Novel Synthesis of α,β-Unsaturated Ketones by the Palladium-Catalyzed Arylation of Ketenes with Aroyl Chlorides or the Decarbonylative Cross-Condensation of Acyl Halides

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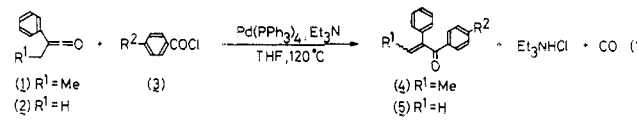
The reaction of alkylphenylketene with aroyl chlorides or the decarbonylative cross-condensation reaction of α-phenylacetyl chlorides with aroyl chlorides in the presence of triethylamine and a catalytic amount of a palladium complex gives α,β-unsaturated ketones in high yields. For example, reaction of ethylphenylketene with 4-methoxybenzoyl chloride catalyzed by $Pd(PPh_3)_4$ gives 1-(4-methoxyphenyl)-2-phenyl-2-buten-1-one in 86% yield. Reaction of 2-phenylbutyryl chloride with 4-methoxybenzoyl chloride catalyzed by $PdBr(Ph)(PPh_3)_2$ gives 1-(4-methoxyphenyl)-2-phenyl-2-buten-1-one in 97% yield by the decarbonylative cross-condensation.

Ketenes are very useful reagents for organic synthesis[1] and have been often postulated to be key intermediates in the transition metal catalyzed activation of carbon monoxide.[2] Several stoichiometric reactions of ketenes with organometallic compounds have been reported.[3] However, little is known about catalytic processes.[4] We intended to build up novel catalytic cycles via ketene–palladium complexes and have reported some palladium-catalyzed reactions of ketenes with various organic compounds; i.e., (1) reaction of diphenylketene with terminal acetylenes to give disubstituted acetylenes,[5] (2) reaction of ketenes with allylic acetates to give 1,3-dienes,[6] and (3) reaction of allylic carbonates to give α-allylated esters.[6] In the course of our study, we have found a novel palladium-catalyzed arylation reaction of alkylphenylketenes with aroyl chlorides to give α,β-unsaturated ketones.[7] This reaction lead us to the decarbonylative cross-condensation reaction of acyl halides and the preliminary results have been reported.[8] In this paper we report the scope and the details of the arylation reaction of ketenes with aroyl chlorides and the decarbonylative cross-condensation of acyl halides.

Results

(i) Arylation Reaction of Alkylphenylketenes with Aroyl Chlorides. Reaction of ethylphenylketene (**1**) or methylphenylketene (**2**) with aroyl chlorides (**3**) in the presence of triethylamine and a catalytic amount of tetrakis(triphenylphosphine)palladium gave a mixture of *E* and *Z* α,β-unsaturated ketones **4** or **5**, respectively (eq 1). The reaction proceeds at 120 °C in tetrahydrofuran accompanied by the formation of triethylammonium chloride



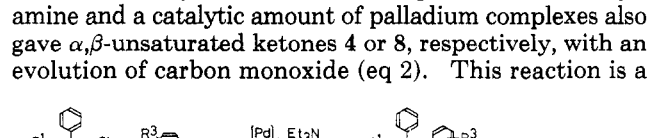
(1) R^1 = Me (2) R^1 = H (3) (4) R^1 = Me (5) R^1 = H

and an evolution of carbon monoxide. Results are shown in Table I. Benzoyl chloride (**3a**) reacted with ethylphenylketene to give a mixture of (*E*)- and (*Z*)-1,1-diphenyl-2-buten-1-one (**4a**) in 46% yield (*E*/*Z* = 3:2). 4-Methoxybenzoyl chloride (**3b**) and 4-methylbenzoyl chloride (**3c**) gave the corresponding ketones (**4b,c**) in high yields (runs 7 and 8). The yield of the product derived from 4-chlorobenzoyl chloride (**3e**) was lower (run 10). Benzoyl bromide offers no advantage over the chloride (run 2). Use of pyridine instead of triethylamine resulted in lower yield (run 3). Benzene and acetonitrile were not suitable solvents for this reaction (runs 4 and 5). When the reaction was performed in triethylamine, the yield of (**4a**) reduced to 22% (run 6). In the cases of low product yields, aroyl chlorides were recovered and 3,4-diphenyl-3-hexene and 1-phenyl-1-propene were produced as byproducts. When methoxybenzoyl chloride was used, 3,4-diphenyl-3-hexene was produced in 4% yield. In other cases, yields of 3,4-diphenyl-3-hexene were ca. 10%. Yields of 1-phenyl-1-propene were less than 2% in all cases.

The reaction of methylphenylketene (**2**) with **3b** gave 1-(4-methoxyphenyl)-2-phenyl-2-propen-1-one (**5b**) in 43% yield (run 11). In this reaction several uncharacterized byproducts were detected by GLC analysis; however, further identification was not performed.

Use of acid chlorides such as acetyl chloride, trimethylacetyl chloride, cyclohexylcarbonyl chloride, cinnamoyl chloride, or 2-furoyl chloride in place of **3** was unsucessful.

(ii) Decarbonylative Cross-Condensation Reaction of Acyl Halides. Reaction of alkylphenylacetyl chloride **6** or **7** with aroyl chlorides **3** in the presence of triethylamine and a catalytic amount of palladium complexes also gave α,β-unsaturated ketones **4** or **8**, respectively, with an evolution of carbon monoxide (eq 2). This reaction is a



(6) R^1 = Me, R^2 = H (7) R^1R^2 = $-(CH_2)_5-$ (3) (4) R^1 = Me, R^2 = H (8) R^1R^2 = $-(CH_2)_5-$

cross-condensation reaction between two kinds of acyl halides accompanied by decarbonylation and elimination of 2 mol of hydrogen chloride. The selectivity for the cross-condensation was excellent, and the ketones derived by homocondensation of acyl halides were not detected at all. Results are summarized in Tables II and III. 2-

(1) Brady, W. P. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; p 279.
(2) (a) For example, see: Bodbar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926. (b) Bodnar, T. W.; Crowford, E. J.; Cutler, A. R. *Organometallics* **1986**, *5*, 947.
(3) (a) Kinugasa, K.; Agawa, T. *Organomet. Chem. Synth.* **1972**, *1*, 427. (b) Baba, A.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1975**, *87*, 247. (c) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *152*, 255. (d) Herrmann, W. A.; Gimeno, J.; Weichmann, J. *J. Organomet. Chem.* **1981**, *213*, C26. (e) Hong, P.; Sonogashira, K.; Hagihara, N. *J. Organomet. Chem.* **1981**, *219*, 363. (f) Ungvary, F. *J. Chem. Soc., Chem. Commun.* **1984**, 824. (g) Musco, A.; Porzio, W.; Destri, S.; Gatti, G.; Grassi, A.; Longo, P. *J. Organomet. Chem.* **1986**, *301*, 237.
(4) (a) Hong, P.; Sonogashira, K.; Hagihara, N. *Tetrahedron Lett.* **1971**, 1105. (b) Hong, P.; Yamazaki, H.; Sonogashira, K. *Chem. Lett.* **1978**, 535.
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(6) (a) Mitsudo, T.; Kadokura, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1539. (b) Mitsudo, T.; Kadokura, M.; Watanabe, Y. *J. Org. Chem.* **1987**, *52*, 1695.
(7) Mitsudo, T.; Kadokura, M.; Watanabe, Y. *Tetrahedron Lett.* **1985**, *26*, 5143.
(8) Kadokura, M.; Mitsudo, T.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 252.

