JOC Article

Et_2Zn-Mediated Rearrangement of Bromohydrins

Lezhen Li,[‡] Peijie Cai,[‡] Qingxiang Guo,[‡] and Song Xue*,[†]

Department of Applied Chemistry, Tianjin University of Technology, Tianjin, 300191, China, and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China

xuesong@ustc.edu.cn

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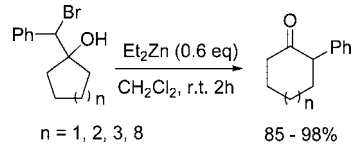
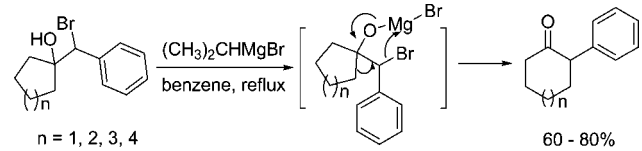


A simple and highly efficient method for the rearrangement of bromohydrins mediated by Et_2Zn to synthesize carbonyl compounds was described. Various β-bromo alcohols were treated with 0.6 equiv of Et_2Zn to form a zinc complex in CH_2Cl_2 at room temperature for 2 h, followed by 1,2-migration to give the corresponding carbonyl compounds. This remarkable and clean rearrangement is general for acyclic and cyclic bromohydrins, and a variety of ring-expansive and -contractive carbonyl compounds were obtained in good to excellent yields according to the feature of the starting bromohydrins. The functional group tolerance of organozinc reagents in this reaction will be useful in organic synthesis. The scope and limitations of this rearrangement process were also investigated.

Introduction

The rearrangement reactions play an important role in modern organic synthesis. Among those rearrangements, ring-expansive reactions[1] to obtain medium and large rings have been the focus of much research for several decades and continue to be an active and rewarding research area. Halohydrins, especially bromohydrins, are one of the most useful and versatile substrates in organic synthesis due to their high reactivity[2] and easy availability through a variety of methods.[3] The frequently used reactions of bromohydrins are their rearrangement to corresponding carbonyl compounds.[4,5] Previously, Sisti et al.[6] reported an efficient ring-expansive procedure entailing the decomposition of the magnesium salts of appropriate bromo-

SCHEME 1



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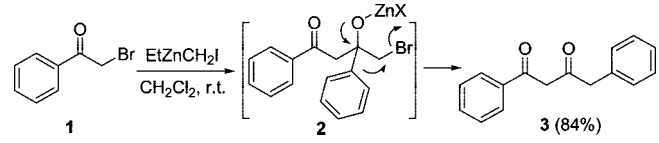

† Tianjin University of Technology.
‡ University of Science and Technology of China.

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(4) (a) Tsuji, J.; Nagashima, H.; Sato, K. *Tetrahedron Lett.* **1982**, *23*, 3085. (b) Piva, O. *Tetrahedron Lett.* **1992**, *33*, 2459. (c) Dolenc, D.; Harej, M. *J. Org. Chem.* **2002**, *67*, 312. (d) Cho, S.; Kang, S.; Keum, G.; Kang, S. B.; Han, S. Y.; Kim, Y. *J. Org. Chem.* **2003**, *68*, 180. (e) Sisti, A. J.; Vitale, A. C. *J. Org. Chem.* **1972**, *37*, 4090.

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(6) (a) Sisti, A. J. *J. Org. Chem.* **1968**, *33*, 453. (b) Sisti, A. J. *Tetrahedron Lett.* **1967**, *52*, 5327. (c) Sisti, A. J. *J. Org. Chem.* **1968**, *33*, 3953. (d) Sisti, A. J.; Rusch, G. M. *J. Org. Chem.* **1974**, *39*, 1182. (e) Sisti, A. J.; Meyers, M. *J. Org. Chem.* **1973**, *38*, 4431. (f) Sisti, A. J. *J. Org. Chem.* **1970**, *35*, 2670.

