

Intramolecular Barbier reaction in water: cyclopentane and cyclohexane ring closure

ALEKSANDAR IVKOVIĆ, RADOMIR MATOVIĆ[#] and RADOMIR N. SAIČIĆ^{*,#}

Faculty of Chemistry, University of Belgrade, Studentski trg 16, P. O. Box 158, YU-11000 Belgrade
and ICTM – Center for Chemistry, Njegoševa 12, YU-11001 Belgrade, Yugoslavia

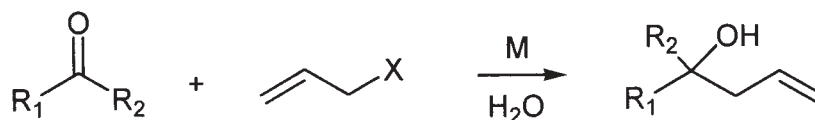
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Zinc or indium promoted intramolecular Barbier reactions of aldehydes containing a suitably positioned allylic or propargylic halide unit afford unsaturated cyclic alcohols in moderate yields.

Keywords: Barbier reactions, cyclisation, allylation, allenes, zinc, indium.

INTRODUCTION

Barbier type allylation of carbonyl compounds in aqueous media has become an important method of carbon-carbon bond formation (Scheme 1).¹ The reaction allows for a high yield, chemoselective synthesis of homoallylic alcohols from carbonyl compounds under environmentally friendly conditions, and is amenable to stereo- and enantiocontrol. Among the many metals that can serve as reaction promoters, zinc and indium have found the most widespread use, owing to the mild reaction conditions and the experimental simplicity of the procedure.



M = Zn, In, Sn, Al, Bi

X = Cl, Br, I

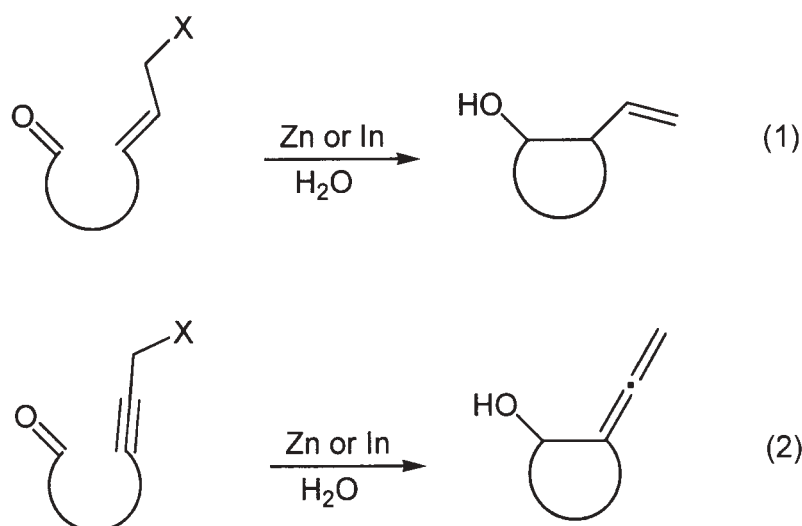
Scheme 1.

In contrast to the extensive synthetic application at the intermolecular level, the intramolecular Barbier reaction, which would provide a useful way to cyclic structures,

[#] Serbian Chemical Society active member.

^{*} e-mail address: rsaicic@chem.bg.ac.yu

has remained mostly unexplored. The rare examples from the literature include tin/aluminium promoted cyclizations under strongly acidic conditions,² indium mediated enlargements of carbo-³ and heterocyclic rings,⁴ as well as three examples of carbocycle formation in the presence of indium.⁵ We have endeavoured to investigate the possibility of the construction of five and six membered rings *via* the zinc and indium mediated allylation of aldehydes under aqueous conditions, and to compare the efficiency of the two reagents for the synthetic transformation delineated in Scheme 2. In addition to the reactions of aldehydes containing allylic halide moiety, which would afford 2-vinylcycloalkanol type products (Eq. 1), we were also interested in the reactions of substrates containing propargylic halide substructure, which would lead to allene derivatives (Eq. 2).

