

Transition-Metal-Free Reductive Deoxygenative Olefination with CO₂

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Supporting Information

ABSTRACT: A new transition-metal-free reductive deoxygenative olefination of phosphorus ylides with CO_2 , an abundant and sustainable C1 chemical feedstock, is described. This catalytic CO_2 fixation afforded β -unsubstituted acrylates and vinyl ketones in good yields with broad scope and good functional group tolerance under mild reaction conditions. Cost-effective and easily handled



polymethylhydrosiloxane was used as a reductant. Bis(silyl) acetal was proved to be the key intermediate in this reductive functionalization of CO_2 .

The development of new carbon-carbon (C-C) bondforming reactions based on sustainable chemical feedstock constitutes a fundamental task in synthetic organic chemistry. As an abundant, nontoxic, cost-effective, and renewable onecarbon source, carbon dioxide (CO₂) has been widely utilized as a C1-synthon in both academic and industrial laboratories.¹ In this respect, transformations of CO₂ into valuable C₂ and high chemicals have gained considerable attention in recent years. These transformations can be possibly divided into two types of reactions, oxygen-retaining C-C bond-forming reactions and deoxygenative C-C bond-forming reactions (Scheme 1a). In the first case, the past decade has witnessed a great advance in transition-metal-catalyzed carboxylation,²



 INo noble metal catalyst
 Low pressure of CO2
 I Scalable reaction

 I Cost-effective reductant
 Mild reaction conditions
 Valuable products

formylation,³ and hydroxymethylation⁴ reactions with CO_2 affording the corresponding carboxylic acids (derivatives), aldehydes, and alcohols. However, the high cost of transition metals and the risk of heavy metal residues may hamper the application of these methods in pharmaceutical industry. Accordingly, transition-metal-free carboxylations with CO_2 have been developed via photocatalysis⁵ or under basic conditions.⁶ Alternatively, deoxygenative C–C bond-forming reactions are less studied. It was not until recently that transition-metal-catalyzed deoxygenative methylation of arenes was achieved with high pressures of CO_2 (20 atm) and H₂ (40 atm) at high temperatures.⁷

Alkenes are one of the fundamental chemicals and reaction intermediates in synthetic chemistry and chemical industry. In this regard, development of new synthetic routes toward alkenes is highly desirable. Among the numerous reported methods, the Wittig reaction of phosphorus ylides and carbonyl compounds is the most well-known due to its easy operation, good functional group tolerance, and ready availability of the starting materials.⁸ In 1966, Matthews et al. first reported that nucleophilic addition of phosphorus ylides to CO2 afforded phosphonium–CO₂ inner salts easily (Scheme 1b).⁹ This kind of salt could be transformed into other products, such as ketene, carboxylic acids, etc.¹⁰ Notably, Zhou, Lu, and coworkers recently used it as a stable catalyst for efficient CO₂ transformation.¹¹ In 1996, Gong and co-workers disclosed a Wittig-type reaction of strongly nucleophilic phosphorus ylide $Me_3P = CH_2$ to Aresta's Ni-CO₂ complex $(PCy_3)_2Ni(CO_2)$,¹² producing a nickel ketene complex (Scheme 1c).¹³ Recently, we reported a reductive tandem C-C and C-N bond-forming reaction with CO_2 , in which CO_2 was reduced as a bridging methylene group.¹⁴ A bis(silyl)acetal from CO_2 was proposed as the intermediate, which has reactivity similar to that of formaldehyde. Continuing our interest in the development of new C-C bond-forming reactions with CO_2 , we hypothesized

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that alkenes could be generated by reaction of phosphorus ylides and CO_2 under suitable reductive conditions with bis(silyl)acetal as the intermediate. Herein, we reported a transition-metal-free reductive deoxygenative olefination with CO_2 using cost-effective and easily handled polymethylhydrosiloxane (PMHS) as a reductant (Scheme 1d).

