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2-Allylisourea as an Effective Agent for Direct α-Allylation of Ketone and Aldehyde Assisted by Palladium(0) under Neutral Conditions

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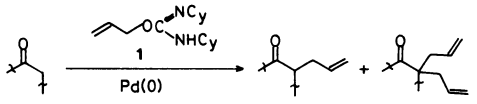
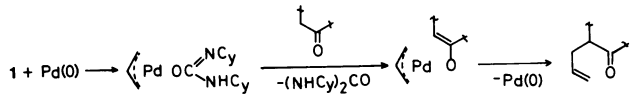
Direct α-allylation of a variety of ketones and aldehydes with 2-allylisourea took place in the presence of a catalytic amount of a palladium(0) complex under neutral and mild conditions. Scope and limitations of this novel method have been investigated.

The palladium-assisted allylation of active hydrogen compounds of pK_a's 10—17 is known to take place smoothly with a variety of allylic compounds,[1a] i.e., esters,[1b] ethers,[1b] alcohols,[1b] amines,[1b] sulfones,[1c] ammonium halides,[1d] sulfonium halides,[1d] nitro derivatives,[1e] and phosphates.[1f] The reaction pathway via π-allylpalladium intermediates is widely accepted.[1a] Usually the reaction is carried out under basic conditions to convert the active hydrogen compounds into their conjugate bases. However alkali metal enolates derived from ketones tend not to readily undergo this allylation.[2] Several improvement have been made including the change of the palladium catalyst[3] and metal enolates used.[4] Recently decarboxylative α-allylation of ketones under neutral conditions using allyl keto carboxylates and allyl enol carbonates have also been exploited.[5]

2-Alkylisourea can be used as the alkylating agent[6] for active hydrogen compounds such as hydrogen chloride, carboxylic acids, phenols, and imides. 2-Allylisourea is employed as an agent for the palladium-catalyzed allylation of imides[6f] and amides.[6g] Previously, we reported briefly that 2-allyl-1,3-dicyclohexylisourea (**1**) was an effective agent for



α-allylation of simple ketones.[7] That is the first example of the direct α-allylation of ketone assisted by palladium(0) under neutral conditions. A likely mechanism is as follows. The isourea **1** oxidatively adds to palladium(0) to afford a π-allylpalladium complex and the isourea anion. The anion thus formed is basic enough to abstract an α-proton of a ketone to produce the ketone enolate. Then the enolate attacks the π-allyl group on the palladium to afford the observed product.



In this paper, we report the extension of this method to a variety of ketones and aldehydes and also describe the related reactions.

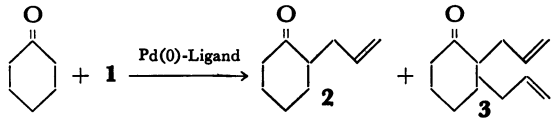
Results and Discussion

2-Allylic-substituted isoureas were prepared from allylic alcohols and dicyclohexylcarbodiimide (DCC) in the presence of a catalytic amount of copper(I) chloride.[8] The allylation reaction was carried out simply by mixing a substrate (1.0 equiv) and an allylic-substituted isourea (1.0 equiv) in the presence of a palladium(0) complex combined with PPh_3 or $Ph_2PCH_2CH_2PPh_2$ (dppe) as the catalyst.

α-Allylation of Ketone. Initially, several reaction parameters were examined using cyclohexanone as a probe for α-allylation with **1**. The results are shown in Table 1. Allylation occurred selectively toward monoallylation in tetrahydrofuran (THF), 1,4-dioxane, diethylene glycol dimethyl ether (diglyme), benzene, and acetonitrile, but the yields were modest. The reaction proceeded efficiently in dipolar, aprotic solvents, i.e., dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPT), and *N,N*-dimethylformamide (DMF). Although monoallylation was main in these solvents, considerable diallylation also took place. This effect of solvent was similar to that observed usually in the alkylation of the metal enolate of a ketone.[9]

The effect of ligand was examined in DMF solvent. Tributylphosphine completely suppressed the reaction. A moderate yield toward monoallylation resulted with triphenylphosphine as ligand. The allylation took place efficiently by the use of ditertiary phosphines [$R_2P(CH_2)_nPR_2$; R=Ph (n= 2, 3, 4), R=Me (n=2)]. Substantial diallylation occurred at the same time. The diarsine ligand $Ph_2As(CH_2)_2AsPh_2$ afforded a catalytically less active species. The effectiveness of the bidentate phosphine ligand has been demonstrated in the palladium-catalyzed allylation.[5c,10] The effect is ascribed to its tendency to generate a cationic (π-allyl)palladium intermediate which is more active than the neutral

