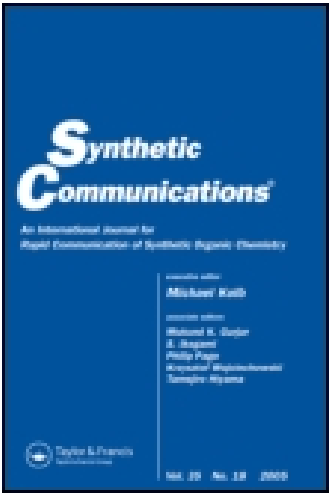

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Synthetic Potential of the Reaction of Allylic Phosphonium Ylides with α, β-Unsaturated Carbonyl Compounds

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SYNTHETIC POTENTIAL OF THE REACTION OF ALLYLIC PHOSPHONIUM YLIDES WITH α, β-UNSATURATED CARBONYL COMPOUNDS

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Abstract: The reaction of triphenylphosphonium-2-propenylide (**14**) with mesityl oxide (**9**) is shown to proceed *via* initial Michael addition followed by trans ylidation and an intramolecular Wittig condensation to yield 1,5,5-trimethyl-1,3-cyclohexadiene (**10**) as the reaction product.

Allylic (**1**) and ethyl acetoacetate derived (**2**) carbanions, which are stabilized by various phosphorus and sulphur substituents, are ambident nucleophiles that may react as α- or γ-anions with appropriate electrophiles, e.g. activated acetylenes[1], allylic phosphonium[2] and sulphonium[3] salts, and α,β-unsaturated carbonyl compounds.[4-6] An allylidenephosphonium ylide (**1**, X = Ph_3P^+) may therefore in principle react with α,β-unsaturated carbonyl systems (**3**) to yield reaction products that resulted from initial C_α-C_1, C_α-C_3, C_γ-C_1, and C_γ-C_3 interaction. The last mode of interaction may formally be regarded as an initial Michael addition of the phosphonium ylide (**1**) to the α, β-unsaturated electrophile (**3**), followed by trans ylidation (**6** → **7**) and an intramolecular Wittig condensation of (**7**), thus leading to the formation of variously substituted cyclohexadienes (**4**).

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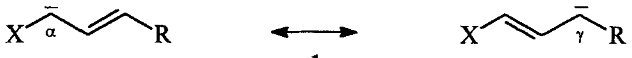

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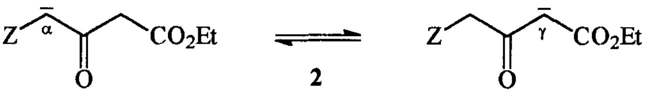

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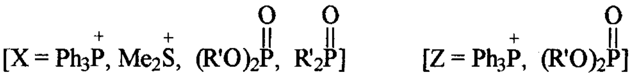
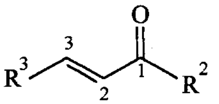


$[X = Ph_3\overset{+}{P},\ Me_2\overset{+}{S},\ (R'O)_2\overset{\overset{O}{\|}}{P},\ R'_2\overset{\overset{O}{\|}}{P}]$ $[Z = Ph_3\overset{+}{P},\ (R'O)_2\overset{\overset{O}{\|}}{P}]$



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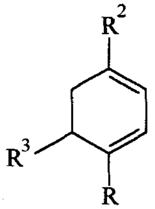

