DOI: 10.1002/ejoc.200901105

# New Cyclotrimerization of Aldehydes to Cyclopentenone or Tetrahydrofuran Induced by Dibromotriphenylphosphorane

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**Keywords:** Aldehydes / Aldol reactions / Cyclotrimerization / Phosphorus

α-Mono- or α-dialkylated aldehydes undergo cyclotrimerization in the presence of dibromotriphenylphosphorane ($PPh_3Br_2$) to afford cyclopentenones or tetrasubstituted tetrahydrofurans in good yields. These transformations proceed by a tandem aldol dimerization/Nazarov reaction or a tandem aldol dimerization/Prins cyclization.

## Introduction

One of the oldest methods allowing the formation of selective carbon–carbon and carbon–oxygen bonds makes use of aldehydes as starting materials. Whereas the aldolization of two aldehyde units is fully reported to yield unsaturated aldehydes,[1] the self-reaction of three aldehyde units is documented to generate different families of compounds (Figure 1): the condensation of aldehydes mediated by bases or Lewis acids[2] or recently by L-proline[3] is reported to give unsaturated aldehydes and triketides [Equation (1)]. The cyclotrimerization of aldehydes catalyzed by bromine,[4] acetonyltriphenylphosphonium bromide,[5] and protic or Lewis acids[6] is well known to afford 1,3,5-trioxanes [Equation (2)]. 2-Deoxyribose-5-phosphate aldolase[7] (DERA, EC 4.1.2.4) as well as L-proline[3b] are reported to catalyze the tandem aldol condensation of aldehydes to trideoxyhexoses [Equation (3)]. The self-condensation of propionaldehyde with an ammonium salt is known to lead to cyclopentenone as a byproduct [Equation (4)].[8] More recently, the first asymmetric self-aldol reaction of acetaldehyde catalyzed by diarylprolinol yielded its trimer acetal [Equation (5)].[9] Enolizable aldehydes underwent trimerization by the aldol-Tishchenko reaction to produce 1,3-diol monoesters [Equation (6)].[10,11]

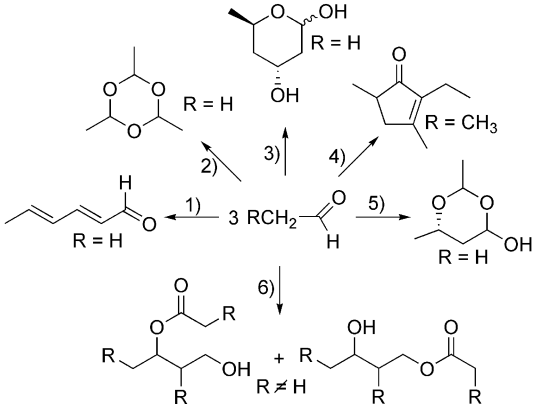


Figure 1. The products of the usual trimerization reactions of aldehydes.

Note, whereas the self-cyclization of aldehydes is well documented, to the best of our knowledge the difference of reactivity of α-mono- and α-dialkylated aldehydes has never been examined. In this paper we report the trimerization of these two types of aldehydes, which yields cyclopentenones or tetrahydrofurans, respectively.

## Results and Discussion

During the course of our study on dibromotriphenylphosphorane ($PPh_3Br_2$), a reagent well known to promote bromination reactions[12] and the deprotection of acetal groups under mild conditions,[13] we discovered that $PPh_3Br_2$ gives rise to a new cyclotrimerization of aldehydes.

Although aldehyde polymerizations are known to be initiated by tertiary phosphanes,[14] their condensation has not been studied with dibromotriphenylphosphorane. We report herein our results of a variety of aldehydes submitted to treatment with $PPh_3Br_2$.

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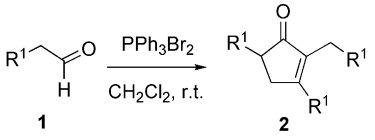
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901105.

First, the reactions of α-substituted aldehydes ($R^1$ = alkyl) **1** in the presence of $PPh_3Br_2$ in $CH_2Cl_2$ was studied. The results are summarized in Table 1. The reaction of propanal (**1a**) with $PPh_3Br_2$ afforded a single product identified as 2-ethyl-3,5-dimethylcyclopenten-2-one (**2a**; entry 1, 68% yield).[8a] The self-condensation of butanal (**1b**) under identical reaction conditions furnished 3,5-diethyl-2-propylcyclopenten-2-one (**2b**; entry 2, 64% yield).

Table 1. Trimerization of monosubstituted aldehydes **1**.[a]



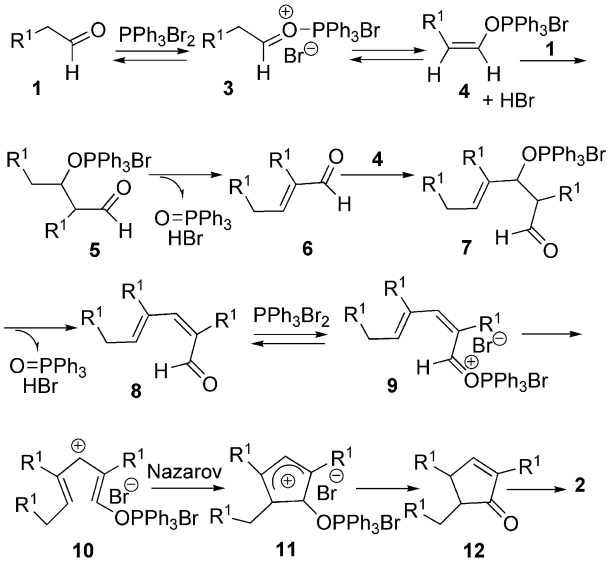

**1** **2**

| Entry | Aldehyde | Product | Yield [%][b] |
|---|---|---|---|
| 1 | **1a** ($R^1$ = $CH_3$) | **2a** | 68 |
| 2 | **1b** ($R^1$ = $CH_3CH_2$) | **2b** | 64 |

[a] Reaction conditions: 1 equiv. aldehyde **1**, 1 equiv. $PPh_3Br_2$ in $CH_2Cl_2$ (1 M) at room temperature, 3 h. [b] Isolated yields.

