JOC Article

Unexpected Catalyst for Wittig-Type and Dehalogenation Reactions

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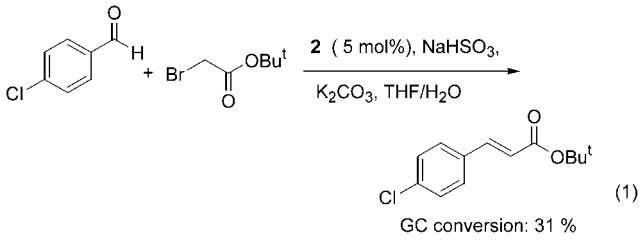
A novel catalyst **2** for Wittig-type and dehalogenation reactions was developed. In the presence of triphenyl phosphite, a wide variety of aldehydes could react with α-bromoacetates to afford α,*β*-unsaturated esters or ketones in high yields with excellent *E*-stereoselectivity when 1−2 mol % of compound **2** was used. Compound **2** was also an effective catalyst for reductive dehalogenation of α-bromocarbonyl compounds. The mechanisms for the above reactions were also proposed.

Introduction

Much attention has been paid to the development of catalytic reactions in the past decades. Although the Wittig reaction and its variants have been extensively studied and are used as one of the most important synthetic methods for construction of carbon−carbon double bonds,[1] research on the catalytic olefination processes is still in its infancy. In the literature, Huang et al. reported the first example of a catalytic Wittig-type reaction by use of 20 mol % tributylarsine or dibutyl telluride in 1989.[2] To the best of our knowledge, no more reports appeared until last year. In our continuing studies on ylides in organic synthesis,[3] we found that PEG-telluride[4] is a better catalyst for Witttig-type reactions than $^{n}Bu_2Te$ or $^{n}Bu_3As$ and the catalyst loading could be reduced to 2 mol %. To investigate the mechanism of the aforementioned reaction, the telluronium salt **1** was synthesized. Surprisingly, salt **1** decomposed quickly in the presence of water and a stable, odorless compound **2**[5,6] was obtained (Scheme 1). Thus, we assumed initially that compound **2** was an inactive species and its formation would lead to the loss of activity of dibutyl telluride in the catalytic cycle. This assumption could also explain the deactivation of the recovered PEG-telluride.[6] To verify this assumption, we tried a catalytic reaction of 4-chlorobenzaldehyde with bromoacetate using compound **2** instead of Bu_2Te. Unexpectedly, the reaction proceeded well and afforded the desired product in 31% yield (eq 1). Further studies showed that the odorless compound **2** was also an excellent catalyst for the Wittig-type reaction. In this paper, we report Wittig-type olefination and dehalogenation reactions catalyzed by compound **2**.



(1)

GC conversion: 31 %

Results and Discussion

Catalytic Wittig-Type Reaction. After the observation that compound **2** could catalyze a Wittig-type reaction, we optimized the reaction conditions to improve its catalytic efficiency. It was found that when $P(OPh)_3$ was used as the reducing reagent instead of $NaHSO_3$, the olefination reaction of *p*-chlorobenzaldehyde afforded the corresponding product in excellent yield in the presence of 1 mol % compound **2** (entry 4, Table 1).

(1) (a) Hoffmann, R. W. *Angew. Chem., Int. Ed.* **2001**, *40* (8), 1411. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (c) Nicolaou, K. C.; Härter, M. W.; Gunzner, J. L.; Nadin, A. *Liebigs Ann./Recueil* **1997**, 1283 and references therein. (d). Kolodiazhnyi, O. I. *Phosphorus Ylides: Chemistry and Application in Organic Synthesis*; Wiley-VCH: New York, 1999. (e) Forsyth, C. J.; Ahmed, F.; Cink, R. D.; Lee, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 5597. (f) Smith, A. B., III; Beauchamp, T. J.; LaMarche, M. J.; Kaufman, M. D.; Qiu, Y.; Arimoto, H.; Jones, D. R.; Kobayshi, K. *J. Am. Chem. Soc.* **2000**, *122*, 8654. (g) White, J. D.; Carter, R. G.; Sundermann, K. F.; Wartmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 5407.

(2) (a) Shi, L.; Wang, W.; Wang, Y.; Huang, Y.-Z. *J. Org. Chem.* **1989**, *54*, 2028. (b). Li, S.-W. Ph.D. Thesis, Shanghai Institute of Organic Chemistry, 1990.

