ammonia was allowed to evaporate. The resultant mixture was diluted with 10% aqueous K_2CO_3 (50 mL) and extracted with ether (200 mL). The ether solution was concentrated and chromatographed over silica gel (25% ether/75% petroleum ether) to afford 0.69 g (64%) of **17** as light yellow needles: mp 168–169 °C; IR (KBr) 1680 (C=O) cm^{-1}; ^1H NMR (300 MHz, Me_2SO-d_6) δ 7.2–7.9 (m, 11, Ar H), 7.00 (d, J = 2 Hz, 1, Ar H), 6.37 (d, J = 8 Hz, 1, Ar H), 4.15 (s, 1, CH); ^{13}C NMR (75 MHz, MeSO-d_6) δ 165.1 (C-2), 138.8, 137.1, 134.5, 130.3, 129.6, 129.1, 129.0, 129.0, 128.9, 128.6, 127.6, 126.2, 124.4, 118.2, 63.4 (C-3), 60.6 (C-4); MS, m/e (relative intensity) 347 (M^+, 70), 319 (100), 290 (70), 254 (52), 228 (77). Anal. Calcd for $C_{21}H_{14}ClNO_2$: C, 72.51; H, 4.06; N, 4.03. Found: C, 72.41; H, 4.00; N, 4.08.

2′-Benzoyl-4′-chloro-*N*-phenyl-2-iodoacetanilide (18). A solution of **16** (3.90 g, 11.2 mmol) in acetone (30 mL) and a solution of sodium iodide (1.77 g, 11.8 mmol) in acetone (15 mL) were mixed and heated under reflux for 10 min. The solution was allowed to cool to room temperature and filtered through celite. The filtrate was again heated under reflux for 10 min, cooled to room temperature, and filtered through Celite. The filtrate was concentrated and dissolved in a solution of THF (10 mL) and ether (100 mL). A small amount of precipitated salt was removed by filtration through Celite. The ether solution was concentrated and the solid recrystallized from MeOH to give 4.40 g (83%) of **18** as yellow prisms: mp 129 °C; IR (KBr) 1660 (C=O) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.0–8.1 (m, 13, Ar H), 3.60 (s, 2, CH_2). Anal. Calcd for $C_{21}H_{15}ClINO_2$: C, 53.02; H, 3.18; N, 2.94. Found: C, 52.93; H, 3.03; N, 2,86.

2′-Benzoyl-4′-chloro-*N*-phenyl-2-azidoacetanilide (19). A solution of **18** (2.5 g, 5.26 mmol) in Me_2SO (20 mL) and a solution of sodium azide (0.68 g, 10.52 mmol) in Me_2SO (20 mL) and water (5 mL) were mixed and allowed to stand for 2 h. The mixture was poured into water (100 mL) and extracted with ether (200 mL). The ether extract was washed with water (75 mL) and concentrated. The residue was taken up in MeOH (25 mL) and allowed to stand for 3 h to deposit 1.86 g (90%) of **19** as beige prisms: mp 100–101 °C; IR (KBr) 2110 (N_3), 1680 and 1670 (C=O) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.0–8.1 (m, 13, Ar H), 3.70 (s, 2, CH_2). Anal. Calcd for $C_{21}H_{15}ClN_4O_2$: C, 64.53; H, 3.88; N, 14.34. Found: C, 64.15; H, 3.60; N, 14.01.

7-Chloro-1,3-dihydro-1,5-diphenyl-2*H*-1,4-benzodiazepin-2-one (21). A solution of **19** (1.40 g, 3.58 mmol) in THF (5 mL) and a solution of triphenylphosphine (1.03 g, 3.93 mmol) in ether (10 mL) were mixed and allowed to stand under a nitrogen atmosphere for 24 h. The mixture was concentrated and chromatographed over silica gel (60% ether/40% petroleum ether) to afford, after recrystallization from MeOH, 1.16 g (94%) of **21** as colorless prisms: mp 196–197 °C; IR (KBr) 1690 (C=O), 1615 (C=N) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.8 (m, 12, Ar H), 6.9 (d, 1, Ar H_9), 4.95 (d, J = 10 Hz, 1, CH_2), 4.00 (d, J = 10 Hz, 1, CH_2); ^{13}C NMR (75 MHz, Me_2SO-d_6) δ 168.8, 167.8 (C-2, C-5), 143.1, 141.3, 138.8, 131.2 (C-1′, C-1″, C-8, C-10), 129.1 (C-11), 131.8, 129.6, 129.4, 128.7, 128.6, 127.6, 126.8 (C-2′, C-2″, C-3′, C-3″, C-4′, C-4″, C-6, C-7, C-9), 57.7 (C-3). Anal. Calcd for $C_{21}H_{15}ClN_2O$: C, 72.72; H, 4.37; N, 8.08. Found: C, 72.43; H, 4.10; N, 8.08.

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Supplementary Material Available: Table III, experimental details of crystal of **21**; Table IV, atomic coordinates and isotropic thermal parameters; Table V, bond lengths; Table VI, bond angles; Table VII, H-atom coordinates and thermal parameters; and Table VIII, anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

Palladium-Catalyzed Decarboxylation–Allylation of Allylic Esters of α-Substituted β-Keto Carboxylic, Malonic, Cyanoacetic, and Nitroacetic Acids

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Decarboxylation–allylation of allylic β-keto carboxylates using $Pd(OAc)_2$–PPh_3 or $Pd_2(dba)_3$·$CHCl_3$–dppe as a catalyst proceeds smoothly to give α-allylated ketones. The reaction is highly regioselective. In some cases, diallylated ketones are obtained with allylic esters bearing an active proton(s). Also rhodium, molybdenum, and nickel complexes are active catalysts in this reaction. Similarly allylic esters of α-substituted malonates, cyanoacetates, and nitroacetate undergo the palladium-catalyzed decarboxylation–allylation to afford allylated acetate, acetonitrile, and nitromethane, respectively. The mechanisms of these palladium-catalyzed decarboxylation–allylations are discussed.