This self-condensation of aldehydes **1** provides a new one-pot strategy for the preparation of substituted cyclopentenones **2**, the essential moiety of prostaglandin derivatives that have various biological activities[15] and that are a structural feature found in numerous natural products.[16] Generally, the preparation of cyclopentenones requires a multistep synthesis, the key step being a Pauson–Khand reaction,[17] or an intermolecular Horner–Wadsworth–Emmons reaction of diketophosphonate,[18] or other types of cycloaddition reactions.[19] To the best of our knowledge, the only example of a cross-condensation reaction between an acyclic ketone and an aldehyde catalyzed by zirconium chloride at 200 °C was reported to afford polysubstituted cyclopentenones.[20]

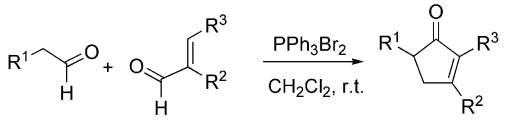
To make sure that the cyclotrimerization of aldehyde **1** into cyclopentenone **2** was mediated by $PPh_3Br_2$, **1** was allowed to self-react in $CH_2Cl_2$ in the absence of $PPh_3Br_2$. In this case the reaction did not proceed and aldehyde **1** was totally recovered. The reaction did not occur either when aldehyde **1** was treated with anhydrous HBr in $CH_2Cl_2$. These investigations allowed us to confirm that the reaction was mediated by $PPh_3Br_2$ and we propose the mechanism depicted in Scheme 1. We speculate that the reaction first proceeds by activation of aldehyde **1** with $PPh_3Br_2$ to afford oxonium intermediate **3**. This Lewis acid–aldehyde conjugate evolves to phosphorane enolate **4**, which undergoes aldol condensation with aldehyde **1** to give the aldolization product **5**. The release of triphenylphosphane oxide and hydrogen bromide affords the corresponding α,β-unsaturated aldehyde **6**. Aldehyde **6** then reacts with **4** to give **7**, which yields α,β- and δ,γ-unsaturated aldehyde **8**. Activation of **8** with $PPh_3Br_2$ leads to oxonium **9**, which evolves to pentadienylic cation **10**, which undergoes a Nazarov-like mechanism involving conrotatory ring-closure to give cyclic carbocation **11**.[21] Carbocation **11** is subjected to deprotonation and rearrangement to afford cyclopentenone **12**, which isomerizes to the corresponding substituted cyclopentenone **2** bearing the double bond with the highest degree of substitution. This type of cycloisomerization of pentadienal **8** to cyclopentenone **2** through a Nazarov mechanism appears to be largely unknown.[22]




Scheme 1. Proposed reaction mechanism for the trimerization of **1**.

This one-step self-condensation of aldehyde **1**, proceeding by a tandem aldol dimerization/Nazarov reaction to give cyclopentenone **2**, has no precedent in the literature. To validate our proposed mechanism and especially the involvement of the α,β-unsaturated aldehyde (intermediate **6**, Scheme 1), we next carried out the reactions of aldehydes **13** and alkyl aldehydes **1** with $PPh_3Br_2$ (Table 2).

Table 2. Cross-coupling reactions of aldehydes **1** and **13**.[a]




**1** **13** **14**

| Entry | Aldehyde **1** $R^1$ | Aldehyde **13** $R^2$ | $R^3$ | Product | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | $CH_3CH_2$ | $CH_3$ | $CH_3$ | **14a** | 52 |
| 2 | $(CH_3)_2CH$ | $CH_3$ | $CH_3$ | **14b** | 25 |
| 3 | $CH_3$ | $CH_3$ | $C_5H_{11}$ | **14c** | 20 |
| 4 | $CH_3CH_2$ | $CH_3$ | H | **14d** | 66 |
| 5 | $CH_3CH_2$ | H | H | – | 0 |

[a] Reaction conditions: 1 equiv. aldehyde **1**, 1 equiv. aldehyde **13**, 1 equiv. $PPh_3Br_2$ in $CH_2Cl_2$ (1 M) at room temperature, 3 h. [b] Isolated yields.

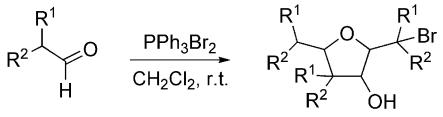
As we predicted, the cross-reactions of aldehydes **1** and **13** gave rise to the corresponding 2,3,5-trisubstituted cyclopentenones **14**. The condensation of *trans*-2,3-dimethylacrolein (**13**) and butanal with $PPh_3Br_2$ afforded cyclopentenone **14a** in 52% yield (entry 1, Table 2). When 3-methylbutyraldehyde and *trans*-2,3-dimethylacrolein were treated with $PPh_3Br_2$, the cyclopentenone **14b** was obtained in 25% yield (entry 2). The reaction of propionaldehyde and 2-meth-

yloct-2-enal yielded cyclopentenone **14c** in 20% yield (entry 3). Thus, the presence of a bulkier substituent either at the $R^1$ position of aldehyde **1** or at the $R^3$ position of **13** (entries 2 and 3, Table 2) resulted in a substantially reduced yield (25% cyclopentenone **14b** and 20% of **14c**, respectively). Conversely, methacrolein (**13**; $R^2 = CH_3$, $R^3 = H$, entry 4, Table 2) reacted with propanal (**1**) to give **14d** in the highest yield obtained (66%, entry 4). In accordance with our proposed mechanism, acrolein failed to react with propanal (entry 5, Table 2). The intermediate carbocation **11** may not be sufficiently stabilized for this substrate.