0022-3263/87/1952-3186$01.50/0

Table I. Arylation Reaction of Alkylphenylketenes with Aroyl Chlorides To Give α,β-Unsaturated Ketones[a]

run	ketene	ArCOCl	Solvent	product	yield,[b] %	Z:E[c]
1	Ph(Et)C=C=O (1)	C_6H_5COCl (3a)	THF	MeCH=C(Ph)COC_6H_5 (4a)	46	3:2
2	1	C_6H_5COBr	THF	4a	39	
3	1	3a	THF	4a	29[d]	
4	1	3a	benzene	4a	23	
5	1	3a	CH_3CN	4a	14	
6	1	3a	Et_3N	4a	22[e]	
7	1	4-$MeOC_6H_4COCl$ (3b)	THF	MeCH=C(Ph)COC_6H_4-4-OMe (4b)	86 (74)	2:3
8	1	4-MeC_6H_4COCl (3c)	THF	MeCH=C(Ph)COC_6H_4-4-Me (4c)	77 (60)	2:3
9	1	4-PhC_6H_4COCl (3d)	THF	MeCH=C(Ph)COC_6H_4-4-Ph (4d)	66 (32)	1:1
10	1	4-ClC_6H_4COCl (3e)	THF	MeCH=C(Ph)COC_6H_4-4-Cl (4e)	32 (30)	1:1
11	Ph(Me)C=C=O (2)	4-$MeOC_6H_4COCl$ (3b)	THF	CH_2=C(Ph)COC_6H_4-4-OMe (5b)	43	

[a] Ketene (1 mmol), aroyl chloride (1 mmol), Et_3N (2 mmol), $Pd(PPh_3)_4$ (0.03 mmol), solvent 2.5 mL, 120 °C, 5 h. [b] Determined by GLC using an internal standard. Isolated yields are given in parentheses. [c] Determined by ^1H NMR. [d] Pyridine (2 mmol) was used instead of Et_3N. [e] Et_3N (2.5 mL) was used as a solvent.

Table II. Cross-Condensation Reaction of 2-Phenylbutyryl Chloride with Aroyl Chlorides To Give α,β-Unsaturated Ketones[a]

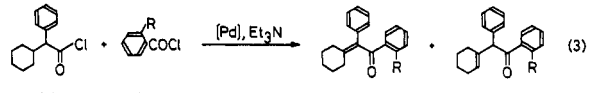
run	ArCOCl	[Pd][b]	product	temp, °C	yield,[c] %
1	C_6H_5COCl (3a)	A	MeCH=C(Ph)COC_6H_5 (4a)	120	46
2	3a	B	4a	120	73
3	3a	B	4a	140	95 (57)
4	4-$MeOC_6H_4COCl$ (3b)	A	MeCH=C(Ph)COC_6H_4-4-OMe (4b)	120	86 (70)
5	3b	B	4b	120	96
6	3b	B	4b	140	97
7	4-MeC_6H_4COCl (3c)	A	MeCH=C(Ph)COC_6H_4-4-Me (4c)	120	77 (60)
8	3c	B	4c	120	87
9	3c	B	4c	140	88
10	4-PhC_6H_4COCl (3d)	A	MeCH=C(Ph)COC_6H_4-4-Ph (4d)	120	66 (32)
11	3d	B	4d	120	89
12	3d	B	4d	140	94
13	4-ClC_6H_4COCl (3e)	A	MeCH=C(Ph)COC_6H_4-4-Cl (4e)	120	32
14	3e	B	4e	120	69
15	3e	B	4e	140	72 (55)
16	4-$NO_2C_6H_4COCl$ (3f)	A	MeCH=C(Ph)COC_6H_4-4-NO_2 (4f)	120	0
17	2-$MeOC_6H_4COCl$ (3g)	B	MeCH=C(Ph)COC_6H_4-2-OMe (4g)	140	62[d]
18	2-MeC_6H_4COCl (3h)	B	MeCH=C(Ph)COC_6H_4-2-Me (4h)	140	54[e]
19	3-MeC_6H_4COCl (3j)	B	MeCH=C(Ph)COC_6H_4-3Me (4j)	140	88 (71)
20	3-ClC_6H_4COCl (3k)	B	MeCH=C(Ph)COC_6H_4-3-Cl (4k)	140	43

[a] 2-Phenylbutyryl chloride (3 mmol), aroyl chloride (3 mmol), Et_3N (9 mmol), [Pd] (0.09 mmol), THF 9 mL, 5 h. [b] Palladium complex: A; $Pd(PPh_3)_4$; B, $PdBr(Ph)(PPh_3)_2$. [c] Determined by GLC using an internal standard. E:Z was almost 1:1 except runs 17 and 18. Isolated yields are given in parentheses. [d] E:Z = 5:1. [e] E:Z = 10:1.

Phenylbutyryl chloride (6) reacted with 3 to give 1,2-diphenyl-2-buten-1-one derivatives 4 as a mixture of E and Z isomers (E/Z = 1:1) (Table II). When $Pd(PPh_3)_4$ was employed as a catalyst, yields of ketones 4 were affected by the substituents in 3. Benzoyl chlorides with an electron-donating substituent at the para position gave the product in high yield in contrast to an electron-withdrawing one (runs 4, 7, 10, and 13). The same tendency was also observed in the reaction of the ketene with aroyl chlorides as described above. 4-Nitrobenzoyl chloride did not give the corresponding ketone at all (run 16).

Much greater yields were achieved by using bromophenylbis(triphenylphosphine)palladium(II) as a catalyst. With this catalyst, yield of the ketone 4 became higher than that in the reaction with $Pd(PPh_3)_4$ and formation of the byproduct such as 3,4-diphenyl-3-hexene was suppressed. For example, the yield of 4e increased from 32% to 69% (run 14). Further, at 140 °C para-substituted benzoyl chlorides 3a–e gave the products almost quantitatively regardless of the nature of substituents (runs 3, 6, 9, 12, and 15). Ortho- and meta-substituted benzoyl chlorides gave the corresponding ketones 4g,h,j,k in moderate to high yields. 2-Methoxybenzoyl chloride (3g) and 2-methylbenzoyl chloride (3h) gave the corresponding E isomer preferentially (E/Z = 5:1, 10:1, respectively).

