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Oxo-Rhenium-Catalyzed Radical Addition of Benzylic Alcohols to Olefins

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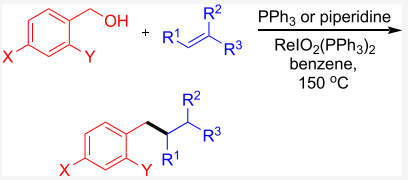
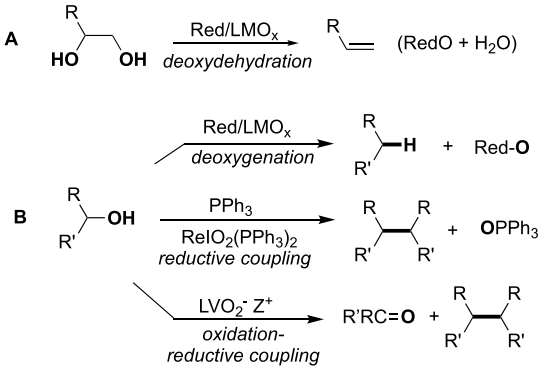
ABSTRACT: Although carbon radicals generated from a variety of alcohol derivatives have proven valuable in coupling and addition reactions, the direct use of alcohols as synthetically useful radical sources is less known. In this report, benzylic alcohols are shown to be effective radical precursors for addition reactions to alkenes when treated with triphenylphosphine or piperidine with the catalyst $ReIO_2(PPh_3)_2$ (**I**).



INTRODUCTION

The search for sustainable transformations of oxygen-rich renewable resources has stimulated widespread efforts to discover and develop new reactions for the refunctionalization and defunctionalization of alcohols and polyols.[1] A recent focus in the field of biomass conversion catalysis has been on the deoxydehydration (DODH) of polyols, in which vicinal hydroxyl groups are eliminated to produce unsaturated products (Scheme 1A).[1c] DODH reactions are catalyzed by oxo-metal compounds of Re,[2−4] Mo,[5−8] and V,[9] employing a variety of reducing agents, including PPh_3,[2] H_2,[10,11] sulfite,[12,13] secondary and benzylic alcohols,[14−16] elements,[17] and hydroaromatics.[18]

Scheme 1. Reductive Deoxygenation of Glycols and Monools



In recent studies, we discovered that benzylic and allylic mono-alcohols undergo a novel reductive coupling reaction with triphenylphosphine catalyzed by $ReIO_2(PPh_3)_2$ (**I**) (Scheme 1B).[19] In contrast, oxovanadium complexes were found to catalyze redox disproportionation of benzylic and allylic alcohols (Scheme 1B), resulting in coproduction of carbonyl products and the reductively coupled hydrocarbon dimers.[20] Experimental and computational studies of the rhenium-[19,21] and vanadium-catalyzed[22] reductive coupling reactions point to the intermediacy of carbon radicals that are generated by the facile homolytic C−O cleavage of reduced metal−alkoxide intermediates. This novel transformation is a rare example of C−C bond formation from alcohol substrates.

The established methods for generating alkyl radicals typically employ alkyl halides, xanthates,[23] oxalates,[24] benzoates,[25] and phosphites[26] as precursors, all of which are prepared from the corresponding alcohols. Recently, alkylarenes,[27] arylacetic acids,[28] benzylamines,[29] and benzylsilanes[30] have also been demonstrated as benzylic radical sources. However, the direct use of alcohols as C-radical precursors, as implicated in the oxo−metal reductive coupling reactions (Scheme 1B), and their application to C−C bond formation are less known.[31] In recent studies, low-valent titanium reagents have been shown to stoichiometrically promote reductive reactions of activated (benzylic and allylic) alcohols, undergoing deoxygenation,[32] dimerization to hydrocarbons,[33] or addition to electron-deficient alkenes.[34]

Radical reactions that form C−C bonds by addition to unsaturated substrates are well-known and useful processes in organic synthesis.[35−37] The ability of oxo−metal complexes to activate C−O bonds in the DODH and reductive coupling of alcohols prompted us to investigate and report here on their ability to catalyze radical addition reactions of alcohols.

RESULTS AND DISCUSSION

We began the investigation examining the addition reaction between benzyl alcohol (**1A**) and 1,1-diphenylethylene (DPE, **2A**) in the presence of $ReIO_2(PPh_3)_2$ (**I**) and PPh_3 as reducing

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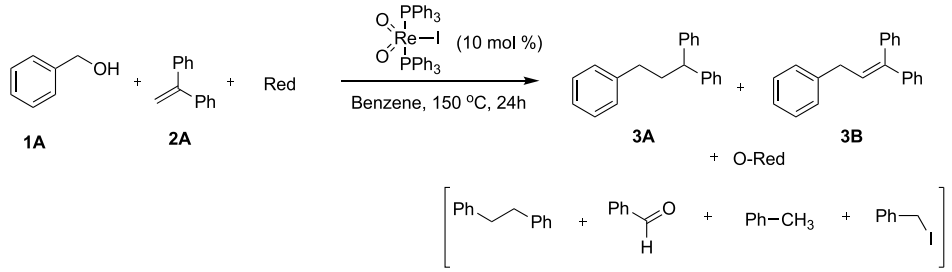
Scheme 2. Optimization of the Benzyl Addition Reaction of DPE 2A