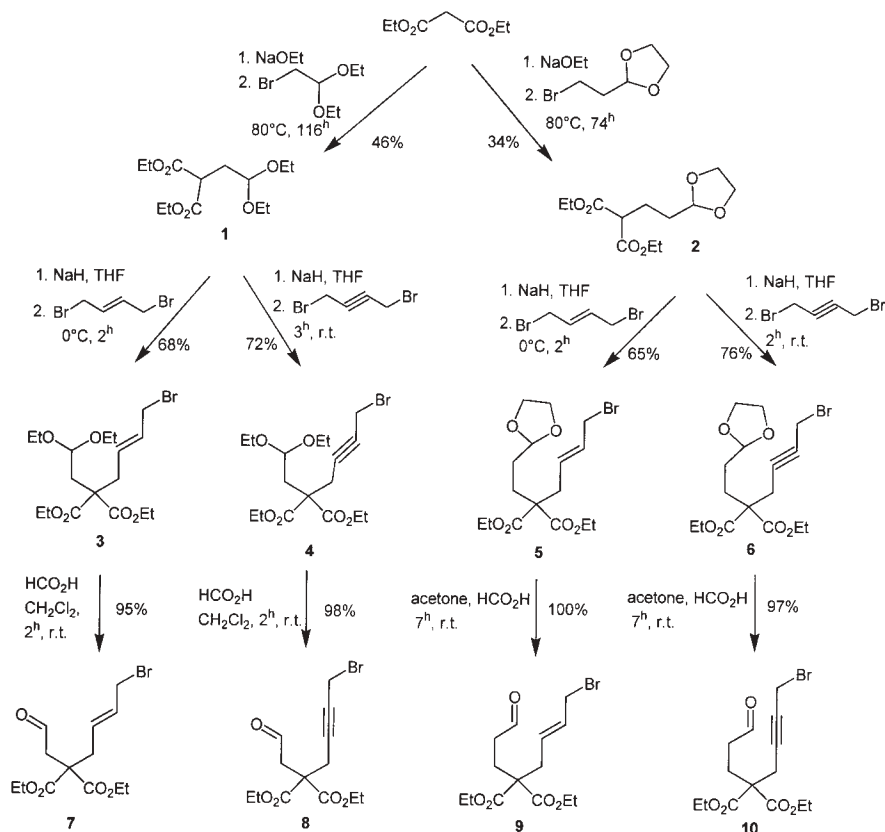


Scheme 2.

RESULTS AND DISCUSSION

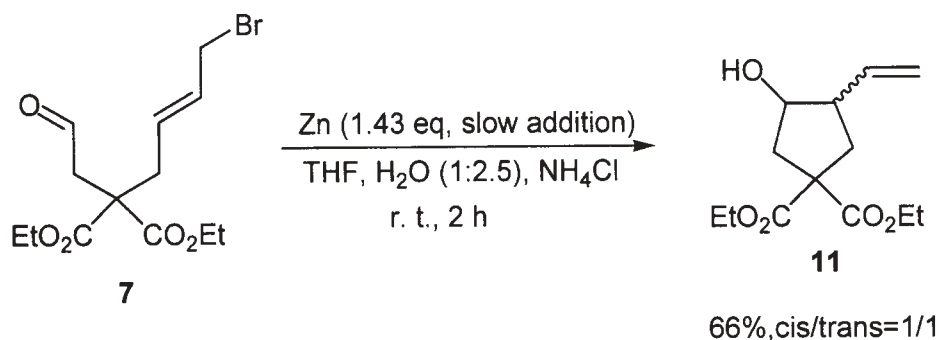
The starting compounds were prepared in a straightforward manner, as exemplified in Scheme 3. The reaction of diethyl malonate with bromoacetaldehyde diethylacetal afforded the alkylated product **1**, which was further submitted to a second alkylation with 1,4-dibromo-2-butene, or 1,4-dibromo-2-butyne, to afford the corresponding bromoacetals **3** and **4**. Acidic deprotection of the bromoacetals **3** and **4** furnished the bromoaldehydes **7** and **8** – precursors for the Barbier reaction. Homologated bromoaldehydes **9** and **10** were prepared in a similar way, substituting 3-bromopropanal dioxolane for bromoacetaldehyde diethylacetal in the first alkylation step.

In the first cyclization experiment a solution of bromoaldehyde **7** in a mixture THF/saturated aqueous NH_4Cl was treated with zinc powder, which was added in small portions (Scheme 4). Upon completion of the addition TLC indicated a clean conversion of the starting compound into a new product, which was isolated in 66 % yield and identified as 2-vinylcyclopentanol derivative **11** (mixture of diastereoisomers, *cis* : *trans* = 1 : 1).

