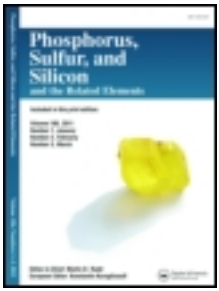

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ORGANOPHOSPHOROUS CHEMISTRY: SELECTIVE TRANSFORMATION OF BENZOIN TO BENZIL, DESYL BROMIDE, OR BENZYL PHENYL KETONE

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ORGANOPHOSPHOROUS CHEMISTRY: SELECTIVE TRANSFORMATION OF BENZOIN TO BENZIL, DESYL BROMIDE, OR BENZYL PHENYL KETONE

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Reaction of benzoin with dibromotriphenylphosphorane under various conditions has been closely investigated. Benzoin was selectively converted to desyl bromide by treatment with dibromotriphenylphosphorane in the presence of triethylamine, while benzyl phenyl ketone was formed in the presence of an excess amount of triphenylphosphine. On the other hand, benzoin was effectively oxidized to benzil by treatment with only bromine. The mechanism of producing these was also proposed. Desyl bromide was formed from the reaction of benzoin with dibromotriphenylphosphorane as a primary product and converted to benzyl phenyl ketone via the Perkow reaction, and benzil was formed by the oxidation of benzoin by bromine. When triethylamine or triphenylphosphine was used as an added base, these bases trapped free bromine, and the oxidation product, benzil, was formed in low yield. In the presence of triphenylphosphine as a base, the Perkow reaction of desyl bromide proceeded smoothly to give benzyl phenyl ketone preferentially, while in the presence of triethylamine, replacement of the hydroxy group to bromide occurred mainly.

Keywords: dibromotriphenylphosphorane; benzoin; benzil; desyl bromide; benzyl phenyl ketone

INTRODUCTION

Organophosphorus compounds are frequently used for selective organic syntheses.[1] Among them, dihalotriphenylphosphorane (Ph_3PX_2, X = Cl, Br, I) is a useful reagent for substitution of the hydroxy group,[2] dehydra-

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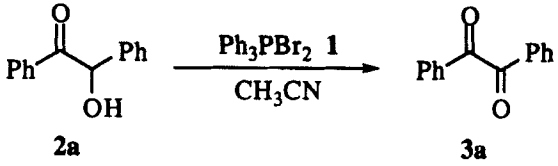
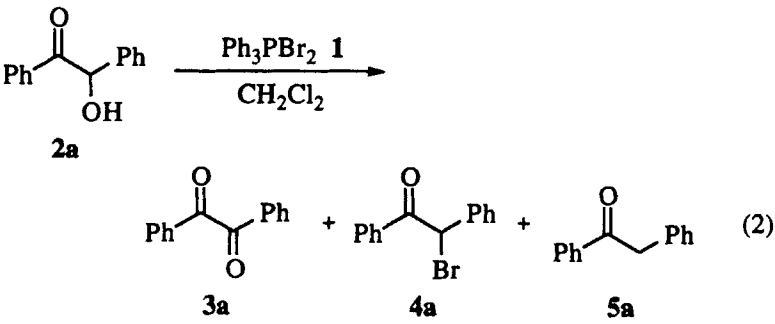
tion,[3] and deoxygenation.[3a][4] In these reactions, Ph_3PX_2 is functioning as a reductant or as a reagent for substitution, but not as an oxidative reagent. In 1972, Ho reported the oxidation of benzoin (**2a**) to benzil (**3a**) by dibromotriphenylphosphorane (**1**) (eq. 1).[5] As this oxidative ability of **1** could potentially establish a new reaction for Ph_3PX_2, we reinvestigated this reaction.



2a **3a** (1)[5]

We found that the reaction of **2a** and **1**, which was prepared by mixing an equimolar amount of triphenylphosphine and bromine, yielded **3a** in lower yield (55%) than that (90%) in the study by Ho, accompanied by desyl bromide (**4a**) (14%) and benzyl phenyl ketone (**5a**, 28%) (eq. 2), and the molar ratio of triphenylphosphine and bromine very sensitively affected their yields. Further investigation of this reaction enabled the selective transformation of **2a** to these three compounds. Here we wish to report the results in detail.



