A New Route for Generation of α-λ^3-Iodanyl Ketones via Ester Exchange of (*Z*)-(*β*-Acetoxyvinyl)-λ^3-iodanes: Their Nucleophilic Substitutions with Halides and Sulfur and Phosphorus Nucleophiles

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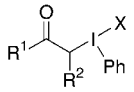
An efficient method for generation of α-λ^3-iodanyl ketones from (*Z*)-(2-acetoxyvinyl)(phenyl)-λ^3-iodanes was developed. The method involves ester exchange of (*Z*)-2-acetoxyvinyl-λ^3-iodanes with methanol in the presence of triethylamine. α-λ^3-Iodanyl ketones react with a variety of nucleophiles such as halides, thiols, phosphines, phosphinic acids, and phosphates, under the conditions which produce α-functionalized carbonyl compounds probably via an S_N2 pathway.

Introduction

It has been generally accepted that α-λ^3-iodanyl ketones of general structure **1** are key intermediates in the oxidation of carbonyl compounds at the α-carbon atom



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by λ^3-organoiodanes under acidic and basic conditions.[1] For instance, (diacetoxyiodo)benzene brings about oxidation of ketones in acetic acid−acetic anhydride in the presence of sulfuric acid to give α-acetoxy ketones, in which intermediate formation of α-λ^3-iodanyl ketones **1** (X = OAc) is believed to be involved.[2] α-λ^3-Iodanyl ketones **1** are highly reactive toward the attack of nucleophiles, probably via an S_N2 pathway with reductive elimination of iodobenzene, and thus have never been isolated.[3] This is due to the very high nucleofugality of the λ^3-phenyliodanyl groups, which show a leaving group ability about 10^6 times greater than that of the superleaving group, triflate.[4]

α-λ^3-Iodanyl ketones **1** with various heteroatom ligands such as OH,[5] OMe,[6] OAc,[7] $OCOCF_3$,[8] OTs,[3] OMs,[9] $OP(O)(OPh)_2$,[10] $OP(O)R_2$,[11] and N_3[12] can be generated in situ from carbonyl compounds or silyl enol ether derivatives by the reaction with λ^3-organoiodanes. In most of these organoiodanes **1**, the ligand X is introduced to the α-carbon atom of the carbonyl compounds regioselectively with reductive elimination of iodobenzene. α-λ^3-Iodanyl ketones **1** with BF_4 as ligand X are known and react with a variety of carbon nucleophiles including silyl enol ethers, olefins, and allylsilanes.[13] Oxidation of alkynes with λ^3-organoiodanes is an efficient alternative for generation of α-λ^3-iodanyl ketones **1** and affords α-hydroxy, α-trifluoroacetoxy, and α-phosphoryloxy ketones and/or their further oxidation products.[14−16]

(1) (a) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. (b) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. (c) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431. (d) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers: New York, 1992.

(2) Mizukami, F.; Ando, M.; Tanaka, T.; Imamura, J. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 335.

(3) α-λ^3-Iodanyl *β*-diketones are known. 2-Dimedonyl(phenyl)iodonium tosylate has been prepared from dimedone by the reaction with [hydroxy(tosyloxy)iodo]benzene in good yield as a white solid, which on heating in acetonitrile affords 2-tosyloxydimedone. See: Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.

(4) The leaving process of λ^3-phenyliodanyl groups involves an energetically favorable reduction of the hypervalent iodine(III) to the normal valency (i.e., PhI) with octet structure. This is the origin of the high leaving group ability. Therefore, a nucleofuge such as the λ^3-aryliodanyl group is termed a hyperleaving group. See: (a) Ochiai, M. In *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: New York, 1999; Chapter 12. (b) Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360.

(5) (a) Moriarty, R. M.; Hu, H.; Gupta, S. C. *Tetrahedron Lett.* **1981**, *22*, 1283. (b) Moriarty, R. M.; Hou, K.-C. *Tetrahedron Lett.* **1984**, *25*, 691. (c) Moriarty, R. M.; Prakash, O.; Freeman, W. A. *J. Chem. Soc., Chem. Commun.* **1984**, 927. (d) Moriarty, R. M.; Engerer, S. G.; Prakash, I.; Gill, U. S.; Freeman, W. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1715.

(6) Moriarty, R. M.; Rani, N.; May, E. J.; Guo, L.; Prakash, O. *J. Chem. Res., Synop.* **1998**, 32.

(7) (a) Moriarty, R. M.; Hu, H. *Tetrahedron Lett.* **1981**, *22*, 2747. (b) Tamura, Y.; Yakura, T.; Shirouchi, Y.; Haruta, J. *Chem. Pharm. Bull.* **1985**, *33*, 1097.

(8) Moriarty, R. M.; Berglund, B. A.; Penmasta, R. *Tetrahedron Lett.* **1992**, *33*, 6065.

(9) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 210.

(10) Koser, G. F.; Lodaya, J. S.; Ray, D. G.; Kokil, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 2987.

(11) Moriarty, R. M.; Condeiu, C.; Tao, A.; Prakash, O. *Tetrahedron Lett.* **1997**, *38*, 2401.

(12) Moriarty, R. M.; Vaid, R. K.; Ravikumar, V. T.; Vaid, B. K.; Hopkins, T. E. *Tetrahedron* **1988**, *44*, 1603.

(13) (a) Zhdankin, V. V.; Tykwinski, R.; Caple, R.; Berglund, B.; Kozmin, A. S.; Zefirov, N. S. *Tetrahedron Lett.* **1988**, *29*, 3703. (b) Zhdankin, V. V.; Mullikin, M.; Tykwinski, R.; Berglund, B.; Caple, R.; Zefirov, N. S.; Kozmin, A. S. *J. Org. Chem.* **1989**, *54*, 2605. (c) Zefirov, N. S.; Samoniya, N. S.; Kutateladze, T. G.; Zhdankin, V. V. *Zh. Org. Khim.* **1991**, *27*, 220.

(14) (a) Merkushev, E. B.; Karpitskaya, L. G.; Novosel'tseva, G. I. *Dokl. Akad. Nauk SSSR* **1979**, *245*, 607. (b) Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *Tetrahedron Lett.* **1985**, *26*, 3837. (c) Vasil'eva, V. P.; Khalfina, I. L.; Karpitskaya, L. G.; Merkushev, E. B. *Zh. Org. Khim.* **1987**, *23*, 2225. (d) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Prakash, I. *J. Org. Chem.* **1988**, *53*, 6124. (e) Haruta, J.; Nishi, K.; Matsuda, S.; Akai, S.; Tamura, Y.; Yakura, T.; Kita, Y. *J. Org. Chem.* **1990**, *55*, 4853.

(15) Koser, G. F.; Chen, X.; Chen, K.; Sun, G. *Tetrahedron Lett.* **1993**, *34*, 779.

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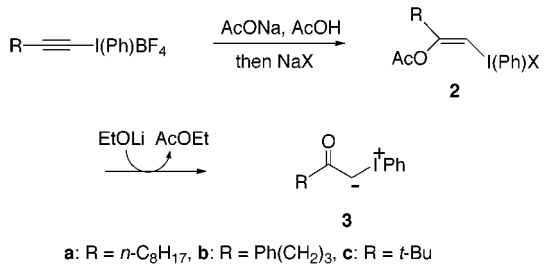
Scheme 1



Recently, we found that ester exchange between (*Z*)-(2-acetoxyvinyl)(phenyl)-λ^3-iodanes **2** (X = BF_4) and EtOLi in THF at −78 °C generates monocarbonyl iodonium ylides **3** quantitatively with liberation of ethyl acetate (Scheme 1).[17] The monocarbonyl iodonium ylides **3** are moderately nucleophilic and undergo alkylidene transfer to aldehydes and activated imines to give α,*β*-epoxy ketones and 2-acylaziridines stereoselectively in good yields. On the basis of the reported data that the introduction of the λ^3-phenyliodanyl group raises the CH acidity of malonic esters by approximately 8 orders of magnitude,[18] the acidity (pK_a) of the α-methylene protons of α-λ^3-iodanyl ketones **1** (R^2 = H) would be estimated to be around 12. In fact, iodonium ylide **3a** (R = *n*-C_8H_{17}) still survives even in the presence of excess amounts of ethanol with a pK_a value of 15.9 and reacts with benzaldehyde, yielding the corresponding α,*β*-epoxy ketone under these conditions.[17a]

