

**SYNTHESIS VIA ULTRASOUND: A CONVENIENT SYNTHESIS  
OF 6-(4-TOLYL)HEPT-1-ENE AND  
6-(2-OXO-4-METHYLCYCLOHEX-3-EN-1-YL)HEPT-1-ENE**

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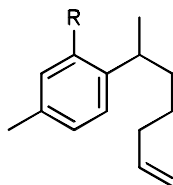
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6-(4-Tolyl)hept-1-ene (*I*) and 6-(2-oxo-4-methylcyclohex-3-en-1-yl)hept-1-ene (*II*), monocyclic nor-sesquiterpenes from aerial parts of South African *Senecio digitalifolius*, have been synthesized using ultrasonic waves and tandem phenylation reduction.

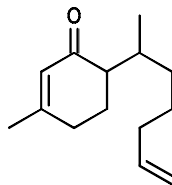
Bohlmann and Zdero have isolated 6-(4-tolyl)hept-1-ene (*I*) and 6-(2-oxo-4-methylcyclohex-3-en-1-yl)hept-1-ene (*II*), monocyclic norsesquiterpenes from the aerial parts of South African *Senecio digitalifolius* DC (ref.<sup>1</sup>). On the basis of detailed spectral studies, structures *I* and *II* have been assigned to these compounds. Literature<sup>2-4</sup> reports multistep synthesis of both compounds, albeit in low yields. Herein, we report a simple, elegant and straightforward synthesis of *I* and *II* via the use of ultrasonic waves and tandem phenylation reduction<sup>5</sup> in overall yields 72% and 70%, respectively.

Zinc-copper couple catalyzed conjugate addition<sup>6</sup> of methyl vinyl ketone with allyl bromide under sonochemical aqueous conditions afforded hept-6-en-2-one (*III*). Tan-

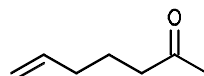


*I*, R = H

*IV*, R = OCH<sub>3</sub>



*II*



*III*

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dem phenylation reduction of compound *III* with 4-bromotoluene in lithium–ammonia gave compound *I*. Compound *III* on reaction with 2-bromo-5-methylanisole in lithium–ammonia–tetrahydrofuran followed by Birch reduction of the resultant product furnished pure compound *II* in good yield.

## EXPERIMENTAL

$^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{CCl}_4$  on a Varian EM-390 (90 MHz) spectrometer utilizing tetramethylsilane as internal standard; chemical shifts in ppm ( $\delta$ -scale), coupling constants ( $J$ ) in Hz. IR spectra of thin films were recorded on a Perkin–Elmer infra-red 337 spectrophotometer (wavenumbers in  $\text{cm}^{-1}$ ). Unless otherwise stated all organic extracts were dried over anhydrous sodium sulfate. Silica gel (ASC, Bombay) impregnated with calcium sulfate was used for TLC.

### Hept-6-en-2-one (*III*)

To the zinc–copper couple, prepared under nitrogen from zinc (1.56 g, 24 mmol) and copper(I) iodide (0.95 g, 5 mmol) in ethanol–water (9 : 1, 20 ml) in a 100 ml reaction vessel using sonicator Model XL 2015 (20 kHz) was added methyl vinyl ketone (0.70 g, 10 mmol) and allyl bromide (1.8 g, 15 mmol) and the mixture sonicated further for 45 min. The product thus obtained was quenched with saturated brine and filtered, ethanol was evaporated under reduced pressure and the residue extracted with ether. The ether extract was washed twice with water and then with brine to obtain the crude material, which was chromatographed over silica gel using hexane–ethylacetate (95 : 5) as eluent furnishing pure compound *III*, yield 0.89 g (80%).  $^1\text{H}$  NMR spectrum: 1.2 m, 2 H ( $-\text{CH}_2-$ ); 1.8 m, 2 H ( $=\text{CH}-\text{CH}_2-$ ); 2.06 s, 3 H ( $-\text{COCH}_3$ ); 2.3 m, 2 H ( $-\text{CH}_2\text{CO}-$ ); 4.97 – 5.40 m, 2 H ( $-\text{CH}=\text{CH}_2$ ); 5.6 – 6.1 m, 1 H ( $-\text{CH}=\text{CH}_2$ ). IR spectrum: 2 960, 2 930, 2 850, 1 710, 1 640, 1 470, 1 270, 1 030, 935, 800. For  $\text{C}_7\text{H}_{12}\text{O}$  (112.2) calculated: 75.0% C, 10.8% H; found: 74.9% C, 10.8% H.