The cross-condensation reaction using α-cyclohexylphenylacetyl chloride (7) gave α-cyclohexylidenebenzyl phenyl ketone derivatives (8) in high yields (Table III). The effects of substituents in aroyl chlorides 3 were negligibly small in contrast to those in the reactions of 2-phenylbutyryl chloride (6). Yields of the products were satisfactory even when $Pd(PPh_3)_4$ was used as a catalyst and amounts of byproducts were very small. The reactions of 2-methoxybenzoyl chloride (3g) or 2-chlorobenzoyl chloride (3i) gave a mixture of α,β- and β,γ-unsaturated ketones (eq 3). The ratios of 8g/8g′ and 8i/8i′ were 2/3 and 4/5, respectively.



(7) (3g) R=OMe (3i) R=Cl (8g) (8i) (8g′) (8i′) 8g/8g′ = 2/3 8i/8i′ = 4/5

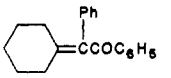
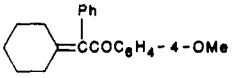
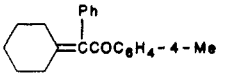
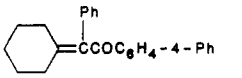
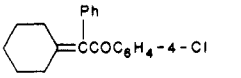
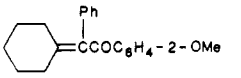
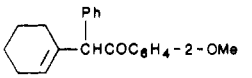
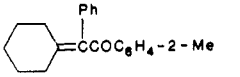
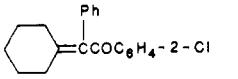
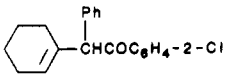
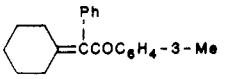
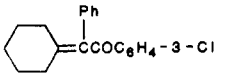
In this cross-condensation reaction, acid chlorides such as phenylacetyl chloride, acetyl chloride, and dichloroacetyl chloride which are precursors of monosubstituted or non-aryl-containing ketenes did not give the corresponding products.

The complexes $Pd(PPh_3)_4$ and $PdBr(Ph)(PPh_3)_2$ did not catalyze the condensation reaction of ketenes and other organic halides which do not have β-hydrogens, e.g., benzyl bromide, β-bromostyrene, 1-bromophenylacetylene, phenacyl bromide, and methyl chloroformate.

Discussion

The present two reactions are considered to be essentially identical. It is well-known that acyl halides which

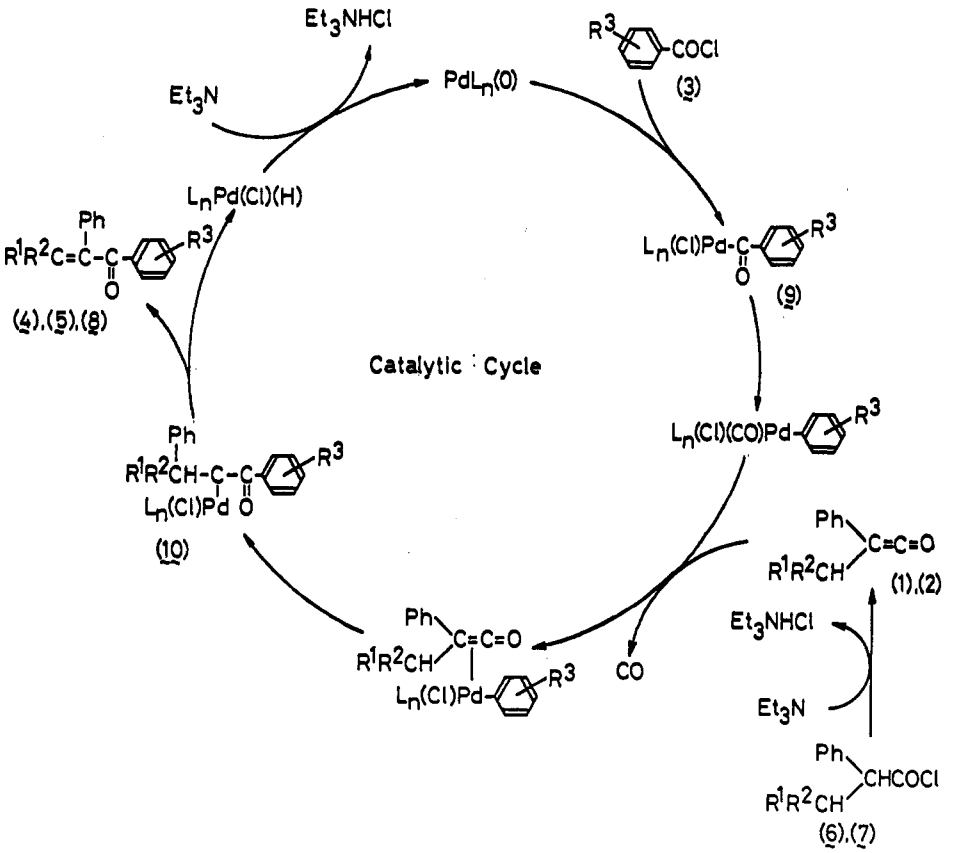
Table III. Cross-Condensation Reaction of α-Cyclohexylphenylacetyl Chloride with Aroyl Chlorides To Give α,β-Unsaturated Ketones[a]

run	ArCOCl	[Pd][b]	product	temp, °C	yield,[c] %
1	C_6H_5COCl (**3a**)	A	 **8a**	120	63 (38)
2	**3a**	A	**8a**	140	71
3	**3a**	B	**8a**	140	87
4	4-$MeOC_6H_4COCl$ (**3b**)	A	 **8b**	120	68 (46)
5	**3b**	A	**8b**	140	72
6	**3b**	B	**8b**	140	83
7	4-MeC_6H_4COCl (**3c**)	A	 **8c**	120	57 (40)
8	**3c**	A	**8c**	140	75
9	**3c**	B	**8c**	140	82
10	4-PhC_6H_4COCl (**3d**)	A	 **8d**	140	83 (57)
11	**3d**	B	**8d**	140	95
12	4-ClC_6H_4COCl (**3e**)	A	 **8e**	140	66 (36)
13	**3e**	B	**8e**	140	81
14[d]	2-$MeOC_6H_4COCl$ (**3g**)	B	 **8g**  **8g′** (**8g**/**8g′** = 2/3)	140	89[e] (86)
15[d]	2-MeC_6H_4COCl (**3h**)	B	 **8h**	140	97 (86)
16[d]	2-ClC_6H_4COCl (**3i**)	B	 **8i**  **8i′** (**8i**/**8i′** = 4/5)	140	(72)[e]
17[d]	3-MeC_6H_4COCl (**3j**)	B	 **8j**	140	95 (86)
18[d]	3-ClC_6H_4COCl (**3k**)	B	 **8k**	140	(71)

[a] α-Cyclohexylphenylacetyl chloride (3 mmol), aroyl chloride (3 mmol), Et_3N (9 mmol), [Pd] (0.09 mmol), THF 9 mL, 5 h. [b] Palladium complex: A, $Pd(PPh_3)_4$; B, $PdBr(Ph)(PPh_3)_2$. [c] Determined by GLC using an internal standard. The values in parentheses show isolated yields. [d] Bu_2O was used as a solvent. [e] Total yield of isomers.

