L-Proline catalysed Michael additions of different active methylene compounds to α-enones in ionic liquid

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Dedicated to Professor E. Lukevics on the occasion of his 70th birthday

Abstract
L-Proline catalysed Michael addition of different active methylene compounds to α-enones in [bmim]PF_6 was studied. Only 5 mol% of L-proline was necessary to achieve good yields of the products, but practically no stereoselectivity was observed. Reactions went smoothly with methyl vinyl ketone, benzylideneacetone as well as chalcone. Only medium yields of the product were isolated at additions to cyclohex-2-ene-1-one.

Keywords: Michael addition, α-enones, L-proline, ionic liquids

Introduction

The Michael addition is one of the most frequently used C–C bond forming reactions in organic synthesis.[1–5] Great progress has been achieved for the asymmetric versions of this reaction.[6–8] Additionally, asymmetric Michael addition to nitroalkenes is also known.[9] One of the most frequently used classes of catalysts in asymmetric Michael additions are Cinchona alkaloids and their derivatives[10,11] as well as BINOL-based heterobimetallic catalysts.[12] Asymmetric reactions catalysed by small organocatalysts have become very attractive in recent years.[13–18] Yamaguchi *et al*. were the first who used rubidium salt of L-proline as the catalyst at addition of nitroalkanes to cyclic enones[19–21] as well as di(*i*-propyl) malonate to prochiral enones and enals.[20] Reactions proceeded with high stereoselectivity up to 76–84% ee. Neutral organocatalysts have been used by Jørgensen for Michael additions of nitroalkanes[22] and dibenzyl malonate[23] to benzylideneacetone and aliphatic aldehydes to vinyl ketones.[24] L-Proline alone was found to be rather ineffective catalyst (up to 15% conversion, 20% ee), but its catalytic efficiency raised considerably after addition of up to 80 mol% of *trans*-2,5-dimethylpiperazine or piperazine as described by Hannesian.[25] In all cases 10–20 mol% of the catalyst has to be used and reaction

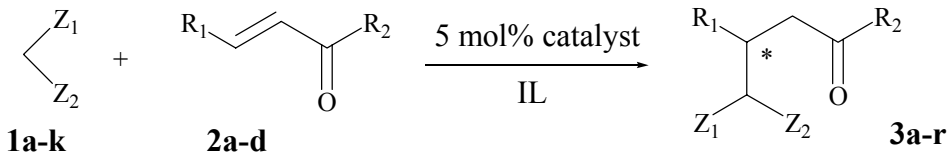
times were 20–180 h. Reasonable results were achieved also by Barbas *et al*.[26] at Michael additions of cyclic as well as acyclic ketones to alkylidenemalonates when 20 mol% of (*S*)-2-[(1-pyrrolidyl)methyl]pyrrolidine was used as the catalyst. While our work was in progress, an interesting paper was published by Jørgensen and co-workers.[27] They tested several organocatalysts for Michael additions of cyclic β-dicarbonyl compound to α,β-unsaturated ketones and the best catalyst was found to be (*S,S*)-(-)-4,5-diphenylimidazoline-2-carboxylic acid. He also described organocatalytic asymmetric domino Michael-Aldol reactions of β-ketoesters to α,β-unsaturated ketones.[28] Prieto found[29] that chiral imidazolidine-2-yltetrazole is an excellent catalyst for Michael addition of nitroalkanes to benzylideneacetone and similar compounds. McMillan's catalyst gave very good ee with just medium yields at Michael additions of aldehydes to methyl vinyl ketone, but yields were rised after addition of 4-ethoxycarbonylcatechol[30]. Ley et al. described that the best catalyst for Michael addition of ketones to nitrostyrene[31] and similarly of nitroalkanes to cyclohexenone as well as benzylideneacetone[32,] and dimethyl malonate[33] to the same acceptors found was 5-pyrrolidin-2-yltetrazole. They screened a range of solvents and found that dichloromethane is the best solvent, but reaction time is rather long 2-3 days and the best ee as well as the best yields were achieved after addition of equivalent amount of base (piperidine or piperazine)

