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Reactivity of Aldehydes with Semi-Stabilised Arsonium Ylide Anions: Synthesis of Terminal (*E*)-1,3-Dienes

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Abstract: A study of the reactivity of semi-stabilised arsonium ylide anions in olefination reactions is presented. The different ylide anions were generated by the addition of *n*BuLi to various arsonium halide derivatives: $[Ph_2As(R)R']^+X^-$, where R and R′ are methyl, allyl, prenyl or benzyl groups. By using diallyldiphenylarsonium bromide (R = R′ = allyl) an olefination protocol was optimised allowing the efficient transformation of aliphatic aldehydes into terminal 1,3-dienes with a high selectivity for the *E* isomer (*E*/*Z* ratios ranging from 90:10 to 97:3). The olefination reactions of aldehydes with dissymmetric arsonium halides (R ≠ R′) are very chemoselective; with arsonium ylide anions the benzyl moiety is more reactive than the allyl moiety which is much more reactive than prenyl and methyl groups. Based on the experimental results, a mechanism is proposed for the reaction.

Keywords: 1,3-dienes · alkenes · arsenic · olefination · ylide anions · ylides

Introduction

The Wittig reaction, discovered in 1953,[1] is widely recognised as a good method for the olefination of aldehydes and ketones.[2] The stereochemistry of the olefination reaction is strongly dependent on the type of ylide and the exact reaction conditions. Reactive and stabilised phosphorus ylides can be structurally tuned to give either (*Z*) or (*E*)-olefins with high selectivity.[3] However, semi-stabilised (or moderately reactive) phosphorus ylides, bearing mildly conjugating substituents (α-1-alkenyl, α-1-alkynyl, α-1-aryl, α-1-heteroaryl, α-1-halo, α-1-alkoxy) often show no great stereoselective preference in the olefination of carbonyl compounds.[4] Efficient protocols for the construction of unsubstituted terminal (*E*)-1,3-dienes (R-CH=CHCH=CH_2) with semi-stabilised phosphorous ylides involve the use of α-deprotonated allylic diphenylphosphine oxides[5] and phosphonates.[6] With aliphatic aldehydes, these reagents lead to the formation of dienes having *E*/*Z* ratios in the range of 99:1 to 94:6 in moderate-to-good yields (45–78%). High *cis* selectivity in the synthesis of unsubstituted terminal 1,3-dienes was achieved by using *ortho*-substituted triphenylphosphorus ylides, albeit in low-to-moderate yields as a result of steric congestion (12%, *E*/*Z* 2:98, from heptanal).[7]

Arsonium ylides are interesting reagents for carbonyl olefination reactions as they are reported to be stronger nucleophiles than the corresponding phosphonium ylides. The increased negative charge density at the carbon centre of arsonium ylides as compared with phosphonium ylides accounts for the difference in reactivity observed.[8] It is known that the reactions of semi-stabilised arsonium ylides with carbonyl compounds result in a mixture of olefin and epoxide products.[9] Hsi and Koreeda have demonstrated that the use of LiHMDS or KHMDS in the generation of the ylide from allyltriphenylarsonium tetrafluoroborate directs the reaction towards the formation of epoxides or olefins, respectively.[10] By using KHMDS, unsubstituted terminal (*E*)-1,3-dienes were obtained in moderate-to-good yields from hindered aliphatic and aromatic aldehydes with no traces of the corresponding (*Z*)-1,3-dienes. In an attempt to improve the selectivity of the reaction of arsonium semi-stabilised ylides with aldehydes, our group reported the synthesis of the first arsonium ylide anion. The dibenzyl ylide anion obtained reacts with hexanal in THF/HMPA (5:1) and leads exclusively to alkene formation with an *E*/*Z* ratio of >99:1.[11] Similar results were obtained with benzyl(2-hydroxyethyl)arsonium ylide anions in the presence of HMPA.[12] The dibenzylarsonium ylide anion converts only one equivalent of aldehyde to the olefination product, whereas a similar phosphonium ylide anion converts two equivalents of aldehyde.[13] It was

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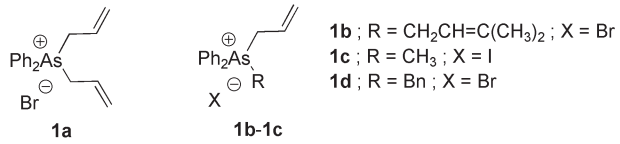
suggested that the arsonium oxide anion, produced by olefination of the first equivalent of aldehyde, reacts with a second equivalent of the aldehyde, but that the β-hydroxyarsine oxide intermediate formed does not react further to form an olefin.[11] This hypothesis was supported by the observation that lithiomethyl(diphenyl)arsine oxide reacts with aldehydes to give a stable β-hydroxyarsine oxide derivative.[14]

In the course of our studies it became apparent that an efficient method for the synthesis of a variety of unsubstituted terminal (*E*)-1,3-dienes was needed. In our exploration of new synthetic methodologies we investigated the use of arsonium allylic ylide anions. Herein is presented the synthesis of diallyldiphenylarsonium bromide **1a** and the study of the reactivity of the corresponding ylide anion in the presence of aldehydes (Scheme 1). The results show that terminal

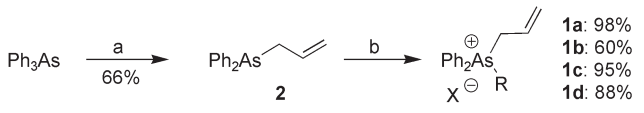


Scheme 1. Structure of diphenylarsonium halide derivatives **1a–d**.

(*E*)-1,3-dienes are obtained in good yields and with high selectivities (*E*/*Z* 90:10 to 97:3). Three other diphenylarsonium halides derivatives **1b–d** have also been synthesised and the reactivity of the corresponding ylide anions in olefination reactions studied (Scheme 1). The results show that **1b** and **1c** exclusively transfer the allyl chain to the aldehydes, whereas **1d** transfers the benzyl chain with high selectivity. Based on these observations and complementary deuteriation experiments, a mechanism is proposed for the reaction.

