Chemistry of Natural Compounds, Vol. 32, No. 6, 1996

PHEROMONES OF INSECTS AND THEIR ANALOGS. LIV. SYNTHESIS OF DODEC-9E-EN-1-OL AND ITS ACETATE — COMPONENTS OF THE SEX PHEROMONE OF *Sparganothis pilleriana*

V. N. Odinokov, R. R. Vakhidov, R. N. Shakhmaev, and V. V. Zorin

UDC 542.91+547.473+632.936.2

Using the Claisen rearrangement in the construction of a double bond with the E configuration, we have synthesized dodec-9E-en-1-ol and its acetate, which are components of the sex pheromone of Sparganothis pilleriana.

The sex pheromone of the vine leaf-roller moth *Sparganothis pilleriana*, which damages the leaves and fruit of the vine, consists of a mixture (1:9) of dodec-9E-en-1-ol (1) and its acetate (2) [1]. A number of syntheses of (1) and (2) are known [2-13] in which various approaches are used in the construction of the double bond with the E configuration; for example, via acetylene derivatives, the opening of a cyclopropane ring, and the metathesis and Knoevenagel reactions.

The Claisen rearrangement has recommended itself as a stereospecific method of synthesizing unsaturated aldehydes and carboxylic acid esters [14, 15]. We have reported the use of this reaction in the synthesis of tridec-4E-en-1-yl acetate [16, 17].

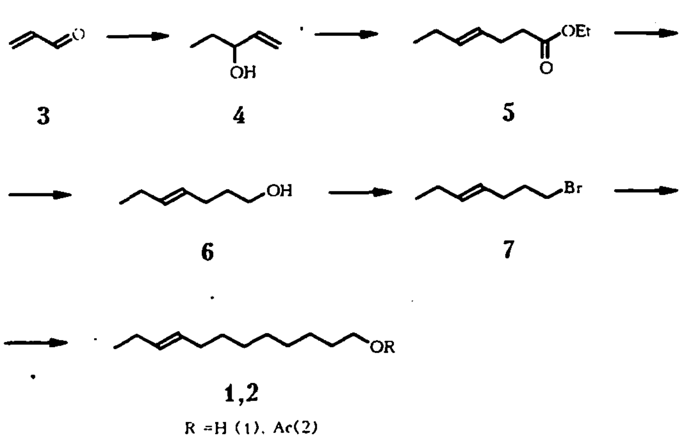
Pheromones with a double bond more remote from the functional group than in the initial products of the Claisen reaction can be synthesized via the products of the thermal rearrangement of secondary allyl alcohols by converting them into, for example, the corresponding alk-4E-enyl bromides, followed by coupling with the appropriate α,ω-bifunctional compounds. We have tried this approach in the synthesis of the pheromones (1) and (2).

The initial compound in the proposed scheme of synthesis was acrolein (3), the coupling of which with ethyl bromide gave the secondary allyl alcohol (4) The rearrangement of (4) into ethyl hept-4E-enoate (5) took place smoothly on heating with triethyl orthoacetate in the presence of acetic acid. The exclusively E configuration of the ester (5) obtained followed from the presence in its IR spectrum of an intense absorption band at $\nu = 965$ cm^{-1}, corresponding to the out-of-plane deformation vibrations of a C=C bond of the E configuration, and the absence of the absorption in the $\nu = 700$-820 cm^{-1} region that is characteristic for a double bond with the Z configuration. The stereochemical individuality of compound (5) was confirmed by GLC on a capillary column.

The subsequent transformations of synthon (5), leading to the desired compounds (1) and (2), included the hydride reduction of the enoate (5) to hept-4E-en-1-ol (6) and its conversion into the corresponding bromide (7), followed by the interaction of the latter with 5-(2-tetrahydropyran-1-yl)oxypent-1-ylmagnesium bromide catalyzed by the CuI—bipyridyl system, which led to the desired coupling product. The acid hydrolysis of this gave the alcohol (1) — one of the desired products — which was converted in the usual way into the other desired product — the acetate (2). The sterochemical individuality of compounds (1) and (2) was confirmed by GLC analysis on a capillary column.

Scientific Research Institute of Fine Organic Synthesis of the Academy of Sciences, Republic of Belarus. Ufa State Petroleum Technical University. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 936-939, November-December, 1996. Original article submitted May 11, 1996.