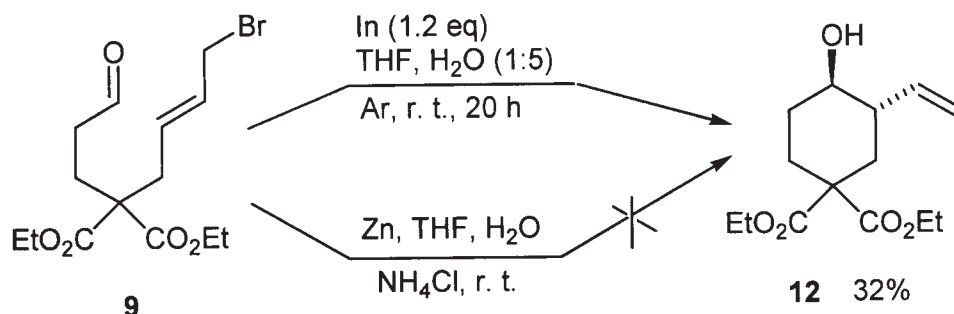


Scheme 3.

Surprisingly, under the identical experimental conditions as above, bromoaldehyde **9** failed to cyclize, the reaction giving rise to a complex mixture of products (Scheme 5). When the reaction was performed under high dilution, TLC indicated the formation of a minor amount of **12**. A similar result was obtained when the reaction was performed in anhydrous DMF, indicating that the cyclization is unfavourable, and that intermolecular reactions predominate. However, the indium promoted reaction with



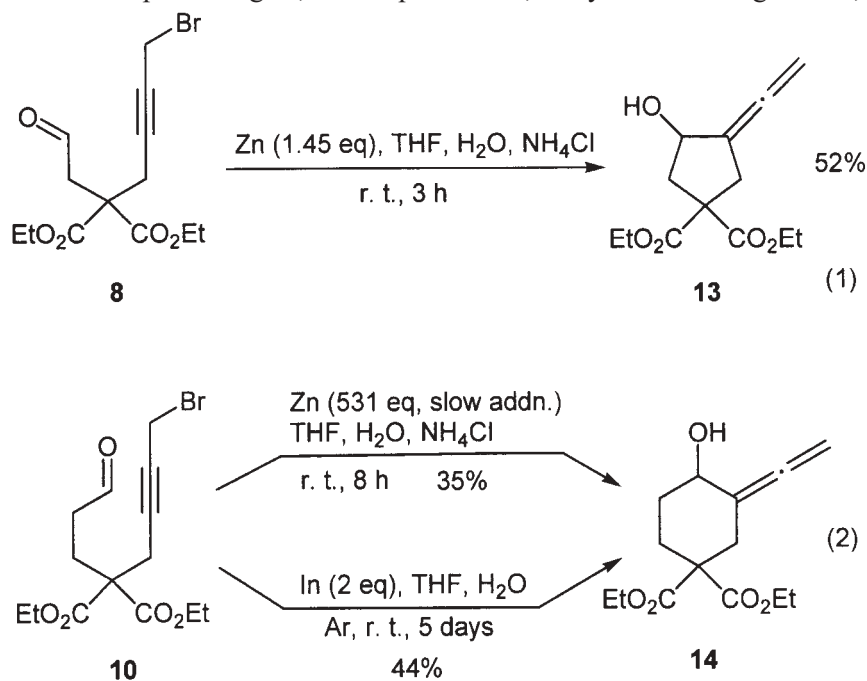
Scheme 4.



Scheme 5.

this substrate afforded the desired 2-vinylcyclohexanol derivative **12** in 32 % isolated yield. It is noteworthy that **12** was obtained as a single stereoisomer, the configuration of which was not determined, but was tentatively assigned as *trans*.

Next, the cyclization reactions of acetylenic aldehydes **8** and **10** were investigated. Submitting the substrate **8** to the standard reaction conditions with zinc resulted in a clean conversion into the allenic cyclopentane derivative **13**, which was isolated in 52 % yield (Scheme 6). The homologue **10** also afforded the expected ethynylidenecyclohexanol derivative **14**, albeit in lower, 35 % yield. In this case the reaction took much longer, and required a large excess of zinc for completion. Again, indium proved to be a superior reagent, with respect to zinc, for cyclohexane ring closure, as in



Scheme 6.

the indium mediated cyclization the allene derivative **14** was isolated in a somewhat improved 44 % yield.