Table 1. Allylation of Cyclohexanone with **1**[a]



Solvent	Ligand	Temp °C	Time h	Product yield/%[b] 2	3
THF	PPh_3	r.t.	5	13	0
	PPh_3	reflux	4 (2)[d]	37 (56)[d]	0 (5)[d]
	dppe	reflux	3	41	3
1,4-Dioxane	PPh_3	reflux	2	20	0
Diglyme[c]	PPh_3	60	1	13	0
Benzene	PPh_3	r.t.	48	9	0
Acetonitrile	PPh_3	r.t.	3	9	0
	PPh_3	60	5	37	10
	dppe	r.t.	3	15	0
HMPT	dppe	r.t.	1	56	42
DMSO	PPh_3	r.t.	4	78	22
	dppe	r.t.	0.25	65	35
DMF	PPh_3	r.t.	15	40	6
	PBu_3	60	3	0	0
	$Me_2P(CH_2)_2PMe$	r.t.	0.25	20	42
	$Ph_2P(CH_2)_nPPh_2$				
	$n=2$(dppe)	0	5	61	30
		r.t.	1	67	32
	$n=3$	r.t.	1	63	37
	$n=4$	r.t.	1	67	33
	$Ph_2As(CH_2)_2AsPh_2$	60	3	15	0

a) General procedure A. b) By GLC based on **1**. c) Diethylene glycol dimethyl ether. d) With addition of lithium acetate.

one toward nucleophilic reactions.[5c,11]

Noteworthy is the inclination of THF as a solvent to afford a monoallylation product although the yield is unsatisfactory in general. In order to increase monoallylation, the effects of added inorganic salts, i.e., lithium acetate, sodium acetate, and lithium bromide, were examined with a [$Pd(PPh_3)_3$] catalyst. Addition of lithium acetate (0.16 equiv) afforded the monoallyl ketone in a significantly increasing yield. The formation of the diallyl ketone was only modest. In contrast, sodium acetate and lithium bromide did not gave influence respectably.

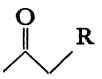
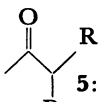
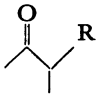
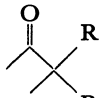
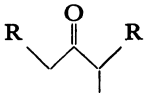
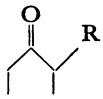
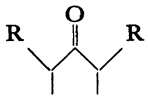
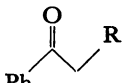
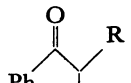
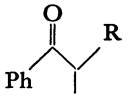
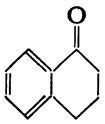
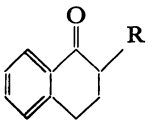
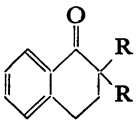
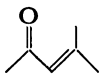
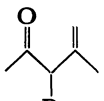
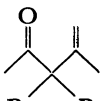
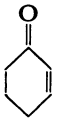
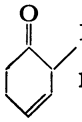
Enol trimethylsilyl ether from cyclohexanone also participated in the reaction involving 2-allylisourea. Somewhat slower reaction was observed compared to that of the original ketone with a slight increase in the mono/di ratio.

Table 2 shows the results of α-allylation of various ketones with **1** in DMF at ambient temperature in the presence of a palladium(0)–dppe catalyst. α,α-Diallylation predominated for acetone. Ethyl methyl ketone was allylated exclusively at the methylene carbon. These observations indicate that this allylation reaction involving **1** and ketone is controlled thermodynamically. Diethyl ketone afforded α-mono- and α,α'-diallylated products. Exclusive diallylation occurred for acetophenone. Propiophenone was selectively converted to the monoallylated product, whereas α-tetralone gave mainly the diallylation product. As a rule the allylation of simple ketones with **1** in DMF solvent by a palladium(0)–dppe catalyst afforded mainly or exclusively di- and trialkylated derivatives.

α,β-Unsaturated ketones, e.g., mesityl oxide and 2-cyclohexenone, reacted with **1** to produce α-allyl-β,γ-unsaturated ketones. Abstraction of the γ-hydrogen followed by allylation at the α-position will afford the observed products.

