

Synthesis of Intermediate Product 8-Cis, Trans-Dodectenyl Acetate

YuldashevIkbol Shukuralievich, Khaitbaev Alisher Khamidovich, Khaitbaev Khamid, Babaev Bahrom Nurillaevich

Department Chemistry of natural compounds, Faculty of Chemistry National University of Uzbekistan, Tashkent.
Uzbekistan

ABSTRACT: Pheromones are one of the components of low molecular weight bioregulators - substances with a relatively small molecular weight, high biological activity and performing various functions in living organisms. Using synthetic pheromones, you can easily influence the behavior of insects without harming other organisms in their environment. The insect pheromones known today are molecules of a linear structure with a content of no more than four asymmetric centers. In this regard, it was of theoretical and practical interest to synthesize and study 8-cis, trans-dodecenylyl acetate. As a result of the synthesis of 2-triphenylphosphinoxy-tetrahydro-2H-pyran bromide insect pheromones can be synthesized as *G.molesta*, *G.batrachopa*, *G.funebrana*, *G.lobarzewskii*, *Eucosmanotantes* and others.

KEYWORDS: pheromone, agroecosystem, synthesisstage, optimization.

I. INTRODUCTION

In recent decades, the concept of an integrated plant protection system has been developed and actively developed in science and practice in agriculture and forestry, into which the use of pheromones, biologically active substances produced by insects themselves to transmit information to individuals of their own species, fits best [1-3].

Having learned how to synthesize pheromones artificially, a person got the opportunity to order insects and control their behavior. The simplest and most obvious way to use this unique opportunity was to order pests to go into traps. Thus, you can either completely get rid of them, or at least accurately determine the moment of their appearance and quantity in order to further develop an effective plan of struggle.

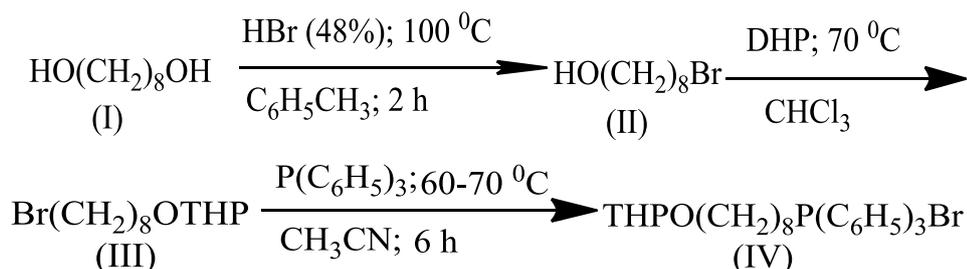
Using synthetic substances that are identical in structure and composition to natural pheromones, it is possible to organize the management of the population of a certain species of phytophagous insects in order to maintain it at a reasonable level while maintaining the balance of the agroecosystem [4-6].

This approach is devoid of the disadvantages that are inherent in the use of pesticides, including biodegradable ones. When using pheromones, insects do not become addicted to the drugs used [7-10].

Therefore, the priority of research is the synthesis of insect pheromone to regulate their numbers.

In order to obtain intermediates of the pheromone synthesis process, we have carried out studies to optimize of the reaction synthesis steps. The influence of the concentration and nature of the reagents, the nature of the solvent, and the duration of the reaction on the efficiency of the process was investigated.

Synthesis of the final product of insect pheromone proceeds in steps, the second can be represented as follows:



II. EXPERIMENTAL

General Methods. IR spectra were recorded on the IRTracer-100 (Shimadzu Corp.) spectrophotometer. Structure controls were conducted by means of ^1H NMR spectra recorded on a NMR spectrometer operating at 400 MHz. Chemical shifts were referenced to internal TMS.

1. Synthesis of 8-bromooctanol-1 (II). In a two-neck flask equipped with a reflux condenser, 15.4 g (0.15 mol) of octanediol, 2 g of tetrabutylammonium bromide, 18 ml of 46% hydrobromic acid (0.15 mol) and 70 ml of toluene were placed. The reaction mixture was boiled at 100°C for 2 hours. The reaction mixture was washed first with 40 ml of water, then with a 2% alkali solution until neutral, dried with anhydrous sodium sulfate. After distillation of the solvent under reduced pressure ($75\text{--}78^\circ\text{C} / 14\text{ mm Hg}$), 8-bromooctanol-1 was obtained, which was purified by the method of column chromatography. Eluent hexane:ether (2:1). Yield 15.1 g (69%). $R_f=0.46$ (system: hexane-ether 2: 1).

IR (neat): ν_{max} 3650–3200, 3000–2840, 1475–1450, 1080–1000, 720– 770, 700–500 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , ppm): δ 1.29 [6H, s], 1.42 [2H, qn], 1.56 [2H, qn], 1.85 [2H, qn], 2.17 [1H, s], 3.40 [2H, t], 3.64 [2H, t].