agent in benzene. The reaction was carried out under conditions reported for the reductive coupling—that is, 0.2 M benzene at 150 °C in a sealed tube for 24 h. The addition product **3A** was isolated, albeit in low yield (10%), and confirmed by spectroscopic analysis, accompanied by the unexpected unsaturated product **3B** (10%) (Scheme 2). At 1.0 M concentration of the reactants, the combined yield of **3A**/**3B** increased to 48% at 70% conversion (see the Supporting Information, Table S1). Gas chromatography−mass spectrometry (GC−MS) analysis of the reaction mixtures revealed the coproduction of other benzyl alcohol derived byproducts, including toluene, benzaldehyde, benzyl iodide (from precatalyst), and bibenzyl, products observed in the reductive coupling reactions (in the absence of alkene).[19,21] Further optimization studies evaluated the effects of reactant ratios on the reaction efficiency (Table 1). The adduct yields were

Table 1. Reaction Optimization−Reactant Stoichiometry with PPh_3 Reductant[a]

entry	**1A** (mmol)	**2A** (mmol)	PPh_3 (mmol)	% Conv.[b]	% yield (**3A** + **3B**)[c]
1	1.2	1.0	1.0	85[b]	38 (23 + 19)
2	1.0	2.0	1.0	80[b]	47 (25 + 22)
3	2.0	1.0	1.0	87[a]	52 (31 + 21)
4	2.0	1.0	2.0	91[a]	70 (44 + 26)
5	2.0	1.0	5.0	82[a]	33 (20 + 13)

[a]The indicated quantities of reactants and catalysts, $ReIO_2(PPh_3)_2$ (**I**, 0.10 mmol), and 1.0 mL of benzene were heated in a sealed tube for 24 h at 150 °C. [b]% conversion based on the limiting reagent. [c]Yield determined by NMR with DMF as the internal standard.

modestly improved by employing an excess of either the alkene (entry 1 vs 2) or the alcohol (entry 2 vs 3). The yield of **3A**/**B** was significantly improved to 70% by increasing the amount of triphenylphosphine (entry 4), but a further increase to 5 equiv suppressed both conversion and yield (entry 5). Several high boiling solvents of low and medium polarity were also tested in the reaction of Scheme 2 (at reflux or at 150 °C), but the conversions and yields were inferior to those in benzene (see the Supporting Information, Table S3).

Regarding the pathway to form the unsaturated product **3B**, the saturated product **3A** was found to be unchanged when heated at 150 °C with catalyst **I** and piperidine. Similarly, the unsaturated product **3B** was also unchanged under the same conditions. These results show that the products do not interconvert under the reaction conditions and suggest that they are either formed by independent pathways or from a common intermediate. This could be a result of disproportionation of the intermediate benzyl radical adduct of DPE[38] or competing H-atom transfer from the intermediate radical by a rhenium-hydroxo species (vide infra).

The effectiveness of other potential reductants was also evaluated (Table 2). Phosphines of varying steric and

Table 2. Survey of Prospective Reductants in the Benzylation of Diphenylethylene[a]

entry	reductant	% conversion[b]	% yield (**3A** + **3B**)[c]
1	P(*o*-Tol)$_3$	87	35 (20 + 15)
2	P(C_6H_{11})	92	40 (22 + 18)
3	PBu_3	50	14 (10 + 4)
4	PPh_2Me	55	44 (21 + 23)
5	$Ph_2PCH_2CH_2PPh_2$ (DPPE)	0	0 (0 + 0)
6	pyridine	87	35 (20 + 15)
7	2,4,6-trimethylpyridine	92	40 (22 + 18)
8	4-dimethylaminopyridine	50	14 (10 + 4)
9	$C_5H_{11}N$ (piperidine)	99	87 (55 + 32)[c] /83 (52 + 31)[d]
10	$C_4H_8NCH_3$ (1-methylpyrrolidine)	55	44 (21 + 23)
11	isopropanol	95	95 (50 + 45)[e]

[a]BnOH (2.0 mmol), DPE **2A** (1.0 mmol), reductant—phosphine (2.0 mmol), amine (1.0 mmol), or isopropanol (2.0 mmol), and catalyst **I** (0.10 mmol) in 1.0 mL of benzene were heated at 150 °C for 24 h. [b]% conversion based on DPE **2A**. [c]Yield determined by NMR with DMF as the internal standard. [d]Isolated yield. [e]72 h reaction time.

electronic characteristics were tested in the reaction (entries 1−5), but all were inferior to PPh_3. Likely chelating DPPE completely suppressed the reaction (entry 5), probably by blocking alcohol coordination and activation. A number of nitrogen-based prospective reductants were also tested (entries 6−10). Among these, the secondary amine piperidine gave the best conversion and yield of the adducts (entry 9), 99 and 87%, respectively. GC−MS analysis showed that the major piperidine-derived product detected was *N*-benzyl-piperidine; $OPPh_3$ and benzaldehyde were also found as oxidation byproducts. The particular chemical role(s) played by piperidine in these reactions, for example, a base, ligand, or reductant, is yet unclear. Finally, isopropanol (2 mM) was also found to be an effective but gradual, reductant for the benzylation of DPE (entry 11).

The catalytic efficiency of a few commercially available oxorhenium derivatives for the benzyl alcohol/DPE/piperidine reaction was assessed under the standard conditions (Table 3, entries 2−4). Only $MeReO_3$ was used to afford a moderate yield of the adducts. It was also found that decreasing the loading of catalyst **I** to 5% slowed the reaction considerably, decreasing the conversion and yield (Table 3, entry 5).