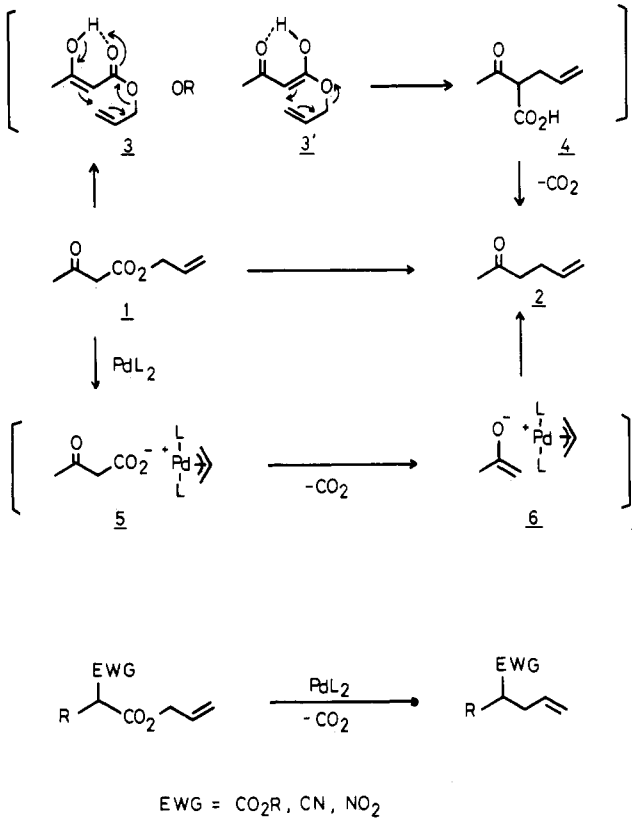
Introduction

Thermal decarboxylative rearrangement of allylic β-keto carboxylates **1** to afford γ,δ-unsaturated ketones **2** as shown in Scheme I is known as the Carroll reaction.[1,2] The reaction is useful for carbon–carbon bond formation and successfully applied to some terpene syntheses. However, the reaction requires high temperature (usually higher than 180 °C) and is sensitive to structure of the substrates. Recently it was found that the reaction can be accelerated by the use of bases such as aluminum alkoxides,[3] collidine,[4] sodium acetate,[5] sodium hydride,[6] or LDA.[7] The Carroll

(1) Carroll, M. F. *J. Chem. Soc.* **1940**, 1226.
(2) Kimel, W.; Cope, A. C. *J. Am. Chem. Soc.* **1943**, *65*, 1992.
(3) Cookson, R. C.; Parsons, D. J. *J. Chem. Soc., Chem. Commun.* **1976**, 990. Kimel, W.; Sax, N. W.; Kaiser, S.; Eichmann, G. G.; Chase, G. O.; Ofner, A. *J. Org. Chem.* **1958**, *23*, 153.
(4) Narwid, J. A.; Cooney, K. E.; Uskokovic, M. R. *Helv. Chim. Acta* **1974**, *57*, 771.
(5) Camps, F.; Canela, R.; Coll, J.; Messeguer, A.; Poca, A. *Tetrahedron Lett.* **1978**, *34*, 2179.
(6) Tanabe, M.; Hayashi, K. *J. Org. Chem.* **1980**, *102*, 862.
(7) Wilson, S. R.; Prince, M. F. *J. Org. Chem.* **1984**, *49*, 722.

0022-3263/87/1952-2988$01.50/0

Scheme I



EWG = CO_2R, CN, NO_2

reaction can be explained as [3,3]-sigmatropic rearrangement, which proceeds via the chelated enol forms such as **3** or **3'**. On the other hand, it is well-known that various allylic esters undergo several palladium-catalyzed reactions. Particularly, the allylation of nucleophiles is a well-established reaction.[8] In these palladium-catalyzed reactions, at first allylic esters react with a palladium–phosphine complex to form (π-allyl)palladium complexes, which then react with nucleophiles. As an extension of the palladium-catalyzed reactions of allylic esters, we were interested in a reaction of allyl β-keto carboxylates. We expected that the palladium–phosphine complex should catalyze the Carroll reaction under milder conditions, although the mechanism is different. In the palladium-catalyzed reaction of allyl β-keto carboxylates, at first (π-allyl)palladium complex **6** is formed by oxidative addition and decarboxylation as an intermediate, and subsequent intramolecular allylation gives the allylated ketones **2**. As expected, we have found that the palladium–phosphine complex catalyzes the expected decarboxylation–allylation of allylic esters of β-keto carboxylic acids smoothly at lower temperatures.[9] Tsuda and coworkers reported a similar palladium-catalyzed reaction independently.[10] Furthermore, in addition to allyl β-keto carboxylates, we found that allylic esters of α-substituted malonates, cyanoacetates, and nitroacetate undergo a similar decarboxylation–allylation. In other words, we established that the reaction is possible with carboxylates substituted by a carbanion-stabilizing, electron-withdrawing group at the α-position. A part of these studies has been given as communications,[9,11] and details of the reaction are presented in this paper.

It should be noted here that the palladium-catalyzed decarboxylation–allylation is competitive with the decarboxylation–dehydrogenation to afford α,β-unsaturated ketones[12] by slight modification of reaction conditions, and the details of which will be presented in a separate paper. Also as a related reaction, we observed the palladium-catalyzed decarboxylation–allylation of allyl 1-alkenyl carbonates to give γ,δ-unsaturated ketones.[13]

Results and Discussion

The palladium-catalyzed decarboxylation–allylation can be carried out smoothly by using $Pd(OAc)_2$–PPh_3 as a catalyst with or without solvents. Most conveniently, the reaction can be carried out in THF at 25–65 °C. Reactions of several allylic esters of β-keto acids were carried out and results are shown in Table I. The reaction of (*E*)-1-methyl-2-butenyl acetoacetate (**7**) with a catalytic amount of $Pd(OAc)_2$–PPh_3 at 90 °C without a solvent gave (*E*)-4-methyl-5-hepten-2-one (**8**) in 74% yield. On the other hand, the thermal reaction of **7** in the presence or absence of $Al(O\text{-}i\text{-}Pr)_3$ did not take place even at 200 °C, showing that the thermal reaction is sensitive to the structure of substrates.[3] The palladium-catalyzed reaction proceeds at temperatures much lower than the thermal reaction reported in the literature.[1,2] Furthermore, the palladium-catalyzed decarboxylation–allylation proceeds even in the absence of an active hydrogen at α-position of β-keto carboxylates. The thermal Carroll rearrangement, which is believed to proceed via an enolate, is not possible with these compounds. For example, the palladium-catalyzed reaction of allyl 2,2-diallylacetoacetate (**9**) gave the 1,1,1-triallylacetone (**10**) in 73% yield without giving regioisomers. In other words, the palladium-catalyzed allylation proceeds without proton transfer during the reaction, and the allyl group is introduced at the same carbon which is attached to the carboxylate group, even though it is a more crowded carbon. Because thermal reaction is impossible with this substrate, the mechanisms of the thermal and palladium-catalyzed Carroll reactions are different. Thus the palladium-catalyzed reaction can be utilized for the formation of quaternary carbon centers by the reaction of α,α-disubstituted esters, which is impossible by the thermal reaction.

The high regioselectivity of the reaction was also observed by the reaction of α,α'-disubstituted 2-[(allyloxy)carbonyl]cyclohexanone **29** to form α,α,α'-trisubstituted cyclohexanone **30**. In the usual organic reactions, regioselective formation of the enolate from α,α'-disubstituted cyclohexanones and subsequent regioselective alkylation are difficult. Thus the palladium-catalyzed decarboxylation–allylation offers an efficient method for the regioselective allylation of α,α'-disubstituted ketones.