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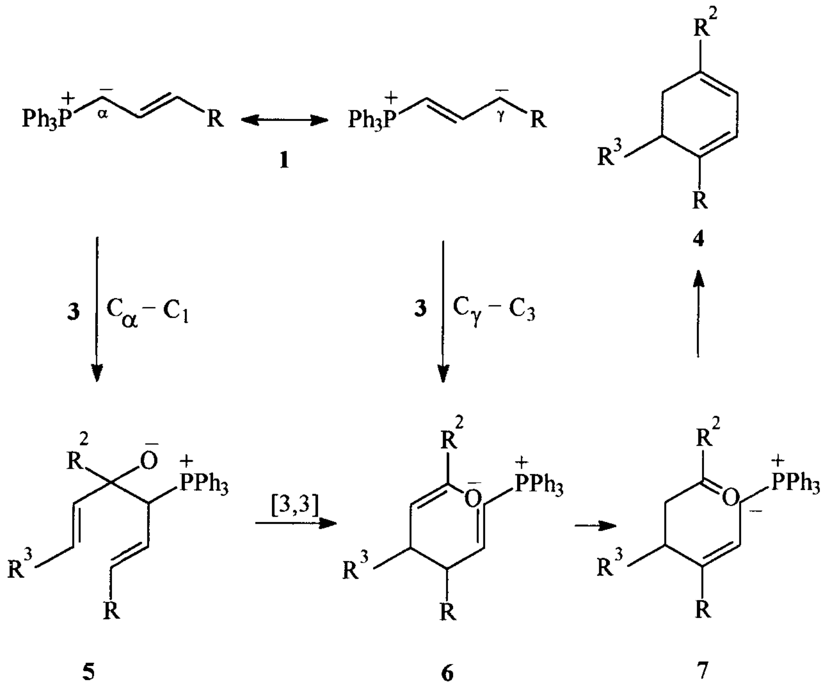
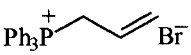
Formation of the intermediate C_γ-C_3 adduct (**6**) may also be regarded as the result of initial C_α-C_1 interaction followed by a fast oxy-Cope rearrangement of the adduct (**5**).[7] The obvious synthetic potential of this mode of interaction prompted us to investigate the course of this useful reaction by implementing the phosphonium salt (**8**), mesityl oxide (**9**), and butyllithium as starting materials. Dauben and co-workers[8] reported that this condensation produced the cyclohexadiene (**10**) in an isolated yield of 50%. In our hands an isolated yield of 57 % was realized, but quantitative GC analysis of the partially concentrated ethereal reaction mixture confirmed a yield of 78% and the total absence of the open-chain polyene (**11**).

The ambident character of the phosphonium ylide (**12**) was demonstrated by quenching a filtered solution of this compound, which was generated by treatment of the salt (**8**) with butyllithium in ether medium, with 47% aqueous hydrogen bromide at −20, 0, and 22 °C, respectively, to yield in each case the





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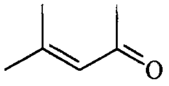

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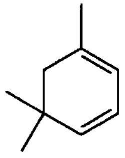

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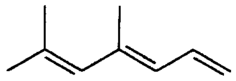

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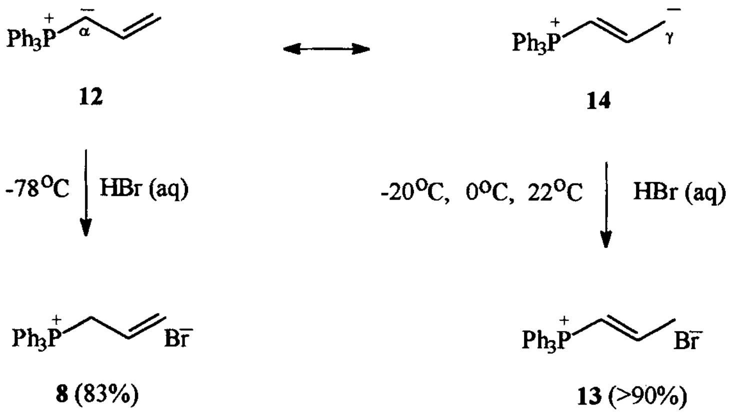
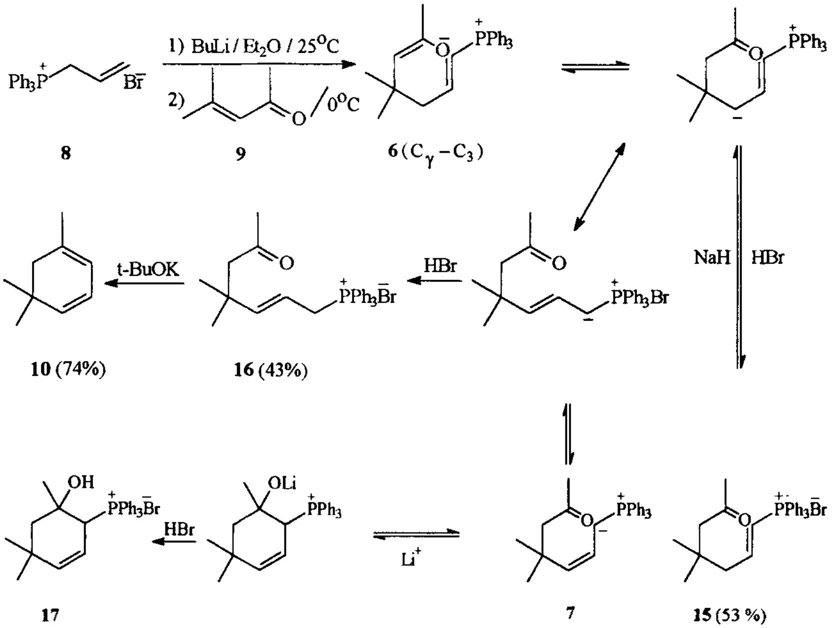
vinylphosphonium salt (**13**) as the sole product. When this procedure was repeated at −78 °C, the allylphosphonium salt (**8**) was formed exclusively.

