

INSECT PHEROMONES AND THEIR ANALOGS.

XIX. PREPARATION OF α -GERANYL PROPIONATE - THE MAIN COMPONENT OF THE SEX PHEROMONE OF SAN JOSE SCALE*

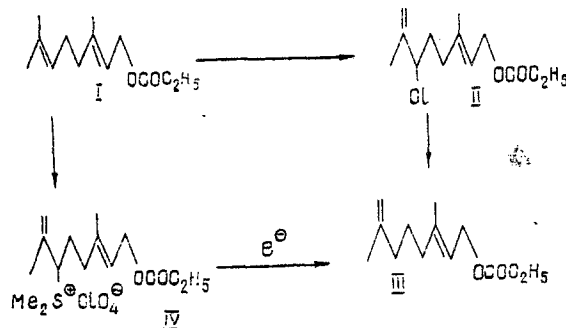
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UDC 542.91:632.936.2

Two methods of synthesizing α -geranyl propionate - a component of the sex pheromone of San Jose scale - have been developed: the hydride reduction of the corresponding 6-chloro derivative and the electrochemical reduction of the 6-dimethylsulfonium derivative.

α -Geranyl propionate (III) is a component of the sex pheromone of San Jose scale Quadraspidiotus perniciosus and exhibits attractant activity in relation to this dangerous polyphagous insect [2]. A whole series of syntheses of this compound are known [3-11]. From the point of view of practical interest, methods based on the isomerization of the isopropylidene fragment of the geraniol molecule into an isopropenyl fragment appeared to be of interest [5-7].

In the present paper we consider another two examples of this approach which are based on the reduction of the known [5] chloride (II) and the sulfonium salt (IV). The former was obtained in high yield by the reaction of geranyl propionate (I) with SO_2Cl_2 in CH_2Cl_2 at -60°C in the presence of pyridine. A study of different variants of reductive dehalogenation [5, 13-16] as applied to (II) showed that it can be realized most effectively (without affecting the double bonds in the ester group) in the $\text{Zn-NiCl}_2\text{-PPh}_3\text{-NaI-DMFA-H}_2\text{O}$ system [16]. The yield of the desired propionate (III) (62%) in this case was higher than when the $\text{NaBH}_4\text{-LiI}$ system was used as reducing agent [5].



An alternative route to the synthesis of (III) consists of the electrochemical reduction of the salt (IV), which is formed smoothly and quantitatively when (I) is treated with the reagent $\text{DMSO}-(\text{CF}_3\text{CO})_2\text{O-LiClO}_4$. The electrolysis of (IV) with a controlled potential at a mercury cathode in aqueous ethanolic solution (pH 5.3, acetate buffer) leads to (III) in moderate yield.

The spectral characteristics (IR, PMR, ^{13}C NMR) of the samples of the propionate (III) synthesized by the two methods under consideration agreed with those published previously [5] for this compound.

*For the preceding communication, see [1].

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EXPERIMENTAL

PMR spectra of solutions in CDCl_3 were measured on a Tesla BS-567 (100 MHz) spectrometer relative to TMS. ^{13}C NMR spectra were obtained on a JEOL FX-90 Q (22.5 MHz) instrument in CDCl_3 .

6-Chloro-3,7-dimethylocta-2E,7-dien-1-ol Propionate (II). A solution of 1.33 g (9.83 mmole) of SO_2Cl_2 in 5 ml of CH_2Cl_2 was added over 5 min to a vigorously stirred (Ar) solution of 1.59 g (7.56 mmole) of (I) and 0.78 g (9.83 mmole) of pyridine in 15 ml of CH_2Cl_2 at -60°C . The reaction mixture was heated to 0°C over 10 min and was then diluted with ether and neutralized with saturated aqueous NaHCO_3 solution. The aqueous layer was separated off and extracted with ether, and the combined organic layer was washed with water, dried with MgSO_4 , and evaporated in vacuum, and the residue (~2 g) was chromatographed on 60 g of SiO_2 . Elution with hexane-ether (97:3) gave 1.63 g (88%) of (II), bp $104-106^\circ\text{C}$ (1 mm), n_D^{20} 1.4730; compare [5]. PMR spectrum (δ , ppm): 1.12 t ($J = 7$ Hz, 3H, CH_3); 1.72 s and 1.85 s (6H, $\text{CH}_3\text{C}=\text{C}$); 1.8-2.2 m (4H, CH_2), 2.38 q ($J = 7$ Hz, 2H, CH_2CO); 4.38 t ($J = 6$ Hz, 1H, CHCl); 4.58 d ($J = 7$ Hz, 2H, CH_2O); 4.87 and 4.98 s (2H, $\text{H}_2\text{C}=\text{C}$); 5.43 t ($J = 7$ Hz, 1H, $\text{HC}=\text{C}$). ^{13}C NMR spectrum (δ , ppm): 9.16 (CH_3CH_2); 16.32 and 17.01 (CH_3); 27.52 (CH_2CH_3); 34.40 (C^5); 36.46 (C^4); 60.95 (C^1); 65.94 (C^6); 140.16 (C^3); 114.21 (C^8); 144.17 (C^7); 174.19 ($\text{C}=\text{O}$).