After developing the optimized reaction conditions for the benzylation of DPE, the sensitivity of the reaction to the

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Table 3. Effects of Catalyst and Its Loading on the Reaction Efficiency and Selectivity[a]

entry	Re-catalyst	% conversion[b]	% yield (3A + 3B)[c]
1	$ReIO_2(PPh_3)_2$ (I)	99	87 (55 + 32)
2	NH_4ReO_4	35	12 (8 + 4)
3	Bu_4NReO_4	0	0 (0 + 0)
4	$MeReO_3$	80	56 (35 + 21)
5	$ReIO_2(PPh_3)_2$ (I)[d]	45	22 (10 + 12)

[a]BnOH (2.0 mmol), DPE **2A** (1.0 mmol), piperidine (1.0 mmol), Re-catalyst (10 mol %, 0.10 mmol), 1.0 mL of benzene, 150 °C in a sealed tube, and 24 h. [b]% Conversion based on DPE **2A**. [c]Yield determined by NMR with DMF as the internal standard. [d]5 mol % **I** (0.05 mmol) used under the same conditions as in[a].

electronic characteristic of the alcohol was investigated by conducting reactions between DPE (**2A**) and a set of electronically varied 4-substituted benzyl alcohols (Table 4, entries 1−5). All five alcohols afforded moderate yields of a mixture of saturated and unsaturated addition products. The more electron-deficient alcohols **1C** and **1E** reacted gradually, requiring a longer reaction time to achieve complete conversion. These results indicate that a moderate range of electronic character of the benzylic alcohol is tolerated in the reaction. A brief survey of the reactions between DPE and some other activated alcohols (e.g., benzhydrol and allylic alcohols) catalyzed by **I** typically afforded mostly the hydrocarbon dimers derived from the alcohol and low yields of the radical addition products (see the Supporting Information, Scheme S1).

The scope of benzylation of various unsaturated substrates was then evaluated using the optimized procedure with piperidine as the reductant. The results are summarized in Table 4 according to Scheme 3. A series of electron-deficient

Scheme 3. Substrate Scope of Rhenium-Catalyzed Benzylation of Alkenes

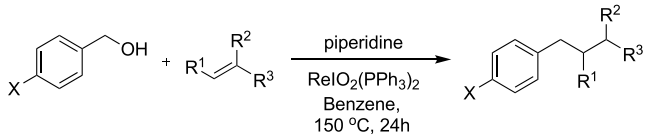
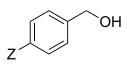
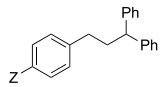
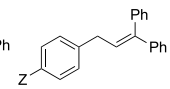
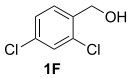
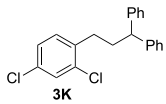
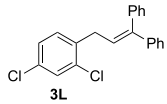
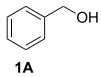
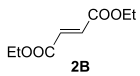
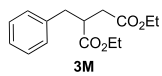
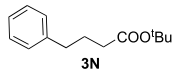
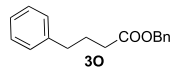
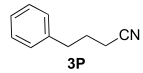
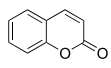
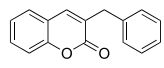
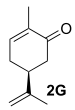
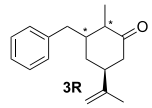
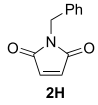
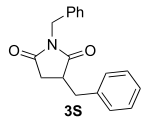
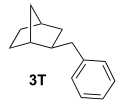


Table 4. Scope and Efficiency of Re-Catalyzed Benzylation of Alkenes

Entry	Alcohol	Alkene	Product	Yield[a,b]
1-4	 1B (Z=OMe) 1C (Z=Cl) 1D (Z=Me) 1E (Z=F)	 2A	 3C 3E 3G 3I	 3D 3F 3H 3J	73 (1.5:1) 75 (1.2:1)[c] 68 (1.0:1) 62 (0.7:1)[d]
5	 1F	2A	 3K	 3L	78 (1.6:1)[d]
6	 1A	 2B	 3M	68
7	1A	 2C	 3N	50
8	1A	 2D	 3O	52
9	1A	 2E	 3P	20[c]
10	1A	 2F	 3Q	80
11	1A	 2G	 3R	61[c,e]
12	1A	 2H	 3S	32[c]
13	1A	 2I	 3T	62[c,f]

[a]Alcohol (2.0 mmol), alkene (1.0 mmol), piperidine (1.0 mmol), **I** (0.1 mmol), 1.0 mL of benzene, 150 °C in a sealed tube, and 24 h. [b]Isolated yield following chromatography. [c]48 h reaction time. [d]5d reaction time. [e]Mixture of diastereomers. [f]9:1 exo/endo.