Results and Discussion

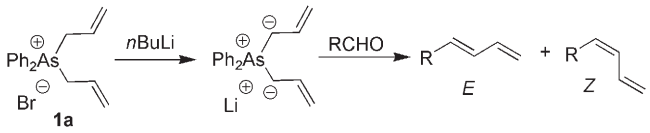
Synthesis of diphenylarsonium halide derivatives: Compounds **1a–d** were synthesised by following the strategy described by our group for the formation of dibenzyldiphenylarsonium bromide.[11] Starting from commercially available triphenylarsine, this strategy allows the synthesis in two steps of diphenylarsonium halide derivatives bearing two different substituents: $[Ph_2As(R)R']^+X^-$, where R and R′ are methyl, allyl, prenyl or benzyl groups (Scheme 2). In the



Scheme 2. Synthesis of diphenylarsonium halide derivatives **1a–d**. Reagents and conditions: a) 1) Li, THF, 12 h at RT; 2) *t*BuCl, THF, 2 h, 0 °C→RT; 3) allyl bromide, THF, 18 h, 0 °C→RT; b) RX, CH_3CN, 24 h at reflux for **1a**,**b**, at RT for **1c**,**d**.

first step, lithium diphenylarsine, which is prepared in situ by treatment of triphenylarsine with lithium in THF, is treated with allyl bromide, to afford allyldiphenylarsine (**2**). During the reaction, the addition of one equivalent of *tert*-butyl chloride is necessary to quench the phenyllithium formed as a side product. Compound **2** is purified by distillation under vacuum and should be kept under an inert atmosphere. In the second step, **2** is quaternised with an halogenated compound in acetonitrile to give **1a–d** in good yields.

Reactivity of diallyldiphenylarsonium bromide 1a with aldehydes: Compound **1a** was the first arsonium bromide that we synthesised with the aim of studying a new methodology for the synthesis of unsubstituted terminal (*E*)-1,3-dienes (R-CH=CHCH=CH_2) from aldehydes (Scheme 3).



Scheme 3. Synthesis of (*E*)-1,3-dienes from aldehydes and the ylide anion generated from **1a**.

Hexadecanal was used to optimise the experimental conditions. The treatment of one equivalent of **1a** with two equivalents of *n*BuLi and subsequent addition of the aldehyde led to the expected diene with an *E*/*Z* ratio of 90:10

Table 1. Optimisation of the conditions for the reactions between diphenylarsonium halide **1a** and hexadecanal.[a]

Entry	*n*BuLi [equiv]	Hexadecanal [equiv]	Yield[b] [%]	*E*/*Z* ratio
1	2	1	40	90:10
2	3	3	76	94:6
3	3.5	3.5	73	92:8

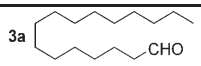
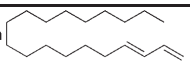
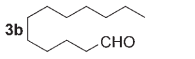
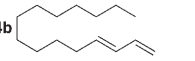
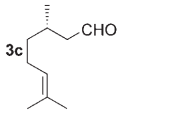
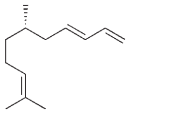
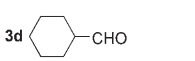
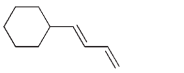
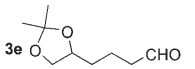
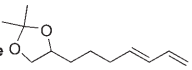
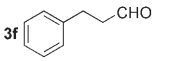
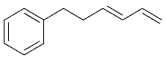
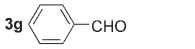
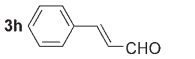
[a] Diphenylarsonium halide **1a** was treated with *n*BuLi in THF/HMPT (5:1) at −35 °C for 3 h before addition of hexadecanal at −78 °C. After 24 h at room temperature and hydrolysis, nonadeca-1,3-diene was extracted and purified as an inseparable mixture of *E* and *Z* isomers. [b] Yields are based on **1a**.

(Table 1, entry 1). The *E*/*Z* ratio and yield increased when three equivalents of *n*BuLi and aldehyde were used; nonadeca-1,3-diene was obtained in 76% yield and with a 94:6 *E*/*Z* ratio (Table 1, entry 2). Larger quantities of reactants led to a decrease in both yield and stereoselectivity (Table 1, entry 3). As described for other arsonium ylide anions, no reaction was observed in the absence of HMPT. Yields never exceeded 100% suggesting that **1a** can convert only one equivalent of aldehyde to the diene product; a similar reactivity was observed with the arsonium ylide anion produced from dibenzyldiphenylarsonium bromide.[11]

The quantitative formation of the arsonium ylide anion under the optimised experimental conditions was confirmed by deuteriation. The dark red solution resulting from the treatment of **1a** with three equivalents of *n*BuLi was quenched by the addition of DCl in D_2O; the ^1H NMR spectrum of the arsonium salt thus obtained (with a yield of 90% after purification) showed the insertion of one deuterium atom into the α position of each of the allylic groups of **1a**.

The reactivity of **1a** with other aldehydes was then studied. Hexadecanal and dodecanal reacted similarly, giving the terminal (*E*)-1,3-dienes **4a** and **4b** in good yields and with very good *E*/*Z* ratios (Table 2, entries 1 and 2). Steric hindrance at the α or β position of the aldehyde leads to a decrease in the reaction yield, but not in the stereoselectivity (Table 2, entries 3 and 4). Furthermore, the reaction worked equally well in the presence of a protected 1,2-diol (Table 2, entry 5). Reaction of **1a** with dihydrocinnamaldehyde led to the expected terminal 1,3-diene **4f**, albeit with a lower stereoselectivity (*E*/*Z* 90:10, entry 6). Finally, the use of benzaldehyde as well as *trans*-cinnamaldehyde led to complex mixtures from which the expected products could not be purified (Table 2, entries 7 and 8). These results are similar to the best results obtained with lithiated allylic phosphonates in terms of yield and selectivity.[5] The stereoselectivities are slightly lower than those obtained with α-deprotonated allylic diphenylphosphine oxides, although they lead to better yields.[6] No traces of epoxide products were detected in our olefination reactions, which can be the case when using semi-stabilised arsonium ylides.