2. Synthesis of 2-(8-bromooctyloxy)-tetrahydro-2H-pyran (III). In a two-neck flask equipped with a reflux condenser, 2 g of 8-bromooctanol-1 were placed in 20 mL of chloroform, p-toluenesulfonic acid and 0.81 g of dihydropyran were heated at 70°C for 8 hours. The progress of the reaction was monitored by TLC (hexane: ether 4: 1). After distilling off the solvent, the reaction product $\text{Br}(\text{CH}_2)_8\text{OTHP}$ was purified by column chromatography (eluent hexane:ether 4:1). Yield 1.93 g (69%), $R_f= 0.78$ (system: hexane-ether 4:1).

IR(neat) ν_{max} 3000–2840, 1600–1575, 1475–1450, 1310–1230, 1110–1340, 1190–990, 1055–870, 720–770 cm^{-1} . ^1H -NMR (400 MHz, CDCl_3) δ 4.56 (1H, m), 3.88–3.70 (2H, m), 3.51–3.34 (2H, m), 3.39 (2H, t, $J = 6.8\text{ Hz}$, H-8), 1.48 (4H, m), 1.56 (6H, m), 1.41–1.32 (8H, m, $-\text{CH}_2-$).

3. Synthesis of 2-triphenylphosphinoctyloxy-tetrahydro-2H-pyran bromide (IV). In a round bottom flask, 2 g of 8-bromooctane-hydroxy-THP were placed in 20 ml of acetonitrile and 2.7 g of triphenylphosphine. The reaction mixture was boiled at a temperature of $60\text{--}70^\circ\text{C}$ for 6 hours. The course of the reaction was monitored by TLC (hexane-ether 3:1). After distilling off the solvent, the resulting complex was purified by the method of column chromatography. Eluent hexane-ether 3:1. Yield 2.45 g (67.7%).

IR(neat) ν_{max} 3000–2840, 1600–1575, 1475–1450, 1310–1230, 1110–1340, 1190–990, 1055–870, 720–770 cm^{-1} .

III. RESULTS AND DISCUSSION

The processes of studies have been conducted to optimize the stages of synthesis. The influence of the concentration and nature of the reagents, the nature of the solvent, the temperature and the duration of the reaction on the efficiency of the process was investigated.

According to the results of the nature of the solvent (such as benzene, 43.5%; heptane, 53%; toluene, 59%), the reaction time (within 1 hour - 58%; 2 hours - 69%; 3 hours - 61%) and temperatures (carried out at the boiling point of solvents), as well as the optimal conditions for the synthesis of 8-chloro- and 8-bromooctanols from 1,8-octanediol were determined. It was also revealed that although bromooctanol is obtained with a relatively high yield (2 hours, 70%), its color, in contrast to chlorooctanol (2 hours, 50%), varies with time.

The optimal conditions for the protection of chloro- and bromooctanols with dihydropyran in chloroform were determined. In the study of the influence of the duration of the reaction (4 hours-23%; 12 hours-32.5%; 16 hours-43.3%; 20 hours-40%), temperatures ($22\text{--}25^\circ\text{C}$ -77%; $75\text{--}80^\circ\text{C}$ 47%) and the amount of catalyst (0.01 g, 0.1 g) - para-toluenesulfonic acid found that although the protection efficiency of bromooctanol is relatively high, the color of the product, unlike the chlorooctanol protection product, changes with time and is relatively unstable.

The optimal conditions for the third stage of the synthesis, the preparation of a complex of 8-halogen-oxydihydropyran with triphenylphosphine, have been determined. When studying the effect of the nature of the solvent (toluene, acetonitrile, dimethylformamide), reaction time (4, 6, 8 hours) and temperature ($50\text{--}60$, $60\text{--}70$, $70\text{--}80^\circ\text{C}$) reaction, it was found that the relatively high efficiency of the process, as in the case of obtaining chlorine-containing and bromine-containing, reaches when carrying out the reaction at a temperature of $70\text{--}80^\circ\text{C}$ and for 6 hours in the medium of acetonitrile. It was exposed that under these conditions, the efficiency of the reaction to obtain the bromine-containing complex is higher (64.7%) than chlorine-containing (45.3%).

Equations

1. The optimal conditions for the two stages of the synthesis were determined, the structures of the obtained intermediate compounds were confirmed by the method of IR-spectroscopy.



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2. Conducted research on the optimization of the stages of synthesis. The influence of the concentration and nature of the reagents, the nature of the solvent, the temperature and the duration of the reaction on the efficiency of the process was investigated.
3. Optimal conditions for the protection of bromoethanol with dihydropyran in chloroform were determined.

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