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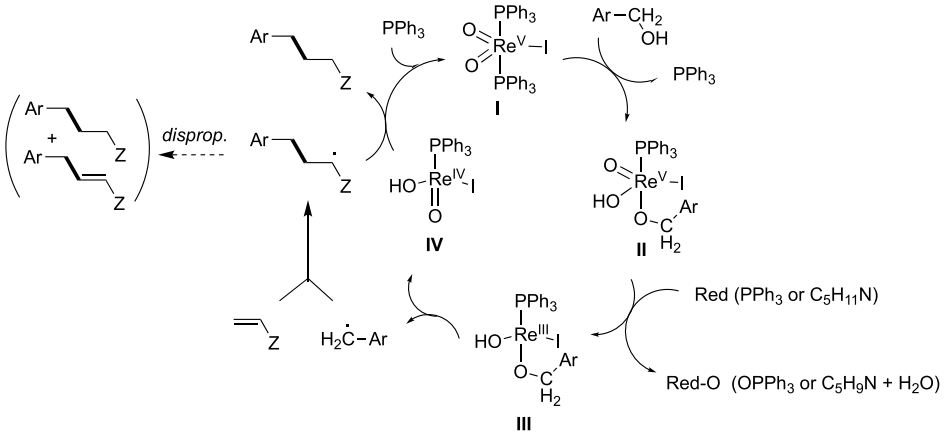
Scheme 4. Suggested Catalytic Cycle for Alcohol-Based Radical Addition to Alkene Catalyzed by $ReIO_2(PPh_3)_2$ (I)



olefins (entries 6–12) were found to be suitable acceptors. Diethyl fumarate reacted with benzyl alcohol (1:2) to give 2-benzyldiethylsuccinate (**3M**) in 68% isolated yield (entry 6). No unsaturated adduct was detected by GC–MS, but a small amount of transesterification product (ca. 10–20%) was indicated. Similarly, *tert*-butyl and benzyl acrylate underwent Re-catalyzed addition producing the corresponding addition products (**3N** and **3O**) in 50 and 52% yield, respectively (entries 7 and 8). Acrylonitrile gave the corresponding adduct (**3P**) in only 20% yield after 48 h at 150 °C (entry 9), which may be the result of competing thermal polymerization of this sensitive alkene. On the other hand, *N*-benzyl maleimide was converted to its benzylated derivative (**3S**) in moderate yield (entry 12). In contrast to the above reactions, which gave exclusively saturated addition products, C-3 benzylation of coumarin was achieved in 80% yield while producing only the unsaturated **3Q** (entry 10). The benzyl radical apparently attacks at the C3 of coumarin to generate the more stable benzylic radical, probably followed by H-atom abstraction.[39] Finally, an addition reaction between benzyl alcohol and the strained 2-norbornene gave *exo*-benzyl norbornane (**3T**) as the major product along with a small amount of the endo isomer (9:1) in a moderate 62% combined yield (entry 13). Use of isopropanol as a reductant with these alkenes gave inferior conversion/yields. Screening reactions of BnOH with other representative types of unsaturated substrates, e.g., vinyl ethers (electron-rich), alkynes, diazenes, and imines, with piperidine/**I**, typically showed little/no adduct formation but produced rather bibenzyl, toluene, and benzaldehyde (see the Supporting Information, Scheme S2), suggesting their low addition reactivity with the relatively stable benzylic radicals.

Supported by our recent experimental and computational studies of the reductive coupling of alcohols catalyzed by **I**,[21] we suggest the operation of the catalytic pathway for the radical additions outlined in Scheme 4. Beginning with alcohol association with **I**, the O-transfer reduction of the Re(V)-alkoxide **II** by PPh_3 (or piperidine or BnOH) would produce Re(III)-alcoholate **III**. Homolytic C–O bond scission of **III** would give the Re(IV)-oxyl species **IV** and benzyl radical. Our recent studies of the reductive coupling of benzylic (and allylic) alcohols by the same reductant/catalyst combination, PPh_3/**I**, support the intermediacy of C-free radicals from: (1) the product distribution-dimeric hydrocarbons (R–R) and/or the reduced hydrocarbon (R–H);[19] (2) the selectivity, unsymmetrical allylic alcohols giving regioisomeric mixtures;[19] (3) DFT-B3LYP computations that indicate a very low Re(III,IV)O–R bond dissociation energy (20–25 kcal/mol);[21] and (4) the observed addition products and selectivity in the current study, that is, the ready additions to EWG–alkenes, consistent with the nucleophilic character of benzyl radicals[40] (and inconsistent with electrophilic intermediates, e.g., carbocations). The C-radical can then be trapped by olefin to give the adduct radical, which can either disproportionate[38] (when alkene = diphenylethylene) or H-abstract from the Re-OH species **IV** (for other alkenes) to give the reduced product and regenerate **I**. We note that the enthalpy of this latter H-transfer step is estimated to be quite favorable (ca. −47 kcal/mol) by DFT/B3LYP computation.

CONCLUSIONS

The Re-catalyzed addition of alcohol-derived benzylic radicals to olefins is an effective method for producing addition products. The reactions are most efficient with electron-deficient or strained alkenes. Our efforts are continuing to expand the utility of metal-promoted C–O cleavage and C–C bond-forming reactions with respect to the alcohol scope, coupling partner, catalyst activity, and economy.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in oven-dried glassware unless otherwise specified. The reactants were obtained commercially and used without further purification. Benzene was distilled from sodium/benzophenone under nitrogen. Analytical thin-layer chromatography was performed on silica gel plates (Merck 60F254) and visualized with a UV lamp (254 nm). Flash chromatography was performed over silica gel (60–120 mesh). ^{1}H NMR spectra were recorded at 300 or 400 MHz in $CDCl_3$ (unless otherwise specified) at ambient temperature and processed using MestReNova software; chemical shifts were given in parts per million from tetramethylsilane with the solvent as an internal reference ($CDCl_3$ δ 7.26 ppm); ^{13}C NMR spectra were recorded at 75 or 100 MHz in $CDCl_3$ (unless otherwise specified), and the chemical shifts were reported in parts per million from tetramethylsilane with the solvent as an internal reference ($CDCl_3$ δ 77.2 ppm); coupling constants (J) were reported in Hertz (Hz). Gas chromatograms were collected on a Shimadzu GC-2014 equipped with an AOC 20i+s autosampler, with a 3% SE-54 packed column, and a FID detector. GC–MS data were obtained using an Agilent 6890 N GC with 5973 MDS equipped with an Agilent HP-5 column (30 m × 250 μm × 0.25 μm). High-resolution mass spectrometry (HRMS) data and liquid chromatography mass spectrometry data were obtained on an Agilent 6545-QTOF W/1290 high-performance liquid chromatography mass spectrometer. Characterization data for previously reported com-