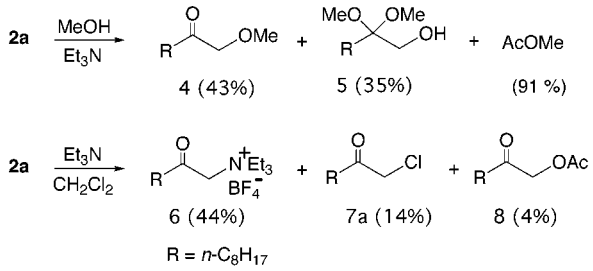
We envisioned that generation of the monocarbonyl iodonium ylides **3** in the presence of an appropriate proton source with similar acidity (pK_a = 12) makes it possible to protonate the iodonium ylides **3**, producing α-λ^3-iodanyl ketones **1** (R^2 = H). We now report a method for in situ generation of α-λ^3-iodanyl ketones **1** from (*Z*)-(2-acetoxyvinyl)(phenyl)-λ^3-iodanes **2** (X = BF_4) via ester exchange reaction of the *β*-acetoxy group, and their nucleophilic substitutions with halides and sulfur and phosphorus nucleophiles.[19]

Results and Discussion

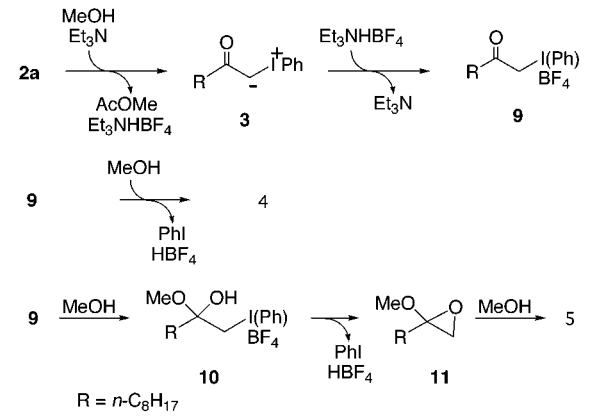
Generation of α-λ^3-Iodanyl Ketones. Exposure of (*Z*)-(2-acetoxy-1-decenyl)(phenyl)-λ^3-iodane **2a** (X = BF_4) to triethylamine (1.1 equiv) in MeOH at room temperature for 1 h gave α-methoxy ketone **4** (43%) and α-hydroxy dimethyl acetal **5** (35%), along with the formation of methyl acetate (91%). Without triethylamine, **2a** was quantitatively recovered unchanged. Interestingly, changing the solvent from methanol to dichloromethane resulted in a decrease in the rate of the reaction (at room temperature for 5 h) and gave a mixture of products: (2-oxoalkyl)triethylammonium tetrafluoroborate **6** (44%), α-chloro ketone **7a** (14%), and α-acetoxy ketone **8** (4%) (Scheme 2).

Formation of α-methoxy ketone **4** and α-hydroxy dimethyl acetal **5** in methanol strongly suggests the intermediacy of α-λ^3-iodanyl ketone **9**, and a possible

Scheme 2



Scheme 3



mechanism for the reaction is shown in Scheme 3. High-yield formation of methyl acetate clearly indicates the intervention of ester exchange between *β*-acetoxyvinyliodane **2a** and MeOH to produce monocarbonyl iodonium ylide **3**. The Et_3NHBF_4 (pK_a = 11.0) produced during the reaction undergoes proton transfer to the iodonium ylide **3**, yielding α-λ^3-iodanyl ketone **9**.[20] Alternatively, α-λ^3-iodanyl ketone **9** might be directly produced via triethylamine-mediated ester exchange of vinyliodanes **2a** with MeOH. Nucleophilic attack of methanol on α-iodanyl ketone **9** at the α-position gives rise to the α-methoxy ketone **4**, probably via an S_N2 pathway. On the other hand, attack of methanol upon the carbonyl group of **9** produces hemiacetal **10**, which, in turn, undergoes intramolecular reductive cyclization with formation of epoxide **11**. The oxirane **11** would be attacked by another methanol at the acetal carbon atom with formation of α-hydroxy dimethyl acetal **5**. α-Methoxy ketone **4** might also be produced by nucleophilic attack of methanol at the other carbon atom of the oxirane ring of **11**.

The mechanism for formation of α-hydroxy dimethyl acetal **5** from α-λ^3-iodanyl ketone **9**, shown in Scheme 3, was originally proposed by Moriarty and co-workers in the oxidation of ketones with (diacetoxyiodo)benzene in alkaline methanol.[5] They demonstrated that the label (^{18}O) of the carbonyl oxygen of the ketones was incorporated into the hydroxyl group of the α-hydroxy dimethyl acetal **5** produced.[1a]

In dichloromethane, the major product (2-oxoalkyl)-ammonium salt **6** will be produced probably via an S_N2 displacement of ketone **9** by triethylamine. The solvent dichloromethane may also act as a nucleophile in S_N2 displacement of ketone **9**, yielding α-chloro ketone **7a**. Dichloromethane can react with a highly electron-deficient species, such as a carbenoid and a carbocation,

(16) Ochiai, M.; Kunishima, M.; Fuji, K.; Nagao, Y. *J. Org. Chem.* **1989**, *54*, 4038.

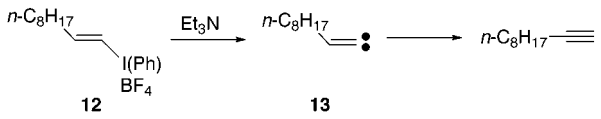
(17) (a) Ochiai, M.; Kitagawa, Y.; Yamamoto, S. *J. Am. Chem. Soc.* **1997**, *119*, 11598. (b) Ochiai, M.; Kitagawa, K. *Tetrahedron Lett.* **1998**, *39*, 5569. (c) Ochiai, M.; Kitagawa, Y. *J. Org. Chem.* **1999**, *64*, 3181.

(18) Neiland, O. Y.; Karele, B. Y. *Zh. Org. Khim.* **1971**, *7*, 1611.

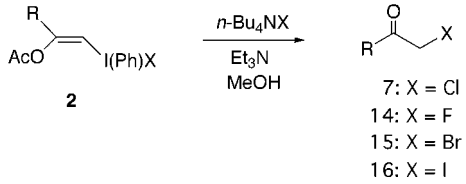
(19) A part of this work has been reported in a preliminary form: Ochiai, M.; Nishi, Y.; Nishitani, J.; Chen, D.-W.; Hashimoto, S.; Tsuchimoto, Y. *J. Chem. Soc., Chem. Commun.* **2000**, 1157.

(20) Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1992.

Scheme 4



Scheme 5



and transfer the chlorine atom.[21] The presence both of the strongly electron-withdrawing λ^3-phenyliodanyl group with a large Hammett σ value ($\sigma_p = 1.37$)[22] and of the acyl group makes the α-carbon atom of **9** highly electron-deficient, and thereby nucleophile displacement of ketone **9** with dichloromethane becomes possible.

Triethylamine readily abstracts an α-vinylic hydrogen of simple vinyl(phenyl)-λ^3-iodane **12** to produce 1-decyne via the intermediacy of alkylidene carbene **13** (Scheme 4).[23] This α-elimination pathway was not detected for reactions of β-acetoxyvinyliodane **2a**. This is probably due to the presence of the β-acetoxy group in **2a**. We believe that the electron-withdrawing λ^3-phenyliodanyl group of **2a** highly activates the ester carbonyl group toward the attack of nucleophiles,[22] which makes the triethylamine-catalyzed ester exchange with methanol more facile than the α-elimination pathway.