Table 2. Reactions between diphenylarsonium halide **1a** and aldehydes.[a]

Entry	Aldehyde **3**	Product **4**	Yield[b] [%]	*E*/*Z* ratio
1			76	94:6
2			79	94:6
3			72	97:3
4			41	93:7
5			85	94:6
6			64	90:10
7		–	0	–
8		–	0	–

[a] Diphenylarsonium halide **1a** was treated with *n*BuLi (3 equiv) in THF/HMPT (5:1) at −35 °C for 3 h before addition of the aldehyde (3 equiv) at −78 °C. The reactions were stopped after 24 h at room temperature. [b] Yields correspond to purified compounds and are based on **1a**.

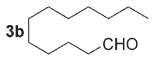
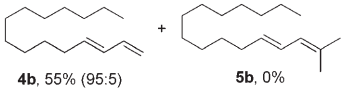
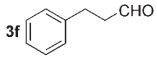
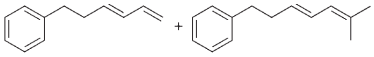
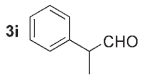
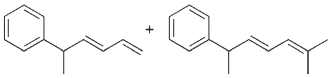
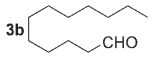
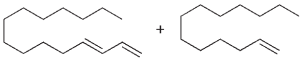
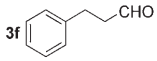
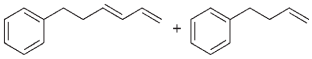
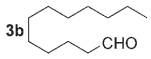
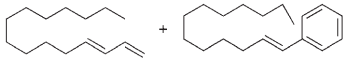
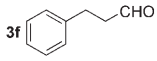
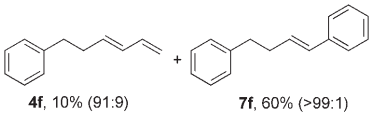
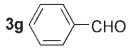
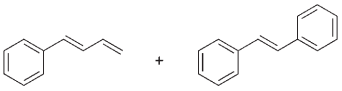
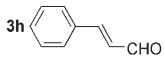
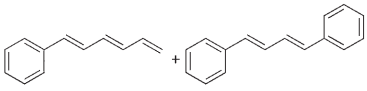
Reactivity of diphenylarsonium halide derivatives 1b–d: The results presented above suggest that diallyldiphenylarsonium bromide **1a**, in the presence of *n*BuLi, olefinates 1 equivalent of aldehyde. Therefore, only one of the two allylic groups on **1a** is transferred during the process; the second one does not give an olefination product. Arsonium halides **1b–d** bearing different substituents were then synthesised to study the chemoselectivity of their olefination reactions with aldehydes.

Following the experimental protocol optimised for **1a**, arsonium halides **1b–d** were treated with 3 equivalents of *n*BuLi and 3 equivalents of aldehydes (Table 3). Arsonium halides **1b** and **1c** reacted with excellent selectivities as only unsubstituted terminal 1,3-dienes (R-CH=CHCH=CH_2) were formed (Table 3, entries 1–5). These results demonstrate that aldehydes react with a very high selectivity with the deprotonated allyl chain of the ylide anions obtained from **1b** and **1c**. The deprotonated prenyl chain of the **1b** ylide anion and the deprotonated methyl group in the **1c** ylide anion do not produce olefination adducts. With **1b**,**c** the stereoselectivities of the olefination reactions are very high (*E*/*Z* > 98:2). Diene **4f** was obtained from dihydrocinnamaldehyde and bifunctional ylide anions **1b**,**c** with *E*/*Z* ratios higher than that obtained with the diallyl ylide anion **1a** (compare Table 2, entry 6 and Table 3, entries 2 and 5). In the olefination of dodecanal and dihydrocinnamaldehyde with **1d** the selectivity is lower as two different alkenes are isolated (Table 3, entries 6 and 7). The major products **7b** and **7f** result from the transfer of the deprotonated benzyl chain of the ylide anion **1d** to the aldehydes; the side-products **4b** and **4f** result from the transfer of the deprotonated allyl chain. In each case the (*E*)-alkene was formed with high stereoselectivity. Interestingly, with benzaldehyde, *trans*-stilbene **7g** was obtained as the only reaction product (Table 3, entry 8). This reflects the unreactivity of benzaldehyde with the ylide anion obtained from **1a** and the higher reactivity of the benzyl chain of **1d** relative to its allyl chain. Similarly, olefination of *trans*-cinnamaldehyde in the presence of **1d** led to diphenylbutadiene **7h** as the only reaction product (Table 3, entry 9). Products **7b** and **7f–h** were obtained as pure *E* isomers; this stereospecificity was previously observed with dibenzyldiphenylarsonium bromides.[11]

To conclude, our results highlight the following hierarchy in the reactivity of the ylide anion side chains with aldehydes: benzyl > allyl ⩾ prenyl and methyl.

Mechanistic hypotheses: Herein we present our hypotheses for the rationalisation of the reactivity of the semi-stabilised arsonium ylide anions **1a–d**. The selectivities observed for the reactions of aldehydes with the ylide anions generated from **1b–d** was not expected. Indeed, in dianionic systems, electrophiles are expected to react with the less stable anionic site.[15] By considering the ylide anions generated from **1b–d** as dianionic systems, it is reasonable to state that

Table 3. Reactions between diphenylarsonium halides **1b–d** and aldehydes.[a]

Entry	Aldehyde	Arsonium halide	Products, yield[b] (*E*/*Z* ratio)
1		**1b**	 **4b**, 55% (95:5) **5b**, 0%
2		**1b**	 **4f**, 55% (92:8) **5f**, 0%
3		**1b**	 **4i**, 70% (95:5) **5i**, 0%
4		**1c**	 **4b**, 50% (95:5) **6b**, 0%
5		**1c**	 **4f**, 55% (96:4) **6f**, 0%
6		**1d**	 **4b**, 29% (98:2) **7b**, 63% (>99:1)
7		**1d**	 **4f**, 10% (91:9) **7f**, 60% (>99:1)
8		**1d**	 **4g**, 0% **7g**, 56% (>99:1)
9		**1d**	 **4h**, 0% **7h**, 53% (>99:1)

