OL | Organic Letters

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

Letter

pubs.acs.org/OrgLett

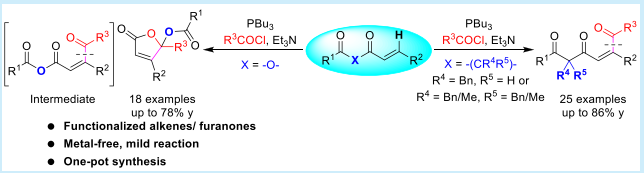
Organophosphane-Promoted Synthesis of Functionalized α,β-Unsaturated Alkenes and Furanones via Direct β-Acylation

Yan-Cheng Liou, Yin-Hsiang Su, Kuan-Chun Ku, Athukuri Edukondalu, Chun-Kai Lin, You-Syuan Ke, Praneeth Karanam, Chia-Jui Lee, and Wenwei Lin*

Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingchow Road, Taipei 11677, Taiwan, R.O.C.

Supporting Information

ABSTRACT: We report a phosphine-mediated direct β-acylation of α,β-unsaturated 1,3-diketones with acyl chlorides and a base. Functionalized furanones were also prepared by the reaction of cinnamic acid and acyl chloride according to our protocol via β-acylation. Our studies revealed that α,β-unsaturated 1,3-diketones with an electron-donating group at the second position favor the formation of β-acylated products, whereas those with oxygen, such as anhydrides, favor furanones via an unprecedented C-acylation/cyclization sequence.

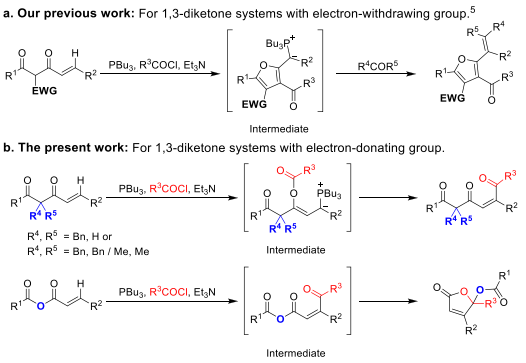


Phosphine-mediated reactions of electron-deficient alkenes have emerged as a powerful tool in organic synthesis to construct biologically active and medicinally useful compounds.[1] Owing to the divergent mechanistic roles played by the phosphonium species, their study greatly benefits the development of a new type of organophosphane-mediated reaction.[2] On the contrary, the direct transformation of electron-deficient alkene C−H bonds into C−C bonds is a fundamental and important challenge and has substantial benefits in organic synthesis.[3] Such methods are mostly developed by utilizing organometallic reagents and transition-metal catalysts.[4] Considering the prominence of this transformation in organic synthesis, the development of efficient methods is highly desirable due to their potential to construct complex molecules.

Previously, we demonstrated a novel method for the synthesis of furocoumarins and cyano-substituted furans from cinnamoyl-4-hydroxy-chromenones and 2-cinnamoyl-cyanoacetophenones by using PBu_3 and acyl chloride via the C-acylation/cyclization sequence (Scheme 1a).[5] As part of our efforts in the exploration of organophosphane chemistry,[6] we were interested in the extension of this reaction by designing appropriate α,β-unsaturated carbonyl compounds. Here we report a new method for the synthesis of functionalized α,β-unsaturated 1,3-diketones and furanones from respective α,β-unsaturated 1,3-diketones and acids/anhydrides via direct β-acylation (Scheme 1b). This result was quite surprising because it resulted in the β-acylation adduct, as opposed to our hypothesis that the presence of acyclic compounds might facilitate the betaine formation and result in a Wittig product.