Nucleophilic Substitution with Halides. When α-λ^3-iodanyl ketones **9** were generated from (*Z*)-2-acetoxyvinyliodanes **2** (X = BF_4) by the room temperature reaction with triethylamine−MeOH in the presence of sodium or tetrabutylammonium halides, nucleophilic substitution took place, and α-halo ketones (α-chloro **7**, α-bromo **15**, and α-iodo **16**) were obtained in good yields (Scheme 5, Table 1). In the reaction with sodium fluoride, no substitution with fluoride was observed, but instead, large amounts of α-methoxy ketone **4** and α-hydroxy dimethyl acetal **5** were formed (Table 1, entry 1). Very interestingly, even without triethylamine, iodanyl ketone **9** is apparently generated in methanol and produces α-bromo ketones **15**, although the rate of the reaction seems to slow considerably (compare Table 1, entries 6−8). In addition to α-bromo ketone **15a** (75%), formation of benzyl acetate (66%) in the reaction of **2a** in the presence of benzyl alcohol in dichloromethane provides additional evidence for the ester exchange mechanism (Table 1, entry 10).

It has been reported that exposure of stable iodonium ylides, derived from 1,3-diketones, to hydrochloric acid in methanol results in the formation of 2-chloro 1,3-diketones via nucleophilic substitution on the intermediate 2-(λ^3-phenyliodanyl) 1,3-diketones with chloride.[24,25]

Table 1. Nucleophilic Substitution of α-λ^3-Iodanyl Ketones 9 with Halides[a]

entry	**2** (X = BF_4)	equiv of Et_3N	halide	solvent	time (h)	α-halo ketone	yield (%)[b]
1	**2a**	1.1	NaF	MeOH	3	**14a**	0[c]
2	**2a**	1.1	NaCl	MeOH	1	**7a**	63
3	**2a**	1.1	NaBr	MeOH	1	**15a**	85
4	**2a**	1.1	NaI	MeOH	1	**16a**	71
5	**2a**	1.1	Bu_4NCl	MeOH	1	**7a**	69
6	**2a**	1.1	Bu_4NBr	MeOH	1	**15a**	84
7	**2a**	0.2	Bu_4NBr	MeOH	24	**15a**	71
8	**2a**		Bu_4NBr	MeOH	1	**15a**	33[d]
9	**2a**	1.1	Bu_4NBr	CH_2Cl_2	9	**15a**	50
10	**2a**	1.1	Bu_4NBr	CH_2Cl_2[e]	1	**15a**	75[f]
11	**2a**	1.1	Bu_4NI	MeOH	1	**16a**	71
12	**2b**	1.1	Bu_4NBr	MeOH	1	**15b**	64

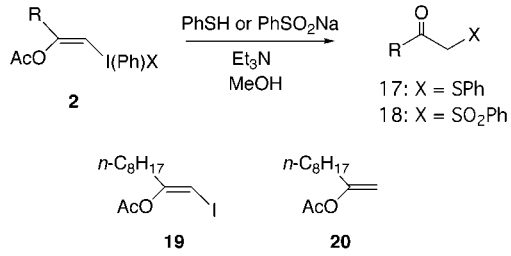
[a] Reactions were carried out using 1.2 equiv of a halide at 25 °C under nitrogen. [b] Isolated yields. [c] α-Methoxy ketone **4** (47%) and α-hydroxy dimethyl acetal **5** (33%) were obtained. [d] Iodane **2a** (53%) was recovered. [e] Reaction was carried out in the presence of benzyl alcohol (5 equiv). [f] Benzyl acetate (66%) was obtained.

Table 2. Substitution of α-λ^3-Iodanyl Ketones 9 with Sulfur Nucleophiles[a]

entry	**2** (X = BF_4)	base	nucleophile (equiv)	solvent	product	yield (%)[b]
1	**2a**	Et_3N	PhSH (2)	MeOH	**17a**	36[c]
2	**2a**	Et_3N	$PhSO_2Na$ (3)	MeOH	**18a**	56[d]
3	**2a**	EtOLi	PhSH (3)	THF[e]	**17a**	65
4	**2b**	EtOLi	PhSH (3)	THF[e]	**17b**	77
5	**2c**	EtOLi	PhSH (3)	THF[e]	**17c**	78

[a] Reactions were carried out using 1.1 equiv of a base at 0 °C for 1 h under nitrogen. [b] Isolated yields. [c] β-Acetoxyvinyl iodide **19** (19%) and terminal olefin **20** (20%) were obtained. [d] α-Hydroxy dimethyl acetal **5** (15%) was obtained. [e] Reaction temperature −78 °C to room temperature.

Scheme 6



Nucleophilic Substitution with Sulfur Nucleophiles. Reaction of λ^3-iodanes **2** in the presence of thiophenol as a nucleophile gave a mixture of products: treatment of **2a** with triethylamine in MeOH in the presence of thiophenol (2 equiv) at 0 °C afforded the desired sulfide **17a**, but in only 36% yield (Table 2, entry 1). In this reaction, large amounts of (*Z*)-β-acetoxyvinyl iodide **19** (19%) and terminal olefin **20** (20%) were also obtained. The use of sodium benzenesulfinate (3 equiv) as a nucleophile afforded β-keto sulfone **18a** in moderate yield (56%) (Scheme 6).

The formation of olefins **19** and **20** suggests the simultaneous occurrence of another process that competes with the desired ester exchange reaction of **2a**. The competing reaction probably involves a single-electron transfer to highly electron-deficient λ^3-iodane **2a**, gener-

(21) (a) White, E. H.; McGirk, R. H.; Aufdermarsh, C. A.; Tiwari, H. P.; Todd, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 8107. (b) Pirrung, M. C.; Zhang, J.; Lackey, K.; Sternbach, D. D. Brown, F. *J. Org. Chem.* **1995**, *60*, 2112.

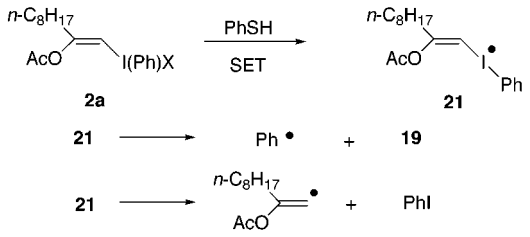
(22) Mironova, A. A.; Maletina, I. I.; Iksanova, S. V.; Orda, V. V.; Yagupolskii, L. M. *Zh. Org. Chem.* **1989**, *25*, 306.

(23) (a) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565. (b) Ochiai, M.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3135. (c) Ochiai, M.; Sueda, T.; Uemura, K.; Masaki, Y. *J. Org. Chem.* **1995**, *60*, 2624.

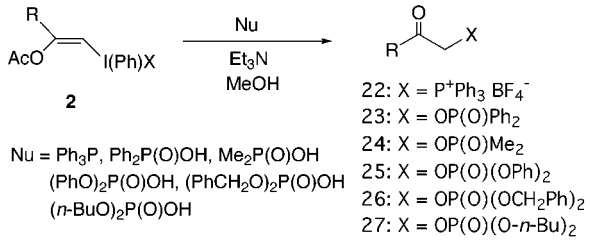
(24) (a) Neiland, O. *Zh. Org. Khim.* **1965**, *1*, 1858. (b) Coats, S. J.; Wasserman, H. H. *Tetrahedron Lett.* **1995**, *36*, 7735.

(25) Interestingly, Hara and Yoneda reported direct fluorination of β-ketoesters using *p*-(difluoroiodo)toluene and a HF−pyridine complex. Hara, S.; Sekiguchi, M.; Ohmori, A.; Fukuhara, T.; Yoneda, N. *J. Chem. Soc., Chem. Commun.* **1996**, 1899.