2a **3a** **4a** **5a** (2)

RESULTS

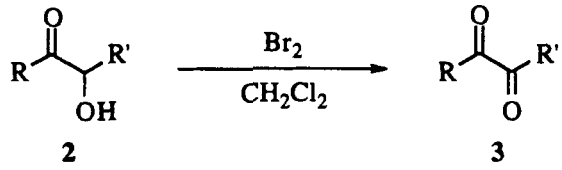
Oxidation of benzoin 2a to benzil 3a

First we investigated the effect of solvent. Product distributions of the reactions using CH_2Cl_2, CH_3CN, and toluene as solvents were basically similar, even though the solution of **1** was homogeneous in CH_2Cl_2 and was heterogeneous in CH_3CN and toluene. The solution of **1** prepared from an equimolar amount of triphenylphosphine and bromine in CH_2Cl_2 was homogeneous and pale. The pale color of this solution was different from the orange color described in literature[5] and an excess of bromine was considered to present in the literature preparation. Therefore, **2a** was allowed to react with bromine, and consequentially oxidation of **2a** to **3a** was observed to proceed smoothly and almost quantitatively (eq. 3). This oxidation of α-hydroxy carbonyl compounds to α-keto carbonyl compounds by bromine was applied to other structurely similar substrates (Table I). The derivatives, ethyl mandelate (**2d**), and 3-hydroxy-1-phenyl-4-hexanone (**2e**) were oxidized efficiently in 24–48 h at room temperature to give **3** in high isolated yield. In the case of **2c**, products due to bromination of the aromatic ring was mainly formed accompanied by **3c** in only 30% yield.

TABLE I Reaction of α-hydroxy carbonyl compounds **2** with Br_2[a]

entry	*substrate*			*time (h)*	*yield[b] of 3 (%)*
		R	*R'*		
1	**2a**	Ph	Ph	48	95
2	**2b**	4-MeC_6H_4	4-MeC_6H_4	24	84
3	**2c**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	24	30
4[c]	**2d**	EtO	Ph	48	70
5	**2e**	Et	$PhCH_2CH_2$	48	74

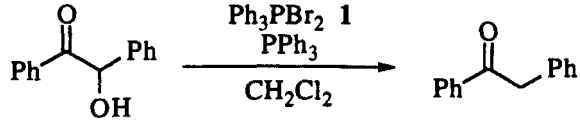
[a] Reaction conditions: bromine 2 mmol, substrate 2 mmol, CH_2Cl_2 15 mL, room temperature [b]Isolated yield [c] Ethyl mandelate was recovered in 12% isolated yield.



2 **3** (3)

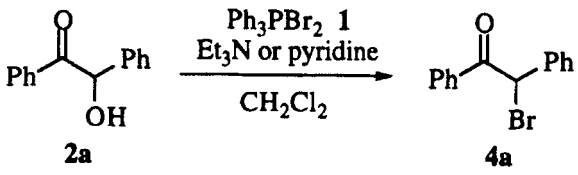
Transformation of 2a to 4a or 5a

It was suggested from the above results that the oxidation of **2a** to **3a** could proceed by the free bromine. To minimize the amount of free bromine in the reaction mixture, we employed the addition of phosphine or amine as a bromine trapping agent. The reaction of **2a** with **1** in the presence of an equimolar amount of triphenylphosphine to **1** gave **5a** in 92% isolated yield (eq. 4). On the other hand, **4a** was obtained by addition of triethylamine or pyridine as a base for the reaction of **2a** with **1** in 72–75% isolated yield (eq. 5). These results indicated that the addition of triphenylphosphine caused reduction of the hydroxymethylene group to a methylene group, and the addition of amines gave rise to replacement of the hydroxy group by bromide.