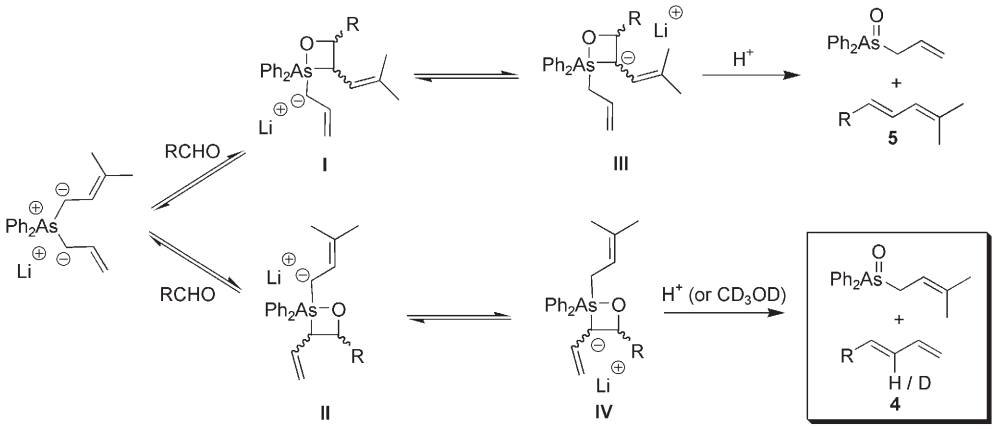
[a] Diphenylarsonium halides **1b–d** were treated with *n*BuLi (3 equiv) in THF/HMPT (5:1) at −35 °C for 3 h before addition of the aldehyde (3 equiv) at −78 °C. The reactions were stopped after 24 h at room temperature. [b] Yields correspond to purified compounds (0 % is indicated if the compound was not formed in the reaction) and are based on **1b–d**.

1) for **1b**, the allyl anion is more stable than the prenyl anion (electron-donating effects of the two methyl groups), 2) for **1c**, the allyl anion is more stable than the methyl anion and 3) for **1d**, the benzyl anion is more stable than the allyl anion (electron delocalisation onto the phenyl ring). In each case the major olefination adduct observed results from the reaction of the aldehyde with the more stable anionic site of the ylide anion.

Our first mechanistic hypothesis was based on the reactivities of the phosphonium ylide anions[13] and on the previous study of the dibenzylarsonium ylide anion.[11] As presented in the introduction of this report, it is generally accepted that in both cases a first equivalent of aldehyde reacts with the ylide anion and leads to an olefination adduct and to a phosphonium or arsonium oxide anion. These intermediates then react with a second equivalent of aldehyde to give a β-hydroxyphosphine oxide or a β-hydroxyarsine oxide. In the latter case, the intermediate is expected to be too stable to evolve further and generate an olefin adduct.[14] Despite several attempts we could not trap or observe a β-hydroxyarsine oxide intermediate in the reaction media. When **1a** or **1b** was used the only arsenic-based reaction adducts that we could detect were allyldiphenylarsine oxide and prenyldiphenylarsine oxide, respectively, which were not expected on the basis of the initial mechanistic hypothesis. These observations suggest that the mechanism involved in the reactions of semi-stabilised arsonium ylide anions **1a–d** with aldehydes is different to the one involved in the reaction of the corresponding phosphonium species.

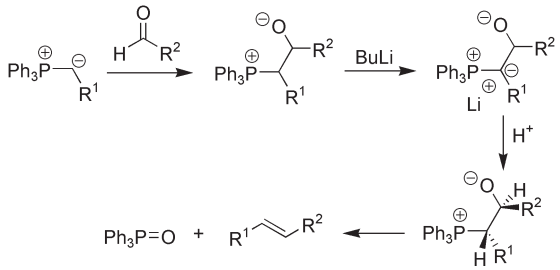
For reasons of clarity our mechanistic hypothesis will be illustrated with the arsonium bromide **1b** (Scheme 4). The initial attack of the arsonium ylide anion on the carbonyl carbon atom of the aldehyde produces oxaarsetane **I** or **II**. Oxaarsetane **I** is favoured kinetically and thermodynamically because the residual anionic charge in **I** is stabilised more than the residual anionic charge in **II**. Intermediate **I** should lead to the olefination adduct **5**, but this adduct was not observed experimentally. To rationalise our results we suggest that oxaarsetane **I** can revert back to the ylide anion and aldehyde and that **II** might evolve into a more stable intermediate. We suggest that oxaarsetanes **I** and **II** are in equilibrium with the intermediates **III** and **IV** through an intramolecular transmetallation reaction. This process is facilitated thanks to the high acidity of the allylic protons in semi-stabilised ylide anions.[16] Such an equilibrium was presented by McKenna and Walker in order to rationalise the high *E*/*Z* ratios obtained in the reactions of aldehydes with semi-stabilised phosphonium ylide anions (an equilibrium forms between *cis*- and *trans*-oxaphosphetane anions).[13]

Intermediate **IV** is expected to be more stable than **III**; the anionic charge on **III** is destabilised by the electron-donating effects of the two methyl groups of the prenyl chain. Intermediate **IV** would naturally lead, after protonation, to the unsubstituted terminal 1,3-diene **4** and to prenyldiphenylarsine oxide, which was detected as a major side product in our reaction mixtures. According to this mechanism the formation of the arsine oxide from **IV** prevents the olefination of a second equivalent of aldehyde.



Scheme 4. Mechanism proposed for aldehyde olefination by the ylide anion generated from **1b**.

Concerning the stereoselectivity of the olefination process, intermediates **III** and **IV** can be compared with the β-oxidophosphonium ylides obtained in SCOOPY-type reactions (α-substitution plus carbonyl olefination via β-oxido phosphorus ylides).[17] In this procedure a β-oxidophosphonium, resulting from the addition of a phosphonium ylide to an aldehyde, is deprotonated by a strong base to give a stable β-oxidophosphonium ylide which is subsequently trapped by an electrophile (Scheme 5). If a proton donor is used, the β-oxidophosphonium ylide is capable of stereospecific protonation to form the *threo* betaine which is the precursor of the (*E*)-olefin. Similarly, it can be expected that protonation of **III** or **IV** would lead to the (*E*)-olefin with high stereoselectivity, which rationalises our experimental observations.



Scheme 5. Illustration of the SCOOPY-type mechanism for the synthesis of (*E*)-olefins from a phosphonium ylide and an aldehyde.

