LOW-MOLECULAR-MASS BIOREGULATORS.
II. SYNTHESIS OF METHYL (±)-TETRADECA-2E,4,5-TRIENOATE - THE SEX PHEROMONE OF *Acanthoscelides obtectus*

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A preparative method has been developed for obtaining methyl (±)-tetradeca-2E,4,5-trienoate — the racemate of the sex pheromone of the dried-bean beetle. Using methyl 4-chlorotetradec-5-ynoate as an example, a detailed study has been made of the dependence of the regiochemistry of reduction on the activity of a zinc-copper couple, the methods of its activation, and the acidity of the proton donor.

The dried-bean beetle *Acanthoscelides obtectus* (Bruchidae, Coleoptera) is a pest of various types of beans under natural conditions and in grain stores [1, 2]. It is distributed almost worldwide. In the USSR, the area of distribution includes Transcaucasia, the Black Sea coast of the Caucasus, and Krasnodar territory, Rostov province, and the southern regions of the Ukraine. From an extract of males of the dried-bean beetle possessing attractiveness for females of the species, in 1970 Horler isolated and identified methyl (—)-tetradeca-2E,4,5-trienoate. Later, various approaches to the synthesis of the desired compound were developed which include the construction of the allene block by the reduction of THP ethers of a substituted propargyl alcohol [5, 6], the Claisen orthoester rearrangement [7], and the reduction of secondary propargyl halides [8, 9]. The construction of the E-double bond was performed with the aid of the Wittig reaction [4, 9], by the stereoselective reduction of a chemical bond [5], by the cis-addition of allenyl cuprates to an activated triple bond [10], and by the dehydrogenation of a saturated synthon through the production of an intermediate organoselenium compound and its subsequent oxidation [7]. The absolute configuration of the pheromone was established by the stereoselective synthesis of both of its enantiomers [11, 12].

There is no information in the literature on the comparative activity of the racemic pheromone and its optically active forms under field conditions [12]. It has been reported only that the racemate has an excitatory activity on females of the pest and is presumably a short-distance attractant; however, under laboratory conditions it is inferior in activity to the natural material [13]. It is obvious that the creation of a biopheromone preparation intended for monitoring and the fight against the dried-bean beetle is an urgent problem.

We have developed a preparative method for obtaining the racemate methyl (±)-tetradeca-2E,4,5-trienoate. The synthesis included the use of vinylacetylene as the starting material and was effected by a $C_8 + C_4 + C_2$ scheme. In the first stage, alkylation of the sodium derivative of vinylacetylene with octyl iodide in liquid ammonia was carried out with the production of dodec-1-en-3-yne (I). The latter was lactonized at the double bond in accordance with a procedure developed previously [14], including the interaction of the substrate with acetic acid in the presence of a one-electron oxidant — manganese(III) acetate. The reaction took place in the manner of an oxidative cycloaddition: the α-carboxymethyl radical generated from the addend under the action of an initiator added to the double bonds of the substrate with the subsequent cyclization of the propargyl radical adduct $C_8H_{17}C{\equiv}CCHCH_2CH_2COOH$ through the carbonyl group [15]. The lactonization product — 5-tetradec-5-yn-4-olide (II) — was converted by the subsequent action of thionyl chloride and methanol [16] into the key intermediate — methyl 3-chlorotetradec-5-ynoate (III).*

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*In the preparation of compound (III) a strict observance of the procedure described is necessary, otherwise the formation of considerable amounts of a solvolysis product — methyl 4-methoxytetradec-5-ynoate — is observed.

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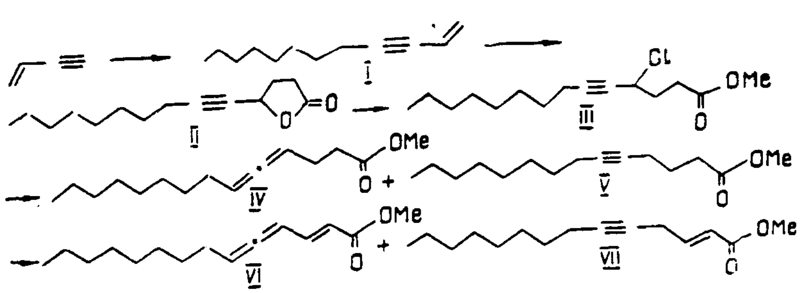

The following stage, according to the selected strategy of synthesis, consisted in the reduction of compound (III) by the zinc—copper couple or by zinc in acetic acid with the aim of obtaining methyl tetradeca-4,5-dienoate (IV). Preliminary experiments had shown that, together with the desired compound (IV), its regio-isomer — methyl tetradeca-5-ynoate (V) — was formed. Analysis of the literature revealed the absence of exhaustive information on the regiochemistry of the reduction of analogous systems [17-23] and, in particular, its dependence of the activity of the zinc—copper couple, the methods of its activation, and the acidity of the proton donor. It must be mentioned that these investigations were carried out by one and the same method [18] in the period 1940-1967, because of which, to establish the structures of the reduction products and their ratio, only IR spectroscopy in combination with chemical methods was used. The main types of structures studied were secondary and tertiary propargyl chlorides containing a terminal triple bond [17-21, 23]. The only example of the reduction of a secondary propargyl chloride with a disubstituted triple bond was described in [22], the authors of which identified the corresponding allene compound as the sole reaction product with the aid of IR spectroscopy.