Scheme 7



Scheme 8



a: R = *n*-C_8H_{17}, **b**: R = Ph$(CH_2)_3$, **c**: R = *t*-Bu

ating the vinyl(phenyl)iodanyl radical **21** (Scheme 7).[26,27] Radical **21** would decompose by two paths, one leading to phenyl radical and β-acetoxyvinyl iodide **19**, and the other to β-acetoxyvinyl radical and iodobenzene. β-Acetoxyvinyl radical abstracts a hydrogen atom from thiophenol and affords the terminal olefin **20**. Single-electron transfer does not seem to be important in the reaction with sodium benzenesulfinate, which gives β-keto sulfone **18a** in moderate yield.

To avoid the undesirable single-electron transfer, the monocarbonyl iodonium ylide **3** was pregenerated from **2** by the reaction with EtOLi in THF, prior to the addition of thiophenol. It is likely that the addition of thiophenol with a pK_a value of 8.4[28] can cause rapid protonation of the ylide **3** with formation of the α-λ^3-iodanyl ketone **9**, which reacts with thiophenol or its anion to give β-keto sulfide **17**. This alternative procedure was found to exclusively inhibit the competing single-electron-transfer process and afforded the desired β-keto sulfides **17a**−**c** in good yields (Table 2, entries 3−5).

Nucleophilic Substitution with Phosphorus Nucleophiles. α-λ^3-Iodanyl ketones **9** also undergo substitutions by the reaction with phosphorus nucleophiles, such as phosphines, phosphinic acids, and phosphates (Scheme 8). Treatment of **2a** (X = BF_4) with triethylamine in the presence of triphenylphosphine (2 equiv) in MeOH at room temperature, after acidification of the reaction mixture with 5% aqueous HBF_4 solution, afforded (2-oxodecyl)phosphonium tetrafluoroborate **22a** in 89% yield. β-Keto phosphonium salts **22b** and **22c** were also obtained in good yields (Table 3, entries 1−3).

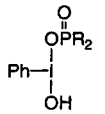
In these reactions, β-keto phosphonium ylide **28** seems to be produced, which makes possible Wittig olefination with aldehydes (Scheme 9). The formation of phosphonium ylide **28** is compatible with the reported acidity of acetonyl(triphenyl)phosphonium salt **22d** (R = Me, pK_a = 6.6), more acidic than Et_3NHBF_4.[29] We have reported that, after treatment of **2** with triethylamine in the presence of triphenylphosphine in MeOH at room temperature, addition of an aldehyde to the reaction mixture and then heating at 60 °C resulted in the formation of α,β-unsaturated ketones with high *trans* selectivity.[19]

The nucleophilicity of diphenylphosphinic acid seems to be lower than that of triphenylphosphine: thus, reaction of **2a** (X = BF_4) with triethylamine and diphenylphosphinic acid in MeOH gave the desired α-ketol diphenylphosphinate **23a** in only 18% yield (Table 3, entry 4). In this reaction, the solvent methanol rather than diphenylphosphinic acid acts as a major nucleophile toward α-λ^3-iodanyl ketone **9**, and large amounts of α-methoxy ketone **4** (38%) and α-hydroxy dimethyl acetal **5** (15%) were produced. Nucleophilic attack of methanol on α-λ^3-iodanyl ketone **9** is reduced to a negligibly small extent by using both dichloromethane as a solvent instead of methanol and limited amounts of methanol (2 equiv). Under these conditions, α-ketol diphenylphosphinate **23a** was obtained in 78% yield (Table 3, entry 5). Vinyl-λ^3-iodanes **2b** and **2c** were also converted into ketol diphenylphosphinates **23b** and **23c** in high yields.

Similarly, the reaction with dimethylphosphinic acid afforded α-ketol dimethylphosphinates **24a**−**c** in yields of 77−98% (Table 3, entries 8−10). Dimethylphosphinate **24** seems to be labile toward hydrolysis,[30] and in fact, partial hydrolysis of **24** was observed on purification by silica gel thin-layer chromatography.

Diphenyl, dibenzyl, and dibutyl phosphates also underwent S_N2 displacement of α-λ^3-iodanyl ketone **9** in dichloromethane in the presence of methanol (2 equiv) and afforded α-phosphoryloxy ketones **25**−**27** in good to excellent yields (Table 3, entries 11−17). However, attempted nucleophilic substitutions of **9** with trimethyl phosphite, yielding β-keto phosphonates,[31] and with trimethyl phosphate, yielding α-ketol phosphate,[32] were found to be fruitless.

α-Phosphoryloxy ketones have been prepared by Koser and co-workers by direct α-oxyphosphorylation of ketones using phosphoryloxy(phenyl)-λ^3-iodanes **29** and **30**.[10,33] The direct α-oxyphosphorylation of ketones was proposed to involve nucleophilic substitution of α-λ^3-iodanyl ketones, generated in situ, with diphenyl and dibenzyl phosphates. α-Ketol dimethylphosphinates and diphenylphosphinates were prepared by α-phosphinylation of carbonyl compounds using λ^3-phenyliodanes **31** and **32**.[11]



29: R = OPh
30: R = OCH_2Ph
31: R = Me
32: R = Ph

In conclusion, we have developed a new, efficient method for in situ generation of α-λ^3-iodanyl ketones from

(26) For nomenclature, see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(27) For generation of [9-I-2] iodanyl radicals, see: (a) Chen, D.-W.; Ochiai, M. *J. Org. Chem.* **1999**, *64*, 6804. (b) Ochiai, M.; Ito, T.; Takahashi, H.; Nakanishi, A.; Toyonari, M.; Sueda, T.; Goto, S.; Shiro, M. *J. Am. Chem. Soc.* **1996**, *118*, 7716. (c) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 3917. (d) Beringer, F. M.; Falk, R. A. *J. Chem. Soc.* **1964**, 4442. (e) Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1. (f) Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* **1993**, *58*, 943. (g) Mubarak, M. S.; Peters, D. G. *J. Org. Chem.* **1985**, *50*, 673.

(28) Oae, S. *Organic Chemistry of Sulfur*; Plenum: New York, 1977.

(29) (a) Fliszar, S.; Hudson, R. F.; Salvadori, G. *Helv. Chim. Acta* **1963**, *46*, 1580. (b) Johnson, A. W.; Amel, R. T. *Can. J. Chem.* **1968**, *46*, 461.

(30) Ramirez, F.; Marecek, J. F. *Synthesis* **1985**, 449.

(31) Kim, D. Y.; Mang, J. Y.; Oh, D. Y. *Synth. Commun.* **1994**, *24*, 629.

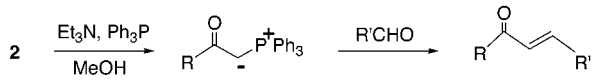
(32) Popov, K. A.; Polozov, A. M.; Tcherezov, S. V. *Tetrahedron Lett.* **1997**, *38*, 1859.

Table 3. Substitution of α-λ^3-Iodanyl Ketones 9 with Phosphorus Nucleophiles[a]

entry	2 (X = BF_4)	equiv of Et_3N	nucleophile (equiv)	solvent	additive (equiv)	time (h)	product	yield (%)[b]
1	**2a**	1.1	Ph_3P (2)	MeOH		1	**22a**	89
2	**2b**	1.1	Ph_3P (2)	MeOH		1	**22b**	66
3	**2c**	1.1	Ph_3P (2)	MeOH		1	**22c**	53(96)[c]
4	**2a**	2.5	$Ph_2P(O)OH$ (1.2)	MeOH		1	**23a**	18[d]
5	**2a**	1.1	$Ph_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	17	**23a**	78
6	**2b**	1.1	$Ph_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	48	**23b**	87
7	**2c**	1.1	$Ph_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	24	**23c**	88
8	**2a**	1.1	$Me_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	6	**24a**	98
9	**2b**	1.1	$Me_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	4	**24b**	93[c]
10	**2c**	1.1	$Me_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	6	**24c**	77(100)[c]
11	**2a**	2.0	$(PhO)_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	96	**25a**	47[c]
12	**2a**	2.0	$(PhCH_2O)_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	48	**26a**	83
13	**2b**	2.0	$(PhCH_2O)_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	21	**26b**	84
14	**2c**	2.0	$(PhCH_2O)_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	35	**26c**	71
15	**2a**	2.0	$(n\text{-}BuO)_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	7	**27a**	80
16	**2b**	2.0	$(n\text{-}BuO)_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	25	**27b**	69
17	**2c**	2.0	$(n\text{-}BuO)_2P(O)OH$ (2)	CH_2Cl_2	MeOH (2)	6	**27c**	64

[a] Reactions were carried out at 25 °C under nitrogen. [b] Isolated yields. [c] ^1H NMR yields. [d] α-Methoxy ketone **4** (38%) and α-hydroxy dimethyl acetal **5** (15%) were obtained.

