Wittig Ethylidenation of Ketones: Reagent Control of *Z*/*E* Selectivity

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Disubstituted alkenes can be prepared from aldehydes with excellent stereocontrol using the conventional Wittig reagent $Ph_3P{=}CHCH_3$ (*Z*-selective)[1,2] or the phosphole-derived reagents 1 (DBP ylides[3a] and 2 (BTP ylides)[3b] (*E*-selective) (Chart I). Selective Wittig reactions of ketones have also been reported, but here the results appear to be substrate-dependent.[4,5] Still and co-workers have demonstrated that excellent levels of *Z*-selectivity are possible in the ethylidenation reactions of acyclic α-alkoxy ketones $RC(O)CH_2OR'$ with $Ph_3P{=}CHCH_3$ (R = *n*-alkyl).[5a] Similar *Z*-selectivity is observed with cyclic α-alkoxy ketones,[5b] with 17-keto steroids (C_α = quaternary carbon; $C_{\alpha'}$ = ring methylene carbon),[4a] and with certain other α-substituted ketones,[4b,c] including the following example from our laboratory. Thus, 3-methyl-2-butanone (3) reacted with lithium-free $Ph_3P{=}CH(CH_2)_2Ph$, prepared from 4 and KHMDS (potassium hexamethyldisilazide), to give 5, 81:19 *Z*:*E* based on ^{13}C evidence. These examples resemble the selectivity pattern for reactions of alkylidenetriphenylphosphoranes with simple aldehydes.[1]

There are other reports that describe *E*-selective or nonselective reactions between seemingly analogous ylides $Ph_3P{=}CHR$ and ketones.[4d-g] We suspected that variations in experimental conditions might be responsible for the puzzling data, and we therefore examined the ethylidenation reactions of a series of simple ketones. Both the conventional reagent $Ph_3P{=}CHCH_3$, and also the phosphole-derived ylides 1 and 2 were used in the present study, all under standardized lithium-free conditions. The results (Table I) reveal that surprising levels of selectivity are often possible in the trisubstituted alkene products and that 1 and 2 are consistently *E*-selective. On the other hand, the $Ph_3P{=}CHCH_3$ data follow no simple pattern with regard to *Z*:*E* selectivity.

Table I. *Z*:*E* Ratios for Ketone Wittig Reactions[a]

ketone	$Ph_3P{=}CHCH_3$	EtDBP=CHCH₃ (1)	PhBTP=CHCH₃ (2)
6	96:4 (68%)	18:82 (70%)	9:91 (69%)
7	78:22 (68%)	4:96 (59%)	9:91 (69%)
8	77:23 (70%)	12:88 (67%)	2:98 (68%)
9	14:86 (82%)	11:89 (73%)	6:94 (70%)
10[b]	7:93 (80%)	10:90 (89%)	
11[c]	29:71 (38%)[d]	<2:98 (67%)	
12	94:6[e]	13:87 (60%)	35:65 (73%)
13	97:3[e]	12:88 (67%)	25:75 (80%)

[a] Product ratios were determined by NMR analysis of *E*/*Z* alkene mixtures. Yields are based on alkene isolated by chromatography. [b] Reference 10. [c] Reference 11. [d] This experiment was conducted with an ylide concentration of about 0.2 M. The optimized method was not tried due to poor *E*:*Z* selectivity. [e] These ratios are taken from ref 5.

The procedure for ketone olefination was based on literature precedents[4a,d,6] and on our preliminary experiments using ketone 3 and $Ph_3P{=}CHCH_2CH_2Ph$. When the ylide was made from 4 and butyllithium (ca. 0.2 M in THF), the reaction with 3 at rt formed a precipitate. Prolonged heating at 60 °C (24 h) produced only traces (<5%) of alkene 5. When the same experiment was performed using KHMDS as the base to generate the ylide (0.2 M in THF), the ylide color faded slowly overnight at 60 °C and the alkene was formed normally (*Z*:*E* = 73:27, yield 53%). A similar experiment was then performed using a 0.75 M solution of the ylide (from 1.1 equiv of 4 and 1.0 equiv of KHMDS). The ylide slurry was stirred at −78 °C and 0.8–0.9 equiv of the ketone was added as a neat liquid to avoid diluting the ylide, and the cooling bath was then removed. As the pot temperature approached 20 °C, the ylide color began to fade noticeably, and >80% conversion was observed within 2 h at room temperature. The isolated yield of 5 improved to 71% after chromatography (*Z*:*E* = 81:19).