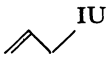
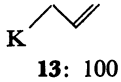
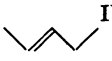
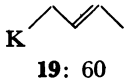
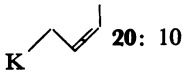
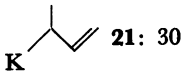
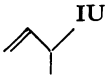
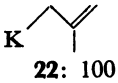
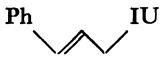
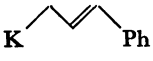
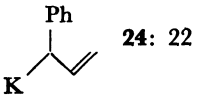
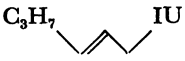
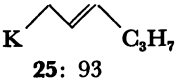
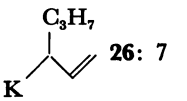
Usually α-alkylation of ketone with alkyl halide or sulfonate has been carried out using a strong base. Normally there are a number of obstacles; a) self-condensation; b) polyalkylation; c) non-regioselective alkylation for unsymmetrical ketones. The obstacle a) was completely eliminated by this neutral allylation means. Although palladium(0)–dppe was an effective catalyst in DMF solvent, polyallylation was usually accompanied. Effective monoallylation was accomplished only for propiophenone. A considerable improvement toward monoallylation of cyclohexanone was attained by the addition of

Table 2. Allylation of Ketone with **1**[a)]

Ketone	Time/h	Product yield/%[b)]
	5	 **4**: 8  **5**: 63
	3	   **6**: 51 **7**: 33 **8**: 7
	1	  **9**: 37 **10**: 43
	3	 **11**: 4  **12**: 96
	1	 **13**: 90
	1	 **14**: 17  **15**: 67
	24	 **16**: 45  **17**: 22
	5	 **18**: 31

a) General procedue B. R=allyl. b) Based on **1** by GLC.

Table 3. Allylation of Propiophenone with Allylic-Substituted Isourea[a)]

Isourea	Temp °C	Yield %[b)]	Product ratio %[c)]
	r.t.	90[d)]	 **13**: 100
	60	87	 **19**: 60
			 **20**: 10
			 **21**: 30
	60	75	**19**: 62, **20**: 10, **21**: 28
	60	77	 **22**: 100
	60	84	 **23**: 78
			 **24**: 22
	80	74	 **25**: 93
			 **26**: 7

a) General procedure C. IU=-OC(NHCy)(=NCy); Cy=cyclohexyl. K=PhCOCHCH$_3$. b) Isolated yield based on **1**. c) Determined by GLC. d) GLC yield.

lithium acetate with [Pd(PPh$_3$)$_3$] as the catalyst in THF solvent. Addition of lithium acetate was also effective to the other ketones. Thus, the monoallylation of diethyl ketone, acetophenone, and mesityl oxide increased from 5, 22, and 9% into 6, 34, and 20%, respectively (LiOAc, 0.2 equiv; [Pd(PPh$_3$)$_3$], THF, reflux, 2 h). As for the obstacle c), the regioselectivity of allylation is left to thermodynamic control.

Extension of this method was attempted intramolecularly to make a ring. The allylic isourea derived from 8-hydroxy-6-octen-2-one was submitted to the reaction at 100 °C for 2 h in DMF with a palladium(0)-dppe catalyst. However the only product isolated was 5,7-octadien-2-one (62% yield). Exclusive 1,4-elimination took place.

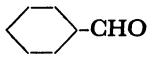
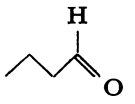
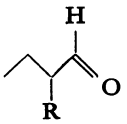
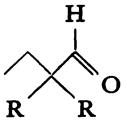
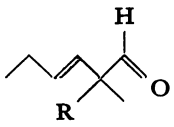
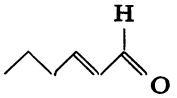
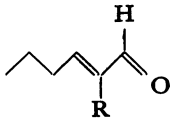
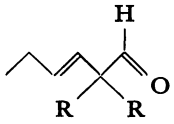
As propiophenone was selectively converted to the monoallylation product with 2-allylisourea, the regiochemistry with respect to the allylic group and the stereochemistry around the double bond were investigated with this ketone employing several 2-allylic-substituted isoureas. The results are summarized in Table 3. The less substituted site of the allylic system in the isourea reacted preferentially. The composition of the products from 2-(1-methyl-2-propenyl)isourea was analogous to that from (*E*)-2-butenylisourea. This indicates that the intermediate from each should be same. Initial (*E*)-geometry around the double bond was retained during the reaction except for the partial loss observed in the (*E*)-2-butenylisourea case. These results support the intermediacy of a π-allylpalladium species having the *syn*-configuration predoninantly.[12)]