2a **5a** (4)

Other α-hydroxy carbonyl compounds were employed for the reaction with **1** in the presence of PPh_3or NEt_3 (eq. 6 and Table II). Benzoin derivatives **2b-c** were converted to benzyl phenyl ketone derivatives (**5b-c**) selectively by **1** with triphenylphosphine, but less selectively to **4b-c** by **1** in the presence of NEt_3. In case of ethyl mandelate (**2d**), ethyl



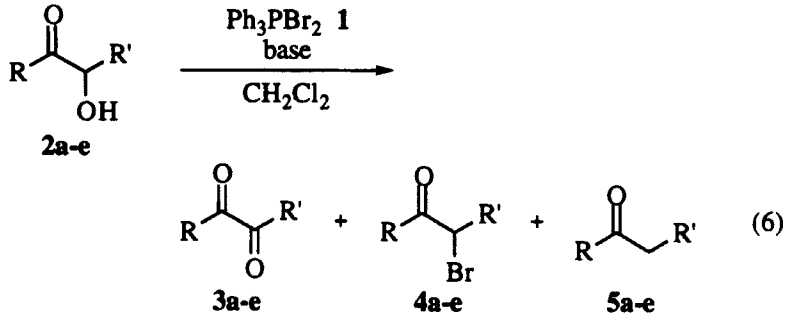
(5)

α-bromophenylacetate (**4d**) was the major product whether bases were added or not. Adding NEt_3 increased the yield of **4d** (70%), while addition of PPh_3 did not affect the yield. When 3-hydroxy-1-phenyl-4-hexanone (**2e**) was subjected to **1** in the presence of PPh_3, the unexpected diketone **3e** was the sole isolatable product (61%), and using NEt_3 did not give **3e**, **4e**, or **5e**.

TALBE II Reaction of α-hydroxy carbonyl compounds **2** with dibromotriphenylphosphorane **1**[a]

entry	*substrate*	*additive*	*time (h)*	*yield of products*[b] *(%)*		
				3	*4*	*5*
1	**2a**	none	48	55	14	28
2	**2a**	Ph_3P	48	2	trace	92
3	**2a**	Et_3N	48	8	75	trace
4	**2b**	Ph_3P	24	-	-	78
5	**2b**	Et_3N	24	13	41	13
6	**2c**	Ph_3P	24	-	-	82
7	**2 c**	Et_3N	24	11	38	trace
8	**2d**	Ph_3P	48	-	43	-
9	**2d**	Et_3N	48	trace	70	-
10	**2e**	Ph_3P	48	61	-	-
11	**2 e**	Et_3N	48	-	-	-

[a] Reaction conditions: triphenylphosphine 2 mmol, bromine 2 mmol, substrate 2 mmol, base 2 mmol, CH_2Cl_2 15 mL, room temperature [b] Isolated yield.



(6)

Instead of Ph_3PBr_2 (**1**), dichloro- and diiodo-triphenylphosphorane were also allowed to react with benzoins **2a-c** and **2d** in the presence or absence of PPh_3 or NEt_3. α-Chloro carbonyl compounds **4a-d** were produced in the range of 22 to 76% yield accompanied by recovered substrates, and there was no oxidation product **3** and no reduction product **5**, when Ph_3PCl_2 was used. In case of Ph_3PI_2, **2a** was recovered at room temperature.

DISCUSSION

Oxidation reaction

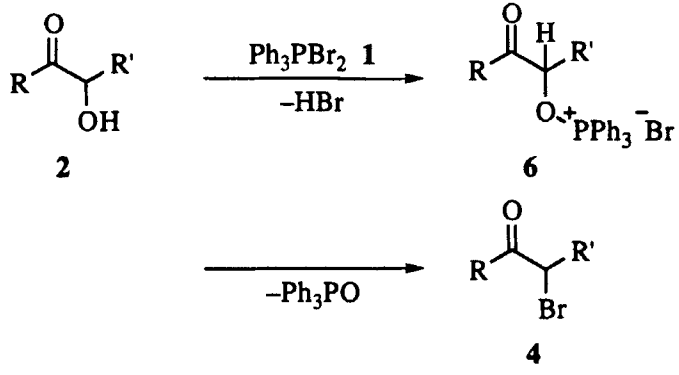
In the oxidation of **2a** with **1** described in literature,[5] reagent **1** prepared in CH_3CN was orange in color and that solution was used directly. It is well known that crystal of **1** analyzed by X-ray was colorless,[6] but triphenylphosphine tetrabromide was orange.[7] The orange color in literature can be considered to be caused from using larger than stoichiometric quantity of bromine. Bromine is known to oxidize some kinds of alcohols to carbonyl compounds,[8] and our experimental results demonstrated that bromine oxidized **2a** to **3a**. Consequently, it was clear that **3a**, only product described in literature, is an oxidation product of **2a** with bromine.