Initially, we treated dibenzylated α,β-unsaturated 1,3-diketone (**1a**) with Bu_3P and benzoyl chloride (**2a**) in the presence of Et_3N in CH_2Cl_2 under Wittig reaction conditions (Table 1). Two products, **3aa** and **4aa**, were obtained in 87% yield and a trace amount of yield, respectively, within 1 h

Scheme 1. (a) Synthesis of Furans and (b) β-Acylation of α,β-Unsaturated 1,3-Diketones and Anhydrides



(entry 1). To our surprise, the obtained product **3aa** was further characterized as a β-acylation adduct. In such an instance, we have realized that the carbon center between two ketone groups plays a very crucial role to control the reaction pathways to provide different products. Previously, we have also reported the first β-acylation of 2-arylidene-1,3-indandiones with acyl chlorides and a base catalyzed by organophosphane.[7]

The examination of several other phosphines could not enhance the yield of the **3aa** because most of the phosphines were found to be ineffective, except for PEt_2Ph and PMe_2Ph (entries 1−4). The evaluation of other factors such as the reaction media and the base (entries 5−8) established CH_2Cl_2 as a better solvent and Et_3N as an optimal base. (See the SI.) Next, the effect of the stoichiometry of PBu_3 was also tested, and the results indicated that the β-acylation product **3aa**

Received: September 3, 2019

DOI: 10.1021/acs.orglett.9b03116
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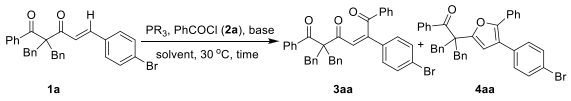
Table 1. Optimization of the Reaction Conditions[a]



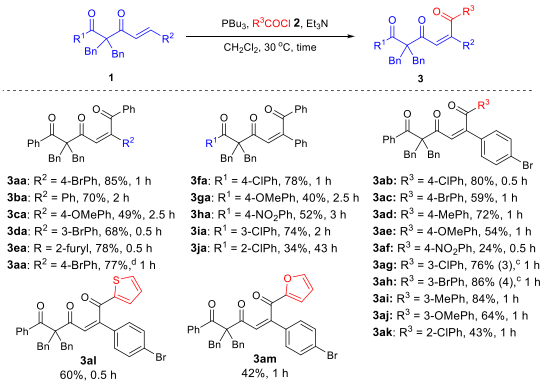
entry	PR_3	solvent	base	t (h)	3aa (%)[b]
1	PBu_3	CH_2Cl_2	Et_3N	1	87 (trace)[c]
2	PPh_3	CH_2Cl_2	Et_3N	1	
3	PMe_2Ph	CH_2Cl_2	Et_3N	1	53 (5)[c]
4	PEt_2Ph	CH_2Cl_2	Et_3N	1	78 (1)[c]
5	PBu_3	CH_2Cl_2	DIPEA	2	80 (2)[c]
6	PBu_3	THF	Et_3N	1	65 (3)[c]
7	PBu_3	CH_3CN	Et_3N	1	75 (3)[c]
8	PBu_3	$C_2H_4Cl_2$	Et_3N	1	79
9[d]	PBu_3	CH_2Cl_2	Et_3N	18	19
10[e]	PBu_3	CH_2Cl_2	Et_3N	1	28

[a]Reactions were carried out with compound **1a** (0.1 mmol), PR_3 (1.2 equiv), PhCOCl (**2a**) (1.1 equiv), and base (1.2 equiv) in dry solvent (0.5 mL) under argon at 30 °C. [b]Yield of the product **3aa** was determined by NMR analysis of the crude reaction mixture using Ph_3CH as an internal standard. [c]NMR yield of the product **4aa**. [d]PBu_3 (0.2 equiv). [e]PBu_3 (0.5 equiv).

could be obtained in good yield only when a stoichiometric amount of PBu_3 was employed (entries 9 and 10). Finally, the most suitable conditions for the reaction were determined as listed in entry 1.

With the optimal conditions in hand, we next investigated the substrate scope, and the results are shown in Scheme 2.