Unfortunately, the allylation involving γ,γ-disubstituted allylic system, i.e., prenyl and geranyl, did not occur by a palladium(0)-dppe catalyst. Instead 1,4-elimination of the isoureas proceeded exclusively to afford isoprene and myrcene/ocimene, respectively. Several papers dealt with 1,4-elimination of allylic compounds to dienes by palladium catalysts.[13] For comparison, we studied the 1,4-elimination of geranyl- and nerylisourea in the absence of ketone in some detail. Geranylisourea was converted to myrcene, (*E*)-, and (*Z*)-ocimene in the ratio 24:58:18 (DMF, 120 °C, 5 h; total yield 67%). Another experiment in THF afforded the same products in the ratio 67:21:12 (r.t., 48 h; total yield 99%). Nerylisourea gave the trienes in the ratio 77:16:7 (DMF, 120 °C, 5 h; total yield 58%). Thus the selectivity of the 1,4-elmination reaction involving allylic isourea was comparable to that involving allylic acetate,[13a] but was not to be compared with that involving allylic acetate and organozinc compounds.[13c]

Allylation of Aldehyde. Results are shown in Table 4. Generally direct alkylation of aldehydes with alkyl halide is not possible, because base treatment of aldehydes normally gives rapid aldol condensations. Only those aldehydes bearing one α-hydrogen have been alkylated in moderate yield by the use of a phase-transfer catalyst.[14] The present method enabled the effective allylation of cyclohexanecarbaldehyde having one α-hydrogen. Diallylation was predominant for butanal with a [$Pd(PPh_3)_3$] catalyst in DMF as solvent. The results obtained here were remarkable because aldol condensation was not observed. The reaction of butanal in THF solvent was very sluggish to afford monoallylation product in a low yield (<7%). With dppe as ligand, both α,α-diallylation and aldol-type condensation of butanal took place in DMF solvent. α,β-Unsaturated aldehyde, i.e., (*E*)-2-hexenal, was also α,α-diallylated giving a β,γ-unsaturated aldehyde.

In order to get the scope and the limitations of this neutral allylation method, various types of compounds were subjected to the reaction. Simple esters, nitriles, and 1-alkynes did not participate in this allylation under the standard reaction conditions (Pd(0)-dppe, DMF, r.t., 3 h), the pK_a values for which are higher than 24. In contrast, methyl phenylacetate and phenylacetonitrile were reactive to afford 2-phenyl-4-pentenoate (91%) and 2-phenyl-4-pentenenitrile (27%)/ 2-allyl-2-phenyl-4-pentenenitrile (34%)/ *N*-allylphenylethenimine (29%), respectively. Thus the introduction of a phenyl group facilitated the reaction. Indene (pK_a 20) and fluorene (pK_a 23) were reactive to yield 3-allyl-1*H*-indene (61%, monoallylation followed by the double bond isomerization)/ 1,1-diallyl-1*H*-indene (14%, diallylation) and 9-allyl-9*H*-fluorene (43%)/ 9,9-diallyl-9*H*-fluorene (51%), respectively. In the suggested scheme described earlier, the isourea anion generated in situ functions as a base to abstract a proton from the nucleophile. Although the exact pK_a value for the conjugate acid of the isourea anion is not available from current literatures, it seems probable that the generation of the conjugate anion is not sufficient for the compound of pK_a value higher than 24.

Table 4. Allylation of Aldehyde with **1**[a]

Aldehyde	Ligand	Time / h	Product yield / %[b]
	dppe	1	 **27**: 92
	PPh_3	1	 Trace
			 **28**: 41
	dppe	2	**28**: 29
			 **29**: 41
	dppe	2	 **30**: 15
			 **31**: 61
	PPh_3	20	**30**: Trace, **31**: 63

a) General procedure D. R=allyl. b) GLC yield based on **1**.

Experimental

General. IR spectra were recorded on a Shimadzu IR 430 spectrometer. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-FX60Q and/or a Hitachi R-24A instrument using $CDCl_3$ as the solvent. The chemical shifts are expressed in parts per million downfield from the internal tetramethylsilane, and signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; m, multiplet. Mass spectra were recorded on a JEOL D-300 instrument. GLC analyses were performed on either Shimadzu GC-3AH, Shimadzu GC-6AM, or Hitachi 164 instrument, using the following columns: Column A, 20% Silicone DC-550, 3 m; Column B, 10% FFAP, 3 m; Column C, 20% Silicone GE SE-52, 2 m; Column D, 3% Silicone OV-1, 2 m.