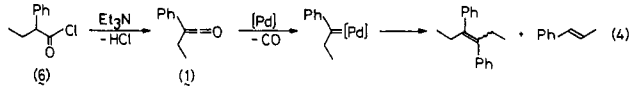
have α-hydrogen react with triethylamine or pyridine to give ketenes by dehydroahlogenation. Actually in the reaction of **6** with **3**, the IR spectra of the reaction mixture shows a characteristic absorption at 2098 cm^{-1}, which can be assigned to ethylphenylketene (**1**). Thus the cross-condensation reaction proceeds via ketenes generated from the corresponding acyl halides, **6** or **7**, by dehydrochlorination with triethylamine.

Scheme I



α,β-Unsaturated ketones are useful intermediates in organic synthesis[9] and a number of synthetic methods have been known, however, the method for α,β-unsaturated ketones **4** may be unsatisfactory,[10] and methods for **8** have not been reported so far.

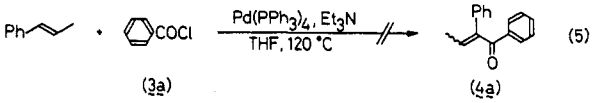
Ethylphenylketene (**1**) is somewhat labile under the present reaction conditions; some byproducts, such as 3,4-diphenyl-3-hexene and 1-phenyl-1-propene, which are derived by decomposition of **1**, were produced. These byproducts may be formed by palladium-catalyzed decarbonylation of ketene via a palladium–carbene complex (eq 4). Dimerization or 1,2-hydrogen shift of the carbene



ligand would give 3,4-diphenyl-3-hexene or 1-phenyl-1-propene, respectively. Rhodium and cobalt complex catalyzed decarbonylation of diphenylketene has been known to give tetraphenylethylene via a carbene complex.[11,12] 1,2-Hydrogen shift reaction of the carbene ligand leading to olefin has been reported by E. O. Fischer.[13] Cyclohexylphenylketene derived from acyl halide **7** is more stable against such decarbonylation probably because of its steric hindrance. Amounts of byproducts from decomposition of cyclohexylphenylketene were very small. In the reactions using ketene **1** or acyl halide **6**, yields of the products **4** seem to depend on the substituent in **3**; however, such tendency is not observed in the reactions using **7** and in the reactions using $PdBr(Ph)(PPh_3)_2$.

In the cross-condensation reaction of **7** with ortho-substituted benzoyl chloride **3g** or **3i**, β,γ-unsaturated ketone **8g′** or **8i′** was obtained together with α,β-unsaturated ketone, **8g** or **8i**. Ketones **8g′** and **8i′** would be produced by the isomerization of **8g** and **8i** mediated by a palladium hydride species.

It should be considered that 1-phenyl-1-propene, which may be derived according to eq 4, is one of the possible intermediates; however, the reaction of 1-phenyl-1-propene with **3a** did not give the ketone **4a** under the same reaction conditions employed (eq 5).



In the early stage of this study, we mentioned a possible mechanism containing a palladium–carbene intermediate.[7] By this assumption, the carbonyl group in the product must originate from benzoyl chloride **3**. However, a detailed study using an isotope ruled out the assumption. The reaction using ^{13}C-labeled benzoyl chloride with **6** or **7** revealed that the carbonyl group in the product must arise from **6** or **7**, because no isotope enrichment was observed by ^{13}C NMR. On the basis of these observations, we propose the alternative mechanism (Scheme I).

The oxidative addition of benzoyl chloride **3** to a zerovalent coordinatively unsaturated palladium complex gives acyl complex **9**, and decarbonylation of **9** gives a phenyl–Pd species. Coordination and insertion of the ketene into the phenyl–palladium bond followed by β-hydrogen elimination from **10** gives the product. Reduction of the remaining Pd(II) complex by triethylamine regenerates Pd(0) species. In the β-hydrogen elimination step, abstraction of H_a or H_b in **10′** gives the *E* or *Z* isomer, respectively (eq 6).

(9) For example, see: House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: New York, 1972.
(10) Ranfaing, J.; Combaut, G.; Giral, L. *Bull. Soc. Chim. Fr.* **1974**, 1048.
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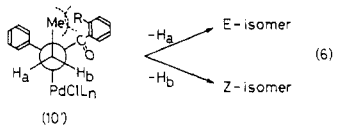
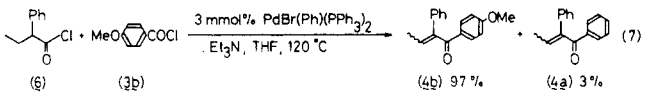


(6)

(10)

When 2-methoxy or 2-chlorobenzoyl chloride was used, abstraction of H_a would be preferential because of the steric repulsion between the substituent *R* on the 2-position and the methyl group.

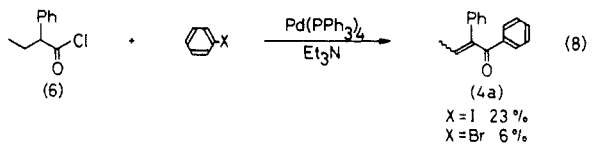
In the reaction using $PdBr(Ph)(PPh_3)_2$ as a catalyst, the product derived from the catalyst was formed. For example, the reaction of **3b** with **6** gave the ketone **4a** as well as **4b** in the yield which is consistent with the amount of catalyst (eq 7). This result suggests that in the initial stage



(6) (3b) (4b) 97 % (4a) 3 % (7)

of the reaction, insertion of ketene into a Pd–phenyl bond in the catalyst gives **4a** and a coordinatively unsaturated palladium species which starts the following catalytic cycle. This reaction is the first example of the insertion of ketene into an aryl–Pd bond.

When the present reaction was performed with aryl halides instead of acyl halide **3**, the yield of the α,β-unsaturated ketone was lower (eq 8). From iodobenzene, the desired ketone (**4a**) was obtained in 23% yield, and biphenyl was formed in 27% yield. From bromobenzene,



(6) (4a) (8)

X = I 23 %
X = Br 6 %

decomposition of the intermediate, ethylphenylketene, to 1-phenyl-1-propene was preferential (85%) and yield of **4a** was only 6%. Most of bromobenzene was recovered. This result suggests that use of aroyl chlorides as a precursor of Pd–phenyl species is profitable for the yield as well as the selectivity for the cross-condensation. In the palladium-catalyzed arylation of alkenes with aroyl chlorides, it has been also reported that aroyl chlorides offer the advantage over the related aryl halides.[14]

Conclusion

Several palladium-catalyzed ketone syntheses have been reported.[15] Generally, these ketone syntheses are achieved by coupling reaction of aryl halides with tin or zinc compounds and by carbonylation of aryl halides or aryldiazonium salts. The present reaction is the first example of α,β-unsaturated ketone synthesis from two kinds of acyl halides accompanied by decarbonylation. Decarbonylation of acyl halides has been so far known; however, examples applied to an efficient organic synthesis involving carbon–carbon bond formation reaction are rare.[16] The palladium-catalyzed arylation of ketenes with aroyl chlorides and the decarbonylative cross-condensation reaction of acyl halides via the insertion of ketene into a phenyl–palladium bond has been revealed to be a versatile novel synthetic method for α,β-unsaturated ketones which are difficult to obtain by other methods.