(3) (a) Huang, Y.-Z.; Tang, Y.; Zhou, Z.-L.; Huang, J.-L. *J. Chem. Soc., Chem. Commun.* **1993**, 7. (b) Huang, Y.-Z.; Tang, Y.; Zhou, Z.-L.; Xia, W.; Shi, L.-P. *J. Chem. Soc., Perkin Trans. 1* **1994**, 893. (c) Tang, Y.; Huang, Y.-Z.; Dai, L.-X.; Chi, Z.-F.; Shi, L.-P. *J. Org. Chem.* **1996**, *61*, 5762. (d) Tang, Y.; Huang, Y.-Z.; Dai, L.-X.; Sun, J.; Xia, W. *J. Org. Chem.* **1997**, *62*, 954. (e) Tang, Y.; Chi, Z.-F.; Huang, Y.-Z.; Dai, L.-X.; Yu, Y.-H. *Tetrahedron* **1996**, *52*, 8747. (f) Huang, Y.-Z.; Tang, Y.; Zhou, Z.-L. *Tetrahedron* **1998**, *54*, 1667. (g) Ye, S.; Yuan, L.; Huang, Z.-Z.; Tang, Y.; Dai, L.-X. *J. Org. Chem.* **2000**, *65*, 6257. (h) Ye, S.; Tang, Y.; Dai, L.-X. *J. Org. Chem.* **2001**, *66*, 5717.

(4) Huang, Z.-Z.; Ye, S.; Xia, W.; Tang, Y. *Chem. Commun.* **2001**, 1384.

(5) (a) This compound may be toxic. (b) Zhou, Z.-L.; Shi, L.-L.; Huang, Y.-Z. *Synth. Commun.* **1991**, *21*, 1027.

(6) Huang, Z.-Z.; Ye, S.; Xia, W.; Yu, Y.-H.; Tang, Y. *J. Org. Chem.* **2002**, *67*, 3096.

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SCHEME 1

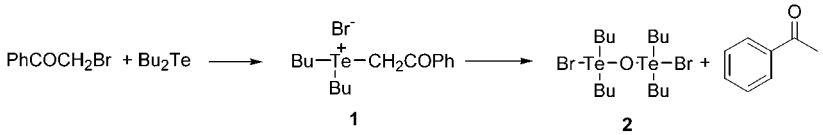
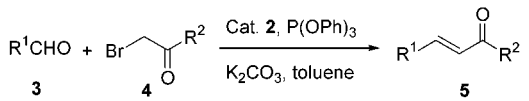
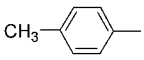
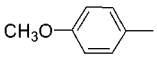
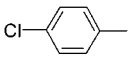
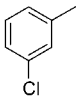
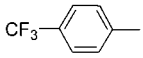
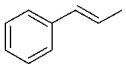
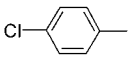
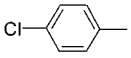
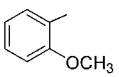
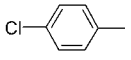


TABLE 1. Data for Wittig-Type Reactions Catalyzed by Compound 2[a]



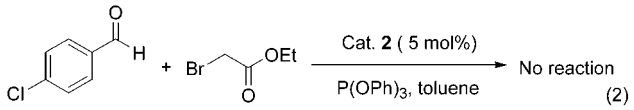
3 4 5

Entry	R^1	R^2	**2** (mol%)	Reaction time (h)	Yield[b] (%)	E / Z
1		OEt	2	36	100 (**5a**)	> 99:1
2		OEt	2	46	99 (**5b**)	> 99:1
3		OEt	2	72	94 (**5c**)	> 99:1
4		OEt	1	48	91 (**5d**)	> 99:1
5		OEt	2	45	98 (**5e**)	> 99:1
6		OEt	2	45	99 (**5f**)	> 99:1
7		OEt	2	46	97 (**5g**)	> 99:1
8		OEt	2	42	100 (**5h**)	> 99:1
9		OEt	2	46	80 (**5i**)	> 99:1
10	$CH_3(CH_2)_8$-	OEt	2	31	80 (**5j**)	> 99:1
11		OEt	2	46	98 (**5k**)	> 96:4
12		OBu^t	2	19	99 (**5l**)	> 99:1
13		Ph	2	18	95 (**5m**)	>89:11
14		OEt	2	24	97 (**5n**)	> 99:1
15[c]		OEt	0	48	0	0

[a] Reaction conditions: aldehyde (0.50 mmol); bromide (0.70 mmol); $P(OPh)_3$ (0.90 mmol); K_2CO_3 (0.65 mmol); compound **2** (0.01 mmol); toluene (2 mL). [b] Isolated yield. [c] 69% of *p*-chlorobenzaldehyde can be recovered.

To determine the generality, a variety of structurally different aldehydes and bromides were employed in this reaction (Table 1). It was found that both aliphatic and aromatic aldehydes worked well with high stereoselectivity in good to excellent yields. As shown in Table 1, various aromatic aldehydes (entries 1−7, 14), as well as a heteroaromatic aldehyde (entry 8, Table 1), gave excellent yields with nearly exclusive *E*-stereoselectivity, which was comparable to typical Wittig reactions of stablized ylides. Aliphatic aldehydes, such as cyclo-

hexanecarboxaldehyde and decyl aldehyde (entries 9, 10) also participated in this reaction to give the corresponding olefins in good yields. *trans*-Cinnamic aldehyde (entry 11) could be highly stereoselectively converted to the corresponding diene ester in high yield. Other bromides, such as *tert*-butyl bromoacetate and *ω*-bromoacetophenone (entries 12, 13), were also investigated in this reaction condition. Both of them reacted readily with *p*-chlorobenzaldehyde to afford the corresponding products in excellent yields. A controlled experiment showed that no Wittig-type olefination product was formed in the absence of catalyst **2** (entry 15). It is worth noting that base was necessary for this reaction. In the absence of K_2CO_3, aldehyde was recovered quantitatively (eq 2).