Materials. 2-Allylic-substituted isoureas were prepared according to the published method.[8] An allylic alcohol (0.1 mol) and DCC (0.1 mol) were heated at 60—80 °C in the presence of a catalytic amount of copper(I) chloride (70 mg) till the absorptions of DCC disappeared in the IR spectrum. The reaction mixture was diluted with dicloromethane and filtered. The filtrate was washed with aqueous ammonia solution to remove the catalyst. The organic layer was washed with water, and dried over sodium sulfate. Although the isoureas thus obtained could be distilled under high vacuum (~10^{-4} mmHg*), they were sufficiently pure for the present allylation reactions.

General Procedure A for Allylation of Cyclohexanone with 1 (Table 1). Cyclohexanone (491 mg, 5 mmol) and **1** (1.32 g, 5 mmol) were reacted in a given solvent (10 cm^3) in the presence of a palladium catalyst under the conditions described in Table 1 under nitrogen. The palladium catalyst employed was $[Pd(PPh_3)_3]$[15] (89 mg, 0.1 mmol) or $[Pd(dba)_2]$[16] (58 mg, 0.1 mmol)-ligand (ligand/Pd=3 for the monodentate ones; ligand/Pd=1 for the bidentate ones). The reaction was analyzed by GLC (column A, 150 °C). Analytical samples were obtained by preparative GLC (column C, 140 °C).

2-Allyl-1-cyclohexanone (2): ^{1}H NMR δ=1.00—2.80 (m, 11H), 4.80—5.30 (m, 2H), 5.35—6.30 (m, 1H). ^{13}C NMR δ=212.17, 136.44, 116.11, 50.28, 42.02, 37.77, 33.37, 27.90, 24.94. IR (neat) 3080, 1710, 1640, 990, 910 cm^{-1}.

A Mixture of 2,2- and 2,6-Diallyl-1-cyclohexanone (3): ^{1}H NMR δ=1.08—2.65 (m, ca. 8H), 2.21—2.43 (m, ca. 4H), 4.70—5.18 (m, 4H), 5.36—6.18 (m, 2H). IR (neat) 3080, 1700, 1640, 990, 910 cm^{-1}.

Allylation of Cyclohexanone with 1 with Addition of Lithium Acetate. A mixture of the isourea **1** (5 mmol), cyclohexanone (5 mmol), $[Pd(PPh_3)_3]$ (0.1 mmol), and lithium acetate (53 mg, 0.8 mmol) was stirred for 2 h in refluxing THF (10 cm^3). GLC analysis (column A, 150 °C) showed that the yields of mono- and diallylcyclohexanone were 56 and 5%, respectively.

General Procedure B for Allylation of Ketones with 1 (Table 2). A DMF solution (10 cm^3) of a ketone (5 mmol) and **1** (1.32 g, 5 mmol) was stirred for 1—24 h at an ambient temperature in the presence of $[Pd(dba)_2]$ (58 mg, 0.1 mmol)-dppe (40 mg, 0.1 mmol) under nitrogen. The reaction was analyzed by GLC. Analytical samples were obtained by either preparative GLC (G) or column chromatography (C) on silica gel according to general procedure C. The products **4**,[17] **11**,[18] and **13**[18] were identified by the comparison of their ^{1}H NMR and IR spectra with those reported earlier.

3-Allyl-5-hexen-2-one (5): G (column A, 160 °C). ^{1}H NMR δ=2.18 (s, 3H), 2.20—2.40 (m, 4H), 2.40—2.92 (m, 1H), 4.80—5.18 (m, 4H), 5.38—6.02 (m, 2H). IR (neat) 1718, 1640, 990, 918 cm^{-1}.

3-Methyl-5-hexen-2-one (6): G (column A, 160 °C). ^{1}H NMR δ=1.07 (d, 3H), 2.09 (s, 3H), 1.93—3.00 (m, 3H), 4.80—5.45 (m, 2H), 5.39—6.09 (m, 1H). IR (neat) 3090, 1708, 1640, 985, 910 cm^{-1}.

3-Allyl-3-methyl-5-hexen-2-one (7): G (column A, 160 °C). ^{1}H NMR δ=1.08 (s, 3H), 2.06 (s, 3H), 2.20—2.35 (m, 4H), 4.80—5.18 (m, 4H), 5.36—6.07 (m, 2H). IR (neat) 3090, 1708, 1640, 990, 910 cm^{-1}.