From the experiments performed, the following conclusions can be made: In all cases cyclizations proceed with *exo*-selectivity, giving rise to the smaller of two possible rings, as expected.⁶ Intramolecular Barbier reaction promoted by zinc under aqueous conditions offers a potentially useful synthetic approach to both vinyl- and allenic cyclopentane derivatives. Under these conditions cyclohexane ring closure is less efficient, requires longer reaction times and excess metallic reagent for completion, and affords cyclic products in lower yields. Although it is not common to invoke conformational constraints as an explanation for the lack of reactivity of an open chain system toward cyclohexane ring closure, the failure of the bromoaldehyde **9** to undergo zinc mediated cyclization (as well as the relatively low yield in the indium promoted reaction of the same substrate), can only be explained by unfavourable stereoelectronic effects. These effects may be reinforced by intramolecular complexation of the metal cation with the carbonyl group of the allylmetal intermediate. Cyclic, stereochemically biased systems might be better precursors for cyclohexane formation than the open ones. The reaction times are much longer in the indium promoted reactions, but indium appears to be a superior reagent with respect to zinc, especially for difficult to cyclize substrates (*e.g.*, **9**). Further investigations are needed to establish the scope and limitations of the reaction.

EXPERIMENTAL

General remarks

All chromatographic separations were performed on Silica, 10-18, 60A, ICN Biomedicals. Standard techniques were used for the purification of reagents and solvents. NMR spectra were recorded on a Varian Gemini 200, ¹H-NMR at 200 MHz, ¹³C-NMR at 50 MHz, for samples in deuterated chloroform. Chemical shifts are expressed in ppm using tetramethylsilane as internal standard, coupling constants (*J*) are in Hz. IR spectra were recorded on a Perkin-Elmer 457 grating FT instrument, and are expressed in cm⁻¹. Mass spectra were obtained on a Finnigan ITDS 700 instrument. GC analyses were performed on a Varian 3400 instrument, equipped with Varian 4270 integrator, VOCOLTM column (105 m, ID: 0.53 mm, film thickness 3.0 μm), carrier gas H₂, 10 ml/min, FI detector. Petroleum-ether refers to the fraction with distillation range 70–90 °C.

Synthesis of precursors

Diethyl 2,2-diethoxyethylmalonate (1). Diethyl malonate (21.42 g; 20.4 mL; 0.133 mol) was added dropwise, with stirring, to a solution of sodium ethoxide, prepared from sodium (3.08 g; 0.133 mmol) and absolute ethanol (120 mL). After 30 min, 2-bromoacetaldehyde diethylacetal (26 g; 20.5 mL; 0.133 mol) was added dropwise, and the reaction mixture was refluxed with stirring for 116 h. The course of the reaction was monitored by GC. Upon completion, ethanol was removed under reduced pressure, water (200 mL) was added, and the reaction mixture was extracted with dichloromethane (5 × 100 mL). The combined organic extract was washed with saturated aqueous NaHCO₃, dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure. Distillation under reduced pressure afforded 17 g (46 %) of the title compound **1**, as a colourless liquid, *E*_{0.15} 94–101 °C.

¹H-NMR: 4.55 (*t*, *J* = 5.7, 1H); 4.20 (*q*, *J* = 7.0, 4H); 3.73–3.40 (*m+s*, 5H); 2.23 (*ABq*, *J*₁ = 6.5, *J*₂ = 1.6, 2H); 1.27 (*t*, *J* = 7.3, 6H); 1.19 (*t*, *J* = 7.1, 6H); ¹³C-NMR: 169.33; 100.72; 61.83; 61.38; 48.05; 32.68; 15.13; 13.97; IR_{film}: 1751, 1736, 1466, 1270, 1240; MS/CI_{isobutane}: 277 (MH⁺).

Diethyl 2-(2,5-dioxacyclopentyl)ethylmalonate (2). This compound was obtained according to the previous procedure, the reaction lasted 74 h. Yield: 34 %, colourless liquid, $E_{0.25}$ 108–111 °C.