In an effort to isolate the initial coupling product of the ylide (**12**) and mesityl oxide (**9**), an ethereal solution of (**12**) was filtered under positive argon pressure and the filtrate treated with the ketone (**9**) (1.8 moles) at 0°C. The reaction



mixture was then stirred for 30 minutes at 0 °C and the reaction terminated by the addition of a slight excess of 47% aqueous hydrogen bromide. ^{31}P NMR analysis of the ether insoluble material revealed the presence of the vinyl salt (**15**) (δ_P 18.24, 53 %, NMR), allyl salt (**16**) (δ_P 21.23, 5 %, NMR), triphenylphosphine oxide (δ_P 28.69), and a component to which the structure (**17**) (δ_P 22.62, 5 %, NMR) was tentatively ascribed, in an approximate relative ratio of 10:1:3:1, respectively. Although the very hygroscopic vinyl salt (**15**) could not be crystallized, even after extraction a small amount of residual triphenylphosphine oxide from (**15**) with ether, its structure and configuration could unequivocally be substantiated by NMR analysis. When a suspension of the crude vinyl salt (**15**), which contained less than 10% of the allyl salt (**16**) as an impurity, and sodium hydride (1.1 moles) in ether was heated at reflux temperature for 20 hours, the pure allyl salt (**16**) could be crystallized after protonation from the ether insoluble reaction product which consisted of (**15**) (18 %, NMR), (**16**) (43%, NMR), and triphenylphosphine oxide in an approximate relative ratio of 2:5:2 according to ^{31}P NMR analysis. Treatment of the pure allyl salt (**16**) with potassium *tert*-butoxide under similar reaction conditions yielded the cyclohexadiene (**10**) in 74% yield on account of GC analysis of the partially concentrated ethereal filtrate.



Since we have shown that the allyl salt (**8**) was formed exclusively when an ethereal solution of the ylide (**12**) was quenched with 47% aqueous hydrogen bromide at −78 °C, the possibility does exist that the ylide (**12**) may react in a similar fashion with other electrophiles at low temperatures. In order to evaluate this possibility, a filtered solution of the ylide (**12**) in ether was treated at −78 °C with an excess of mesityl oxide (**9**) (1.8 moles) and the reaction terminated after two hours at −78 °C by the addition of 47% aqueous hydrogen bromide. The ether insoluble material consisted of the allyl salt (**8**) (δ_P 21.13) and vinyl salt (**15**) (δ_P 18.23) in an approximate ratio of 7:6 according to ^{31}P NMR analysis. Even at this low temperature no indications could be found that the hydroxyphosphonium salt corresponding to the C_α-C_1 coupling product (**5**) was formed at all. Our results therefore strongly indicate that the condensation of the phosphonium ylide (**12**) with mesityl oxide (**9**) proceeds *via* initial C_γ-C_1 interaction[7] as a viable option under these circumstances.

EXPERIMENTAL

All operations were carried out in an argon atmosphere. NMR spectra were recorded for solutions in deuteriochloroform (unless otherwise indicated) on Varian *FT 80* and *VXR 300* instruments, while mass spectra were taken on a *Varian Mat 311 A* spectrometer. Multiplicities were confirmed by APT and SFORD experiments.