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TABLE 1. Et_2Zn-Mediated Rearrangement of Acyclic Tertiary Bromohydrins

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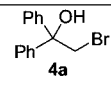
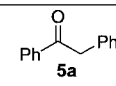
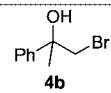
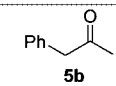
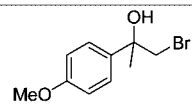
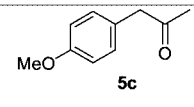
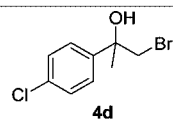
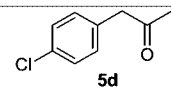
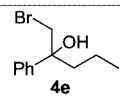
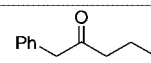
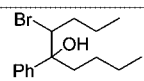
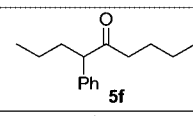
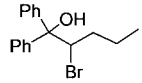
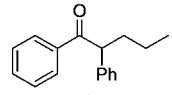
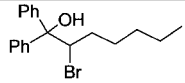
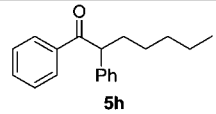
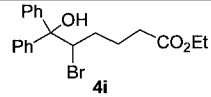
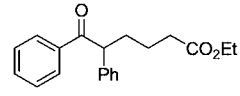
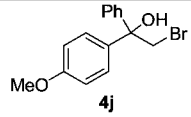
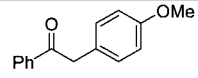
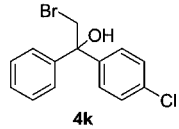
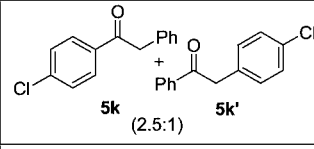
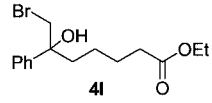
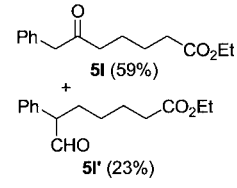
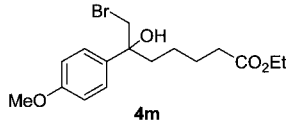
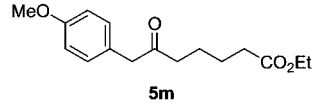
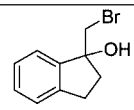
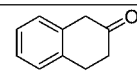
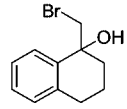
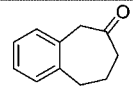
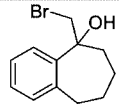
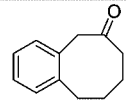
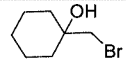
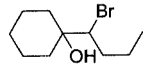
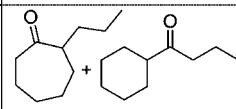
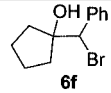
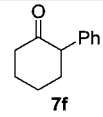
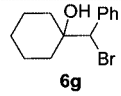
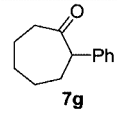
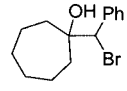
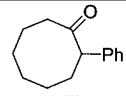
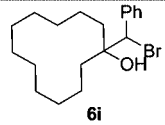
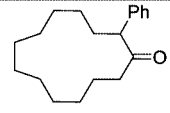
1	 **4a**	 **5a**	98 (96)[b]
2	 **4b**	 **5b**	93
3	 **4c**	 **5c**	95
4	 **4d**	 **5d**	86
5	 **4e**	 **5e**	94
6	 **4f**	 **5f**	96
7	 **4g**	 **5g**	96
8	 **4h**	 **5h**	95
9	 **4i**	 **5i**	93
10	 **4j**	 **5j**	96
11	 **4k**	 **5k** (2.5:1) **5k'**	93[c]
12	 **4l**	 **5l** (59%) + **5l'** (23%)	82
13	 **4m**	 **5m**	92