Stereochemistry of the decarboxylation–allylation of allyl 1-methyl-5-*tert*-butyl-2-oxocyclohexanecarboxylate

(8) Our recent work on the allylation via (π-allyl)palladium intermediates: Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523. Recent reviews on organic reactions via (π-allyl)palladium intermediates: Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140. Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1980; p 37. Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. Trost, B. M.; Verhoeven, T. R. *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; Vol. 8, p 799. Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic: New York, 1985; p 117. Trost, B. M. *J. Organomet. Chem.* **1986**, *300*, 263. Tsuji, J. *J. Organomet. Chem.* **1986**, *300*, 281.

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(11) Tsuji, J.; Minami, I.; Shimizu, I. *Chem. Lett.* **1984**, 1721.

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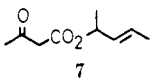
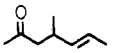
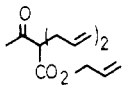
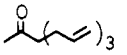
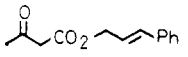
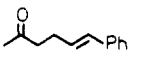
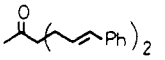
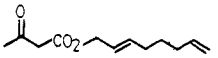
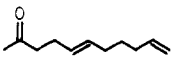
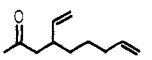
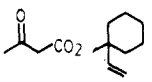
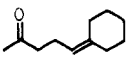
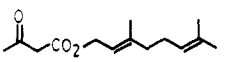
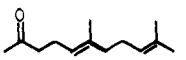
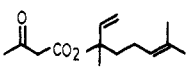
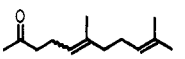
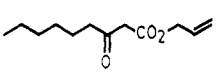
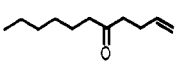
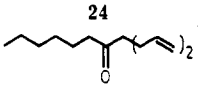
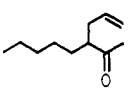
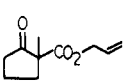
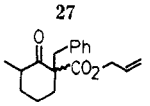
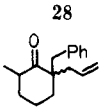
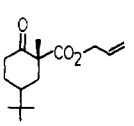
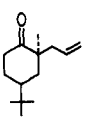
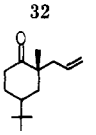
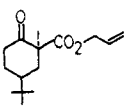
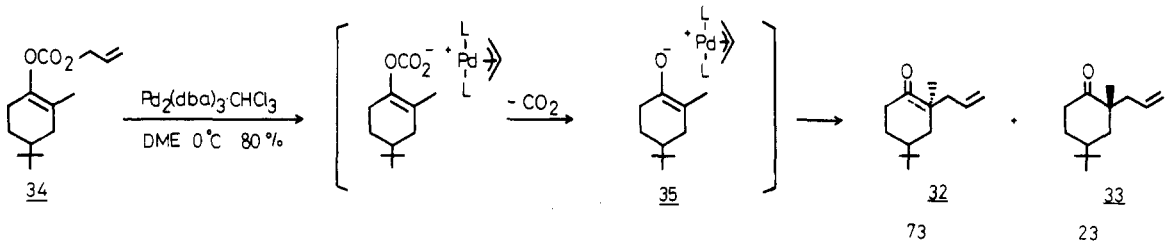
Table I

run	substrate	solv	temp, °C	time, h	product	yield, %
1	 **7**		90	1	 **8**	74
2	 **9**	THF	65	2	 **10**	73
3	 **11**	THF	65	1	 **12**	52
					 **13**	21
4	 **14**	THF	65	0.2	 **15**	24
					 **16**	8
					diallylated products	32
5[a]	 **17**	*t*-BuOH	50	1	 **18**	51
6[a]	 **19**	*t*-BuOH	50	4	 **20**	44
7[a]	 **21**	*t*-BuOH	50	2	 **22**	56 (*E*:*Z* = 3:2[c])
8	 **23**	THF	6	2	 **24**	34[c]
					 **25**	33[c]
					 **26**	5[c]
9	 **27**	THF	65	1	 **28**	81
10[b]	 **29**	THF	80	1	 **30**	68
11	 **31a**	PhH	80	1	 **32**	78[c] (**32**:**33** = 1.9:1[c])
					 **33**	
12	**31a**	THF	65	2	**32**, **33**	87[c] (**32**:**33** = 3:1[c])
13	**31a**	*t*-BuOH	65	1	**32**, **33**	79[c] (**32**:**33** = 3:1[c])
14	 **31b**	THF	65	1	**32**, **33**	65[c] (**32**:**33** = 3:1[c])

[a] Reaction was carried out in the presence of NaH. [b] $Pd_2(dba)_3 \cdot CHCl_3$ was used instead of $Pd(OAc)_2$. [c] Calculated by GLC analysis.

Scheme II

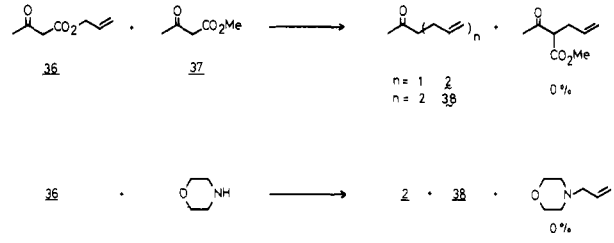


(31) was studied by using the axial and equatorial esters **31a** and **31b**. The reaction of both **31a** and **31b** in THF gave two stereoisomers in a similar ratio, showing that the stereochemistry was not retained in the reaction. The axial allylation of cyclohexanone was favorable, and its ratio increased in a polar solvent. Also we obtained **32** and **33** in a similar ratio by the palladium-catalyzed reaction of allyl 1-alkenyl carbonate **34**. Thus, (π-allyl)palladium enolate complex **35**, formed by oxidative addition–decarboxylation,[13] is a reasonable intermediate in the reactions of **31a**, **31b**, and **34** (Scheme II). The observed selectivity is similar to that observed in base-induced alkylation of cyclohexanones with alkyl halides.[14]

