Tetrahedron Letters 51 (2010) 6690–6694

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Mechanistic studies of the phosphine-catalyzed homodimerization of ketoketenes

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ARTICLE INFO

Article history:
Received 12 September 2010
Accepted 6 October 2010
Available online 20 October 2010

Keywords:
Disubstituted ketenes
Ketoketenes
Ketoketene dimers
β-Lactones
Diastereoselectivity
Ketenes
Phosphonium enolate
Enolates
Phosphines

ABSTRACT

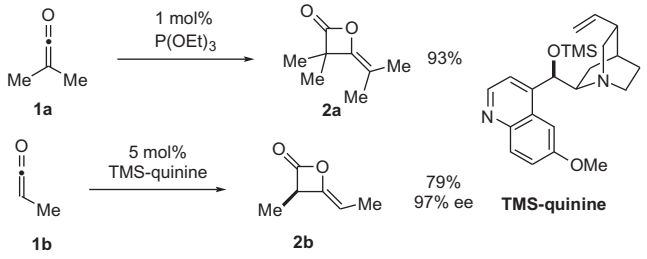
The mechanism of PBu_3-catalyzed homodimerization of ketoketenes has been explored and compared with that of the previously reported trialkylphosphite-mediated reactions. NMR studies of the PBu_3-catalyzed reaction implicated the involvement of tetravalent phosphonium intermediates. Phosphonium intermediates in the catalytic cycle were trapped through reaction with trimethylsilyl chloride and 4-chlorobenzaldehyde, and the resulting products were characterized. A method for the stoichiometric generation of phosphonium enolates was developed as a result of these studies. No evidence was obtained for the involvement of pentacovalent phosphorane intermediates in trialkylphosphine-catalyzed ketoketene homodimerization reactions, in contrast with the mechanism of the trialkylphosphite-mediated homodimerization of dimethylketene. An X-ray crystal structure analysis of methylphenylketene dimer showed that it possesses *Z*-geometry about the exocyclic olefin.

Dimerization of ketenes is an important reaction for accessing β-lactones.[1–3] Elam and Bentrude independently showed that dimethylketene could be homodimerized using trialkylphosphites as nucleophilic catalysts.[1c–f]

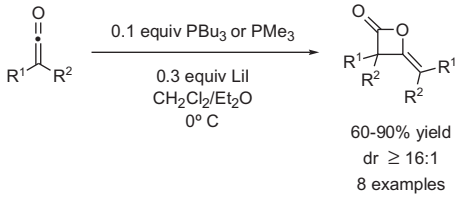
In 1996 Calter showed that a nucleophilic catalyst system (TMS-quinine or TMS-quinidine) could catalyze the homodimerization of aldoketenes with high enantioselectivity (Scheme 1).[2] While aldoketene dimer β-lactones have been used extensively in the synthesis of polyketides (polypropionates) by Calter et al., ketoketene dimers have received less attention due to the paucity of general methods for their preparation.[3–5]

In 2008, our group reported a versatile trialkylphosphine catalytic system which provided a general method for ketoketene (disubstituted ketene) homodimerization (Scheme 2).[4] A range of ketoketene dimer β-lactone products were obtained in good to excellent yields and with excellent diastereoselectivity (Scheme 2).[4]

We have recently demonstrated the synthetic potential of ketoketene dimers by showing that they can undergo highly diastereoselective ring-opening reactions to afford, for example, 1,3-diketones (dr up to 90:10).[4c]



Scheme 1. Literature examples for homodimerization of ketenes.



Scheme 2. Phosphine-catalyzed homodimerization of ketoketenes.