We started our research by choosing commercially available phosphorus ylide 1 as a model substrate to test our hypothesis. We were glad to find that the desired alkene product 2 was obtained in 65% yield using TBD as a catalyst and phenylsilane (PhSiH₃) as a reductant in CH₃CN with CO₂ (1 atm) for the first attempt (Table 1, entry 1). Further investigation of the

Table 1. Development of the Reductive Deoxygenative Olefination with CO_2

$BnO \xrightarrow{O} PPh_3 + CO_2 + reductant \xrightarrow{10 mol \% catalyst}_{solvent, 100 °C, 12 h} BnO \xrightarrow{O} H H$					
1	(1 atm)			NMe ₂	2
	TBD	DBU	DABCO	DMAP	
entry	catalyst	reductant (x e	quiv)	solvent	yield ^a (%)
1	TBD	$PhSiH_3(2)$		CH ₃ CN	65
2	DBU	$PhSiH_3(2)$		CH ₃ CN	44
3	DABCO	$PhSiH_3(2)$		CH ₃ CN	43
4	DMAP	$PhSiH_3(2)$		CH ₃ CN	68
5	DMAP	$PhSiH_{3}(2)$		DMF	70
6	DMAP	$PhSiH_3(2)$		THF	18
7	DMAP	Ph_2SiH_2 (3)		DMF	77
8	DMAP	Ph ₃ SiH (6)		DMF	0
9	DMAP	(EtO) ₃ SiH	(6)	DMF	8
10	DMAP	PMHS (6)		DMF	59
11	Cs ₂ CO ₃	PMHS (6)		DMF	73
12	Na_2CO_3	PMHS (6)		DMF	51
13	NaOEt	PMHS (6)		DMF	43
14	NaO ^t Bu	PMHS (6)		DMF	89
15 ^b	NaO ^t Bu	PMHS (6)		DMF	43
16 ^c	NaO ^t Bu	PMHS (6)		DMF	0
17 ^d	NaO ^t Bu	PMHS (6)		DMF	90 (83)
18 ^e		PMHS (6)		DMF	42
19 ^e		$PhSiH_3(2)$		CH ₃ CN	0
20 ^f	NaO ^t Bu	PMHS (6)		DMF	0

^{*a*}All of the reactions were carried out on a 0.2 mmol scale in 2 mL of solvent at 100 °C in a sealed 25 mL screw Schlenk tube; the yield was determined by GC with *n*-dodecane as internal standard. ^{*b*}At 80 °C. ^{*c*}At 25 °C. ^{*d*}With 0.5 mmol of 1; isolated yield in parentheses. ^{*e*}No catalyst. ^{*f*}Without CO₂.

catalysts showed that DMAP, a common and inexpensive organic base, gave a slightly higher yield (entry 4 and Table S1). Switching the solvent from CH_3CN to DMF afforded 2 with a slightly higher yield (entry 5). However, other common solvents, such as THF, dioxane, DCM, and toluene, produced 2 in low yields (entry 6 and Table S2). Then a series of reductants were tested. Diphenylsilane (Ph_2SiH_2) gave a better result (entry 7). Other reductants gave no reaction or afforded 2 in very low yields, such as triphenylsilane and triethoxysilane (entries 8 and 9). To our delight, a promising yield was also obtained when polymethylhydrosiloxane (PMHS),¹⁵ an abundant chemical waste with nontoxicity, low cost, and high moisture stability from silicone chemistry, was used (entry 10).

Considering that inorganic bases can be disolved slightly in highly polar DMF, a variety of inorganic bases were tested in DMF with PMHS (Table S4). Most inorganic bases afforded 2 in good yields, such as Cs_2CO_3 , Na_2CO_3 , and KOEt (entries 11–13). The best result was obtained when NaO^tBu , a strong base in DMF, was used (entry 14). Lower yield was observed when the temperature was reduced from 100 to 80 °C (entry 15). No reaction occurred at room temperature (entry 16). An 83% isolated yield was obtained when the reaction was conducted with 0.5 mmol of 1 (entry 17). Surprisingly, the reaction still occurred in DMF without catalyst, albeit in low yield (entry 18). This result may be attributed to the weak basicity of DMF because no reaction occurred without CO_2 , indicating that the carbon source is not from DMF (entry 20).

