

LICKOR-Promoted 1,2-elimination in 1,1-dimethoxy-2-phenylethane and 1,1-dimethoxy-2-phenylpropane: synthesis of substituted enol ethers and alkynes

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Dimethyl acetals of phenylacetaldehyde **1a** and 2-phenylpropionaldehyde **1b**, upon treatment with 1.25 equiv. of LICKOR reagent, undergo 1,2-elimination (THF at -95°C) promoted by metallation at the benzylic site, and afford the corresponding enol ethers in the *E*-form. When the substrate is treated with an excess of the base (2.5 equiv.), further hydrogen-metal exchange takes place at the α -vinyl site of the elimination product, and carbonyl electrophiles can be added to the carbanionic intermediate yielding allyl alcohols. Experimental procedures are given for the conversion of the α -substituted derivatives into carbonyl compounds, according to an inverse polarity approach. Moreover, allyl alcohols synthesised starting from acetal **1a**, can be transformed into prop-2-ynyl alcohols by treatment with LICKOR base.

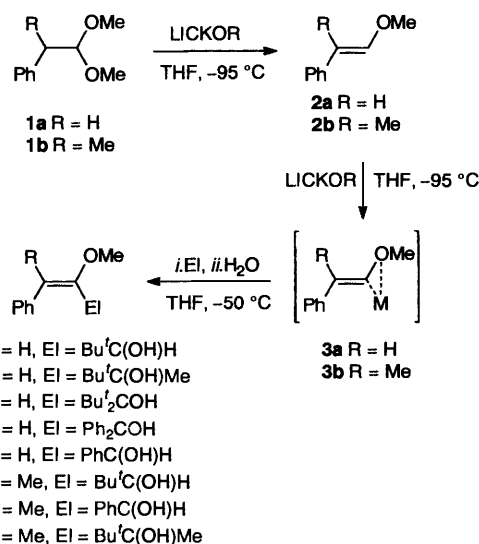
Schlosser and co-workers have discovered and deeply explored the use of mixed metal bases in organic synthesis,¹ and in particular the synthetic potential of an equimolar mixture of butyllithium and potassium *tert*-butoxide (LICKOR reagent) is well documented.² In recent studies we have reported that LICKOR base promotes transformation of α,β -unsaturated acetals into α -substituted 1-ethoxybuta-1,3-dienes.³ In contrast, addition and substitution products predominate when acetals derived from acrolein and crotonaldehyde are treated with alkylolithium reagents.⁴

The present paper deals with the details of our work on the reaction of 1,1-dimethoxy-2-phenylethane **1a** and 1,1-dimethoxy-2-phenylpropane **1b** with carbonyl electrophiles, in the presence of LICKOR superbase. The reaction proceeds through two consecutive metallations that lead to an α -metallated enol ether. Carbonyl electrophiles add to the carbanionic intermediate affording α -substituted derivatives that can be subsequently transformed into carbonyl compounds and alkynes, depending on the structure and reaction conditions.

Results and discussion

The reaction of acetals **1a** and **1b** with 1.25 equiv. of LICKOR in THF at -95°C is initiated by metallation at the benzylic position, which is immediately followed by β -elimination to give the enol ethers **2a,b**. In this context, the metallation of 2-benzyloxirane has been previously accomplished:⁵ the acidity enhancing effect of the phenyl substituent and the ring strain provide enough driving force to overcome the reluctance of the alkoxy group to act as a leaving group. In the case of **1a,b**, the excess of metal cation insures coordination to the methoxy group, and enhances its nucleofugality.⁶ Enol ethers **2a,b** can be further metallated by LICKOR reagent (1.25 equiv.) affording α -metallated intermediates **3a,b**,⁷ that react with carbonyl compounds. Working in the presence of 2.5 equiv. of LICKOR base, the reaction gives directly allyl alcohols in good yields, after the addition of the electrophile. The results are reported in Table I and the products shown in Scheme 1.