Scheme 9



28

(*Z*)-(2-acetoxyvinyl)(phenyl)-λ^3-iodanes via ester exchange reaction of the β-acetoxy group. α-λ^3-Iodanyl ketones are highly reactive species and undergo substitution with a variety of nucleophiles such as halides, thiols, phosphines, phosphinic acids, and phosphates, probably via an S_N2 pathway.

Experimental Section

General Procedures. For general experimental details, see ref 17a. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel F-254. Kieselgel 60 (230−400 mesh) was used for flash chromatography. ^{31}P NMR chemical shifts are referenced to a sample of 85% H_3PO_4 (sealed capillary) in $CDCl_3$.

(*Z*)-(2-Acetoxy-1-decenyl)(phenyl)-λ^3-iodane **2a** (X = BF_4) was prepared according to a literature method.[17c] (*Z*)-(2-Acetoxy-5-phenyl-1-pentenyl)(phenyl)-λ^3-iodane **2b** (X = BF_4) and (*Z*)-(2-acetoxy-3,3-dimethyl-1-butenyl)(phenyl)-λ^3-iodane **2c** (X = BF_4) were prepared from 1-alkynyl(phenyl)-λ^3-iodane[34] via Michael addition of acetic acid in the presence of sodium acetate according to a literature procedure.[17c]

Data for **2b** (X = BF_4): white powder; mp 60−62 °C; IR (KBr) 1762, 1062 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (br d, J = 8.0 Hz, 2H), 7.60 (br t, J = 7.4 Hz, 1H), 7.44 (br dd, J = 8.0, 7.4 Hz, 2H), 7.34−7.06 (m, 5H), 6.65 (s, 1H), 2.64 (t, J = 7.4 Hz, 2H), 2.60 (t, J = 7.4 Hz, 2H), 2.24 (s, 3H), 1.82 (quint, J = 7.4 Hz, 2H); FAB MS *m*/*z* 407 [(M − BF_4)$^+$]. Anal. Calcd for $C_{19}H_{20}BF_4IO_2$: C, 46.19; H, 4.08. Found: C, 46.23; H, 4.15.

Data for **2c** (X = BF_4): colorless prisms; mp 89−91 °C (recrystallized from dichloromethane−diethyl ether); IR (KBr) 1769, 1063 (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02 (br d, J = 7.5 Hz, 2H), 7.65 (br t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 6.85 (s, 1H), 2.40 (s, 3H), 1.20 (s, 9H); FAB MS *m*/*z* 345 [(M − BF_4)$^+$]. Anal. Calcd for $C_{14}H_{18}BF_4IO_2$: C, 38.92; H, 4.20. Found: C, 38.70; H, 4.18.

Reaction of 2a with Triethylamine in Methanol. To a stirred solution of 1-decenyl-λ^3-iodane **2a** (X = BF_4) (30 mg, 0.062 mmol) in methanol (1.5 mL) was added triethylamine (6.9 mg, 0.068 mmol) under nitrogen at room temperature, and the mixture was stirred for 1 h. After addition of water, methanol was evaporated under an aspirator vacuum. The mixture was extracted with dichloromethane, and the combined organic phase was washed with water and brine. The organic phase was filtered and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (hexanes−ethyl acetate, 10:1) to give 1-methoxy-2-decanone (**4**) (4.9 mg, 44%) and 1-hydroxy-2-decanone dimethyl acetal (**5**) (4.8 mg, 35%). In a separate experiment, the yield (91%) of methyl acetate was determined by analytical GC (hexane as the internal standard). Data for **4**:[35] colorless oil; ^1H NMR ($CDCl_3$) δ 4.01 (s, 2H), 3.42 (s, 3H), 2.43 (t, J = 7.3 Hz, 2H), 1.7−1.5 (m, 2H), 1.43−1.12 (m, 10H), 0.88 (t, J = 5.9 Hz, 3H). Data for **5**: colorless oil; IR (neat) 3486 (br), 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.56 (d, J = 6.1 Hz, 2H), 3.23 (s, 6H), 1.74−1.48 (m, 2H), 1.4−1.1 (m, 12H), 0.87 (t, J = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 102.1, 61.4, 48.3, 31.9, 31.9, 29.9, 29.5, 29.3, 23.6, 22.7, 14.1; MS *m*/*z* (relative intensity) 187 [(M − OMe)$^+$, 100], 105 (34), 101 (19), 71 (11), 57 (20); HRMS *m*/*z* calcd for $C_{11}H_{23}O_2$ [(M − OMe)$^+$] 187.1698, found 187.1700.

Reaction of 2a with Triethylamine in Dichloromethane. To a stirred solution of 1-decenyl-λ^3-iodane **2a** (X = BF_4) (30 mg, 0.062 mmol) in dichloromethane (1.5 mL) was added triethylamine (6.9 mg, 0.068 mmol) under nitrogen at room temperature, and the mixture was stirred for 5 h. After addition of water, the mixture was extracted with dichloromethane, and the combined organic phase was washed with water and brine. The organic phase was filtered and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (hexanes−ethyl acetate, 10:1) to give (2-oxodecyl)triethylammonium tetrafluoroborate (**6**) (9 mg, 44%), 1-chloro-2-decanone (**7a**) (1.7 mg, 14%), and 1-acetoxy-2-decanone (**8**)[16] (0.5 mg, 4%). Data for **6**: white solid; IR (KBr) 1726, 1090 (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.41 (s, 2H), 3.58 (q, J = 7.3 Hz, 6H), 2.61 (t, J = 7.3 Hz, 2H), 1.70−1.47 (m, 2H), 1.35−1.15 (m, 10H), 1.33 (t, J = 7.3 Hz, 9H), 0.88 (t, J = 6.5 Hz, 3H); HRMS (FAB) *m*/*z* calcd for $C_{16}H_{34}NO$ [(M − BF_4)$^+$] 256.2640, found 256.2646. Data for **7a**:[36] colorless oil; ^1H NMR ($CDCl_3$) δ 4.08 (s, 2H), 2.59 (t, J = 7.4 Hz, 2H), 1.70−1.50 (m, 2H), 1.40−1.17 (m, 10H), 0.88 (t, J = 6.1 Hz, 3H).

General Procedure for the Synthesis of an α-Halo Ketone. A Typical Example (Table 1, Entry 6): 1-Bromo-2-decanone (15a). To a stirred solution of 1-decenyl-λ^3-iodane **2a** (X = BF_4) (30 mg, 0.062 mmol) and Bu_4NBr (24 mg, 0.07 mmol) in methanol (1.5 mL) was added triethylamine (6.9 mg,

(33) (a) Koser, G. F.; Chen, K.; Huang, Y.; Summers, C. A. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1375. (b) Koser, G. F.; Huang, Y.; Chen, K.; Calvo, K. C. *J. Chem. Soc., Perkin Trans. 1* **1995**, 299.

(34) Ochiai, M.; Kunishima, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 4501.

(35) Collman, J. P.; Winter, S. R.; Clark, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 1788.

(36) Rieke, R. D.; Brown, J. D.; Wu, X. *Synth. Commun.* **1995**, *25*, 3923.