Next, to extend the scope of our method, we studied the reactions of α-disubstituted ($R^1$,$R^2$ = alkyl) aldehydes **15** with $PPh_3Br_2$. Surprisingly, aldehydes **15**, submitted to our typical reaction conditions, gave new trimerization products identified as tetrasubstituted tetrahydrofurans **16**.[23] The results are summarized in Table 3.

Table 3. Trimerization of disubstituted aldehydes **15**.[a]




**15** **16**

| Entry | Aldehyde **15** | | Product | Yield [%][b] |
|---|---|---|---|---|
| | $R^1$ | $R^2$ | | |
| 1 | $CH_3$ | $CH_3$ | **16a**[c] | 70 |
| 2 | $CH_3CH_2$ | $CH_3$ | **16b** | 55 |
| 3 | $CH_3CH_2$ | $CH_3CH_2$ | **16c** | 58 |
| 4 | $-CH_2(CH_2)_3CH_2-$ | | **16d** | 60 |
| 5 | $-CH_2(CH_2)_2CH_2-$ | | **16e** | 43 |

[a] Reaction conditions: 1 equiv. aldehyde, 1 equiv. $PPh_3Br_2$ in $CH_2Cl_2$ (1 M) at room temperature, 3 h. [b] Isolated yields. [c] In the case of product **16a**, two isomers were separated: minor isomer **16aa** (10% yield), major isomer **16ab** (60% yield).

The self-reaction of isobutyraldehyde with $PPh_3Br_2$ in $CH_2Cl_2$ afforded the polysubstituted tetrahydrofuran **16a** in 70% yield (entry 1, Table 3). The same self-condensation reaction was realized with 2-methylbutyraldehyde and 2-ethylbutyraldehyde to yield compounds **16b** and **16c** (entries 2 and 3, 55 and 58% yields, respectively). Aldehydes α-substituted by a five- or six-membered carbocycle afforded the corresponding polysubstituted tetrahydrofurans **16d** and **16e** (entries 4 and 5, 60 and 43% yield, respectively).

The X-ray structure of **16ab**[24] was determined and the resulting ORTEP plot is shown in Figure 2. It confirms the expected oxygen-containing five-membered ring product.

The trimerization reactions of α-disubstituted aldehydes allow a new and easy one-pot access to tetrahydrofurans, important heterocycle constituents in many bioactive natural products.[25] We propose a possible reaction mechanism to explain the formation of tetrahydrofuran **16** starting from aldehyde **15** (Scheme 2).

First, the reaction follows the same path as that proposed in Scheme 1: Activation of aldehyde **15** with $PPh_3Br_2$ affords oxonium **17** which evolves to phosphorane enolate **18** and then undergoes aldol condensation with aldehyde **15** to

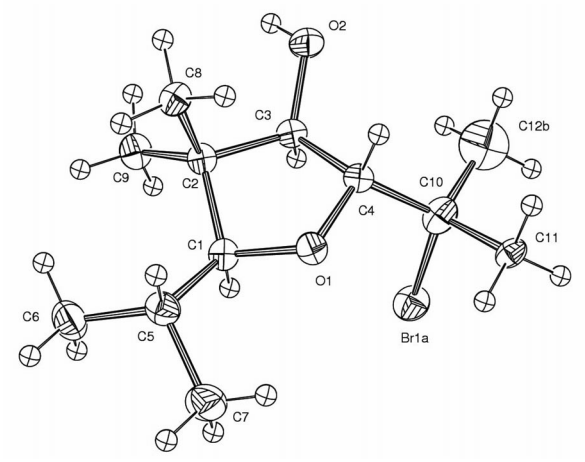
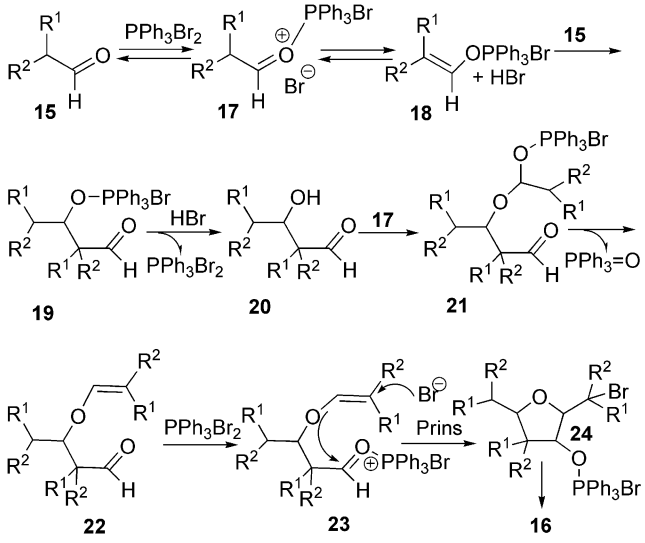



Figure 2. ORTEP drawing of the X-ray structure of tetrahydrofuran **16ab**.



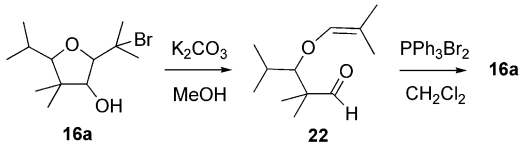

Scheme 2. Possible mechanism for the formation of substituted tetrahydrofurans **16**.

furnish aldolization product **19**. The substituents $R^1$ and $R^2$ in the α position of aldehyde **19** prevent the transformation into the corresponding α,β-unsaturated aldehyde (similar to aldol **5** yielding **6** in Scheme 1). The release of $PPh_3Br_2$ from **19** furnishes **20**, which reacts with activated aldehyde **17** to afford **21**. Compound **21** evolves to enol ether **22** with the release of triphenylphosphane oxide. Subsequent activation of the carbonyl moiety affords **23**, which yields through a Prins[26] reaction type mechanism intermediate **24**, which finally leads to tetrahydrofuran **16**.