1. Condensation of *allylidenetriphenylphosphonium ylide* (12) with *mesityl oxide* (9)

Butyllithium in hexane (1.26 M, 16.61 cm^3, 20.93 mmol) and ether (10 cm^3) was added dropwise to a stirred suspension of dry, powdered *allyltriphenylphosponium bromide* **(8)** (10.07 g, 26.29 mmol) in ether (70 cm^3). The resulting red mixture was stirred for 1 h at room temperature, whereafter freshly distilled *mesityl oxide* **(9)** (4.65 g, 47.41 mmol) in ether (10 cm^3) was added dropwise. The mixture was stirred for 21 h at room temperature, refluxed for 12 h, allowed to cool to room temperature and added to an excess of water. After separation of the ethereal layer, the aqueous layer was extracted and the combined extracts dried ($MgSO_4$). Distillation of the residue from the ether extract over a Vigreax column yielded *1,5,5-trimethyl-1,3-cyclohexadiene* **(10)** of > 98 % purity according to gaschromatographic analysis on a 20 m *SUPEROX* column (1.84 g, 57 %), b.p. 131-3 °C (lit.[9] 130-3°C); λ_{max} 260 nm; δ_H 0.96 (s, 3H), 1.74 (s, 3H), 1.96 (s, 2H), 5.20-5.80 (m, 3H); δ_C 23.54 (CH_3), 28.14 (2 × CH_3), 31.68 (>C<), 43.82 (CH_2), 117.98 (=CH), 122.25 (=CH), 134.34 (>C=), 134.59 (=CH). M^+, 122.1090. Calcd. for C_9H_{14} : M, 122.1095.

2. Protonation of *allylidenetriphenylphosphonium ylide* (12) at different temperatures

a) At 22 °C

Butyllithium in hexane (1.25 M, 22.63 cm^3, 28.29 mmol) and ether (10 cm^3) was added dropwise to a stirred solution of dry, powdered *allyltriphenylphosphonium bromide* **(8)** (10.07 g, 26.29 mmol) in ether (70 cm^3). The resulting red mixture was stirred for 1 h at 22 °C, filtered under argon pressure and the filtrate stirred at 22 °C for an additional 30 min. Aqueous hydrogen bromide (47%, 31.55 mmol) was added to the filtrate and a brown suspension resulted, which was filtered. The precipitate was washed with ether (3 × 50 cm^3), dissolved in chloroform, dried ($MgSO_4$), the solvent evaporated and the residue dried under vacuum to yield *(E)-prop-1-en-1-yl-triphenylphosponium bromide* **(13)** (9.02 g, 90 %) as a brown powder. Crystallization from dichloromethane/ acetone gave white crystals of the *vinyl salt* **(13)**, m.p. 210-215 °C; δ_P 18.40; δ_H 2.36 (ddd, J_{PH} 2.40 Hz, J_{HH} 6.55 and 1.60 Hz, 3H), 6.65 (ddq, J_{PH} 21.90 Hz, J_{HH} 16.50 and 6.50 Hz, 1H), 7.38-7.97 (m, arom. H and =CH, 16H); δ_C 21.86 (J_{PC} 19.9 Hz, CH_3), 110.36 (J_{PC} 86.3 Hz, =CH), 118.16 (J_{PC} 90.7 Hz, 3 × arom. C), 130.59 (J_{PC} 12.8 Hz, 6 × arom. C), 133.89 (J_{PC} 9.5 Hz, 6 × arom. C), 135.33 (J_{PC} 3.0 Hz, 3 × arom. C), 159.73 (J_{PC} 2.6 Hz, =CH).

b) At 0 °C

This experiment was conducted as in (a), but quenching of the phosphonium ylide **(12)** with 47 % aqueous hydrogen bromide was performed at 0 °C to yield the vinyl salt, *(E)-prop-1-en-1-yl-triphenylphosphonium bromide* **(13)** (90 %), δ_P 18.39, as a white powder.

c) At -20 °C

This experiment was conducted as in (a), but quenching of the phosphonium ylide **(12)** with 47 % aqueous hydrogen bromide was performed at -20 °C to yield the vinyl salt, *(E)-prop-1-en-1-yl-triphenylphosphonium bromide* **(13)** (> 99 %), δ_P 18.37, as a white powder.

d) At -78 °C

This experiment was conducted as in (a), but quenching of the phosphonium ylide

(12) with 47 % aqueous hydrogen bromide was performed at -78 °C to yield the allyl salt, *allyltriphenylphosphonium bromide* **(8)** (82 %), δ_P 21.15, as a white powder.