To validate our mechanistic hypotheses, we made several attempts to trap intermediate **IV** with a deuterium donor. The best result was obtained when arsonium bromide **1b** was treated at −35 °C with *n*BuLi (3 equiv) in THF for 3 h, followed by the addition of dihydrocinnamaldehyde (3 equiv) at −78 °C. After 2 h at −78 °C, the solution was quenched with deuteriated methanol. After column chromatography, the expected (*E*)-1,3-diene **4f** was obtained with a yield of 21 %. ^{1}H NMR analysis showed the insertion of deuterium in the expected position of the 1,3-diene moiety of **4f** with a 64 % deuterium/hydrogen ratio (Figure 1, bottom). This result is indirect, but strong proof of the formation of intermediate **IV** in the reaction process (Scheme 4). Other similar deuteriation experiments were performed, but with longer reaction times at −78 °C or room temperature using a variety of deuterium donors (D_2O, DCl, CD_3OD). These experiments gave **4f** in higher yields, but with lower deuterium insertion, which suggests that intermediate **IV** was neutralised in the reaction mixture. We have not yet determined the mechanism for the in situ neutralisation of intermediate **IV**; the use of [D_8]THF

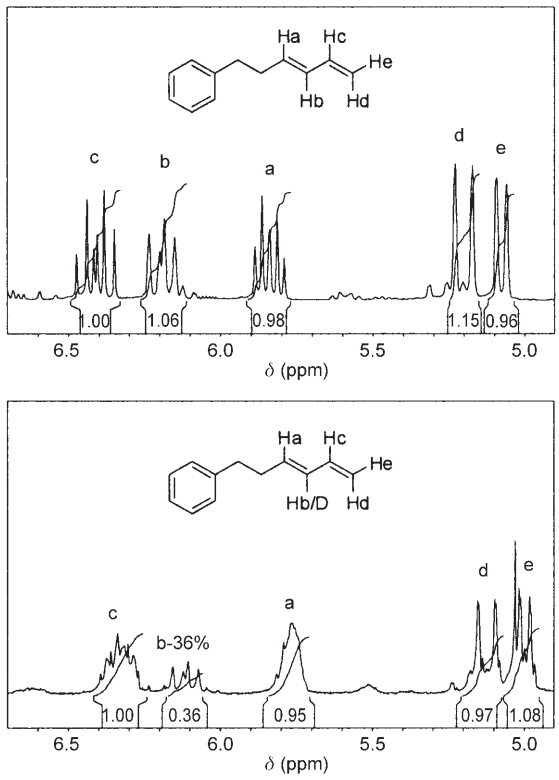


Figure 1. ^{1}H NMR spectra of hydrogenated (top) and deuteriated (bottom) **4f** (*E*/*Z* 92:8).

did not lead to the deuteriation of compound **4**, the excess of aldehyde might be responsible for the protonation of **IV**.

In the optimised experimental procedure three equivalents of *n*BuLi are used; the excess *n*BuLi probably reacts with the excess aldehyde although it could also participate in the deprotonation of intermediate **II** (as in a SCOOPY-type reaction) leading to a β-oxidoarsonium ylide anion. We consider this chemical pathway unlikely because, in the various deuteriation experiments, no deuterium atom insertion was detected in the prenylarsine oxide produced.

Conclusion

In conclusion, we have proposed a new protocol for the synthesis of unsubstituted terminal (*E*)-1,3-dienes from aldehydes using semi-stabilised arsonium ylide anions. The ylide anion was generated from diallyldiphenylarsonium bromide **1a** and allowed the olefination of one equivalent of aldehyde. Starting from various aliphatic aldehydes the dienes were obtained in good yields and with high stereoselectivities (*E*/*Z* ratios ranging from 90:10 to 97:3). The study of arsonium semi-stabilised ylide anions bearing two different anionic substituents (methyl, allyl, prenyl or benzyl) allowed us to propose a mechanism for the olefination reaction. The key step of this mechanism is an intramolecular transmetallation process leading to intermediate **IV** which is closely related to the β-oxidophosphonium ylides observed in SCOOPY-type reactions. Stereospecific protonation of **IV** leads to the formation of an *E* olefination adduct and an arsine oxide. The mechanism proposed for this reaction is different to the mechanism reported for the olefination of carbonyl compounds by phosphonium ylide anions.

Experimental Section

General methods: All experiments were carried out under argon. Commercially available aldehydes were freshly distilled prior to use. THF and diethyl ether were distilled from sodium and benzophenone. HMPT was distilled over calcium hydride and stored over 4 Å molecular sieves under argon. Acetonitrile and DCM were distilled over sodium hydride. TLC was performed on Merck silica gel $60F_{54}$ and were detected by using UV light at 254 nm and vanilline. Silica gel (Merck 60, 40–63 μm) was used for flash column chromatography. NMR spectra were recorded at 200 or 300 MHz for ^{1}H NMR and 50 or 75 MHz for ^{13}C NMR, using chloroform as the internal reference (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). Infra-red spectra (KBr discs or CsI films) were recorded on a Perkin-Elmer apparatus (1600 FT-IR). Fusion points were recorded on a Reichert-Jung (Thermo Galen) apparatus. Elemental analyses were performed by the Service Central d'Analyses du CNRS at Vernaison (France). The *E*/*Z* ratios were calculated from the integration values of the ^{1}H NMR spectra.

(Prop-2-enyl)diphenylarsine (2): Lithium (3.4 g, 0.49 mol) was added to a solution of triphenylarsine (50 g, 0.16 mol) in THF (250 mL). After a few minutes, the solution became dark red and stirring was maintained for 24 h. Excess lithium was then removed by cannulating the solution into another flask under argon. A solution of *tert*-butyl chloride (18 mL, 0.16 mol) in THF (40 mL) was added dropwise at 0 °C to destroy the phenyllithium formed during the reaction. The mixture was stirred for 2 h at room temperature and became pale red. Then allyl bromide (29.7 mL, 0.34 mol) in THF (40 mL) was added dropwise. The pale yellow solution obtained was stirred for 18 h at room temperature. The mixture was then diluted with diethyl ether and hydrolyzed with water. The organic extract was washed with brine, dried with magnesium sulfate and concentrated under vacuum. The crude product was then distilled under reduced pressure to afford **2** (29.06 g, 66 %) as a colourless oil. B.p. 109–113 °C/0.1 mmHg. ^{1}H NMR (200 MHZ, $CDCl_3$): $\delta = 7.50$–7.30 (m, 10H), 6.0–5.75 (m, 1H), 5.04–4.94 (m, 2H), 2.87 ppm (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 140.2$, 134.0, 133.0, 128.4, 116.1, 32.8 ppm; IR (CsI): $\tilde{\nu} = 3068$, 3052, 2971, 2911, 1581, 1481, 1434, 1075, 735 cm^{-1}.