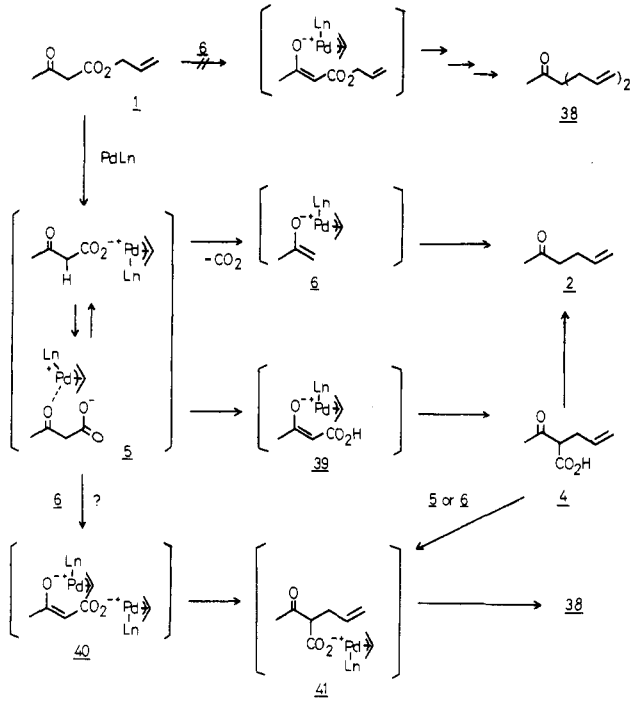
If the reaction is assumed to proceed via (π-allyl)palladium enolate complex, the following mechanism for the reaction of **1** to **2** is suggested. First, the oxidative addition of the Pd(0) species to the allylic ester gives (π-allyl)palladium β-keto carboxylate complex **5**, which undergoes facile decarboxylation to give (π-allyl)palladium enolate complex **6**. Formation of several metal enolate complexes from metal β-keto carboxylates by decarboxylation is known, but generally, the reaction requires high temperatures. Compared with harder lithium, tin, or silicon cations, the palladium cation is soft enough to release the carboxylate anion easily. This is why the decarboxylation of the palladium carboxylate complex takes place below 65 °C or even at a room temperature. Then the enolate anion of **6** attacks the (π-allyl)palladium cation to afford γ,δ-unsaturated ketone **2**. At the same time, the Pd(0) species is regenerated. It is well-known that stabilized carbanions such as β-keto esters and malonates react with (π-allyl)palladium complexes smoothly. On the other hand, hard carbanions such as lithium enolate of ketones do not react easily. But in the present case, the (π-allyl)palladium enolate complex generated by oxidative addition–decarboxylation reacts smoothly to give α-allyl ketones, suggesting that a (π-allyl)palladium enolate is much more reactive than lithium enolate.[15]

Unlike the thermal reaction, in addition to the expected allyl ketones, the formation of diallylated products was observed in the palladium-catalyzed reaction of some allylic β-keto carboxylates. For example, considerable amounts of the diallylated products were obtained in the reaction of acetoacetates **11**, **14**, and **23**. The formation of the diallylated products is somewhat difficult to explain, if we assume that the palladium-catalyzed reaction is intramolecular. Therefore, we carried out the following studies in order to understand the mechanism of the diallylation. As a competitive reaction, the reaction of allyl acetoacetate (**36**) was carried out in the presence of methyl acetoacetate (**37**). No allylation of methyl acetoacetate was observed and diallyl acetone was a major product. Also *N*-allylmorpholine was not obtained in the reaction of **36** with morpholine (Scheme III).

Scheme III



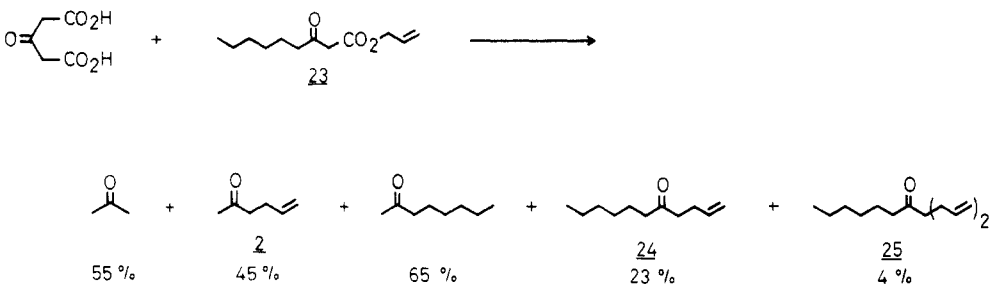
Scheme IV



Simple intermolecular proton transfer between the keto ester **1** and (π-allyl)palladium enolate complex **6** followed by allylation before decarboxylation–allylation seems to be negligible in this case, since methyl acetoacetate or morpholine was not allylated with allyl acetoacetate even though diallyl acetone was obtained (Scheme IV). Therefore, intramolecular proton transfer of palladium complex **5** is plausible. The α-carbonyl group in the (π-allyl)palladium β-keto carboxylate **5** is activated by a chelating effect. Then (π-allyl)palladium enolate acid **39** undergoes intramolecular allylation to give α-allyl β-keto acid **4**, which decarboxylates to give the α-allyl ketone **2**. When the decarboxylation of **4** to give **2** is slower than the ligand-exchange reaction, diallylation takes place. We carried out the following competitive reaction in order to confirm possibility of the conversion of **4** to **41** and subsequently to diallylated ketone **38**. By the reaction of acetonedicarboxylic acid (instead of unstable acetoacetic acid) with an equimolar amount of the allyl β-keto carboxylate **23**, 5-hexen-2-one (**2**) was obtained in 45% yield

(14) Conia, J. M.; Briet, P. *Bull. Soc. Chim. Fr.* **1966**, 3881, 3888.
(15) Fiaud, M. C.; Malleron, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 1159.

Scheme V



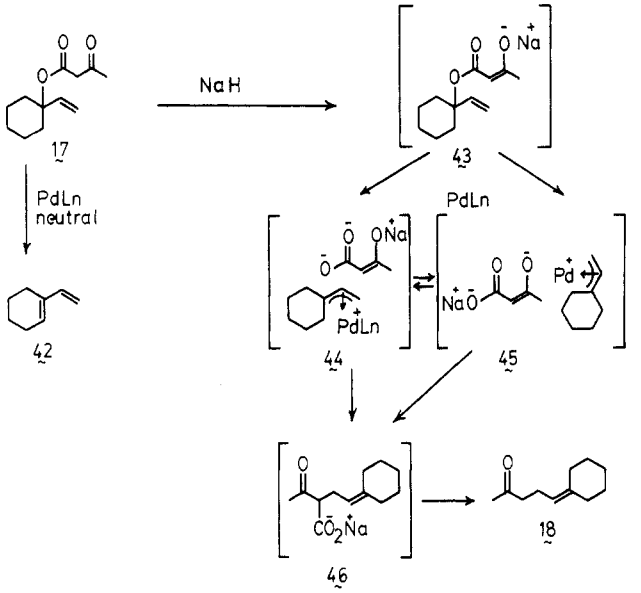
(Scheme V) in addition to 2-octanone and 1-undecen-5-one. As another supporting evidence, Tsuda and co-workers reported the formation of γ,δ-unsaturated ketones by the palladium-catalyzed reaction of β-keto acids with allyl acetate.[10] The possibility of decarboxylation–allylation or intramolecular proton transfer is dependent on the acidity of the methylene protons. Also formation of bis(π-allyl)palladium complex **40** from **5** followed by stepwise allylation (**40** to **41**) and decarboxylation–allylation (**41** to **38**) is also another understandable possibility.[16]

In the reaction of unsymmetrical allylic esters of acetoacetates, **11**, **17**, **19**, and **21**, the reaction took place exclusively at the less hindered terminal position of the allyl groups. However, the two monoallylated products **15** and **16** were obtained in a ratio of 3:1 from 2,7-octadienyl acetoacetate **14**. Under the same conditions, linalyl acetoacetate (**21**) gave geranylacetone (**20**) and nerylacetone (**22**) in a ratio of 3:2, but geranyl acetoacetate (**19**) was converted to **20** with retention of *E* configuration.