In recent years, ionic liquids have emerged as frequently used "green" solvents for many organic reactions including transition metal and biocatalysed reactions.[34–41] Ionic liquids have been used also for addition of thiols to α,β-unsaturated ketones.[42] Dell'Anna found that [bmim]BF_4 is a good solvent for addition of acetylacetone to methyl vinyl ketone when $Ni(acac)_2$ is used as the catalyst.[43] Yadav described [bmim]BF_4 as an excellent solvent for Michael additions of β-ketoesters to methyl vinyl ketone, cyclohexenone and cyclopentenone when copper(II) triflate was used as the catalyst.[44] Simultaneously, with Loh[45] we have found that ionic liquids are also excellent solvents for L-proline-catalysed aldol reactions.[46] Chowdari described L-proline catalysed asymmetric Mannich reactions in ionic liquids.[47] We have found, that L-proline in ionic liquids is a very good catalyst for Michael addition of aliphatic aldehydes and ketones to β-nitrostyrenes.[48] High yield reactions and reasonable enantioselectivities using just 5 mol% of the L-proline were attained. Rasalkar very recently described L-proline catalysed Michael addition of ketones to nitrostyrene.[49] He tested several ionic liquids and 1-methoxyethyl-3-methylimidazolium methanesulfonate ([MOEMIM]OMs) was found to be the best. In order to achieve good yields it was necessary to prolong the reaction time up to 60 hours and catalyst loading had to be increased up to 40 mol% to achieve 75% ee. Very recently Hagiwara described[50] organocatalysed addition of aliphatic aldehydes to methyl vinyl ketone in ionic liquid [bmim]PF_6. 2-(*S*)-(1-Morpholinomethyl)piperidine was found to be the best organocatalyst, but the yields of the product were only medium with 11–51% ee. We have performed in ionic liquids also organocatalytic Michael additions of thiophenols[51] and even Michael addition of thiols without any catalyst[52].

The aim of this work was to explore whether ionic liquids can be used as the solvents for L-proline catalysed Michael additions of different active methylene compounds to α- enones.

Results and Discussion

The organocatalysed Michael additions of C-nucleophiles are usually performed in conventional solvents and the most frequently used substrates are methyl vinyl ketone, benzylideneacetone, and esters of benzylidenemalonic acid. The best results were achieved when aliphatic aldehydes or ketones were used as the reagents. This is not a surprise, because *L*-proline, or bases derived from it, can form reactive intermediates (enamines) with both of them. (Scheme 1, Fig. 1,2, Table1)



Scheme 1. Michael addition of methylene active compounds to α,β-unsaturated enones.