Diallyldiphenylarsonium bromide (1a): A solution of **2** (1.23 g, 4.55 mmol) and allyl bromide (1.14 mL, 13.20 mmol) in acetonitrile (2.5 mL) was refluxed for 24 h. The solvent was removed under vacuum and the solid obtained was dissolved in dry DCM. The reaction product was precipitated by addition of dry diethyl ether to afford **1a** (1.74 g, 98 %) as white crystals. F.p. 142–144 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 7.83–7.60 (m, 10H), 5.88–5.65 (m, 1H), 5.45 (d, $J = 16.9$ Hz, 1H), 5.26 (d, $J = 9.9$ Hz, 1H), 4.44 ppm (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 133.6$, 132.9, 130.3, 124.7, 124.6, 120.2, 113.9, 29.8 ppm; IR (KBr): $\tilde{\nu} = 3054$, 3010, 2934, 2881, 2799, 1634, 1436, 1405, 1202, 1084, 990, 743 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}AsBr$ (391.18): C 55.27, H 5.15, As 19.15, Br 20.43; found: C 55.21, H 5.21, As 18.65, Br 20.45.

(3-Methylbut-2-ene)(prop-2-enyl)diphenylarsonium bromide (1b): A solution of **2** (1.21 g, 4.47 mmol) and 1-bromo-3-methylbut-2-ene (1.51 mL, 12.98 mmol) in acetonitrile (2.5 mL) was refluxed for 24 h. The solvent was removed under vacuum and the solid obtained was dissolved in dry DCM. The reaction product was precipitated by addition of dry diethyl ether to afford **1b** (1.12 g, 60 %) as white crystals. F.p. 122–124 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.80$–7.54 (m, 10H), 5.83–5.65 (m, 1H), 5.45 (d, $J = 16.9$ Hz, 1H), 5.28 (d, $J = 9.9$ Hz, 1H), 5.14 (t, $J = 8.6$ Hz, 1H), 4.47 (d, $J = 7.7$ Hz, 2H), 4.40 (d, $J = 8.6$ Hz, 2H), 1.62 (s, 3H), 1.37 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 142.6$, 133.0, 132.6, 129.8, 124.5, 123.9, 120.0, 109.2, 29.5, 25.6, 25.2, 18.0 ppm; IR (KBr): $\tilde{\nu} = 3016$, 2931, 2903, 1654, 1636, 1438, 938, 746 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{24}AsBr$ (419.23): C 57.30, H 5.77, As 17.87, Br 19.06; found: C 57.01, H 5.93, As 17.78, Br 18.88.

Methyl(prop-2-enyl)diphenylarsonium iodide (1c): A solution of **2** (1.19 g; 4.44 mmol) and methyl iodide (0.80 mL, 12.86 mmol) in acetonitrile (2.5 mL) was stirred at room temperature for 24 h. The solvent was removed under vacuum and the solid obtained was dissolved in dry DCM. The reaction product was precipitated by addition of dry diethyl ether to afford **1c** (1.73 g, 95 %) as white crystals. F.p. 141–142 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.87$–7.58 (m, 10H), 5.89–5.71 (m, 1H), 5.64 (d, $J = 16.8$ Hz, 1H), 5.35 (d, $J = 9.8$ Hz, 1H), 4.35 (d, $J = 3.3$ Hz, 2H), 4.40 (d, $J = 8.6$ Hz, 2H), 2.79 ppm (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 133.6$, 132.1, 130.4, 125.0, 124.2, 121.5, 30.4, 7.7 ppm; IR (KBr): $\tilde{\nu} = 3054$, 3018, 2971, 2936, 2895, 1632, 1438, 1338, 1201, 997, 747 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{18}AsI$ (412.14): C 46.63, H 4.40, As 18.18, I 30.79; found: C 46.56, H 4.56, As 18.00, I 30.70.

(Benzyl)(prop-2-enyl)diphenylarsonium bromide (1d): A solution of **2** (1.26 g, 4.68 mmol) and benzyl bromide (1.61 mL, 13.57 mmol) in acetonitrile (2.5 mL) was stirred at room temperature for 24 h. The solvent was removed under vacuum and the solid obtained was dissolved in dry DCM. The reaction product was precipitated by addition of dry diethyl ether to afford **1d** (1.82 g, 88 %) as white crystals. F.p. 159–161 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.70$–7.46 (m, 10H), 7.27–7.12 (m, 5H), 5.78–5.59 (m, 1H), 5.38 (d, $J = 16.8$ Hz, 1H), 5.24 (d, $J = 9.9$ Hz, 1H), 5.09 (s, 2H), 4.41 ppm (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ 133.1, 132.8, 129.8, 128.7, 128.3, 127.7, 124.3, 124.0, 119.7, 32.0, 28.9 ppm; IR (KBr): $\tilde{\nu} = 3048$, 3017, 2932, 2880, 2802, 1636, 1605, 1492, 1323, 995, 744 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{22}AsBr$ (441.23): C 59.89, H 5.03, As 16.98, Br 18.11; found: C 59.25, H 5.04, As 16.30, Br 17.95.

General procedure for the olefination reaction: The arsonium salt **1a** (0.50 g, 1.28 mmol) was suspended in THF (25 mL) and HMPT (5 mL) −35 °C.[18] Then a solution of *n*-butyllithium (1.6 M in hexanes, 2.55 mL, 4.08 mmol)[19] was added dropwise and the dark red mixture was stirred at −35 °C for 3 h. The solution was then cooled to −78 °C and a solution of aldehyde (4.08 mmol) in THF (9 mL) was added dropwise. After

10 min at −78 °C, the solution was allowed to warm to room temperature and stirring was continued for 24 h. Diethyl ether was then added and the reaction mixture was hydrolyzed with water. The organic extracts were washed with brine, dried with magnesium sulfate and concentrated under vacuum. The crude mixture was then purified on silica gel using cyclohexane/diethyl ether (95:5) as eluent.