### 6-(4-Tolyl)hept-1-ene (*I*)

In a metal ammonia reaction vessel containing a stirred mixture of lithium (2.8 g, 400 mmol) in anhydrous ether (100 ml) was slowly added a solution of 4-bromotoluene (8.55 g, 50 mmol) in dry ether (70 ml). After 1 h, the solution of hept-6-en-2-one (*II*; 2.8 g, 25 mmol) in anhydrous ether (80 ml) was added slowly and stirred further for 1 h. Liquid ammonia (250 ml) was slowly added to prevent excessive splattering. Once a dark blue colour of the mixture was established, ammonium chloride (29.4 g, 550 mmol) was added carefully to discharge the blue colour and ammonia was allowed to evaporate. Then the residue had been partitioned between aqueous sodium chloride solution and ether, the aqueous layer was extracted with ether and the combined organic layer was dried, concentrated and distilled under reduced pressure to obtain pure *I*, yield 4.23 g (90%).  $^1\text{H}$  NMR spectrum: 0.95 d, 3 H ( $J = 6$ ,  $-\text{CH}_3$ ); 1.23 m, 4 H ( $-\text{CH}_2-$ ); 1.8 m, 2 H ( $-\text{CH}_2-\text{CH}=\text{}$ ); 2.3 s, 3 H (Ar- $\text{CH}_3$ ); 2.57 m, 1 H (Ar-CH); 4.9 – 5.2 m, 2 H ( $-\text{CH}=\text{CH}_2$ ); 5.8 m, 1 H ( $-\text{CH}=\text{CH}_2$ ); 7.2 s, 4 H ( $4 \times \text{Ar-H}$ ). IR spectrum: 2 980, 2 940, 2 880, 1 470, 1 380, 760. For  $\text{C}_{14}\text{H}_{20}$  (188.3) calculated: 89.3% C, 10.7% H; found: 89.1% C, 10.9% H.

### 6-(2-Methoxy-4-methylphenyl)hept-1-ene (*IV*)

Title compound was prepared by above mentioned procedure from 2-bromo-5-methylanisole (10.05 g, 50 mmol), yield 4.79 g (88%).  $^1\text{H}$  NMR spectrum: 1.1 d, 3 H,  $J = 7$ , ( $-\text{CH}_3$ ); 1.35 m, 2 H ( $-\text{CH}_2-$ ); 1.85 m, 2 H ( $-\text{CH}_2-\text{CH}=\text{}$ ); 2.2 s, 3 H (Ar- $\text{CH}_3$ ); 3.08 m, 1 H (Ar-CH); 3.72 s, 3 H ( $-\text{OCH}_3$ ); 4.97 – 5.23

2 H ( $-\text{CH}=\text{CH}_2$ ); 5.7 m, 1 H ( $-\text{CH}=\text{CH}_2$ ); 6.4 – 6.97, 3 H (Ar-H). IR spectrum: 2 990, 2 960, 2 860, 1 490, 910. For  $\text{C}_{15}\text{H}_{22}\text{O}$  (218.3) calculated: 82.5% C, 10.2% H; found: 82.3% C, 10.4% H.

6-(2-Oxo-4-methylcyclohex-3-en-1-yl)hept-1-ene (*II*)

Compound *IV* (3.0 g, 13.8 mmol) in dry ether (16 ml) was added to anhydrous liquid ammonia (52 ml) with stirring and to this homogeneous solution was added lithium (0.48 g, 6.8 mmol) in small pieces during 10 min. After stirring for 30 min, absolute alcohol (3.0 ml) was added dropwise during 30 min, when bluish-brown colour disappeared completely. Ammonia was allowed to evaporate; solid residue was decomposed with cold water and extracted with ether ( $3 \times 50$  ml). The combined ether extract was washed with saturated brine. Evaporation of ether gave an oil which after hydrolysis with 10% HCl for 30 min was cooled and extracted with ether ( $2 \times 50$  ml). The ethereal layer was washed with 5% sodium hydrogen carbonate solution and dried. Evaporation of the solvent followed by column chromatography on alumina using ether–light petroleum (3 : 2) gives compound *II*, yield 1.4 g (49%).  $^1\text{H}$  NMR spectrum: 0.85 d, 3 H,  $J = 7$  ( $-\text{CH}_3$ ); 1.2 – 1.5 m, 6 H ( $3 \times -\text{CH}_2-$ ); 1.9 m, 2 H (ring  $-\text{CH}_2-\text{C}=\text{C}-$ ); 1.92 s, 3 H ( $=\text{C}-\text{CH}_3$ ); 2.05 m, 2 H (chain  $-\text{CH}_2-\text{CH}=\text{C}-$ ); 2.3 m, 1 H ( $-\text{CH}(\text{CH}_3)-$ ); 4.97 – 5.40 m, 2 H ( $-\text{CH}=\text{CH}_2$ ); 5.85 m, 2 H ( $2 \times -\text{CH}=\text{C}-$ ). IR spectrum: 3 020, 1 670, 1 620, 990, 905. For  $\text{C}_{14}\text{H}_{22}\text{O}$  (206.3) calculated: 81.5% C, 10.7% H; found: 81.1% C, 10.5% H.

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