[a] Isolated yield after flash chromatography. [b] 3.0 equiv of Furukawa reagent ($EtZnCH_2I$) was used. [c] Ratio of the two compounds was determined by ^1H NMR spectra.

hydrins in benzene under reflux conditions. Reactions of 1-(α-bromobenzyl)-1-cycloalkanols with isopropyl magnesium bro-

TABLE 2. Et_2Zn-Mediated Rearrangement of Cyclic Tertiary β-Bromo Alcohols to Form Ring-Expansive Carbonyl Compounds

Entry	Substrate	Product	Yield (%)[a]
1	 **6a**	 **7a**	95[b]
2	 **6b**	 **7b**	99
3	 **6c**	 **7c**	97
4	 **6d**	NR[c]	-
5	 **6e**	 **7e** **7e'** (4.7:1)	92[d]
6	 **6f**	 **7f**	85
7	 **6g**	 **7g**	98
8	 **6h**	 **7h**	95
9	 **6i**	 **7i**	98

[a] Isolated yield after flash chromatography. [b] 0.6 equiv of Furukawa reagent ($EtZnCH_2I$) was used. [c] NR = no reaction. [d] Ratio of the two isomers was determined by GC-MS analysis.

mide gave rise to the corresponding ring-expansive α-phenyl ketones in good yields (Scheme 1).[6a]

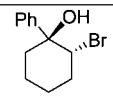
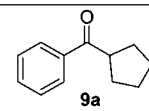
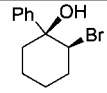
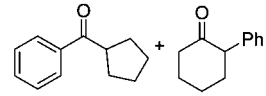
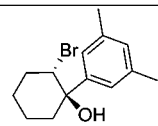
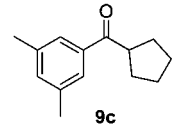
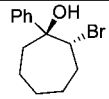
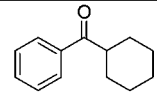
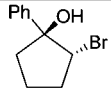
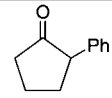
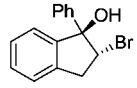
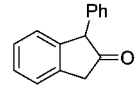
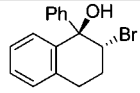
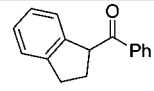
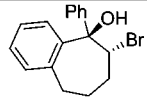
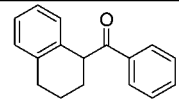
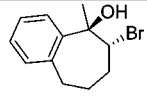
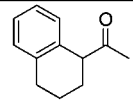
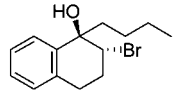
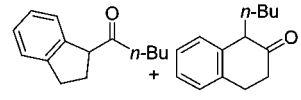
Recently, our group reported an efficient procedure to synthesize β-diketones from α-bromoketones using the Furukawa reagent under mild conditions.[7] The key intermediate **2** was the zinc complex of bromohydrin, which was derived from the self-condensation of α-bromoketone in the presence of $EtZnCH_2I$. Similar to the decomposition of the magnesium salts of bromohydrins, the zinc complex **2** proceeded through 1,2-migration to give the desired β-diketone (Scheme 2). Inspired by this work, we hypothesized that the reaction of bromohydrins with organozinc reagents would easily form the zinc complex of bromohydrins and generate the corresponding carbonyl compounds. In view of a broader functional group

(7) Li, L. Z.; Cai, P. J.; Xu, D.; Guo, Q. X.; Xue, S. *J. Org. Chem.* **2007**, *72*, 8131.

(8) Matsubara had reported a stereoselective pinacol-type rearrangement of 2,3-epoxy alcohols promoted by bis(iodozincio)methane: Matsubara, S.; Yamamoto, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 2837.