(*E*)-Nonadeca-1,3-diene (4a): Compound **4a** was obtained from **1a** and palmitaldehyde (**3a**) in 76% yield as a mixture of isomers (*E*/*Z* 94:6) following the general olefination procedure. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.76–6.56 (m, 0.06H), 6.32 (ddd, J = 17.0, 10.2, 10.1 Hz, 0.94H), 6.06 (dd, J = 15.2, 10.2 Hz, 1H), 5.71 (dt, J = 15.2, 6.9 Hz, 0.94H), 5.37–5.59 (m, 0.06H), 5.09 (dd, J = 17.0, 1.8 Hz, 1H), 4.96 (dd, J = 10.1, 1.8 Hz, 1H), 2.30–2.03 (m, 2H), 1.50–1.10 (m, 26H), 0.87 ppm (t, J = 6.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.4, 135.6, 132.4, 130.8, 116.6, 114.5, 32.6, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 27.8, 22.7, 14.1 ppm; IR (CsI): $\tilde{\nu}$ = 3086, 2925, 2854, 1795, 1652, 1603, 1464, 1377, 1001, 949, 722 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{36}$ (264.50): C 86.28, H 13.72; found: C 86.15, H 13.70.

(*E*)-Pentadeca-1,3-diene (4b): Compound **4b** was obtained from **1a** and dodecanal (**3a**) in 79% yield as a mixture of isomers (*E*/*Z* 94:6) following the general olefination procedure. Comparison of the spectral data with the literature[20] confirmed the identity of compound **4b**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.76–6.56 (m, 0.06H), 6.33 (ddd, J = 17.0, 10.2, 10.1 Hz, 0.94H), 6.06 (dd, J = 15.2, 10.2 Hz, 1H), 5.71 (dt, J = 15.2, 6.9 Hz, 0.94H), 5.59–5.37 (m, 0.06H), 5.09 (dd, J = 17.0, 1.8 Hz, 1H), 4.95 (dd, J = 10.1, 1.8 Hz, 1H), 2.30–2.03 (m, 2H), 1.50–1.10 (m, 18H), 0.89 ppm (t, J = 6.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.4, 135.6, 133.1, 132.4, 130.8, 116.6, 114.5, 32.6, 31.9, 29.6, 29.5, 29.4, 29.2, 27.8, 22.7, 14.1 ppm; IR (CsI): $\tilde{\nu}$ = 3086, 2925, 2854, 1793, 1652, 1603, 1465, 1378, 949, 722 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{28}$ (208.39): C 86.46, H 13.54; found: C 86.39, H 13.51.

(*S*,3*E*)-6,10-Dimethylundeca-1,3,9-triene (4c): Compound **4c** was obtained from **1a** and (−)-1-citronellal (**3c**) in 72% yield as a mixture of isomers (*E*/*Z* 97:3) following the general olefination procedure. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.34 (ddd, J = 16.8, 10.2, 10.1 Hz, 1H), 6.05 (dd, J = 15.1, 10.2 Hz, 1H), 5.71 (dt, J = 15.1, 7.6 Hz, 1H), 5.14–5.04 (m, 2H), 4.96 (dd, J = 9.9, 1.7 Hz, 1H), 2.23–1.85 (m, 4H), 1.69 (s, 3H), 1.61 (s, 3H), 1.43–1.10 (m, 3H), 0.88 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.4, 134.0, 132.2, 131.1, 124.9, 114.5, 40.0, 36.8, 32.9, 25.7, 19.5, 17.6 ppm; IR (CsI): $\tilde{\nu}$ = 3059, 2962, 2921, 1798, 1651, 1602, 1455, 1377, 1260, 1002, 897, 739 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{22}$ (178.32): C 87.56, H 12.44; found: C 87.55, H 12.39.

(3*E*)-Buta-1,3-dienylcyclohexane (4d): Compound **4d** was obtained from **1a** and cyclohexanecarbaldehyde (**3d**) in 41% yield as a mixture of isomers (*E*/*Z* 93:7) following the general olefination procedure. Comparison of the spectral data with the literature[21] confirmed the identity of compound **4d**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.78–6.59 (m, 0.07H), 6.31 (ddd, J = 16.8, 10.2, 10.1 Hz, 0.93H), 6.03 (dd, J = 15.2, 10.2 Hz, 1H), 5.66 (dd, J = 15.2, 6.8 Hz, 0.93H), 5.40–5.22 (m, 0.07H), 5.10 (dd, J = 16.8, 1.6 Hz, 1H), 4.97 (dd, J = 10.1, 1.6 Hz, 1H), 2.03–1.94 (m, 1H), 1.86–1.56 (m, 5H), 1.37–1.00 ppm (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.1, 139.3, 137.7, 132.6, 128.4, 114.6, 40.6, 36.7, 33.3, 32.8, 26.2, 26.0, 25.9 ppm; IR (CsI): $\tilde{\nu}$ = 2926, 2852, 1651, 1604, 1448, 1002, 950, 893 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{16}$ (136.24): calcd C 88.16, H 11.84; found: C 88.05, H 11.82.

(4*E*)-4-Hepta-4,6-dienyl-2,2-dimethyl-1,3-dioxolane (4e): Compound **4e** was obtained from **1a** and 5,6-*O*-isopropylidenehexanal (**3e**)[22] in 85% yield as a mixture of isomers (*E*/*Z* 94:6) following the general olefination procedure. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.75–6.54 (m, 0.06H), 6.28 (ddd, J = 16.8, 10.3, 10.2 Hz, 0.94H), 6.03 (dd, J = 15.2, 10.2 Hz, 1H), 5.70 (dt, J = 15.2, = 6.8 Hz, 0.94H), 5.55–5.37 (m, 0.06H), 5.09 (dd, J = 16.8, 1.7 Hz, 1H), 4.94 (dd, J = 10.3, 1.7 Hz, 1H), 4.13–4.00 (m, 2H), 3.55–3.46 (m, 1H), 2.20–2.05 (m, 2H), 1.69–1.30 ppm (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.1, 134.6, 132.1, 132.0, 131.4, 117.1, 114.9, 108.7, 75.9, 72.1, 69.4, 66.8, 33.1, 32.7, 32.4, 27.6, 26.9, 25.7, 25.3, 25.1 ppm; IR (CsI): $\tilde{\nu}$ = 3085, 2986, 2935, 2865, 1802, 1732, 1651, 1603, 1456, 1370, 1248, 1157, 859, 737 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{20}O_2$ (196.29): C 73.43, H 10.27; found: C 73.41, H 10.26.