Experimental Section

2-Phenylbutyryl chloride and α-cyclohexylphenylacetyl chloride were prepared from the corresponding carboxylic acid by a treatment with thionyl chloride.[17] Ethylphenylketene and methylphenylketene were prepared according to the method reported for diphenylketene.[18] All aroyl chlorides are commercial products are distilled before use. ^{13}C-labeled benzoyl chloride was synthesized from the corresponding acid. Tetrahydrofuran (THF), butyl ether (Bu_2O), and triethylamine were dried and distilled just before use. $Pd(PPh_3)_4$[19] and $PdBr(Ph)(PPh_3)_2$[20] were prepared by the published methods.

Analytical Procedure. Identification of the products were confirmed by ^{13}C NMR, ^1H NMR, FT-IR, MS, and elemental analysis. All boiling points and melting points are uncorrected. ^{13}C NMR spectra were recorded on a JEOL JNM FX-100 spectrometer at 25.05 MHz using tetramethylsilane as an internal standard. ^1H NMR spectra were recorded on a JEOL JNM FX-100 or a NICOLET NT-300NB spectrometer at 100 or 300 MHz, respectively. FT-IR spectra were measured on a NICOLET 5-MX spectrometer as films or as KBr disks. Elemental analyses were performed at the Laboratory for Organic Elemental Microanalysis at the Faculty of Pharmaceutical Science at Kyoto University. Mass spectra (MS) were obtained on a Hitachi RM-50GC spectrometer. High-resolution mass spectra (HRMS) were obtained on a Hitachi M-80 spectrometer. GLC analyses were performed on a Shimadzu GC-4CM equipped with a column (3 mm i.d. × 1.5 m) packed with silicone SE-30 (5% on Chromosorb W).

Arylation Reaction of Alkylphenylketene with Aroyl Chlorides. Reaction of ethylphenylketene with 4-methoxybenzoyl chloride is representative. A mixture of ethylphenylketene (1 mmol, 0.146 g), 4-methoxybenzoyl chloride (1 mmol, 0.13 mL), triethylamine (2 mmol, 0.28 mL), and $Pd(PPh_3)_4$ (0.03 mmol, 0.035 g) in 2.5 mL of dry degassed THF was placed in a 50-mL stainless steel autoclave under an argon atmosphere and stirred at 120 °C for 5 h. The solvent was removed in vacuo, and the residue was extracted with 3 mL of ether. The precipitates were filtered off, and the filtrate was concentrated and subjected to column chromatography (Alumina, Merck 1097, eluted with hexane/ethyl acetate) to give a mixture of (*E*)- and (*Z*)-1-(4-methoxyphenyl)-2-phenyl-2-buten-1-one (0.187 g, 74%).

General Procedure for the Decarbonylative Cross-Condensation Reaction. Reaction of 2-phenylbutyryl chloride with benzoyl chloride is representative. A mixture of 2-phenylbutyryl chloride (3 mmol, 0.51 mL), benzoyl chloride (3 mmol, 0.35 mL), triethylamine (9 mmol, 1.3 mL), and $PdBr(Ph)(PPh_3)_2$ (0.09 mmol, 0.072 g) in 9 mL of THF was placed in a stainless steel autoclave under an argon atmosphere and stirred at 140 °C for 5 h (or a mixture in 9 mL of Bu_2O was placed in a two-necked reactor equipped with a reflux condenser and stirred at 140 °C for 5 h). The solvent was removed in vacuo, and the residue was extracted with 10 mL of ether. The precipitates were filtered off, and the filtrate was subjected to Kugelrohr distillation to give a mixture of (*E*)- and (*Z*)-1,2-diphenyl-2-buten-1-one (0.38 g, 57%).

(*Z*)- and (*E*)-1,2-Diphenyl-2-buten-1-one (4a): colorless oil; Kugelrohr distillation [120 °C (0.4 mmHg)]; ^{13}C NMR ($CDCl_3$) δ 197.5 (s), 142.8 (s), 139.5 (dq), 138.4 (s), 135.7 (s), 131.8 (d), 129.5 (d), 128.6 (d), 128.2 (d), 128.0 (d), 127.4 (d), 15.6 (q); ^1H NMR (300 MHz, $CDCl_3$) δ 7.19–7.98 (m, Ar, 10 H), 6.59 (q, J = 7.1 Hz, *E*), 6.34 (q, J = 7.1 Hz, *Z*), 1.88 (d, J = 7.1 Hz, CH_3, *E*), 1.75 (d, J = 7.1 Hz, CH_3, *Z*); IR (neat) 1668, 1595, 1577 cm^{-1}; HRMS, m/z calcd for $C_{16}H_{14}O$ 222.1045, found 222.1050.

(*Z*)- and (*E*)-1-(4-Methoxyphenyl)-2-phenyl-2-buten-1-one (4b): colorless oil; Kugelrohr distillation [140 °C (0.1 mmHg)]; ^{13}C NMR ($CDCl_3$) δ 197.7 (s), 196.3 (s), 164.1 (s), 163.1 (s), 142.7 (s), 142.0 (s), 137.6 (s), 137.1 (dq), 136.2 (s), 132.2 (d), 130.6 (d), 129.8 (d), 129.5 (d), 128.7 (d), 128.3 (d), 127.6 (d), 127.5 (d), 126.0 (d), 125.8 (d), 114.1 (d), 113.5 (d), 55.3 (q), 15.5 (q), 15.3 (q); ^1H NMR (300 MHz, $CDCl_3$) δ 7.20–7.96 (m, Ar, 9 H), 6.49 (q, J =

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7.1 Hz, *E*), 6.30 (q, *J* = 7.1 Hz, *Z*), 3.83 (s, OCH_3, 3 H), 1.88 (d, *J* = 7.1 Hz, CH_3, *E*), 1.75 (d, *J* = 7.1 Hz, CH_3, *Z*); IR (neat) 1655, 1601 cm^{-1}; HRMS, *m/z* calcd for $C_{17}H_{16}O_2$ 252.1148, found 252.1147.

(*Z*)- and (*E*)-1-(4-Methylphenyl)-2-phenyl-2-buten-1-one (4c): colorless crystal; mp 89–91 °C; ^{13}C NMR ($CDCl_3$) δ 198.1 (s), 144.3 (s), 141.9 (s), 138.1 (dq), 137.5 (s), 134.3 (s), 129.6 (d), 129.4 (d), 128.7 (d), 128.5 (d), 128.1 (d), 127.4 (d), 126.2 (d), 125.8 (d), 21.6 (q), 15.4 (q); ^1H NMR (300 MHz, $CDCl_3$) δ 7.17–7.88 (m, Ar, 9 H), 6.53 (q, *J* = 7.1 Hz, *E*), 6.31 (q, *J* = 7.1 Hz, *Z*), 2.37 (s, $ArCH_3$, CH), 1.87 (d, *J* = 7.2 Hz, CH_3, *E*), 1.74 (d, *J* = 7.1 Hz, CH_3, *Z*); IR (KBr) 1658, 1603, 1570 cm^{-1}; HRMS, *m/z* calcd for $C_{17}H_{16}O$ 236.1200, found 236.1221.