The elimination reaction yields selectively intermediates **2a,b** in the *E*-configuration. The *E*-configuration of enol ether **2a** has been deduced from the J_{trans} coupling constant (13 Hz) between the α - and β -vinylic protons in the ^1H NMR spectrum. For



Scheme 1 Reaction of acetals **1a,b** with carbonyl compounds, in the presence of LICKOR reagent: synthesis of allyl alcohols

Table I Allyl alcohols obtained by the treatment of acetals **1a,b** with carbonyl compounds, in the presence of LICKOR reagent^a

Electrophile	Substrate	Product	Yield (%) ^b
Bu ^t CHO	1a	4a	72
Bu ^t COMe	1a	4b	64
Bu ^t ₂ CO	1a	4c	57
Ph ₂ CO	1a	4d	83
PhCHO	1a	4e	95
Bu ^t CHO	1b	4f	87
PhCHO	1b	4g	81
Bu ^t COMe	1b	4h	68

^a Substrate (5.0 mmol), Bu^tLi (12.5 mmol), Bu^tOK (12.5 mmol), electrophile (5.0 mmol), THF (10 cm³), *T* = from -95 to -50°C .

^b Isolated yield of purified product.

compound **2b** irradiation of the olefinic hydrogen atom gives rise to an Overhauser enhancement of the signal assigned to the

Table 2 Prop-2-ynyl alcohols obtained by the treatment of acetals **1a** with carbonyl compounds, in the presence of LICKOR reagent^a

Electrophile	Product	Yield (%) ^b
Bu ^t CHO	5a	37
Bu ^t COMe	5b	84
Bu ^t ₂ CO	5c	35
Ph ₂ CO	5d	84

^a Substrate (5.0 mmol), Bu^tLi (20.0 mmol), Bu^tOK (20.0 mmol), electrophile (5.0 mmol), THF (10 cm³), *T* = from -95 to 25 °C.
^b Isolated yield of purified product.

Table 3 Acid-catalysed reaction of α -substituted enol ethers **4a-e**^a

Enol ether	Product	Yield (%) ^b
4a	6a	80
4b	6b	75
4c	6c	80
4d	6d	67
4e	6e	70

^a Substrate (2.5 mmol), catalyst (0.02 mol dm⁻³ HCl), solvent (MeOH-H₂O, 4:1; 25 cm³), *T* = 25 °C. ^b Isolated yield of purified product.

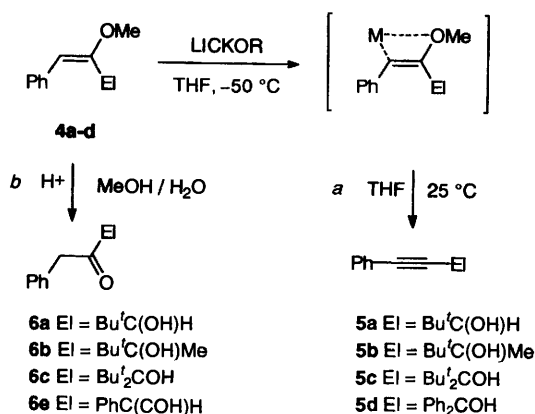
Ph and OMe groups which indicates the *E*-configuration. Moreover, irradiation of the Me allyl hydrogen atoms caused an NOE of the signal assigned to the aromatic hydrogens.

To our knowledge, there are no methods in the literature for the conversion of simple acetals into alkynes.⁸ The hydrohalogeno-elimination of dihalides or vinylic halides is by far the most important way of introducing a triple bond into a molecule.⁹ In experiments carried out at -95 °C in the presence of 4.0 equiv. of LICKOR superbase, and of 1.0 equiv. of **1a** and pivaldehyde, two compounds were obtained. After column chromatography (cyclohexane-diethyl ether, 90:10), allyl alcohol **4a** was separated (45%) from 4,4-dimethyl-1-phenylpent-1-yn-3-ol **5a** (15%). This result suggests that with a large excess of base, as the addition product **4a** forms, it undergoes β -metallation and 1,2-elimination, affording **5a**. Prop-2-ynyl alcohol **5a** can be obtained pure from intermediate enol ethers **4a** by further treatment with 2.0 equiv. of LICKOR superbase in THF at -95 °C. Moreover, alkynes **5a-d** can be obtained starting from **1a** in a one-pot synthesis, working in the presence of 4.0 equiv. of LICKOR and, after the addition of a suitable electrophile, stirring the reaction mixture at 25 °C for 0.5 h before the addition of water. The results are reported in Table 2 and the products shown in Scheme 2, route *a*. Unlike compounds **4a-d**, derivative **4e** does not undergo further β -elimination, probably because metallation occurs at the more acidic benzyl carbon.