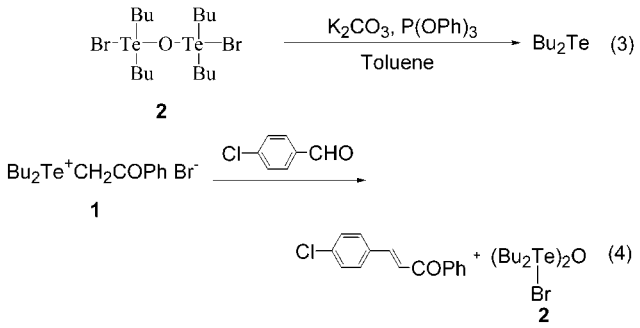
Mechanism. To understand the catalytic process in detail, we first examined the reaction in the absence of aldehyde and bromide. It was found that compound **2** could be converted readily into Bu_2Te when a mixture of compound **2** (0.1 mmol), $P(OPh)_3$ (0.2 mmol), and K_2CO_3 (0.5 mmol) in toluene was heated in an 80 °C oil bath (Scheme 2, eq 3). Additionally, we found that telluronium salt **1** could react directly with aldehyde to afford the α,*β*-unsaturated ketone, as described by Huang et al.[7] In this reaction, compound **2** was also isolated (Scheme 2, eq 4).

According to the above observations, together with the mechanism suggested by Huang,[2] two mechanisms shown in Scheme 3 are probably operative in this reaction. In mechanism I, compound **2** was first reduced to dibutyl telluride (**8**), which reacted with bromide to form telluronium salt **1**. Salt **1** reacted directly with aldehyde to afford the desired olefin **5** and recycled compound **2** to complete the catalytic cycle. Another path maybe proceed via an ylide route. Reaction of dibutyl telluride with bromoacetate yielded salt **1**. Salt **1**, followed by deprotonation, reacted with aldehyde to afford compound **5** and tellurium oxide **7**. Compound **7** was readily reduced by $P(OPh)_3$ to regenerate dibutyl telluride (Scheme 3).

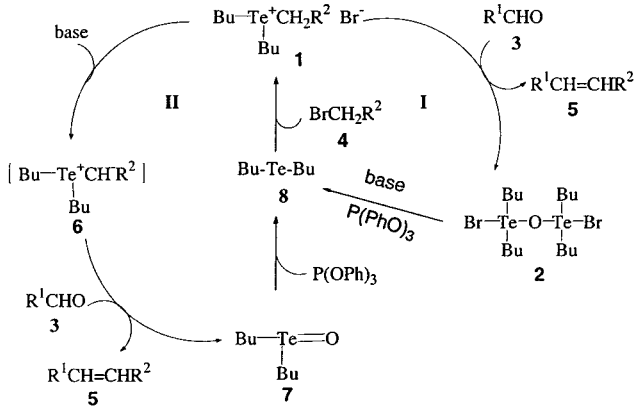
Catalytic Dehalogenation. During our preparation of compound **2** by hydrolysis of telluronium salt **1**, acetophenone was detected (Scheme 1). On the basis of this finding, together with the above-described catalytic process, we designed the catalytic cycle in Scheme 4 and found that the dehalogenation reaction catalyzed by compound **2** worked well.[8]

In the presence of 1 mol % compound **2**, when $NaHSO_3$ was used as the reducing agent, the dehalogenation

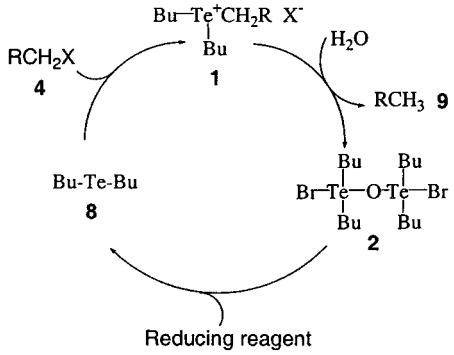
SCHEME 2



SCHEME 3



SCHEME 4



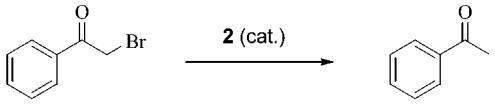
reaction was base-dependent (entries 1−5, Table 2). And $NaHCO_3$ was the most appropriate one. Although THF, acetone, CH_3CN, and H_2O could be used as the reaction solvents (entries 8−13), the best one was a mixture of DMF and water. Without compound **2**, the dehalogenation reaction was exceedingly slow (entry 22, Table 2). After optimization of the reaction conditions (entries 6−7, 14−21), the most efficient one was the use of $P(OPh)_3$ as the reducing agent, a mixture of DMF and H_2O (6/0.5, v/v) as the solvent, and 1 mol % of compound **2** as the catalyst.