(9) Curtin, D. Y.; Schmuckler, S. *J. Am. Chem. Soc.* **1955**, *77*, 1105.

TABLE 3. Et_2Zn-Promoted Rearrangement of Cyclic Tertiary β-Bromo Alcohols to Form Ring-Contractive Carbonyl Compounds

Entry	Substrate	Product	Yield (%)[a]
1	 **8a**	 **9a**	98
2	 **8b**	 **9a** (8%) **7f** (84%)	92
3	 **8c**	 **9c**	99
4	 **8d**	 **9d**	99
5	 **8e**	 **9e**	85
6	 **8f**	 **9f**	87[b]
7	 **8g**	 **9g**	99
8	 **8h**	 **9h**	95
9	 **8i**	 **9i**	86
10	 **8j**	 **9j** (39%) **9j'** (55%)	94

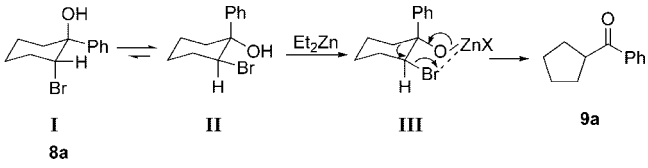
[a] Isolated yield after flash chromatography. [b] 0.6 equiv of Furukawa reagent ($EtZnCH_2I$) was used.

tolerance of organozinc reagents than that of Grignard reagents, it is worthwhile to study the rearrangement reaction of bromohydrins mediated by organozinc reagents to synthesize carbonyl compounds. In this paper, we wish to report our results.

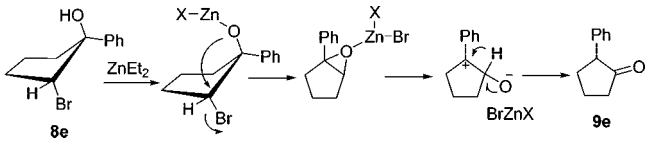
Results and Discussion

Initially, we carried out the rearrangement reaction of bromohydrins using the organozinc species $EtZnCH_2I$. Treatment of 4-bromo-3-hydroxy-1,3-diphenylbutan-1-one **2** with 3.0

SCHEME 3. Pinacol-Type Rearrangement Mediated by Et_2Zn



SCHEME 4. "Epoxide" Rearrangement Mediated by Et_2Zn



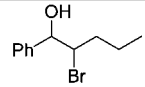
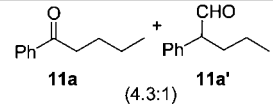
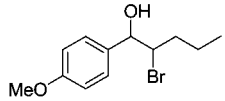
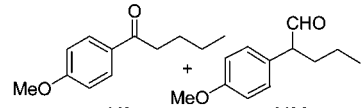
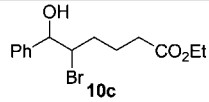
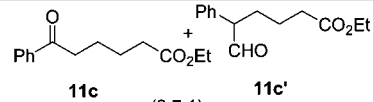
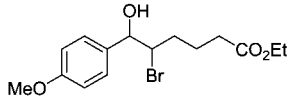
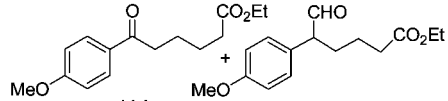
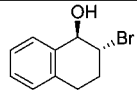
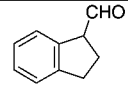
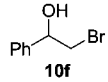
equiv of $EtZnCH_2I$ in CH_2Cl_2 at room temperature for 5 h gave the resulting β-diketone **3** in 88% yield. But, when $EtZnCH_2I$ was replaced by Et_2Zn, the reaction afforded a complicated mixture and the β-diketone **3** was not detected by TLC. Therefore, the Furukawa reagent ($EtZnCH_2I$) is considered to be crucial for the rearrangement of bromohydrins. Next, the reaction process was employed to the rearrangement of other bromohydrins prepared from simple alkenes.[3] Reaction of 2-bromo-1,1-diphenylethanol **4a** with 3.0 equiv of $EtZnCH_2I$ in CH_2Cl_2 at room temperature for 2 h gave rise to the resulting ketone **5a** in 96% yield. However, reaction of bromohydrin **4b** under the same reaction conditions gave the desired product 1-phenylpropan-2-one **5b** in 60% yield along with 35% yield of 1-phenylpropan-2-ol, which was formed from the reduction of compound **5b** by the Furukawa reagent. It was found that the rearrangement reaction of **4b** proceeded smoothly when Et_2Zn, in place of the Furukawa reagent, was used. The yield of ketone **5b** increased to 93%, and the reductive product 1-phenylpropan-2-ol was not found. To evaluate the optimal amount of Et_2Zn, 1-bromo-2-phenylpropan-2-ol **4b** was chosen as a typical substrate. The amount of Et_2Zn which ranged from 3.0 to 0.6 equiv has no obvious effect on the yield of **5b**. However, a lower yield was obtained when less than 0.6 equiv of Et_2Zn was employed in this reaction. So, the rearrangement of bromohydrins was carried out by 0.6 equiv of Et_2Zn in CH_2Cl_2 at room temperature for 2 h. Meanwhile, an iodohydrin such as 1-iodo-2-phenylpropan-2-ol was employed to this reaction to give the same product **5b** in comparable yield (92%).