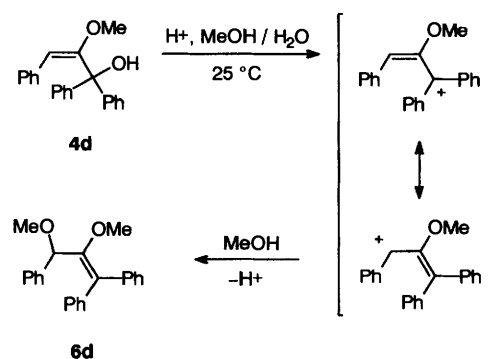
The metallation of **2a,b** takes place selectively at the α -position, as the methoxy substituent probably favours the dihapto carbanion through a neighbouring group effect (Scheme 1, structure **3a,b**).^{10,†}

The reaction products **4a-h** contain a vinyl ether moiety which can be further elaborated and converted into the

† Intermediate **2b** might undergo metallation at either of two different sites: *i.e.* either the α -vinylic or the γ -allylic terminus. Hydrogen-metal exchange takes place selectively at the vinylic position. Analogous regioselectivity was found for (*E*)-1-ethoxy-3-methylbuta-1,3-diene. In that case, some computational data show energy differences between the allylic and vinylic structures (0.90 and -23.95 kcal mol⁻¹ for Li and K, respectively), that agree with the experimental regioselectivity, K being expected to be the counter-ion of the intermediate carbanion (see ref. 10).

**Scheme 2** Reaction of enol ethers **4a-d**, in the presence of LICKOR reagent: synthesis of prop-2-ynyl alcohols (route *a*); acid catalysed conversion of enol ethers **4a-c** and **4e** into carbonyl compounds (route *b*)

corresponding carbonyl compound in high isolated yield,^{7,11} according to an umpolung approach (Scheme 2, route *b*).¹² Hydrolysis of the adducts can be achieved under mild conditions (aqueous methanolic 0.02 mol dm⁻³ HCl, 25 °C), and the results are reported in Table 3. Similar conditions appear to be applicable to most of the compounds in Table 1. In contrast, the acid-catalysed reaction of compound **4d** proceeds *via* a different pathway: the acidic reaction firstly promotes the protonation of the allylic alcohol and the formation of a carbocation intermediate. Subsequent nucleophilic attack by methanol results in 2,3-dimethoxy-1,1,3-triphenylprop-1-ene **6d** (Scheme 3).

**Scheme 3** Acid-catalysed conversion of enol ether **4d** into 2,3-dimethoxy-1,1,3-triphenylprop-1-ene **6d**

Experimental

Flasks and all the equipment used for the generation and reaction of moisture-sensitive compounds were flame dried under argon. Where a temperature of -95 °C is indicated an acetone-liquid nitrogen slush bath was used; 'room temperature' is denoted as 25 °C. Anhydrous tetrahydrofuran (THF) was obtained by distillation over sodium wire-benzophenone after a persistent blue colour of sodium diphenylketyl was observed.¹³ Bu^tLi (1.4 mol dm⁻³ solution in cyclohexane) was purchased from Aldrich. Bu^tOK, obtained from Merck, was sublimed *in vacuo* (0.1 Torr) prior to the reaction. All commercially available chemicals were reagent grade and were used without further purification. ¹H NMR spectra were recorded at 60 or 300 MHz as CDCl₃ solutions, using tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) are given in Hz, and coupling patterns are described by the abbreviations: s (singlet),

d (doublet), q (quartet), m (multiplet), br (broad). ^{13}C NMR were recorded at 75.5 MHz as CDCl_3 solutions. Chemical shifts were determined relative to the residual solvent peak (CHCl_3 : 77.0 ppm). A cross linked methyl silicone capillary column (25 m \times 0.2 mm \times 0.33 mm film thickness) was used for GC-MS spectra, which were obtained at a 70 eV ionisation potential. Purification of products was carried out by preparative column chromatography on Merck silica gel 60 with light petroleum (bp 30–60 °C)-diethyl ether, or cyclohexane-diethyl ether as eluent.