This proposed mechanism involves the formation of the enol ether **22**. To gain information about the possible involvement of **22**, we treated the synthesized tetrahydrofuran **16a** with potassium carbonate (1 equiv.) in methanol. This reaction afforded compound **22** in 75% yield (Scheme 3). Compound **22** was then subjected to $PPh_3Br_2$ under our standard trimerization conditions and, as expected, compound **16a** was quantitatively obtained (Scheme 3). This re-

sult highlights the probability of **22** being an intermediate of the trimerization reaction, which is in agreement with our proposed mechanism depicted in Scheme 2.




Scheme 3. Formation and reactivity of aldehyde **22**.

Finally, to confirm that the cyclotrimerization of aldehyde **15** was not an acid-catalyzed reaction, we partially hydrolyzed $PPh_3Br_2$ prior to the reaction (to generate HBr in situ). This process led to a dramatic decrease in the yield of tetrahydrofuran **16a** (5% yield after 48 h of reaction). These investigations have allowed us to propose that the trimerization of α-disubstituted aldehydes **15** to tetrahydrofurans **16** is mediated by $PPh_3Br_2$ and that the enol ether **22** is an intermediate of the reaction.

## Conclusions

We have reported in this paper an original one-pot self-cyclotrimerization reaction of aldehydes induced by dibromotriphenylphosphorane. The transformation of α-monosubstituted aldehydes into polysubstituted cyclopentenones appears to proceed by a tandem aldol dimerization/Nazarov reaction. The self-condensation of α-disubstituted aldehydes with dibromotriphenylphosphorane follows a tandem aldol dimerization/Prins process to furnish substituted tetrahydrofuran derivatives, important structures found in natural products. Further studies aimed at probing the general use of this three-component cyclotrimerization reaction are ongoing.

## Experimental Section

**General:** All reactions were performed in dried glassware under argon. All reagents were purchased from commercial sources, aldehydes were freshly distilled prior to use, and other reactants were used without further purification. Methylene chloride was freshly distilled from $CaH_2$ prior to use. TLC and flash chromatography were, respectively, performed on precoated silica gel 60 F 254 plates and on silica gel 60 (230–400 mesh). $^1H$ and $^{13}C$ NMR spectra were recorded at the indicated field strength in $CDCl_3$; chemical shifts were measured relative to internal TMS. High-resolution mass spectra were recorded with a MALDI-TOF spectrometer (matrix: dihydroxybenzoic acid). Mass spectra were obtained with a Finnigan-4600 quadrupole spectrometer using either a chemical (CI, $NH_3$) or electronic (EI, 70 eV) ionization mode. IR spectra were recorded on NaCl plates as thin films.

**General Procedure A. The Cyclotrimerization Reaction of α-Monosubstituted Aldehyde 1 and of α-Disubstituted Aldehyde 15:** The aldehyde **1** or **15** (4 mmol, 1 equiv.) was added dropwise to a stirred solution of dibromotriphenylphosphorane (4 mmol, 1 equiv.) in $CH_2Cl_2$ (2.5 mL). The yellowish solution, which gradually turned black, was stirred for 4 h at room temperature and then was concentrated under vacuum. $Et_2O$ (3 mL) was added to precipitate triphenylphosphane oxide, which was removed by filtration. The mixture was concentrated under vacuum to afford the crude product which was purified by silica gel column chromatography or by kugelrohr distillation to yield the corresponding trimerization product **2** or **16** from the starting aldehyde **1** or **15**, respectively.

**General Procedure B. Cross-Coupling Reaction of α-Monosubstituted Aldehyde 1 and α,β-Unsaturated Aldehyde 13:** The α,β-unsaturated aldehyde **13** (5.5 mmol, 1 equiv.) followed by the α-monosubstituted aldehyde **1** (5.5 mmol, 1 equiv.) were successively added to a stirred solution of dibromotriphenylphosphorane (5.5 mmol, 1 equiv.) in $CH_2Cl_2$ (3.5 mL). The resulting mixture was stirred for 4 h at room temperature and then concentrated under vacuum. Then $Et_2O$ (3 mL) was added to precipitate triphenylphosphane oxide, which was removed by filtration. The solvent was evaporated under vacuum and the residue was purified by flash chromatography to afford the trimerization product **14**.

**2-Ethyl-3,5-dimethylcyclopent-2-enone (2a):** From propionaldehyde (0.37 mL, 5.2 mmol) and dibromotriphenylphosphorane (2.18 g, 5.2 mmol) in $CH_2Cl_2$ (2.5 mL), the crude cyclopentenone **2a** was obtained following the general procedure A. Kugelrohr distillation under vacuum (15 Torr) at 80 °C or purification by flash chromatography (hexane/$Et_2O$, 9:1) afforded **2a** (162 mg, 68% yield) as a colorless oil. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 2.72 (dd, $^2J$ = 18.3, $^3J$ = 6.7 Hz, 1 H, CH$H'$), 2.33 (t, $J$ = 7.3 Hz, 1 H, C$H$H′), 2.15 (m, 3 H, $CH_3$-C$H$, $CH_3$-C$H_2$), 2.02 (s, 3 H, =CC$H_3$), 1.15 (d, $^3J$ = 7.4 Hz, 3 H, CH-C$H_3$), 0.89 (t, $^3J$ = 7.5 Hz, 3 H, $CH_2$-C$H_3$) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 211.8, 167.7, 140.4, 40.4, 39.4, 16.7, 16.3, 16.0, 12.8 ppm. IR (neat): $\tilde{\nu}$ = 2966, 2930, 2873, 1695, 1646, 1456, 1438, 1385, 1348 $cm^{-1}$. MS (DCI/$NH_3$): $m/z$ = 139 $[MH]^+$, 156 $[MNH_4]^+$. $C_9H_{14}O$ (138.21): calcd. C 78.21, H 10.21; found C 78.41, H 9.98.