With the best reaction conditions in hand, various acyclic tertiary β-bromo alcohols which the hydroxyl group attached on the tertiary carbon atom were submitted to the reaction under the optimal conditions, and the experimental results are summarized in Table 1. Of all the examples examined, the desired α-aryl ketones were afforded in good to excellent yields. Because of a higher migratory ability of the aryl group than that of the alkyl group, β-bromo alcohols were converted into ketones with aryl migration. Clearly, the substituents on the phenyl ring have a slight effect on the reaction. For example, Hammett sigma constants of substituents in the phenyl series ranged from -0.27 (*p*-MeO) to $+0.2$ (*p*-Cl), and the yield of the resulting product **5d** decreased to 86% along with a small amount of 1-(4-chlorophenyl)propan-1-one (5%), which was formed from methyl transfer. The bromohydrins containing long alkyl chains also gave the corresponding products in good isolated yields. The bromohydrin **4j** produced the sole product **5j**, since the *p*-methoxyphenyl group transfers faster than the phenyl group. But, substrate **4k** afforded a 2.5:1 mixture of two isomers **5k** and **5k′**, which might be ascribed to the comparable migratory aptitude of the *p*-chlorophenyl and phenyl groups. The phenyl group transfers faster than the *p*-chlorophenyl group, and **5k** was obtained as the major product. The substrates containing the ester group can also be converted into the corresponding products in high yields. When bromohydrin **4l** was subjected to this reaction, the desired product **5l** was obtained in 59% yield along with a 23% yield of **5l′**. The formation of isomer **5l′** might be ascribed to the competition of the pinacol-type[8] and the "epoxide" rearrangement pathway.[5b] Due to the high migratory aptitude of the *p*-methoxyphenyl group, the rearrangement of the bromohydrin **4m** gave a sole product **5m** in 92% yield.