As shown in Table 3, this catalytic system was proved to be highly efficient for dehalogenation of α-bromocarbonyl compounds. A variety of 2-bromo-substituted phenylethanones were readily reduced in high to excellent yields (entries 1−5, 11, Table 3). It is worth noting that not only α-bromo ketones but also α-chloro ketones worked well (entry 10, Table 3). *gem*-α-Dibromides and di-*tert*-butyl 2-bromomalonate also provided the desired

(7) Huang, X.; Xie, L.; Wu, H. *Tetrahedron Lett.* **1987**, *28*, 801.

(8) For selected references for reductive dehalogenation of α-bromocarbonyl compounds, see: (a) Barrero, A. F.; Alvarez-Manzaneda, E. J.; Chahboun, R.; Meneses, R.; Romera, J. L. *Synlett* **2001**, 485. (b) Park, L.; Keum, G.; Kang, S. B.; Kim, K. S.; Kim, Y. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4462. (c) Ranu, B. C.; Dutta, P.; Sarkar, A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1139. (d) Han, Y.; Huang, Y.-Z. *Tetrahedron Lett.* **1998**, 7751. (e) Zhang, J.; Saito, S.; Takahashi, T.; Koizumi, T. *Heterocycles* **1997**, *45*, 575. (f) Schultz, E. K. V.; Harpp, D. N. *Synthesis* **1998**, 1137. (g) Chatgilialoglu, C.; Guerra, M.; Guerrini, A.; Seconi, G.; Clark, K. B.; Griller, D.; Kanabus-Kaminska, J.; Martinho-Simões, J. A. *J. Org. Chem.* **1992**, *57*, 2427.

TABLE 2. Effects of Reaction Conditions on Dehalogenation



entry	reducing agent	catal (mol %)	solvent (v/v)	temp (°C)	base	yield[a] (%)
1	$NaHSO_3$	1	THF/H_2O (2/0.04)	80	K_2CO_3	22
2	$NaHSO_3$	1	THF/H_2O (2/0.04)	80	$KHCO_3$	23
3	$NaHSO_3$	1	THF/H_2O (2/0.04)	80	Na_2CO_3	11
4	$NaHSO_3$	1	THF/H_2O (2/0.04)	80	$NaHCO_3$	44
5	$NaHSO_3$	1	THF/H_2O (2/0.04)	80	$LiOH·H_2O$	5
6	$NaHSO_3$	1	THF/H_2O (2/0.04)	50	$NaHCO_3$	10
7	$NaHSO_3$	1	THF/H_2O (2/0.04)	23	$NaHCO_3$	4
8	$NaHSO_3$	1	CH_3CN/H_2O (2/0.04)	80	$NaHCO_3$	15
9	$NaHSO_3$	1	DMF/H_2O (2/0.04)	80	$NaHCO_3$	36
10	$NaHSO_3$	1	acetone/H_2O (2/0.04)	80	$NaHCO_3$	14
11	$NaHSO_3$	1	acetone/H_2O (2/0.04)	80	$NaHCO_3$	15
12	$NaHSO_3$	1	DMF/H_2O (1/1)	80	$NaHCO_3$	55
13	$NaHSO_3$	1	H_2O	80	$NaHCO_3$	29
14	$P(OPh)_3$	1	DMF/H_2O (1/1)	80	$NaHCO_3$	77
15	$P(OPh)_3$	1	H_2O/DMF (2/2)	80	$NaHCO_3$	82
16	$P(OPh)_3$	1	H_2O/DMF(4/4)	80	$NaHCO_3$	88
17	$P(OPh)_3$	1	H_2O/DMF (6/6)	80	$NaHCO_3$	99
18	$P(OPh)_3$	1	H_2O/DMF (6/0.5)	80	$NaHCO_3$	99
19	$P(OPh)_3$	1	H_2O	80	$NaHCO_3$	75
20	$P(OPh)_3$	0.5	H_2O/DMF (6/0.5)	80	$NaHCO_3$	58
21	$P(OPh)_3$	0.1	H_2O/DMF (6/0.5)	80	$NaHCO_3$	13
22	$P(OPh)_3$	0	H_2O/DMF (6/0.5)	80	$NaHCO_3$	<5

[a] GC yield.

products in high yields (entries 7−9, 12, Table 1). However, 2-bromocamphor failed (entry 6), most probable owing to the steric hindrance that retarded the formation of telluronium salt.