Scheme 2. Synthesis of Compound 3 via β-Acylation[a,b]



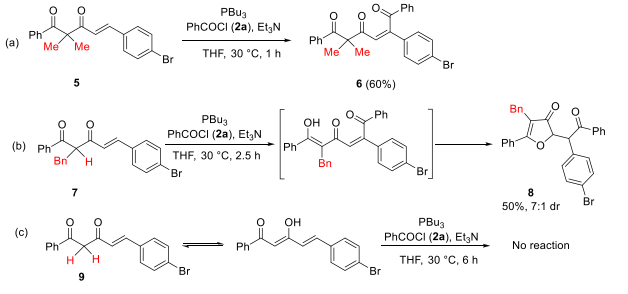
[a]Reactions were carried out with **1** (0.1 mmol), PBu_3 (1.2 equiv), R^3COCl (1.1 equiv), and Et_3N (1.2 equiv) in dry CH_2Cl_2 (0.5 mL) under argon at 30 °C. [b]Isolated yield. [c]NMR yield of the product **4**. [d]Reaction was performed on 2 mmol scale.

Various substrates **1a−e** reacted with PhCOCl (**2a**) to generate the corresponding β-acylated products **3aa−ea** in moderate to good yield. Substrates **1a** and **1d** bearing electron-withdrawing R^2 substitutions provided greater yields of the products **3aa** and **3da** as compared with the substrates **1b** and **1c** with electron-donating R^2 substitutions, irrespective of their position. Notably, substrate **1e** bearing a heteroaryl substitution (R^2 = 2-furyl) also afforded the desired product **3ea** in 78% yield. Next, the effect of R^1 substitution was examined with substrates **1f−j**. It was found that the electronic and steric properties of substituents have a significant impact on the reaction outcome. The diketones **1f** and **1i** bearing chloro group at the para and meta positions, respectively, gave desired products **3fa** and **3ia** in good yield (78 and 74%) within 2 h, whereas **1j** bearing an *ortho*-chloro substitution furnished the product **3ja** in low yield (34%), even after 43 h, as a consequence of steric hindrance.

Furthermore, different acyl chlorides **2b−m** were also tested for the reaction with **1a**. The acyl chlorides **2b** and **2g** with a *para*-chloro and *meta*-chloro substitution furnished the products **3ab** and **3ag** in 76−80% yield, whereas **2k** with an *ortho*-chloro substitution gave the product **3ak** in only 43% yield. Surprisingly, acyl chloride **1f**, having a strongly electron-withdrawing nitro group, resulted in the product **3af** in only 24% yield. In addition, heteroaryl-substituted acyl chlorides, such as **2l** and **2m** (R^3 = 2-thienyl and 2-furyl) also worked well with **1a** to furnish the products **3al** and **3am** in up to 60% yield within 1 h.

Next, the influence of geminal disubstitution on the course of the reaction was investigated. Replacing the sterically bulky benzyl groups with methyl groups also successfully furnished the desired β-acylated product **6** within 1 h in 60% yield (Scheme 3a). However, when a substrate bearing a mono

Scheme 3. Examination of Geminal Disubstitution



substitution **7** was tested, surprisingly, the 3-furanone product **8** was obtained (Scheme 3b). It could be understood that the β-acylation adduct generated would still exist in the enolic form and facilitate the intramolecular oxa-Michael addition, resulting in the 3-furanone product **8**. The structure of 3-furanone **8** was further confirmed by X-ray diffraction analysis. (See the SI.) Furthermore, with an unsubstituted diketone **9**, the reaction did not proceed, and the starting materials could be recovered (Scheme 3c). This could be due to the existence of diketone **9**, predominantly in the enolic form, that renders inertness toward the phospha-Michael addition.

