JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

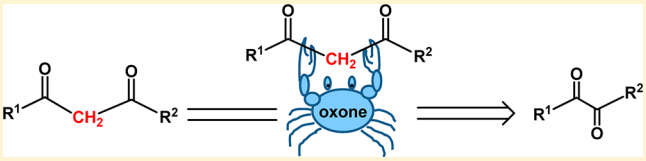
Oxone-Mediated Oxidative Cleavage of β-Keto Esters and 1,3-Diketones to α-Keto Esters and 1,2-Diketones in Aqueous Medium

Anastasios Stergiou, Anna Bariotaki, Dimitris Kalaitzakis, and Ioulia Smonou*

Department of Chemistry, University of Crete, Heraklion 71003, Crete, Greece

Supporting Information

ABSTRACT: A versatile and highly efficient method for the direct synthesis of α-keto esters and 1,2-diketones has been developed. This approach utilizes the oxidative cleavage of a variety of β-keto esters and 1,3-diketones mediated by an Oxone/aluminum trichloride system. The simple one-step oxidation reaction proceeded selectively in aqueous media to afford products in high yields, short reaction times, and environmentally benign conditions.

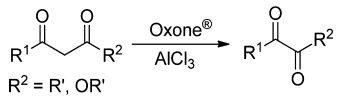


α-Keto esters and 1,2-diketones are very useful compounds for the synthesis of various pharmaceuticals and other organic molecules. They are extensively used as starting materials for intercalation reactions,[1−3] the synthesis of carboxylic acids[4] and heterocyclic compounds,[5] the asymmetric synthesis of α-hydroxy ketones,[6−8] of acyloins, and the direct synthesis of substituted indoles.[9] 1,2-Diketones have also shown interesting applications as photosensitive agents and photoinitiators.[10,11] The practical and efficient synthesis of α-keto esters and 1,2-diketones remains an interesting and challenging goal. Most of the reported synthetic methodologies utilize hazardous and toxic reagents or catalysts,[12−15] while others require complicated time-consuming procedures[16−21] under harsh and unusual conditions.[22−25] Furthermore, in some cases, in an effort to minimize the reaction time, expensive reagents have been utilized.[26,27] An efficient method for the preparation of α-keto esters and 1,2-diketones has been published previously by Yang and co-workers.[28] They successfully demonstrated the synthesis of α-keto esters by the dimethyldioxirane mediated oxidative cleavage of cyanoketophosphoranes. Furthermore, Yuan's research group has utilized iodine as a catalyst for the oxidative cleavage of 1,3-diaryldiketones to 1,2-analogues,[29] while Itoh and co-workers prepared 1,2-diketones by catalytic aerobic decarboxylation of 1,3-diketones in the presence of iodine and under irradiation conditions.[30] In an alternative approach, the same group prepared 1,2-diketones from alkynes with a bromide source.[31] All the above methods produced moderate to good isolated yields. More recently, Zhang and co-workers synthesized 1,2-diketones using $FeCl_3$ as a catalyst and excess of *tert*-butyl nitrite as oxidant.[32] In this case the reactions took place under mild conditions and gave good yields within 12 h. When they used in one case $AlCl_3$ as catalyst, lower efficiency was observed.[32]

The use of Oxone as an oxidizing reagent has grown rapidly the past decade, because of its easy handling, stability, nontoxic nature, and low cost.[33] Oxone's utility has been demonstrated in a great variety of oxidative transformations of many heteroatom-containing compounds.[34−39] However, no studies have been reported to date concerning the employment of an Oxone/$AlCl_3$ system for the oxidative cleavage of β-keto esters and 1,3-diketones for the formation of the corresponding 1,2-dicarbonyl compounds.

Herein, we report a straightforward synthesis of α-keto esters and 1,2-diketones starting from the corresponding β-keto esters and 1,3-diketones, by oxidative cleavage with Oxone and $AlCl_3$ (Scheme 1). This simple one-step reaction takes place in aqueous medium, with high yield, short reaction times, and environmentally benign conditions.

Scheme 1. Oxidative Cleavage of β-Keto Esters and 1,3-Diketones by Oxone/$AlCl_3$



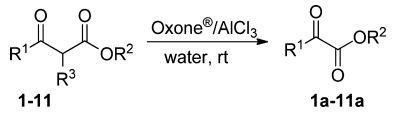
Our intention was to develop a method for the oxidative cleavage of 1,3-dicarbonyl compounds under environmentally benign, mild, and low cost conditions. The initial idea was to employ Oxone in aqueous media, as oxidative reagent for the oxidation of the methylene moiety located between the two carbonyl groups to form a hydroxy group. This compound would then be oxidized in the presence of $AlCl_3$, a Lewis acid activator. As it has been recently reported, $AlCl_3$ in aqueous medium is hydrolyzed to oligomers, $[Al_2(OH_nCl_{6-n})]_m$, which promote oxidative processes.[40]

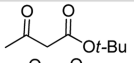
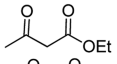
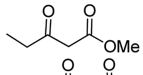
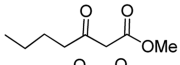
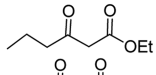
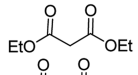
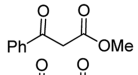
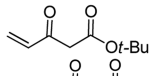
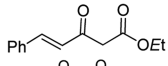
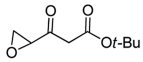
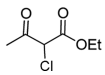
To explore the potential of this reaction, we started our experiments with *tert*-butyl acetoacetate (**1**) and Oxone in aqueous media, without the presence of a Lewis acid. In this case no oxidation occurred even after a period of 24 h. However, the addition of $AlCl_3$ impressively facilitated the oxidation−elimination process in water, producing the corresponding α-keto ester **1a** in 88% conversion after 24 h. To improve the reaction conversion, a variety of substrate

