with dichloromethane. After removal of the solvent, benzene (10 mL) was added to the residue and the mixture was refluxed for 1 h. After evaporation of the solvent, the residue was chromatographed on SiO_2 with ether–hexane to give geranylacetone (**29**, 288 mg, 74%). GLC analysis showed the 5 Z isomer **30** in 8%. By the same procedure as above, neryl carbonate (**31**) was reacted with methyl acetoacetate followed by hydrolysis and decarboxylation to give a 52:48 mixture of 5 E isomer **29** and 5 Z isomer **30** in 54% yield.

General Procedure D for the Allylation of Carbonucleophiles (Tables III and IV). To a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (26 mg, 0.025 mmol) and dppe (39 mg, 0.1 mmol) in dry THF (2 mL) was added a solution of the protected cyanohydrin **39** (108 mg, 0.5 mmol) and diallyl carbonate (**12**, 142 mg, 1 mmol) in dry THF (3 mL). The mixture was stirred at 65 °C for 1 h under argon. The reaction mixture was filtered through a Florisil column followed by chromatographic purification (SiO_2, ether–hexane,

(29) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253–266.

10:1) to give **40** (113 mg, 88%).

40 (diastereomer): IR (film) 1640, 1605, 1500, 920 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.20–2.00 (m, 6 H), 2.38 (t, J = 6 Hz, 2 H), 3.20–4.20 (m, 2 H), 4.10–5.10 (m, 2 H), 5.20 (br, 1 H), 5.30–5.90 (m, 1 H), 7.00–7.80 (m, 5 H). Hydrolysis of **40** (0.1 N HCl) followed by decyanization (2% aqueous NaOH) gave 1-phenyl-2-buten-1-one, which was identical with an authentic sample.

46: IR (film) 1545, 1370, 990, 910 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.96 (t, J = 7 Hz, 3 H), 1.62–2.14 (m, 2 H), 2.42–2.68 (m, 2 H), 4.11–4.58 (m, 1 H), 4.92–5.20 (m, 2 H), 5.40–6.05 (m, 1 H).

47: IR (film) 2950, 1640, 1495, 1450 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.57 (t, J = 7 Hz, 2 H), 3.74 (t, J = 7 Hz, 1 H), 4.90–5.30 (m, 2 H), 5.30–6.20 (m, 1 H), 7.30 (s, 5 H).

48: IR (film) 2220, 990, 915 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.33 (d, J = 6 Hz, 4 H), 4.95–5.33 (m, 6 H), 5.44–6.51 (m, 3 H).

49: ^1H NMR (CCl_4, 60 MHz) δ 1.64 (bs, 6 H), 2.58 (d, J = 7 Hz, 2 H), 3.20–4.20 (m, 2 H), 4.80–6.20 (m, 6 H). Hydrolysis of **49** (0.1 N HCl) followed by decyanization (2% aqueous NaOH) gave 1.5-hexadien-3-one: IR (film) 1680, 1605, 1400, 985, 920 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.38 (dt, J = 5.5 and 1.4 Hz), 4.95–5.26 (m, 2 H), 5.60–6.10 (m, 2 H), 6.10–6.40 (m, 2 H).

51: IR (film) 1740, 995, 910 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.21 (t, J = 7 Hz, 3 H), 2.27–2.46 (m, 2 H), 2.96 (dt, J = 7 and 7 Hz, 1 H), 4.05 (q, J = 7 Hz, 2 H), 4.82–5.17 (m, 4 H), 5.40–6.10 (m, 2 H).

52: IR (film) 1735, 995, 915, 900 cm^{-1}; ^1H NMr (CCl_4, 60 MHz) δ 1.19 (t, J = 7 Hz, 3 H), 1.78 (s, 3 H), 2.35 (m, 2 H), 2.95 (t, J = 7 Hz, 1 H), 4.02 (q, J = 7 Hz, 2 H), 4.28 (br, 2 H), 4.25–5.10 (m, 2 H), 5.24–6.02 (m, 1 H).

53: IR (film) 1730, 995, 905 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.38–2.78 (m, 2 H), 3.50 (t, J = 8 Hz, 1 H), 3.53 (s, 3 H), 4.80–5.10 (m, 2 H), 5.34–6.00 (m, 1 H), 7.19 (br, 5 H).

54: IR (film) 1705, 995, 910 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.90 (s, 3 H), 1.28–1.66 (m, 6 H), 1.83–2.86 (m, 4 H), 2.28 (d, J = 7 Hz, 4 H), 4.66–4.99 (m, 4 H), 5.20–5.90 (7, 3 H). Anal. Calcd for $C_{17}H_{22}O$: C, 85.55; H, 9.90. Found: C, 83.53; H, 9.89.