4-Methyl-1,8-nonadien-5-one (8): G (column A, 160 °C). ^{1}H NMR δ=0.99 (d, 3H), 1.80—2.86 (m, 7H), 4.78—5.20 (m, 4H), 5.34—6.10 (m, 2H). IR (neat) 3080, 1708, 1640, 990, 910 cm^{-1}. MS (70 eV) *m/z* 152 (M^+), 109, 83, 69, 67, 55.

4-Methyl-6-hepten-3-one (9): G (column A, 150 °C). ^{1}H NMR δ=1.08 (d, 3H), 1.10 (t, 3H), 2.54 (q, 2H), 2.05—2.96 (m, 3H), 4.81—5.20 (m, 2H), 5.40—6.25 (m, 1H). ^{13}C NMR δ=214.17, 135.76, 116.56, 47.74, 34.45, 32.24, 16.17, 7.69. IR (neat) 3080, 1710, 1640, 990, 910 cm^{-1}.

4,6-Dimethyl-1,8-nonadien-5-one (10): G (column A, 150 °C). ^{1}H NMR δ=1.03 (dd, 6H), 1.56—2.58 (m, 6H), 4.80—5.16 (m, 4H), 5.32—6.03 (m, 2H). IR (neat) 3070, 1708, 1640, 990, 910 cm^{-1}.

1-Phenyl-2-allyl-4-penten-1-one (12): C (benzene). ^{1}H NMR δ=2.05—2.85 (m, 4H), 3.75 (qu, 1H), 4.77—5.20 (m, 4H), 5.30—6.07 (m, 2H), 7.19—8.00 (m, 5H). IR (neat) 3080, 1680, 1640, 1580, 1445, 990, 910 cm^{-1}.

2-Allyl-3,4-dihydro-1(2*H*)-naphthalenone (14): C (hexane/ethyl acetate=20). ^{1}H NMR δ=1.76—2.84 (m, 5H), 2.88—3.25 (dd, 2H), 4.89—5.41 (m, 2H), 5.49—6.20 (m, 1H), 7.10—8.23 (m, 4H). IR (neat) 3070, 1680, 1640, 990, 910 cm^{-1}.

2,2-Diallyl-1(2*H*, 3*H*, 4*H*)-naphthalenone (15): C (hexane/ethyl acetate=20). ^{1}H NMR δ=2.13 (t, 2H), 2.50 (t, 4H), 3.09 (t, 2H), 4.86—5.51 (m, 4H), 5.55—6.29 (m, 2H), 7.08—8.29 (m, 4H). IR (neat) 3070, 1675, 1640, 990, 910 cm^{-1}.

3-Isopropenyl-5-hexen-2-one (16): G (column C, 140 °C). ^{1}H NMR δ=1.64 (m, 3H), 2.10 (s, 3H), 2.40 (t, 2H), 3.18 (t, 1H), 4.76—5.18 (m, 4H), 5.36—6.08 (m, 1H). IR (neat) 3070, 1710, 1640, 990, 890 cm^{-1}. MS (70 eV) *m/z* 138 (M^+), 97, 95, 81, 67.

3-Allyl-3-isopropenyl-5-hexen-2-one (17): G (column C, 140 °C). ^{1}H NMR δ=1.64 (m, 3H), 2.02 (s, 3H), 2.43 (d, 4H), 4.74—5.40 (m, 6H), 5.44—6.08 (m, 2H). IR (neat) 1710, 1640, 990, 890 cm^{-1}. MS (70 eV) *m/z* 178 (M^+), 136, 93, 83, 81, 55.

2-Allyl-3-cyclohexen-1-one (18): G (column C, 140 °C). ^{1}H NMR δ=1.80—2.75 (m, 7H), 4.75—5.20 (m, 2H), 5.21—6.21 (m, 3H). IR (neat) 3090, 1710, 1640, 990, 912 cm^{-1}. MS (70 eV) *m/z* 136 (M^+), 108, 80, 79, 68.

General Procedure C for Allylation of Propiophenone with Allylic-Substituted Isourea (Table 3). A DMF solution (10 cm^3) of propiophenone (671 mg, 5 mmol) and an allylic-substituted isourea (5 mmol) was stirred for 1 h in the presence of $[Pd(dba)_2]$ (58 mg, 0.1 mmol)-dppe (40 mg, 0.1 mmol) at a given temperature under nitrogen. After being cooled to room temperature, the reaction mixture was diluted with diethyl ether and the *N,N'*-dicyclohexylurea that was formed was filtered off. The filtrate was washed with saturated NaCl solution. The organic layer was dried on $MgSO_4$ and the solvent was removed in vacuo. The products were isolated by column chromatography on silica gel (hexane/ethyl acetete=20). The isomer ratio was determined by GLC.