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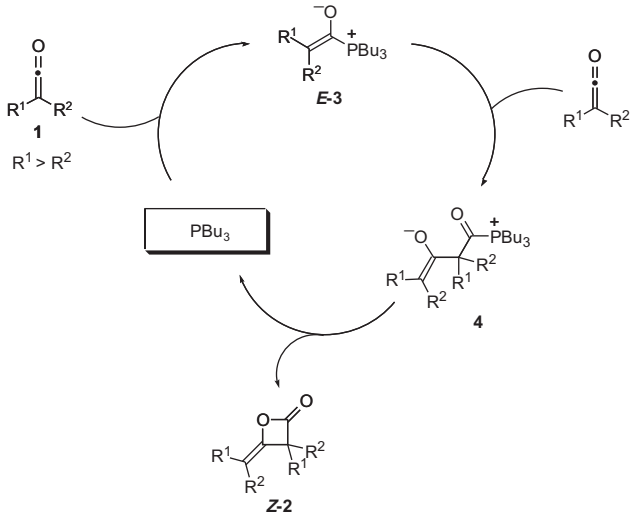
doi:10.1016/j.tetlet.2010.10.026



Scheme 3. Mechanism A for catalytic homodimerization of ketoketenes.

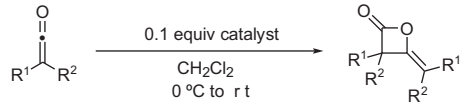
In this Letter, we describe our studies on the mechanism of the phosphine-catalyzed reaction with a range of ketoketene substrates, and compare it to the mechanism of Bentrude's phosphite-mediated dimethylketene dimerization reaction.[1]

We originally postulated that ketoketene dimer **2** was formed through mechanism A presented in Scheme 3.[4b] Nucleophilic attack of the trialkylphosphine catalyst on the less sterically hindered side of the ketoketene **1** (where R^2 = less sterically demanding substituent) would result in the stereoselective formation of phosphonium enolate *E*-**3**.[6] Nucleophilic addition of **3**, through C, to a second molecule of **1** would give rise to a second enolate intermediate **4** (stabilized through a six-membered chelate when LiI is used as an additive). 4-*Exo-trig* cyclization and elimination of the phosphine would result in the generation of ketoketene dimer product *Z*-**2**.

Alternatively in mechanism B (Scheme 4), addition of **3**, through oxygen, to a second molecule of **1** would give rise to enolate **5**. Zwitterion **5** would add to a third molecule of **1** to give enolate **6**, which would undergo cyclization to afford **2** and regenerate **3**.

In this alternative proposal mechanism B (Scheme 4), which is related to the mechanism proposed by Bentrude for the $P(OMe)_3$-mediated dimerization of dimethylketene, **3** (generated through addition of PBu_3 to ketene) would act as the dimerization catalyst.[1] Bentrude and co-workers obtained evidence for the involvement of a pentacovalent phosphorane species **7** ($PR_3 = P(OMe)_3$) in the $P(OMe)_3$-mediated dimerization of dimethylketene by carrying out ^{31}P NMR analysis (δ −53.8 ppm for **7**) of the reaction.[1] The phosphorane was stable enough to be isolated and, indeed, only on heating at >60 °C did Bentrude's group observe decomposition of the pentacovalent species to generate dimethylketene dimer and $P(OMe)_3$. They suggested a mechanism which would involve attack of the O (rather than C) of enolate **3** on a second molecule of ketoketene leading to the formation of a pentacovalent phosphorus species **7**.[1] Mechanism B deviates significantly from Bentrude's original proposal in that **5** (with $PR_3 = PBu_3$) would not cyclize to give **7**, but instead would add, through C of enolate **5**, to another molecule of ketene to give **6**. The electron donating alkyl substituents (of PBu_3) on the phosphonium center of **5** would be expected to stabilize the positively charged phosphorus of **5** to a greater degree than when $P(OMe)_3$ is used, hence disfavoring cyclization to a pentacovalent phosphorane intermediate **7**.[7a] This critical difference would enable catalytic turnover in our system, unlike in Bentrude's system.[1e,4] Interestingly, when Elam carried out the $P(OEt)_3$-catalyzed dimerization of dimethylketene under solventless conditions, less than 0.01 equiv of catalyst was required.[1d] Presumably, catalytic turnover is observed in this situation due to the exothermic nature (90–100 °C) of the neat reaction, resulting in decomposition of **7**.[1d]

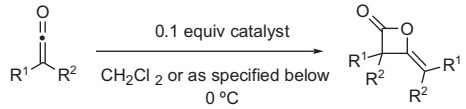
Table 1
Major ^{31}P NMR resonances observed in the nucleophile-catalyzed homodimerization of diphenylketene **1c** to form dimer **2c**[a]



