(for example, with 4-phenyl-1,2,4-triazoline-3,5-dione), fluorination with morpholinosulfur trifluoride to give the 3β-fluorinated adduct, and the subsequent regeneration of the 5,7-double bonds by treating the adduct with a solution of sodium methoanolate in methanol.

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SYNTHESIS OF RACEMIC DOMINCALURE — THE AGGREGATION PHEROMONE OF THE LESSER GRAIN BORER *Rhyzopertha dominica*

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The sec-amyl esters of 2-methylpent-2E-enoic and 2,4-dimethylpent-2E-enoic acids, constituting the aggregation pheromone of the lesser grain borer *Rhyzopertha dominica*, have been synthesized stereospecifically in high yield from the products of the aldol condensation of propionaldehyde and isobutyraldehyde. The 2-methyl- and 2,4-dimethylpent-2E-enals were oxidized to the corresponding acids, which were converted into the chlorides and these into the corresponding sec-amyl esters. The geometric purity of the products was shown by their PMR spectra (250 MHz).

The lesser grain borer *Rhyzopertha dominica* is one of a number of dangerous pests of grain stocks. One of the methods of combating this insect may be the use of its aggregation pheromone, which has recently been identified as a mixture of S-(+)-sec-amyl esters (Ia and b) ("dominicalure") [1]. This pheromone possesses a high attractant activity, and in the present paper we consider a stereospecific synthesis of the racemic forms of both of its components, which have been obtained previously in comparatively low yield from methyl propyl and methyl isobutyl ketones [1].

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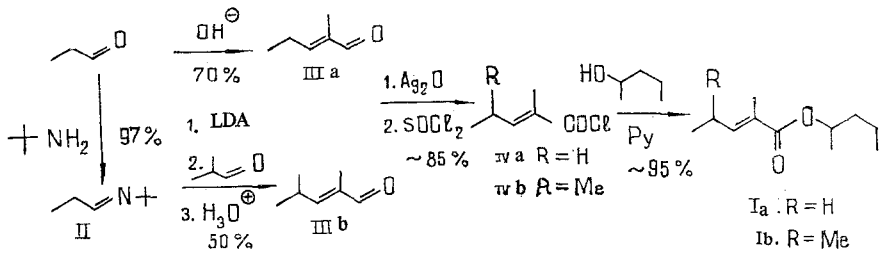
The E-configuration of the unsaturated carbon skeleton of the acid moieties of the molecules of (I) is easy to create from the products of the aldol condensation of propionaldehyde and isobutyraldehyde. Their directed cross-condensation was effected through the stage of the Schiff's base (II), which has been described in the literature [2], and the deprotonation of the latter with the aid of lithium diisopropylamide (LDA).



The known [3, 4] conjugated aldehydes (IIIa and b) obtained as a result were oxidized by Ag_2O almost quantitatively to the corresponding acids which were then converted without isolation into the corresponding chlorides — the (IVa) described previously [3] and the hitherto unknown (IVb), the structure of which was confirmed spectrally.

The treatment of (IVa and b) with sec-amyl alcohol gave the desired esters (Ia and b) quantitatively in a geometric purity (E > 98%), as was reliably deduced from the results of GLC and the PMR spectra, which contained diagnostic [1] signals of the protons of a $CH_3C{=}C$ group at $\delta \sim 1.8$ ppm. The other physicochemical characteristics of the esters (I) synthesized agreed completely with those published for these compounds [1].

EXPERIMENTAL

PMR spectra were measured relative to TMS on a Varian DA-60-IL or a Bruker WM-250 spectrometer. GLC was performed on an LKhM-80 instrument (column 3 m × 3 mm with 15% of Carbowax 20M on Chezasorb AW-HMDS).

2-Methylpent-2E-enal (IIIa). Over 15 min, 24 g (0.4 mole) of propionaldehyde was added to 20 ml of a vigorously stirred 1 N aqueous solution of KOH (20 mmoles). After 5 min, the mixture, which had become hot, was cooled to 25°C and was extracted with ether. The combined extract was neutralized with 5% HCl, washed with saturated NaCl solution, and dried with $MgSO_4$. The ether was evaporated off at 150 mm Hg, and the residue was distilled. This gave 13.7 g (70%) of the aldehyde (IIIa) with bp 50°C (30 mm).

Propylidene-tert-butylamine (II). With stirring, 29 g (0.5 mole) of propionaldehyde was added over 20 min to 36.5 g (0.5 mole) of tert-butylamine, and then, at 5°C, K_2CO_3 was added until the separation of water ceased. The organic layer was separated off, dried with K_2CO_3, and distilled. This gave 55 g (97%) of the azomethine (II) with bp 101-103°C.

2,4-Dimethylpent-2E-enal (IIIb). Over 15 min, a solution of 5.05 g (50 mmoles) of diisopropylamine in 6 ml of THF was added at −20°C (Ar) to 50 ml of a 1 N solution of n-butyllithium (50 mmoles) in hexane. The reaction mixture was stirred at ~25°C for 30 min and then at −15°C for 20 min. A solution of 5.65 g (50 mmoles) of the azomethine (II) in 10 ml of THF and, after 40 min, at −70°C, a solution of 3.6 (50 mmoles) of isobutyraldehyde in 5 ml of THF were added to it. The reaction mixture was heated to 25°C over 1 h, and after 15 min 100 ml of 20% H_2SO_4 was added to it at 0°C. The resulting emulsion was stirred vigorously for 40 min, and the aqueous layer was separated off and carefully extracted with ether. The combined extract was washed with saturated aqueous NaCl solution and dried with $MgSO_4$, the solvent was evaporated off at 150 mm Hg, and the residue was distilled. This gave 2.8 g (50%) of the aldehyde (IIIb), bp 45°C (15 mm), n_D^{19} 1.4465. PMR spectrum ($CDCl_3$, δ, ppm): 1.08 d (J = 7 Hz, 6 H, CH_3CH); 1.75 d (J = 1.5 Hz, 3 H, $CH_3C{=}C$); 2.83 m (1 H, $CHCH_3$); 6.25 dq (J = 10 and 1.5 Hz, 1 H, $HC{=}C$); 9.40 s (1 H, CHO).