Furthermore, we wished to introduce a little diversity to the substrates by incorporating ester and nitrile groups. Under the optimized conditions, ester-bearing substrate **10** afforded the desired β-acylated product **11** in 47% yield whereas the nitrile substrate **12** surprisingly resulted in the Wittig product **13** in 69% yield besides the β-acylated product **14** in only 20% yield (Scheme 4). This gives a vital hint that the 1,3-diketone motif is very crucial for the predominant formation of β-acylated products.

Afterward, the reason for the formation of furan **4aa** in our optimization studies was also investigated. It was speculated that the furan **4aa** might be obtained via the β-acylated product **3aa**. To test our hypothesis, the β-acylated adduct **3aa** was treated with PBu_3 (1.1 equiv) in CH_2Cl_2. After 1 h, **4aa** was obtained in 26% yield. Similarly, **5** afforded furan **15** in 70% yield via the β-acylated product **6** (Scheme 3a) after the reaction time was prolonged to 72 h (Scheme 5). It is evident that the reaction of β-acylated product formation is catalyzed

DOI: 10.1021/acs.orglett.9b03116
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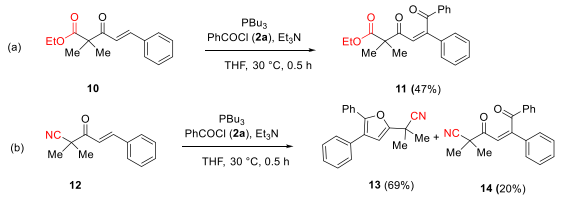
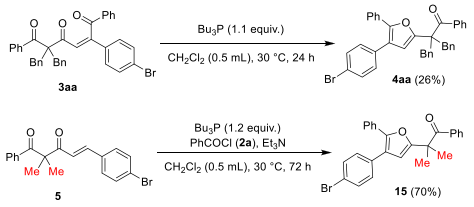
Scheme 4. Examination of Other Compounds



by PBu_3, and a second phospha-Michael addition to **6** leads to the Wittig product **15**.

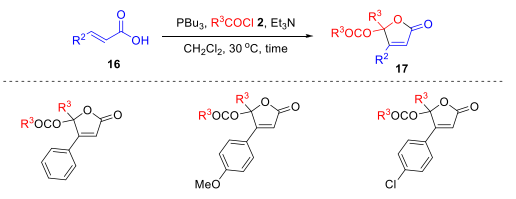
Scheme 5. Generation of Furans 4aa/15 from 3aa/5



Next, we turned our attention to test the reactivity of other 1,3-dicarbonyl compounds such as anhydrides. Accordingly, we have carried out the reaction with cinnamic acid **16a**, 4-BrPhCOCl (**2c**, 2.2 equiv), Et_3N (2.4 equiv), and PBu_3 (1.2 equiv) following our optimized protocol. Surprisingly, instead of β-acylated product, 2-furanone derivative **17ac** was obtained in 51% yield after 3 h. It could be reasoned that the β-acylation adducts generated were reactive enough to undergo a nucleophilic addition with phosphine and generate furanone **17ac**. Owing to the diverse biological applications of furanones,[8] we wished to pursue this study a little further. After a brief screening of phosphines, different bases, solvents, and various other factors, the optimal results were obtained. (See the SI.)

With the optimized reaction conditions established, the scope of the other substrates was investigated (Scheme 6). Various acyl chlorides **2a–j** were tested for the reaction with different acids such as **16a**, **16b**, and **16c**. The results indicate that the acyl chlorides bearing electron-withdrawing groups were more effective for the reaction than the ones that bear electron-donating groups. Moreover, in the case of acids **16a** and **16c**, only moderate yields (up to 51%) of desired

Scheme 6. Synthesis of 2-Furanones 17 via β-Acylation[a,b]



17ab: R^3 = 4-ClPh, 32%, 1.5 h
17ac: R^3 = 4-BrPh, 51%, 3 h
17ae: R^3 = 4-OMePh, 23%, 17 h
17af: R^3 = 4-NO_2Ph, 38%, 1 h
17ag: R^3 = 3-ClPh, 38%, 17 h