3. Condensation of *allylidenetriphenylphosphonium ylide* (12) with *mesityl oxide* (9) at 0 °C followed by quenching with 47 % aqueous hydrogen bromide

Butyllithium in hexane (1.26 M, 68.56 cm^3, 86.39 mmol) and ether (10 cm^3) was added dropwise to a stirred suspension of dry, powdered *allyltriphenylphosphonium bromide* **(8)** (30.08 g, 78.53 mmol) in ether (210 cm^3). The resulting red mixture was stirred at 22 °C for 1 h, filtered under argon pressure and the filtrate stirred at 0 °C for 30 min. Freshly distilled *mesityl oxide* **(9)** (13.88 g, 141.53 mmol) in ether (10 cm^3) was added dropwise to the red solution and the resulting orange suspension stirred at 0 °C for 30 min. The suspension was then quenched by the addition of an excess of aqueous hydrogen bromide (47%, 94.25 mmol), the ice bath removed after 10 min., and the cream coloured precipitate washed with ether. The precipitate was dissolved in dichloromethane, dried ($MgSO_4$), the solvent evaporated and the residue dried under vacuum to yield a brown powder (30.14 g) containing *(E)-4,4-dimethyl-6-oxo-1-hepten-1-yltriphenylphosphonium bromide* **(15)** (δ_P 18.24), *(E)-4,4-dimethyl-6-oxo-2-hepten-1-yltriphenylphosphonium bromide* **(16)** (δ_P 21.23), most probably *4-hydroxy-4,6,6-trimethylcyclohex-1-en-3-yltriphenylphosphonium bromide* **(17)** (δ_P 22.62) and *triphenylphosphine oxide* (δ_P 29.78) in a ratio of 20:2:1:6 according to analysis by ^{31}P NMR.

This material (5.79 g) was dissolved in equal volumes water (200 cm^3) and ether (200 cm^3) to form two bright yellow layers, *i.e.* a *vinyl salt* **(15)** containing aqueous phase and a *triphenylphosphine oxide* containing organic phase. The aqueous phase was extracted with dichloromethane (3 × 200 cm^3), the combined extracts dried ($MgSO_4$), the solvent evaporated and the residue dried under vacuum to yield a yellow, hygroscopic powder (3.55 g), which consisted of the *vinyl salt* **(15)**, ν_{max} 1715 cm^{-1} (C=O); δ_H 1.04 (s, 6H), 2.12 (s, 3H), 2.44 (s, 2H), 2.82 (d, J_{HH} 7.64 Hz, 2H), 6.64 (dd, J_{PH} 22.02 Hz, J_{HH} 16.47 Hz, 1H), 7.47-8.00 (m, arom. H and =CH, 16H); δ_C 27.50 (2 × CH_3), 32.45 (CH_3), 34.45 (J_{PC} 0.9 Hz), 46.96 (J_{PC}, 17.7 Hz, CH_2), 53.34 (CH_2), 111.56 (J_{PC} 84.0 Hz, =CH), 118.11 (J_{PC} 90.8 Hz, 3 × arom. C), 130.60 (J_{PC} 12.9 Hz, 6 × arom. C), 133.82 (J_{PC} 10.6 Hz, 6 × arom. C), 135.41 (J_{PC} 2.9 Hz, 3 × arom. C), 161.06 (J_{PC} 2.0 Hz, =CH), 208.37 (C=O); (M^+ - Br) , 401.2048 and (M^+ - HBr), 400.1977. Calcd. for $C_{27}H_{30}OP$: (M-Br), 401.2034 and for $C_{27}H_{29}OP$: (M-HBr), 400.1956. Attempted recrystallization of the *vinyl salt* **(15)** was unsuccessful.