**3,5-Diethyl-2-propylcyclopent-2-enone (2b):** From butyraldehyde (0.45 mL, 5 mmol) and dibromotriphenylphosphorane (2.10 g, 5 mmol) in $CH_2Cl_2$ (3 mL), the crude cyclopentenone **2b** was obtained following the general procedure A. Purification by flash chromatography (hexane/$Et_2O$, 9:1) afforded **2b** (192 mg, 64% yield) as a yellow oil. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 2.68 (dd, $^2J$ = 18, $^3J$ = 6.5 Hz, 1 H, CHCH$H'$C=) 2.44 (q, $J$ = 7.6 Hz, 1 H, CH-C$H$H′-C=), 2.29–2.10 (m, 3 H, $CH_3CH_2$-C$H$, $CH_3$-C$H_2$-C=), 1.89–1.76 (m, 2 H, $CH_3CH_2$-C$H_2$), 1.43–1.27 (m, 4 H, $CH_3CH_2$-$CH_2$, $CH_3CH_2$-CH), 1.14 (t, $J$ = 7.6 Hz, 3 H, C$H_3$-$CH_2$-C=), 0.92 (t, $J$ = 7.4 Hz, 3 H, $CH_3CH_2$-$CH_2$), 0.88 (t, $J$ = 7.3 Hz, 3 H, $CH_3CH_2$-CH) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 211.9, 173.8, 139.1, 46.2, 34.9, 24.9, 24.6, 24.1, 21.8, 14.0, 12.1, 11.3 ppm. IR (neat): $\tilde{\nu}$ = 2961, 2360, 1697, 1462, 1287, 1175, 839, 709, 588, 503 $cm^{-1}$. HRMS: calcd. for $C_{12}H_{20}O$ 180.1514; found 180.1511.

**5-Ethyl-2,3-dimethylcyclopent-2-enone (14a):** From *trans*-2-methyl-2-butenal (0.5 mL, 5.2 mmol), butyraldehyde (0.46 mL, 5.2 mmol), and dibromotriphenylphosphorane (2.18 g, 5.2 mmol) in $CH_2Cl_2$ (3.5 mL), the crude cyclopentenone **14a** was obtained following the general procedure B. Purification by flash chromatography (hexane/$Et_2O$, 8:2) afforded **14a** (372 mg, 52% yield) as a colorless oil. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 2.65 (dd, $^2J$ = 18.3, $^3J$ = 5.8 Hz, 1 H, CH$H'$), 2.17 (m, 1 H, C$H$H′), 2.03 [s, 3 H, =C($CH_3$)-C=O], 1.83 (m, 1 H, $CH_3CH_2$-C$H$), 1.68 [s, 3 H, CHH′=C(C$H_3$)], 1.35 (m, 2 H, $CH_3CH_2$), 0.93 (t, $^3J$ = 7.1 Hz, 3 H, C$H_3CH_2$) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 211.7, 168.5, 135.6, 46.3, 38.0, 24.5, 17.0, 11.4, 7.9 ppm. IR (neat): $\tilde{\nu}$ = 2963, 2922, 1698, 1655, 1438, 1387, 1328, 1042, 916, 805, 733 $cm^{-1}$. MS (DCI/$NH_3$): $m/z$ = 139 $[MH]^+$. $C_9H_{14}O$ (138.21): calcd. C 78.21, H 10.21; found C 78.09, H 10.05.

**5-Isopropyl-2,3-dimethylcyclopent-2-enone (14b):** From *trans*-2-methyl-2-butenal (0.46 mL, 4.8 mmol), 3-methylbutyraldehyde (0.51 mL, 4.8 mmol), and dibromotriphenylphosphorane (2 g, 4.8 mmol) in $CH_2Cl_2$ (3.2 mL), the crude cyclopentenone **14b** was obtained following the general procedure B. Purification by column chromatography (hexane/$Et_2O$, 8:2) afforded **14b** (183 mg, 25% yield) as a colorless oil. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 2.52–2.18 [m, 4 H, $(CH_3)_2CH$-C*H*, $(CH_3)_2C$*H*-CH, C*HH′*], 2.05 [s, 3 H, =C(C*H*$_3$)-C=O], 1.69 [s, 3 H, CHH′=C(C*H*$_3$)], 0.94 [d, $J$ = 7.8 Hz, 3 H, (C*H*$_3$)$(CH_3)$CH], 0.68 [d, $J$ = 6.6 Hz, 3 H, $(CH_3)$(C*H*$_3$)CH] ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 211.4, 168.8, 136.5, 50.6, 46.7, 33.8, 28.5, 20.7, 16.9, 7.7 ppm. IR (neat): $\tilde{\nu}$ = 2957, 1698, 1650, 1465, 1387, 1328, 1185, 1065 $cm^{-1}$. MS (DCI/$NH_3$): $m/z$ = 153 $[MH]^+$, 170 $[MNH_4]^+$. $C_{10}H_{16}O$ (152.23): calcd. C 78.90, H 10.59; found C 78.75, H 10.55.

