SYNTHESIS OF DODEC-10E-EN-1-YL ACETATE – THE SEX PHEROMONE OF Lithocolletis blancardella

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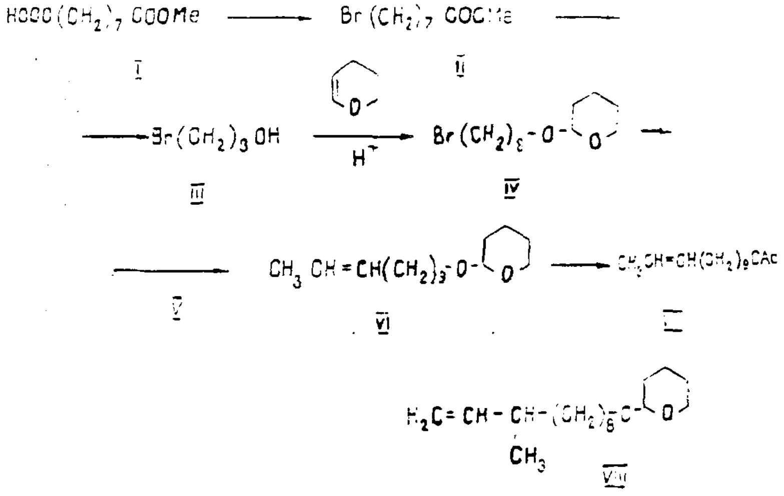
Dodec-10E-en-1-yl acetate – the sex pheromone of the apple leaf miner moth – has been obtained by a four-stage synthesis from monomethyl azelate and crotyl acetate. Its IR, PMR, and mass spectra are given.

Dodec-10E-en-1-yl acetate is a sex attractant of Lithocolletis blancardella (Fabr.), the apple leaf miner moth – a dangerous pest of plants of the order Rosales [1, 2]. Syntheses of this compound via acetylenic intermediates [3, 4] and also with the use of the Wittig reaction [5] are known. We have achieved the synthesis of dodec-10E-en-1-yl acetate (VII) from the readily available monomethyl azelate (I) and crotyl acetate (V) by the following scheme:



Methyl 8-bromooctanoate (II) was obtained from monomethyl azelate (I) by a modified Hunsdiecker reaction [6], and this was converted into 8-bromooctan-1-ol (III) and then into its tetrahydropyranyl ether (IV). The coupling of but-2E-en-1-yl acetate (crotyl acetate) (V) with the Grignard reagent generated from 1-bromo-8-(2-tetrahydropyranyloxy)octane (IV) under the conditions of [7] gave 1-(2-tetrahydropyranyloxy)dodec-10E-ene (VI). The latter was converted by the action of a mixture of acetyl chloride and acetic acid into the required acetate (VII), the yield of which, calculated on the initial monomethyl ester (I), was 10.7%. According to the results of GLC analysis, the final product (VII) contained 8% of 9-methylundec-10-en-1-yl acetate, obviously corresponding to the formation of a regioisomeric product of a S_N2'-substitution reaction in the allyl acetate (V) [8] – 1-(2-tetrahydropyranyloxy)-9-methylundec-10-ene (VIII).

EXPERIMENTAL

IR spectra were taken on a Specord 71 IR spectrometer in CCl_4. The PMR spectra of solutions of the substances under investigation in CCl_4 were measured relative to HMDS on a Varian XL-200 instrument with a working frequency of 200 MHz. Mass spectra were recorded on a

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Varian MAT 311 instrument. GLC analysis was performed on a Chrom-5 instrument with the stationary phase E-301 (10%) on Chromaton N-AW-HMDS with a column temperature of 160°C using helium as the carrier gas in a glass column with dimensions of 3 × 3500 mm.