Conclusion

A novel catalyst for Wittig-type and dehalogenation reactions was developed. Compared to the other catalysts previously reported, this catalyst showed its advantages in its stability, lack of odor, and high catalytic efficiency. The catalytic Wittig-type reaction shown here had a wide scope of suitable substrates. Most of them gave the corresponding Wittig-type products in excellent yields and high *E*-stereoselectivity. The catalytic dehalogenation reaction presents a mild reducing process with high catalytic efficiency. This method represents a method for the selective cleavage of C−X bond in the presence of other functional groups.

Experimental Section

All reaction flasks and equipment for catalytic Wittig type reactions were dried for several hours prior to use, and all reactions were carried out under nitrogen. Aldehydes, bromides, and $P(OPh)_3$, as well as the solvents, were purified according to the standard method before use.

Preparation of Compound 2. A mixture of *n*-butyl telluride (454.8 mg, 1.88 mmol) and *ω*-bromoacetophenone (431.0 mg, 2.16 mmol) was stirred at room temperature for 5 h. The resulting white solid was collected and washed with ether to afford the white powder **1**.[7,14] Yield: 823.0 mg (99%). Mp: 93 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.21 (d, J = 7.2 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 4.48 (s, 2H), 3.22−3.07 (m, 4H), 1.89−1.79 (m, 4H), 1.47−1.35 (m, 4H), 0.92 (t, J = 7.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 194.9, 135.1, 134.1, 128.9, 128.7, 34.2, 27.7, 27.6, 24.4, 13.1 ppm. ^{125}Te NMR ($CDCl_3$/Me_2Te): δ 551.191. MS (ESI): *m*/*z* 363.1 [$(Bu_2)Te^+CH_2(CO)Ph$ (^{130}Te)], 361.1 [$(Bu_2)Te^+CH_2$-(CO)Ph (^{128}Te)], 359.1 [$(Bu_2)Te^+CH_2(CO)Ph$ (^{126}Te)]. IR (KBr): ν = 2962, 1662, 742, 690, 588 cm^{-1}. Anal. Calcd for $C_{16}H_{25}$-BrOTe: C, 43.59; H, 5.72; Br, 18.12. Found: C, 43.38; H, 5.57; Br, 17.50.

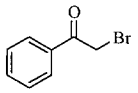
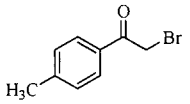
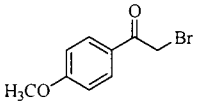
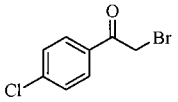
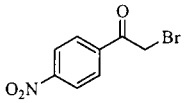
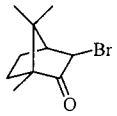
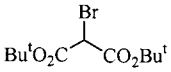
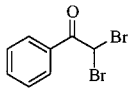
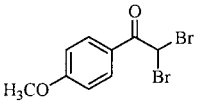
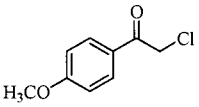
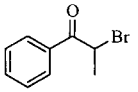
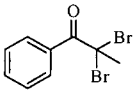
A mixture of compound **1** (0.2433 g, 1.0 mmol) and water (0.02 mL) in CH_2Cl_2/ THF (0.5 mL/0.5 mL) was stirred at room temperature overnight. The yield of acetophenone was determined by GC (mesitylene as internal standard). Yield: 100%. The reaction mixture was filtered, and the filtrate was concentrated. The residue was washed with ether to give the compound **2**[5,6] as white crystals. Yield: 307.8 mg (94%). Mp: 136−138 °C. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.48 (br, 4H), 3.10 (br, 4H), 2.10−1.92 (m, 8H), 1.58−1.47 (m, 8H), 1.00 (t, J = 7.3 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 43.3, 27.2, 24.5, 13.6 ppm. MS (ESI): *m*/*z* 261.1 [$(Bu_2)Te^+(OH)$ (^{130}Te)], 259.1 [$(Bu_2)Te^+(OH)$ (^{128}Te)], 257.1 [$(Bu_2)Te^+(OH)$ (^{126}Te)]. IR (KBr): ν = 2961, 1464, 632, 439 cm^{-1}. Anal. Calcd for $C_{16}H_{36}$-Br_2OTe_2: C, 29.14; H, 5.50; Br, 24.23. Found: C, 29.21; H, 5.75; Br, 24.27.

(A) Typical Procedure for Catalytic Wittig-Type Reactions. A mixture of catalyst **2** (6.6 mg, 0.01 mmol), bromide (0.30 mmol), and $P(OPh)_3$ (0.23 mL, 0.88 mmol) in toluene (1.5 mL) was stirred at 80 °C for 5 min, and then K_2CO_3 (89.8 mg, 0.65 mmol) was added. The resulting suspension was stirred for 1 min, followed by addition of a mixture of aldehyde (0.5 mmol) and bromide (0.40 mmol) in toluene (0.5 mL) in portions within 3.5 h. After the reaction was completed (monitored by