Received: April 30, 2013
Published: June 19, 2013

dx.doi.org/10.1021/jo4009047 | J. Org. Chem. 2013, 78, 7268−7273

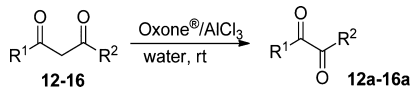
Table 1. Oxidative Cleavage of β-Keto Esters

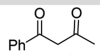
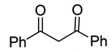
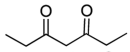
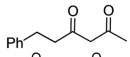


entry	Keto ester	Oxone® (equiv.)	$AlCl_3$ (equiv.)	Time	Isolated yield[a] %
1		2.1	2.3	10 min	93
2		2.1	2.3	10 min	98
3		2.1	2.3	10 min	98
4		2.1	2.3	1 h	96
5		2.1	2.3	20 min	95
6		2.1	2.3	10 min	95
7		4.6	6.4	24 h	98[b]
8		2.1	2.3	15 min	50
9		3.4	3.0	4 h	98[c]
10		2.1	2.3	1.5 h	85
11		1.2	1.0	3 h	98[d]

[a]Conversions were >99% in all cases. [b]With 2.1 equiv Oxone and 2.3 equiv $AlCl_3$ the conversion was 53% in 24 h. [c]With 2.1 equiv Oxone and 2.3 equiv $AlCl_3$ the conversion was 75% in 24 h. [d]With 2.1 equiv Oxone and 2.3 equiv $AlCl_3$ conversion was 99% in 10 min with many impurities.

Table 2. Oxidative Cleavage of 1,3-Diketones



entry	Diketone	Oxone® (equiv.)	$AlCl_3$ (equiv.)	Time	Isolated yield[a] %
12		2.1	2.3	1 h	90
13		3.4	4.3	24 h	98[b]
14		2.1	2.3	5 min	95
15		2.1	2.3	1.5 h	94
16		2.1	2.3	1.5 h	97

[a]Conversions were >99% in all cases. [b]With 2.1 equiv Oxone and 2.3 equiv AlCl3 conversion was 50% in 24 h.

concentrations and ratios of Oxone/$AlCl_3$ equivalents were tested. Thus the highest isolated yield of 93% was obtained by the addition of 2.3 equiv of $AlCl_3$ and 2.1 equiv of Oxone, at room temperature and using water as the solvent. Under these conditions the reaction was much faster (10 min, entry 1, Table 1). The reaction was carried out by simply adding 2.1 equiv of Oxone and 2.3 equiv of $AlCl_3$ in an aqueous solution of 20 mM of **1** at room temperature. We notice here that the equivalents of $AlCl_3$ are rather critical for the completion of the reaction than for the acidity of the mixture. Buffered solution did not have any effect on reactivity. The systematic study of this reaction was carried out by subjecting the series of β-keto esters **1**−**11** to these conditions, and as shown in Table 1, the final products were the corresponding α-keto esters **1a**−**11a** in good to excellent yields. It should be noticed here that there were no solubility problems for the compounds tested in this work.

As shown in Table 1, in entries **1**−**6** the yields were high, while the reactions were completed in very short times (10 min to 1 h). It is interesting to note here that, in the case of unsaturated keto esters (entries **8** and **9**), Oxone did not react with the double bond to form the corresponding epoxide, as was expected on the basis of the literature data.[41−43] More specifically, the reaction of compound **8** with Oxone and $AlCl_3$, gave the desired product **8a** (85%) and an unidentified sideproduct (15%), as determined by gas chromatography. However, the isolated yield was 50% due to partial decomposition during column chromatography purification. Compound **9**, on the other hand, gave exclusively the cleavage

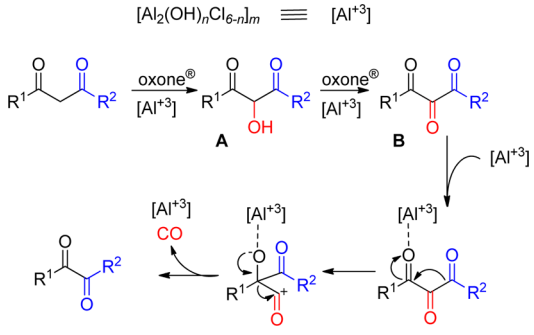
dx.doi.org/10.1021/jo4009047 | J. Org. Chem. 2013, 78, 7268−7273

product **9a**. The reaction with the keto ester **10**, which bears an oxirane moiety, gave only the cleavage product **10a**. Despite the presence of a Lewis acid ($AlCl_3$) and the low pH conditions, the epoxide ring was found to be intact. In the case of the α-Cl-keto ester **11**, after the first 10 min of the reaction, the formation of the desired α-keto ester was accompanied with a considerable amount of side products. However, since the α-carbon is already in a higher oxidative state, the reaction required less $AlCl_3$ and Oxone. Indeed, by decreasing the equivalents of $AlCl_3$ from 2.3 to 1.0 and the equivalents of Oxone from 2.1 to 1.2 (entry **11**), the α-keto ester **2a** was exclusively formed free of any side products. For keto esters **7** and **9** more equivalents of Oxone and $AlCl_3$ were necessary in order to complete the cleavage in a period of 24 h. This may be due to the observed high ratio of enol/keto forms.