On the basis of what has been said above, we undertook a systematic study of the dependence of the regiochemistry of the reduction of compound (III) on the above-mentioned parameters of the reaction with the aim of finding the optimum conditions for its transformation into the allenic ester (IV). The ratio of the regio-isomers (IV) and (V) was determined with the aid of GLC in a capillary column by the method of simple normalization, and also from high-resolution PMR spectra by integrating the signals at 5.13 and 1.79 ppm for compounds (IV) and (V), respectively. The results obtained (Table 1) permit the conclusions that: 1) the regiochemistry of the reduction does not depend on the activity of the zinc—copper couple with a change in the ratio of the active components from 20:1 to 60:1 under the conditions of acid activation (experiments 2 and 3); 2) the regiochemistry of reduction is practically independent of the acidity of the medium: a change in the pK_a value of the proton donor from 19 (tert-C_4H_9OH) to 4.7 (CH_3COOH) caused an increase in the yield of desired compound of not more than 5% (experiments 1, 3, and 4); 3) the use of alkaline activation in the preparation of the zinc—copper couple led to some rise in the selectivity of the process (experiments 3 and 5) but at the same time the side reaction of the transesterification of compounds (IV) and (V) with the formation of ethyl tetradeca-4,5-dienoate and ethyl tetradec-5-ynoate in a ratio of 7:30 was observed; and 4) the highest selectivity of reduction was achieved in the absence of added copper using acetic acid as the proton donor (experiment 6).

Thus, for the preparative production of methyl tetradeca-4,5-dienoate (IV) it is most desirable to perform the reduction of compound (III) by the action of zinc in acetic acid. It must be mentioned that compound (IV) has been described previously as a precursor of the sex pheromone of the dried-bean beetle, but the synthesis was carried out in six stages and the overall

TABLE 1. Regiochemistry of the Reduction of Methyl 4-Chlorotetradec-5-ynoate (III)

Expt. No.	Molar ratio		Activation	Proton donor	Time, h	Temp. °C	Conversion, %	Ratio of products, %		Total yield, %
	Zn/Cu	subst./Zn						IV	V	
1	20 : 1	1 : 6	HCl	tert-C_4H_9OH	6	80	8	62	38	—
2	60 : 1	1 : 6	"	C_2H_5OH	4	75	100	63	37	55.7
3	20 : 1	1 : 6	"	C_2H_5OH	4	75	100	63	37	51,6
4	20 : 1	1 : 6	"	CH_3COOH	3	80	100	68	32	54,6
5	20 : 1	1 : 10	KOH	C_2H_5OH	6	75	100	71	29	36,0*
6	100 : 0	1 : 4	—	CH_3COOH	3	80	100	84	16	68,2

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*The total yield of the transesterification products of compounds (IV) and (V) amounted to 17.5%.

yield was only 11% [7]. The method that we propose for obtaining the desired intermediate is preferable since the number of stages is four and the overall yield amounts to 15%.

The purification of the alkenic ester (IV) from the regio-isomer (V) is difficult to perform on the preparative scale. Therefore, the desired mixture of (IV) and (V) in a ratio of 84:16 was used without additional separation operations in the concluding stage of the synthesis, which consisted in the introduction of an E-double bond into the α,β-position with respect to the methoxycarbonyl group. The method includes the metallation of the α-position of the substrate by the action of lithium diisopropylamide, the production of an intermediate selenoester, and its oxidation by sodium periodate [7]. As was expected, together with the main process of the formation of methyl (±)tetradeca-2E,4,5-trienoate (VI), this sequence of reactions also took place for the minor component — the acetylenic ester (V) — leading to methyl tetradec-2E-en-5-ynoate (VII).

It must be mentioned that compound (VII) has been described in the literature as an intermediate in the synthesis of the sex pheromone of the black carpet beetle — tetradeca-3E,5Z-dienoic acid [24]. According to high-resolution PMR, the $C_{(2)}$–$C_{(3)}$ double bonds in (VI) and (VII) have the E-configuration. Their ratio, determined by integrating the signals at 7.18 and 6.1 ppm, respectively, amounted to 74:26. The desired compound (VI), isolated in the individual state with the aid of column chromatography, had spectral characteristics agreeing with those given in the literature [7]. Its overall yield calculated on the dodec-1-en-3-yne (I) amounted to 10%.