In our reaction using a pale colored CH_2Cl_2 solution of **1**, **3a** was still obtained in considerable amount from **2a**. The pale color of **1** suggested that there was a small amount of free bromine in solution. The equilibrium between **1** and bromine with triphenylphosphine could be a source of free bromine. This speculation is confirmed from the fact that the addition of bases (PPh_3, NEt_3, or pyridine) suppressed the formation of **3a**.

Usually benzils were synthesized from benzoins by several oxidative methods using a combination of metal catalysts and oxidative reagents in literature.[9] This oxidation of benzoins to benzil derivatives by bromine seems to be quite simple and easy because no catalyst was required.

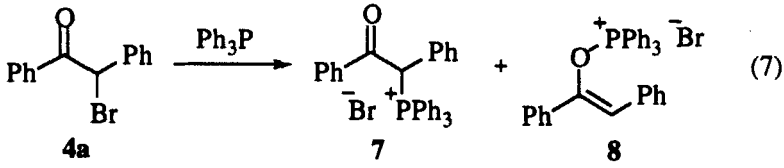
Reaction of 2 with 1 in the presence of bases (PPh_3, NEt_3, or pyridine)

When triphenylphosphine was added, reduction product **5** was formed selectively. Diiodotriphenylphosphorane was reported to promote hydrogenolysis of alcohols, in which replacement of the hydroxy group by iodide first occurs and then reduction of this by hydrogen iodide was suggested as a mechanism.[4a-c] Since dibromotriphenylphosphorane (**1**) is also known to act as a reagent for replacement of the hydroxy group by bromide as in the case of Ph_3PI_2, the hydroxy group in **2** was considered similarly to be transformed to bromide **4** through **6** (Scheme 1). In contrast, hydrogen bromide does not have the same reduction ability as hydrogen iodide. Actually **4a** was not reduced with HBr for 6 h.[10]



2 **6** **4**

On the other hand, the reaction of α-halo ketone with PPh_3 is the well-known Perkow reaction (eq. 7).[11] Two intermediates, keto-phosphonium salt **7** and enol-phosphonium salt **8**, were proposed on the Perkow reaction of desyl bromide with PPh_3, and the ratio of these salts was suggested by the chemical transformation of the salts to benzyl phenyl ketone. We tried to determine the ratio of these salts by ^{31}P NMR analysis. The $^{31}P\{^1H\}$ NMR spectrum of a mixture of an equimolar amount of PPh_3 and **4a** in CD_2Cl_2 is shown in Fig. 1. There were four singlets, which were assigned as PPh_3 at −5.20 ppm, triphenylphosphine oxide at 27.48 ppm, keto-type salt **7** at 16.15 ppm, and enol-type salt **8** at 63.86 ppm. The assignments of salt signals were made by comparison with the standard chemical shifts for C-attached phosphonium salts and O-attached phosphonium salts.[12] It is clear that the enol-type salt **8** was a major species (**8** : **7** = 86 : 14).



4a **7** **8** (7)

At the same time, according to a MOPAC calculation[13] (PM3) on the intermediates from desyl bromide and triphenylphosphine, the enol-type intermediate was more stable (8.17 kcal/mol) than the keto-type intermediate. The difference could be explained by resonance stabilization of the stilbene unit.

In the literature, there was no equilibrium between **7** and **8**, and the enol-type salt **8** was easily hydrolyzed to the enol, while the keto-type salt **7** was not. Concequently, the reduction seemed to be caused by hydrolysis of the enol-phosphonium salt **8** (Scheme 2). Benzoins (**2a-c**) were reduced to benzyl phenyl ketones (**5a-c**) effectively by **1** in the presence of PPh_3 via the Perkow-type intermediates. On the other hand, selectivities for the reaction of **2d-e** were different from those of benzoins. Ethyl mandelate (**2d**) was thought to be converted to bromide (**4d**) at first by **1**. Then, **4d** reacted with PPh_3 slowly to give the keto-type salt, which resulted in a low yield of **4d** but no detectable yield of **5d**.