(*Z*)- and (*E*)-1-(4-Biphenylyl)-2-phenyl-2-buten-1-one (4d): colorless crystal; mp 80–81 °C; ^{13}C NMR ($CDCl_3$) δ 197.6 (s), 196.0 (s), 145.7 (s), 144.2 (s), 141.5 (s), 139.3 (s), 138.5 (dq), 137.1 (s), 136.6 (s), 135.5 (s), 135.1 (s), 129.8 (d), 129.2 (d), 128.5 (d), 128.4 (d), 127.9 (d), 127.7 (d), 127.2 (d), 127.0 (d), 126.8 (d), 126.4 (d), 125.6 (d), 15.5 (q); ^1H NMR (300 MHz, $CDCl_3$) δ 7.27–8.05 (m, Ar, 14 H), 6.62 (q, *J* = 7.2 Hz, *E*), 6.36 (q, *J* = 7.2 Hz, *Z*), 1.90 (d, *J* = 7.2 Hz, CH_3, *E*), 1.79 (d, *J* = 7.2 Hz, CH_3, *Z*); IR (neat) 1666, 1637, 1601, 1558 cm^{-1}; HRMS, *m/z* calcd for $C_{22}H_{18}O$ 298.1357, found 298.1360.

(*Z*)- and (*E*)-1-(4-Chlorophenyl)-2-phenyl-2-buten-1-one (4e): colorless crystal; mp 95–96 °C; ^{13}C NMR ($CDCl_3$) δ 196.6 (s), 141.1 (s), 139.5 (s), 136.8 (s), 134.8 (s), 130.6 (d), 128.7 (d), 128.4 (d), 127.4 (d), 127.0 (dq), 125.5 (d), 15.5 (q); ^1H NMR (300 MHz, $CDCl_3$) δ 7.21–7.90 (m, Ar, 9 H), 6.58 (q, *J* = 7.2 Hz, *E*), 6.34 (q, *J* = 7.2 Hz, *Z*), 1.88 (d, *J* = 7.2 Hz, CH_3, *E*), 1.75 (d, *J* = 7.2 Hz, CH_3, *Z*); IR (KBr) 1666, 1582, 1568 cm^{-1}; HRMS, M/Z calcd for $C_{16}H_{13}ClO$ 256.0655, found 256.0691.

(*Z*)- and (*E*)-1-(2-Methoxyphenyl)-2-phenyl-2-buten-1-one (4g): colorless oil; Kugelrohr distillation [140 °C (0.15 mmHz)]; ^{13}C NMR ($CDCl_3$) δ 197.0 (s), 144.5 (s), 142.1 (dq), 135.2 (s), 133.9 (s), 131.1 (d), 129.8 (d), 128.7 (d), 128.0 (d), 127.8 (d), 127.2 (d), 126.4 (s), 120.2 (dd), 111.3 (dd), 55.5 (q), 15.7 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 6.83–7.79 (m, Ar, 9 H), 6.64 (q, *J* = 7.1 Hz, *E*), 6.17 (q, *J* = 7.1 Hz, *Z*), 3.75 (s, OCH_3, *E*), 3.70 (s, OCH_3, *Z*), 1.83 (d, *J* = 7.1 Hz, CH_3, *Z*), 1.78 (d, *J* = 7.1 Hz, CH_3, *E*); IR (neat) 1660, 1651, 1597 cm^{-1}; HRMS, *m/z* calcd for $C_{17}H_{16}O_2$ 252.1148, found 252.1165.

(*Z*)- and (*E*)-1-(2-Methylphenyl)-2-phenyl-2-buten-1-one (4h): colorless oil; Kugelrohr distillation [120 °C (0.8 mmHg)]; ^{13}C NMR ($CDCl_3$) δ 199.0 (s), 144.5 (s), 144.3 (dq), 139.7 (s), 135.7 (s), 134.9 (s), 130.6 (d), 129.7 (d), 129.5 (d), 128.0 (d), 127.6 (d), 127.4 (d), 125.1 (d), 19.7 (q), 15.9 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.18–7.73 (m, Ar, 9 H), 6.60 (q, *J* = 7.1 Hz, *E*), 6.29 (q, *J* = 7.1 Hz, *Z*), 2.68 (s, $ArCH_3$, *Z*), 2.36 (s, $ArCH_3$, *E*), 1.80 (d, *J* = 7.1 Hz, CH_3, *E*), 1.77 (d, *J* = 7.1 Hz, CH_3, *Z*); IR (neat) 1660, 1651, 1599, 1575 cm^{-1}; HRMS, *m/z* calcd for $C_{17}H_{16}O$ 236.1200, found 236.1158.

(*Z*)- and (*E*)-1-(3-Methylphenyl)-2-phenyl-2-buten-1-one (4j): colorless oil; Kugelrohr distillation [115 °C (0.1 mmHg)]; ^{13}C NMR ($CDCl_3$) δ 198.6 (s), 197.0 (s), 142.8 (s), 141.8 (s), 139.1 (dq), 138.4 (d), 137.8 (s), 137.4 (s), 136.7 (s), 135.8 (s), 134.2 (d), 132.5 (d), 129.9 (d), 129.6 (d), 129.5 (d), 128.5 (d), 128.0 (d), 127.8 (d), 127.4 (d), 127.3 (d), 127.0 (d), 126.8 (d), 126.3 (d), 125.8 (d), 21.2 (q), 15.4 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.18–7.79 (m, Ar, 9 H), 6.56 (q, *J* = 7.1 Hz, *E*), 6.32 (q, *J* = 7.1 Hz, *Z*), 2.37 (s, $ArCH_3$, 3 H), 1.87 (d, *J* = 7.1 Hz, CH_3, *E*), 1.75 (d, *J* = 7.1 Hz, CH_3, *Z*); IR (neat) 1666, 1601, 1583, cm^{-1}; HRMS, *m/z* calcd for $C_{17}H_{16}O$ 236.1200, found 236.1236.

(*Z*)- and (*E*)-1-(3-Chlorophenyl)-2-phenyl-2-buten-1-one (4k): colorless oil; Kugelrohr distillation [140 °C (0.25 mmHg)]; ^{13}C NMR ($CDCl_3$) δ 197.0 (s), 195.3 (s), 142.5 (s), 141.2 (s), 140.6 (dq), 140.1 (s), 138.3 (s), 136.9 (s), 135.2 (s), 135.0 (s), 134.2 (s), 133.3 (d), 131.6 (d), 130.0 (d), 129.5 (d), 129.3 (d), 128.7 (d), 128.2 (d), 127.7 (d), 127.5 (d), 125.8 (d), 15.6 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.17–7.95 (m, Ar, 9 H), 6.61 (q, *J* = 7.2 Hz, *E*), 6.36 (q, *J* = 7.2 Hz, *Z*), 1.89 (d, *J* = 7.2 Hz, CH_3, *E*), 1.80 (d, *J* = 7.2 Hz, CH_3, *Z*); IR (neat) 1668, 1651, 1586 cm^{-1}; HRMS, *m/z* calcd for $C_{16}H_{13}ClO$ 256.0655, found 256.0737.