The method developed for obtaining the sex pheromone of the dried-bean beetle can also be applied to the stereoselective synthesis of optically active forms of the desired compound by performing the asymmetric reduction of the acetylenic chloride (III) [25, 26].

EXPERIMENTAL

PMR spectra were obtained in $CDCl_3$ on Bruker WM-250 (250 MHz) and Varian VXR-400 (400 MHz) instruments; CSs are given in ppm (δ scale) relative to TMS, and SSCCs in Hz. IR spectra of the pure substances were taken in thin layers in a UR-20 instrument. GLC analysis was performed on a Chrom-5 chromatograph with a glass capillary column (0.25 mm × 50 m) with the stationary liquid phase (SLF) XE-60, the carrier gas being nitrogen. Chromato-mass spectra were obtained on a LKB-2091 instrument with a glass capillary column (0.25 mm × 25 m) containing the SLF SE-30 at an energy of the ionizing electrons of 70 eV. Column chromatography was conducted on the sorbent Silicagel L (Chemapol) with a particle size of 40-100 μm, and TLC analysis on Silufol UV-254 plates with a saturated solution of $KMnO_4$ as revealing agent.

The elementary analyses of all the compounds corresponded to the calculated figures.

Dodec-1-en-3-yne (I) was synthesized from vinylacetylene and octyl iodide [27].

Tetradec-5-yn-4-olide (II) was obtained by the interaction of (I) with acetic anhydride in the presence of manganese (III) acetate [1].

Methyl 4-Chlorotetradec-5-ynoate (III). A mixture of 0.9 g (4 mmoles) of (II) and 1.9 g (16 mmoles) of thionyl chloride was boiled with stirring for 5 h and was cooled to 20°C, after which 20 ml of methanol was added dropwise and the mixture was boiled for another 0.5 h. Then it was diluted with an equal volume of water and was extracted twice with ether. The combined ethereal extracts were washed with H_2O and dried ($MgSO_4$). The ether was evaporated off in a vacuum of 14 mm Hg, and the residue was distilled. This gave 0.78 g (71.6%) of (III) with bp 140-142°C (1 mm), n_D^{20} 1.4660.

TLC analysis: R_f 0.62 [hexane—ether (5:1)]. PMR spectrum(250 MHz): 0.88 (3H, t, CH_3, $J_{CH_3\text{-}CH_2}$ = 6.9), 1.26 (10H, br.s, $5CH_2$), 1.51 (2H, t.t, 8-CH_2, $J_{8\text{-}CH_2\text{-}7\text{-}CH_2(9\text{-}CH_2)}$ = 7.0), 2.22 (2H, t.d, 7-CH_2), 2.24 (2H, q, 3-CH_2, $J_{3\text{-}CH_2\text{-}2\text{-}CH_2(4\text{-}H)}$ = 7.5), 2.59 (2H, t, 2-CH_2), 3.68 (3H, s, $COOCH_3$), 4.67 (1H, t.t, 4-H, $J_{4\text{-}H\text{-}7\text{-}CH_3}$ = 2.0). On homonuclear double resonance with the suppression of the 4-H proton, the signals of the 3-CH_2 and 7-CH_2 methylene groups were completely differentiated and appeared in the form of triplets. IR spectrum (ν_{max}, cm^{-1}): 1740 ($COOCH_3$), 2250 ($C\equiv C$).

Methyltetradeca-4,5-dienoate (IV) and Methyl Tetradec-5-enoate (V). A. Zinc dust (390 mg, 6 mmoles) was washed with 1 ml of 3% HCl solution and with 0.5 ml of H_2O and then, with stirring, a solution of 75 mg (0.3 mmole) of $CuSO_4 \cdot 5H_2O$ (molar ratio Zn/Cu 20:1) in 3.7 ml of H_2O was added in portions and was decanted off. The black precipitate that had formed was washed with 1 ml of H_2O and 2 ml of ethanol, and then with 2 ml of absolute ethanol. In the zinc—copper couple so obtained were added 10 ml of absolute ethanol (pH 7.25) and 270 mg (1 mmole) of (III). The reaction mixture was boiled for 4 h (with monitoring by TLC) and filtered, and the bulk of the solvent was distilled off on the water bath (50°C) in a vacuum of 14 mm, after which the contents of the flask were diluted with H_2O and extracted twice with ether. The combined ethereal extracts were dried ($MgSO_4$), the ether was evaporated off, and the residue was distilled from a rotating flask. This gave 123 mg (51.6%) of a mixture of (IV) and (V).