One important reaction observed in the palladium-catalyzed transformation of allylic compounds via (π-allyl)palladium complexes is the formation of 1,3-dienes by the β-hydrogen elimination reaction.[17] The diene-forming reaction was also observed in the reaction of some allylic β-keto carboxylates as a major path. Reaction of the ester of tertiary allyl alcohol **17** with $Pd(OAc)_2$–PPh_3 catalyst in boiling THF gave the 1,3-diene **42** as an elimination product, predominantly. But the reaction of **17** in *t*-BuOH in the presence of NaH at 50 °C for 1 h gave the α-allylated ketone **18** as a major product in 51% yield after chromatographic purification. This allylation is explained to proceed via sodium enolate **43**, which attacks the (π-allyl)palladium moiety directly, or intramolecular transmetalation to form **45**, followed by allylation to **46** (Scheme VI).

The decarboxylation of β-keto carboxylates proceeds smoothly, because the carbanion generated by the decarboxylation is stabilized by ketone group. Thus similar decarboxylation is expected with allyl carboxylates which have other electron-withdrawing groups at the α-position. On the basis of this expectation, we examined the palladium-catalyzed allylation of allyl esters of malonic acid, cyanoacetic acid, and nitroacetic acid. But the reactions were slow and also gave a mixture of products. Then we carried out reaction of the substituted malonates, cyanoacetates, and nitroacetate. The expected decarboxylation–allylation was observed with these substrates, but their reactivities were considerably different depending on the electron-withdrawing groups. Their reactivities were studied briefly with several representative substrates.

Scheme VI



The results are shown in Table II. Disubstituted diallyl malonates are less reactive than allyl β-keto carboxylates, and no reaction took place in boiling THF. The reaction proceeded in boiling dioxane or DMF. The monosubstituted diallyl malonate is more reactive, and the decarboxylation–allylation took place slowly in boiling THF. In DMF, diallylation was observed in 30%. Satisfactory results were obtained in dioxane.

The reaction of substituted allyl cyanoacetates was carried out in dioxane. In this case, no diallylation was observed. However, decarboxylation–protonation was observed in considerable extents as a competing reaction. Substituted allyl nitroacetate is the most reactive and it underwent the decarboxylation–allylation even at −50 °C. In this case, both C-allylation and O-allylation took place without selectivity. At room temperature, the ratio of C- and O-allylation was 1:1. Lower temperature favors the C-allylation, but the selectivity was 2:1 even at −50 °C.

From these results, it can be concluded that the order of reactivity is nitroacetate > β-ketoacetate > cyanoacetate > malonate. From a synthetic viewpoint, reaction of allyl β-keto carboxylates is the most useful since it proceeds in good yields with high chemo- and regioselectivity.

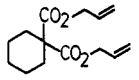
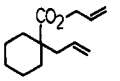
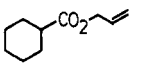
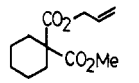
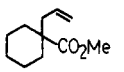
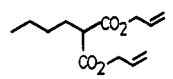
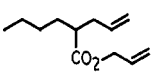
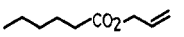
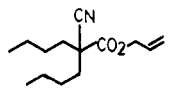
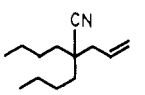
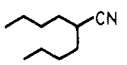
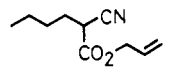
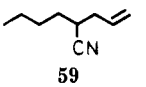
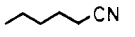
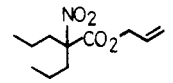
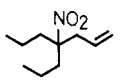
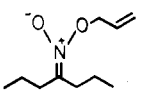
In addition to palladium–phosphine complexes, we have found that rhodium, nickel, ruthenium, and molybdenum complexes are active catalysts in the allylation of carbonucleophiles.[18] They showed considerable catalytic activities in the decarboxylation–allylation reaction of allyl β-keto carboxylates.[11] But their activities are somewhat lower than that of the palladium–phosphine catalyst, and

(16) The formation of a dicopper analogue from copper β-keto carboxylate and its reaction with electrophiles have been reported. For detail, see: Tsuda, T.; Takahashi, S.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 4980.

(17) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075. Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301. Matsushita, H.; Negishi, E. *J. Org. Chem.* **1982**, *47*, 4161.

(18) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 5157. Minami, I.; Shimizu, I.; Tsuji, J. *J. Organomet. Chem.* **1985**, *296*, 269 and references cited therein.

Table II

run	substrate	ligand	solvent	temp, °C	time, h	product	yield, %
1	 **47**	dppe	DMF	120	3	 **48**	65
						 **49**	22
2	 **50**	dppe	DMF	120	5	 **51**	75
3	 **52**	PPh_3	dioxane	100	5	 **53**	76
						 **54**	2
4	 **55**	dppe	dioxane	100	1.5	 **56**	63
						 **57**	24
5	 **58**	PPh_3	dioxane	100	3	 **59**	76
						 **60**	21
6	 **61**	PPh_3	THF	−50	2	 **62**	59
						 **63**	28
7	61	PPh_3	THF	20–25	2	**62** **63**	40 40

higher temperatures and longer reaction time were required.

Experimental Section

General. THF, dioxane, *t*-BuOH, and benzene were distilled over sodium. DMF was distilled over CaH_2. The solvents were stored under argon. $Pd_2(dba)_3{\cdot}CHCl_3$ [tris(dibenzylideneacetone)dipalladium(chloroform)] was prepared by the published procedure.[19] ^1H NMR spectra were measured with either a Hitachi Model R-24A (60 MHz) or a JEOL FX-90Q (90 MHz) instrument. Chemical shifts are given in units in parts per million relative to tetramethylsilane as an internal standard. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (qualtet), m (multiplet), 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 spectrometer. GLC analyses were performed on Shimadzu GC-4C using a column packed with silicone DC 550, and the peak areas were calculated on a Shimadzu Chromatopack C-E1B. TLC analyses were carried out with Merck Kieselgel 60 F_{254} sheet. Column chromatography was performed with Wako gel C 200 in a weight ratio of 10/1–15/1 silica gel/crude product.

(19) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1976**, *65*, 253.

Preparation of Materials. Allylic esters of acetoacetic acids **7**, **11**, **14**, **17**, **19**, and **21** were prepared from the corresponding allylic alcohols and diketene.[7]

1-Methyl-2-butenyl acetoacetate (**7**): ^1H NMR (CCl_4, 60 MHz) δ 1.26 (d, J = 6 Hz, 3 H), 1.70 (d, J = 5 Hz, 3 H), 2.15 (s, 3 H), 3.27 (s, 2 H), 5.00–5.90 (m, 3 H); IR (neat) 1740, 1720, 1650, 1045, 975 cm^{-1}. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.70; H, 8.38. bp 70–75 °C (2 mmHg).