Methyl 8-Bromooctanoate (II). Over 0.5 h, 10.34 g (64.7 mmoles) of bromine in 15 ml of CCl_4 was added to a mixture of 13.07 g (64.7 mmoles) of monomethyl azelate (I) and 10.65 g (49.2 mmoles) of red mercuric oxide in 100 ml of CCl_4 heated to 75°C. The mixture was boiled with stirring for 2 h and was then cooled and the solid matter was filtered off and washed with CCl_4. The filtrate was washed with 5% NaOH solution (3 × 25 ml) and then with water to pH 7 and was dried with $MgSO_4$. After evaporation and distillation, 5.12 g (33.4%) of compound (II) was obtained, with bp 120-122°C/5 mm. PMR spectrum (δ, ppm): 1.1-1.9 (10H, m, CH_2), 2.18 (2H, t, $CH_2{-}C{=}O$, J = 6.8 Hz), 3.26 (2H, t, CH_2Br, J = 6.6 Hz), 3.55 (3H, s, OCH_3).

8-Bromooctan-1-ol (III). With stirring, 4.8 g (20.2 mmoles) of methyl 8-bromooctanoate (II) in 15 ml of absolute ether was added dropwise to a suspension of 1.14 g (30 mmoles) of lithium tetrahydroaluminate in 100 ml of absolute ether at such a rate that the mixture boiled gently. Then it was boiled with stirring for 3 h and was cooled, and the excess of lithium tetrahydroaluminate was decomposed with ice water. The precipitate of Al and Li hydroxides was filtered off and was washed with 50 ml of ether. The ethereal solution was dried with $MgSO_4$ and evaporated. Fractionation of the residue gave 3.38 g (80.1%) of the bromohydrin (III), bp 102-104°C/1 mm, n_D^{20} 1.4805. According to the literature: bp 110-119°C/2 mm [9], n_D^{20} 1.4807 [10].

1-Bromo-8-(2-tetrahydropyranyloxy)octane (IV). By the method of [11], 3.32 g (15.9 mmoles) of the bromohydrin (III) and 2.01 g (23.8 mmoles) of 2,3-dihydropyran, with the addition of 2 drops of concentrated HCl, yielded 4.42 g (94.9%) of the protected bromohydrin (IV), the PMR and IR spectra of which were identical with those given in the literature [11].

1-(2-Tetrahydropyranyloxy)dodec-10E-ene (VI) and Dodec-10E-en-1-yl Acetate (VII). A solution of 1.37 g (12 mmoles) of but-2E-en-1-yl acetate (V) in 12 ml of absolute THF and 10 ml of absolute diethyl ether (−78°C, nitrogen) was treated with 21 ml of a 0.2 M solution of Li_2CuCl_4 in absolute THF and then with the Grignard reagent obtained from 4.39 g (15 mmoles) of 1-bromo-8-(2-tetrahydropyranyloxy)octane (IV) and 0.37 g (15.2 mmoles) of magnesium in 20 ml of absolute THF, and the mixture was stirred at the same temperature for 1 h, at −10°C for 2 h, and at room temperature for 10 h. The 25 ml of saturated NH_4Cl solution and 40 ml of diethyl ether were added to it. The organic layer was separated off and was washed with saturated NaCl solution and dried with $MgSO_4$.

Evaporation of the solvent gave 2.9 g of the crude product (VI), to which 9 ml of a 10:1 mixture of glacial acetic acid and acetyl chloride was added, after which the resulting mixture was left at room temperature for 24 h. After the usual working up and column chromatography [SiO_2, n-hexane−Et_2O (1:1)], 1.14 g (42% in the two stages) of the acetate (VII) was isolated, with n_D^{20} 1.4442 (see [3]). IR spectrum (cm^{-1}): 970 (trans-CH=CH); 1240, 1740 ($OCOCH_3$). PMR spectrum (δ, ppm): 1.1-1.4 (14H, m, CH_2), 1.58 (3H, m, $CH_3{-}C{=}$), 1.89 (3H, s, CH_3CO), 1.90 (2H, m, $={C}{-}CH_2$), 3.93 (2H, t, CH_2OCO, J = 6.8 Hz), 5.2-5.4 (2H, m, CH=CH). Mass spectrum, m/z (%): 226 (M^+; < 0.5), 166 $(M{-}CH_3COOH)^+$ (25), 138(8), 124(9), 110(25), 96(40), 82(65), 68(100), 61(17), 55(60), 43(60), 41(40).

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