PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2014, № 2, p. 58–60

COMMUNICATIONS

Chemistry

SYNTHESIS OF 4-OXO-2(*E*)-DECENAL: PHEROMONE COMPONENT AND ALLOMONE OF SOME TRUE BUGS OF *HEMIPTERA*

M. R. HOVHANNISYAN*

Institute of Organic Chemistry of Scientific-Technological Centre of Organic and Pharmaceutical Chemistry NAS of the Republic of Armenia

In this paper a new method for the synthesis of 4-oxo-2(*E*)-decenal – defensive compound (allomone) and pheromone component of several true bugs of *Hemiptera* based on the 2-propyn-1-ol is described.

***Keywords*:** pheromone, allomone, 4-oxo-2(*E*)-decenal.

Introduction. 4-Oxo-2(*E*)-decenal serves as defensive compound (allomone) and pheromone component of several true bugs of *Hemiptera* [1–4]. Besides, researchers from Spain detected the presence of toxic aldehydes including 4-oxo-2(*E*)-decenal in a sunflower oil heated to frying temperature in an industrial fryer. This substance has been thought to be responsible for cancer and several neurodegenerative diseases, such as Alzheimer's and Parkinson's [5].

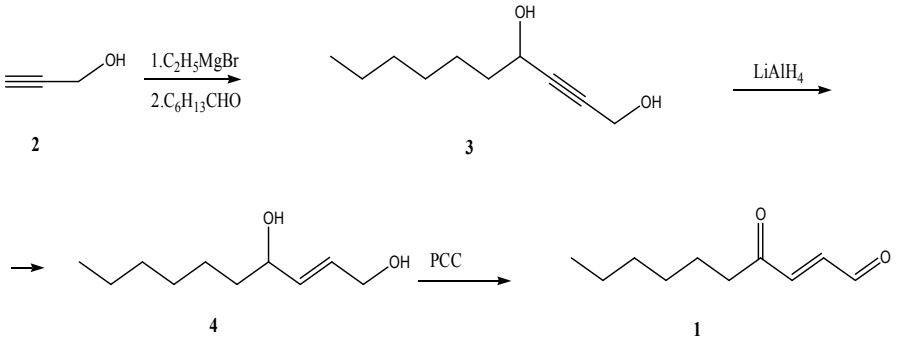
4-Oxo-2(*E*)-decenal **(1)** have a great potential to be used in agriculture (e.g., by affecting the behavior of pests thus increasing the control over them) and biological research. Therefore, it is of a significant importance to set an easy access towards the synthesis of abovementioned compound.

So far, there is only one method for the synthesis of 4-oxo-2(*E*)-decenal described in the literature. Latter is based on the oxidation of 2-*n*-hexylfuran with aqueous *N*-bromosuccinimide to form desired product via cleavage of furan ring [6].

Taking into consideration the growing interest towards this compound and the possibility of its synthesis from commercially available materials, we have developed a new method for the synthesis of 4-oxo-2(*E*)-decenal based on 2-propyn-1-ol (**2**).

At first, as a result of the reaction between 2-propyn-1-ol (**2**) and ethylmagnesium bromide, Jocic reagent was formed, which subsequently was treated with heptanal to produce 2-decyne-1,4-diol (**3**) in 48.2% yield. In the second step of the synthesis triple bond was reduced to corresponding *trans*-alkene by means of lithium aluminium hydride solved in THF. Synthesized 2(*E*)-decene-1,4-diol (**4**) was finally oxidized by pyridinium chlorochromate [7] to form desired product.

* E-mail: mar.yan.00@mail.ru



4-Oxo-2(*E*)-decenal (**1**) was isolated and purified by column chromatography on silica gel.

Overall yield of 4-oxo-2(*E*)-decenal (**1**) is 21.8 %.

Experimental Part. ^{1}H NMR spectra were recorded on Varian Mercury-300 VX spectrometer (300.077 *MHz*). Samples were measured in $CDCl_3$, CCl_4, DMSO-d_6 and signals were referenced to the internal standard (TMS). Infrared spectra were recorded on Specord 75IR spectrometer. Course of reactions was controlled by thin-layer chromatography on Silufol UV-254 (eluent: hexane-ether, colouring reagent: iodine steams and solution of $KMnO_4$). The products were purified by column chromatography on silica gel (L 40/100).

Synthesis of 2-decyne-1,4-diol (3). To the solution of ethylmagnesium bromide, prepared from 10.9 *g* (0.1 *mol*) of ethyl bromide and 2.4 *g* (0.1 *mol*) of magnesium in 70 *mL* of THF, 2.8 *g* (0.05 *mol*) of 2-propyn-1-ol (**2**) was added dropwise. Reaction mixture was refluxed for 3 *h* and cooled down to 0º*C* temperature. Subsequently, 5.7 *g* (0.05 *mol*) of heptanal was added drop by drop and the mixture was kept overnight at room temperature. On the next day the solution was again refluxed for 2 *h* and cooled to 0º*C*. Afterwards, the saturated solution of NH_4Cl was added and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and the solvent of the filtrate was evaporated. Finally, the desired 2-decyn-1,4-diol (**3**) was obtained by distilling (bp 118–120º*C*, 4 *mm* Hg) the residue.