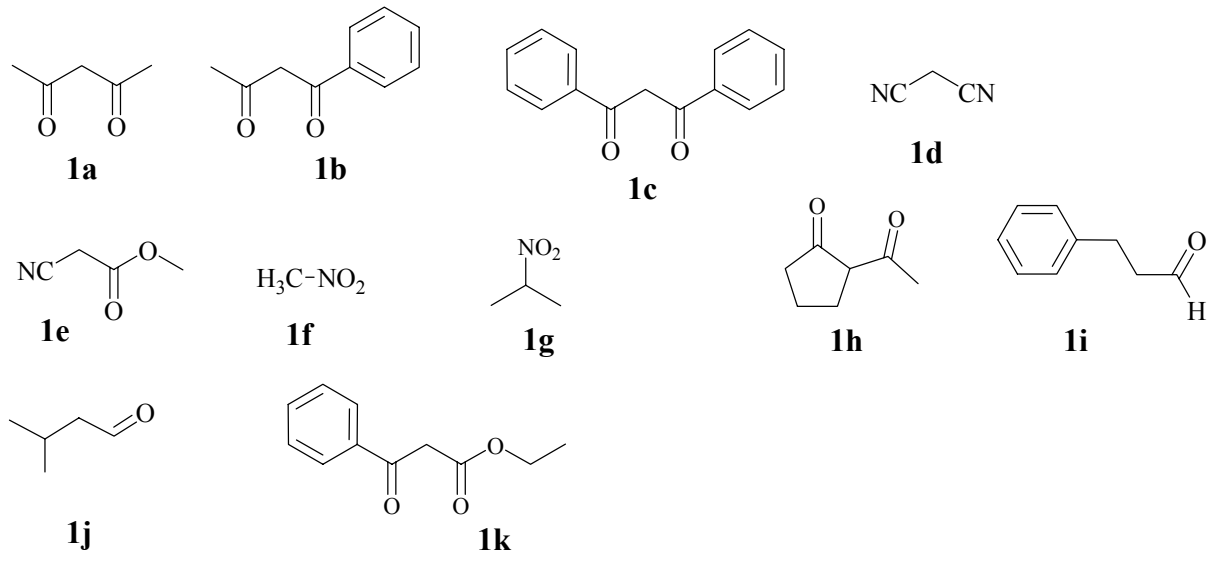


Figure 1. Structures of the nucleophiles.

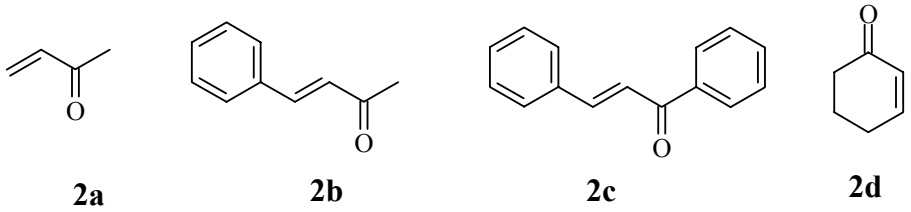


Figure 2. Structures of the enones.

We decided to test if L-proline can catalyse additions of active methylene compounds (which do not form enamines) to methyl vinyl ketone, benzylideneacetone and especially chalcone. We suppose that L-proline can undergo a reaction with α-enone leading to chiral en-iminium ion and subsequent Michel addition could go with some stereoselectivity. Formation of such intermediate was suggested by King *et al*.[53] as well as Gryko[54] for explanation of stereoselectivity of alkylation of indole by enones or Michael addition of 1,3-diketones to methyl vinyl ketone.

Table 1. Results of L-proline catalysed Michael addition of different methylene active compounds to α,β-unsaturated enones in [bmim]PF_6

Entry	Nucleophile	Enone	Conditions	Yield / %	Product
1	**1c**	**2a**	14h /r.t.	88	**3a**
2	**1b**	**2a**	14h /r.t.	68	**3b**
3	**1a**	**2a**	14h /r.t.	42	**3c**
4	**1c**	**2b**	24h /r.t.	34	**3d**
5	**1d**	**2b**	22h /r.t.	70	**3e**
6	**1k**	**2d**	22h /r.t.	32	**3f**
7	**1b**	**2d**	22h /r.t.	41	**3g**
8	**1c**	**2d**	22h /r.t.	37	**3h**
9	**1d**	**2d**	22h /r.t.	18	**3i**
10	**1c**	**2c**	22h /r.t.	19	**3j**
11	**1h**	**2c**	24h / r.t.	29	**3k**
12	**1d**	**2c**	22h /r.t.	74	**3l**
13	**1e**	**2c**	22h /r.t.	56[a]	**3m**
14[b]	**1f**	**2c**	8h / 80°C	86	**3n**
15[c]	**1g**	**2c**	96h / r.t.	63	**3o**
16	**1g**	**2c**	12h / 80°C	31	**3o**
17[d]	**1k**	**2c**	24h / r.t.	35	**3p**
18	**1j**	**2c**	12h / r.t.	19	**3r**
19	**1i**	**2b**	24h / r.t.	76	**4**
20	**1j**	**2b**	22h / r.t.	24	**5**

[a] Diastereomers ratio (7 : 3) was detected by HPLC. [b] Product was not detected at r.t./100 hours. [c] L-Proline salt were used as catalyst at the same conditions. Na-prolinate: chemical yield 76%, 0.8% ee; Li-prolinate: chemical, yield 32%, 7% ee; Ca-prolinate: chemical yield 52%, 3.4% ee; Cu-prolinate: chemical yield 18%, 3.4% ee. [d] Product was isolated in 12% yield using recovered catalyst.