Since the reaction of β-keto esters **1**−**11** with Oxone/$AlCl_3$ leads directly to α-keto esters, (Table 1) in high yields, we investigated the oxidation of 1,3-diketones by applying this powerful oxidative method. To our delight, the reactivity of diketones **12**−**16** (Table 2) toward the Oxone/$AlCl_3$ system was excellent under the same experimental conditions described above. Four starting diketones were acyclic (entries **12**−**15**) and one cyclic (entry **16**). As seen in Table 2, in all cases the corresponding 1,2-diketones **12a**−**16a** were produced in excellent yields and relatively short reaction times (5 min to 1.5 h for **12a**, **14a**−**16a**). For diketone **13**, more equivalents of Oxone and $AlCl_3$ were necessary, in order to complete the cleavage to **13a** within 24 h.

A possible mechanistic approach of this oxidative cleavage metathesis is presented in Scheme 2. The initial step of the

Scheme 2. Proposed Pathway for the Formation of 1,2-Dicarbonyl Compounds 1a−10a and 12a−16a

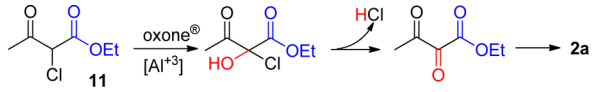


reaction involves the formation of α-hydroxy dicarbonyl compound **A**, followed by a further oxidation to tricarbonyl compound **B**. The oligomer $[Al_2(OH_nCl_{6-n})]_m$ from the hydrolysis of $AlCl_3$ in water is symbolized as $[Al^{3+}]$ (Scheme 2). Activation of the β-keto moiety of **B** by $[Al^{3+}]$ leads to an ester or acyl group rearrangement by the simultaneous elimination of carbon monoxide driving the reaction toward the desired 1,2-dicarbonyl compound.

In the case of α-Cl-keto ester **11**, the formation of the α-keto ester **2a** is rationalized by the mechanism shown in Scheme 3.

In conclusion, we have developed a highly efficient, mild, practical, and convenient method for the synthesis of simple α-keto esters and 1,2-diketones using inexpensive, nontoxic reagents, in aqueous medium. In this oxidative cleavage process, safe and environmentally benign reagents were used. Furthermore, the products were prepared directly from the corresponding 1,3-dicarbonyl compounds, in short reaction

Scheme 3. Proposed Pathway for the Formation of α-Keto Ester 2a Starting from 11



times (10 min to 24 h). It is also important to note that the isolation procedure was very simple and that no side products were formed in most of the cases. The reaction described herein may prove to be a valuable alternative compared to other traditional metal-mediated oxidations.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, the solvents and reagents were reagent grade and were used without any further purification. $AlCl_3$ was in powder form. Dry THF was used after distillation in the presence of metallic Na and benzophenone, into a Soxhlet. Column chromatographic separations were carried out on a flash chromatographic system using silica gel and hexane/ethyl acetate solvent mixtures. For thin layer chromatography (TLC), silica gel plates precoated with 60 F-254 were used. The gas chromatograph (GC) was equipped with an FID detector and a 30 m × 0.25 mm × 0.25 μm capillary column. ^1H NMR spectra were recorded on a 300 or 500 MHz spectrometer in $CDCl_3$ solutions, and ^{13}C NMR spectra were recorded on a 75 MHz or 125 MHz spectrometer in $CDCl_3$, using Me_4Si as the internal standard. Chemical shifts are reported in ppm downfield from Me_4Si. High resolution mass spectra (HRMS) were recorded on ESI-Orbitrap mass spectrometer.

Compounds **7**, **8**, and **15** were synthesized by aldol condensation followed by oxidation. Compound **9** was synthesized by Wittig olefination. Compound **10** was synthesized by an amino acid catalyzed epoxidation of substrate **8**.

General Aldol Condensation Procedure for the Synthesis of Methyl 3-Hydroxy-3-phenylpropanoate, *tert*-Butyl 3-Hydroxy Pent-4-enoate, and 5-Hydroxy-1-phenylhexan-3-one. Under nitrogen atmosphere dry diisopropylamine (462 μL, 3.3. mmol) was dissolved in dry THF (10 mL). The solution was cooled to 0 °C, and *n*-BuLi 1.6 M in hexane (2.0 mL, 3.3 mmol) was added dropwise. After stirring for 15 min at 0 °C, the mixture was cooled to −78 °C, a solution of ester or ketone (3 mmol of methyl acetate, *tert*-butyl acetate, and 4-phenylbutan-2-one, respectively) in dry THF (2 mL) was added, and the mixture was stirred for 20 min at −78 °C. Freshly distilled aldehyde (6 mmol of benzaldehyde or acrylaldehyde and 4.5 mmol of acetaldehyde, respectively) dissolved in 3 mL of dry THF was then added dropwise. After the completion of the reaction, which was observed by TLC analysis, saturated aqueous ammonium chloride (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 15 mL), and the combined organic layers washed with brine (30 mL), dried over anhydrous $MgSO_4$, and evaporated to dryness.

Methyl 3-Hydroxy-3-phenylpropanoate. Methyl acetate (3 mmol, 222 mg) and benzaldehyde (6 mmol, 636 μL) were used according to the general procedure. The reaction was completed in 2 h (450 mg, 83%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 2.68 (m, 2H), 3.62 (s, 3H), 3.77 (broad s, 1H), 5.08 (m, 1H), 7.28 (m, 5H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 43.4, 51.8, 70.3, 125.7 (2C), 127.7, 128.5 (2C), 142.9, 172.5; HRMS (ESI-Orbitrap) *m*/*z* [M − H_2O + H]$^+$ calcd for $C_{10}H_{11}O_2$ 163.0759, found 163.0753.