1-(4-Methoxyphenyl)-2-phenyl-2-propen-1-one (5b): colorless oil; Kugelrohr distillation [135 °C (0.2 mmHg)]; ^{13}C NMR ($CDCl_3$) δ 196.2 (s), 163.6 (s), 148.4 (s), 137.1 (s), 132.3 (d), 129.8 (s), 128.5 (d), 128.3 (d), 126.8 (d), 118.8 (t), 113.6 (d), 55.4 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 6.72–7.98 (m, Ar, 9 H), 5.98 (s, $=CH_2$, 1 H), 5.55 (s, $=CH_2$, 1 H), 3.84 (s, OCH_3, 3 H); IR (neat) 1658, 1599, 1574, 1508 cm^{-1}; MS, *m/z* 238 (M^+).

α-Cyclohexylidenebenzyl phenyl ketone (8a): colorless crystal; mp 80–81 °C; ^{13}C NMR ($CDCl_3$) δ 198.7 (s), 142.4 (s), 137.0 (s), 136.6 (s), 133.4 (s), 133.0 (d), 129.6 (d), 129.2 (d), 128.5 (d), 128.3 (d), 127.0 (d), 33.1 (t), 30.9 (t), 28.2 (t), 27.9 (t), 26.3 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.28–8.04 (m, Ar, 10 H), 2.14–2.31 (m, methylene, 4 H), 1.61 (br s, methylene, 6 H); IR (KBr) 1658, 1591, 1575 cm^{-1}; MS, *m/z* 276 (M^+). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.69; H, 7.28.

α-Cyclohexylidenebenzyl 4-methoxyphenyl ketone (8b): colorless crystal; mp 73.5–74.0 °C; ^{13}C NMR ($CDCl_3$) δ 197.4 (s), 163.6 (s), 141.5 (s), 136.9 (s), 133.6 (s), 131.9 (d), 130.2 (s), 129.1 (d), 128.2 (d), 126.9 (d), 113.8 (d), 55.3 (q), 33.1 (t), 30.8 (t), 28.2 (t), 27.9 (t), 26.4 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 6.85–8.04 (m, Ar, 9 H), 3.81 (s, OCH_3, 3 H), 2.08–2.35 (m, methylene, 4 H), 2.02 (br s, methylene, 6 H); IR (KBr) 1658, 1651, 1599, 1574 cm^{-1}; MS, *m/z* 306 (M^+). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.57; H, 7.33.

α-Cyclohexylidenebenzyl 4-methylphenyl ketone (8c): colorless crystal; mp 77.5–78.0 °C; ^{13}C NMR ($CDCl_3$) δ 198.4 (s), 143.9 (s), 142.0 (s), 136.7 (s), 134.6 (s), 133.6 (s), 129.8 (d), 129.2 (d), 128.2 (d), 127.0 (d), 33.1 (t), 30.9 (t), 28.2 (t), 27.9 (t), 26.4 (t), 21.6 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.17–7.96 (m, Ar, 9 H), 2.36 (s, CH_3, 3 H), 2.11–2.31 (m, methylene, 4 H), 1.60 (br s, methylene, 6 H); IR (KBr) 1660, 1604, 1572 cm^{-1}; MS, *m/z* 290 (M^+). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.88; H, 7.68.

α-Cyclohexylidenebenzyl 4-biphenylyl ketone (8d): colorless crystal; mp 76.5–77.5 °C; ^{13}C NMR ($CDCl_3$) δ 198.3 (s), 145.7 (s), 142.4 (s), 139.8 (s), 136.6 (s), 135.8 (s), 133.5 (s), 130.2 (s), 129.2 (d), 128.8 (d), 128.3 (d), 128.1 (d), 127.2 (d), 33.1 (t), 30.9 (t), 28.2 (t), 28.0 (t), 26.4 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.23–8.13 (m, Ar, 14 H), 2.19–2.32 (m, methylene, 4 H), 1.63 (br s, methylene, 6 H); IR (KBr) 1651, 1628, 1597, 1558 cm^{-1}. Anal. Calcd for $C_{26}H_{24}O$: C, 88.60; H, 6.86. Found: C, 88.71; H, 6.88.

α-Cyclohexylidenebenzyl 4-chlorophenyl ketone (8e): colorless crystal; mp 58–59 °C; ^{13}C NMR ($CDCl_3$) δ 197.4 (s), 143.1 (s), 139.4 (s), 136.3 (s), 135.5 (s), 133.1 (s), 130.9 (d), 129.2 (d), 128.9 (d), 128.4 (d), 127.2 (d), 33.1 (t), 30.9 (t), 28.2 (t), 28.0 (t), 26.3 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.27–7.97 (m, Ar, 9 H), 2.14–2.30 (m, methylene, 4 H), 1.60 (br s, methylene, 6 H); IR (KBr) 1658, 1633, 1585, 1570 cm^{-1}; MS, *m/z* 310 (M^+). Anal. Calcd for $C_{20}H_{19}ClO$: C, 77.28; H, 6.16. Found: C, 77.28; H, 6.13.

Mixture of α-cyclohexylidenebenzyl 2-methoxyphenyl ketone (8g) and α-(1-cyclohexyl)benzyl 2-methoxyphenyl ketone (8g'): pale yellow oil; Kugelrohr distillation [170 °C (0.1 mmHg)]; ^{13}C NMR ($CDCl_3$) δ 200.8 (s), 197.9 (s), 158.3 (s), 143.9 (s), 138.1 (s), 137.2 (s), 136.5 (s), 136.3 (s), 133.2 (d), 132.9 (d), 131.3 (d), 130.5 (d), 129.7 (d), 129.5 (d), 127.9 (d), 127.8 (d), 126.7 (d), 126.5 (d), 124.9 (d), 120.5 (d), 120.1 (d), 111.5 (d), 64.8 (d), 55.4 (q), 32.8 (t), 31.8 (t), 28.4 (t), 28.0 (t), 26.5 (t), 25.4 (t), 23.0 (t), 22.2 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 6.74–7.73 (m, Ar, 9 H), 5.44 (br s), 5.28 (s), 3.79 (s, OCH_3), 3.77 (s, OCH_3), 1.94–2.35 (m, methylene), 1.59 (br s, methylene); IR (neat) 1653, 1597, 1577 cm^{-1}; MS, *m/z* 306 (M^+). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.24; H, 7.21.

α-Cyclohexylidenebenzyl 2-methylphenyl ketone (8h): colorless crystal; mp 87.5–88.5 °C; ^{13}C NMR ($CDCl_3$) δ 200.3 (s), 143.7 (s), 139.1 (s), 136.9 (s), 135.3 (s), 131.6 (d), 131.2 (d), 131.0 (s), 129.0 (d), 128.0 (d), 126.7 (d), 125.2 (d), 32.6 (t), 31.2 (t), 28.1 (t), 27.8 (t), 26.2 (t), 21.3 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.06–7.84 (m, Ar, 9 H), 2.56 (s, CH_3, 3 H), 2.24 (m, methylene, 4 H), 1.59 (br s, methylene, 6 H); IR (KBr) 1657, 1599, 1566 cm^{-1}; MS, *m/z* 290 (M^+). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.95; H, 7.86.