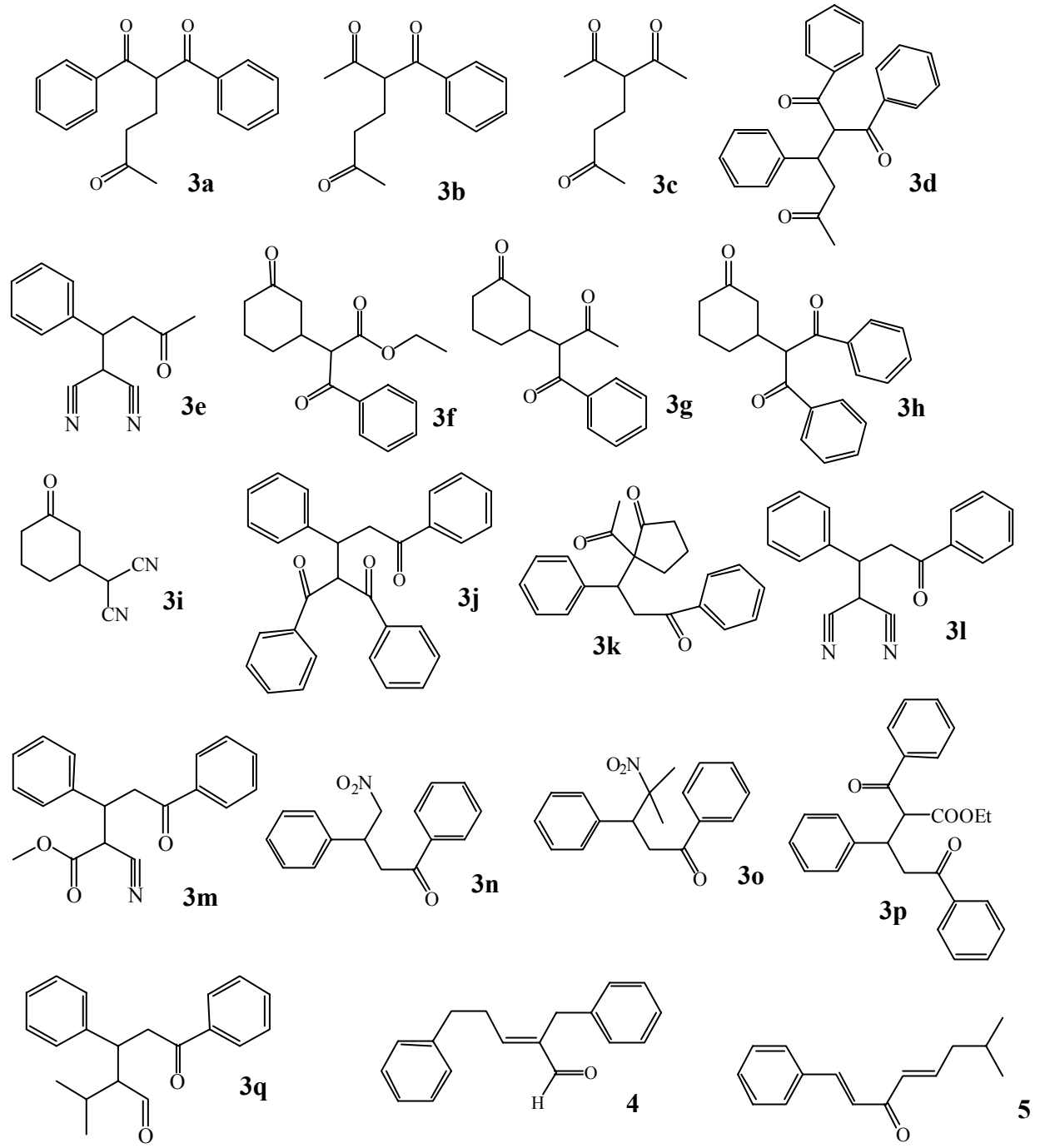


Figure 3. Structures of the products.