2,7-Octadienyl acetoacetate (14): ^1H NMR (CCl_4, 60 MHz) δ 1.30–1.70 (m, 2 H), 1.80–2.30 (m, 4 H), 2.10 (s, 3 H), 3.26 (s, 2 H), 4.46 (d, J = 6 Hz, 2 H), 4.70–5.10 (m, 2 H), 5.10–6.10 (m, 2 H); IR (neat) 1750, 1735, 1645, 975, 920 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.62. Found: C, 68.57; H, 8.87. bp 112–115 °C (2 mmHg).

1-Vinylcyclohexyl acetoacetate (**17**): ^1H NMR (CCl_4, 60 MHz) δ 1.20–2.30 (m, 10 H), 1.80–2.30 (s, 3 H), 2.22 (s, 2 H), 4.80–5.30 (m, 2 H), 6.05 (dd, J = 11 and 18 Hz, 1 H); IR (neat) 1740, 1720, 1645, 970, 930, 910 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.62. Found: C, 68.75; H, 8.71. bp 108–112 °C (2 mmHg).

Allyl 2-Acetyl-2-(2-propenyl)-4-pentenoate (9). A mixture of allyl acetoacetate (4.26 g, 30 mmol), allyl bromide (12 g, 0.1 mmol), and K_2CO_3 (13.8 g, 0.1 mol) in acetone (60 mL) was refluxed for 12 h. After the solvent was removed by evaporation, water was added to the residue, and the mixture was extracted with CH_2Cl_2. Distillation of the crude product gave pure **9** (5.44 g, 82%): ^1H NMR (CCl_4, 60 MHz) δ 2.00 (s, 3 H), 2.53 (d, J = 6 Hz, 4 H), 4.55 (d, J = 5 Hz, 4.70–6.20 (m, 9 H); IR (neat) 1750,

1720, 1650, 1450, 1370, 1285, 1150, 1060, 1000, 930 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16. Found: C, 70.23; H, 8.22. bp 98–102 °C (5 mmHg).

Allyl 3-Oxononanoate (23). To a stirred solution of diallyl carbonate (5 g, 35.2 mmol) and NaH (50% in mineral oil, 2.5 g, 58.5 mmol) in benzene was added dropwise 2-octanone (3.0 g, 23.4 mmol), and the mixture was refluxed for 6 h. HCl (3 N) was added, and the organic layer was extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. After evaporation of the solvent, the residue was distilled in vacuo to give **23** (3.79 g, 79%): ^1H NMR (CCl_4, 60 MHz) δ 1.60–2.00 (m, 11 H), 2.45 (t, J = 6 Hz, 3 H), 3.29 (s, 2 H), 4.52 (d, J = 5 Hz, 2 H), 5.00–6.30 (m, 3 H); IR (neat) 2940, 1740, 1720, 1645, 1630, 995, 935 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.99; H, 9.41. bp 94 °C (3 mmHg).

Allyl 1-(Phenylmethyl)-3-methyl-2-oxocyclohexanecarboxylate (29). The allyl ester **29** was prepared from allyl 3-methyl-2-oxocyclohexanecarboxylate and benzyl bromide in 73% yield as a mixture of cis and trans isomers. Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.37; H, 7.74.

Allyl 1-Methyl-5-*tert*-butyl-2-oxocyclohexanecarboxylate (31). Sodium (50 mg) was dissolved in allyl alcohol (50 mL). Methyl 5-*tert*-butyl-2-oxocyclohexanecarboxylate (3.5 g, 16.5 mmol) was added to the solution, and the resultant mixture was refluxed for 6 h. After the reaction was complete (GLC analysis), most of the solvent was removed by distillation. HCl (3 N) was added to the residue at 0 °C, and the organic layer was extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a crude product, which was used for the alkylation without further purification.

A mixture of allyl 5-*tert*-butyl-2-oxocyclohexanecarboxylate (3.84 g), MeI (2.84 g, 20 mmol), and K_2CO_3 (4.14 g, 30 mmol) in acetone (100 mL) was refluxed for 24 h. After the reaction was complete, most of inorganic salts were removed by filtration. Then the solvent was removed under reduced pressure to give a mixture of cis and trans isomers **31a** and **31b**. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.58. Found: C, 71.68; H, 9.58.

The cis isomer **31a** (676 mg, 16%) and trans isomer **31b** (2.6 g, 63%) were isolated by column chromatography on silica gel.

31a: ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 21.5, 27.4, 32.2, 39.7, 40.3, 44.2, 56.3, 65.7, 118.9, 131.5, 172.8, 207.9.

31b: ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 20.8, 26.5, 27.4, 32.4, 36.7, 37.8, 41.8, 57.8, 65.7, 118.0, 132.1, 172.9, 209.9.

Diallyl 1,1-Cyclohexanedicarboxylate (47). A suspension of NaH (100 mg) and dimethyl 1,1-cyclohexanedicarboxylate (4.56 g, 20 mmol) in allyl alcohol (100 mL) was refluxed for 24 h. After the reaction was complete, diallyl 1,1-cyclohexanedicarboxylate (3.5 g, 75%) was isolated by distillation: ^1H NMR (CCl_4, 60 MHz) δ 1.30–1.75 (m, 6 H), 1.75–2.20 (m, 4 H), 4.40–4.70 (m, 4 H), 4.95–5.50 (m, 4 H), 5.50–6.20 (m, 2 H); IR (neat) 3080, 2940, 1720, 1650, 1450, 995, 930 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.57; H, 7.79. bp 130–131 °C (2 mmHg).

Similarly diallyl butylmalonate (**52**) was prepared from diethyl butylmalonate: ^1H NMR (CCl_4, 60 MHz) δ 0.90 (t, J = 5.0 Hz, 3 H), 1.10–1.60 (m, 4 H), 1.60–2.10 (m, 2 H), 3.25 (t, J = 6.8 Hz, 1 H), 4.50 (d, J = 7.0 Hz, 4 H), 4.90–5.40 (m, 4 H), 5.45–6.20 (m, 2 H); IR (neat) 3150, 2930, 1740, 1640, 990, 930 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.17; H, 8.34.