In the presence of NEt_3, this is a typical substitution reaction of the hydroxy group to bromide (Scheme 1). Triethylamine may act as a nucle-

ophile to convert ammonium salt by the reaction with bromide **4a**, and this was the reason why for the low isolatable yield of **4a**. Interestingly, 3-hydroxy-1-phenyl-4-hexanone (**2e**) was oxidized to **3e** even in the presence of PPh_3 and converted a complex mixture in the presence of NEt_3. Since **2e** is the alkyl ketone, enolization may be a factor why the reaction of **2e** and **1** in the presence of base was not same as the other substrates.

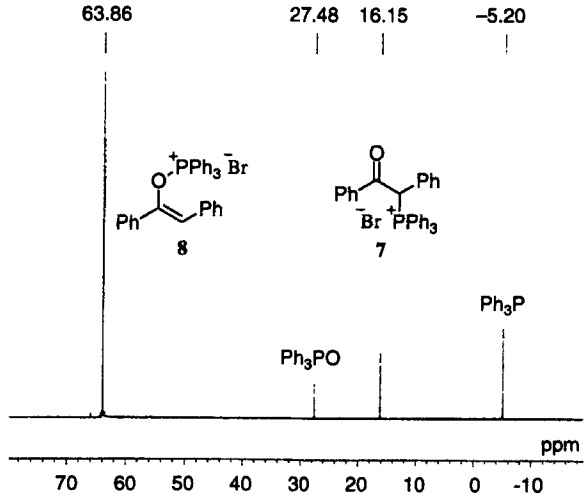
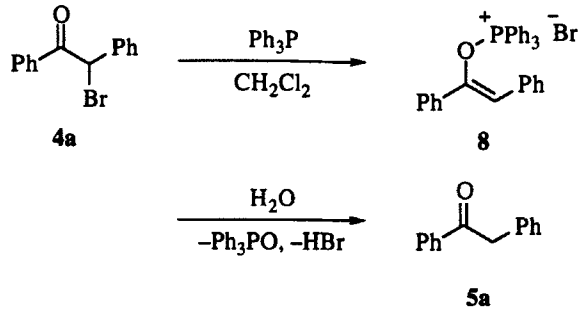


FIGURE 1 $^{31}P\{^1H\}$ NMR Spectrum (CD_2Cl_2) of the mixture of triphenylphosphine and desyl bromide



CONCLUSION

We found that the oxidation of **2** to **3** was not effected by **1** only, but was accomplished selectively by bromine. The reaction of benzoins with **1** in the presence of triethylamine or pyridine gave products in which the hydroxy group was replaced by bromide, while the reduction of benzoins proceeded mainly to give **5** in the presence of triphenylphosphine.

EXPERIMENTAL SECTION

General

All solvents were dried by standard methods and distilled under argon.[14] Commercially available compounds were used without purification. Substrates **2a-2d** were purchased from Wako Pure Chemical Industries, Ltd. or Tokyo Kasei Kogyo Co., Ltd. 3-Hydroxy-l-phenyl-4-hexanone (**2e**) was prepared by modified procedure according to the literature method[15] and was identified by spectroscopic analysis.[16]All products were identified by mp, bp, IR, and/or ^{1}H NMR analyses by comparison with that of authentic amples (**3a**, **3b**, **3c**, **3d**, **4a**, **5a**, and **5c**: as purchased from Aldrich or Tokyo Kasei Kogyo Co., Ltd.; **3e**[17], **4b**[18], **4c**[18], **4d**[19], and **5b**[20]: prepared according to the literatures). Nuclear magnetic resonance (^{1}H and ^{31}P NMR) spectra were measured on a JEOL JNM A-400 (400 MHz and 160 MHz for ^{1}H and ^{31}P, respectively) spectrometer using tetramethylsilane as an internal standard for ^{1}H and 85% H_3PO_4 aq. as an external standard for ^{31}P. IR spectra were measured on a Shimadzu IR-408 spectrometer. Analyses by gas chromatography were performed on a Shimadzu GC-14A (Column packing: 5% Silicone SE-30 on Chromosorb W AW DMCS (80–100 mesh)). Melting points were measured on a Yanako Model MP and were not corrected.