LICKOR Promoted elimination in acetals 1a,b

Under an atmosphere of argon, the solvent was stripped from a solution of Bu^tLi (1.4 mol dm^{-3} solution in cyclohexane; 4.5 cm^3 , 6.25 mmol) under reduced pressure. Pre-cooled (–95 °C) THF (10 cm^3), substrate (5.0 mmol) and sublimed Bu^tOK (0.7 g, 6.25 mmol) were added consecutively to it with stirring at –95 °C.^{14,†} After 3 h at –95 °C the reaction mixture was kept for 1 h at –50 °C, and then quenched at that temperature with water-THF (3:2; 5 cm^3) and allowed to reach 25 °C. The two phases were separated and the aqueous layer was extracted with diethyl ether (3 \times 15 cm^3). The combined organic solutions were washed with brine (2 \times 10 cm^3) and dried (Na_2SO_4). After evaporation of the solvent the residue was purified.

(*E*)-1-Methoxy-2-phenylethene **2a**:¹⁵ δ_{H} (60 MHz) 3.6 (3 H, s), 5.7 (1 H, d, *J* 13), 6.9 (1 H, d, *J* 13) and 7.2 (5 H, br s).

(*E*)-1-Methoxy-2-phenylprop-1-ene **2b**:¹⁶ δ_{H} (60 MHz) 1.9 (3 H, d, *J* 1.4), 3.6 (3 H, s), 6.2 (1 H, q, *J* 1.4) and 7.1 (5 H, br s).

General procedure for the synthesis of α -substituted enol ethers

A solution of Bu^tLi (1 mol dm^{-3} in cyclohexane; 9.0 cm^3 , 12.5 mmol) was evaporated under reduced pressure and the residue dissolved at –95 °C in pre-cooled THF (10 cm^3). The substrate (5.0 mmol) and sublimed Bu^tOK (1.4 g, 12.5 mmol) were added consecutively to the resulting solution with stirring at –95 °C. After 3 h at –95 °C the electrophile (5.0 mmol) was added and the reaction mixture was kept for 1 h at –50 °C. The reaction mixture was then treated at that temperature with aqueous THF (5 cm^3) and allowed to reach 25 °C. After standard work-up (see above) the residue was purified.

(*E*)-2-Methoxy-4,4-dimethyl-1-phenylpent-1-en-3-ol **4a**. Cyclohexane- Et_2O , 85:15. Colourless oil, δ_{H} (60 MHz) 1.0 (9 H, s), 2.4 (1 H, br s), 3.4 (3 H, s), 4.1 (1 H, s), 5.4 (1 H, s) and 7.1 (5 H, br s); *m/z* (relative intensity) 220 (M^+ , 10%), 163 (97), 131 (100), 103 (95), 91 (49) and 57 (73) (Found: C, 76.45; H, 9.2. Calc. for $\text{C}_{14}\text{H}_{20}\text{O}_2$: C, 76.33; H, 3.15%).

(*E*)-2-Methoxy-3,4,4-trimethyl-1-phenylpent-1-en-3-ol **4b**. Cyclohexane- Et_2O , 90:10. Colourless oil, δ_{H} (60 MHz) 1.1 (9 H, s), 1.5 (3 H, s), 3.3 (1 H, br s), 3.6 (3 H, s), 5.6 (1 H, s) and 7.1 (5 H, br s); *m/z* (relative intensity) 177 (M^+ –57, 2%) 131 (100), 103 (99), 102 (21), 77 (74) and 57 (100) (Found: C, 77.0; H, 9.55. Calc. for $\text{C}_{15}\text{H}_{22}\text{O}_2$: C, 76.88; H, 9.46%).