Difficult ketone olefinations have been reported that include most of the key features of the above-optimized procedure.[4a,d,6] The prior workers had recommended the use of 0.8–1.0 M ylide, sodium or potassium bases, excess phosphonium salt over the base, and excess ylide over the ketone. For the most hindered substrates, Fitjer *et al.* recommend the added precautions of preparing the ylide with KO-*t*-Bu in ether or benzene followed by removal of nearly all of the volatile solvents. The ketone is then added to the heated ylide slurry, resulting in good yields even with ketones that contain one or two quaternary α-carbons.[6a] Some of the above precautions were not essential in our experiments, but the absence of lithium ion[7] and the high concentration of ylide[4c,d,6] were absolutely crucial. We have not established whether lithium ion acts simply by catalyzing enolization or whether it interferes

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Chart I

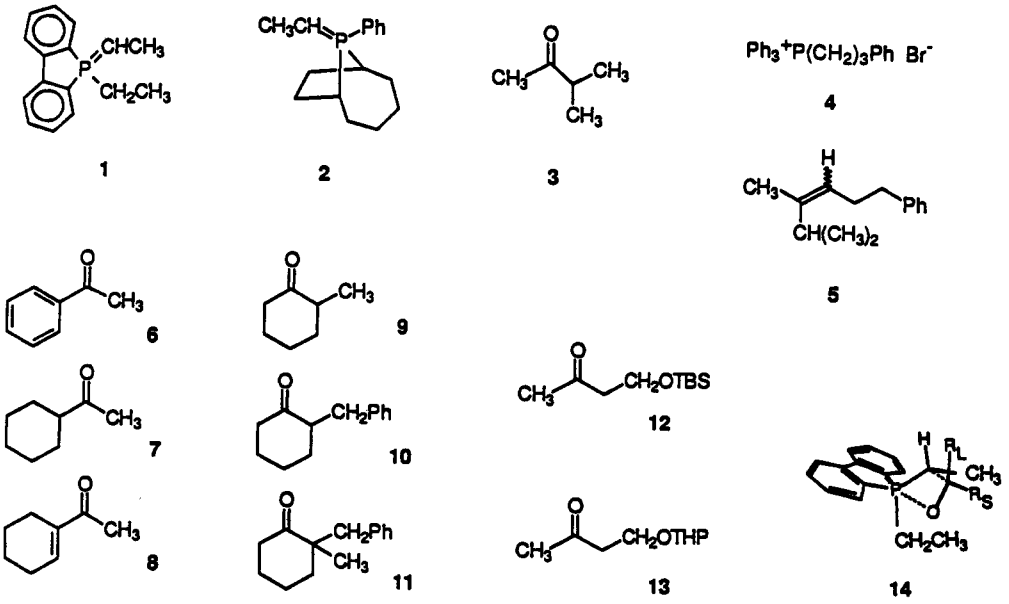

Table II. Characteristic ^{13}C Shifts (ppm) for Allylic Carbons of Trisubstituted Alkenes ($CDCl_3$)

ketone	(*E*)-alkene	(*Z*)-alkene
6	CH_3: δ 19.3, 26.7[a]	CH_3: δ 14.9, 25.4
7	CH: δ 47.2; CH_3: δ 13.1, 13.9[b]	CH: δ 39.1; CH_3: δ 12.5, 19.5
8	CH_3: δ 13.1, 14.1	CH_3: δ 14.5, 22.2
9	CH: δ 38.5; CH_3: δ 12.6[c]	CH: δ 33.1; CH_3: δ 12.2[c]
10	CH: δ 46.0; CH_3: δ 13.0	CH: δ 38.5; CH_3: δ 12.0
13	CH_3: δ 13.2, 13.7	CH_3: δ 13.2, 19.5

[a] Reference 12. [b] Reference 13. [c] Reference 14.

with formation or decomposition of the oxaphosphetane.[1b] However, the beneficial effect of high reactant concentration on reaction rates is self-explanatory because the Wittig reaction is a bimolecular process.