2-Methylpent-2E-enoyl Chloride (IVa). In one portion, a solution of 0.98 g (10 mmoles) of the aldehyde (IIIa) in 20 ml of MeOH was added to a solution of 3.6 g (20 mmoles) of $AgNO_3$ in 15 ml of H_2O and this was followed, with stirring, over 40 min, by 42 ml of a 1 N aqueous solution of NaOH (42 mmoles). After 3 h, the precipitate was filtered off and was washed with hot water and with ether and this ether was used to extract the aqueous filter, which was then acidified with 20 ml of 10% HCl and was carefully extracted with ether. The combined extract

was dried with $MgSO_4$, the solvent was evaporated off in vacuum, and the residue (~1.1 g) was treated with 2.4 g (20 mmoles) of $SOCl_2$. The mixture obtained was heated at 60°C for 1 h, and then the excess of $SOCl_2$ was evaporated in vacuum, and the residue was distilled. This gave 1.13 g (85%) of the acid chloride (IVa), bp 52°C (11 mm). PMR spectrum (CCl_4, δ, ppm): 1.13 t (J = 7 Hz, 3 H, CH_3CH_2); 1.88 d (J = 1.5 Hz, 3 H, $CH_3C{=}C$); 2.29 quintet (J = 7 Hz, 2 H, CH_2); 7.10 to (J = 7 and 1.5 Hz, 1 H, CH).

2,4-Dimethylpent-2E-enoyl Chloride (IVb). Similarly, 1.68 g (15 mmoles) of the aldehyde (IIIb) in 23 ml of MeOH, 5.1 g (30 mmoles) of $AgNO_3$ in 23 ml of H_2O, 63 ml of a 1 N solution of NaOH (63 mmoles), and 3.57 g (30 mmoles) of $SOCl_2$ gave 1.8 g (82%) of the acid chloride (IVb) with bp 57°C (9 mm), n_D^{20} 1.4645. PMR spectrum ($CDCl_3$, δ, ppm): 1.08 d (J = 7 Hz, 6 H, CH_3CH); 1.90 d (J = 1.5 Hz, 3 H, $CH_3C{=}C$); 2.73 m (1 H, $CHCH_3$); 7.00 dq (J = 10 and 1.5 Hz, 1 H, $HC{=}C$).

1-Methylbutyl 2-Methylpent-2E-enoate (Ia). Over 15 min, a solution of 0.8 g (6 mmoles) of the acid chloride (IVa) in 2 ml of ether was added to a stirred solution of 0.62 g (7 mmoles) of sec-amyl alcohol in 4 ml of pyridine. After 2 h, the reaction mixture was diluted with 10 ml of ether, washed free from pyridine with 5% HCl, washed additionally with a saturated aqueous solution of NaCl, and dried with $MgSO_4$. After the solvent had been driven off *in vacuo* and the residue had been distilled 1.05 g (94%) of the ester (Ia) was obtained with bp 59-60°C (3 mm), n_D^{20} 1.4410. PMR spectrum ($CDCl_3$, δ, ppm): 0.90 t (J = 7 Hz, 3 H, $CH_3CH_2CH_2$); 1.05 t (J = 7.5 Hz, 3 H, $CH_3CC{=}C$); 1.2-1.7 m (4 H, CH_2CH_2); 1.23 d (J = 6.5 Hz, 3 H, CH_3CH); 1.82 br.s (3 H, $CH_3C{=}C$); 2.18 quintet (J = 7.5 Hz, 2 H, $CH_2C{=}C$); 4.96 m (1 H, CHO); 6.72 (br.t (J = 7.5 Hz, 1 H, $HC{=}C$).

1-Methylbutyl 2,4-Dimethylpent-2E-enoate (Ib). Similarly, 1.6 g (10.9 mmoles) of the acid chloride (IVb) and 1.23 g (14 mmoles) of sec-amyl alcohol in 5 ml of pyridine gave 2.05 g (95%) of the ester (Ib) with bp 64-65°C (2 mm), n_D^{20} 1.4405. PMR spectrum ($CDCl_3$, δ, ppm), 0.92 t (J = 7 Hz, 3 H, CH_3CH_2); 1.02 d (J = 6.5 Hz, 6 H, $CH_3CHC{=}C$); 1.25 d (J = 6.5 Hz, 3 H, CH_3CHO); 1.2-1.7 m (4 H, CH_2CH_2); 1.83 d (J = 1.5 Hz, 3 H, $CH_3C{=}C$); 2.63 m (1 H, $CH{=}C$); 4.98 m (1 H, CHO); 6.55 dq (J = 10 and 1.5 Hz, 1 H, $HC{=}C$).

SUMMARY

An effective stereospecific method of synthesizing both components of the pheromone of the lesser grain borer from the readily available propionaldehyde and isobutyraldehyde has been developed.

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