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pounds are given in the Supporting Information. $ReIO_2(Ph_3P)_2$ (**I**) was prepared efficiently by the reported method (below).[41]

Preparation of $ReIO_2(PPh_3)_2$ (I). Sodium perrhenate (1.0 g, 3.7 mmol) and triphenylphosphine (5.0 g, 19 mmol) were added to a mixture of 56% hydroiodic acid solution (5.0 mL) and ethanol (30 mL). The reaction was brought to reflux for 15 min. Green crystals of $ReI_2O(OEt)(PPh_3)_2$ formed in the mixture. After cooling to room temperature, the crystals were filtered off, washed with ethanol, and dried under high vacuum. To a mixture of acetone (50 mL) and water (2 mL) was added $ReI_2O(OEt)(PPh_3)_2$ (1.00 g, 0.97 mmol). The green suspension was magnetically stirred at room temperature. After an hour, the suspended crystals changed to violet color. The crystals were filtered off and washed with cold acetone. The product was recrystallized from hot 1:1 benzene/hexanes, giving an 80% yield of $ReIO_2(PPh_3)_2$ (**I**) (0.67 g, 0.78 mmol), which was stored in a desiccator over $CaCl_2$.

General Procedure A for the Addition of Benzyl Alcohol to DPE. Benzyl alcohol (**1A**, 1−2 mmol, 1−2 equiv), DPE (**2A**, 1−2 mmol, 1−2 equiv), the reductant (1−2 mmol, 1−2 equiv), and $ReIO_2(PPh_3)_2$ (**I**) (87 mg, 0.10 mmol, 0.1 equiv) were mixed in 1.0 mL of dry benzene in a 10 mL thick-walled glass tube fitted with a Teflon screw cap/plunger (Ace Glass) and a spin bar. The reaction mixture was purged with nitrogen and heated at 150 °C in a preheated silicone oil bath behind a blast shield for 24 h. The mixture was cooled to room temperature, and an aliquot was removed for analysis by ^{1}H NMR spectroscopy, GC, and GC−MS. The percent conversion and yield of the reaction were determined by NMR using dimethylformamide (DMF) as an internal standard in $CDCl_3$. Integration of the reactant and product NMR peaks relative to the DMF signals was used to determine the percent conversion and yield. The addition products (**3A** and **3B**) were isolated by column chromatography (EtOAc/hexane 1:20) over silica gel eluting with ethyl acetate and hexane and identified by comparison with the spectra of known compounds.

*1,1,3-Triphenylpropane (**3A**).*[42] Colorless oil (141 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (ddd, J = 12.0, 8.3, 1.4 Hz, 2H), 7.55−7.32 (m, 3H), 7.33−6.94 (m, 10H), 3.86 (t, J = 7.7 Hz, 1H), 2.51 (dd, J = 9.3, 6.3 Hz, 2H), 2.39−2.25 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 144.9, 142.2, 128.6, 128.5, 128.4, 128.0, 126.3, 125.9, 50.8, 37.4, 34.2; GCMS [M]$^+$: 272.1.

*1,1,3-Triphenyl-prop-1-ene (**3B**).*[29] Colorless oil (84 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.10 (m, 15H), 6.28 (t, J = 7.6 Hz, 1H), 3.49 (d, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.6, 142.5, 141.1, 139.9, 130.1, 128.6, 128.5, 128.4, 128.2, 127.9, 127.4, 127.3, 127.2, 126.1, 36.1; GCMS [M]$^+$: 270.1.

Optimized General Procedure B for the Addition Reaction to Alkenes. The alcohol (2.0 mmol, 2 equiv), the alkene (1.0 mmol, 1.0 equiv), $ReIO_2(PPh_3)_2$ **I** (87 mg, 0.10 mmol, 0.1 equiv), and piperidine (0.10 mL, 85 mg, 1.0 mmol, 1.0 equiv) were mixed in dry benzene (1 mL) in a 5 mL thick-walled glass tube fitted with a Teflon screw cap/plunger (Ace Glass) and a spin bar. The reaction mixture was purged with nitrogen and heated at 150 °C in a preheated silicone oil bath. The mixture was cooled to room temperature, and an aliquot was removed for analysis by GC and GC−MS. The resulting mixture was separated by column chromatography over silica gel eluting with ethyl acetate and hexane to give the desired addition products (**3C**−**3T**).