**3,5-Dimethyl-2-pentylcyclopent-2-enone (14c):** From 2-methyloct-2-enal (84 mg, 0.6 mmol), propionaldehyde (43 µL, 0.6 mmol), and dibromotriphenylphosphorane (253 mg, 0.6 mmol) in $CH_2Cl_2$ (1.2 mL), the crude cyclopentenone **14c** was obtained following the general procedure B. Silica gel chromatography (hexane/$Et_2O$, 8:2) afforded **14c** (22 mg, 20% yield) as a colorless oil. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 2.73 (dd, $^2J$ = 18.2, $^3J$ = 7.2 Hz, 1 H, CH*H′*), 2.32 (q, $J$ = 7.2 Hz, 1 H, C*H*H′), 2.14 (m, 3 H, $CH_3$-C*H*, $CH_3$-C*H*$_2$-C=), 2.02 (s, 3 H, =C-C*H*$_3$), 1.29 [m, 6 H, $CH_3$(C*H*$_2$)$_3$-$CH_2$], 1.14 (d, $^3J$ = 7.4 Hz, 3 H, CH-C*H*$_3$), 0.86 [t, $^3J$ = 6.7 Hz, 3 H, C*H*$_3$(CH$_2$)$_3$-$CH_2$] ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 212.1, 168.1, 139.4, 40.6, 39.5, 31.7, 28.0, 22.9, 22.4, 17.0, 16.6, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 2959, 2929, 2857, 1699, 1648, 1457, 1385, 1233, 1096, 978, 806, 667, 533 $cm^{-1}$. MS (DCI/$NH_3$): $m/z$ = 181 $[MH]^+$. $C_{12}H_{20}O$ (180.29): calcd. C 79.94, H 11.18; found C 79.74, H 11.06.

**5-Ethyl-3-methylcyclopent-2-enone (14d):** From methacrolein (0.46 mL, 5.55 mmol), butyraldehyde (0.5 mL, 5.55 mmol), and dibromotriphenylphosphorane (2.34 g, 5.55 mmol) in $CH_2Cl_2$ (3.7 mL), the crude cyclopentenone **14d** was obtained following the general procedure B. Silica gel chromatography (hexane/$Et_2O$, 8:2) afforded **14d** (456 mg, 66% yield) as a colorless oil. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 5.86 (d, $J$ = 1.4 Hz, 1 H, =C*H*-C=O), 2.70 (dd, $^2J$ = 18.3, $^3J$ = 6.2 Hz, 1 H, CH*H′*), 2.26 (m, 1 H, C*H*H′), 2.09 (s, 3 H, =C-C*H*$_3$), 1.77 (m, 1 H, $CH_3CH_2$-C*H*), 1.33 (m, 2 H, $CH_3$C*H*$_2$), 0.89 (t, $J$ = 7.3 Hz, 3 H, C*H*$_3$CH$_2$) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 211.2, 177.4, 129.7, 47.6, 38.9, 23.9, 19.1, 11.0 ppm. IR (neat): $\tilde{\nu}$ = 3433, 2962, 2933, 2874, 1696, 1624, 1461, 1431, 1379, 1324, 1287, 1174, 1102, 1051, 966, 838 $cm^{-1}$. MS (DCI/$NH_3$): $m/z$ = 125 $[MH]^+$, 142 $[MNH_4]^+$.

**2-(1-Bromo-1-methylethyl)-5-isopropyl-4,4-dimethyltetrahydrofuran-3-ol (16aa and 16ab):** From 2-methylpropionaldehyde (0.44 mL, 4.82 mmol) and dibromotriphenylphosphorane (2.05 g, 4.82 mmol) in $CH_2Cl_2$ (3.3 mL), the crude **16a** was obtained following the general procedure A. Purification by silica gel chromatography (hexane/$Et_2O$, 8.5:1.5) afforded two major separable diastereoisomers **16aa** and **16ab**: minor diastereoisomer **16aa** (50 mg, 10% yield) as a colorless oil and major diastereoisomer **16ab** (266 mg, 60% yield) as a white solid.

Minor diastereoisomer **16aa**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.67 [d, $^3J$ = 5.2 Hz, 1 H, $(CH_3)_2$C-C*H*-OH], 3.39 [d, $^3J$ = 5.6 Hz, 1 H, -O-C*H*-C$(CH_3)_2$Br], 3.10 [d, $^3J$ = 9.2 Hz, 1 H, $(CH_3)_2$CH-C*H*-O-], 1.82 [s, 3 H, CBr(C*H*$_3$)$(CH_3)$], 1.79 [s, 3 H, CBr$(CH_3)$(C*H*$_3$)], 1.81–1.78 [br. s, 1 H, $(CH_3)_2$C*H*], 1.63–1.55 (br. s, 1 H, O*H*), 1.07 [s, 3 H, C$(CH_3)$(C*H*$_3$)], 1.01 [d, $^3J$ = 7.1 Hz, 3 H, $(CH_3)$(C*H*$_3$)CH], 0.99 [s, 3 H, C(C*H*$_3$)$(CH_3)$], 0.92 [d, $J$ = 6.8 Hz, 3 H, (C*H*$_3$)$(CH_3)$CH] ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 91.7, 91.5, 82.9, 66.0, 43.9, 31.9, 29.5, 28.8, 22.16, 21.2, 21.15, 19.3 ppm. IR (neat): $\tilde{\nu}$ = 2970, 2873, 1466, 1387, 1369, 1223, 1117, 1065, 1041, 980, 759 $cm^{-1}$. MS (EI): $m/z$ = 278, 235, 199, 198, 165, 163, 157, 127, 97, 85, 72, 43. $C_{12}H_{23}BrO_2$ (279.21): calcd. C 51.62, H 8.30; found C 51.49, H 8.39.

