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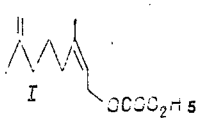
α-Neryl and α-geranyl propionates – components of the sex pheromone of San Jose scale – have been synthesized by the two-stage E/Z-C_5 homologization of isopentenyl iodide.

It is well known that monoterpenoid 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.



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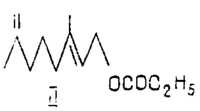

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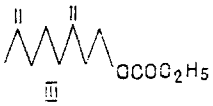

III

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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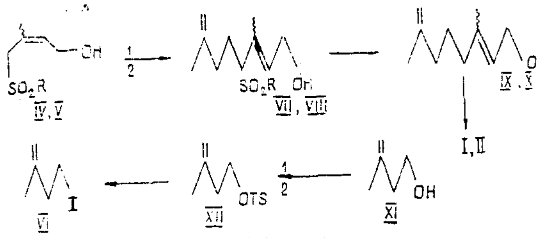
0009-3130/89/2503-0366 $12.50



$R = N(CH_2)_4O$: (IV), (VII); Ph: (V), (VIII)

The deprotonation of (VI) and (V) with the aid of n-BuLi in THF at −40°C followed by the acylation of the intermediate dilithium derivatives with the iodide (VI) led easily to the corresponding Z-sulfonamide (VII) and the E-sulfone (VIII). The structures of these previously unknown substances were reliably confirmed by the results of their physicochemical and elementary analyses. In particular in the PMR spectra of the sulfonamide (VII) the $CH_3{-}C^3$ and $CH_3{-}C^7$ signals characteristic for the Z-isomer were observed at δ 1.90 and 1.75 ppm, and also those at $H_2C{=}C$ groups at 4.70 and 4.8 ppm. The signals of these groups in the spectrum of the sulfone (VIII) were located at δ 1.59, 1.50, 4.50, and 4.60, respectively, which indicates its E-configuration (see [11, 12]).

The reductive desulfonylation of (VII) and (VIII) under the conditions adopted for related materials [10, 11] using Na in NH_3 in the presence of 0.1-0.15 molar equivalent of dibenzo-18-crown-6 (DB18C6) gave the alcohols corresponding to them (IX) and (X), which have previously been converted into the desired propionates (I) and (II). The physicochemical characteristics (boiling points, n_D^{20} values, and PMR and IR spectra) of the alcohols (IX) and (X) and their esters (I) and (II) that have been synthesized were close to those published previously for these substances [1].

The samples of compounds (I) and (II) obtained in this way, which according to GLC had a purity of 95%, exhibited a high biological activity under laboratory and field conditions.

EXPERIMENTAL

The IR spectra of solutions in $CHCl_3$ were taken on a UR-20 instrument. PMR spectra were measured relative to TMS on a Tesla BS-469 (100 MHz) instrument in CCl_4. Mass spectra were obtained on Varian MAT CH-6 instrument at 70 eV. GLC was conducted on Chrom-5 instrument using a 3 × 2500 mm column containing 15% of Carbowax 20 M and a 0.3 × 50,000 mm [sic] column with SP-2340 (FID).

1-Iodo-3-methylbut-3-ene (VI). To a solution of 43 g (0.5 mole) of (XI) in 400 ml of THF stirred (Ar) at 0°C was added, over 20 min, 202 ml of a 2.5 M solution of N-BuLi in hexane (0.505 mole), and then, at the same temperature, 94 g (0.49 mole) of TsCl. The reaction mixture was heated to 25°C over 30 min and was stirred at 25°C for 3 h and was then treated with ether and H_2O. The aqueous layer was separated off and extracted with ether. The combined extract was washed with H_2O, dried with $MgSO_4$, and evaporated in vacuum. This gave 116 g (97%) of the tosylate (XII) in the form of a light yellow oil which was used further without additional purification. A solution of 45 g (0.3 mole) of NaI and 40 g (0.17 mole) of (XII) in 250 ml of acetone was stirred at 25°C for 3 h, and then 200 ml of H_2O was added followed by 1 M solution of $Na_2S_2O_3$ until the coloration had disappeared, and it was extracted with ether. The usual working up of the extract gave 18 g (54%) of (VI) in the form of a light pink liquid with bp 40-42°C (15 mm). PMR spectrum (δ, ppm): 1.71 s (3H, CH_3); 2.53 t (2H, HC^2, J = 7 Hz); 3.17 t (2H, HC^1, J = 7 Hz), 4.71 and 4.79 br.s. (2H, HC^4).