(*E*)-3-tert-Butyl-2-methoxy-4,4-dimethyl-1-phenylpent-1-en-3-ol **4c**. Light petroleum- Et_2O , 85:15. Colourless oil, δ_{H} (60 MHz) 1.1 (18 H, s), 3.2 (1 H, br s), 3.4 (3 H, s), 5.4 (1 H, s) and 7.0 (5 H, br s); *m/z* (relative intensity) 219 (M^+ –57, 20%), 201 (42), 145 (49), 91 (49) and 57 (100) (Found: C, 78.1; H, 10.0. Calc. for $\text{C}_{18}\text{H}_{28}\text{O}_2$: C, 78.21; H, 10.21%).

(*E*)-2-Methoxy-1,1,3-triphenylprop-2-en-1-ol **4d**. Cyclohexane- Et_2O , 97:3. Colourless oil; δ_{H} (60 MHz) 3.1 (1 H, br s), 3.5 (3 H, s), 5.8 (1 H, s) and 7.0–7.3 (15 H, m); *m/z* (relative intensity) 316 (M^+ , 3%), 298 (22), 283 (100), 109 (28) and 77

(28) (Found: C, 83.65; H, 6.45. Calc. for $\text{C}_{22}\text{H}_{20}\text{O}_2$: C, 83.52; H, 6.37%).

(*E*)-2-Methoxy-1,3-diphenylprop-2-en-1-ol **4e**. Cyclohexane- Et_2O , 80:20. Mp 62 °C (light petroleum- Et_2O); δ_{H} (300 MHz) 2.7 (1 H, d, *J* 8), 3.6 (3 H, s), 5.7 (1 H, d, *J* 8), 5.8 (1 H, s) and 7.1 (10 H, m); *m/z* (relative intensity) 240 (M^+ , 20%), 207 (50), 105 (47), 91 (51) and 77 (99) (Found: C, 80.05; H, 6.8. Calc. for $\text{C}_{16}\text{H}_{16}\text{O}_2$: C, 79.97; H, 6.71%).

(*E*)-4-Methoxy-2,2-dimethyl-5-phenylhex-4-en-3-ol **4f**. Cyclohexane- Et_2O , 95:5. Colourless oil; δ_{H} (60 MHz) 0.9 (9 H, s), 1.8 (3 H, s), 3.4 (1 H, br s), 3.5 (3 H, s), 4.2 (1 H, s) and 7.0 (5 H, br s); *m/z* (relative intensity) 234 (M^+ , 5%), 148 (100), 117 (27), 87 (10), 77 (25) and 57 (21) (Found: C, 76.95; H, 9.65. Calc. for $\text{C}_{15}\text{H}_{22}\text{O}_2$: C, 76.9; H, 9.5%).

(*E*)-2-Methoxy-1,3-diphenylbut-2-en-1-ol **4g**. Cyclohexane- Et_2O , 80:20. Colourless oil; δ_{H} (60 MHz) 1.9 (3 H, s), 2.6 (1 H, br s), 3.4 (3 H, s), 5.1 (1 H, s) and 7.1 (10 H, br s); *m/z* (relative intensity) 254 (M^+ , 4%), 222 (18), 105 (35), 77 (100) and 51 (36) (Found: C, 80.2; H, 7.0. Calc. for $\text{C}_{17}\text{H}_{18}\text{O}_2$: C, 80.3; H, 7.1%).

(*E*)-4-Methoxy-2,2,3-trimethyl-5-phenylhex-4-en-3-ol **4h**. Cyclohexane- Et_2O , 80:20. Colourless oil; δ_{H} (60 MHz) 0.9 (9 H, s), 1.1 (3 H, s), 1.3 (3 H, s), 3.4 (1 H, br s), 3.5 (3 H, s) and 7.1 (5 H, br s); *m/z* (relative intensity) 191 (M^+ –57, 4%), 148 (96), 117 (32), 102 (31), 77 (26), 57 (30) and 43 (100) (Found: C, 77.6; H, 9.45. Calc. for $\text{C}_{16}\text{H}_{24}\text{O}_2$: C, 77.4; H, 9.7%).