Entry	R_1	R_2	Nucleophile	^{31}P NMR signals (ppm)	Yield of **2c**[b]
1	Ph	Ph	PBu_3	13.6	67
2	Ph	Ph	PMe_3	—	61
3	Ph	Ph	PPh_3	−5.1	0
4	Ph	Ph	$P(OEt)_3$	7.9	0
5[c]	Ph	Ph	$P(OEt)_3$	−55	0

[a] All reactions were conducted at 0.5 M concentration of ketene in CH_2Cl_2 unless stated otherwise.
[b] Yields are isolated yields.
[c] Reaction conducted with 0.5 equiv of $P(OEt)_3$ at 5.5 M concentration of ketene in Et_2O by Baldwin's group (see Ref. 11).

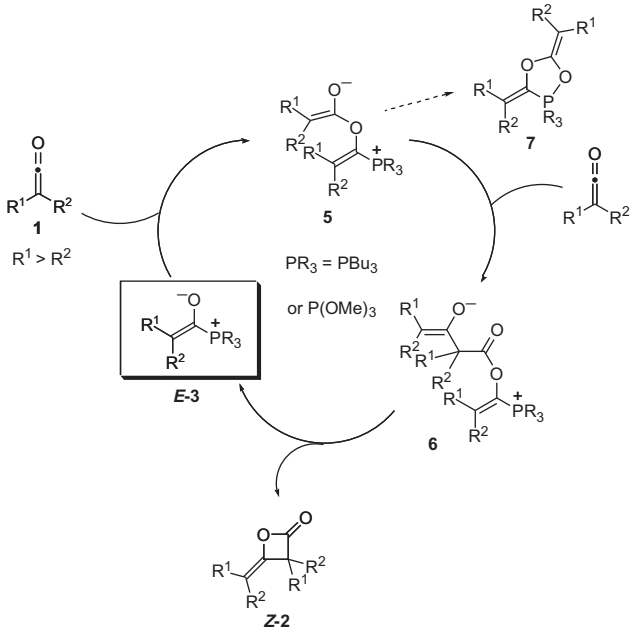
Table 2
Major ^{31}P NMR resonances observed in the nucleophile-catalyzed homodimerization of ketoketenes **1a–f**[a]



Entry	R_1	R_2	Catalyst	^{31}P NMR signals (ppm)	Yield of **2a–f**
1	Et	Ph	PBu_3	34.2	98
2[b]	Et	Ph	PBu_3/LiI	34.3	77
3	Et	Ph	PPh_3	−5.1	0
4	Et	Ph	$P(OEt)_3$	−51.6, −53.3, −55.5, −56.6	0
5	*i*-Bu	Ph	PBu_3	34.3[c], 10.9	84
6[b]	Et	*c*-Hexyl	PBu_3/LiI	—	87[d]
7[e]	Me	Me	PBu_3	33.2, 31.5[c]	73
8	Me	Me	$P(OMe)_3$	−53.8	>99[f]

[a] Yields are isolated yields.
[b] Reaction carried out in CH_2Cl_2/Et_2O.
[c] Major signal.
[d] 1,3-Cyclobutanedione regioisomer.
[e] Reaction carried out in THF at −25 °C.
[f] Reaction performed by Bentrude's group using 0.5 equiv $P(OMe)_3$ in EtOAc, yield after heating to >60 °C, see Ref. 1e.