$^1\text{H-NMR}$: 4.89 (*t*, $J = 4.4$, 1H); 4.20 (*q*, $J = 7.2$, 4H); 4.01–3.81 (*m*, 4H); 3.41 (*t*, $J = 7.4$, 1H); 2.09–1.98 (*m*, 2H); 1.76–1.66 (*m*, 2H); 1.27 (*t*, $J = 7.0$, 6H); $^{13}\text{C-NMR}$: 169.22; 103.69; 64.80; 61.23; 51.49; 31.08; 22.91; 13.95; IR_{film} : 1748, 1733, 1257, 1227; $\text{MS}/\text{CI}_{\text{isobutane}}$: 261 (MH^+).

1-Bromo-5,5-diethoxycarbonyl-7,7-diethoxy-2-heptene (3). To a stirred solution of ester **1** (579 mg; 2.09 mmol) in THF (7 mL), sodium hydride (80 % in mineral oil; 75.4 mg; 1.2 eq) was added at 0 °C. After 15 min, 1,4-dibromo-2-butene (1.118 g; 2.5 eq) was added in one portion, and the reaction mixture stirred for 2 h at that temperature. The reaction mixture was diluted with dichloromethane (30 mL), washed with water (4 × 15 mL), followed by saturated aqueous NaHCO_3 (15 mL), dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. Purification by dry-flash chromatography (eluent: petroleum-ether : ethyl acetate = 9 : 1) afforded 586.1 mg (68 %) of the title compound **3** as a colourless, viscous oil.

$^1\text{H-NMR}$: 5.83–5.60 (*m*, 2H); 4.53 (*t*, $J = 5.6$, 1H); 4.20–4.10 (*m*, 4H); 3.90 (*d*, $J = 7.2$, 2H); 3.72–3.56 (*m*, 2H); 3.53–3.38 (*m*, 2H); 2.72 (*d*, $J = 6.8$, 2H); 2.24 (*d*, $J = 5.6$, 2H); 1.25 (*q*, $J = 7.2$, 6H); 1.18 (*q*, $J = 7.0$, 6H); $^{13}\text{C-NMR}$: 170.56; 130.58; 129.78; 100.05; 61.94; 61.18; 55.15; 36.13; 35.42; 32.21; 15.04; 13.01; IR_{film} : 1733, 1661, 1251, 1206; $\text{MS}/\text{CI}_{\text{isobutane}}$: 407, 409 (MH^+).

1-Bromo-5,5-diethoxycarbonyl-7,7-diethoxy-2-heptyne (4). This compound was prepared according to the procedure described for 1-bromo-5,5-diethoxycarbonyl-7,7-diethoxy-2-heptene (**3**), the reaction lasted 3 h. Purification by dry-flash chromatography (eluent: toluene : ethyl acetate = 975 : 25) afforded 532 mg (72 %) of the title compound **4**, as a colourless oil.

$^1\text{H-NMR}$: 4.54 (*t*, $J = 5.6$, 1H); 4.20 (*q*, $J = 7.2$, 2H); 4.18 (*q*, $J = 7.0$, 2H); 3.87 (*t*, $J = 2.2$, 2H); 3.70–3.59 (*m*, 2H); 3.55–3.43 (*m*, 2H); 2.95 (*t*, $J = 2.4$, 2H); 2.41 (*d*, $J = 5.8$, 2H); 1.25 (*t*, $J = 7.2$, 6H); 1.18 (*t*, $J = 7.0$, 6H); $^{13}\text{C-NMR}$: 169.76; 100.12; 82.43; 78.26; 62.14; 61.51; 54.52; 35.69; 23.38; 15.02; 14.64; 13.88; IR_{film} : 1736, 1250; $\text{MS}/\text{CI}_{\text{isobutane}}$: 409, 407 (MH^+).

1-Bromo-5,5-diethoxycarbonyl-7-(2,5-dioxacyclopent-1-yl)hept-2-ene (5). This compound was obtained according to the procedure described for compound **3**, the reaction lasted 3 h. Purification by dry-flash chromatography (eluent: toluene : acetone = 975 : 25) afforded the title compound **5** in 65 % yield, as a colourless oil.

$^1\text{H-NMR}$: 5.88–5.55 (*m*, 2H); 4.87 (*t*, $J = 4.4$, 1H); 4.19 (*q*, $J = 7.2$, 4H); 3.98–3.94 (*m*, 2H); 3.90 (*d*, $J = 6.8$, 2H); 3.90–3.81 (*m*, 2H); 2.64 (*d*, $J = 6.8$, 2H); 2.03–1.95 (*m*, 2H); 1.63–1.55 (*m*, 2H); 1.25 (*t*, $J = 7.2$, 6H); $^{13}\text{C-NMR}$: 170.79; 130.54; 129.62; 103.88; 64.89; 61.32; 56.93; 35.38; 32.30; 28.47; 26.58; 14.04; IR_{film} : 1730, 1661, 1299, 945; $\text{MS}/\text{CI}_{\text{isobutane}}$: 393, 391 (MH^+).