General procedure for the synthesis of alkynes

Alkynes were synthesised according to the procedure reported above for α -substituted enol ethers, starting from 1.0 equiv. of **1a**, and working in the presence of 4.0 equiv. of LICKOR reagent. After the addition of the electrophile, the mixture was stirred at 25 °C for 0.5 h and then the reaction was quenched by the addition of water.

4,4-Dimethyl-1-phenylpent-1-yn-3-ol **5a**. Cyclohexane- Et_2O , 85:15. Colourless oil; δ_{H} (300 MHz) 1.1 (9 H, s), 2.2 (1 H, br s), 4.2 (1 H, s), 7.3 (3 H, m) and 7.5 (2 H, m); δ_{C} 25.23, 35.97, 71.85, 85.50, 88.08, 122.85, 128.12, 128.14 and 131.52; *m/z* (relative intensity) 188 (M^+ , 10%), 131 (99), 103 (41), 77 (78) and 57 (98) (Found: C, 83.1; H, 8.75. Calc. for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.9; H, 8.6%).

3,4,4-Trimethyl-1-phenylpent-1-yn-3-ol **5b**. Cyclohexane- Et_2O , 90:10. Colourless oil; δ_{H} (300 MHz) 1.1 (9 H, s), 1.5 (3 H, s), 2.2 (1 H, br s), 7.3 (3 H, m) and 7.5 (2 H, m); δ_{C} 24.64, 25.95, 38.32, 74.12, 83.67, 92.80, 122.86, 127.94, 128.07 and 131.43; *m/z* (relative intensity) 145 (M^+ –57, 15%), 131 (100), 91 (31), 89 (15), 77 (30) and 57 (47) (Found: C, 83.35; H, 8.95. Calc. for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.1; H, 9.0%).

3-tert-Butyl-4,4-dimethyl-1-phenylpent-1-yn-3-ol **5c**. Cyclohexane- Et_2O , 85:15. Colourless oil; δ_{H} (300 MHz) 1.3 (18 H, s), 2.0 (1 H, br s), 7.3 (3 H, m) and 7.5 (2 H, m); δ_{C} 29.59, 41.62, 81.41, 85.14, 92.95, 123.19, 127.91, 128.15 and 131.36; *m/z* (relative intensity) 244 (M^+ , 5%), 187 (100), 172 (42), 128 (24), 57 (18) and 43 (92) (Found: C, 83.8; H, 10.05. Calc. for $\text{C}_{17}\text{H}_{24}\text{O}$: C, 83.55; H, 9.9%).

1,1,3-Triphenylprop-2-yn-1-ol **5d**. Cyclohexane- Et_2O , 97:3. Colourless oil; δ_{H} (300 MHz) 3.3 (1 H, br s) and 7.2–7.7 (15 H, m); δ_{C} 74.65, 87.05, 91.70, 122.34, 125.96, 127.16, 127.87, 128.17, 128.54, 131.66 and 144.97; *m/z* (relative intensity) 284 (M^+ , 32%), 207 (27), 178 (58), 105 (60) and 77 (100) (Found: C, 76.2; H, 9.1. Calc. for $\text{C}_{21}\text{H}_{16}\text{O}$: C, 88.7; H, 5.7%).

General procedure for the acid-catalysed reaction of α -substituted enol ethers

Crude enol ether **4a–e** (2.5 mmol) was dissolved in aqueous methanolic (1:4) HCl (0.02 mol dm^{-3} ; 25 cm^3) and stirred at 25 °C for 2–4 h. The reaction was followed by TLC (Et_2O -light petroleum, 40:60). After the disappearance of the spot corresponding to the enol ether, the solution was neutralised with 5% aqueous NaHCO_3 and then evaporated to half its

† It is advisable to control the reaction temperature in order to avoid the formation of (*E*)-3-methyl-1-phenylpent-1-ene and (*E*)-4-methyl-2-phenylhex-2-ene. The by-products are obtained by substitution reactions of the organometallic reagent on **2a** and **2b**, respectively. Analogous substitution reactions have been previously described (see ref. 14).

volume. The residue was extracted with Et₂O (2 × 20 cm³), and the organic phase washed with brine (2 × 20 cm³) and dried. After evaporation of the solvent the crude reaction product was purified.