The optimized procedure was applied to the ethylidenation of a variety of ketones using an initial ylide concentration 0.75 M in 10–20% excess over the ketone. Further rate improvement was possible using the ylide in the same high concentration, but in larger excess. However, this was not necessary for any of the singly branched ketones listed in Table I, and 65–85% conversions were obtained even though there is considerable dilution of reagents as the second-order reaction proceeds. Olefination of the relatively more reactive α-alkoxy ketones could be performed at concentrations of 0.2–0.25 M, according to the procedure of Still *et al.*[5a]

Olefin stereochemistry was assigned using the ^{13}C chemical shift method.[8] Steric compression induces upfield shifts for the key allylic carbons in the (*Z*)-alkene compared to the *E*-isomer, as listed in Table II. Several of the product alkenes have been reported previously (ketones **6**, **7**, **9**, **12**, **13**), and the *Z*/*E* assignments are in agreement.[5a,12,14] In the case of **11**, the *E*-olefin geometry was based on the larger NOE effect between the C-2 methyl group at 0.86 ppm and the vinyl proton at 5.00 ppm by comparison with the *Z*-isomer. NOE results also were used to confirm the ^{13}C assignment in the ethylidene derivatives obtained from 2-methylcyclohexanone (**9**).

Most of the ketones studied afforded synthetically useful product ratios. On the basis of the NMR evidence, $Ph_3P{=}CHCH_3$ is *Z*-selective with the methyl ketones (**6**–**8**). In the latter series, the effect of a single α-alkyl branch point can be nearly as large as the α-oxygen effect discovered by Still *et al.*[5a] On the other hand, $Ph_3P{=}CHCH_3$ is *E*-selective with cyclohexanone derivatives **9**, **10**, and **11**. An earlier study reports a 55:45 *Z*:*E* ratio from the reaction of 2-methylcyclopentanone with $Ph_3P{=}CHCH_3$ under lithium-free conditions.[4f] Apparently, the high *Z*-selectivity observed with cyclopentanones of the 17-keto steroid family is the result of the specific D-ring environment and is not simply the consequence of α-branching in a cyclic ketone. The same conclusion would have to apply to the *E*-selective Wittig reactions of 20-keto steroids in the pregnenolone family. The latter compounds are methyl ketones that should be closely related to ketones **3** or **7**, but their reactions with lithium-free alkylidenetriphenylphosphoranes are reported to be *E*-selective.[4d]

Reactions of the DBP (**1**) and BTP (**2**) ethylides proved to be consistently *E*-selective.[2b,c] No exceptions were encountered among the ketones studied, although the degree of *E*-selectivity varied with the substrate family. Thus, **1** is the preferred reagent for α-alkoxy ketones, while **2** is somewhat better with α,β-unsaturated ketones. The *E*-selective olefination of α-alkoxy ketones with **1** nicely complements the *Z*-selective reactions of Still *et al.*,[5] although the product radios are not as high.

Inconsistent *E*/*Z* selectivity in the $Ph_3P{=}CHCH_3$ + ketone reactions suggests a delicate balance of interdependent kinetic or steric factors. We shall not speculate about the origins of selectivity in these examples. In contrast, *E*-trisubstituted alkenes are formed using **1** and **2** in all cases. In the analogous aldehyde ethylidenations with **1**, *E*-selectivity was explained by arguing that the

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rigid phosphole environment minimizes 1,3-interactions between phosphorus ligands and carbonyl substituents in the developing oxaphosphetane and that selectivity is dominated by 1,2-interactions. By a similar (tentative) argument, the major pathway in the ketone reactions may correspond to a four-center transition state such as 14. The larger ketone substituent is placed *cis* to hydrogen in the developing oxaphosphetane ring and thermal decomposition affords the *E*-trisubstituted alkene. However, other explanations are not ruled out.

Good yields are possible with all three ylides **1**, **2**, and $Ph_3P{=}CHCH_3$ under the optimized conditions. Each reagent has limitations with regard to one or more of the following: predictability, selectivity, or practicality. The conventional ylide $Ph_3P{=}CHCH_3$ is easily available, but the results with a complex substrate are difficult to anticipate. The DBP ylide **1** has the disadvantage that the intermediate oxaphosphetanes must be heated to induce decomposition, but the ring system is now easily available from $Ph_3P{=}O$.[9] By comparison the TBP ylide **2** is considerably more expensive, but oxaphosphetane decomposition occurs without heating.[3b] Ideal reagents for *E*- or *Z*-trisubstituted alkene synthesis remain to be discovered, but useful product ratios are now accessible in most cases where the ketone α- and α'-carbons differ in the degree of branching.