3-Hydroxy-1-phenyl-4-hexanone (2e)

To a tetrahydrofuran solution (100 mL) of trimethylsilyl cyanide (7.4 mL, 55 mmol) and 3-phenylpropanal (6.6 mL, 50 mmol) was added

a catalytic amount of triethylamine (0.50 g, 4.9 mmol) at 0°C under argon atmosphere. The mixture was stirred overnight at the same temperature. To the mixture, the 3.0 M ether solution of ethylmagnesium bromide (20 mL, ca. 60 mmol) was added at -78°C, and the resulting mixture was heated at reflux temperature for 4 h. Then 2.0 M HCl was added to the mixture. After stirring overnight, the organic layer extracted with ether was washed with brain, dried over Na_2SO_4, and concentrated. After column chromatography (silica-gel 60, hexane-ethyl acetate), a pale yellow oil, 3-hydroxy-1-phenyl-4-hexanone (**2e**), was obtained in 1.48 g (15% yield). The products were identified by IR and/or ^1H NMR analyses by comparison with that in the literature.[16]

Reaction of benzoin (2a) with bromine

To a stirred solution of bromine (0.32 g, 2.0 mmol) in dichloromethane (15 mL) at room temperature was added benzoin (**2a**) (0.42 g, 2.0 mmol). After stirring at room temperature for 48 h, the mixture was quenched with saturated sodium thiosulfate aq. and subsequently diluted with water and dichloromethane. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (10 mL × 3). The combined organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated. Recrystallization of the residue from ethanol to give **3a** (0.40 g, 1.9 mmol, 95% yield).

Reaction of 4,4′-dimethylbenzoin (2b) with bromine

To a stirred solution of bromine (0.32 g, 2.0 mmol) in dichloromethane (15 mL) was added **2b** (0.48 g, 2.0 mmol) at room temperature. After stirring at room temperature for 48 h, the mixture was quenched with saturated sodium thiosulfate aq. and subsequently diluted with water and dichloromethane. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (10 mL × 3). The combined organic layer was washed with water and dried over anhydrous magnesium sulfate. The mixture was filtered, concentrated, and separated by column chromatography (silica-gel, hexane-ethyl acetate). Product **3b** was obtained in 84% yield (0.40 g, 1.7 mmol).

Reaction of 4,4′-dimethoxybenzoin (2c) with bromine

Similar procedure of the reaction of **2b** with bromine was emgaged except to use **2c** (0.54 g, 2.0 mmol). Column chromatography (silica-gel, hexane-ethyl acetate) gave **3c** in 30% yield in pure form (0.16 g, 0.6 mmol). There were several products due to bromination on aromatic rings.

Reaction of ethyl mandelate (2d) with bromine

Similar procedure of the reaction of **2b** with bromine was emgaged except to use **2d** (0.36 g, 2.0 mmol). Column chromatographic purification (silica-gel, hexane-ethyl acetate) afforded **3d** in 70% yield (0.25 g, 1.4 mmol).

Reaction of 3-hydroxy-1-phenyl-4-hexanone (2e) with bromine

Similar procedure of the reaction of **2b** with bromine was emgaged except to use **2e** (0.38 g, 2.0 mmol). Column chromatography (silica-gel, hexane-ethyl acetate) gave the oxidation product **3e** in 74% yield (0.29 g, 1.5 mmol).