Mixture of α-cyclohexylidenebenzyl 2-chlorophenyl ketone (8i) and α-(1-cyclohexenyl)benzyl 2-chlorophenyl ketone (8i'): pale yellow oil; Kugelrohr distillation [160 °C (0.3 mmHg)]; ^{13}C NMR ($CDCl_3$) δ 200.8 (s), 196.8 (s), 150.0 (s), 139.8 (s), 138.9 (s), 136.9 (s), 136.7 (s), 135.3 (s), 135.1 (s), 131.3 (d), 131.2 (d), 130.4 (d), 129.8 (d), 129.3 (d), 129.2 (d), 128.2 (d), 128.1 (d), 127.0 (d), 126.7 (d), 126.5 (d), 126.3 (d), 64.6 (d), 32.7 (t), 32.5 (t), 28.3 (t), 28.1 (t), 26.4 (t), 25.5 (t), 22.9 (t), 22.0 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.19–7.51 (m, Ar, 9 H), 5.58 (br s), 5.09 (s),

2.10–2.45 (m, methylene), 1.61 (br s, methylene); IR (neat) 1699, 1668, 1587 cm^{-1}; MS, m/z 310 (M^+). Anal. Calcd for $C_{20}H_{19}ClO$: C, 77.28; H, 6.16. Found: C, 77.10; H, 6.05.

α-Cyclohexylidenebenzyl 3-methylphenyl ketone (8j): colorless crystal; mp 72.0–72.5 °C; ^{13}C NMR ($CDCl_3$) δ 198.6 (s), 141.9 (s), 138.1 (s), 136.9 (s), 136.5 (s), 133.7 (d), 133.4 (s), 129.6 (d), 129.0 (d), 128.2 (d), 128.0 (d), 127.0 (d), 126.8 (d), 32.9 (t), 30.7 (t), 28.1 (t), 27.8 (t), 26.2 (t), 21.1 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.12–7.85 (m, Ar, 9 H), 2.33 (s, CH_3, 3 H), 2.14–2.25 (m, methylene, 4 H), 1.57 (br s, methylene, 6 H); IR (KBr) 1658, 1597 cm^{-1}; MS, m/z 290 (M^+). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.69; H, 7.75.

α-Cyclohexylidenebenzyl 3-chlorophenyl ketone (8k): colorless crystal; mp 60–61 °C; ^{13}C NMR ($CDCl_3$) δ 197.1 (s), 143.5 (s), 138.7 (s), 136.2 (s), 134.8 (s), 133.0 (s), 132.9 (d), 129.8 (d), 129.2 (d), 128.3 (d), 127.7 (d), 127.2 (d), 33.1 (t), 30.9 (t), 28.2 (t), 27.9 (t), 26.2 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.27–7.96 (m, Ar, 9 H), 2.02–2.30 (m, methylene, 4 H), 1.60 (br s, methylene, 6 H); IR (KBr) 1657, 1635, 1587, 1570 cm^{-1}; MS, m/z 310 (M^+). Anal. Calcd for $C_{20}H_{19}ClO$: C, 77.28; H, 6.16. Found: C, 77.12; H, 6.12.

Reaction of 2-Phenylbutyryl Chloride (6) with Aryl Halide. A mixture of 2-phenylbutyryl chloride (1 mmol, 0.17 mL), aryl halide (1 mmol), triethylamine (3 mmol, 0.42 mL), and $Pd(PPh_3)_4$ (0.05 mmol, 0.058 g) in 5 mL of THF was placed in a 50-mL stainless steel autoclave under an argon atmosphere and stirred at 120 °C for 5 h. The product (**4a**) was identified by comparing GLC and FT-IR with those of the authentic sample.

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2-(Chloromethyl)-3,5-dioxahex-1-ene. An Effective Acetonylating Reagent

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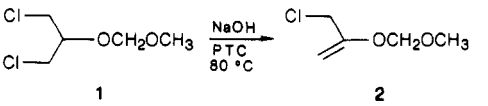
By β-elimination of 2-chloro-1-(chloromethyl)ethyl methoxymethyl ether (1) under solid–liquid phase-transfer catalytic conditions, 2-(chloromethyl)-3,5-dioxahex-1-ene (2) of high purity was readily obtained in 85%. Allyl chloride **2** is found to be stable at ambient conditions and to be a superior reagent as $CH_3COCH_2^+$ synthon for converting active proton-containing compounds such as carboxylic acids, amines, phenols, alcohols, thiols, malonate, β-diketones, β-keto esters, phenylacetonitrile, fluorene, and indene to the corresponding acetonyl derivatives in good to excellent yields (61–93%), usually under phase-transfer catalytic conditions or in a *t*-BuONa–*t*-BuOH system.

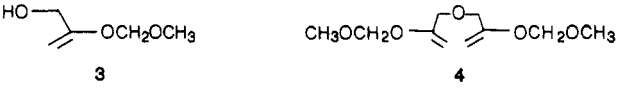
The acetonyl unit is one of the most basic functional groups due to its high and versatile reactivity, and introduction of this group has become a very important operation in organic synthesis. Until now, several kinds of reagents for introduction of acetonyl groups have been described. One of the most useful compounds among them, methoxyallyl bromide, developed by Horning[1] and Jacobson,[2] has attracted attention as a masked electrophilic acetonylation reagent. This reagent, however, requires some care in its preparation and preservation, for example, as they mentioned, high pyrolytic temperatures, inevitable side reactions, difficult isolation, and instability to polymerization.[1-3] Since the review concerning acetonylating reagents was published in 1978,[4] several new methods have been developed. A free-radical acetonylation has been applied successfully,[5] although the vigorous conditions that were necessary for the free-radical reaction led inevitably to isomerization. Kjonaas used dilithio acetoacetate as an acetone enolate equivalent for substitution of halogen by an acetonyl group.[6] Alkylation of

Scheme I



1 2

Scheme II



3 4

β-dicarbonyl compounds with 3-acetoxy-2-chloroprop-1-ene in the presence of palladium(II) acetate as a catalyst was also reported.[7] 3-Acetonyl-2-methyl-1,4-naphthoquinone was synthesized by photochemical reaction of 2-methyl-1,4-naphthoquinone with isopropenyl methyl ether and subsequent oxidation of the photoproduct under acidic conditions.[8] These methods have certain drawbacks either in preparation or use or in both. In our attempts to extend the utility of 2-chloro-1-(chloromethyl)ethyl methoxymethyl ether (1), we have found that **1** is a useful reagent for conversion of hydroxyl compounds to the corresponding acetonyl ethers in good yields.[9] This made us desire the development of an effective method for introducing an acetonyl unit by substituting the protons of other active

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