In order to elucidate information about which mechanism (A or B) is operative in our system, and about the intermediates involved, we carried out extensive ^{31}P NMR spectroscopic studies of the nucleophile-catalyzed homodimerization reaction of ketoketenes **1a–f** (Tables 1 and 2), as well as performing intermediate trapping experiments. In all of these studies, a catalytic amount (0.1 equiv) of the nucleophilic catalyst was used, unless otherwise stated. We initially investigated the dimerization of diphenylketene **1c** (Table 1). PBu_3 and PMe_3 were found to be the only successful homodimerization catalysts. Careful ^{31}P NMR monitoring of the PBu_3-catalyzed reaction (Table 1) revealed a strong signal at 13.6 ppm. We propose that this signal represents a phosphonium enolate based on the region (10–40 ppm) in the ^{31}P NMR spectrum where the signal appears, which is characteristic for a tetravalent phosphonium species.[7] Phosphonium enolates **3–6** were considered to be possible structures for the signal at 13.6 ppm (Scheme 3 and 4). To help distinguish between the

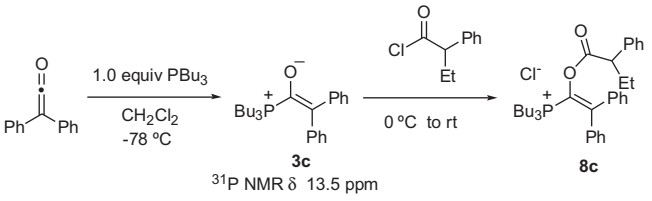


Scheme 4. Mechanism B for catalytic homodimerization of ketoketenes.

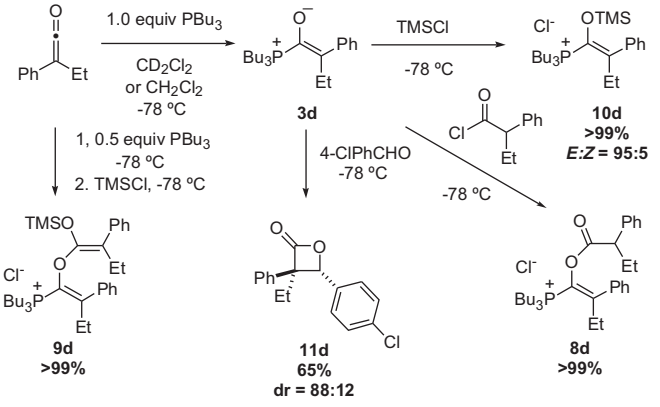
possible enolate structures (**3**–**6**) for the signal at 13.6 ppm, we carried out a number of control experiments. First, we investigated where the ^{31}P NMR resonance of an acylphosphonium derived from diphenylacetyl chloride and PBu_3 would appear. After stirring PBu_3 (1 equiv) and diphenylacetyl chloride (1 equiv) in CH_2Cl_2 for 50 min, a signal was observed at 31.8 ppm. Indeed, based on literature precedent, an acylphosphonium signal would be expected to appear between 28 and 32 ppm, and so structure **4** could be ruled out as a possibility for the signal at 13.6 ppm.[8] Second, when PBu_3 (1 equiv) was added to diphenylketene (1 equiv) in CH_2Cl_2 at −78 °C, the signal for PBu_3 (−30.7 ppm) disappeared completely and was cleanly replaced by a signal at 13.5 ppm (94% of all ^{31}P NMR signals by integration). ^{13}C and ^{1}H NMR analysis of the resulting phosphonium species in CD_2Cl_2 supported our assignment of structure **3** to the signal at 13.6 ppm (in the ^{31}P NMR spectrum).[9] The species giving rise to a signal at 13.6 ppm was also converted into enol ester derivative **8c** and fully characterized, a structure which supports the assignment of structure **3** to the signal at 13.6 ppm (Scheme 5).[10] Therefore, phosphonium enolate **3** appears to be the catalyst resting state in the PBu_3-catalyzed dimerization of diphenylketene. This is presumably due to the attenuated reactivity of **3c** ($R^1 = R^2 = Ph$). The electronically stabilized and sterically hindered nature of **3c** would be expected to slow its reaction with another molecule of diphenylketene.