We next extended the synthetic utility of the rearrangement procedure to cyclic tertiary β-bromo alcohols that Br was not attached on the ring system. A series of bromohydrins were investigated under the same reaction conditions, and the experimental results are shown in Table 2. Treatment of 1-(bromomethyl)-2,3-dihydro-1*H*-inden-1-ol **6a** with 0.6 equiv of Et_2Zn at room temperature for 2 h, even after prolonging the reaction time to 8 h, gave no desired 3,4-dihydronaphthalen-2(1*H*)-one **7a** as judged by the ^1H NMR spectra of the crude reaction mixtures. Interestingly, the corresponding product **7a** was obtained in 95% yield when bromohydrin **6a** reacted with 0.6 equiv of Furukawa reagent ($EtZnCH_2I$) in CH_2Cl_2 for 2 h. The precise reason for this phenomenon is not known at the present time. Reactions of bromohydrins **6b** and **6c** with 0.6 equiv of Et_2Zn gave rise to the ring-expansive products **7b** and **7c** in 99% and 97% yields, respectively. However, no reaction was observed when 1-(bromomethyl)cyclohexanol **6d** as a substrate was submitted to this reaction under the typical reaction conditions. Geissman and Akawie[5b] observed that primary halides do not rearrange unless a good migrating group is involved and that secondary and tertiary halides rearrange regardless of the migrating group. Indeed, substrate **6e** as a secondary bromine worked well and gave two resulting isomers **7e** and **7e′** in 92% total yields. The ratio of the two isomers **7e** and **7e′** determined by GC-MS analysis is 4.7:1. The minor isomer **7e′** might be formed from the "epoxide" rearrangement. Bromohydrins **6f**−**i** on which the bromine atom was attached on the benzyl position were converted to the corresponding ring-expansive α-phenylcycloalkanones **7f**−**i** in high yields under standard reaction conditions.

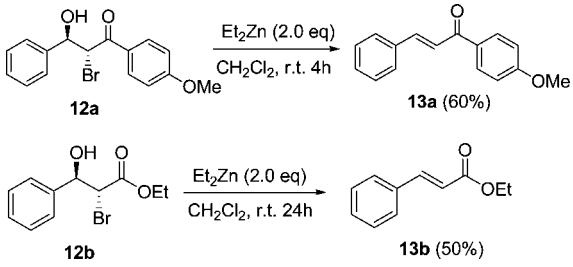
To evaluate the scope of this reaction further, various cyclic tertiary β-bromo alcohols on which the Br atom was attached on the ring system were tested under standard conditions, and the results are summarized in Table 3. These tertiary β-bromo alcohols submitted to the reaction gave rise to the corresponding carbonyl compounds in excellent isolated yields. For example, reaction of *trans*-2-bromo-1-phenylcyclohexanol **8a** with Et_2Zn afforded the ring-contractive cyclopentyl(phenyl)methanone **9a** in 98% yield. At this time, the rearrangement reaction underwent selective alkyl migration to form a ring-contractive product in preference to aryl migration. The fact may be accounted for by differences in the stability of the two conformational isomers **I** and **II** of bromohydrin **8a**. For the tautomeric equilibrium, the isomer **II** is more stable than that of the isomer **I** (Scheme 3). So, the corresponding product **9a** was formed by rearrangement of the intermediate **III** involving a displacement of bromine from its rear by the alkyl group.[9] Treatment of *cis*-2-bromo-1-phenylcyclohexanol **8b** with 0.6 equiv of Et_2Zn afforded α-phenylcyclohexanone **7f** with 82% yield, along with a ring-contractive cyclopentyl(phenyl)methanone **9a** in 8% yield (entry

TABLE 4. Et_2Zn-Induced Rearrangement of Secondary β-Bromo Alcohols

Entry	Substrate	Product	Yield (%)[a]
1	 **10a**	 **11a** + **11a'** (4.3:1)	98[b]
2	 **10b**	 **11b** + **11b'** (1:8.7)	85[b]
3	 **10c**	 **11c** + **11c'** (2.7:1)	90[b]
4	 **10d**	 **11d** + **11d'** (1:8)	80[b]
5	 **10e**	 **11e**	30
6	 **10f**	NR[c]	-

[a] Isolated yield after flash chromatography. [b] Ratio of the two isomers was determined by ^1H NMR spectra. [c] NR = no reaction.