1-Hydroxy-3,7-dimethylocta-2Z,7-diene-4-sulfonmorpholide (VII). Over 5 min, 10 ml of a 1 M solution of n-BuLi in hexane (10 mmole) and, after 40 min, 1.08 g (5.51 mmole) of (VI) were added to a solution of 1.17 g (4.97 mmole) of (IV) [8] in 25 ml of THF being vigorously stirred at −40°C (Ar). The reaction mixture was stirred at −40°C for 30 min and was then heated to 10°C over 4 h and was treated with ether and H_2O. The aqueous layer was separated off, neutralized with 20% H_2SO_4, and extracted with ether. The combined organic layer was washed with 2% $Na_2S_2O_3$ solution and with H_2O, was dried with $MgSO_4$ and evaporated, and the residue was chromatographed on 80 g of SiO_2. Elution with ether gave 1.12 g (74%) of (VII) in the form of a light yellow oil. IR spectrum (ν, cm^{-1}): 760, 820, 850, 960, 1000, 1070, 1115, 1275, 1325, 1355, 1385, 1455, 2865, 2970, 3530. PMR spectrum (δ, ppm): 1.75 and 1.90 br.s. (6H, CH_3); 2.0 m (4H, CH_2); 3.36 m (4H, CH_2N); 3.70 m (4H, CH_2OCH_2); 4.05 m (3H, CH_2O and CHS); 4.70 and 4.78 br.s. (2H, $H_2C{=}C$); 5.89 br.t. (1H, $HC{=}C$, J = 7 Hz). Found, %: C 55.25; H 8.22. M^+ 303. $C_{14}H_{25}NO_4S$. Calculated, %: C 55.42, H 8.31. Molecular mass 303.4.

3,7-Dimethyl-4-phenylsulfonyl-2E,7-dien-1-ol (VIII). Similarly, 6.3 g (27.84 mmole) of (V) [10], 57 ml of a 1 M solution of n-BuLi in hexane (57 mmole), and 5.7 g (29.1 mmole) of (VI) in 100 ml of THF yielded 6.1 g (74%) of (VIII) in the form of a colorless oil. IR spectrum (ν, cm^{-1}): 760, 850, 960, 1000, 1075, 1120, 1270, 1325, 1335, 1390, 1455, 2865, 2925, 2970, 3500. PMR spectrum (δ, ppm): 1.50 and 1.59 br.s. (6H, CH_3); 1.88 m (4H, CH_2); 3.4 m (1H, CHS); 3.96 br.d. (2H, CH_2O, J = 7 Hz); 4.50 and 4.60 br.s. (2H, $H_2C{=}C$); 5.26 br.t. (1H, $HC{=}C$, J = 7 Hz); 7.5-8.0 m (5H, C_6H_5). Found, %: C 65.41; H 7.72. M^+ 294. $C_{16}H_{22}O_3$. Calculated, %: C 65.27; H 7.82. Molecular mass 294.4.

α-Nerol (IX). A solution of 0.61 g (2.01 mmole) of (VII) in 10 ml of THF was added over 5 min to a solution of 0.37 g (16.1 mg-atom) of Na in 50 ml of NH_3 containing 70 mg (0.19 mmole) of DB18C6 and being vigorously stirred at −70°C. The reaction mixture was stirred at −70°C for another 5 min and was then decomposed with an excess of NH_4Cl, the NH_3 was evaporated off, and the residue was diluted with H_2O and extracted with hexane. The usual working up of the extract and chromatography of the substance so obtained on SiO_2 with gradient elution from hexane to ether (up to 60% of the latter) gave 0.23 g (74%) of (IX), bp 125°C (10 mm), n_D^{20} 1.4835 (compare [1]).

α-Geraniol (X). Similarly, 0.59 g (2.0 mmole) of (VIII), 0.37 g (16.1 mg-atom) of Na, and 70 mg (0.19 mmole) of DB18C6 in 50 ml of NH_3 and 10 ml of THF gave, after chromatography under the conditions described above, 0.2 g (65%) of (X), bp 125°C (10 mm), n_D^{20} 1.4815 (compare [1]).

α-Neryl Propionate (I). A solution of 0.77 g (4.99 mmole) of (VIII) and 0.47 g (5.94 mmole) of pyridine in 50 ml of ether being stirred at 20°C was treated with 0.56 g (6.05 mmole) of EtCOCl. The mixture was kept at 25°C for 5 h and, after the usual working up, 0.99 g (94%) of (I) was obtained with bp 120°C (1 mm), n_D^{20} 1.4541 (compare [1]).

α-Geranyl Propionate (II). Similarly, 0.77 g (4.99 mmole) of (IX), 0.47 g (5.94 mmole) of pyridine, and 0.56 g (6.05 mmole) of EtCOCl in 50 ml of ether yielded 1 g (95%) of (II), with bp 120°C (1 mm), n_D^{20} 1.4510 (compare [1]).

SUMMARY

An effective synthesis of α-neryl and α-geranyl propionates has been performed by the two-stage E/Z-C_5 homologization of 3-methylbut-3-en-1-yl iodide.

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