(9) Ogata, M.; Matsumoto, H.; Kida, S.; Shimizu, S.; Tawara, K.; Kawamura, Y. *J. Med. Chem.* **1987**, *30*, 1497.
(10) Uemura, S.; Fukuzawa, S. *J. Chem. Soc., Perkin, Trans. 1* **1986**, 1983.
(11) (a). Hollowood, J.; Jansen, A. B. A.; Southgate, P. J. *J. Med. Chem.* **1967**, *10*, 863. (b). Rich, D. H.; Dhaon, M. K. *Tetrahedron. Lett.* **1983**, 1671.
(12) Aston, J. G.; Newkirk, J. D.; Dorsky, J.; Jenkins, D. M. *J. Am. Chem. Soc.* **1942**, *64*, 1413.
(13) Philip, K.; Bosco, D.; John, V. *Tetrahedron* **2001**, *57*, 8047.
(14) Huang, X.; Xie, L.; Wu, H. *J. Org. Chem.* **1988**, *53*, 4862.

TABLE 3. Dehalogenation Reactions Catalyzed by Compound 2

RX (4) —2 (cat.), $P(OPh)_3$, $NaHCO_3$→ RH (9)

Entry	RX	Cat. (mol%)	Solvent (v/v)	Reaction Time (h)	Yield[a] (%)
1		1	H_2O/DMF: 6 / 0.5	1	(99)
2		1	H_2O/DMF: 6 / 0.5	1	83
3		1	H_2O/DMF: 6 / 0.5	1.5	86
4		1	H_2O/DMF: 6 / 0.5	1	70
5		2	H_2O/THF: 6 / 1	1	61
6		5	H_2O/DMF: 6 / 0.5	5	0[b]
7		5	H_2O/DMF: 6 / 0.5	5	81
8		1	H_2O/DMF: 6 / 0.5	1	(90)
9		1	H_2O/DMF: 6 / 0.5	1.5	90
10		2	H_2O/DMF: 6 / 1	3	89
11		1	H_2O/DMF: 6 / 0.5	3	88
12		5	H_2O/DMF: 6 / 0.5	6	86

[a] Isolated yield. GC yields are given in parentheses. [b] The bromide can be recovered quantitatively.

TLC), the mixture was filtered rapidly through a glass funnel with a thin layer of silica gel (ethyl acetate as the elution). The filtrate was concentrated, and the residue was purified by flash column chromatography to afford the desired product.

Ethyl (*E*)-3-phenylprop-2-enoate[2a] (R_1 = C_6H_5, R_2 = OEt, 5a): yield 88.9 mg (100%); *E*/*Z* > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.70 (d, J = 15.9 Hz, 1H), 7.55−7.52 (m, 2H), 7.40−7.38 (m, 3H), 6.45 (d, J = 15.9 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).

Ethyl (*E*)-3-(4-methylphenyl)prop-2-enoate[2a] (R_1 = *p*-$CH_3C_6H_4$, R_2 = OEt, 5b): yield 94.0 mg (99%); *E*/*Z* > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.59 (d, J = 15.9 Hz, 1H),

7.41 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.32 (d, J = 15.9 Hz, 1H), 3.50 (q, J = 7.0 Hz, 2H), 2.37 (s, 3H), 1.33 (t, J = 7.0 Hz, 3H).

Ethyl (*E*)-3-(4-methoxyphenyl)prop-2-enoate[4] (R_1 = *p*-$CH_3OC_6H_4$, R_2 = OEt, 5c): yield 97.6 mg (94%); E/Z > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.64 (d, J = 16.0 Hz, 1H), 7.47 (d, J = 6.8 Hz, 2H), 6.90 (d, J = 6.8 Hz, 2H), 6.31 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H).

Ethyl (*E*)-3-(4-Chlorophenyl)prop-2-enoate[2a] (R_1 = *p*-ClC_6H_4, R_2 = OEt, 5d). A 1 mol % amount of the catalyst was used. Yield: 95.9 mg (91%). E/Z > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.64 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 6.7 Hz, 2H) 7.36 (dd, J = 6.7 Hz, 2H), 6.41 (d, J = 16.1 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H).

Ethyl (*E*)-3-(3-chlorophenyl)prop-2-enoate[13] (R_1 = *m*-ClC_6H_4, R_2 = OEt, 5e): yield 104.1 mg (99%); E/Z > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.61 (d, J = 16.5 Hz, 1H), 7.51 (s, 1H), 7.40−7.06 (m, 3H), 6.43 (d, J = 15.9 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.3 Hz, 3H).

Ethyl (*E*)-3-(2-chlorophenyl)prop-2-enoate[2a] (R_1 = *o*-ClC_6H_4, R_2 = OEt, 5f): yield 103.0 mg (98%); E/Z > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 8.09 (d, J = 15.9 Hz, 1H), 7.63−7.60 (m, 1H), 7.43−7.31 (m, 1H), 7.31−7.26(m, 2H), 6.43 (d, J = 15.9 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H).