1-Bromo-5,5-diethoxycarbonyl-7-(2,5-dioxacyclopent-1-yl)hept-2-yne (6). This compound was prepared according to the procedure described for 1-bromo-5,5-diethoxycarbonyl-7,7-diethoxy-2-heptyne (**3**), the reaction lasted 3 h. Yield: 76 %, colourless viscous oil.

$^1\text{H-NMR}$: 4.90 (*t*, $J = 4.4$, 1H); 4.21 (*q*, $J = 7$, 4H); 4.02–3.81 (*m+t*, $J = 2.4$, 4H+2H); 2.87 (*t*, $J = 2.4$, 2H); 2.19–2.11 (*m*, 2H); 1.64–1.54 (*m*, 2H); 1.26 (*q*, $J = 7$, 6H); $^{13}\text{C-NMR}$: 169.98; 103.89; 82.20; 78.13; 64.88; 61.62; 56.42; 28.54; 26.40; 23.39; 14.75; 13.98; IR_{film} : 1733, 1266, 1202; $\text{MS}/\text{CI}_{\text{isobutane}}$: 392, 390 (MH^+).

7-Bromo-3,3-diethoxycarbonyl-5-heptenal (7). Formic acid (4 mL) was added to a solution of **3** (1 g; 2.4 mmol) in dichloromethane (6 mL), with stirring at room temperature. The reaction was monitored by TLC (eluent: petroleum-ether : ethyl acetate = 9 : 1). After 7 h the reaction mixture was diluted with dichloromethane (30 mL), washed with water until neutral to litmus, dried over anhydrous Na_2SO_4 , filtered, and evaporated under reduced pressure to give 776 mg (95 %) of the title compound **7** as a colourless oil.

$^1\text{H-NMR}$: 9.72 (*t*, $J = 1.2$, 1H); 5.75–5.65 (*m*, 2H); 4.23 (*q*, $J = 7.0$, 4H); 3.90 (*d*, $J = 6.6$, 2H); 2.98 (*d*, $J = 6.6$, 2H); 2.97 (*d*, $J = 1.4$, 2H); 1.27 (*t*, $J = 7.0$, 6H); $^{13}\text{C-NMR}$: 198.62; 169.67; 131.38;

129.20; 61.92; 54.59; 46.08; 36.33; 31.81; 13.86; IR_{film}: 2872, 2739, 1729, 1661; MS/CI_{isobutane}: 337, 335 (MH⁺).

7-Bromo-3,3-diethoxycarbonyl-5-heptynal (8). Formic acid (6 mL) was added to a solution of **4** (218 mg; 0.537 mmol) in dichloromethane (10 mL), with stirring at room temperature. The reaction was monitored by TLC (eluent: petroleum-ether : ethyl acetate = 8 : 2). After 2 h the reaction mixture was diluted with dichloromethane (30 mL), washed with water until neutral to litmus, dried over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure to give 776 mg (98 %) of the title compound **8** as a colourless oil.

¹H-NMR: 9.77 (*t*, *J* = 0.8, 1H); 4.24 (*q*, *J* = 7.2, 4H); 3.86 (*t*, *J* = 2.2, 2H); 3.22 (*d*, *J* = 1.0, 2H); 3.04 (*t*, *J* = 2.4, 2H); 1.27 (*t*, *J* = 7.0, 6H); ¹³C-NMR: 198.55; 168.71; 81.93; 78.91; 62.22; 53.95; 45.90; 24.11; 14.35; 13.84; IR_{film}: 2850, 2739, 1736, 1287; MS/CI_{isobutane}: 335, 333 (MH⁺).

8-Bromo-4,4-diethoxycarbonyl-6-heptenal (9). A solution of acetal **5** (101 mg; 0.256 mmol) in acetone (4 mL) and formic acid (10 mL) was stirred at room temperature for 7 h. The reaction mixture was diluted with dichloromethane (30 mL), washed with water until neutral to litmus, and evaporated under reduced pressure to give 91 mg (quantitative yield) of the title compound **9** as a colourless, viscous oil.