*1,1-Diphenyl-3-[(4-methoxyphenyl)]propane (**3C**).*[42] It is obtained from 4-methoxybenzyl alcohol (**1B**) (276 mg, 2.0 mmol) and DPE (**2A**) (0.18 mL, 0.18 g, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:20) to give the product as a mixture (**3C** and **3D**). 24 h, colorless oil (220 mg, 73% yield) **3C**/**3D** (1.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.00 (m, 12H) 6.92−6.67 (m, 2H), 3.89 (t, J = 7.7 Hz, 1H), 3.77 (s, 3H), 2.50 (dd, J = 9.2, 6.2 Hz, 2H), 2.3−2.30 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.8, 144.9, 134.2, 129.4, 128.6, 128.0, 126.2, 113.8, 55.3, 50.6, 37.6, 33.2; GCMS [M]$^+$: 302.1.

*1,1-Diphenyl-3-(4-methoxyphenyl)prop-1-ene (**3D**).*[29] 24 h, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.0 (m, 14H), 6.23 (t, J = 7.6 Hz, 1H), 3.77 (s, 3H), 3.40 (d, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.0, 142.3, 142.2, 139.9, 133.1, 130.0, 129.4, 128.4, 128.2, 127.4, 127.2, 127.1, 114.0, 35.1; GCMS [M]$^+$: 300.1.

*1,1-Diphenyl-3-(4-chlorophenyl)propane (**3E**).*[42] It is obtained from 4-chlorobenzyl alcohol (**1C**) (285 mg, 2.0 mmol) and DPE (**2A**) (0.18 mL, 0.18 g, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:20) to give the separable products (**3E** and **3F**, 1.2:1.0); 48 h, colorless oil (125 mg, 41% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38−7.13 (m, 12H), 7.07 (d, J = 8.4 Hz, 2H), 3.90 (t, J = 7.7 Hz, 1H), 2.56 (dd, J = 9.2, 6.1 Hz, 2H), 2.43−2.27 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.7, 140.6, 131.6, 129.9, 128.6, 128.5, 127.9, 126.4, 50.6, 37.3, 33.5; GCMS [M]$^+$: 306.0.

*1,1-Diphenyl-3-(4-chlorophenyl)prop-1-ene (**3F**).*[29] 48 h, colorless oil (103 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.30 (m, 2H), 7.27−7.20 (m, 10H) 7.10 (d, J = 8.4 Hz, 2H), 6.20 (t, J = 7.6 Hz, 1H), 3.42 (d, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.1, 142.3, 139.7, 139.5, 131.9, 129.9, 129.8, 128.7, 128.5, 128.3, 127.5, 127.4, 127.3, 127.1, 35.4; GCMS [M]$^+$: 304.0.

*1,1-Diphenyl-3-(4-methylphenyl)propane (**3G**).*[42] It is obtained from 4-methylbenzyl alcohol (**1D**) (244 mg, 2.0 mmol) and DPE (**2A**) (0.18 mL, 0.18 g, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:19) to give the separable products (**3G** and **3H**, 1.0:1.0). 24 h, colorless oil (97 mg, 34% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43−7.10 (m, 10H), 7.05 (q, J = 8.0 Hz, 4H), 3.91 (t, J = 7.7 Hz, 1H), 2.53 (dd, J = 9.4, 6.0 Hz, 2H), 2.40−2.33 (m, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.9, 139.4, 137.8, 129.0, 128.3, 127.9, 126.1, 50.6, 37.4, 33.6, 21.0; GCMS [M]$^+$: 286.1.

*1,1-Diphenyl-3-(4-methylphenyl)prop-1-ene (**3H**).*[29] 24 h, colorless oil (97 mg, 34% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41−7.15 (m, 10H), 7.13−6.95 (m, 4H), 6.25 (t, J = 7.6 Hz, 1H), 3.43 (d, J = 7.6 Hz, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 142.5, 142.2, 139.8, 139.0, 135.5, 129.9, 129.2, 128.5, 128.3, 128.1, 127.3, 127.1, 127.0, 35.5, 21.0; GCMS [M]$^+$: 284.1.

*1,1-Diphenyl-3-(4-fluorophenyl)propane (**3I**).*[42] It is obtained from 4-fluorobenzyl alcohol (**1E**) (0.23 mL, 0.25 g, 2.0 mmol) and DPE (**2A**) (0.18 mL, 0.18 g, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:19) to give the separable products (**3I** and **3J**, 0.7:1.0). 5d, Colorless oil (74 mg, 26% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47−6.86 (m, 14H), 3.90 (t, J = 7.7 Hz, 1H), 2.55 (dd, J = 9.3, 6.1 Hz, 2H), 2.43−2.26 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 163.0, 144.8, 137.7, 129.8, 128.6, 128.0, 126.4, 115.3, 50.7, 37.6, 33.4. GCMS [M]$^+$: 290.1.

*1,1-Diphenyl-3-(3-(4-fluorophenyl)prop-1-ene (**3J**).*[29] 5d, Colorless oil (106 mg, 36% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44−7.21 (m, 10H), 7.19−7.10 (m, 2H), 7.02−6.94 (m, 2H), 6.23 (t, J = 7.6 Hz, 1H), 3.50−3.37 (d, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 142.8, 142.4, 139.8, 136.7, 136.6, 130.0, 129.9, 129.8, 128.5, 128.3, 127.6, 127.6, 127.4, 127.3, 127.3, 115.5, 115.2, 35.2; GCMS [M]$^+$: 288.1.