55: IR (film) 1700, 990, 910 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.95–2.90 (m, 5 H), 4.80–5.15 (m, 2 H), 5.39–6.15 (m, 1 H), 6.04 (dt, J = 6 and 2 Hz, 1 H), 7.52 (dt, J = 6 and 3 Hz, 1 H).

56: mp 127 °C; IR (KBr) 1640, 1595, 1490, 920 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.38 (bs, 3 H), 2.60–3.40 (m, 2 H), 4.02 and 4.18 (d, J = 4.6 Hz, 1 H), 4.80–5.20 (m, 2 H), 5.20–5.95 (m, 1 H), 7.00–7.60 (m, 9 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 21.0, 31.4, 70.5, 117.7, 127.7, 128.1, 128.5, 128.6, 129.4, 129.7, 131.5, 125.5. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 9.68. Found: C, 71.30; H, 9.76.

57: mp 52 °C; IR (KBr) 1640, 1595, 920 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.45 (bs, 3 H), 2.60–3.00 (m, 2 H), 3.50 (dt, J = 3.8 and 9.0 Hz, 1 H), 4.80–5.80 (m, 6 H), 7.20 (d, J = 8 Hz, 2 H), 7.70 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 21.6, 31.7, 69.3, 118.2, 123.5, 128.3, 129.3, 129.4, 130.0, 133.0, 144.6. Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 66.86; H, 6.75; S, 13.33.

58: IR (film) 3130, 2980, 1640, 1620, 920 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.38 (s, 3 H), 2.30–2.90 (m, 4 H), 4.70–5.40 (m, 6 H), 5.50–6.30 (m, 3 H), 7.00 (d, J = 8 Hz, 2 H), 7.40 (d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 21.5, 35.1, 69.1, 119.1, 120.4, 128.9, 130.8, 131.7, 131.8, 135.1, 144.5. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.65; H, 7.53.

60: IR (film) 1310, 1150, 990, 915, 815, cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.12 (s, 3 H), 1.47 (s, 3 H), 1.53 (s, 3 H), 1.72–2.00 (m, 6 H), 2.22 (s, 3 H), 3.41 (dt, J = 4 and 10 Hz, 1 H), 4.40–5.60 (m, 5 H), 6.71 (d, J = 8 Hz, 2 H), 7.14 (d, J = 8 Hz). Anal. Calcd for $C_{20}H_{28}O_2S$: C, 72.25; H, 8.49; S, 9.64. Found: C, 72.45; H, 8.48; S, 9.91.

Ethyl (*E*)-2,6-Heptadienoate (61). Ethyl 2-vinyl-4-pentenoate (**51**, 158 mg, 1 mmol) was heated at 160 °C in a sealed tube for 18 h. GLC analysis showed the formation of the ester **61** in 74% yield and its isomers (16%) with recovered **51** (9%). An analytical sample of **61** was obtained by preparative GLC. **61**: IR (film) 1715, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.28 (t, J = 7 Hz, 3 H), 2.06–2.42 (m, 4 H), 4.18 (q, J = 7 Hz, 2 H), 4.94–5.13 (m, 2 H), 5.45–6.03 (m, 1 H), 5.83 (d, J = 16 Hz, 1 H), 7.04 (dt, J = 16 and 6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.3 (q), 31.5 (t), 32.1 (t, 60.1 (t), 115.5 (t), 121.9 (d), 137.1 (d), 148.1 (d), 166.5 (s). Anal. Calcd for $C_9H_{15}O_2$: C, 70.10; H, 9.15. Found: C, 70.05; H, 9.04.

(9*E*)-8-(*p*-Tolylsulfonyl)-6,10,14-trimethyl-5,9,13-pentadecatrien-2-one (62). By a similar procedure to the allylation shown in Table III, reaction of geranylsulfone **59** (292 mg, 1 mmol) and the allylic carbonate **37** (400 mg, 2 mmol) and chromatographic purification on SiO_2 gave **62** (185 mg, 45%): IR (film) 2910, 1720, 1300, 1145 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.20 (s, 3 H), 1.54 (s, 3 H), 1.65 (s, 3 H), 1.69 (s, 3 H), 1.99 (s, 3 H), 2.40 (s, 3 H), 1.30–1.95 (m, 10 H), 3.70 (dt, J = 4 and 10 Hz, 1 H), 4.55–5.20 (m, 3 H), 7.17 (d, J = 8 Hz, 2 H), 7.58 (d, J = 8 Hz, 2 H).