Reaction of dibromotriphenylphosphorane (1) with benzoin 2a

This is a typical reaction procedure of **2** and **1**. To a 50 mL flask containing dichloromethane (15 mL) were added bromine (0.32 g, 2.0 mmol) and triphenylphosphine (0.52 g, 2.0 mmol). After stirring for 15 min, benzoin (0.42 g, 2.0 mmol) was added to this mixture, and the resulting mixture was stirred at room temperature for 48 h. Water and dichloromethane were added to the mixture, and the organic layer was separated, washed with sat. sodium thiosulfate aq. and then water, dried over magnesium sulfate, and concentrated. The resulting materials were separated by column chromatography (silica-gel 60, hexane-ethyl acetate) to yield **3a** (0.01 g, 0.04 mmol, 2 % yield), **4a** (2 mg), and **5a** (0.36 g, 1.8 mmol, 92 % yield).

Reaction of 1 with 4,4′-dimethylbenzoin 2b in the presence of PPh_3

This is a typical reaction procedure of **2** and **1** in the presence of PPh_3. To a 50 mL flask containing dichloromethane (15 mL) were added bromine

(0.32 g, 2.0 mmol) and triphenylphosphine (1.04 g, 4.0 mmol). After stirring for 15 min, **2b** (0.48 g, 2.0 mmol) was added to this mixture, and the resulting mixture was stirred at room temperature for 48 h. Water and dichloromethane were added to the mixture, and the organic layer was separated, washed with sat. sodium thiosulfate aq. and then water, dried over magnesium sulfate, and concentrated. The resulting materials were separated by column chromatography (silica-gel 60, hexane-ethyl acetate) to give **5b** (0.35 g, 0.16 mmol, 78 % yield).

Reaction of 1 with 4,4′-dimethoxybenzoin 2c in the presence of PPh_3

Similar procedure of the reaction of **2b** and **1** in the presence of PPh_3 was emgaged except to use **2c** (0.54 g, 2.0 mmol). Column chromatography (silica-gel 60, hexane-ethyl acetate) yielded **5c** (0.42 g, 0.16 mmol, 82 % yield).

Reaction of 1 with ethyl mandelate 2d in the presence of NEt_3

This is a typical reaction procedure of **2** and **1** in the presence of NEt_3. To a 50 mL flask containing dichloromethane (15 mL) were added bromine (0.32 g, 2.0 mmol), triphenylphosphine (0.52 g, 2.0 mmol), and triethylamine (0.20 g, 2.0 mmol). After stirring for 15 min, **2d** (0.36 g, 2.0 mmol) was added to this mixture, and the resulting mixture was stirred at room temperature for 48 h. The mixture was quenched with saturated sodium thiosulfate aq., and subsequently diluted with water and dichloromethane. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (10 mL × 3). Combined organic layer was washed with water and dried over magnesium sulfate. The solution was filtered and concentrated. The resulting materials were separated by column chromatography (silica-gel 60, hexane-ethyl acetate) to give **3d** (3 mg) and **4d** (0.34 g, 0.14 mmol, 70 % yield).

Reaction of 1 with 3-hydroxy-1-phenyl-4-hexanone 2e in the presence of PPh_3

Similar procedure of the reaction of **2b** and **1** in the presence of PPh_3 was emgaged except to use **2e** (0.38 g, 2.0 mmol). Column chromatography

(silica-gel 60, hexane-ethyl acetate) gave **3e** (0.23 g, 0.12 mmol, 61 % yield).

Reaction of desyl bromide 4a with PPh_3

To a 25 mL flask were added dichloromethane (7.5 mL), **4a** (0.28 g, 1.0 mmol), and PPh_3 (0.26 g, 1.0 mmol). The mixture was stirred at room temperature for 2 h. Water and dichloromethane were poured to this mixture. Separated organic layer was washed with saturated sodium thiosulfate aq. and then with water. After concentration, the resulting materials were separated by column chromatography (silica-gel 60, hexane-ethyl acetate) to give **5a** (0.18 g, 0.94 mmol, 94% yield).

$^{31}P\{^1H\}$ NMR study of the mixture of 4a and PPh_3 in CD_2Cl_2

To a 5 mmϕ NMR tube were added PPh_3 (52 mg, 0.2 mmol), **4a** (55 mg, 0.2 mmol), and CD_2Cl_2 (1 mL), succesively. This sample was subjected to NMR mesurement. ^{31}P NMR (160 MHz) δ -5.20, 16.15, 27.48, 63.86.

Acknowledgements
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