17ba: R^3 = Ph, 44%, 13 h
17bb: R^3 = 4-ClPh, 59%, 12 h
17bc: R^3 = 4-BrPh, 63%, 12 h
17bg: R^3 = 3-ClPh, 78%, 12 h
17bg: R^3 = 3-ClPh, 76%,[c] 12 h
17bh: R^3 = 3-BrPh, 73%, 14 h
17bi: R^3 = 3-MePh, 45%, 14 h
17bj: R^3 = 3-OMePh, 59%, 14 h

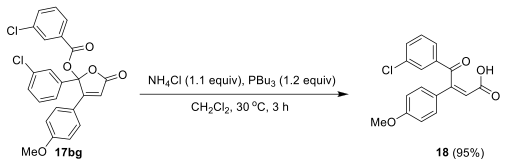
17ca: R^3 = Ph, 36%, 13 h
17cb: R^3 = 4-ClPh, 39%, 12 h
17cc: R^3 = 4-BrPh, 36%, 12 h
17ce: R^3 = 4-OMePh, 26%, 40 h
17cg: R^3 = 3-ClPh, 38%, 17 h
17ch: R^3 = 3-BrPh, 39%, 13 h

[a]Reactions were carried out with compound **16** (0.3 mmol), R^3COCl (2.2 equiv), Et_3N (2.4 equiv), and PBu_3 (1.2 equiv) in dry CH_2Cl_2 (1.5 mL) under argon at 30 °C. [b]Isolated yield of the product **17**. [c]Reaction was performed on a 1 mmol scale.

furanones were obtained. It was delightful to find that the cinnamic acid derivative **16b** was more suitable for the reaction because it provided a good to high yield of the corresponding furanones (up to 78%).

To investigate the mechanism for the formation of furanone **17**, several control experiments have been done to confirm the intermediates like ketene, the β-acylated adduct, and the reactivity of anhydride and imide.[9] Unfortunately, the reaction of α,β-unsaturated imide **23** with PBu_3, benzoyl chloride, and Et_3N was unsuccessful in furnishing the desired product, and only **24** and **25** were obtained under the standard reaction conditions.[10] To our delight, the reaction of furanone **17bg** with PBu_3 and NH_4Cl afforded the β-acylated cinnamic acid **18** in 90% yield (Scheme 7). It is evident that the furanone **17** further reacts with PBu_3 to undergo the reversible reaction.

Scheme 7. Control Experiment for β-Acylated Compound of 18



On the basis of these results, a plausible reaction mechanism is proposed in Scheme 8. The reaction is initiated by the Michael addition of PBu_3 to **1**, giving rise to the zwitterion **I** that undergoes O-acylation with acyl chloride **2** to result in phosphonium salt **II**. The protonation by Et_3N generates ylide **III**, which, upon subsequent intramolecular cyclization, generates the betaine intermediate **IV**. The carbonyl group of ketone functionality then presumably facilitates the cleavage of the C–O bond and the expulsion of PBu_3 to afford the corresponding β-acylated product **3** via intermediate **V**. Notably, upon prolonging the reaction time, the regenerated PBu_3 triggers a second Michael addition onto product **3**, leading to oxaphosphetane **XI** via zwitterionic species **X**. The subsequent elimination of phosphine oxide from **XI** results in the formation of furan product **4**. This could be the reason for the utilization of a stoichiometric amount of phosphine.

On the contrary, the addition of PBu_3 to the α,β-unsaturated anhydride **19** (formed from acid **16** and acyl chloride **2**) generates a ketene-bearing phosphonium salt **VI**, the presence of which was confirmed by HRMS analysis.[9] The deprotonation of ketene **VI** by Et_3N leads to ylide **VII**, which undergoes C-acylation with mixed anhydride to generate intermediate **VIII**. Furthermore, the addition of carboxylate onto the carbonyl of the ketene species **VIII** leads to **IX**, which upon losing PBu_3 gives β-acylated intermediate **20**. The Michael addition of PBu_3 to **20** and the subsequent cyclization results in **XII** via intermediate **X**. The addition of a carboxylate anion to **XII** results in the expulsion of PBu_3 to afford furanones **17**.