Dimethyl(2,6-dimethyl-8-propionyloxyocta-1,6E-dien-3-yl)sulfonium Perchlorate (IV). A stirred (Ar) solution of 1.76 g (8.37 mmole) of (I) in 15 ml of CH_2Cl_2 at -30°C was treated successively with 1.31 g (16.77 mmole) of DMSO, 1.34 g (12.59 mmole) of LiClO_4 , and, after 5 min, 3.52 g (16.74 mmole) of $(\text{CF}_3\text{CO})_2\text{O}$. The reaction mixture was warmed to -10°C over 20 min and was stirred at this temperature for 1.5 h and it was then diluted with CH_2Cl_2 , neutralized with saturated aqueous NaHCO_3 solution, washed with water, dried with MgSO_4 , and evaporated in vacuum. The oily residue was twice precipitated with ether from solution in CH_2Cl_2 and was subjected to vacuum. This gave 2.75 g (89%) of the salt (IV) in the form of a viscous light yellow oil, which was used further without additional purification.

α -Geranyl Propionate (III). A. A suspension of 0.33 g (5.05 mg-at.) of Zn, 0.16 g (1.07 mmole) of NaI, 0.21 g (1.62 mmole) of NiCl_2 , and 0.25 g (0.95 mmole) of PPh_3 in 5 ml of $\text{DMFA-H}_2\text{O}$ (24:1) was stirred (Ar) at 50°C for 15 min, and was then treated with a solution of 0.7 g (2.86 mmole) of (II) in 3 ml of $\text{DMFA-H}_2\text{O}$ (24:1). The reaction mixture was stirred at 50°C for 1 h and was then diluted with water and extracted with ether. The extract was dried with MgSO_4 and evaporated, and the residue (~0.6 g) was chromatographed on 20 g of SiO_2 under the conditions used for (II). This gave 0.37 g (62%) of (III) in the form of a colorless oil.

B. The electrolysis of (IV) using a II 5848 potentiostat was performed in a cell with a glass diaphragm. The cathode was the bottom mercury pool and the anode platinum gauze, the comparison electrode being a saturated calomel electrode.

A current (100 \rightarrow 10 mA, $E = -1$ V) was passed through the stirred catholyte - 15 ml of aqueous AcOK solution (pH 5.3)-ethanol (1:1) containing 0.6 g (1.62 mmole) of (IV) - for 1.5 h. Then the mercury was separated off, and the reaction mixture was diluted with water and extracted with ether. The usual treatment of the extract and chromatography under the conditions given above led to 70 mg (20%) of (III). The IR, PMR, and ^{13}C NMR spectra of the samples of (III) prepared in this way were practically identical with those given in [5].

SUMMARY

Two methods for synthesizing α -geranyl propionate - a component of the sex pheromone of San Jose scale - have been developed: the hydride reduction of the corresponding 6-chloro derivative and the electrochemical reduction of the 6-dimethylsulfonium derivative.

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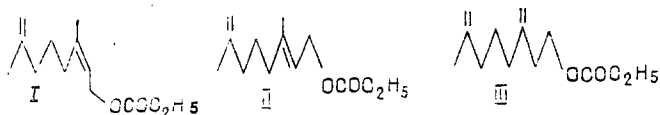
SYNTHESIS OF α -NERYL AND α -GERANYL PROPIONATES - COMPONENTS OF THE SEX PHEROMONE OF SAN JOSE SCALE

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UDC 542.91:632.936.2

α -Neryl and α -geranyl propionates - components of the sex pheromone of San Jose scale - have been synthesized by the two-stage E/Z- C_5 homologization of isopentenyl iodide.

It is well known that monoterpene propionates, mainly of the α -series, are active components of the sex pheromone of a quarantine pest of a large number of thermophilous crops - San Jose scale. Among such components the propionates (I-III), in particular, have been identified [1, 2]. Syntheses of compounds (I) and (II) based on the addition of isohexenyl cuprates to methylacetylenes [2, 3], the alkylation of acetoacetic ester derivatives [4, 5], and the isomerization of the terminal isoprene unit of neryl and geranyl propionates [6, 7] are known.



In the present paper we consider a directed synthesis of the α -isomeric propionates (I) and (II) based on the isoprene Z-hydroxysulfonamide (IV) [8, 9] and the E-hydroxysulfone (V) [10]. These sulfonyl derivatives served as the basic "building blocks" in the construction of the desired molecules. As an auxiliary material we selected 3-methylbut-3-en-1-yl iodide (VI), prepared by a standard method from the industrially available 2-methylallyl carbinol (XI) through the stage of the unstable tosylate (XII), which, like (VI), was characterized spectrally.

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