0.068 mmol) under nitrogen at room temperature, and the mixture was stirred for 1 h. After addition of water, methanol was evaporated under an aspirator vacuum. The mixture was extracted with diethyl ether, and the combined organic phase was washed with water and brine. The organic phase was filtered and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (hexanes−ethyl acetate, 10:1) to give **15a** (12.1 mg, 84%) as a colorless oil:[37] ^{1}H NMR ($CDCl_3$) δ 3.89 (s, 2H), 2.65 (t, J = 7.3 Hz, 2H), 1.72−1.50 (m, 2H), 1.4−1.15 (m, 10H), 0.88 (t, J = 6.0 Hz, 3H).

Data for 1-Iodo-2-decanone (16a):[38] ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 2H), 2.70 (t, J = 7.7 Hz, 2H), 1.7−1.5 (m, 2H), 1.37−1.2 (m, 10H), 0.88 (t, J = 6.0 Hz, 3H).

Data for 1-Bromo-5-phenyl-2-pentanone (15b): colorless oil; IR (neat) 1715, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35−7.13 (m, 10H), 3.85 (s, 2H), 2.66 (t, J = 7.4 Hz, 2H), 2.65 (t, J = 7.4 Hz, 2H), 1.96 (quint, J = 7.4 Hz, 2H); MS m/z (relative intensity) 240 (M^+, 3), 161 (10), 147 (6), 104 (100), 91 (37).

Reaction of 2a with Triethylamine and Thiophenol (Table 2, Entry 1). To a stirred solution of 1-decenyl-λ^3-iodane **2a** (X = BF_4) (30 mg, 0.062 mmol) and thiophenol (13 mg, 0.12 mmol) in methanol (1.5 mL) was added triethylamine (7.1 mg, 0.07 mmol) under nitrogen at room temperature, and the mixture was stirred for 1 h. After addition of water, methanol was evaporated under an aspirator vacuum. The mixture was extracted with dichloromethane, and the combined organic phase was washed with water and brine. The organic phase was filtered and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (hexanes−ethyl acetate, 15:1) to give 1-phenylthio-2-decanone (**17a**) (5.9 mg, 36%), (*Z*)-2-acetoxy-1-iodo-1-decene (**19**) (3.7 mg, 19%), and 2-acetoxy-1-decene (**20**) (2.4 mg, 20%). Data for **17a**:[39] colorless plates; mp 53−54 °C (recrystallized from dichloromethane−hexane); ^{1}H NMR ($CDCl_3$) δ 7.40−7.15 (m, 5H), 3.67 (s, 2H), 2.58 (t, J = 7.4 Hz, 2H), 1.65−1.45 (m, 2H), 1.37−1.17 (m, 10H), 0.87 (t, J = 6.2 Hz, 3H). Data for **19**: colorless oil; IR ($CHCl_3$) 1755, 1180 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.81 (s, 1H), 2.35 (t, J = 7.4 Hz, 2H), 2.23 (s, 3H), 1.55−1.38 (m, 2H), 1.36−1.18 (m, 10H), 0.88 (t, J = 6.1 Hz, 3H); MS m/z (relative intensity) 324 (M^+, 7), 282 (28), 197 (12), 184 (21), 155 (47), 95 (45), 81 (52), 43 (100); HRMS m/z calcd for $C_{12}H_{21}O_2I$ (M^+) 324.0586, found 324.0587. The (*Z*)-stereochemistry of **19** was established by observation of an NOE enhancement between the vinylic and allylic protons. Data for **20**:[40] colorless oil; ^{1}H NMR (CDCl3) δ 4.75−4.68 (m, 2H), 2.20 (t, J = 7.3 Hz, 2H), 2.14 (s, 3H), 1.55−1.20 (m, 12H), 0.88 (t, J = 6.1 Hz, 3H).

Data for 1-Phenylsulfonyl-2-decanone (18a): white solids; IR (KBr) 1718, 1301, 1154 cm^{-1}; ^{1}H NMR (CDCl3) δ 7.89 (br d, J = 7.2 Hz, 2H), 7.70 (br t, J = 7.2 Hz, 1H), 7.58 (br t, J = 7.2 Hz, 2H), 4.14 (s, 2H), 2.70 (t, J = 6.8 Hz, 2H), 1.70−1.45 (m, 2H), 1.40−1.15 (m, 10H), 0.89 (t, J = 6.5 Hz, 3H); MS m/z (relative intensity) 296 (M^+, 3), 199 (48), 198 (45), 154 (57), 141 (47), 134 (100), 125 (70), 77 (83); HRMS m/z calcd for $C_{16}H_{24}O_3S$ (M^+) 296.1446, found 296.1456.

General Procedure for the Synthesis of an α-Phenylthio Ketone. A Typical Example (Table 2, Entry 3): Ketone 17a. To a stirred solution of 1-decenyl-λ^3-iodane **2a** (X = BF_4) (30 mg, 0.062 mmol) in THF (6 mL) was added a 0.43 M THF solution of EtOLi (0.145 mL, 0.062 mmol) at −78 °C under argon, and the mixture was stirred for 20 min. After addition of a solution of thiophenol (21 mg, 0.19 mmol) in THF (0.2 mL), the mixture was stirred for 1 h at −78 °C. The reaction mixture was allowed to warm to room temperature over 8 h, quenched with water, and extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Preparative TLC (hexanes−ethyl acetate, 10:1) gave **17a** (10.8 mg, 65%).

Data for 5-Phenyl-1-phenylthio-2-pentanone (17b): white powder; IR (KBr) 1707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37−7.09 (m, 10H), 3.64 (s, 2H), 2.59 (t, J = 7.4 Hz, 2H), 2.58 (t, J = 7.4 Hz, 2H), 1.89 (quint, J = 7.4 Hz, 2H); MS m/z (relative intensity) 270 (M^+, 41), 166 (48), 147 (92), 91 (100); HRMS m/z calcd for $C_{17}H_{18}OS$ (M^+) 270.1078, found 270.1055. Anal. Calcd for $C_{17}H_{18}OS$: C, 75.52; H, 6.71. Found: C, 75.18; H, 6.70.

Data for 3,3-Dimethyl-1-phenylthio-2-butanone (17c):[41] colorless oil; IR ($CHCl_3$) 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45−7.16 (m, 5H), 3.96 (s, 2H), 1.19 (s, 9H).

General Procedure for the Synthesis of a Phosphonium Salt. A Typical Example (Table 3, Entry 1): (2-Oxodecyl)triphenylphosphonium Tetrafluoroborate (22a). To a stirred solution of 1-decenyl-λ^3-iodane **2a** (X = BF_4) (30 mg, 0.062 mmol) and triphenylphosphine (35 mg, 0.13 mmol) in methanol (2.5 mL) was added triethylamine (6.9 mg, 0.068 mmol) under nitrogen at room temperature, and the mixture was stirred for 1 h. After addition of water, methanol was evaporated under an aspirator vacuum. The mixture was acidified by the addition of 5% aqueous HBF_4 solution at 0 °C and extracted with chloroform, and the combined organic phase was washed with water. The organic phase was filtered and concentrated under an aspirator vacuum to give an oil, which was washed several times with hexane and diethyl ether by decantation at −78 °C to give **22a** (27.5 mg, 89%) as a white solid: IR (KBr) 1709, 1084 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.85−7.55 (m, 15H), 4.93 (d, $^2J_{HP}$ = 12.2 Hz, 2H), 2.79 (t, J = 7.1 Hz, 2H), 1.57−1.37 (m, 2H), 1.29−1.08 (m, 10H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 202.9 ($^2J_{CP}$ = 7.3 Hz), 134.9, 133.6 ($^2J_{CP}$ = 9.2 Hz), 130.3 ($^3J_{CP}$ = 12.9 Hz), 118.5 ($^1J_{CP}$ = 88.3 Hz), 44.2 ($^3J_{CP}$ = 3.7 Hz), 37.9 ($^1J_{CP}$ = 58.8 Hz), 31.7, 29.3, 29.0, 28.7, 23.2, 22.6, 14.1; ^{31}P NMR ($CDCl_3$) δ 20.6; HRMS (FAB) m/z calcd for $C_{28}H_{34}OP$ [$(M - BF_4)^+$] 417.2347, found 417.2379.