Sodium tetraphenylborate (3.03 g, 8.86 mmol) in 96% ethanol (20 cm^3) was added to a stirred solution of the *vinyl salt* **(15)** (3.55 g, 7.38 mmol) in 96% ethanol (10 cm ^{3}) at room temperature. The resulting light yellow precipitate was collected by filtration after 2 h and the solid dried under vacuum to yield *(E)-4,4-dimethyl-6-oxo-1-hepten-1-yltriphenylphosphonium tetraphenylborate* as a brown powder (4.22 g, 79 %), which could not be recrystallized; δ_H (d_6-DMSO) 0.92 (s, 6H), 1.98 (s, 3H), 2.33 (s, 2H), ~2.5 (d, J_{HH} ~ 7.8 Hz, 2H), 6.57-7.35 (m, arom. H, BPh_4, and =CH, 21H), 7.44-7.97 (m, arom.H, PPh_3, and =CH, 16H); δ_C (d_6-DMSO) 21.26 (J_{PC} 20.1 Hz, CH_2), 26.87 (2 × CH_3), 31.77 (CH_3), 33.72 (J_{PC} 1.0 Hz, >C<), 52.46 (CH_2), 111.00 (J_{PC} 83.9 Hz, =CH), 118.19 (J_{PC} 90.2 Hz, 3 × arom. C), 130.21 (J_{PC} 12.8 Hz, 6 × arom. C), 133.69 (J_{PC} 10.7 Hz, 6 × arom. C), 134.86 (3 × arom. C), 121.42 (4 × arom. C, BPh_4), 125.18 (J_{BC} 2.8 Hz, 8 × arom. C, BPh_4), 135.51 (J_{BC} 1.4 Hz, 8 × arom. C, BPh_4), 163.33 (J_{BC} 49.3 Hz, 4 × arom. C, BPh_4), 160.19 (J_{PC} 2.1 Hz, =CH), 207.85 (C=O).

4. Treatment of *(E)-4,4-dimethyl-6-oxo-1-hepten-1-yltriphenylphosphonium bromide* (15) with potassium *tert*-butoxide

A suspension of dry, powdered *(E)-4,4-dimethyl-6-oxo-1-hepten-1-yltriphenyl-*

phosphonium bromide **(15)** (18.89 g, 39.29 mmol) and freshly sublimed potassium *tert*-butoxide (4.84 g, 43.11 mmol) in ether (300 cm^3) was stirred at 22 °C for 1 h and then refluxed for 19 h. The mixture was filtered and the red ethereal filtrate washed with water (3 × 200 cm^3), dried ($MgSO_4$) and distilled to yield *1,5,5-trimethyl-1,3-cyclohexadiene* **(10)** (1.48 g, 31 %).

5. Treatment of *(E)-4,4-dimethyl-6-oxo-1-hepten-1-yltriphenylphosphonium bromide* (15) with sodium hydride

A suspension of dry, powdered *(E)-4,4-dimethyl-6-oxo-1-hepten-1-yltriphenylphosphonium bromide* **(15)** (25.01 g, 51.98 mmol) and oil-free sodium hydride (1.37 g, 57.09 mmol) in ether (500 cm^3) was stirred at 22 °C for 1 h and then refluxed for 19 h and filtered. The residue on the filter was thoroughly washed with ether (3 × 30 cm^3), dissolved in dichloromethane, and the dichloromethane solution washed with water and dried ($MgSO_4$). Evaporation of the solvent yielded a solid which was dried under vacuum to give a brown powder (19.37 g) which consisted of a 43:100:39 mixture of *(E)-4,4-dimethyl-6-oxo-1-hepten-1-yltriphenylphosphonium bromide* **(15)** (δ_P 18.25), *(E)-4,4-dimethyl-6-oxo-2-hepten -1-yltriphenylphosphonium bromide* **(16)** (δ_P 21.19), and *triphenylphosphine oxide* (δ_P 28.72) according to analysis by ^{31}P NMR.

The *allyl salt* **(16)** started to precipitate when this powder was refluxed with acetone. The mixture was then cooled (0 °C), filtered and the white crystals dried under vacuum to yield the *allyl salt* **(16)** (4.71 g, 19 %). Recrystallization of this material from dichloromethane/ acetone gave the pure *allyl salt* **(16)**, m.p. 212-216 °C, ν_{max} 1700 cm^{-1} (C=O); δ_P 21.23; δ_H 0.96 (s, 6H), 1.95 (s, 3H), 2.38 (s, 2H), 4.71 (ddd, J_{PH} 14.74 Hz, J_{HH} 7.32 and 1.24 Hz, 2H), 5.19 (ddt, J_{PH} 5.01 Hz, J_{HH} 15.64 and 7.32 Hz, 1H), 6.04 (ddt, J_{PH} 5.38 Hz, J_{HH} 15.64 and 1.25 Hz, 1H), 7.66-7.92 (m, arom.H, 15H); δ_C 27.05 (CH_3), 27.08 (CH_3), 27.94 (J_{PC} 48.8 Hz, CH_2), 31.81 (CH_3), 36.24 (J_{PC} 2.4 Hz, >C<), 53.79 (J_{PC} 2.4 Hz, CH_2), 110.96 (J_{PC} 9.8 Hz, =CH), 118.28 (J_{PC} 84.8 Hz, 3 × arom. C), 130.28 (J_{PC} 12.8 Hx, 6 × arom. C), 134.13 (J_{PC} 9.8 Hz, 6 × arom. C), 134.89, (J_{PC} 3.1 Hz, 3 × arom. C), 150.11 (J_{PC} 13.1 Hz, =CH), 207.35 (C=O); (M^+ - Br), 401.2047 and (M^+ - HBr), 400.1957. Calcd. for $C_{27}H_{30}OP$: (M - Br), 401.2034 and for $C_{27}H_{29}OP$: (M - HBr), 400.1956. Found: C, 67.42; H, 6.32; P, 6.40. Required: C, 67.36; H, 6.28; P, 6.43.