The use of less basic phosphorus-centered catalysts proved to be an ineffective strategy for catalyzing the dimerization of diphenylketene (Table 1, entries 3 and 4). To understand why this was so, we analyzed these reactions by ^{31}P NMR spectroscopy. In the case of PPh_3, no signal for a phosphonium enolate was observed, with only a signal for free PPh_3 (^{31}P NMR δ −5.1 ppm). From this, we suggest that PPh_3 is too sterically hindered and not sufficiently nucleophilic to generate a significant amount of phosphonium enolate at equilibrium. $P(OEt)_3$ is less sterically hindered and functions as a better nucleophile than PPh_3 but the resulting enolate **3** (^{31}P NMR δ 7.9 ppm) is presumably too stabilized, due to the electron withdrawing alkoxy groups, to undergo further reaction with diphenylketene under our conditions (0.5 M concentration of ketene in CH_2Cl_2). However, it should be noted that Baldwin's group found that when $P(OEt)_3$ (1 equiv) was used under more concentrated conditions (5 M concentration of ketene in Et_2O) it could react with diphenylketene (2 equiv) to form a pentacovalent phosphorane which gave a ^{31}P NMR signal at −55 ppm (Table 1, entry 5).[11]

We next examined the nucleophile-catalyzed dimerization of ethylphenylketene **1d** (Table 2, entries 1–4). We had previously found it necessary to use LiI as an additive in order to reduce trimer formation and favor dimer formation in the PBu_3-catalyzed reaction.[4b] However, this strategy was found to be only necessary for alkylarylketenes possessing a $-CH_3$ substitutent due to the greater reactivity of these ketenes vis-à-vis more sterically hindered ketenes (R^1 = Et, *i*-Bu, Ph). The dimerization of ethylphenylketene proceeded efficiently when PBu_3 was used as the nucleophilic catalyst, both in the presence and in the absence of lithium iodide (Table 2, entry 1 vs entry 2) to provide the desired dimer in good to excellent yields (77–98%). The same resting state of the catalyst was observed in both cases, that is, a tetravalent phosphonium species giving rise to a strong signal at 34 ppm. The first enolate **3d** was not observed under the catalytic reaction conditions, as judged by the absence of a signal between 10 and 20 ppm. It appears in these cases that a tetravalent phosphonium intermediate other than **3** (Schemes 3 and 4) is giving rise to the signal at 34 ppm. This is presumed to be due to the enhanced reactivity and lower stability of **3d** relative to diphenylketene-derived enolate **3c**, and so the resting state of the catalyst is strongly dependent upon the structure of the ketoketene. To clarify the structure of the observed intermediate (**4**, **5** or **6**), we attempted to prepare and characterize it through a modification of the reaction conditions. At −78 °C, PBu_3 (ca. 0.6 equiv) was added quickly to a dilute solution of ethylphenylketene (1 equiv) in CH_2Cl_2 (0.05 M concentration of ketene in CH_2Cl_2). Monitoring by ^{31}P NMR showed the formation of a species giving a major signal at 34 ppm. TMSCl (2 equiv) was then added at −78 °C to trap the intermediate. The resulting product was characterized and was determined to be silylketene acetal **9d**, a derivative of **5d** (Schemes 4 and 6), which lends support to the proposal of mechanism B as being operative in the dimerization of ketoketenes.[12] To test this mechanistic proposal we



Scheme 5. Trapping of phosphonium enolate **3c** with an acyl chloride.



Scheme 6. Synthetic potential of phosphonium enolate **3d**.

prepared **3c** in quantitative fashion, as before, through the reaction of PBu_3 (1 equiv) with diphenylketene (1 equiv). The resulting relatively stable enolate **3c** was then added to a solution of ethylphenylketene. The dimerization of ethylphenylketene was observed to proceed efficiently (yield of **2c** = 95%). ^{31}P NMR monitoring indicated that **3c** was present in high concentration for much of the reaction, while another species (**5**, ^{31}P NMR δ 34 ppm) was gradually formed. While such a result supports the notion of **3** being the true dimerization catalyst (mechanism B), we cannot rule out the possibility that PBu_3 is being formed in a reversible fashion from **3** or **5**, and that PBu_3 itself is actually the active catalyst.