***tert*-Butyl 3-Hydroxy-pent-4-enoate.** *tert*-Butyl acetate (3 mmol, 348 mg) and acrylaldehyde (6 mmol, 395 μL) were used according to the general procedure. The reaction was completed in 2 h (500 mg, 90%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.43 (s, 9H), 2.43 (m, 2H), 3.24 (broad s, 1H), 4.44 (m, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.83 (ddd, *J* = 17.2, 10.5, 5.5 Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 28.0 (3C), 42.1, 69.0, 81.3, 115.0, 138.9, 171.6; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_9H_{16}O_3Na$ 195.0992, found 195.0993.

5-Hydroxy-1-phenylhexan-3-one. 4-Phenylbutan-2-one (3 mmol, 450 μL) and acetaldehyde (4.5 mmol, 264 μL) were used.

dx.doi.org/10.1021/jo4009047 | J. Org. Chem. 2013, 78, 7268−7273

The reaction was completed in 2 h. The residue was purified using silica gel chromatography (hexane/ethyl acetate, v/v, 5/1) (489 mg, 85%); ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.17 (d, J = 6.3 Hz, 3H), 2.53 (m, 2H), 2.76 (t, J = 7.3 Hz, 2H), 2.89 (t, J = 7.3 Hz, 2H), 3.07 (br s, 1H), 4.22 (m, 1H), 7.24 (m, 5H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 22.4, 29.4, 44.9, 50.8, 63.8, 126.2, 128.2 (2C), 128.5 (2C), 140.7, 210.9; HRMS (ESI-Orbitrap) m/z [M + H]$^+$ calcd for $C_{12}H_{17}O_2$ 193.1228, found 193.1223.

General Jones Oxidation for the Synthesis of Methyl 3-Oxo-3-phenylpropionate (7), *tert*-Butyl 3-Oxopent-4-enoate (8), and 6-Phenylhexane-2,4-dione (15).[44] A 1 mmol portion of the corresponding hydroxy ester or hydroxy ketone (methyl 3-hydroxy-3-phenylpropanoate, *tert*-butyl 3-hydroxy-pent-4-enoate, and 5-hydroxy-1-phenylhexan-3-one, respectively) was dissolved in 5 mL of acetone. The mixture was cooled in an ice bath and Jones reagent (1.08 mmol, 360 μL, dissolved in 1 mL acetone) was added dropwise. After the addition of the Jones reagent, the reaction mixture was allowed to warm slowly to room temperature. After the completion of the reaction, which was observed by TLC analysis, 2-propanol (2.65 mmol, 200 μL) was added to quench the excess of Jones reagent. Then a solution of sodium phosphate buffer pH 8 (6 mL, 200 mM) was added and the mixture was extracted with diethyl ether (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to dryness. No purification was needed.

Methyl 3-Oxo-3-phenylpropionate (7). Methyl 3-hydroxy-3-phenylpropanoate (1 mmol, 178 mg) and Jones reagent (360 μL) were used according to the general procedure. The reaction was completed in 1 h. The product appeared as a mixture of keto−enol forms in a 4/1 ratio. (175 mg, 98%); keto form: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 3.74 (s, 3H), 4.00 (s, 2H), 7.45 (m, 2H), 7.59 (dd, J = 8.4, 7.3 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 45.7, 52.5, 128.50 (2C), 128.53, 128.79 (2C), 131.3, 167.9, 192.4; enol form: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 3,79 (s, 3H), 5.67 (s, 1H), 7.45 (m, 2H), 7.59 (dd, J = 8.4, 7.3 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 12.50 (s, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 51.4, 87.0, 126.1 (2C), 130.1, 133.8 (2C), 135.9, 171.5, 173.5; HRMS (ESI-Orbitrap) m/z [M + H]$^+$ calcd for $C_{10}H_{11}O_3$ 179.0703, found 179.0700.

***tert*-Butyl 3-Oxopent-4-enoate (8).** *tert*-Butyl 3-hydroxy-pent-4-enoate (1 mmol, 172 mg) and Jones reagent (360 μL) were used according to the general procedure. The reaction was completed in 1 h. The product appeared as a mixture of keto−enol forms in a 1/1 ratio. (165 mg, 97%); keto form: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.44 (s, 9H), 3.51 (s, 2H), 5.90 (d, J = 11.2 Hz, 1H), 6.23 (d, J = 17.6 Hz, 1H), 6.37 (dd, J = 17.6, 11.2 Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 28.2, 47.8, 81.1, 121.8, 135.8, 168.1, 193.0; enol form: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si): 1.47 (s, 9H), 4.96 (s, 1H), 5.47 (dd, J = 6.1, 5.9 Hz, 1H), 6.04 (d, J = 5.9 Hz, 2H), 11.91 (s, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) 27.9 (3C), 81.9, 93.4, 129.7, 131.4, 166.3, 172.5; HRMS (ESI-Orbitrap) m/z [M + H]$^+$ calcd for $C_9H_{15}O_3$ 171.1021, found 171.1012.

6-Phenylhexane-2,4-dione (15). 5-Hydroxy-1-phenylhexan-3-one (1 mmol, 192 mg) and Jones reagent (360 μL) were used. The reaction was completed in 1 h. (185 mg, 97%); ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 2.05 (s, 3H), 2.62 (dd, J = 7.9, 7.4 Hz, 2H), 2.95 (dd, J = 7.9, 7.4 Hz, 2H), 5.49 (s, 1H), 7.25 (m, 5H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 24.6, 31.3, 39.8, 99.8, 126.0, 128.1 (2C), 128.3 (2C), 140.5, 190.8, 193.1; HRMS (ESI-Orbitrap) m/z [M + H]$^+$ calcd for $C_{12}H_{15}O_2$ 191.1072, found 191.1064.