¹H-NMR: 9.75 (*s*, 1H); 5.84–5.61 (*m*, 2H); 4.20 (*q*, *J* = 7.2, 4H); 3.90 (*d*, *J* = 7.0, 2H); 2.65 (*d*, *J* = 6.8, 2H); 2.50 (*t*, *J* = 8.2, 2H); 2.17 (*t*, *J* = 7.4, 2H); ¹³C-NMR: 200.51; 170.40; 130.81; 129.16; 61.43; 56.39; 38.88; 36.09; 31.97; 24.92; 13.90; IR_{film}: 2850, 2727, 1729, 1661, 1299, 1266; MS/CI_{isobutane}: 351, 349 (MH⁺).

8-Bromo-4,4-diethoxycarbonyl-6-heptynal (10). This compound was obtained according to the procedure described for compound **9**. Yield: 97 %, colourless oil.

¹H-NMR: 9.77 (*t*, *J* = 1.4, 1H); 4.29–4.16 (*m*, 4H); 3.88 (*t*, *J* = 2.4, 2H); 2.88 (*t*, *J* = 2.2, 2H); 2.58–2.48 (*m*, 2H); 2.39–2.30 (*m*, 2H); 1.27 (*t*, *J* = 7.2, 6H); ¹³C-NMR: 200.44; 169.54; 81.67; 78.48; 61.72; 55.77; 38.80; 24.70; 23.83; 14.42; 13.82; IR_{film}: 2832, 2728, 1730, 1270; MS/CI_{isobutane}: 349, 347 (MH⁺).

Cyclization reactions of the bromoaldehydes **7**, **8**, **9** and **10**

4,4-Diethoxycarbonyl-2-vinylcyclopentanol (11) (Barbier reaction promoted by Zn). To a vigorously stirred mixture of **7** (288 mg; 0.856 mmol), THF (0.4 mL) and saturated aqueous NH₄Cl (1 mL), zinc powder was added in small portions, at room temperature. The reaction was monitored by TLC, and zinc was added until no more starting compound could be detected in the reaction mixture (the reaction was completed upon the addition of 80 mg; 1.42 eq of Zn). The reaction mixture was diluted with dichloromethane (20 mL), washed with water (3 × 15 mL), saturated aqueous NaHCO₃ (10 mL), dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. Purification by dry-flash chromatography (eluent: benzene : acetone = 95 : 5) afforded 143 mg (66 %) of the title compound **11**, as a colourless viscous oil, 1:1 mixture of *cis* and *trans* isomers.

¹H-NMR (for the more polar isomer according to TLC): 5.83–5.65 (*m*, 1H); 5.19–5.06 (*m*, 2H); 4.27–4.14 (*m*, 4H); 3.96–3.93 (*br. s*, 1H, OH); 2.68–2.47 (*m*, 3H); 2.24–1.97 (*m*, 3H); 1.26 (*t*, *J* = 7.2, 3H); 1.25 (*t*, *J* = 7.0, 3H); ¹³C-NMR (for the mixture of isomers): 173.01; 172.57; 172.39; 171.96; 138.38; 135.91; 117.22; 116.15; 76.57; 74.93; 61.67; 61.52; 58.30; 56.75; 51.54; 49.26; 42.47; 40.99; 36.76; 35.93; 13.84; IR_{film}: 3600–3100 (*br.*), 1729, 1642, 1260; MS/CI_{isobutane}: 257 (MH⁺).

4,4-Diethoxycarbonyl-2-vinylcyclohexanol (12) (Barbier reaction promoted by In). A suspension of **9** (73 mg; 0.209 mmol), THF (0.45 mL), water (1.8 mL) and indium powder (32 mg; 1.2 eq) was vigorously stirred at room temperature, under an argon atmosphere, for 20 h. The reaction mixture was diluted with dichloromethane (15 mL), washed with water (2 × 10 mL), saturated aqueous NaHCO₃ (10 mL), dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. Purification by column chromatography (eluent: benzene : acetone = 95 : 5) afforded 18 mg (32 %) of the title compound **12** as a colourless oil (single stereoisomer).