Experimental Section

General. The phosphonium salts $DBP^+(CH_2CH_3)_2I^-$ and $PhBTP^+CH_2CH_3I^-$ were prepared using established procedures.[3] The salt $Ph_3P^+(CH_2)_3PhBr^-$ (**4**) was prepared by conventional alkylation of Ph_3P with 3-phenyl-1-bromopropane.[1] The ketones 2-methylbutanone (**3**), acetophenone (**6**), acetylcyclohexane (**7**), 1-acetyl-1-cyclohexene (**8**), and 2-methylcyclohexanone (**9**) were purchased from Aldrich. 2-Benzylcyclohexanone (**10**) and 2-benzyl-2-methylcyclohexanone (**11**) and the α-alkoxy ketones **12** and **13** were prepared according to literature precedents.[5,10,11] Solutions of KHMDS were prepared in a centrifuge tube by dissolving solid KHMDS (Aldrich) in dry THF (distilled from sodium benzophenone) under nitrogen. A small amount of suspended material was removed by centrifugation. Cannula transfer of the supernatant solution was then done into a special flask fitted with a three-way stopcock to allow easy nitrogen purge and syringe transfer. The KHMDS was then titrated using the method of Ireland *et al.*[15]

4,5-Dimethyl-1-phenyl-3-hexene (5). To a stirred suspension of (3-phenylpropyl)triphenylphosphonium bromide (**4**) (0.231 g, 0.50 mmol) in 0.17 mL of dry THF under N_2 was added a solution of KHMDS in THF (0.43 mL, 1.05 M, 0.45 mmol, 0.90 equiv). After the solution was stirred for 5 min at rt, the ylide solution was cooled to −78 °C. Ketone **3** (47 μL, 0.45 mmol, 0.90 equiv) was added dropwise via microliter syringe as a neat liquid and the mixture was stirred for 5 min at −78 °C. The resulting mixture was then warmed to rt by removal of the cooling bath. During this period, the ylide color gradually discharged, and additional precipitate formed. The resulting suspension was stirred at rt for 2 h, diluted with pentane (20 mL), and washed with water (10 mL) and brine (10 mL). The organic fraction was then dried ($MgSO_4$), and the solvent was removed (aspirator). Purification by filtration chromatography (silica gel, 1 × 5 cm; eluent, hexane) produced **5** (60 mg, 71% yield): analytical TLC on silica gel (hexane) R_f = 0.70; molecular ion calcd for $C_{14}H_{20}$ 188.15649, found m/e = 188.1575, error = 5 ppm; IR (neat, cm^{-1}) 2961, C—H; 1604, C=C; 1453, =C—H. *Z* isomer: 500-MHz NMR ($CDCl_3$, ppm) 7.28–7.15 (5 H, m), 5.09 (1 H, t, J = 7.1 Hz), 2.76 (1 H, sept, J = 6.9 Hz), 2.64–2.61 (2 H, m), 2.34–2.28 (2 H, m), 1.58 (3 H, s), 0.90 (6 H, d, J = 6.9 Hz); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 142.1, 141.2, 128.4, 128.2, 125.6, 122.9, 36.5, 29.3, 28.5, 20.8, 18.0. *E* isomer: 500-MHz NMR ($CDCl_3$, ppm) 7.28–7.15 (5 H, m), 5.21–5.17 (1 H, m), 2.64–2.61 (2 H, m), 2.34–2.28 (2 H, m), 2.21 (1 H, sept, J = 6.8 Hz), 1.49 (3 H, s), 0.97 (6 H, d, J = 6.8 Hz); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 142.3, 141.8, 128.5, 128.1, 125.6, 121.1, 36.8, 36.2, 29.8, 21.5, 13.3.

Optimized Procedure for Ethylidenation of Ketones with $Ph_3P{=}CHCH_3$ or $BTP{=}CHCH_3$. The same procedure was used as described above. Thus, a thick slurry of $Ph_3P^+CH_2CH_3Br^-$ (1.5 mmol) with 0.4 mL of dry THF was stirred vigorously at room temperature while KHMDS (1.05 M, 1.30 mL, 1.36 mmol) was added dropwise under nitrogen. After addition was complete, the mixture was stirred for 5 min and then cooled to −78 °C and the ketone (0.8 mmol) was added neat. The same method was used on smaller scale to prepare alkenes using the BTP ylide from $PhBTP^+CH_2CH_3I^-$ and KHMDS. Reactions with the α-alkoxy ketones **12** and **13** were performed according to the procedure of Still *et al.*[5a] using 0.25 M solutions of the appropriate ylide.