Major diastereoisomer **16ab**: M.p. 58 °C[24]. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.88 [d, $^3J$ = 7.2 Hz, 1 H, $(CH_3)_2$C-C*H*-OH], 3.49 [d, $^3J$ = 7.6 Hz, 1 H, -O-C*H*-C$(CH_3)_2$Br], 3.15 [d, $^3J$ = 7.2 Hz, 1 H, $(CH_3)_2$CH-C*H*-O-], 1.90–1.85 (br. s, 1 H, O*H*), 1.81 [s, 3 H, CBr(C*H*$_3$)$(CH_3)$], 1.79–1.77 [br. s, 1 H, $(CH_3)_2$C*H*], 1.78 [s, 3 H, CBr$(CH_3)$(C*H*$_3$)], 1.11 [s, 3 H, C(C*H*$_3$)$(CH_3)$], 1.00 [d, $^3J$ = 6.4 Hz, 3 H, (C*H*$_3$)$(CH_3)$CH], 0.96 [s, 3 H, C$(CH_3)$(C*H*$_3$)], 0.88 [d, $^3J$ = 6.8 Hz, 3 H, $(CH_3)$(C*H*$_3$)CH] ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 90.9, 86.2, 81.7, 69.2, 44.3, 31.6, 29.8, 29.2, 23.9, 21.0, 18.5, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 2970, 2873, 1466, 1387, 1369, 1223, 1117, 1065, 1041, 980, 759 $cm^{-1}$. MS (EI): $m/z$ = 278, 235, 199, 198, 165, 163, 157, 127, 97, 85, 72, 43. $C_{12}H_{23}BrO_2$ (279.21): calcd. C 51.62, H 8.30; found C 51.46, H 8.33.

CCDC-735049 (for **16ab**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**2-(1-Bromo-1-methylpropyl)-5-*sec*-butyl-4-ethyl-4-methyltetrahydrofuran-3-ol (16b):** From 2-methylbutyraldehyde (0.43 mL, 4 mmol) and dibromotriphenylphosphorane (1.69 g, 4 mmol) in $CH_2Cl_2$ (3 mL), the crude **16b** was obtained following the general procedure A. Purification by silica gel chromatography (hexane/EtOAc, 8.5:1.5) afforded a mixture of inseparable diastereoisomers **16b** (236 mg, 55% yield) as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.82 [d, $^3J$ = 5.4 Hz, 1 H, $(CH_3)$$(C_2H_5)$C-C*H*-OH], 3.61 [d, $^3J$ = 6.2, 1 H, -O-C*H*-CBr$(CH_3)$$(C_2H_5)$], 3.32 [d, $^3J$ = 6.0 Hz, 1 H, $(CH_3)$$(C_2H_5)$CH-C*H*-O-], 3.27–3.20 (m, 1 H, O*H*), 1.98–1.90 [m, 2 H, CBr$(CH_3)$$(CH_3CH_2)$], 1.69 [s, 3 H, CBr(C*H*$_3$)$(CH_3CH_2)$], 1.68–1.62 [br. s, 1 H, $(CH_3)$$(C_2H_5)$C*H*-], 1.54–1.47 [m, 2 H, $(CH_3)$$(CH_3CH_2)$CH-], 1.15–1.05 [m, 2 H, $(CH_3)$C(C*H*$_2$CH$_3$)], 1.09 [t, $^3J$ = 7.1 Hz, 3 H, CBr$(CH_3)$(C*H*$_3$CH$_2$)], 1.05–0.90 [m, 9 H, (C*H*$_3$)$(C_2H_5)$CH-, $(CH_3)$C$(CH_2CH_3)$, (C*H*$_3$)-C$(CH_2CH_3)$], 0.88 [t, $^3J$ = 7.0 Hz, 3 H, $(CH_3)$$(CH_3CH_2)$CH-] ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 91.4, 90.9, 86.9, 86.5, 79.0, 73.1, 47.2, 35.9, 34.1, 30.1, 27.6, 25.2, 16.3, 15.8, 10.9 ppm. IR (neat): $\tilde{\nu}$ = 3461, 2968, 2937, 2878, 1458, 1381, 1064, 1004, 787 $cm^{-1}$. MS (DCI/$NH_3$): $m/z$ = 241, 258, 338 $[M(^{79}Br) + NH_4]^+$, 340 $[M(^{81}Br) + NH_4]^+$. $C_{15}H_{29}BrO_2$ (321.29): calcd. C 56.07, H 9.10; found C 56.29, H 9.03.

**2-(1-Bromo-1-ethylpropyl)-4,4-diethyl-5-(1-ethylpropyl)tetrahydrofuran-3-ol (16c):** From 2-ethylbutyraldehyde (0.62 mL, 5 mmol) and dibromotriphenylphosphorane (2.11 g, 5 mmol) in $CH_2Cl_2$ (5 mL), the crude **16c** was obtained following the general procedure A. Purification by silica gel chromatography (hexane/$Et_2O$, 8:2) afforded a mixture of inseparable diastereoisomers **16c** (351 mg, 58% yield) as an orange oil. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 3.96 [d, $^3J$ = 6.3 Hz, 1 H, $(C_2H_5)_2$C-C*H*-OH], 3.61 [d, $^3J$ = 4.3 Hz, 1 H, -O-C*H*-C$Br(C_2H_5)_2$], 3.51 [d, $^3J$ = 6.3 Hz, 1 H, $(C_2H_5)_2$CH-C*H*-O-], 2.11–1.92 [m, 4 H, O*H*, $(C_2H_5)_2$C*H*-, CBr$(C_2H_5)$$(CH_3CH_2)$], 1.61–1.29 [m, 10 H, 5$(CH_3)$(C*H*$_2$)], 1.07–0.81 [m, 18 H, 6(C*H*$_3$)$(CH_2)$] ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 87.0, 86.3, 80.2, 49.4, 40.5, 40.1, 31.6, 31.7, 30.7, 24.6, 24.2, 23.5, 23.0, 20.8, 11.4, 10.9, 9.5 ppm. IR (neat): $\tilde{\nu}$ = 3515, 2965, 2878, 1460, 1381, 1109, 1070, 839, 557 $cm^{-1}$. MS (DCI/$NH_3$): $m/z$ = 380 $[M(^{79}Br)NH_4]^+$, 382 $[M(^{81}Br)NH_4]^+$. $C_{18}H_{35}BrO_2$ (363.37): calcd. C 59.50, H 9.71; found C 59.40, H 9.61.