Preparation of Allyl Methyl Cyclohexane-1,1-dicarboxylate (50). A solution of *n*-butyllithium in hexane (1.55 N, 20 mL, 30 mmol) was added dropwise to a solution of diisopropylamine (3 g, 40 mL, 30 mmol) in THF (100 mL) at 0 °C under nitrogen. After addition was complete, the solution was cooled to −78 °C, and then a solution of methyl cyclohexanecarboxylate (2.84 g, 20 mmol) in THF (20 m) was added dropwise. The resultant mixture was stirred for 1 h, and a solution of allyl chloroformate (3.62 g, 30 mmol) in THF (20 mL) was added in one portion. The mixture was allowed to warm to 25–30 °C and then stirred for 1 h. After the reaction was complete (GLC analysis), the reaction mixture was diluted with CH_2Cl_2 and washed with NH_4Cl solution and brine. **50** was isolated by distillation (4.0 g, 90%): ^1H NMR (CCl_4, 60 MHz) δ 1.40–1.70 (m, 6 H), 1.70–2.10 (m, 4 H), 3.65 (s, 3 H), 4.45–4.70 (m, 2 H), 5.00–5.50 (m, 2 H), 5.50–6.25 (m, 1 H); IR (neat) 2940, 2860, 1730, 1645, 1450, 990, 935 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.7; H, 8.02. Found: C, 63.96; H, 8.07. bp 78–79 °C (1 mmHg).

Allyl 2-Butyl-2-cyanohexanoate (55). **55** was prepared by the dialkylation of allyl cyanoacetate (6.25 g, 50 mmol) with *n*-butyl iodide (27.6 g, 150 mmol) using K_2CO_3 (34.5 g, 250 mmol) in boiling acetone (100 mL) in 86% yield after distillation: ^1H NMR (CCl_4, 60 MHz) δ 0.65–1.05 (m, 6 H), 1.05–1.55 (m, 8 H), 1.55–2.20 (m, 4 H), 4.40–4.80 (m, 2 H), 4.85–5.45 (m, 2 H), 5.45–6.15 (m, 1 H); IR (neat) 2930, 2850, 2230, 1740, 1640, 1450, 990, 935 cm^{-1}. Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.86; H, 9.71; N, 5.81.

Similarly **58** was prepared by the monoalkylation of allyl cyanoacetate (6.25 g, 50 mmol) with *n*-butyl iodide (9.2 g, 50 mmol) using K_2CO_3 (6.9 g, 50 mmol) in boiling acetone (100 mL) in 83% yield after distillation: ^1H NMR (CCl_4, 60 MHz) δ 0.70–1.10 (m, 3 H), 1.10–1.60 (m, 4 H), 1.60–2.10 (m, 2 H), 3.30 (t, J = 6.5 Hz, 1 H), 4.42 (d, J = 5 Hz, 2 H), 4.95–5.40 (m, 2 H), 5.45–6.15 (m, 1 H); IR (neat) 2950, 2850, 2240, 1745, 1645, 1450, 990, 935 cm^{-1}. Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.42; H, 8.36; N, 7.87.

Allyl 2-Nitro-2-propylpentanoate (61). A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (260 mg, 0.5 mmol), PPh_3 (520 mg, 2 mmol), methyl nitroacetate (5.95 g, 50 mmol), and allyl methyl carbonate (13.9 g, 120 mmol) in dry THF (50 mL) was stirred for 6 h at 25–30 °C under argon. After the reaction was complete, the resultant mixture was filtered through Florisil. Methyl 2-allyl-2-nitro-4-pentenoate (8.24 g, 89%) was isolated by distillation. Then the diallylated product was converted to **61** by hydrogenation (H_2, Pd/C) and transesterification: ^1H NMR (CCl_4, 60 MHz) δ 0.70–1.80 (m, 10 H), 1.80–2.23 (m, 4 H), 4.45–4.60 (m, 2 H), 4.90–5.35 (m, 2 H), 5.40–6.05 (m, 1 H); IR (neat) 2970, 2890, 1760, 1670, 1650, 1550, 1470, 935 cm^{-1}; bp 80 °C (1 mmHg).

General Procedure for the Palladium-Catalyzed Decarboxylation–Allylation of Allyl β-keto Carboxylates (Table I). A solution of allyl β-keto carboxylate (10 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), and PPh_3 (104 mg, 0.4 mmol) in dry THF (20 mL) was refluxed under argon. Then the allylated product was isolated by distillation or column chromatography on silica gel.

4-(*E*)-Methyl-5-hepten-2-one (**8**): ^1H NMR (CCl_4, 60 MHz) δ 0.95 (d, J = 6 Hz, 3 H), 1.60 (d, J = 4 Hz, 3 H), 1.98 (s, 3 H), 5.10–5.40 (m, 2 H); IR (neat) 1710, 960 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.15; H, 11.18. Found: C, 76.02; H, 11.15.

3,3-Diallyl-5-hexen-2-one (**10**). ^1H NMR (CCl_4, 60 MHz) δ 1.98 (s, 3 H), 1.90–2.40 (m, 8 H), 4.70–6.00 (m, 9 H); IR (neat) 1700, 1638, 1435, 1372, 1200, 1010, 940 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O$: C, 80.45; H, 10.18. Found: C, 80.45; H, 10.30.

6-Phenyl-2-(3-phenyl-2-propenyl)-5-hexen-3-one (**13**). ^1H NMR ($CDCl_3$, 90 MHz) δ 2.16 (s, 3 H), 2.20–2.60 (m, 2 H), 2.60–2.85 (m, 1 H), 6.09 (dt, J = 15.8, 6.6 Hz, 2 H), 6.43 (d, J = 15.8 Hz, 2 H), 7.10–7.50 (m, 10 H); IR (neat) 3020, 2900, 1710, 1595, 1495, 960, 730, 685 cm^{-1}.

5,10-Undecadien-2-one (**15**): ^1H NMR (CCl_4, 60 MHz) δ 1.10–1.80 (m, 2 H), 1.98 (s, 3 H), 1.80–2.60 (m, 8 H), 4.70–5.20 (m, 2 H), 5.20–6.00 (m, 3 H); IR (neat) 2900, 1705, 1640, 1160 cm^{-1}.

1-Undecen-5-one (**24**): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.88 (t, J = 6.2 Hz, 3 H), 1.00–1.80 (m, 8 H), 2.00–2.69 (m, 6 H), 4.80–5.20 (m, 2 H), 5.72 (ddt, J = 16.8, 10.8, and 6.3 Hz, 1 H); IR (neat) 2950, 1710, 1640, 990, 105 cm^{-1}.

4-Allyl-1-undecen-5-one (**25**): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.88 (t, J = 5.9 Hz, 3 H), 1.00–1.70 (m, 8 H), 2.00–2.80 (m, 7 H), 4.80–5.20 (m, 4 H), 5.71 (ddt, J = 17.5, 9.0, and 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.0, 22.5, 23.3, 28.9, 31.7, 35.4, 42.9, 51.3, 116.9, 135.4, 212.9; IR (neat) 2920, 2705, 2640, 995, 915, 720 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.97; H, 11.50.

3-Allyl-2-octanone (**26**): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.87 (t, J = 5.9 Hz, 3 H), 1.26 (br s, 8 H), 2.11 (s, 3 H), 1.94–2.14 (m, 3 H), 5.72 (ddt, J = 17.5, 9.7, and 6.8 Hz, 1 H); IR (neat) 2920, 2850, 1710, 1640, 920, 725 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.56; H, 11.84.