Ethyl 3-Oxo-5-phenylpent-4-enoate (9).[45,46] *A. Preparation of Ylide Ethyl 3-Oxo-4-(triphenylphosphoranylidene) Butanoate.* For the synthesis of the stabilized ylide ethyl 3-oxo-4-(triphenylphosphoranylidene) butanoate, triphenyl phosphine (63.6 mmol, 16.7 g) and ethyl 4-chloro-3-oxobutanoate (70 mmol, 9.46 mL) in 50 mL toluene were stirred for 24 h at 50 °C. The solid product was washed with toluene and then distilled water was added until the solid is dissolved. The mixture was extracted with two portions of diethyl ether. Saturated $NaHCO_3$ was added to the aqueous phase until pH 8. The solid product was filtrated through a Buchner funnel, washed twice with distilled water and twice with diethyl ether and evaporated to dryness. (15 g, 60%); ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.27 (t, J = 7.1 Hz, 3H), 3.35 (s, 2H), 3.80 (d, J_{P-H} = 24.9 Hz, 1H), 4.20 (q, 2H, J = 7.1 Hz), 7.5 (m, 15H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 14.2 (2C), 48.3, 48.5, 51.5, 53.0, 60.4 (2C), 126.0 (2C), 127.2 (2C), 128.7 (2C), 128.9 (2C), 132.1 (4C), 133.0 (2C), 133.2 (2C), 170.7 (2C), 184.00 (2C).

B. Wittig Olefination of Ethyl 3-Oxo-4-(triphenylphosphoranylidene) Butanoate with Benzaldehyde. A 2 mmol portion of ethyl 3-oxo-4-(triphenylphosphoranylidene) butanoate (780 mg) and 4 mmol of benzaldehyde (407 μL) were added in dry THF (10 mL), and the mixture was left overnight to reflux. After the completion of the reaction, most of the solvent was evaporated, and hexane (3 mL) was added to precipitate phosphine oxides, which were removed by filtration through a silica pad. The silica pad was washed with hexane/ethyl acetate (2/1) mixture (6 mL), and the organic layer was evaporated to dryness. The residue was purified using silica gel flash chromatography (hexane/ethyl acetate, v/v, 70/1). The product appeared as a mixture of keto−enol forms in a 1.5/1 ratio. (196 mg, 45%). Keto form: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.26 (t, 3H), 3.70 (s, 2H), 4.22 (q, 2H), 6.81 (d, J = 15.9 Hz, 1H), 7.34 (m, 6H); enol form: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.26 (t, 3H), 4.22 (q, 2H), 5.17 (s, 1H), 6.43 (d, J = 10.5 Hz, 1H), 7.34 (m, 6H), 12.00 (s, 1H); ^{13}C NMR of keto−enol mixture (75 MHz; $CDCl_3$; Me_4Si) δ 14.1, 14.2, 47.6, 60.2, 61.4, 91.9, 121.9, 125.2, 127.5 (2C), 128.5 (2C), 128.8 (2C), 129.0 (2C), 129.3, 130.9, 134.1, 135.3, 136.7, 144.5, 167.3, 169.2, 172.8, 191.9; HRMS (ESI-Orbitrap) m/z [M + H]$^+$ calcd for $C_{13}H_{15}O_3$ 219.1021, found 219.1012.

***tert*-Butyl 3-(Oxiran-2-yl)-3-oxopropanoate (10).**[47] *tert*-Butyl-3-oxo-pentenoate (1 mmol, 170 mg), hydrogen peroxide (3 mmol, 830 μL 30% solution), and L-arginine (0.2 mmol, 35 mg) were dissolved in 2 mL of absolute MeOH, and 2 mL of distilled water was added. The reaction mixture was stirred for 5 h at rt. After the reaction's completion brine solution and diethyl ether were added. The mixture was stirred vigorously for 30 min. The aqueous layer was extracted with diethyl ether, and the combined organic phases were evaporated to dryness. The residue was purified using silica gel chromatography (hexane/ethyl acetate, v/v, 15/1). The product appeared as a mixture of keto−enol forms in a 4/1 ratio (120 mg, 65%). Keto form: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.47 (s, 9H), 2.95 (m, 1H), 3.02−3.06 (m, 1H), 3.30 (s, 2H), 3.51 (m, 1H); enol form: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.49 (s, 9H), 2.95 (m, 1H), 3.02−3.06 (m, 1H), 3.30 (m, 1H), 5.18 (s, 1H,), 12.08 (s, 1H); ^{13}C NMR of keto−enol mixture (75 MHz; $CDCl_3$; Me_4Si) δ 27.9, 28.2, 29.7, 44.5, 46.0, 47.5, 49.6, 53.5, 82.4, 91.6, 165.6, 200.4; HRMS (ESI-Orbitrap) m/z [M + H]$^+$ calcd for $C_9H_{15}O_4$ 187.0965, found 187.0969.

General Procedure for the Oxidative Cleavage of the Corresponding 1,3-Diketones and β-Keto Esters. A 1 mmol portion (except in the case of compound **10** where 0.56 mmol was used) of the corresponding 1,3-diketone or β-keto ester (20 mM) was dissolved in 50 mL of distilled water. Oxone (2.1−4.6 equiv) and $AlCl_3$ (1.0−6.4 equiv) were added, and the mixture was stirred at room temperature for 5 min to 24 h. The reaction was monitored by TLC. After completion of the reaction, a saturated solution of Rochelle salt (5 mL) was added. The mixture was extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to dryness. Further purification was achieved using flash column chromatography (silica gel, hexane/ethyl acetate, v/v, 15:1).