(3*E*)-Hexa-3,5-dienylbenzene (4f): Compound **4f** was obtained from **1a** and 3-phenylpropanal (**3f**) in 64% yield as a mixture of isomers (*E*/*Z* 90:10) following the general olefination procedure. Comparison of the spectral data with the literature[23] confirmed the identity of compound **4f**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.23 (m, 5H), 6.83–6.63 (m, 0.10H), 6.41 (ddd, J = 16.8, 11.6, 10.2 Hz, 0.90H), 6.19 (dd, J = 15.0, 11.6 Hz, 1H), 5.84 (dt, J = 15.0, 6.7 Hz, 0.90H), 5.67–5.43 (m, 0.10H), 5.20 (dd, J = 16.8, 1.7 Hz, 1H), 5.07 (dd, J = 10.2, 1.7 Hz, 1H), 2.82 (t, J = 9.7 Hz, 2H), 2.68–2.43 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.8, 137.2, 134.2, 132.2, 131.5, 130.8, 128.4, 128.3, 125.9, 117.1, 115.0, 35.9, 35.7, 34.3, 29.5 ppm; IR (CsI): $\tilde{\nu}$ = 3061, 3026, 2927, 1710, 1602, 1495, 1089, 904, 747 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{14}$ (158.25): C 91.08, H 8.92; found: C 90.97, H 8.89.

(2*E*)-(1-Methylpenta-2,4-dienyl)benzene (4i): Compound **4h** was obtained from **1b** and 2-methyl-2-phenylethanal (**3i**) in 70% yield as a mixture of isomers (*E*/*Z* 95:5) following the general olefination procedure. Comparison of the spectral data with the literature[24] confirmed the identity of compound **4i**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.19 (m, 5H), 6.95–6.77 (m, 0.05H), 6.44 (ddd, J = 16.8, 10.1, 10.0 Hz, 0.95H), 6.19 (dd, J = 15.2, 10.0 Hz, 1H), 5.99 (dd, J = 15.2, 6.5 Hz, 0.95H), 5.67 (m, 0.05H), 5.24 (dd, J = 16.8, 1.7 Hz, 1H), 5.11 (dd, J = 10.1, 1.7 Hz, 1H), 4.14–3.98 (m, 0.05H), 3.70–3.55 (m, 0.95H), 1.52 ppm (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 139.6, 137.3, 129.7, 128.0, 127.3, 126.3, 115.8, 42.3, 21.2 ppm; IR (CsI): $\tilde{\nu}$ = 3064, 3027, 2928, 1802, 1602, 1492, 1451, 1008, 905, 699 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{14}$ (158.25): C 91.08, H 8.92; found: C 91.05, H 8.90.

(*E*)-1-Phenyltridec-1-ene (7b): Compound **7b** was obtained from **1d** and dodecanal (**3b**) in 63% yield as the pure *E* isomer following the general olefination procedure. Comparison of the spectral data with the literature[25] confirmed the identity of compound **7b**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.18 (m, 5H), 6.41 (d, J = 15.3 Hz, 1H), 6.25 (dt, J = 15.3, 6.9 Hz, 1H), 2.23 (q, J = 6.9 Hz, 2H), 1.51–1.31 (m, 20H), 0.93 ppm (t, J = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.3, 131.6, 130.0, 128.8, 127.1, 126.2, 33.4, 32.3, 30.0, 29.9, 29.7, 29.6, 23.0, 14.5 ppm; IR (CsI): $\tilde{\nu}$ = 3081, 3060, 3025, 2955, 2924, 2853, 1494, 1466, 962, 742, 691 cm^{-1}.

(1*E*)-1,4-Diphenylbut-1-ene (7f): Compound **7f** was obtained from **1d** and 3-phenylpropanal (**3f**) in 60% yield as the pure *E* isomer following the general olefination procedure. Comparison of the spectral data with the literature[26] confirmed the identity of compound **7f**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.51–7.27 (m, 10H), 6.57 (d, J = 15.9 Hz, 1H), 6.40 (dt, J = 15.9, 6.3 Hz, 1H), 2.94 (t, J = 8.0 Hz, 2H), 2.73–2.62 ppm (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.7, 137.7, 130.4, 130.0, 128.5, 128.4, 126.9, 126.0, 125.9, 35.9, 34.8 ppm; IR (film): $\tilde{\nu}$ = 3058, 3025, 2933, 2850, 1945, 1872, 1748, 1651, 1599, 1494, 1457, 1433, 1071, 964, 739 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{16}$ (208.31): C 92.26, H 7.74; found: C 92.05, H 7.72.

***trans*-Stilbene (7g)**: Compound **7g** was obtained from **1d** and benzaldehyde (**3g**) in 56% yield as the pure *E* isomer following the general olefination procedure. Comparison of the spectral data with the Aldrich database confirmed the identity of compound **7g**. ^{1}H NMR (300 MHZ, $CDCl_3$): δ = 7.45 (d, J = 7.3 Hz, 4H), 7.33–7.19 (m, 6H), 7.05 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3, 128.7, 128.6, 127.6, 126.5 ppm.

***trans*,*trans*-1,4-Diphenylbuta-1,3-diene (7h)**: Compound **7h** was obtained from **1d** and cinnamaldehyde (**3h**) in 53% yield as the pure *E* isomer following the general olefination procedure. Comparison of the spectral data with the Aldrich database confirmed the identity of compound **7g**. ^{1}H NMR (300 MHZ, $CDCl_3$): δ = 7.46 (t, J = 7.2 Hz, 4H), 7.35 (d, J = 7.2 Hz, 4H), 7.27–722 (m, 2H), 7.02–6.93 (m, 2H), 6.74–6.64 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 133.0, 129.4, 128.8, 127.7, 126.5 ppm.

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