From the results given in Table 1 it follows, that additions of β-diketones **1a–c** to methylvinyl ketone **(2a**) went smoothly and reasonable yields of the products were achieved after 14 h (Table 1, Entries 1–3). Similarly additions of dibenzoylmethane (**1c**) as well as malononitrile (**1d)** to benzylideneacetone **(2b**) proceeded also well (Table 1, Entries 4, 5), but practically without any stereoselectivity (4–6% ee). We made also attempts on addition of

hydrocinnamaldehyde **(1i**) to benzylideneacetone (**2b)** but instead of the Michael adduct we isolated as the only compound the product of Claisen-Schmidt autocondensation **4**. This is in contradiction with the literature,[23,42] where such a compound was isolated as a minor product, but these authors have used different organocatalysts. We also made attempts on the addition of 3-methylbutanal (**1j)** to the same Michael acceptor **2b** but just condensation product of aldehyde with benzylideneacetone **5** was isolated in 24% yield (Table 1, Entry 20).

Additions to cyclohex-2-ene-1-one (**2d)** were also tested (Table 1, Entries 6–9), but these reactions did not perform well and just 18–41% yields of nearly racemic products were isolated.

The greatest attention was paid to Michael additions to chalcone **2c**. It can be concluded, that additions of ß-diketones **1c** and **1h** to chalcone (**2c)** (Table 1, Entries 10, 11) were less favoured than analogous additions to methyl vinyl ketone (**2a)** or to benzylideneacetone (**2b)**, and just 19 or 29% yield of the products **3j** and **3k** were obtained. Similar results were achieved also on addition of ethyl benzoylacetate (**1k)** (Table 1, Entry 17) and methyl cyanoacetate (**1e)** which proved to be a better donor (Table 1, Entry 13). Attempts at additions of simple aldehydes and ketones were performed too. The addition of 3-methylbutanal (**1j)** gave after 12 h 19% yield of product **3r**, but reaction of cyclohexanone failed. To our surprise the attempts on addition of diethyl malonate to chalcone failed as well and no product was detected even after 100 h. The best results were achieved on additions of malononitrile (**1d)** (Table 1, Entry 12) (74% yield) and nitromethane **1f** (Table 1, Entry 14) (86% yield), but the temperature had to be elevated to 80°C, as no product was detected after 100 h at room temperature. 2-Nitropropane (**1g)** proved to be less reactive and just 63% yield of the product **3o** was isolated after 96 h at room temperature and 31% of **3o** was isolated after 12 h heating at 80°C (Table 1, Entries 15,16). No enantioselectivity was observed also in these additions to chalcone. This indicates that an en-iminium intermediate can not play any role in these Michael additions and mechanism should go *via* different route and proline acts, the most probably just as basic catalyst. This is supported by the fact that L-proline benzylester is a better catalyst (91% yield) and its HCl adduct is a worse catalyst (55% yield).

Conclusions

We have shown that ionic liquid [bmim]PF_6 is a suitable solvent for L-proline catalysed Michael additions of different donors (carbonyl compounds) to α,β-unsaturated enones. Only 5 mol% of L-proline are necessary to reach reasonable to high yields but a long reaction time was necessary (14–24 h), while Lee[32,33] has used on equivalent of piperidine as an additional catalyst to get similar yields of the product for reactions carried out in dichloromethane. The reactions proceed smoothly with methyl vinyl ketone, benzylideneacetone as well as chalcone. Additions to cyclohex-2-ene-1-one afforded products in medium yields.

Experimental Section

General Procedures. NMR spectra were measured on a Varian Gemini 2000 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR); tetramethylsilane was used as an internal standard. MS spectra were measured at Micromass ZMD ESI (80 eV) system, substances were dissolved in acetonitrile/water (80/20 v/v) mixture. Elemental analysis were performed on Carlo Erba instrument. Enantioselectivity for the purified products was determined by HPLC (Krüss P3002RS instrument) on chiral column Chiralcel OD-H using *n*-hexane/2-propanol (90/10 v/v) as an eluent and cellulose tris(3,5-dimethylphenylcarbamate) coated on 5 μm silica-gel as a packing composition. MS data were obtained on HPLC-MS instrument Hewlett Packard, Agilent 1100 Series MSD. Organocatalysts and starting material were purchased in reagent grade (Aldrich, Acros, Fluka, Merck) and used without further purification. Ionic liquids were purchased from Solvent Innovation Co. and from Merck Co.