***tert*-Butyl 2-Oxopropanoate (1a).** *tert*-Butyl acetoacetate (1 mmol, 144 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 10 min (139 mg, 93%); ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.51 (s, 9H), 2.44 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 23.6, 27.5 (3C), 86.4, 161.8, 191.3; HRMS (ESI-Orbitrap) m/z [M + H]$^+$ calcd for $C_7H_{13}O_3$ 145.0864, found 145.0857.

Ethyl 2-Oxopropanoate (2a). Ethyl acetoacetate (1 mmol, 130 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 10 min (114 mg, 98%); ^{1}H NMR (300 MHz; $CDCl_3$;

dx.doi.org/10.1021/jo4009047 | J. Org. Chem. 2013, 78, 7268−7273

Me_4Si) δ 1.33 (t, J = 7.1 Hz, 3H), 2.47 (s, 3H), 4.35 (q, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 13.7, 23.4, 64.6, 163.3, 191.3; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_5H_9O_3$ 117.0551, found 117.0542.

Methyl 2-Oxobutanoate (3a). Methyl 3-oxopentanoate (1 mmol, 130 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 10 min (114 mg, 98%); ^1H NMR (500 MHz; $CDCl_3$; Me_4Si) δ 1.19 (t, J = 7.2 Hz, 3H), 2.88 (q, 2H, J = 7.2 Hz), 3.91 (s, 3H) ppm; ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 8.5, 29.3, 54.8, 164.0, 195.1; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_5H_9O_3$ 117.0551, found 117.0542.

Methyl 2-Oxohexanoate (4a). Methyl 3-oxoheptanoate (1 mmol, 158 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 1 h (138 mg, 96%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 0.93 (t, J = 7.3 Hz, 3H), 1.36 (m, 2H), 1.67 (m, 2H), 2.84 (t, J = 7.3 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 13.6, 21.9, 26.2, 35.4, 54.8, 164.0, 194.3; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_7H_{13}O_3$ 145.0864, found 145.0855.

Ethyl 2-Oxopentanoate (5a). Ethyl 3-oxohexanoate (1 mmol, 158 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 20 min (137 mg, 95%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 0.94 (t, J = 7.4 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.66−1.78 (m, 2H), 2.78 (t, J = 6.9 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 13.3, 13.7, 17.7, 37.6, 64.5, 163.4, 194.0; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_7H_{13}O_3$ 145.0864, found 145.0859.

Ethanedioic Acid, 1,2-Diethylester (6a). Diethyl malonate (1 mmol, 160 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 10 min (139 mg, 95%); ^1H NMR (500 MHz; $CDCl_3$; Me_4Si) δ 1.34 (t, J = 7.1 Hz, 6H), 4.36 (q, J = 7.1 Hz, 4H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 13.7 (2C), 64.6 (2C), 162.8 (2C); HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_6H_{11}O_4$ 147.0657, found 147.0649.

Methyl 2-Oxo-2-Phenylacetate (7a). Methyl 3-oxo-3-phenylpropanoate (1 mmol, 178 mg, 20 mM), Oxone (4.6 mmol, 2.828 g), and $AlCl_3$ (6.4 mmol, 853 mg) were used according to the general procedure. The reaction was completed in 24 h (161 mg, 98%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 3.85 (s, 3H), 7.46 (dd, J = 7.8, 7.6 Hz, 2H), 7.60 (dd, J = 7.8, 7.2 Hz, 1H), 8.03 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 55.0, 128.7 (2C), 130.1 (2C), 130.7, 134.3, 164.6, 183.3; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_9H_9O_3$ 165.0551, found 165.0546.

***tert*-Butyl 2-Oxobut-3-enoate (8a).** *tert*-Butyl 3-oxopent-4-enoate (1 mmol, 170 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mgr) were used according to the general procedure. The reaction was completed in 15 min (78 mg, 50%); ^1H NMR (500 MHz; $CDCl_3$; Me_4Si) δ 1.51 (s, 9H), 6.00 (d, J = 10.2 Hz, 1H), 6.61 (d, J = 16.9 Hz, 1H), 6.79 (dd, J = 16.9, 10.2 Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 27.5 (3C), 86.4, 128.2, 133.2, 161.8, 182.7; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_8H_{13}O_3$ 157.0864, found 157.0854.

Ethyl 2-Oxo-4-phenylbut-3-enoate (9a). Ethyl 3-oxo-5-phenylpent-4-enoate (1 mmol, 218 mg, 20 mM), Oxone (3.4 mmol, 2.090 g), and $AlCl_3$ (3 mmol, 400 mg) were used according to the general procedure. The reaction was completed in 4 h (200 mg, 98%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.34 (t, 3H, J = 7.1 Hz), 4.40 (q, 2H, J = 7.1 Hz), 7.18 (d, 1H, J = 15.7 Hz), 7.43 (m, 3H), 7.61 (m, 2H), 7.91 (d, J = 15.7 Hz, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 13.8, 64.6, 117.2, 128.9 (3C), 129.1 (3C), 131.6, 133.8, 148.4, 163.5, 183.1; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{12}H_{13}O_3$ 205.0864, found 205.0854.