(9*E*)-6,10,14-Trimethyl-5,9,13-pentadecatrien-2-one (63) by Desulfonylation of 62. By a procedure reported by Trost[30] desulfonylation of **62** was carried out. To a solution of **62** (416 mg, 1 mmol) and Na_2HPO_4 (568 mg, 4 mmol) in dry MeOH (10 mL) was added 5% sodium amalgam (2.0 g) at −20 °C. The reaction mixture was poured into water, extracted with ether, washed with saturated NH_4Cl solution and brine, and dried over $MgSO_4$. After removal of the solvent, the crude product was eluted on SiO_2 with hexane–ether (5:1) to give trienes (130 mg, 49%), which were found to be 5:1 mixture of 5*E* and 5*Z* isomers and identical with authentic samples by GLC analysis.[31]

Registry No. **11**, 17422-12-7; **12**, 15022-08-9; **13**, 85217-68-1; **14**, 74562-19-9; **15**, 591-87-7; **16**, 1746-13-0; **17**, 3066-75-9; **18**, 107-18-6; **19**, 557-40-4; **20**, 81112-28-9; **21**, 85217-75-0; **22**, 85217-69-2; **23**, 85217-77-2; **24**, 85217-70-5; **25**, 95514-48-0; **26**, 95514-49-1; **27**, 95587-38-5; **28**, 85217-72-7; **29**, 3796-70-1; **30**, 3879-26-3; **31**, 85217-73-8; **32**, 95514-50-4; (*E*)-**33**, 95514-51-5; (*Z*)-**33**, 95514-52-6; **34**, 85217-74-9; (*E*)-**35**, 95514-53-7; (*Z*)-**35**, 95514-54-8; **36**, 95514-55-9; **37**, 92747-33-6; (*E*)-**38**, 95514-56-0; (*Z*)-**38**, 95514-57-1; **39**, 41865-47-8; **40**, 95514-58-2; **41**, 35466-83-2; **42**, 16308-66-0; **43**, 70122-88-2; **44**, 70122-89-3; **45**, 16308-68-2; **46**, 72760-81-7; **47**, 5558-87-2; **48**, 923-52-4; **49**, 95514-59-3; **50**, 1617-18-1; **51**, 42998-16-3; **52**, 64861-90-1; **53**, 14815-73-7; **54**, 95514-60-6; **55**, 61020-32-4; **56**, 71376-51-7; **57**, 85217-80-7; **58**, 84603-00-9; **59**, 53254-60-7; **60**, 95514-61-7; **61**, 95514-62-8; **62** (isomer 1), 95514-63-9; **62** (isomer 2), 95514-64-0; **63** (isomer 1), 1117-51-7; **63** (isomer 2), 1117-52-8; CH_2=$CHCH_2CN$, 109-75-1; CH_2=CHCH(OTHP)CN, 95514-65-1; CH_3CH(OTHP)CN, 17224-04-3; CH_2=$C(CH_3)CH_2CO_2Et$, 1617-19-2; OCH_2CH_2OP-$OCH_2CH_2CH_3$, 53969-09-8; PPh_3, 603-35-0; $P(OPh)_3$, 101-02-0; $P(OEt)_3$, 122-52-1; $Mo(CO)_6$, 13939-06-5; $CH_3COCH_2CO_2Me$, 105-45-3; $CH_2(CO_2Et)_2$, 105-53-3; $CH_3(CH_2)_2NO_2$, 108-03-2; $PhCH_2CN$, 140-29-4; $PhCH_2CO_2Me$, 101-41-7; trichloromethyl chloroformate, 503-38-8; 1-phenyl-2-buten-1-one, 495-41-0; 2-cyclopenten-1-one, 930-30-3; cyclohexanone, 108-94-1; benzyl *p*-tolyl sulfone, 5395-20-0; allyl *p*-tolyl sulfone, 3112-87-6; 2-allylcyclohexanone, 94-66-6; 4a-methyl-3,4,4a,5,6,7-hexahydro-2-(1*H*)-naphthalenone, 22789-80-6; $Pd_2(dba)_3CHCl_3$, 52522-40-4; Dppe, 1663-45-2.

(30) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477–3478.

(31) An authentic sample as a 3:1 *E*/*Z* mixture was prepared by Wittig reaction of geranylacetone and [4,4-(ethylenedioxy)-pentyl]phosphonium salt[32] followed by hydrolysis.

(32) Crombie, L.; Hemesley, P.; Pattenden, G. *J. Chem. Soc.* **1969**, 1016–1024.