Data for (2-Oxo-5-phenylpentyl)triphenylphosphonium Tetrafluoroborate (22b): pale yellow oil; IR (neat) 1715, 1058 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.84−7.58 (m, 15H), 7.30−7.06 (m, 5H), 4.90 (d, $^2J_{HP}$ = 11.8 Hz, 2H), 2.86 (t, J = 7.3 Hz, 2H), 2.53 (t, J = 7.3 Hz, 2H), 1.82 (quint, J = 7.3 Hz, 2H); FAB MS m/z 423 [$(M - BF_4)^+$].

Data for (3,3-Dimethyl-2-oxobutyl)triphenylphosphonium Tetrafluoroborate (22c): white powder; mp 162−165 °C; IR (KBr) 1698, 1084 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.85−7.58 (m, 15H), 5.0 (d, $^2J_{HP}$ = 12.4 Hz, 2H), 1.18 (s, 9H); FAB MS m/z 361 [$(M - BF_4)^+$]. The salt **22c** was contaminated with a small amount of impurity.

General Procedure for the Synthesis of an α-Ketol Phosphinate and an α-Phosphoryloxy Ketone. A Typical Example (Table 3, Entry 5): 2-Oxodecyl Diphenylphosphinate (23a). To a stirred solution of 1-decenyl-λ^3-iodane **2a** (X = BF_4) (30 mg, 0.062 mmol), diphenylphosphinic acid (27 mg, 0.12 mmol), and methanol (4 mg, 0.12 mmol) in dichloromethane (4 mL) was added triethylamine (6.9 mg, 0.068 mmol) under nitrogen at room temperature, and the mixture was stirred for 17 h. After addition of water, the mixture was extracted with ethyl acetate, and the combined organic phase was washed with water. The organic phase was filtered and concentrated under an aspirator vacuum to give an oil, which was purified by preparative TLC (hexanes−ethyl acetate, 2:1) to give **23a** (17.1 mg, 78%) as a colorless oil: IR (neat) 1737, 1231, 1132, 1055, 731, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.86 (dd, J = 7.4 Hz, $^3J_{HP}$ = 12.3 Hz, 4H), 7.63−7.40 (m, 6H), 4.55 (d, $^3J_{HP}$ = 7.8 Hz, 2H), 2.47 (t, J = 7.6 Hz, 2H), 1.73−1.50 (m, 2H), 1.35−1.15 (m, 10H), 0.87 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 205.0 ($^3J_{CP}$ = 6.1 Hz), 132.6 ($^4J_{CP}$ = 3.1 Hz), 131.7 ($^2J_{CP}$ = 10.7 Hz), 130.5 ($^1J_{CP}$ = 137.3 Hz), 128.7 ($^3J_{CP}$ = 12.2 Hz), 67.8 ($^2J_{CP}$ = 6.2 Hz), 38.9, 31.8, 29.3, 29.1, 29.1, 23.2, 22.6, 14.1; ^{31}P NMR ($CDCl_3$) δ −27.3; MS m/z (relative intensity) 372 (M^+, 0.4), 231 (100), 201 (34), 92 (16), 77 (13); HRMS m/z calcd for $C_{22}H_{29}O_3P$ (M^+) 372.1854, found 372.1838.

Data for 2-Oxo-5-phenylpentyl Diphenylphosphinate (23b): colorless oil; IR ($CHCl_3$) 1740, 1240 (br), 1135, 1035

(37) Samuelsson, B.; Stallberg, G. *Acta Chem. Scand.* **1963**, *17*, 810.
(38) Antonioletti, R.; D'Auria, M.; Mico, A. D.; Piancatelli, G.; Scettri, A. *Tetrahedron* **1983**, *39*, 1765.
(39) Yoshida, J.; Nakatani, S.; Isoe, S. *J. Org. Chem.* **1993**, *58*, 4855.
(40) Hartstock, F. W.; Wayner, D. D. M. *Tetrahedron Lett.* **1994**, *35*, 8137.
(41) Matano, Y.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1739.

cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.84 (br dd, J = 8.0 Hz, $^3J_{HP}$ = 12.6 Hz, 4H), 7.63−7.40 (m, 6H), 7.35−7.08 (m, 5H), 4.52 (d, $^3J_{HP}$ = 7.8 Hz, 2 H), 2.61 (t, J = 7.3 Hz, 2H), 2.50 (t, J = 7.3 Hz, 2H), 1.92 (quint, J = 7.3 Hz, 2H); ^{31}P NMR ($CDCl_3$) δ −27.3; MS *m/z* (relative intensity) 378 (M^+, 5), 287 (4), 274 (100), 231 (62), 219 (30), 201 (53). 159 (31), 91 (46), 77 (27); HRMS *m/z* calcd for $C_{23}H_{23}O_3P$ (M^+) 378.1385, found 378.1391.

Data for 3,3-Dimethyl-2-oxobutyl Diphenylphosphinate (23c): colorless needles; mp 105−107 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1736, 1231, 1131, 1050, 1007, 731, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.97−7.83 (m, 4H), 7.60−7.40 (m, 6H), 4.86 (d, $^3J_{HP}$ = 7.8 Hz, 2H), 1.10 (s, 9H); ^{31}P NMR ($CDCl_3$) δ −27.2; MS *m/z* (relative intensity) 316 (M^+, 7), 259 (68), 231 (100), 201 (71), 149 (58), 77 (47); HRMS *m/z* calcd for $C_{18}H_{21}O_3P$ (M^+) 316.1228, found 316.1204. Anal. Calcd for $C_{18}H_{21}O_3P$: C, 68.34; H, 6.69. Found: C, 68.34; H, 6.66.

Data for 2-Oxodecyl Dimethylphosphinate (24a): colorless oil; IR (neat) 1734, 1307, 1211, 1063, 942, 877 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.60 (d, $^3J_{HP}$ = 10.3 Hz, 2H), 2.43 (t, J = 7.4 Hz, 2H), 1.70−1.50 (m, 2H), 1.59 (d, $^2J_{HP}$ = 14.2 Hz, 6H), 1.40−1.18 (m, 10H), 0.88 (t, J = 6.3 Hz, 3H); MS *m/z* (relative intensity) 248 (M^+, 7), 163 (23), 150 (65), 109 (75), 108 (78), 95 (90), 78 (99), 77 (100); HRMS *m/z* calcd for $C_{12}H_{25}O_3P$ (M^+) 248.1541, found 248.1534.

Data for 2-Oxo-5-phenylpentyl Dimethylphosphinate (24b): colorless oil; IR (neat) 1734, 1307, 1212, 1070, 941, 876 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.36−7.12 (m, 5H), 4.56 (d, $^3J_{HP}$ = 10.2 Hz, 2H), 2.65 (t, J = 7.3 Hz, 2H), 2.44 (t, J = 7.3 Hz, 2H), 1.95 (quint, J = 7.3 Hz, 2H), 1.57 (d, $^2J_{HP}$ = 14.2 Hz, 6H); MS *m/z* (relative intensity) 254 (M^+, 3), 150 (100), 147 (17), 108 (56), 91 (64), 78 (42), 77 (32); HRMS *m/z* calcd for $C_{13}H_{19}O_3P$ (M^+) 254.1072, found 254.1096.

Data for 3,3-Dimethyl-2-oxobutyl Dimethylphosphinate (24c): colorless oil; IR (neat) 1726, 1308, 1211, 1051, 1000, 941, 877 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.87 (d, $^3J_{HP}$ = 10.7 Hz, 2H), 1.59 (d, $^2J_{HP}$ = 14.2 Hz, 6H), 1.19 (s, 9H); MS *m/z* (relative intensity) 192 (M^+, 2), 135 (37), 108 (100), 95 (26), 78 (84), 77 (35), 57 (63); HRMS *m/z* calcd for $C_8H_{17}O_3P$ (M^+) 192.0915, found 192.0922.