Preparation of Trisubstituted Alkenes Using $DBP^+(CH_2CH_3)_2I^-$. Because the intermediate oxaphosphetanes derived from DBP ylides require heating to induce decomposition to the alkene and phosphine oxide,[3a] the following experimental modifications to the general procedure were made. After addition of the ketone (0.90 equiv) and warming to rt, the reaction mixture was transfered by cannula under nitrogen pressure into a thick-walled tube suitable for sealing. The tube was cooled to −78 °C, evacuated, and sealed under vacuum, and the reaction mixture was then heated at 100 °C (oil bath temperature) for 30 min. Alternatively, the reaction was conducted from the start in a specially modified round bottom flask to which a condenser had been directly fused. In this way, the reaction mixture could be taken directly from −78 °C to rt to 100 °C without the need for transfer to a second reaction vessel. Workup and isolation procedures remained the same.

Product Alkenes. In all cases, the alkenes were isolated using filtration chromatography as *E*/*Z* mixtures. Isomers were not separated, and NMR signals were deduced from spectra of the mixtures.

(*Z*)- and (*E*)-2-Phenyl-2-butene. Both (*Z*)- and (*E*)-2-phenyl-2-butene are known compounds, although the literature characterization data are incomplete.[16] Analytical TLC on silica gel: hexane, R_f = 0.48; molecular ion calcd for $C_{10}H_{12}$ 132.09390, found m/e = 132.0927, error = 9 ppm; base peak = 117 amu; IR ($CHCl_3$, cm^{-1}) 2956, C—H; 1585, C=C. *Z* isomer: 500-MHz NMR ($CDCl_3$, ppm) 7.35–7.18 (5 H, m), 5.56 (1 H, qq, J = 6.9, 1.5 Hz), 2.02 (3 H, dq, J = 1.6, 1.5 Hz), 1.59 (3 H, dq, J = 6.9, 1.6 Hz); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 141.8, 136.7, 128.0, 127.9, 126.3, 121.5, 25.4, 14.9. *E* isomer: 500-MHz NMR ($CDCl_3$, ppm) 7.37–7.19 (5 H, m), 5.86 (1 H, qq, J = 6.8, 1.3 Hz), 2.02 (3 H, dq, J = 1.3, 1.2 Hz), 1.79 (3 H, dq, J = 6.8, 1.2 Hz); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) δ 138.8, 134.9, 128.8, 128.0, 125.8, 125.5, 26.7, 19.3.

(*Z*)- and (*E*)-2-Cyclohexyl-2-butene. (*E*)-2-Cyclohexyl-2-butene is a known compound.[13] Data for both isomers are provided for comparison purposes. Analytical TLC on silica gel: hexane, R_f = 0.58; molecular ion calcd for $C_{10}H_{18}$ 138.14085, found m/e = 138.1409, error = 0 ppm; IR ($CHCl_3$, cm^{-1}) 2932, C—H; 1664, C=C. *Z* isomer: 500-MHz NMR ($CDCl_3$, ppm) 5.13 (1 H, q, J = 6.7 Hz), 2.44–2.40 (1 H, m), 1.81–1.72 (2 H, m), 1.60 (3 H, d, J = 1.5 Hz), 1.69–1.62 (2 H, m), 1.56 (3 H, dq, J = 6.7, 1.6 Hz), 1.49–1.44 (2 H, m), 1.35–1.11 (4 H, m); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 140.8, 117.5, 39.1, 30.7, 26.7, 26.6, 26.3, 26.2, 19.5, 12.5. *E* isomer: 500-MHz NMR ($CDCl_3$, ppm) 5.22–5.17 (1 H, m), 1.85–1.78 (1 H, m), 1.76–1.72 (2 H, m), 1.68–1.63 (2 H, m), 1.56 (3 H, d, J = 5.5 Hz), 1.57 (3 H, s), 1.31–1.10 (6 H, m); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 141.1, 115.9, 47.2, 31.8, 26.7, 26.6, 26.3, 26.2, 13.9, 13.1.