*1,1-Diphenyl-3-(2,4-dichlorophenyl)propane (**3K**).* It is obtained from 2,4-dichlorobenzyl alcohol (**1F**) (354 mg, 2.0 mmol) and DPE (**2A**) (0.18 mL, 0.18 g, 1.0 mmol) using the optimized general procedure B (5 d) isolated by column chromatography on silica gel with ethyl acetate and hexane (3:97) to give the separable products (**3K** and **3L**, 1.6:1.0). Colorless oil (163 mg, 48% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.21 (m, 9H), 7.21−7.08 (m, 3H), 7.03 (d, J = 8.2 Hz, 1H), 3.93 (t, J = 7.8 Hz, 1H), 2.76−2.48 (m, 2H), 2.44−2.20 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.5, 138.5, 134.7, 132.3, 131.3, 129.4, 128.7, 127.9, 127.1, 126.4, 51.2, 35.5, 32.0; GCMS [$^{35\text{-Cl, }35\text{-Cl}}$M]$^+$: 340.1, [$^{35\text{-Cl, }37\text{-Cl}}$M]$^+$: 342.1, [$^{37\text{-Cl, }37\text{-Cl}}$M]$^+$: 344.1. The compound did not ionize by ESI−MS, preventing acquisition of HRMS.

*1,1-Diphenyl-(3-(2,4-dichlorophenyl)prop-1-ene (**3L**).* Colorless oil (102 mg, 30% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47−

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6.95 (m, 13H), 6.19 (t, J = 7.5 Hz, 1H), 3.52 (d, J = 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 143.9, 142.2, 139.6, 137.3, 134.7, 132.6, 131.0, 129.9, 129.3, 128.5, 128.3, 127.5, 127.4, 127.2, 125.4, 125.3, 33.3; GCMS $[M]^+$: 338.1; HRMS (ESI-TOF) m/z: $[M - H]^-$ calcd for $C_{21}H_{15}Cl_2$, 337.0556; found, 337.0547.

*Diethyl 2-Benzylsuccinate (**3M**).*[43] It is obtained from benzyl alcohol (**1A**) (0.21 mL, 0.22 g, 2.0 mmol) and diethyl fumarate (**2B**) (0.17 mL, 0.17 g, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:10) to give the product **3M**; 24 h, colorless oil (179 mg, 68% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.38−7.07 (m, 5H), 4.11 (q, J = 7.1 Hz, 2H), 4.09 (q, J = 7.1 Hz, 2H), 3.18−2.95 (m, 2H), 2.84−2.56 (m, 2H), 2.48−2.28 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.4, 171.9, 138.3, 129.1, 128.6, 126.7, 60.8, 60.7, 43.2, 37.9, 35.3, 14.2, 14.2; GCMS $[M]^+$: 264.1.

*tert-Butyl-4-phenylbutanoate (**3N**).*[44] It is obtained from benzyl alcohol (**1A**) (0.21 mL, 0.22 g, 2.0 mmol) and *tert*-butyl acrylate (**2C**) (0.15 mL, 0.13 g, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:10) to give the product **3N**; 24 h, colorless oil (110 mg, 50% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.39−7.34 (m, 1H), 7.33−7.27 (m, 1H), 7.23−7.15 (m, 3H), 2.74−2.53 (m, 2H), 2.24 (t, J = 7.5 Hz, 2H), 2.00−1.80 (m, 2H), 1.45 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.0, 141.7, 128.6, 128.4, 126.0, 80.2, 35.2, 35.0, 28.2, 26.9; GCMS $[M]^+$: 220.1.

*Benzyl-4-phenylbutanoate (**3O**).*[45] It is obtained from benzyl alcohol (**1A**) (0.21 mL, 0.22 g, 2.0 mmol) and benzyl acrylate (**2D**) (0.16 mL, 0.16 g, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:10) to give the product (**3O**); 24 h, pale yellow oil (132 mg, 52% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42−7.21 (m, 10H), 5.12 (s, 2H), 2.65 (t, J = 7.5 Hz, 2H), 2.39 (t, J = 7.5 Hz, 2H), 1.99 (quin, J = 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.5, 141.5, 136.1, 128.7, 128.6, 128.5, 128.4, 128.3, 126.1, 66.3, 35.2, 33.7, 26.6; GCMS $[M]^+$: 254.1.

*4-Phenylbutanenitrile (**3P**).*[46] It is obtained from benzyl alcohol (**1A**) (0.21 mL, 0.22 g, 2.0 mmol) and acrylonitrile (**2E**) (60 μL, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:20) to give the product (**3P**); 48 h, pale yellow oil (29 mg, 20% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.39−7.08 (m, 5H), 2.79 (t, J = 7.4 Hz, 2H), 2.33 (t, J = 7.4 Hz, 2H), 2.01 (quin, J = 7.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 139.8, 128.8, 128.6, 126.7, 119.7, 34.5, 27.1, 16.5; GCMS $[M]^+$: 145.1.

*3-Benzyl-2H-chromen-2-one (**3Q**).*[39] It is obtained from benzyl alcohol (**1A**) (0.21 mL, 0.21 g, 2.0 mmol) and coumarin (**2F**) (146 mg, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:10) to give the product (**3Q**); 24 h, white solid (188 mg, 80% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.48−7.44 (t, J = 7.6 Hz, 1 H), 7.38−7.28 (m, 8 H), 7.24−7.20 (t, J = 7.6 Hz, 1 H), 3.90 (s, 2 H) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 161.5, 152.9, 139.2, 137.5, 130.7, 129.3, 129.2, 128.6, 127.3, 126.7, 124.2, 119.3, 116.2, 36.4; GCMS $[M]^+$: 236.1.