Reaction of Propiophenone with (*E*)-2-Butenylisourea: A Typical Procedure. Propiophenone (671 mg, 5 mmol) and (*E*)-2-butenylisourea (1.39 g, 5 mmol) were stirred in DMF (10 cm^3) at 60 °C for 1 h under nitrogen in the presence of

* 1 mmHg=133.322 Pa.

[Pd(dba)$_2$] (58 mg, 0.1 mmol)-dppe (40 mg, 0.1 mmol). The products were obtained according to the general procedure C after purification by column chromatography on silica gel eluting with hexane–ethyl acetate (20:1). Yield 818 mg (87%). Samples for spectroscopic analysis of the isomers **19**, **20**, and **21** were obtained by preparative GLC (column B, 160 °C).

(*E*)-2-Methyl-1-phenyl-4-hexen-1-one (19): G. ^{1}H NMR δ=1.16 (d, 3H), 1.60 (d, 3H), 1.90—2.70 (m, 2H), 3.10—3.80 (m, 1H), 5.20—5.60 (m, 2H), 7.26—8.00 (m, 5H). IR (neat) 1680, 965 cm^{-1}. MS *m/z* (70 eV) 188 (M$^+$), 173, 145, 134, 106, 105, 77.

(*Z*)-Isomer (20): G. This was isolated in an impure state, being contaminated by the (*E*)-isomer. ^{1}H NMR δ=1.20 (d, 3H), 1.60 (d, 3H), 2.12—2.56 (m, 2H), 3.20—3.72 (m, 1H), 5.24—5.56 (m, 2H), 7.17—8.04 (m, 5H). IR (neat) 1680 cm^{-1}. MS *m/z* (70 eV) 188 (M$^+$), 105, 77.

2,3-Dimethyl-1-phenyl-4-penten-1-one (21): G. ^{1}H NMR δ=1.00 (d, 3H), 1.12 (d, 3H), 2.28—2.96 (m, 1H), 3.04—3.80 (m, 1H), 4.76—5.16 (m, 2H), 5.40—6.12 (m, 1H), 7.18—8.05 (m, 5H). IR (neat) 1680, 990, 910 cm^{-1}. MS (70 eV) *m/z* 188 (M$^+$), 134, 106, 105, 77.

2,4-Dimethyl-1-phenyl-4-penten-1-one (22): C (hexane/ethyl acetate=20). ^{1}H NMR δ=1.16 (d, 3H), 1.72 (s, 3H), 2.03—2.80 (m, 2H), 3.17 (q, 1H), 4.71 (m, 2H), 7.25—8.03 (m, 5H). IR (neat) 1685, 1655, 890 cm^{-1}. MS (70 eV) *m/z* 188 (M$^+$), 106, 105, 83, 77.

(*E*)-2-Methyl-1,5-diphenyl-4-penten-1-one (23): G (column D, 200 °C). ^{1}H NMR δ=1.16 (d, 3H), 1.96—2.92 (m, 2H), 3.16—3.80 (m, 1H), 6.08 (dt, 1H), 6.36 (d, 1H), 6.92—8.04 (m, 10H). IR (neat) 1680, 960 cm^{-1}. MS *m/z* (70 eV) 250 (M$^+$), 235, 117, 115, 105.

2-Methyl-1,3-diphenyl-4-penten-1-one (24): G (column D, 200 °C). ^{1}H NMR δ=1.24 (d, 3H), 3.60—3.96 (m, 2H), 4.68—5.28 (m, 2H), 5.60—6.18 (m, 1H), 6.88—8.08 (m, 10H). IR (neat) 1680, 990, 910 cm^{-1}. MS (70 eV) *m/z* 250 (M$^+$), 235, 117, 105, 77.

(*E*)-2-Methyl-1-phenyl-4-octen-1-one (25): G (column D, 160 °C). ^{1}H NMR δ=0.84 (t, 3H), 1.20 (d, 3H), 1.10—1.60 (m, 2H), 1.68—2.76 (m, 4H), 3.16—3.80 (m, 1H), 5.20—5.55 (m, 2H), 7.25—8.08 (m, 5H). IR (neat) 1680, 965 cm^{-1}. MS *m/z* (70 eV) 216 (M$^+$), 173, 134, 106, 105, 77.