General experimental procedure. Ionic liquid (1 mL) was degassed by stirring under reduced pressure (oil pump), then catalyst (5 mol%) and the chosen enone **2** (1.0 mmol) were added and the mixture was stirred for 15 min at room temperature. Nucleophile **1** (1.5 mmol) was then added and the resulting reaction mixture was stirred intensively for specified time and temperature (see Tables 1–3). Product was extracted by several portions of diethyl ether and the combined extracts were evaporated *in vacuo* and purified by column chromatography on SiO_2 (hexane/ethyl acetate 4 : 1 or hexane/dichloromethane 2 : 1). Products were isolated as pure materials and their structure was proved by ^{1}H NMR spectra and new compounds were completely characterised.

Characterization of the products. The spectroscopic characteristics of already known products **3a**[56], **3b**[57], **3c**[58], **3e**[59], **3f**[60], **3g**[61], **3i**[62], **3j**[63], **3l**[64], **3m**[65], **3n**[66], **3o**[67], **3p**[68], **3q**[66] and **4**[70] were in agreement with published data. New compounds were fully characterized as stated below.

2-Benzoyl-1,3-diphenylhexane-1,5-dione (3d). Yield 34%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66–7.50 (m, 15H), 5.52 (d, 1H), 4.11 (m, 1H), 3.23 (d, 2H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.4, 195.0, 144.9, 139.8, 131.5, 127.4, 126.7, 126.2, 125.8, 124.8, 58.6, 50.1, 41.6, 28.3. Elemental analysis calcd. for $C_{25}H_{22}O_3$: C 81.06, H 5.99; found C 81.06, H 5.99.

2-(3-Oxocyclohexyl)-1,3-diphenylpropane-1,3-dione (3h). Yield 37.5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (t, 4H), 7.56 (m, 2H), 7.44 (m, 4H), 5.23 (d, 1H, J = 8.7Hz), 3.041(m, 1H), 2.42–2.17 (m, 3H), 2.05–1.93 (m, 2H), 1.62–1.25 (m, 2H), 0.88 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.6, 194.6, 194.4, 136.6, 133.8, 129.1, 129.0, 128.7, 62.6, 45.9, 41.2, 39.5, 29.5, 24.8. Elemental analysis calcd. for $C_{21}H_{20}O_3$: C 78.73, H 6.29; found C 78.82, H 6.18.

2-Acetyl-2-(3-oxo-1,3-diphenylpropyl)cyclopentanone (3k). Yield 29%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (dd, 2H, J = 8.7Hz), 7.51 (t, 1H), 7.42 (m, 2H), 7.25–7.19 (m, 5H), 4.54 (dd, 1H, J = 10.8Hz, J = 3.6Hz), 3.67 (dd, 1H, J = 17.7Hz, J = 10.8Hz), 2.86 (dd, 1H, J = 17.7Hz, J = 3.3Hz), 2.73 (m, 1H), 2.24 (s, 3H), 2.13–2.04 (m, 2H), 1.61–1.50 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 214.7, 204.2, 197.2, 138.7, 136.7, 133.4, 129.7, 128.9, 128.5, 128.1, 127.4, 73.7, 43.9,

39.7, 39.0, 26.7, 26.5, 19.7. Elemental analysis calcd. for $C_{22}H_{22}O_3$: C 79.02, H 6.63; found C 79.11, H 6.70.

7-Methyl-1-phenylokta-1,4-dien-3-one (5). Yield 24%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (m, 1H), 7.82 (m, 2H), 7.57 (m, 3H), 7.00 (t, 1H), 6.95 (t, 1H), 6.43 (d, 1H, J = 15.6Hz), 2.21 (t, 2H), 1.82 (m, 1H), 0.95 (2, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 146.2, 145.6, 132.6, 130.0, 128.8, 128.3, 127.3, 126.8, 40.1, 26.8, 21.0. Elemental analysis calcd. for $C_{15}H_{18}O$: C 84.07, H 8.47; found C 84.19, H 8.52; MS: m/z = 215 ($M+H^+$, pos. mode).

Acknowledgements

We are grateful to Dr. E. Solčaniová and her staff for NMR measurements. This work was supported by the Slovak Grant Agency VEGA, grant No. 1/0072/03.

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