With the optimized reaction conditions in hand, we began to examine the scope of the reductive deoxygenative olefination reaction. As illustrated in Table 2, the α carbonyl phosphorus ylide 5 was synthesized in situ from commercially available acyl chloride 3 and alkyl phosphonium bromide salt 4 under simple conditions and used directly in the reductive deoxygenative olefination without further purification. A series of terminal alkenes 6 were obtained in good to excellent yields. Simple ethyltriphenylphosphonium bromide 4a was first selected as a model substrate for the investigation of various acyl chlorides. A good yield of 6a was obtained with benzyl carbonochloridate 3a (entry 1). Benzoyl chloride (3b) was then tested and afforded 6b in good yield (entry 2). The electron-donating group (Me, MeO, CF_3O and electron-withdrawing group (CF_3) on the para-position of benzoyl chlorides were all well tolerated and produced the corresponding alkenes 6 in good yields (entries 3-6). Meanwhile, benzoyl chlorides bearing halogen substituents (F, Cl, Br, I) reacted smoothly, affording vinyl ketones 6 in good yields (entries 7-10). The moderate yield of 6l obtained with 2,4,6-trimethylbenzoyl chloride may be attributed to the steric hindrance of the *o*-dimethyl group (entry 12). In addition, reactions using 2-naphthoyl chloride (3m) and heteroaryl acyl chloride (3n and 3o) as starting materials provided 6 in good yield (entries 13-15). Next, long-chain alkyl triphenylphosphonium bromides were tested, and the corresponding 6p, 6q, and 6r were obtained in good yields (entries 16-18). When (cyclopropylmethyl)triphenylphosphonium bromide was used in this reaction, a low yield of 6s was obtained, but no ring-opening product was detected, indicating that no α carbonyl radical was formed in the reaction (entry 19). At last, isophthaloyl dichloride was employed as substrate, and the corresponding 6t was obtained in good yield (entry 20). Unfortunately, no reaction occurred when simple alkyl triphenylphosphorus ylide without an α carbonyl group was used, maybe because of its lower stability in our reaction system.

To test the scalability of the present reaction, a gram-scale reaction was carried out with 5 mmol of benzoyl chloride **3b** as substrate, and the desired product **6b** was obtained in 90% isolated yield (Scheme 2).

To gain some preliminary insight into the reaction mechanism, we carried out some experiments as shown in Scheme 3. Bis(triethylsilyl)acetal 7 was synthesized according the reported procedure.¹⁶ The reaction of phosphorus ylide 1 with 7 afforded 2 in 88% yield under the standard conditions without silane and CO_2 (eq 1). As expected, olefin 2 was also obtained in 86% yield under the standard conditions with triethylsilane as reductant (eq 2). This indicates that bis(silyl)-



Table 2. Scope of the Transition-Metal-Free Reductive Deoxygenative Olefination with CO_2^{a}

"The reaction was conducted on 0.5 mmol scale of 3; isolated yields are provided. "With 0.25 mmol of 3t and 1.05 mmol of 4a.

Scheme 2. Gram-Scale Reaction



Scheme 3. Mechanistic Experiments



acetal may be the intermediate in the reductive deoxygenative olefination reaction with CO_2 .

On the basis of our experiments, a plausible reaction pathway is proposed in Scheme 4. First, reduction of CO_2 with silane produces bis(silyl)acetal I efficiently through a formoxysilane intermediate in the presence of catalytic amount of base. This Scheme 4. Plausible Reaction Pathway for the Reductive Deoxygenative Olefination



two-step reduction has also been suggested by Wang and Zhang in the reduction of CO_2 with hydrosilane.¹⁷ Then nucleophilic addition of phosphorus ylide to bis(silyl)acetal I affords phosphonium intermediate II. Subsequent elimination produces alkene product and generates triphenylphosphine oxide¹⁸ and silyl ether.

In summary, we have developed the first transition-metal-free reductive deoxygenative olefination reaction for the synthesis of terminal alkenes with CO₂. A series of β -unsubstituted acrylates

and vinyl ketones have been obtained in good yields using costeffective PMHS under mild conditions. A bis(silyl)acetal was proved to be the key intermediate. Further investigation of the reaction mechanism and expansion of the reductive C–C bondforming reactions with CO₂ are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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(18) Triphenylphosphine oxide was obtained in 75% isolated yield under the standard conditions (Table 1, entry 17).