Ethyl (*E*)-3-(4-trifluoromethylphenyl)prop-2-enoate[4] (R_1 = *p*-$CF_3C_6H_4$, R_2 = OEt, 5g): yield 118.5 mg (97%); E/Z > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.70 (d, J = 16.1 Hz, 1H), 7.64 (s, 4H), 6.51 (d, J = 16.1 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).

Ethyl (*E*)-3-(2-furyl)prop-2-enoate[2a] (R_1 = furyl, R_2 = OEt, 5h): yield 82.9 mg (100%); E/Z > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.48 (d, J = 1.4 Hz, 1H), 7.43 (d, J = 15.7 Hz, 1H), 6.60 (d, J = 3.3 Hz, 1H), 6.47 (dd, J = 1.7, 3.3 Hz, 1H), 6.32 (d, J = 15.7 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H).

Ethyl (*E*)-3-cyclohexylprop-2-enoate[2a] (R_1 = C_6H_{11}, R_2 = OEt, 5i): reaction scale 1.0 mmol; yield 146.6 mg (80%); E/Z > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.92 (dd, J = 6.9, 15.8 Hz, 1H), 5.77 (dd, J = 15.8, 1.0 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.20−2.15 (m, 1H), 1.78−1.64 (m, 4H), 1.36−1.12 (m, 9H).

Ethyl (*E*)-dodec-2-enoate[4] (R_1 = $CH_3(CH_2)_8$, R_2 = OEt, 5j): reaction scale 1.0 mmol; yield 182.6 mg (80%); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 6.97 (dt, J = 15.7, 6.9 Hz, 1H), 5.81 (dt, J = 15.7, 1.4 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.23−2.15 (m, 2H), 1.47−1.27 (m, 17H), 0.88 (t, J = 6.7 Hz, 3H).

Ethyl (*E,E*)-5-phenylpent-2, 4-dienoate[2a] (R_1 = C_6H_5CH=CH, R_2 = OEt, 5k): yield 100.1 mg (98%); E/Z > 96:4; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) for trans isomer δ 7.49−7.38 (m, 3H), 7.38−7.30 (m, 3H), 6.90−6.87 (m, 2H), 5.99 (d, J = 15.2 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) for cis isomer δ 8.21−8.11(m, 1H), 7.54−7.46 (m, 2H), 7.38−7.26 (m, 3H), 6.90−6.71 (m, 2H), 5.73 (d, J = 11.6 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.3 Hz, 3H).

***tert*-Butyl (*E*)-3-(4-chlorophenyl)prop-2-enoate[4] (R_1 = *p*-ClC_6H_4, R_2 = OBu^t, 5l)**: yield 237.5 mg (93%); E/Z > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.53 (d, J = 15.9 Hz, 1H), 7.44 (d, J = 7.0 Hz, 2H), 7.34 (d, J = 7.0 Hz, 2H), 6.34 (d, J = 15.8 Hz, 1H), 1.53 (s, 9H).

(*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-enone[2a] (R_1= *p*-ClC_6H_4, R_2 = Ph, 5m): yield: 116.2 mg (95%); E/Z > 89:11; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) for trans isomer δ 8.02 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 15.7 Hz, 1H), 7.59−7.48 (m, 6H), 7.39 (d, J = 8.4 Hz, 2H); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) for cis isomer δ 7.98−7.94 (m, 2H), 7.55−7.52 (m, 2H), 7.45−7.36 (m, 3H); 7.26−7.21 (m, 2H); 6.95 (d, J = 12.8 Hz, 1H), 6.68 (d, J = 12.9 Hz, 1H).

Ethyl (*E*)-3-(2-methoxyphenyl)prop-2-enoate[13] (R_1 = *o*-$CH_3OC_6H_4$, R_2 = OEt, 5n): yield 199.2 mg (97%); E/Z > 99:1; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.99 (d, J = 15.9 Hz, 1H), 7.51 (dd, J = 8.0, 1.7 Hz, 1H), 7.35 (td, J = 7.8, 1.8 Hz, 1H), 6.99−6.90 (m, 2H), 6.52 (d, J = 16.2 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H).

(B) Typical Procedure for Dehalogenation Reactions. To a mixture of catalyst **2** (6.6 mg, 0.01 mol) and bromide (1.0 mmol) in DMF/H_2O (0.5 mL/6.0 mL) was added $P(OPh)_3$ (0.36 mL, 1.4 mmol). The mixture was stirred at 80 °C for 5 min, and then $NaHCO_3$ (0.1680 g, 2.0 mmol) was added. The resulting suspension was stirred for 1 h. After the reaction was completed it was analyzed with GC (mesitylene as the internal standard) or the mixture was filtered rapidly through a glass funnel with a thin layer of silica gel (ethyl acetate for elution). The filtrate was concentrated, and the residue was purified by flash column chromatography to afford the desired product.

Dehalogenation of 2-bromo-1-phenylethanone: GC yield 99%.

Dehalogenation of 2-Bromo-1-(4-methylphenyl)ethanone. The 2-bromo-1-(4-methylphenyl)ethanone substrate was synthesized (94% yield) according to the literature.[9] ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.88 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.43 (s, 2H), 2.42 (s, 3H).