2-Methyl-1-phenyl-3-vinylhexan-1-one (26): G (column D, 160 °C). ^{1}H NMR δ=0.80 (t, 3H), 1.10 and 1.14 (d, 1.5H and d, 1.5H; due to the asymmetric carbon), 1.04—1.60 (m, 4H), 2.16—2.72 (m, 1H), 3.10—3.90 (m, 1H), 4.60—5.20 (m, 2H), 5.24—5.96 (m, 1H), 7.36—8.08 (m, 5H). IR (neat) 1680, 995, 910 cm^{-1}. MS (70 eV) *m/z* 216 (M$^+$), 173, 134, 105, 77.

General Procedure D for Allylation of Aldehydes with 1 (Table 4). A DMF solution (10 cm^3) of an aldehyde (5 mmol) and **1** (1.32 g, 5 mmol) was stirred for 1—20 h at an ambient temperature in the presence of [Pd(PPh$_3$)$_3$] (89 mg, 0.1 mmol) or [Pd(dba)$_2$] (58 mg, 0.1 mmol)-dppe (40 mg, 0.1 mmol) under nitrogen. The reaction was analyzed by GLC. Analytical samples were obtained by preparative GLC.

1-Allylcyclohexanecarbaldehyde (27): G (column C, 140 °C). ^{1}H NMR δ=1.10—2.01 (m, 8H), 2.15 (d, 2H), 4.80—5.22 (m, 2H), 5.26—6.07 (m, 1H), 9.44 (s, 1H). IR (neat) 3070, 1725, 1640, 990, 910 cm^{-1}.

2-Allyl-2-ethyl-4-pentenal (28): G (column C, 140 °C). ^{1}H NMR δ=0.85 (t, 3H), 1.58 (q, 2H), 2.27 (d, 4H), 4.85—5.33 (m, 4H), 5.35—6.14 (m, 2H), 9.42 (s, 1H). IR (neat) 3080, 1725, 1640, 990, 910 cm^{-1}.

(*E*)-2-Allyl-2-ethyl-3-hexenal (29): G (column C, 140 °C). ^{1}H NMR δ=0.82 (t, 3H), 0.98 (t, 3H), 1.65 (q, 2H), 1.81—2.31 (m, 2H), 2.37 (d, 2H), 4.81—5.26 (m, 2H), 5.30—6.07 (m, 3H), 9.30 (s, 1H). ^{13}C NMR δ=202.83, 135.70, 127.95, 118.38, 117.88, 36.79, 36.16, 26.19, 25.51, 13.72, 7.97. IR (neat) 3080, 1725, 1645, 990, 970, 910 cm^{-1}.

Reaction of (*E*)-2-Hexenal with 1: A Typical Procedure. (*E*)-2-Hexenal (491 mg, 5 mmol) and **1** (1.32 g, 5 mmol) were stirred for 2 h in DMF (10 cm^3) at an ambient temperature under nitrogen in the presence of [Pd(dba)$_2$] (58 mg, 0.1 mmol)-dppe (40 mg, 0.1 mmol). A mixture of the starting aldehyde, **30**, and **31** was obtained according to the general procedure C after chromatographic work-up on silica gel eluting with hexane–ethyl acetate (20:1). Samples for spectroscopic analysis of the product **30** and **31** were obtained by GLC (column C, 170 °C). Quantitative analyses were performed on GLC (column C, 170 °C).

(*E*)-2-Allyl-2-hexenal (30): ^{1}H NMR δ=0.95 (t, 3H), 1.22—1.87 (m, 2H), 2.45 (q, 2H), 3.00 (d, 2H), 4.73—5.21 (m, 2H), 5.32—6.19 (m, 1H), 6.53 (t, 1H), 9.36 (s, 1H). The chemical shift (δ=9.36) of the formyl proton indicated the presence of an (*E*)-double bond.[19] IR (neat) 3080, 1685, 1640, 990, 910 cm^{-1}. MS (70 eV) *m/z* 138 (M$^+$), 95, 81, 79, 67, 53.

(*E*)-2,2-Diallyl-3-hexenal (31): ^{1}H NMR δ=0.99 (t, 3H), 1.80—2.40 (m, 2H), 2.38 (d, 4H), 4.83—5.26 (m, 4H), 5.36—6.12 (m, 4H), 9.37 (s, 1H). IR (neat) 3080, 1725, 1640, 995, 975, 915 cm^{-1}. MS (70 eV) *m/z* 178 (M$^+$), 137, 93, 79, 67.

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