0009-3130/96/3206-0912$15.00 ©1997 Plenum Publishing Corporation



EXPERIMENTAL

IR spectra were taken on a Microlab 620MX spectrometer (in a film), and PMR spectra on a Tesla BS-587A instrument (working frequency 80 MHz) in the solvent $(CD_3)_2CO$; chemical shifts are given on the δ scale relative to HMDS. GLC analysis was conducted on a Chrom-5 instrument: stationary phase SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm), working temperature 50-250°C, carrier gas helium. Compounds (1), (2) and (5) were additionally analyzed on a Carlo Erba instrument with a 0.2 mm × 20 m glass capillary column, working temperature 50-200°C. TLC was conducted on Silufol plates with a fixed layer of SiO_2. The elementary analyses of the compounds synthesized corresponded to the calculated values.

Pent-1-en-3-ol (4). With vigorous stirring and cooling (1 h, −10 to −15°C) a solution of 8.4 g (0.15 mole) of acrolein in 30 ml of abs. diethyl ether was added dropwise to the Grignard reagent obtained from 18.7 g (0.165 mole) of ethyl bromide and 3.65 g (0.15 g-atom) of magnesium turnings in 200 ml of diethyl ether. Stirring was continued for another 0.5 h, after which the mixture was cooled to 0°C and 50 ml of water was carefully added. The aqueous layer was separated off and was extracted with ether (3 × 50 ml). The combined organic layers were dried with Na_2SO_4 and evaporated. The residue was distilled, to give 9.90 g (74%) of the alcohol (4), bp 114-116°C, n_D^{19} 1.4228 , see [18]. IR spectrum (ν, cm^{-1}): 3350 (OH); 1640, 995, 920 ($HC{=}CH_2$) The PMR spectrum was identical with that given in [19].

Ethyl Hept-4E-enoate (5). A mixture of 4.76 g (0.55 mole) of the alcohol (4), 32.4 g (0.185 mole) of triethyl orthoacetate, and 0.2 g of acetic acid was stirred at 100°C for 6 h, with the ethanol liberated being distilled off. Then the reaction mixture was cooled to room temperature and, after the addition of 100 ml of diethyl ether, it was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was distilled in vacuum, giving 6.54 g (76%) of the ester (5), bp 81-83°C (10 mm Hg), n_D^{19} 1.4160. IR spectrum (ν, cm^{-1}): 1745 (C=O), 1645, 965 (E-CH=CH). PMR spectrum (δ, ppm): 0.85 (t, 3H, J = 6 Hz, H-7), 1.12 (t, 3H, J = 6 Hz, CH_3CH_2O), 1.7-2.05 (m, 4H, H-3, H-6), 2.22 (t, 2H, J = 2 Hz, H-2), 4.00 (q, 2H, J = 6 Hz, CH_3CH_2O), 5.4-5.8 (m, 2H, H-4, H-5).

Hept-4E-en-1-ol (6). With stirring (Ar, 0-5°C), 3.9 g (25 mmole) of the ester (5) was added dropwise over 1 h to a suspension of 1.09 g (12 mmole) of $LiAlH_4$ in 50 ml of abs. diethyl ether. After being heated to room temperature, the reaction mixture was stirred for 2 h, and it was then cooled to 0°C and 20 ml of water was added dropwise over 0.5 h. The solution was decanted off and the residue was washed with ether (20 ml). The combined ethereal solution was washed with saturated NaCl solution, dried with Na_2SO_4, and evaporated. The residue was distilled, giving 2.23 g (78%) of the alcohol (6), n_D^{16} 1.4205. IR spectrum (ν, cm^{-1}: 3350 (OH); 965 (E-CH=CH). The PMR spectrum was identical with that given in [20].

1-Bromohept-4E-ene (7). With stirring and cooling (−10 to −15°C), 1.76 g (16 mmole) of the alcohol (6) was added over 2 h to a mixture of 4.75 g (17.5 mmole) of PBr_3 and 0.68 g of pyridine in 50 ml of abs. diethyl ether, and the mixture was left at room temperature for two days. Then 20 ml of ice-cooled water was added, the organic layer was separated off, and the aqueous layer was extracted with ether (2 × 25 ml). The combined ethereal solution was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with Na_2SO_4, and evaporated. The residue was chromatographed (SiO_2, pentane), giving 2.23 g (81%) of the bromide (7), n_D^{17} 1.4484. IR spectrum (ν, cm^{-1}): 1635, 970 ($E\text{-}CH{=}CH_2$); 640 (C—Br). The PMR spectrum was identical with that given in [21].

Dodec-9E-en-1-ol (1). A suspension of 0.38 g (1.8 mmole) of CuI in 10 ml of abs. THF was treated with 0.7 g of 2,2′-bipyridyl and the mixture was stirred (Ar, 20°C) for 0.5 h and was then cooled to 2°C, and a solution of 0.79 g (4.4 mmole) of the bromide (7) in 5 ml of abs. HF was added. The mixture was stirred for 15 min and then the Grignard reagent prepared from 1.10 g of 5-(2-tetrahydropyran-1-yl)oxypent-1-yl bromide (obtained in accordance with [22]) and 0.11 g (4.4 mmole) of magnesium turnings in 10 ml of abs. THF was added dropwise, and the reaction mixture was stirred at 2°C for 2 h and at 20°C for 16 h and was then boiled for 4 h.