*3-Benzyl-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one (**3R**).* It is obtained from benzyl alcohol (**1A**) (0.21 mL, 0.22 g, 2.0 mmol) and *S*-carvone (**2G**) (0.15 mL, 0.15 g, 1.0 mmol) using the optimized general procedure B (48 h) isolated by column chromatography on silica gel with ethyl acetate and hexane (1:10) to give the product (**3R**) as a mixture of stereoisomers; pale yellow oil (148 mg, 61% yield). IR (KBr) 3084, 3062, 3026, 2970, 2933, 1710, 1645, 1602, 1494, 1452, 1377, 1217, 1029, 893, 748, 732, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.37−7.00 (m, 5H), 4.85−4.57 (m, 2H), 2.97−2.04 (m, 7H), 2.03−1.42 (m, 5H), 1.17 (dd, J = 19.5, 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 213.8, 212.9, 147.4, 146.9, 140.3, 140.0, 129.4, 129.2, 128.9, 128.5, 128.5, 126.2, 111.4, 110.0, 49.5, 48.5, 46.3, 43.8, 43.3, 42.2, 40.9, 40.8, 40.5, 40.2, 36.1, 33.3, 32.5, 30.9, 21.4, 20.8, 14.5, 12.1; GCMS $[M]^+$: 242.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{23}O$, 243.1749; found, 243.1760.

*1,3-Dibenzylpyrrolidine-2,5-dione (**3S**).*[47] It is obtained from benzyl alcohol (**1A**) (0.21 mL, 0.22 g, 2.0 mmol) and *N*-benzylpyrrolidine-2,5-dione (**2H**) (187 mg, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:10) to give the product (**3S**); 48 h, pale yellow oil (82 mg, 32% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.38−7.16 (m, 7H), 7.16−7.03 (m, 3H), 4.62 (s, 2H), 3.23−3.03 (m, 2H), 2.96−2.80 (m, 1H), 2.69 (dd, J = 18.4, 8.9 Hz, 1H), 2.51−2.34 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.1, 176.1, 136.9, 135.7, 129.1, 128.9, 128.8, 128.7, 128.0, 127.1, 42.5, 41.3, 36.4, 33.2; GCMS $[M]^+$: 279.1.

*2-Benzylbicyclo[2.2.1]heptane (**3T**).*[48] It is obtained from benzyl alcohol (**1A**) (0.21 mL, 0.22 g, 2.0 mmol) and norbornene (**2I**) (94 mg, 1.0 mmol) using the optimized general procedure B isolated by column chromatography on silica gel with ethyl acetate and hexane (1:20) to give the product (**3T**); 48 h, colorless oil (115 mg, 62% yield) (exo isomer/endo isomer 9/1, data for major isomer). ^1H NMR (300 MHz, $CDCl_3$): δ 7.38−7.02 (m, 5H), 2.55 (dd, J = 13.7, 8.3 Hz, 1H), 2.42 (dd, J = 13.6, 7.4 Hz, 1H), 2.30−2.13 (m, 1H), 2.06−1.90 (m, 1H), 1.75 (qd, J = 7.9, 4.5 Hz, 1H), 1.65−0.81 (m, 8H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 142.0, 129.1, 128.3, 125.7, 43.8, 42.9, 40.5, 38.0, 36.9, 35.2, 30.2, 29.0; GCMS $[M]^+$: 186.1.

Thermal Stability Test of 1,1,3-Triphenylpropane (3A) in the Presence of Catalyst I/Piperidine. 1,1,3-Triphenylpropane **3A** (54 mg, 0.20 mmol), $ReIO_2(PPh_3)_2$ (**I**) (17 mg, 0.020 mmol), and piperidine (20 μL, 0.20 mmol) were mixed in dry benzene (0.2 mL) in a 2 mL thick-walled glass tube fitted with a Teflon screw cap/plunger (Ace Glass) and a spin bar. The reaction mixture was purged with nitrogen and heated at 150 °C in a preheated silicone oil bath for 24 h. The mixture was cooled to room temperature, and an aliquot was removed for analysis by ^1H NMR spectroscopy, GC, and GC−MS.

Stability Test of 1,1,3-Triphenylprop-1-ene (3B) in the Presence of I/Piperidine. 1,1,3-Triphenyl-prop-1-ene **3B** (54.0 mg, 0.20 mmol), $ReIO_2(PPh_3)_2$ (**I**) (17 mg, 0.020 mmol), and piperidine (20 μL, 0.20 mmol) were mixed in dry benzene (0.2 mL) in a 2 mL thick-walled glass tube fitted with a Teflon screw cap/plunger (Ace Glass) and a spin bar. The reaction mixture was purged with nitrogen and heated at 150 °C in a preheated silicone oil bath for 24 h. The mixture was cooled to room temperature, and an aliquot was removed for analysis by ^1H NMR spectroscopy, GC, and GC−MS.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.9b03150.

Reaction procedures, reaction optimization studies, and characterization data for reaction products (^1H NMR spectra, unit resolution GC−mass spectra, HRMS, and ^{13}C NMR data for new compounds) (PDF)

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Notes

The authors declare no competing financial interest.

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