In summary, we have demonstrated the novel metal-free synthesis of β-acylated α,β-unsaturated 1,3-diketones and 2-furanones by utilizing the α,β-unsaturated 1,3-diketones and α,β-unsaturated acids, respectively, in the presence of PBu_3, acyl chloride, and a base. We have also developed the novel concept of β-acylation of α,β-unsaturated carbonyl compounds utilizing organophosphane, illustrated by using two conceptual prerequisite substrates (1,3-diketone and anhydride), to provide corresponding products in moderate to good yield.

DOI: 10.1021/acs.orglett.9b03116
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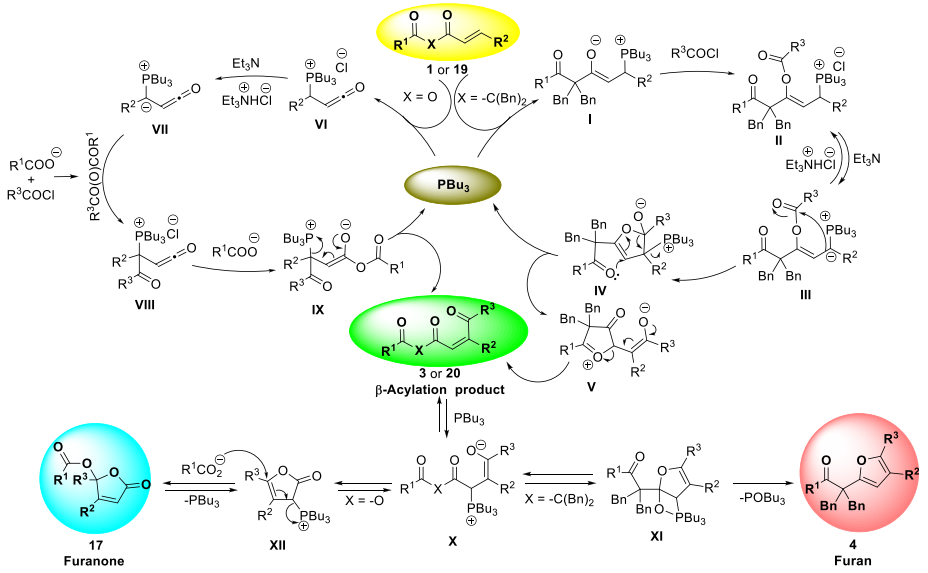
Scheme 8. Plausible Mechanism for the *β*-Acylation



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03116.

Optimization data, experimental procedures, characterization data, and spectra of all compounds (PDF)

Accession Codes

CCDC 1484673, 1561009−1561010, 1845180, and 1947032 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wenweilin@ntnu.edu.tw.

ORCID

Yan-Cheng Liou: 0000-0002-1013-0808
Athukuri Edukondalu: 0000-0003-4593-3843
Praneeth Karanam: 0000-0003-3982-3525
Wenwei Lin: 0000-0002-1121-072X

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Ministry of Science and Technology of the Republic of China (MOST 107-2628-M-003-001-MY3) for financial support.

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(9) Several control experiments have been done. The intermediates **22**−**26** were characterized by NMR, and the ketene phosphonium salt **VI** was confirmed by the HRMS analysis. For the experimental details, see the Supporting Information.

(10) Imide derivative **23** (nitrogen between both of the ketone groups) has been examined to get desired furanones, but only **24** and **25** were obtained; see the Supporting Information.

DOI: 10.1021/acs.orglett.9b03116
Org. Lett. XXXX, XXX, XXX−XXX