***tert*-Butyl 2-(Oxiran-2-yl)-2-oxoacetate (10a).** *tert*-Butyl 3-(oxiran-2-yl)-3-oxopropanoate (0.56 mmol, 105 mg, 20 mM), Oxone (1.3 mmol, 798 mg), and $AlCl_3$ (1.2 mmol, 160 mg) were used according to the general procedure. The reaction was completed in 1.5 h (146 mg, 85%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.55 (s, 9H), 3.04−3.11 (m, 2H), 3.94 (m, 1H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 27.5 (3C), 49.0, 50.0, 87.2, 161.2, 188.9. HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_8H_{13}O_4$ 173.0814, found 173.0804.

Ethyl 2-Oxopropanoate (2a) derived from the oxidation of compound 11. Ethyl 2-choro-3-oxobutanoate (1 mmol, 164 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (1 mmol, 133 mg) were used according to the general procedure. The reaction was completed in 3 h (114 mg, 98%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.33 (t, J = 7.1 Hz, 3H), 2.47 (s, 3H), 4.35 (q, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 13.7, 23.4, 64.6, 163.3, 191.3; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_5H_9O_3$ 117.0551, found 117.0542.

Phenylpropane-1,2-dione (12a). 1-Phenylbutane-1,3-dione (1 mmol, 162 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 1 h (133 mg, 90%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 2.44 (s, 3H), 7.46 (t, J = 7.8 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 8.05 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 24.9, 128.7 (2C), 130.6 (2C), 130.7, 134.5, 185.9, 192.2; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_9H_9O_2$ 149.0602, found 149.0593.

1,2-Diphenylethane-1,2-dione (13a). 1,3-Diphenylpropane-1,3-dione (1 mmol, 224 mg, 20 mM), Oxone (3.4 mmol, 2.090 g), and $AlCl_3$ (4 mmol, 537 mg) were used according to the general procedure. The reaction was completed in 24 h (208 mg, 98%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 7.40 (dd, J = 7.9, 7.6 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.97 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 128.7 (4C), 130.5 (4C), 131.5 (2C), 134.2 (2C), 185.3 (2C); HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{14}H_{11}O_2$ 211.0759, found 211.0751.

Hexane-3,4-dione (14a). Heptane-3,5-dione (1 mmol, 114 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 5 min (108 mg, 95%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.15 (t, J = 7.2 Hz, 6H), 2.82 (q, J = 7.2 Hz, 4H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 8.4 (2C), 30.3 (2C), 197.4 (2C); HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_6H_{11}O_2$ 115.0759, found 115.0752.

5-Phenylpentane-2,3-dione (15a). 6-Phenylhexane-2,4-dione (1 mmol, 190 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 1.5 h (165 mg, 94%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 2.41 (s, 3H), 2.96−3.02 (m, 2H), 3.11−3.18 (m, 2H), 7.19−7.25 (m, 5H); ^{13}C NMR (125 MHz; $CDCl_3$; Me_4Si) δ 23.4, 30.2, 38.7, 126.5, 128.4 (2C), 128.6 (2C), 139.8, 193.6, 195.4; HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_{11}H_{13}O_2$ 177.0914, found 177.0910

Cyclopentane-1,2-dione (16a). Cyclohexane-1,3-dione (1 mmol, 112 mg, 20 mM), Oxone (2.1 mmol, 1.291 g), and $AlCl_3$ (2.3 mmol, 306 mg) were used according to the general procedure. The reaction was completed in 1.5 h. (95 mg, 97%); ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 2.00 (quintet, 2H), 2.47 (t, J = 7.0 Hz, 4H); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 19.6, 32.9 (2C), 178.7 (2C); HRMS (ESI-Orbitrap) m/z $[M + H]^+$ calcd for $C_5H_7O_2$ 99.0446, found 99.0440.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: smonou@chemistry.uoc.gr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the project "IRAKLITOS II - University of Crete" of the Operational Programme for Education and Lifelong Learning 2007−2013 (E.P.E.D.V.M.) of the NSRF (2007−2013), which is cofunded by the European Union (European Social Fund) and National Resources. We are also thankful to the PROFI (Proteomics Facility at IMBB-FORTH) for performing all the HRMS analyses.