Dehalogenation: yield 111.0 mg (83%). ^{1}H NMR for 4-methylphenylethanone (300 MHz, $CDCl_3$/TMS): δ 7.86 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H).

Dehalogenation of 2-Bromo-1-(4-methoxyphenyl)ethanone. The 2-bromo-1-(4-methoxyphenyl)ethanone substrate was synthesized (80% yield) according to the literature.[9] ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.98 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 4.41 (s, 2H), 3.89 (s, 3H).

Dehalogenation: yield 129.4 mg (86%). ^{1}H NMR for 4-methoxyphenylethanone (300 MHz, $CDCl_3$/TMS): δ 7.95 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 7.8 Hz, 2H), 3.88 (s, 3H), 2.56 (s, 3H).

Dehalogenation of 2-Bromo-1-(4-chlorophenyl)ethanone. The solvent used was H_2O/DMF = 6 mL/1 mL. Yield of dehalogenation: 107.5 mg (70%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) for 4-chlorophenylethanone: δ 7.91 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 2.60 (s, 3H).

Dehalogenation of 2-Bromo-1-(4-nitrophenyl)ethanone. A 2 mol % amount of the catalyst was used. The solvent used was H_2O/THF = 6 mL/1 mL. Yield: 101.0 mg (61%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) for 4-nitrophenylethanone: δ 8.33 (d, J = 9.0 Hz, 2H), 8.12 (d, J = 9.0 Hz, 2H), 2.69 (s, 3H).

Dehalogenation of Di-*tert*-butyl 2-Bromomalonate. The di-*tert*-butyl 2-bromomalonate substrate was synthesized (40% yield) according to the literature.[11] ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 4.67 (s, 1H), 1.50 (s, 18H).

Dehalogenation. A 5 mol % amount of the catalyst was used. Yield: 175.0 mg (81%). ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.19 (s, 2H), 1.48 (s, 18H).

Dehalogenation of 2,2-Dibromophenylethanone. The 2,2-dibromophenylethanone substrate was synthesized (43% yield) according to the literature as a byproduct.[12] ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.10−8.07 (m, 2H), 7.65−7.62 (m, 1H), 7.55−7.52 (m, 2H), 6.72 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 185.8, 134.3, 130.6, 129.5, 128.8, 39.7 ppm. IR (film): ν = 1694.36, 1592.45, 800.91 cm^{-1}. MS (EI) [*m*/*z* (rel intensity)]: 280 (0.23), 278 (0.47), 276 (0.24), 105 (100).

Dehalogenation: GC yield 90%.

Dehalogenation of 2,2-Dibromo-1-(4-methoxyphenyl)-ethanone. The 2,2-dibromo-1-(4-methoxyphenyl)ethanone substrate was synthesized (13% yield) according to the literature as a byproduct.[9] ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.09 (d, J = 9.3 Hz, 2H), 6.98 (d, J = 9.3 Hz, 2H), 6.67 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 184.6, 164.5, 132.1, 123.2, 114.2, 55.7, 40.1 ppm. IR (film): ν = 1677.74, 1600.78, 845.56, 809.69 cm^{-1}. MS (EI) [*m*/*z* (rel intensity)]: 310 (1.86), 308 (3.63), 306 (1.97) 135 (100).

Dehalogenation: yield 134.5 mg (90%).

Dehalogenation of 2-Chloro-1-(4-methoxyphenyl)ethanone. This reaction was carried out in H_2O/DMF = 6 mL/1 mL for 5 h by using 5 mol % catalyst. Yield: 133.7 mg (89%).

Dehalogenation of 2-Bromo-1-phenylpropanone. The 2-bromo-1-phenylpropanone substrate was synthesized (1.5 equiv of bromine, glacial acetic acid, 55% yield) according to the literature.[10] ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.04 (d, J = 6.9 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.52−7.47 (m, 2H), 5.31 (q, J = 6.7 Hz, 1H), 1.91 (t, J = 6.6 Hz, 3H).

Dehalogenation: yield 115.6 mg (86%); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.99−7.96 (m, 2H), 7.59−7.54 (m, 1H), 7.50−7.44 (m, 2H), 3.02 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H).

Dehalogenation of 2,2-Dibromo-1-phenylpropanone. The 2,2-dibromo-1-phenylpropanone substrate was synthesized (1.5 equiv of bromine, glacial acetic acid, 40% yield) according to the literature.[10] ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.41 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.50−7.45 (m, 2H), 2.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 188.1, 133.4, 131.5, 131.2, 127.8, 57.8, 37.6 ppm. IR (film): ν = 1679.79, 1593.76, 804.79 cm^{-1}. MS (EI) [m/z (rel intensity)]: 294 (0.36), 292 (0.69), 290 (0.37), 105 (100).

Dehalogenation: yield 115.6 mg (86%). A 5 mol % amount of the catalyst was used.

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