(*Z*)- and (*E*)-2-(1-Cyclohexenyl)-2-butene: analytical TLC on silica gel, hexane, R_f = 0.55; molecular ion calcd for $C_{10}H_{16}$ 136.12510, found m/e = 136.1250, error = 1 ppm; IR ($CHCl_3$, cm^{-1}) 2930, C—H; 1668, C=C. *Z* isomer: 500-MHz NMR ($CDCl_3$, ppm) 5.42–5.37 (1 H, m), 5.20 (1 H, qq, J = 6.7, 1.6 Hz), 2.09–2.05 (2 H, m), 2.01–1.96 (2 H, m), 1.73–1.70 (3 H, dq, J = 1.6, 1.5 Hz), 1.70–1.54 (4 H, m), 1.59 (3 H, dq, J = 6.7, 1.5 Hz); ^{13}C NMR (125

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MHz {H}, $CDCl_3$, ppm) 139.4, 137.7, 123.4, 118.9, 27.4, 25.0, 23.2, 22.9, 22.2, 14.5. *E* isomer: 500-MHz NMR ($CDCl_3$, ppm) 5.80–5.78 (1 H, m), 5.58 (1 H, q, J = 7.0 Hz), 2.19–2.11 (4 H, m), 1.76 (3 H, s), 1.71 (3 H, d, J = 7.0 Hz), 1.73–1.60 (2 H, m), 1.59–1.54 (2 H, m); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 137.6, 136.2, 122.1, 118.1, 25.8, 25.7, 23.0, 22.4, 14.1, 13.1.

(*Z*)- and (*E*)-2-Methylethylidenecyclohexane. Although both (*Z*)- and (*E*)-2-methylethylidenecyclohexane are reported several times in the literature,[14,17] only ^{13}C NMR data are given as characterization.[14] Analytical TLC on silica gel: hexane, R_f = 0.62; molecular ion calcd for C_9H_{16} 124.12510, found m/e = 124.1252, error = 0 ppm; IR ($CHCl_3$, cm^{-1}) 2930, C—H; 1420, =C—H. *Z* isomer: 500-MHz NMR ($CDCl_3$, ppm) 5.10 (1 H, dq, J = 6.8, 2.2 Hz), 2.92–2.28 (1 H, m), 2.27–2.19 (1 H, m), 1.84–1.08 (7 H, m), 1.58 (3 H, dd, J = 2.0 Hz), 1.06 (3 H, d, J = 7.5 Hz); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 143.6, 115.0, 33.1, 32.5, 29.7, 28.5, 21.1, 17.9, 12.2. *E* isomer: 500-MHz NMR ($CDCl_3$, ppm) 5.12 (1 H, q, J = 6.6 Hz), 2.51 (1 H, dt, J = 13.5, 4.8 Hz), 2.09–2.04 (1 H, m), 1.82–1.06 (7 H, m), 1.59 (3 H, dt, J = 6.6, 1.1 Hz), 1.01 (3 H, d, J = 6.7 Hz); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 144.1, 112.3, 38.5, 36.8, 27.9, 27.8, 25.6, 18.7, 12.6.

(*Z*)- and (*E*)-2-Benzylethylidenecyclohexane: analytical TLC on silica gel, hexane, R_f = 0.33; molecular ion calcd for $C_{15}H_{20}$ 200.15649, found m/e = 200.1561, error = 2 ppm; base peak = 109 amu; IR (neat, cm^{-1}) 3040, C—H; 2930, C—H; 1600, C=C. *Z* isomer: 200-MHz NMR ($CDCl_3$, ppm) 7.26–7.11 (5 H, m), 5.13 (1 H, q, J = 6.6 Hz), 2.80–2.70 (2 H, m), 2.40–2.20 (2 H, m), 2.20–2.00 (1 H, m), 1.90–1.20 (6 H, m), 1.58 (3 H, d, J = 6.6 Hz); ^{13}C NMR (90 MHz (DEPT), $CDCl_3$, ppm) 141.5, 141.0, 129.0, 128.0, 126.0, 117.0, 38.5, 38.0, 33.5, 30.5, 28.5, 21.5, 12.0. *E* isomer: 200-MHz NMR ($CDCl_3$, ppm) 7.26–7.11 (5 H, m), 5.13 (1 H, q, J = 6.6 Hz), 2.90 (1 H, dd, J = 13.0, 6.0 Hz), 2.60 (1 H, dd, J = 13.0, 9.0 Hz), 2.40–2.20 (2 H, m), 2.20–2.00 (1 H, m), 1.90–1.20 (6 H, m), 1.58 (3 H, d, J = 6.6 Hz); ^{13}C NMR (90 MHZ (DEPT), $CDCl_3$, ppm) 142.5, 142.0, 129.0, 128.0, 126.0, 114.5, 46.0, 39.0, 33.0, 28.0, 27.0, 24.5, 13.0.