Data for Diphenyl 2-Oxodecyl Phosphate (25a): colorless oil; IR (neat) 1739, 1289, 1191, 1026, 957 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.43−7.15 (m, 10H), 4.71 (d, $^3J_{HP}$ = 9.0 Hz, 2H), 2.43 (t, J = 7.5 Hz, 2H), 1.65−1.45 (m, 2H), 1.35−1.15 (m, 10H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 204.1 ($^3J_{CP}$ = 6.0 Hz), 150.3 ($^2J_{CP}$ = 7.6 Hz), 129.9, 125.7, 120.1 ($^3J_{CP}$ = 4.5 Hz), 71.5 ($^2J_{CP}$ = 6.0 Hz), 38.6, 31.8, 29.3, 29.2, 29.1, 23.0, 22.6, 14.1; ^{31}P NMR ($CDCl_3$) δ −11.4; MS *m/z* (relative intensity) 404 (M^+, 20), 311 (100), 264 (17), 175 (89), 166 (58), 141 (18), 77 (40), 57 (62); HRMS *m/z* calcd for $C_{22}H_{29}O_5P$ (M^+) 404.1753, found 404.1746.

Data for Dibenzyl 2-Oxodecyl Phosphate (26a): colorless oil; IR (neat) 1738, 1278, 1016 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37−7.33 (m, 10H), 5.13 (dd, J = 11.9 Hz, $^3J_{HP}$ = 8.9 Hz, 2H), 5.08 (dd, J = 11.9 Hz, $^3J_{HP}$ = 8.9 Hz, 2H), 4.44 (d, $^3J_{HP}$ = 9.2 Hz, 2H), 2.36 (t, J = 7.4 Hz, 2H), 1.54 (quint, J = 7.4 Hz, 2H), 1.34−1.18 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 204.8, 135.6 ($^3J_{CP}$ = 7.3 Hz), 128.7, 128.6, 128.1, 70.4 ($^2J_{CP}$ = 5.4 Hz), 69.7 ($^2J_{CP}$ = 5.4 Hz), 38.5, 31.8, 29.3, 29.1, 23.0, 22.6, 14.1; ^{31}P NMR ($CDCl_3$) δ −0.5; MS *m/z* (relative intensity) 432 (M^+, 0.5), 341 (15), 235 (36), 104 (95), 91 (100), 69 (82), 57 (42); HRMS *m/z* calcd for $C_{24}H_{33}O_5P$ (M^+) 432.2066, found 432.2089.

Data for Dibenzyl 2-Oxo-5-phenylpentyl Phosphate (26b): colorless needles; mp 41.5−43 °C (recrystallized from dichloromethane−hexane); IR (KBr) 1738, 1260, 1041, 991, 741, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47−7.10 (m, 15H), 5.11 (dd, J = 11.9 Hz, $^3J_{HP}$ = 8.5 Hz, 2H), 5.06 (dd, J = 11.9 Hz, $^3J_{HP}$ = 8.5 Hz, 2H), 4.41 (d, $^3J_{HP}$ = 9.3 Hz, 2H), 2.59 (t, J = 7.2 Hz, 2H), 2.37 (t, J = 7.2 Hz, 2H), 1.88 (quint, J = 7.2 Hz, 2H); MS *m/z* (relative intensity) 438 (M^+, 2), 347 (5), 249 (16), 231 (11), 104 (23), 91 (100). Anal. Calcd for $C_{25}H_{27}O_5P$: C, 68.48; H, 6.21. Found: C, 68.36; H, 6.21.

Data for Dibenzyl 3,3-Dimethyl-2-oxobutyl Phosphate (26c): colorless oil; IR (neat) 1729, 1278, 999, 881, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.42−7.30 (m, 10H), 5.15 (dd, J = 11.6 Hz, $^3J_{HP}$ = 8.3 Hz, 2H), 5.10 (dd, J = 11.6 Hz, $^3J_{HP}$ = 8.3 Hz, 2H), 4.75 (d, $^3J_{HP}$ = 10.3 Hz, 2H), 1.13 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 207.6 ($^3J_{CP}$ = 4.5 Hz), 135.8 ($^3J_{CP}$ = 7.6 Hz), 128.6, 128.5, 128.1, 69.6 ($^2J_{CP}$ = 6.1 Hz), 67.0 ($^2J_{CP}$ = 6.1 Hz), 42.7, 26.1; ^{31}P NMR ($CDCl_3$) δ −0.0; MS *m/z* (relative intensity) 376 (M^+, 2), 285 (13), 179 (48), 104 (61), 91 (100), 57 (32); HRMS *m/z* calcd for $C_{20}H_{25}O_5P$ (M^+) 376.1440, found 376.1435.

Data for Dibutyl 2-Oxodecyl Phosphate (27a): colorless oil; IR (neat) 1740, 1279, 1029 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.54 (d, $^3J_{HP}$ = 9.5 Hz, 2H), 4.11 (q, J = 6.8 Hz, $^3J_{HP}$ = 6.8 Hz, 4H), 2.48 (t, J = 7.4 Hz, 2H), 1.73−1.56 (m, 6H), 1.42 (sext, J = 7.3 Hz, 4H), 1.33−1.20 (m, 10H), 0.94 (t, J = 7.3 Hz, 6H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 205.1, 70.4 ($^2J_{CP}$ = 6.1 Hz), 68.0 ($^2J_{CP}$ = 6.1 Hz), 38.6, 32.2 ($^3J_{CP}$ = 7.6 Hz), 31.8, 29.3, 29.1, 29.1, 23.1, 22.6, 18.7, 14.1, 13.6; MS *m/z* (relative intensity) 364 (M^+, 1), 224 (22), 169 (100), 113 (60), 99 (20), 57 (21); HRMS *m/z* calcd for $C_{18}H_{37}O_5P$ (M^+) 364.2379, found 364.2371.

Data for Dibutyl 2-Oxo-5-phenylpentyl Phosphate (27b): colorless oil; IR (neat) 1738, 1278, 1029 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37−7.10 (m, 5H), 4.52 (d, $^3J_{HP}$ = 9.3 Hz, 2H), 4.09 (q, J = 7.0 Hz, $^3J_{HP}$ = 7.0 Hz, 4H), 2.64 (t, J = 6.5 Hz, 2H), 2.49 (t, J = 6.5 Hz, 2H), 1.95 (quint, J = 6.5 Hz, 2H), 1.67 (quint, J = 7.0 Hz, 4H), 1.41 (sext, J = 7.0 Hz, 4H), 0.94 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 204.7 ($^3J_{CP}$ = 6.1 Hz), 141.2, 128.4, 126.1, 70.4 ($^2J_{CP}$ = 6.1 Hz), 68.0 ($^2J_{CP}$ = 6.1 Hz), 37.7, 34.9, 32.2 ($^3J_{CP}$ = 6.1 Hz), 24.4, 18.6, 13.6; ^{31}P NMR ($CDCl_3$) δ −0.4; MS *m/z* (relative intensity) 370 (M^+, 18), 266 (100), 211 (34), 154 (56), 113 (37), 99 (39), 91 (54); HRMS *m/z* calcd for $C_{19}H_{31}O_5P$ (M^+) 370.1909, found 370.1909.

Data for Dibutyl 3,3-Dimethyl-2-oxobutyl Phosphate (27c): colorless oil; IR (neat) 1731, 1278, 1030, 998 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.85 (d, $^3J_{HP}$ = 9.9 Hz, 2H), 4.11 (q, J = 7.3 Hz, $^3J_{HP}$ = 7.3 Hz, 4H), 1.68 (quint, J = 7.3 Hz, 4H), 1.42 (sext, J = 7.3 Hz, 4H), 1.19 (s, 9H), 0.94 (t, J = 7.3 Hz, 6H); MS *m/z* (relative intensity) 308 (M^+, 1),251 (25), 169 (99), 139 (53), 113 (100), 99 (36), 57 (86); HRMS *m/z* calcd for $C_{14}H_{29}O_5P$ (M^+) 308.1753, found 308.1751.

Supporting Information Available: ^{1}H or ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internat at http://pubs.acs.org.

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