3-Hydroxy-4,4-dimethyl-1-phenylpentan-2-one 6a. Light petroleum–Et₂O, 60:40. Colourless oil; δ_H(60 MHz) 0.9 (9 H, s), 3.1 (1 H, br s), 3.65 (2 H, s), 3.75 (1 H, s) and 7.0 (5 H, br s); *m/z* (relative intensity) 188 (M⁺ – 18, 4%), 120 (40), 91 (96), 57 (100) and 41 (97); ν_{max}(neat)/cm⁻¹ 3400 and 1700 (Found: C, 75.9; H, 8.65. Calc. for C₁₃H₁₈O₂: C, 75.7; H, 8.8%).

3-Hydroxy-3,4,4-trimethyl-1-phenylpentan-2-one 6b. Light petroleum–Et₂O, 60:40. Colourless oil; δ_H(60 MHz) 0.9 (9 H, s), 1.1 (3 H, s), 3.3 (1 H, br s), 3.7 (2 H, s) and 7.1 (5 H, br s); *m/z* (relative intensity) 220 (M⁺, 8%), 131 (100), 91 (41), 77 (41) and 57 (44); ν_{max}(neat)/cm⁻¹ 3450 and 1710 (Found: C, 76.1; H, 9.25. Calc. for C₁₄H₂₀O₂: C, 76.3; H, 9.15%).

3-tert-Butyl-3-hydroxy-4,4-dimethyl-1-phenylpentan-2-one 6c. Light petroleum–Et₂O, 60:40. Colourless oil; δ_H(60 MHz) 0.9 (9 H, s), 1.1 (9 H, s), 3.3 (2 H, s), 3.7 (1 H, br s) and 7.1 (5 H, br s); *m/z* (relative intensity) 245 (M⁺ – 17, 100%), 91 (25), 85 (25), 37 (100) and 43 (29); ν_{max}(neat)/cm⁻¹ 3450 and 1720 (Found: C, 78.0; H, 9.8. Calc. for C₁₇H₂₆O₂: C, 77.8; H, 10.0%).

2,3-Dimethoxy-1,1,3-triphenylprop-1-ene 6d. Light petroleum–Et₂O, 90:10. Mp 129 °C (light petroleum–Et₂O); δ_H(300 MHz) 3.35 (3 H, s), 3.40 (3 H, s), 4.9 (1 H, s) and 7.1–7.9 (15 H, m); *m/z* (relative intensity) 330 (M⁺, 61%), 298 (100), 255 (44), 121 (28) and 77 (17); ν_{max}(CHCl₃)/cm⁻¹ 3450 and 1710 (Found: C, 83.75; H, 6.65. Calc. for C₂₃H₂₂O₂: C, 83.6; H, 6.7%).

1-Hydroxy-1,3-diphenylpropan-2-one 6e. Light petroleum–Et₂O, 70:30. Colourless oil; δ_H(60 MHz) 3.6 (2 H, s), 4.1 (1 H, d, *J* 8), 5.1 (1 H, d, *J* 8) and 7.1 (10 H, m); *m/z* (relative intensity) 208 (M⁺ – 18, 26%), 121 (15), 107 (47), 105 (93) and 77 (100); ν_{max}(CHCl₃)/cm⁻¹ 3450 and 1710 (Found: C, 76.75; H, 6.1. Calc. for C₁₅H₁₄O₂: C, 79.6; H, 6.2%).

Acknowledgements

This work was supported by grants from the MURST, from the Italian CNR, and from the 'Progetto Strategico Tecnologie Chimiche'.

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Paper 5/03793J

Received 13th June 1995

Accepted 6th July 1995