The reaction mixture was treated with 10 ml of saturated aqueous NH_4Cl and stirred for 1 h, the organic layer was separated off, and the aqueous layer was extracted with diethyl ether (3 × 20 ml). The combined organic solution was evaporated, and a solution of the residue in 20 ml of ethanol containing 0.06 g of TsOH was stirred at room temperature for 24 h and was evaporated. The new residue was dissolved in 50 ml of diethyl ether, and this solution was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with Na_2SO_4, and evaporated. The residue was chromatographed (SiO_2, hexane—ether (1:1)), giving 0.51 g (62%) of the alcohol (1). IR spectrum (ν, cm^{-1}): 3350 (OH); 1635, 965 (E-CH=CH). The PMR spectrum was identical with that given in [13].

Dodec-9E-en-1-yl Acetate (2). A mixture of 0.19 g (1.05 mmole) of the alcohol (1), 2 ml of abs. pyridine, and 2.5 ml of acetic anhydride was kept at room temperature for two days, and then, after the addition of 20 ml of diethyl ether, it was washed successively with 10% HCl and with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2, hexane—ether (9:1)), giving 0.20 g (81%) of the acetate (2). Its IR and PMR spectra were identical with those given in [13].

REFERENCES

1. P. Saglio, E. Priesner, S. Discoins, and M. Gallois, C. R. Acad. Sci, **D.284**, No. 20, 2007 (1977).
2. C. A. Henrick, Tetrahedron, **33**, No. 15, 1845 (1977).
3. G. K. Roshka, A. M. Sorochinskaya, and B. G. Kovalev, New Methods in Plant Protection [in Russian], Kishinev, Part 4 (1982), p. 14.
4. N. Popovici, A. A. Botar, A. Baravas, I. Oprean, and F. Hodosan, J. Prakt. Chem., **325**, No. 1, 17 (1983).
5. O. P. Vig, G. L. Kad, A. Subharval, V. Dodra, and S. Sharma, J. Indian Chem. Soc., **66**, No. 4, 233 (1989).
6. I. Oprean, M. Ciupe, L. Jansca, and F. Hodosan, J. Prakt. Chem., **329**, No. 2, 283 (1987).
7. V. Fiandanese, G. Marchese, F. Naso, and L. Ronzini, J. Chem. Soc., Perkin Trans. I, No. 6, 1115 (1985).
8. Nand Singh Krishna, Singh Mamorama, and Misra Ram Achal, Indian J. Chem., **32B**, No. 4, 431 (1993).
9. C. Conevet, T. Roeder, O. Vostrocsky, and H. J. Bestmann, Chem. Ber., **118**, No. 3, 1115 (1980).
10. O. P. Vig, M. L. Sharma, N. K. Varma, and M. Neera, Indian J. Chem., **19B**, No.8, 692 (1980).
11. K. Yokoi and Y. Matsubara, J. Jpn. Oil Chem. Soc., **28**, No. 9, 623 (1978).
12. J. Levisalles and D. Villemint, Tetrahedron, **36**, No. 22, 3181 (1980).
13. L. N. Zakharkin and E. A. Petrushkina, Zh. Org. Khim., **18**, 1623 (1982).
14. O. P. Vig, M. L. Sharma, N. K. Varma, and N. Malik, Indian J. Chem., **20B**, No. 10, 860 (1981).
15. S. C. Sinka and E. Keinan, J. Am. Chem. Soc., **115**, No. 11, 4891 (1993).
16. V. N. Odinokov, R. R. Vakhidov, R. N. Shakhmaev, and N. V. Gil'vanova, Khim. Prir. Soedin., 490 (1995).
17. V. N. Odinokov, R. R. Vakhidov, and R. N. Shakhmaev, Khim. Prir. Soedin., 905 (1995).
18. A. A. Potekhina, Properties of Organic Compounds [in Russian], Khimiya, Leningrad (1984), p. 278.
19. S. E. Denmark, H. Harman, and K. White, J. Org. Chem., **52**, No. 18, 4031 (1987).
20. H. J. Bestmann, K. H. Koschatzky, W. Schatzke, J. Suess, and O. Vostrovsky, Liebigs Ann. Chem., **9**, 1705 (1981).
21. L. Crambe and R. D. Wyvill, J. Chem. Soc., Perkin Trans. I, No. 9, 1994 (1985).
22. S. W. Baldwin, J. D. Wilson, and J. Aube, J. Org. Chem., **50**, No. 23, 4432 (1985).