SCHEME 5. Et_2Zn-Mediated Reductive Elimination of Bromohydrins to Form Olefins



2, Table 3). When **8e** as a five-membered ring substrate was submitted to this reaction, the ring-contractive product was not detected, but α-phenylcyclopentanone **9e** was obtained in 85% yield. It seems likely that the formation of compound **9e** is attributed to the migration of the phenyl group. In fact, the phenyl group does not transfer in this case, while the zinc−oxygen group rearranges (Scheme 4). The "epoxide" pathway of the rearrangement might involve the displacement of the β-bromine atom by a nucleophilic attack of the oxygen atom, followed by migration of the hydrogen atom to form **9e.** Similar to the formation of **9e**, substrate **8f** also proceeded through the "epoxide" pathway to generate the corresponding ketone **9f**. In this instance, the Furukawa reagent ($EtZnCH_2I$), replaced by Et_2Zn, must be used for the reaction. Otherwise, no desired ketone **9f** was formed under the same reaction conditions. When the β-bromo alcohols containing the seven-membered ring were employed in this process, the ring-contractive products **9d**, **9h**, and **9i** were obtained with 99%, 95%, and 86% yields, respectively (entries 4, 8, and 9, Table 3). However, the β-bromo alcohol **8j** gave a mixture of ketones **9j** and **9j′**. The major product **9j′** might be generated by the epoxide pathway of rearrangement.

Extension of this reaction process to tertiary bromohydrins confirms its generality and utility. Our attention was next turned to explore Et_2Zn-induced rearrangement of secondary β-bromo alcohols that the hydroxyl group was attached to on the secondary carbon position. Several substrates were prepared to investigate the regioselectivity and the migratory ability of the groups. The corresponding results were summarized in Table 4. Reaction of 2-bromo-1-phenylpentan-1-ol **10a** with 0.6 equiv of Et_2Zn provided a mixture of **11a** and **11a′** in 98% yield. The ratio of the two isomers **11a** and **11a′** was 4.3:1 which was determined by ^1H NMR spectroscopic analysis. It is concluded from the case that the migratory ability of the hydrogen is higher than that of the phenyl group. While bromohydrin **10b** was subjected to the reaction, the major product **11b′** formed by the migration of the *p*-methoxylphenyl group was obtained with good yield along with a minor isomer (**11b**). The migratory ability of *p*-methoxylphenyl > H > phenyl is proved to be congruous to the classical theory. The bromohydrins containing long alkyl chains and an ester group performed in the reaction

to give similar experimental results. Cyclic β-bromo alcohol **10e** afforded the desired ring-contractive product **11e** in only 30% yield. The lower yield of this reaction may be accounted for by the formation of polymers that are insolvable in organic solvent. No reaction was found when 2-bromo-1-phenylethanol **10f** was submitted to 0.6 equiv of Et_2Zn or $EtZnCH_2I$ under the typical reaction conditions.

It is notable that when bromohydrins derived from electron-deficient olefins were submitted to the reaction the rearrangement products were not detected, but olefins were obtained (Scheme 5). For example, treatment of substrate **12a** with 2.0 equiv of Et_2Zn in CH_2Cl_2 at room temperature for 5 h gave 4′-methoxychalcone **13a** in 60% isolated yield. The high stereochemistry (*E*) of the product olefin was determined by comparison of the NMR spectrum of the authentic olefin. It seems likely that the pathway of the formation of olefins might proceed through the reductive elimination of HBrO from the bromohydrins.[10] Reaction of bromohydrin **12b** with 0.6 equiv of Et_2Zn afforded the corresponding ethyl (*E*)-cinnamate **13b** in 15% yield along with the recovered starting **12b**. The yield of **13b** increased to 50% when 2.0 equiv of Et_2Zn was used and the reaction time was prolonged to 24 h.