Surprisingly given the highly reactive nature of ethylphenylketene, the first phosphonium enolate **3d** was formed with good conversion through the quick addition of 1 equiv of PBu_3 to 1 equiv of ethylphenylketene at −78 °C (Scheme 6). In this way a tetravalent phosphonium enolate species, which gave a ^{31}P NMR (CD_2Cl_2) δ at 13.4 ppm, was generated. Phosphonium enolate **3d** was trapped cleanly through reaction with TMSCl at −78 °C to give the corresponding silyl enol ether **10d** quantitatively with an olefin isomer ratio = 95:5. The major olefin is presumed to be the *E*-isomer by analogy with the stereochemical outcome of the addition of nucleophiles to disubstituted ketenes reported by Tidwell and co-workers.[6] Compound **10d** gave a ^{31}P NMR (CD_2Cl_2) δ at 32.6 ppm (major isomer).[13] Alternatively **3d**, generated quantitatively, could be engaged in a formal [2 + 2] cycloaddition with 4-chlorobenzaldehyde to give **11d** (65%, dr = 88:12), with the *trans*-isomer being the major isomer.[14] Therefore, this stoichiometric method of phosphonium enolate generation represents a promising new avenue for ketene reaction development, given the lack of a stoichiometric variant available to other catalytic systems, for example, alkaloid and ferrocenylamine catalytic systems.[2,15]

Phosphonium enolate intermediates were also observed when the PBu_3-catalyzed dimerization of other ketenes, such as isobutylphenylketene and dimethylketene, were monitored using ^{31}P NMR analysis (Table 2, entry 5 and 7). Indeed, pentacovalent phosphorane intermediates were only ever detected when trialkylphosphites were used as reaction promoters (Table 2, entries 4 and 8). Dialkylketenes gave the β-lactone or 1,3-cyclobutanedione regioisomer when exposed to PBu_3 catalysis, depending upon the alkyl substituents chosen. Dimethylketene was efficiently dimerized to give the β-lactone when tri-*n*-butylphosphine was used as the catalytic system. On the other hand, cyclohexylethylketene was dimerized to give 1,3-cyclobutanedione exclusively, rather than the β-lactone regioisomer (Table 2, entry 6). The switch in regioselectivity may be due to the higher reactivity of cyclohexylethylketene-derived enolate **6f** at C, compared to the lower reactivity of dimethylketene- or alkylarylketene-derived enolates **6** at C.

The major olefin isomer of the ketoketene dimer β-lactones was determined to be the *Z*-isomer by an X-ray crystal structure analysis of methylphenylketene dimer **2g** (see Supplementary data). This is the isomer that would be expected based on an analysis of the reaction mechanism. A nucleophile would be expected to add to the side of the ketene that is less sterically hindered in order to minimize steric interactions in the transition state leading to **3**, **5,** and **6** (Scheme 4). Arising from this situation A[1,3] strain would be minimized in product **2**. Diastereoselectivity (*Z*-isomer: *E*-isomer >16:1 in most cases) in ketene dimerization is extremely important given the need to access enolates stereoselectively, following ring-opening, in order for them to be broadly useful in synthesis.[3,4]

In conclusion, we have carried out mechanistic investigations of the PBu_3-catalyzed homodimerization of ketoketenes, and this has led us to consider mechanism B as the most likely mechanism. We have demonstrated that trialkylphosphine-catalyzed homodimerizations involve tetravalent phosphonium enolate intermediates, which enable catalytic turnover in our system, even under mild conditions (0 °C or −25 °C). No evidence was observed for the involvement of pentacovalent phosphorus intermediates in the PBu_3-catalyzed reaction. Knowledge of the structures of the intermediates is expected to have implications for the design of chiral phosphine catalysts suitable for imparting asymmetric induction in reactions of ketenes. Furthermore, we have shown that phosphonium enolate intermediates involved in PBu_3-catalyzed ketene dimerizations may be trapped through reaction with various electrophiles, hinting at the potential of these enolates for the development of new synthetic methodologies. Future work will focus on a kinetics investigation of the catalytic system, and on the application of the catalytic system to complex molecule synthesis.[16]

Acknowledgments

We thank the National Science Foundation (Grant Nos. CHE-0911483 to N.J.K., CHE-0722547 to K.A.W., and CHE-0821487 for NMR facilities at Oakland University), and Oakland University (N.J.K.) for financial support of this work.