Yield 4.1 *g* (48.2 %), R_f 0.37 (hexane–diethyl ether, 2:1). IR spectrum, *v*, cm^{-1}: 2220 (C≡C), 3635 (OH). ^{1}H NMR (CCl_4); δ , *ppm*: 0.88 t (*J*=6.8 *Hz*, 3H); 1.20–1.66 m (8 H); 1.71–1.82 m (2H); 1.85 br. s (2H, OH); 4.25–4.33 m (2H).

Synthesis of 2(E)-decen-1,4-diol (4). To a suspension of 2.27 *g* (0.06 *mol*) lithium aluminum hydride in 40 *mL* of anhydrous THF was added 2.4 *g* (0.014 *mol*) of 2-hexyn-1,4-diol (**3**) in 10 *mL* of anhydrous ether at 0º*C* under argon. The reaction mixture was stirred for 2.5 *h* at room temperature, cooled to from –6 to –8 º*C*, and treated with 2.3 *mL* of water, 2.3 *mL* of 15% sodium hydroxide solution, and 6.8 *mL* of water. The precipitate was filtered off and washed with diethyl ether. The filtrate was dried over sodium sulfate. After the solvents removal, the residue was purified by column chromatography (hexane–diethyl ether, 9:1).

Yield 1.9 *g* (79.2 %), R_f (hexane–diethyl ether, 2:1). IR spectrum, *v*, cm^{-1}: 980 (trans. C=C), 3020 (C=C), 3630 (OH). ^{1}H NMR (DMSO- *d*6); δ , *ppm*: 0.88 t (*J*=6.8 *Hz*, 3H); 1.20–1.66 m (10 H); 2.91 br. s (2 H, OH); 4.12 d (*J*=7.2 *Hz*, 1 H); 4.18 kv (*J*=7.2 *Hz*, 1 H); 5.58 m (2 H) [7].

Synthesis of 4-oxo-2(E)-decenal (1). To the suspension of pyridinium chlorochromate (8.64 *g*, 0.02 *mol*) in 10 *mL* dichloromethane was drop by drop added 0.7 *g* (0.004 *mol*) of 2(*E*)-decen-1,4-diol solved in 4 *mL* dichloromethane under nitrogen atmosphere at room temperature. Reaction mixture was stirred for 5 *h* and subsequently extracted with Et_2O (3×50 *mL*). After, combined organic layers were dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The remaining crude material was purified by column chromatography to give the desired product.

Yield 0.4 *g* (57 %). R_f 0.42 (hexane–diethyl ether, 4:1). IR spectrum, *ν*, cm^{-1}: 980 (*E*–C=C), 1590 (C=C), 1700 (C=O), 2730 (CHO). ^{1}H NMR ($CDCl_3$); *δ, ppm*: 0.92 t (*J*= 7.0 *Hz*, 3H, H^{10}); 1.24–1.66 m (8H, H^6, H^7, H^8, H^9); 2.58 t (*J*= 7.22 *Hz*, 1H, H^5); 6.78 dd (J_1 =7.2 *Hz*, J_2 =16.2 *Hz*, 1H, H^2); 6.88 d (*J*= 16.2 *Hz*, 1H, H^3); 9.74 d (*J* =7.2 *Hz*, 1H, H^1) [6].

Received 16.06.2014

REFERENCES

1. **Borges M., Aldrich J.R.** Instar-Specific Defensive Secretions of Stink Bugs (*Hemiptera*: *Pentatomidae*). // Experientia, 1992, v. 48, p. 893.
2. **Pavis C., Malosse C., Ducrot P. H., Descoins C.** Dorsal Abdominal Glands in Nymphs of Southern Green Stink Bug, *Nezara Viridula* (L.) (*Hemiptera*: *Pentatomidae*): Chemistry of Secretions of Five Instars and Role of 4-Oxo-(*E*)-2-decenal, Compound Specific to First Instars. // J. Chem. Ecol., 1994, v. 20, № 9, p. 2213.
3. **Fávaro C.F., Mauro A.C., Rodrigues M., Aldrich J.R., Zarbin P.H.G.** Identification of Semiochemicals in Adults and Nymphs of the Stink Bug *Pallantia macunaima* Grazia (*Hemiptera*: *Pentatomidae*). // J. Braz. Chem. Soc., 2011, v. 22, № 1, p. 58.
4. **Noge K., Kimura H., Abe M., Becerra J.X., Tamogami S.** Antibacterial Activity of 4-Oxo-(*E*)-2-hexenal from Adults and Nymphs of the Heteropteran, *Dolycoris baccarum* (*Hemiptera*: *Pentatomidae*). // Biosci. Biotechnol. Biochem., 2012, v. 76, № 10, p. 1975.
5. **Guillen M.D., Uriarte P.S.** Aldehydes Contained in Edible Oils of a Very Different Nature After Prolonged Heating at Frying Temperature: Presence of Toxic Oxygenated *α,β*-Unsaturated Aldehydes. // Food Control, 2012, v. 24, № 1–2, p. 50.
6. **Moreira J.A., Millar J.G.** Short and Simple Syntheses of 4-Oxo-(*E*)-2-hexenal and Homologs: Pheromone Components and Defensive Compounds of *Hemiptera*. // J. Chem. Ecol., 2005, v. 31, № 4, p. 965.
7. **Ho H.-Y., Millar J.G.** Compounds in Metathoracic Glands of Adults and Dorsal Abdominal Glands of Nymphs of the Stink Bugs, *Chlorochroa uhleri*, *C. sayi* and *C. ligata* (*Hemiptera*: *Pentatomidae*). // Zoological Studies, 2001, v. 40, № 3, p. 193.