■ REFERENCES

(1) Méndez-Andino, J.; Paquette, L. A. *Org. Lett.* **2000**, *2*, 1263−1265.
(2) Balskus, E. P.; Méndez-Andino, J.; Arbit, R. M.; Paquette, L. A. *J. Org. Chem.* **2001**, *66*, 6695−6704.
(3) Bortolini, O.; Fantin, G.; Fogagnolo, M.; Giovannini, P. P.; Venturi, V.; Pacifico, S.; Massi, A. *Tetrahedron* **2011**, *67*, 8110−8115.
(4) Khurana, J. M.; Sharma, P.; Gogia, A.; Kandpal, B. M. *Org. Prep. Proced.* **2007**, *39*, 185−202.
(5) Khan, F. A.; Dash, J.; Sudheer, C. *Chem.—Eur. J.* **2004**, *10*, 2507−2519.
(6) Hayakawa, R.; Sahara, T.; Shimizu, M. *Tetrahedron Lett.* **2000**, *41*, 7939−7942.
(7) Sinisterra, J.-V.; Molinary, F.; Alcántara, A.-R.; Domínguez De Maria, P. *Acc. Chem. Res.* **2010**, *43*, 288−299.
(8) Giovannini, P. P.; Fantin, G.; Massi, A.; Venturi, V.; Pedrini, P. *Org. Biomol. Chem.* **2011**, *9*, 8038−8045.
(9) Cabrera, A.; Sharma, B. P.; Ayala, M.; Rubio-Perez, L.; Amézquita-Valencia, M. *Tetrahedron Lett.* **2011**, *52*, 6758−6762.
(10) Matsuschita Electric Industrial Co. Ltd.; Patent JP56098203; *Chem. Abstr.* **1981**, *95*, 188163.
(11) Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. *J. Photochem. Photobiol. A* **2003**, *159*, 103−114.
(12) McKillop, A.; Swann, B. P.; Ford, M. E.; Taylor, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 3641−3645.
(13) Cofré, P.; Ross, B.; Sobbkowiak, A.; Sawyer, D. T.; Kanofsky, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1936−1942.
(14) Antoniotti, S.; Duñach, E. *J. Mol. Catal. A: Chem.* **2004**, *28*, 135−145.
(15) Taydakov, I. V.; Nelyubina, Y. V. *Tetrahedron Lett.* **2013**, *54*, 1704−1706.
(16) Wolfe, S.; Inglold, C. F. *J. Am. Chem. Soc.* **1983**, *105*, 7755−7757.
(17) Tymonko, S. A.; Nattier, B. A.; Mohan, R. S. *Tetrahedron Lett.* **1999**, *40*, 7657−7659.
(18) Che, C. M.; Yu, W.-Y.; Chan, P.-M.; Cheng, W.-C.; Peng, S.-M.; Lau, K.-C.; Li, W.-K. *J. Am. Chem. Soc.* **2000**, *122*, 11380−11392.
(19) Paleo, M. R.; Calaza, M. I.; Graña, P.; Sardina, F. J. *Org. Lett.* **2004**, *6*, 1061−1063.
(20) Katritzky, A.-R.; Zhang, D.; Kirichenko, K. *J. Org. Chem.* **2005**, *70*, 3271−3274.
(21) Mecinović, J.; Hamed, R. B.; Schofield, C. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2796−2800.
(22) Yusubov, M. S.; Zholobova, G. A.; Vasilevsky, S. F.; Tretyakov, E. V.; Knight, D. W. *Tetrahedron* **2002**, *58*, 1607−1610.
(23) Wan, Z.; Jones, C. D.; Mitchell, D.; Pu, J. Y.; Zhang, T. Y. *J. Org. Chem.* **2006**, *71*, 826−828.
(24) Ren, W.; Xia, Y.; Ji, S.-J.; Zhang, Y.; Wan, X.; Zhao, J. *Org. Lett.* **2009**, *11*, 1841−1844.
(25) Gao, A.; Yang, F.; Li, L.; Wu, Y. *Tetrahedron* **2012**, *68*, 4950−4954.
(26) Saikia, P.; Laskar, D.-D.; Praiaparat, D.; Sandhu, J. S. *Tetrahedron Lett.* **2002**, *43*, 7525−7526.
(27) Kobayashi, S.; Miyamura, H.; Akiyama, R.; Ishida, T. *J. Am. Chem. Soc.* **2005**, *127*, 9251−9254.
(28) Wong, M. K.; Yu, C.-W.; Yuen, W.-H.; Yang, D. *J. Org. Chem.* **2001**, *66*, 3606−3609.
(29) Yuan, Y.; Zhu, H. *Eur. J. Org. Chem.* **2012**, *2*, 329−333.
(30) Tada, N.; Shomura, M.; Nakayama, H.; Miura, T.; Itoh, A. *Synlett* **2010**, *13*, 1979−1983.
(31) Nobuta, T.; Tada, N.; Hattori, K.; Hirashima, S.; Miura, T.; Itoh, A. *Tetrahedron Lett.* **2011**, *52*, 875−877.
(32) Huang, L.; Cheng, K.; Yao, B.; Xie, Y.; Zhang, Y. *J. Org. Chem.* **2011**, *76*, 5732−5737.
(33) Hussain, H.; Green, I. R.; Ahmed, I. *Chem. Rev.* **2013**, *113*, 3329−3371.
(34) Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. *Synlett* **1999**, *6*, 777−779.
(35) Travis, B. R.; Sivakumar, M.; Hollist, G. O.; Borhan, B. *Org. Lett.* **2003**, *5*, 1031−1034.
(36) Yan, J.; Travis, B. R.; Borhan, B. *J. Org. Chem.* **2004**, *69*, 9299−9302.
(37) Desai, L. V.; Malik, H. A.; Sanford, M. S. *Org. Lett.* **2006**, *8*, 1141−1144.
(38) Wang, Y. R.; Chu, W. *Water Res.* **2011**, *45*, 3883−3889.
(39) Cui, L.-Q.; Liu, K.; Zhang, C. *Org. Biomol. Chem.* **2011**, *9*, 2258−2265.
(40) Wu, S.; Ma, H.; Lei, Z. *Tetrahedron* **2010**, *66*, 8641−8647.
(41) Shaw, H. *Ind. Eng. Chem. Res.* **1995**, *34*, 3761−3765.
(42) Bohé, L.; Kammoun, M. *Tetrahedron Lett.* **2004**, *45*, 747−751.
(43) Shu, H.-Y.; Perlmutter, D.; Bortolini, O.; Fantin, G.; Fogagnolo, M.; Mari, L. *Tetrahedron* **2006**, *62*, 4482−4490.
(44) Zibuck, R.; Streider, J. *Organic Synthesis*; Wiley: New York, 1998; Collect. Vol. *IX*, p 432.
(45) Wittig, G.; Schöllkopf, U. *Chem. Ber.* **1954**, *87*, 1318−1330.
(46) Wittig, G.; Haag, W. *Chem. Ber.* **1955**, *88*, 1654−1666.
(47) Kim, J.; Jung, S.; Park, S.; Park, S. *Tetrahedron Lett.* **2011**, *52*, 2866−2868.