**3-(1-Bromocyclohexyl)-1-cyclohexyl-2-oxaspiro[4.5]decan-4-ol (16d):** From cyclohexanecarbaldehyde (0.6 mL, 5 mmol) and dibromotri-

phenylphosphorane (2.11 g, 5 mmol) in $CH_2Cl_2$ (5 mL), the crude **16d** was obtained following the general procedure A. Purification by silica gel chromatography (hexane/$Et_2O$, 8.5:1.5) afforded a mixture of diastereoisomers **16d** (400 mg, 60% yield) as a colorless oil.

Major diastereoisomer **16d**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 4.08 (m, 1 H, -C*H*-OH), 3.55 [d, $^3J$ = 4.8 Hz, 1 H, -O-C*H*-CBr-$(CH_2)_5$-], 3.10 [d, $^3J$ = 7.3 Hz, 1 H, -$(CH_2)_5$-CH-C*H*-O-], 1.97–0.89 [m, 32 H, O*H*, -$(CH_2)_5$-C*H*-, 15-$(CH_2)_5$-] ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 93.3, 90.1, 47.5, 38.3, 37.9, 35.0, 30.7, 30.6, 29.0, 28.4, 26.4, 26.2, 26.0, 25.2, 24.1, 22.5, 22.1 ppm. IR (neat): $\tilde{\nu}$ = 3468, 2930, 2852, 1447, 1247, 1116, 1048, 904, 735 cm$^{-1}$. MS (DCI/$NH_3$): *m*/*z* = 416 [M($^{79}$Br)$NH_4$]$^+$, 418 [M($^{81}$Br)$NH_4$]$^+$. $C_{21}H_{35}BrO_2$ (399.41): calcd. C 63.15, H 8.83; found C 63.05, H 8.90.

**3-(1-Bromocyclopentyl)-1-cyclopentyl-2-oxaspiro[4.4]nonan-4-ol (16e):** From cyclopentanecarbaldehyde (0.6 mL, 5.6 mmol) and dibromotriphenylphosphorane (2.37 g, 5.6 mmol) in $CH_2Cl_2$ (5.5 mL), the crude **16e** was obtained following the general procedure A. Purification by silica gel chromatography (pentane/$Et_2O$, 9:1) afforded a mixture of diastereoisomers **16e** (285 mg, 43% yield) as a colorless oil.

Major diastereoisomer **16e**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.69 (br. s, $^3J$ = 1.6 Hz, 1 H, O*H*), 4.15 (d, $^3J$ = 7.2 Hz, 1 H, -C*H*-OH), 3.84 [d, $^3J$ = 7.2 Hz, 1 H, -O-C*H*-CBr-$(CH_2)_4$-], 3.56 [d, $^3J$ = 9.2 Hz, 1 H, -$(CH_2)_4$-CH-C*H*-O-], 2.36–2.30 [m, 4 H, CBr-$(CH_2)_2$-$(CH_2)_2$], 2.06–1.95 [m, 1 H, -$(CH_2)_4$-C*H*-], 1.92–1.84 (m, 4 H, 2-$CH_2$-), 1.81–1.35 (m, 16 H, 8-$CH_2$-) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 89.1, 84.8, 82.9, 82.1, 55.7, 40.9, 40.5, 38.5, 33.9, 31.2, 29.2, 26.8, 26.0, 25.8, 25.5, 25.4, 24.3, 23.0 ppm. IR (neat): $\tilde{\nu}$ = 3470, 2930, 2852, 1447, 1247, 1116, 1048, 730 cm$^{-1}$. $C_{18}H_{29}BrO_2$ (357.33): calcd. C 60.50, H 8.18; found C 60.40, H 8.25.

**2,2,4-Trimethyl-3-(2-methylpropenyloxy)pentanal (22):** Compound **16a** (1 g, 4 mmol) was added to a solution of ground potassium carbonate (0.52 g, 4 mmol) in methanol (20 mL) at 0 °C. The mixture was stirred for 3 h at room temperature and then was hydrolyzed with water (20 mL). $Et_2O$ was added (20 mL) and the organic layer was separated, dried with magnesium sulfate, and the solvent removed under vacuum at 0 °C. Purification by silica gel chromatography (hexane/$Et_2O$, 8:1) afforded aldehyde **22** (595 mg, 75% yield). NMR (200 MHz, $CDCl_3$): $\delta$ = 9.71 (s, 1 H, *H*-C=O), 5.81 [br. s, 1 H, *H*C=C$(CH_3)_2$], 3.42 [d, $^3J$ = 3.7 Hz, 1 H, -O-*H*C-CH$(CH_3)_2$], 1.97–1.78 [m, 1 H, C*H*$(CH_3)_2$], 1.61 [s, 3 H, ($CH_3$)$(CH_3)$C=], 1.53 [s, 3 H, $(CH_3)$($CH_3$)C=], 1.11 [s, 3 H, C($CH_3$)$(CH_3)$], 1.08 [s, 3 H, C$(CH_3)$($CH_3$)] 0.91 [t, $^3J$ = 7.0 Hz, 6 H, CH($CH_3$)$_2$] ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 205.5, 142.9, 107.8, 91.7, 90.7, 51.1, 30.2, 21.9, 20.0, 18.8, 17.4, 14.9 ppm. IR (neat): $\tilde{\nu}$ = 2964, 2927, 2876, 1724, 1689, 1470, 1390, 1337, 1182, 1160, 1047, 989, 886, 821 cm$^{-1}$. MS (DCI/$NH_3$): *m*/*z* = 199 [MH]$^+$.

**Supporting Information** (see also the footnote on the first page of this article): General experimental procedures and characterization data for compounds **2a**,**b**, **14a**–**d**, **16aa**,**ab**, **16b**–**e**, and **22**, and the crystallographic data of compound **16ab** in CIF format.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Received: September 28, 2009
Published Online: January 4, 2010

  