6. Treatment of *(E)-4,4-dimethyl-6-oxo-2-hepten-1-yltriphenylphosphonium bromide* (16) with potassium *tert*-butoxide

A suspension of a mixture of dry, powdered *(E)-4,4-dimethyl-6-oxo-2-hepten-1-yltriphenylphosphonium bromide* **(16)** (4.23 g, 8.79 mmol) and freshly sublimed potassium *tert*-butoxide (1.08 g, 9.67 mmol) in ether (100 cm^3) was stirred at room temperature for 1 h. The resulting red mixture was then refluxed for 19 h, washed with water (3 × 75 cm^3), dried ($MgSO_4$), the solvent evaporated, and the oily residue cooled to room temperature to yield white crystals of *triphenylphosphine oxide* (1.19 g, 77 %), m.p. (ether) 157 °C; δ_P 28.98, which was collected by filtration. Distillation of the residue from the filtrate gave *1,5,5-trimethyl-1,3-cyclohexadiene* **(10)** (0.71 g, 66 %).

7. Condensation of *allylidenetriphenylphosphonium ylide* (12) with *mesityl oxide* (9) at -78 °C and quenching of the reaction mixture with 47 % aqueous hydrogen bromide

Butyllithium in hexane (1.23 M, 70.24 cm^3, 86.39 mmol) and ether (30 cm^3) was added dropwise to a stirred suspension of dry, powdered *allyltriphenylphosphonium bromide* **(8)** (30.08 g, 78.53 mmol) in ether (210 cm^3). The red mixture was stirred at room temperature for 1 h, filtered under argon pressure and the filtrate stirred at -78 °C in a dry ice/ acetone bath. Freshly distilled *mesityl oxide*

(9) (13.87 g, 141.43 mmol) in ether (30 cm^3) was added dropwise, the light orange suspension stirred at -78 °C for 2 h and the reaction quenched by the addition of an excess of 47 % aqueous hydrogen bromide (94.24 mmol). The cooling bath was removed, the mixture allowed to warm to room temperature, the orange precipitate thoroughly washed with ether, dissolved in dichloromethane and dried ($MgSO_4$). Evaporation of the solvent yielded a solid residue which was dried under vacuum to give a brown powder (27.24 g) which consisted of a mixture of *allyltriphenylphosphonium bromide* **(8)** (δ_P 21.13) and *(E)-4,4-dimethyl-6-oxo-1-hepten-1-yltriphenylphosphonium bromide* **(15)** (δ_P 18.23) in a ratio of 100:86 according to ^{31}P NMR analysis. Recrystallization of this mixture from acetone yielded the pure *allyl salt* **(8)** (5.21 g, 17 %) according to NMR analysis; δ_H 4.74 (ddt, J_{PH} 15.4 Hz, J_{HH} 6.9 and 1.1 Hz, 2H), 5.40 (dddt, J_{PH} 4.5 Hz, J_{HH} 9.7, 1.3 and 1.0 Hz, 1H), 5.58 (dddt, J_{PH} 5.1 Hz, J_{HH} 16.9, 1.3 and 1.1 Hz, 1H), 5.73 (dddt, J_{PH} 5.0 Hz, J_{HH} 17.0, 9.7 and 7,0 Hz, 1H), 7.65-7.89 (m, arom.H, 15H).

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