Conclusions

In summary, we have described a new procedure of synthesizing carbonyl compounds from β-bromo alcohols using organozinc species Et_2Zn or $EtZnCH_2I$. The rearrangement reaction involves mild conditions, high efficiency, functionality tolerance, and using a substoichiometric amount of Et_2Zn (60 mol %). This method is general for bromohydrins and permits regioselective syntheses of α-aryl ketones. A variety of ring-expansive and -contractive carbonyl compounds were also obtained with good to excellent isolated yields.

Experimental Section

General Procedure for Et_2Zn-Mediated Rearrangement of Bromohydrins. Et_2Zn (30 μL, 0.3 mmol) was added to a solution of bromohydrins (0.5 mmol) in dry dichloromethane (3 mL) at 0 °C under nitrogen. After stirring at room temperature for 2 h, the mixture was quenched by saturated aqueous ammonium chloride solution and extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine and then dried over anhydrous magnesium sulfate, filtered, and concentrated in a vacuum to give the crude products, which were purified by column chromatography packed with silica gel using petroleum ether/ethyl acetate (20:1) as eluent to afford the corresponding products.

1,2-Diphenylethanone (5a): White solid; Mp 59–60 °C (Lit.[11] 59–60 °C); ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm) 7.91 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.2 Hz, 2H), 7.26−7.16 (m, 5H), 4.19 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm) 197.1, 136.9, 134.6, 133.2, 129.5, 128.7, 128.7, 128.7, 126.9, 45.5; IR (neat; cm^{-1}) υ 2962, 1685, 1076, 801, 699. HRMS (EI): calcd for $C_{14}H_{12}O$ (M^+), 196.0888; found, 196.0894.

Ethyl 7-(4-Methoxyphenyl)-6-oxoheptanoate (5m): Colorless oil (128.0 mg, 92% yield); ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm) 7.11 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.11 (q, J = 7.2 Hz, 2H), 3.79 (s, 3H), 3.60 (s, 2H), 2.44 (t, J = 6.6 Hz, 2H), 2.25 (t, J = 6.6 Hz, 2H), 1.57−1.52 (m, 4H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm) 208.3, 173.3, 158.7, 130.4, 126.3, 114.2, 60.2, 55.2, 49.2, 41.2, 34.0, 24.3, 23.1, 14.2; IR (neat; cm^{-1}) υ 2936, 1713, 1512, 1032, 812. HRMS (EI): calcd for $C_{16}H_{22}O_4$ (M^+), 278.1518; found, 278.1511.

General Procedure for Furukawa Reagent ($EtZnCH_2I$) Promoted Rearrangement of Bromohydrins. A 25 mL round-bottom flask was equipped with a stir bar and charged with freshly distilled methylene chloride (3 mL) and diethyl zinc (30 μL, 0.3 mmol) under an atmosphere of nitrogen at 0 °C. Methylene iodide (24 μL, 0.3 mmol) was added dropwise via syringe under nitrogen, and the resulting white suspension was stirred for 20 min. Bromohydrins (0.5 mmol) were added rapidly, and the ice bath was removed. The mixtures were allowed to stir at room temperature for 2 h until TLC indicated complete consumption of the starting bromohydrins. The reaction mixtures were quenched by saturated aqueous ammonium chloride solution and extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine and then dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give the crude products, which were purified by column chromatography packed with silica gel using petroleum ether/ethyl acetate (20:1) as eluent to afford the corresponding products.

1-Phenyl-1*H*-inden-2(3*H*)-one (9f): White solid (90.5 mg, 87% yield); Mp 49−51 °C (Lit.[12] 49−50 °C); ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm) 7.27−7.03 (m, 9H), 4.60 (s, 1H), 3.60 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm) 213.9, 141.4, 138.2, 137.4, 128.9, 128.6, 128.1, 128.0, 127.4, 126.2, 125.0, 59.9, 43.1; IR (KBr; cm^{-1}) υ 1753.

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Supporting Information Available: Detailed experimental procedures and characterization data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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