2-Allyl-2-methylcyclopentanone (**28**): ^1H NMR ($CDCl_3$, 90 MHz) δ 1.01 (s, 3 H), 1.74–1.95 (m, 2 H), 2.10–2.32 (m, 2 H), 4.93–5.15 (m, 2 H), 5.49–6.02 (m, 1 H); IR (neat) 3065, 2960, 1740, 1640 cm^{-1}.

2-Allyl-2-(phenylmethyl)-6-methylcyclohexanone (**30**, mixture of diastereomers): ^1H NMR ($CDCl_3$, 90 MHz) δ 1.03/1.10 (d, J = 7.1 Hz, 3 H), 1.20–2.02 (m, 9 H), 2.82/2.88 (s, 2 H), 4.80–5.20

(m, 2 H), 5.40–6.00 (m, 1 H), 6.67–7.40 (m, 5 H). Anal. Calcd for $C_{17}H_{22}O$: C, 84.24; H, 9.14. Found: C, 84.31; H, 9.23.

Palladium-Catalyzed Reaction of 17 in the Presence of NaH in *t*-BuOH. A mixture of 17 (420 mg, 2 mmol), NaH (100 mG), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), and PPh_3 (104 mg, 0.4 mmol) in *t*-BuOH (20 mL) was stirred for 4 h at 50 °C. After the reaction was complete (TLC and GLC analyses), the reaction mixture was neutralized and extracted with CH_2Cl_2. Then pure 18 (169 mg, 51%) was isolated by column chromatography on silica gel.

General Procedure for the Palladium-Catalyzed Decarboxylation–Allylation of α-Substituted Allyl Cyanoacetates, Malonates, and Nitroacetate (Table II). A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (26 mg, 0.05 mmol) an dppe (40 mg, 0.1 mmol) in dry DMF (3 mL) was stirred for 10 min at 20–25 °C under argon. To this solution, a solution of allyl ester (1 mmol) in dry DMF (0.5 mL) was added, and the resultant solution was stirred under argon. After the reaction was complete (TLC and/or GLC anaylses), the allylated product was isolated by column chromatography on silica gel.

Allyl 1-allylcyclohexanecarboxylate (48): ^1H NMR ($CDCl_3$, 90 MHz) δ 1.00–1.78 (m, 10 H), 2.22 (d, J = 12 Hz, 2 H, 4.58 (d, J = 5.4 Hz, 2 H), 5.00–5.42 (m, 4 H), 5.46–6.18 (m, 2 H); IR (neat) 2980, 1730, 1640, 1450, 990, 930 cm^{-1}.

Methyl 1-allylcyclohexanecarboxylate (51): ^1H NMR (CCl_4, 60 MHz) δ 0.70–2.00 (m, 10 H), 2.11 (d, J = 7 Hz, 2 H), 3.52 (s, 3 H), 4.60–5.00 (m, 1 H), 5.00–5.60 (m, 1 H); IR (neat) 2900, 2850, 1725, 1640, 1450, 1200, 1140 cm^{-1}.

Allyl 2-allylhexenoate (53): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.88 (t, J = 5.7 Hz, 3 H), 1.04–1.80 (m, 6 H), 2.00–2.60 (m, 3 H), 4.76 (d, J = 6.5 Hz, 2 H), 4.90–5.44 (m, 4 H), 5.44–6.12 (m, 2 H); IR (neat) 3180, 2940, 1730, 1640, 1450, 995, 920 cm^{-1}.

5-Allyl-5-cyanononane (56): ^1H NMR ($CDCl_3$, 90 MHz) δ 1.00–1.78 (m, 10 H), 2.22 (d, J = 12.0 Hz, 2 H), 4.58 (d, J = 5.4 Hz, 2 H), 5.00–5.42 (m, 4 H), 5.46–6.18 (m, 2 H); IR (neat) 2980, 1730, 1640, 1450, 990, 930 cm^{-1}.

4-Cyano-1-octene (59): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.70–1.10 (m, 3 H), 1.10–1.80 (m, 6 H), 2.10–2.70 (m, 3 H), 5.12 (d, J = 17 Hz, 2 H), 5.48–6.10 (m, 1 H); IR (neat) 3080, 2950, 2240, 1640, 1460, 990, 920 cm^{-1}.

4-Allyl-4-nitroheptane (62): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.80–1.48 (m, 10 H), 1.72–2.04 (m, 4 H), 2.66 (d, J = 7.2 Hz, 2 H), 4.96–5.35 (m, 2 H), 5.32–5.88 (m, 1 H); IR (neat) 3070, 2960, 1640, 1550, 1460, 990, 920 cm^{-1}.

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Alkylation of Pentaerythritol by Phase-Transfer Catalysis. 3. Influence of the Tetrahedral Structure of Pentaerythritol on the Rate and Selectivity of the Phase-Transfer-Catalyzed Reaction

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The rates and selectivity of the phase-transfer-catalyzed etherification of pentaerythritol [2,2-bis(hydroxymethyl)-1,3-propanediol] and ethylenetetramethanol [2,3-bis(hydroxymethyl)-2-butene-1,4-diol] have been compared under similar phase-transfer alkylation conditions. The results described herein clearly indicate that the tetrahedral structure of pentaerythritol explains the successful alkylation results pointed out in previous papers.

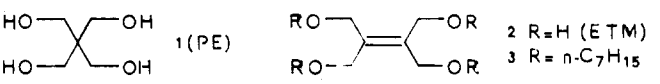
In our previous papers, we have discussed the selectivity of the alkylation of pentaerythritol[1] (PE) and provided an explanation for the formation of a mixture of tri- and tetraethers. The role of the solubility of the phase-transfer catalyst and the excess of sodium hydroxide, which are the key factors for the completion of this PTC reaction, were also reported.[2]

However, no explanation has been given why such a hydrophilic polyalcohol reacts so easily and so rapidly under phase-transfer conditions.[3]

Recently, we have had an opportunity[4] to develop a new synthetic route to the 2,3-bis(hydroxymethyl)-2-butene-1,4-diol (2) (ETM), a tetraalcohol with four primary hydroxyl functions but without the tetrahedral spatial conformation of the CH_2OH groups of PE (Chart I).

In the present work, we have compared the selectivity and the rates of formation of *n*-heptyl ethers for these two

Chart I



polyalcohols under PTC conditions.

Results and Discussion

Alkylation of **2** by *n*-heptyl bromide was accomplished with a large excess of sodium hydroxide (80 equiv) and tetrabutylammonium bromide as the catalyst. By monitoring the reaction by GC, it was first observed that the reaction was very slow. After 2 h, the organic phase was composed of only 5% of the tetra-*n*-heptyl ether of ETM (**3**) and 34% of di-*n*-heptyl ether (Figure 1).

The presence of di-*n*-heptyl ether is fully consistent with the hydrolysis of the halide by the hydroxide anions in the organic phase.[5] The newly formed 1-heptanol is then transformed into the symmetrical ether by a classical PTC process.[6]

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