Supplementary data

Supplementary data (characterization data and procedures for the preparation of **2a**, **2f**, **3c**, **8c**, **8d**, **9d**, **10d**, and **11d**, and X-ray crystal structure data for methylphenylketene dimer **2g**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.026.

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9. *Selected characterization data for* **3c**: ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.76–6.85 (m, 10H), 1.70–1.26 (m, 18H), 0.88 (t, J = 7.1 Hz, 9H); ^{13}C NMR (50 MHz, CD_2Cl_2): δ 151.1 (d, J = 47.3 Hz), 143.3, 143.0, 141.6, 135.2, 128.9, 127.8, 126.5, 123.0, 115.1 (d, J = 65.7 Hz), 25.1, 24.5 (d, J = 13.9 Hz), 20.4 (d, J = 40.8 Hz), 13.7; ^{31}P NMR (81 MHz, CD_2Cl_2): δ 13.5.
10. *Characterization data for* **8c**: IR υ max (thin film): 1765, 1718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.80–7.12 (m, 15H), 3.32 (t, J = 7.6 Hz, 1H), 2.21–1.18 (m, 20H), 0.92 (t, J = 7.2 Hz, 3H), 0.86 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 156.6 (d, J = 17 Hz), 136.9, 136.9, 135.1, 130.9, 129.8, 129.3, 129.1 (d, J = 7 Hz), 128.7, 128.6, 128.4, 128.1, 128.0, 127.5, 53.1, 25.7, 23.8 (d,

J = 8 Hz), 23.5 (d, J = 17 Hz), 20.7 (d, J = 46 Hz), 13.2, 11.3; ^{31}P NMR (162 MHz, 85% H_3PO_4, $CDCl_3$): δ 35.4; (M^++Na) HRMS Anal. Calcd for $C_{36}H_{48}O_2P$: 543.3386 (m/z). Found: 543.3387.

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12. *Characterization data for* **9d**: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for major product: δ 7.71–7.34 (m, 10H), 2.79 (dq, J = 1.8, 7.5 Hz, 2H), 2.42–2.31 (m, 6H), 1.97–1.44 (m, 14H), 1.46 (t, J = 7.3 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 9H), 0.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) for major product: δ 170.7, 147.6 (d, J = 23.9 Hz), 129.8, 129.3 (d, J = 11.8 Hz), 129.1, 129.1, 128.4, 128.4, 128.0, 127.4, 126.2, 116.4, 28.2 (d, J = 8.0 Hz), 24.1 (d, J = 4.4 Hz), 23.8, 23.6, 20.5, 13.5, 11.5, 11.5, 1.3; ^{31}P NMR (162 MHz, 85% H_3PO_4, CH_2Cl_2): δ 34.1 (minor, 5% of all ^{31}P species), 33.7 (major, 85% of all ^{31}P species), 33.5 (minor, 10% of all ^{31}P species).
13. *Characterization data for* **10d**: IR ν_{max} (thin film): 2960, 1690, 1465, 1253 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, TMS at −78 °C) δ 7.67–7.56 (m, 3H), 7.42–7.31 (m, 2H), 2.74 (q, J = 7.5 Hz, 2H), 2.28–2.17 (m, 4H), 1.89–1.48 (m, 14H), 1.21–1.04 (m, 12H), 0.59 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2 at −78 °C) δ 145.2 (d, J = 28.2 Hz), 135.7 (d, J = 11.1 Hz), 128.2, 128.0, 127.9, 127.0, 25.3, 23.3 (d, J = 14.7 Hz), 23.1, 19.3 (d, J = 47.1 Hz), 12.9, 11.8, −0.7; ^{31}P NMR (162 MHz, 85% H_3PO_4 at −78 °C, CD_2Cl_2) δ 32.5 (major: 95% of all ^{31}P species), 32.2 (minor: 5% of all ^{31}P species).
14. Spectroscopic data for **11d** agreed with that previously reported in: Mondal, M.; Ibrahim, A. A.; Wheeler, K. A.; Kerrigan, N. J. *Org. Lett.* **2010**, *12*, 1664–1667.
15. Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 1578–1579.
16. A preliminary kinetics investigation has shown that the reaction rate is dependent upon catalyst concentration.