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(*Z*)- and (*E*)-2-Benzyl-2-methylethylidenecyclohexane: analytical TLC on silica gel, hexane, R_f = 0.66; molecular ion calcd for $C_{16}H_{22}$ 214.17215, found m/e = 214.172, error = 1 ppm; base peak = 123 amu; IR ($CDCl_3$, cm^{-1}) 2970, C—H; 2930, C—H; 1650, C=C. *Z* isomer: 200-MHz NMR ($CDCl_3$, ppm) 7.25–7.00 (5 H, m), 5.28 (1 H, q, J = 7.0 Hz), 3.08 (1 H, d, J = 13.1 Hz), 2.7–1.00 (11 H, m), 2.48 (1 H, d, J = 13.1 Hz), 1.15 (3 H, s). *E* isomer: 200-MHz NMR ($CDCl_3$, ppm) 7.25–7.00 (5 H, m), 5.00 (1 H, q, J = 7.0 Hz), 2.95 (1 H, AB q, J = 13.1 Hz), 2.70–1.00 (8 H, m), 2.54 (1 H, AB q, J = 13.1 Hz), 1.57 (3 H, dd, J = 7.0, 1.1 Hz), 0.86 (3 H, s).

(*Z*)- and (*E*)-1-(Tetrahydropyranyloxy)-2-methyl-2-butene. The title compounds have been reported, but without characterization data.[5a] Analytical TLC on silica gel: 1:4 ether/hexane, R_f = 0.46, 0.58; molecular ion calcd for $C_{10}H_{18}O_2$ 170.13064, found m/e = 170.1304, error = 1 ppm; IR (neat, cm^{-1}) 2932, C—H; 1015, C-O; 1424, =C—H. *Z* isomer: 500-MHz NMR ($CDCl_3$, ppm) 5.52 (1 H, qq, J = 7.0, 1.7 Hz), 4.61 (1 H, t, J = 6.7 Hz), 4.12 (2 H, s), 3.97–3.89 (1 H, m), 3.58–3.49 (1 H, m), 1.90–1.50 (6 H, m), 1.80–1.78 (3 H, m), 1.61 (3 H, d, J = 7.0 Hz); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 132.4, 121.2, 97.4, 73.0, 65.3, 30.6, 25.5, 22.0, 19.5, 13.2. *E* isomer: 500-MHz NMR ($CDCl_3$, ppm) 5.44 (1 H, qq, J = 7.0, 1.5 Hz), 4.61 (1 H, t, J = 6.7 Hz), 4.12 (1 H, d, J = 11.1 Hz), 3.92–3.85 (1 H, m), 3.85 (1 H, d, J = 11.1 Hz), 3.55–3.48 (1 H, m), 1.90–1.50 (6 H, m), 1.64 (3 H, d, J = 7.0 Hz), 1.68 (3 H, s); ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) 132.6, 122.4, 97.4, 73.0, 62.0, 30.6, 25.5, 19.5, 13.7, 13.2.

(*Z*)- and (*E*)-1-(Dimethyl-*tert*-butylsiloxy)-2-methyl-2-butene. The title compounds have been reported, but without characterization data.[5a] Analytical TLC on silica gel: 1:3 ether/hexane, R_f = 0.65, 0.75; molecular ion calcd for $C_{11}H_{24}OSi$ 200.15964, found m/e = 200.1599, error = 1 ppm; IR (neat, cm^{-1}) 2930, C—H; 1472, =C—H; 1080, C-C. *Z* isomer: 200-MHz NMR ($CDCl_3$, ppm) 5.40–5.30 (1 H, m), 4.15 (2 H, s), 1.72–1.71 (3 H, m), 1.60 (3 H, d, J = 6.8 Hz), 0.89 (9 H, s), 0.06 (6 H, s). *E* isomer: 200-MHz NMR ($CDCl_3$, ppm) 5.52–5.44 (1 H, m), 3.99 (2 H, s), 1.68–1.57 (6 H, m), 0.89 (9 H, s), 0.07 (6 H, s).

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