$^1\text{H-NMR}$: 5.75–5.57 (*m*, 1H); 5.28–5.17 (*m*, 2H); 4.24 (*q*, $J = 7.0$, 2H); 4.16 (*q*, $J = 7.2$, 2H); 3.31 (*dt*, $J_1 = 10.4$, $J_2 = 4.4$, 1H); 2.48–2.35 (*m*, 2H); 2.15–1.32 (*m*, 6H); 1.28 (*t*, $J = 7.2$, 3H); 1.23 (*t*, $J = 7.2$, 3H); $^{13}\text{C-NMR}$: 171.85; 170.54; 139.12; 118.01; 71.77; 61.52; 61.32; 54.37; 47.16; 35.32; 30.13; 29.63; 14.01; 13.92; IR_{film} : 3600–3100, 1732, 1642, 1239, 1205; $\text{MS/CI}_{\text{isobutane}}$: 271 (MH^+).

4,4-Diethoxycarbonyl-2-ethenylidenecyclopentanol (13). This compound was obtained according to the procedure described for compound **11**. Purification by column chromatography (eluent: benzene : acetone = 96 : 4) afforded 77 mg (52 %) of the title compound **13** as a colourless oil.

$^1\text{H-NMR}$: 4.97–4.88 (*m*, 2H); 4.74 (*br. s*, 1H, OH); 4.28–4.15 (*m*, 4H); 3.28–3.18 (*m*, 1H); 2.95 (*dt*, $J_1 = 16.6$, $J_2 = 4.8$, 1H); 2.56–2.31 (*m*, 3H); 1.27 (*t*, $J = 7.0$, 3H); 1.26 (*t*, $J = 7.0$, 3H); $^{13}\text{C-NMR}$: 203.35; 172.20; 171.04; 104.55; 78.95; 73.32; 61.91; 61.69; 58.47; 42.61; 36.31; 13.88; IR_{film} : 3600–3100, 1964, 1731, 1261, 1194, 861; $\text{MS/CI}_{\text{isobutane}}$: 255 (MH^+).

4,4-Diethoxycarbonyl-2-ethenylidenecyclohexanol (14). *Method A (Zn promoted cyclization)*. Zinc powder (5 g; 45 mmol; 318 eq) was added in small portions, within 8 h, to a vigorously stirred mixture of THF (62.5 mL), saturated aqueous NH_4Cl (120 mL) and compound **10**, at ambient temperature. Standard work-up, followed by purification by column chromatography (eluent: benzene : acetone = 95 : 5) afforded 13.5 mg (35 %) of the compound **14** as a colourless oil.

Method B (In promoted cyclization): A suspension of indium powder (69.4 mg; 0.604 mmol; 2 eq), bromoaldehyde **10** (105 mg; 0.302 mmol), THF (0.7 mL) and water (2.7 mL) was vigorously stirred at ambient temperature, under an argon atmosphere, for 5 days. Standard work-up afforded 36 mg (44 %) of the compound **14**.

$^1\text{H-NMR}$: 4.92–4.88 (*m*, 2H); 4.27–4.11 (*m*, 5H); 3.05–2.97 (*m*, 1H); 2.57 (*dt*, $J_1 = 13.8$, $J_2 = 2.8$, 1H); 2.41–2.31 (*m*, 1H); 2.11–1.64 (*m*, 3H); 1.26 (*t*, $J = 7.2$, 3H); 1.24 (*t*, $J = 7.0$, 3H); $^{13}\text{C-NMR}$: 202.42; 170.98; 170.38; 101.72; 78.33; 67.73; 61.51; 61.37; 55.20; 33.20; 31.60; 28.06; 13.96; IR_{film} : 3600–3100, 1964, 1729, 1447, 1115, 858.

ИЗВОД

ИНТРАМОЛЕКУЛСКА BARBIER-OVA REAKCIJA U VODI: SINTEZA PETOČLANIH I ŠESTOČLANIH PRSTENOVA

ALEKSANDAR IVKOVITŠ, RAĐOMIR MATOVIĆ и RAĐOMIR N. SAIČIĆ

Хемијски факултет, Универзитет у Београду, Студенјски брџ 16, п. бр. 158, 11000 Београд и ИХТМ – Центар за хемију, Њеђошева 12, 11001 Београд

Алдехиди који у погодном положају поседују алил-халогенидну или пропаргил-халогенидну структурну јединицу реагују у воденим условима са цинком или индијумом, при чему настају незасићени циклични алкохоли у умереним приносима.

(Примљено 3. августа 2001)

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