The reaction was carried out similarly at a Zn/Cu molar ratio of 60:1 and with the use of tert-butanol and acetic acid as the media. The yields and ratios of the products of the reduction of (IV) and (V) are given in Table 1, and their physicochemical constants and spectral characteristics in experiment C.

B. A solution of 86 mg (0.5 mole) of $CuCl_2 \cdot 2H_2O$ in 0.4 ml of H_2O was added to a suspension of 650 mg (10 mmoles) of zinc dust in 1 ml of H_2O heated to the boil (molar ratio 20:1). The resulting precipitate was washed with hot H_2O (2 × 1 ml), and then a solution of 0.91 g of KOH in 5.4 ml of H_2O was added and the mixture was heated at 90°C for 15 min. In this process the precipitate was observed to swell (longer heating led to a loss of activity by the zinc—copper couple). The catalyst obtained was washed with hot H_2O (3 × 3 ml) and then it was suspended in 20 ml of hot absolute ethanol and to this suspension (pH 9.8) was added 270 ml (1 mmole) of (III) dropwise. The reaction mixture was boiled for 6 h and was worked up as described in the preceding experiment.

Distillation yielded 130 mg of a mixture containing, according to the results of chromato-mass spectroscopy [130°C (18 min) → 2°C min → 230°C] 47% of (IV), 19% of (V) [(IV):(V) ratio 71:29; total yield 36%], 24% of ethyl tetradeca-4,5-dienoate [m/z (%): 252 (M^+, 21.5), 207 (10.3), 164 (11.3), 154 (62.1), 126 (11.0), 125 (11.1), 121 (11.6), 112 (12.2), 111 (14.8), 108 (10.6), 107 (14.8), 95 (17.1), 93 (29.7), 91 (10.3), 83 (15.3), 82 (30.4), 81 (100), 80 (98.5), 79 (55.4), 77 (16.6), 69 (16.2), 68 (15.3), 67 (47.1), 57 (12.1), 55 (40.6), 53 (10.4)], and 10% of ethyl tetradec-5-ynoate (ratio 70:30, total yield 17.5%) [m/z (%): 252 (M^+, 14.8), 207 (11.8), 164 (12.8), 154 (62.0), 136 (11.1), 135 (17.6), 125 (13.9), 124 (12.5), 121 (12.6), 112 (12.5), 111 (16.5), 109 (11.2), 107 (19.9), 97 (16.6), 96 (14.9), 95 (17.8), 93 (38.4), 91 (18.1), 88 (20.7), 83 (19.9), 82 (14.2), 81 (86.6), 80 (100), 79 (58.0), 78 (11.8), 77 (17.1), 71 (12.3), 70 (13.4), 68 (10.1), 67 (66.5), 65 (13.9), 61 (26.4), 60 (29.5), 57 (19.9), 55 (59.1), 53 (12.5)].

C. A suspension of 260 mg (4 mmoles) of zinc dust in 10 ml of glacial acetic acid was treated with 270 mg (10 mmoles) of (III) and the mixture was heated at 80°C for 3 h. Then it was filtered and the filtrate was diluted with an equal volume of H_2O again, and was dried ($MgSO_4$). The ether was evaporated off and the residue was distilled from a rotating flask. This gave 162 mg (68.2%) of a mixture of (IV) and (V), T_{bath} = 160-170°C (1 mm). The (IV):(V) ratio according to the results of capillary GLC (T_c = 176°C, T_{evap} = 230°C, T_{FID} = 250°C, P = 1.6 MPa, t_{ret}(IV) = 9 20 , t_{ret}(V) = 9 50) ratio 84:16.

TLC analysis: R_f 0.65 [hexane—ether (5:1), one spot]. PMR spectrum (250 MHz): (IV) 1.96 [2H, m, 3-CH_3 (under the conditions of suppression of the signal of the allene protons at 5.13 ppm, the signal of the group under consideration was converted intro a triplet, $J_{7\text{-}CH_2\text{-}8\text{-}CH_2}$ = 6.9)], 5.13 (2H, five main lines in the form of a quintet, 4-H, 6-H); (V) 1.79 (2H, t.t, 3-CH_2, $J_{3\text{-}CH_2\text{-}2\text{-}CH_2(4\text{-}CH_2)}$ = 7.2), 2.13 (2H, t.t, 7-CH_2, $J_{7\text{-}CH_2\text{-}8\text{-}CH_2}$ = 7.0, $J_{7\text{-}CH_2\text{-}4\text{-}CH_2}$ = 2.3), 2.22 (2H, t.t 4-CH_2); (IV) + (V) 0.88 (6H, t, 2CH_3, $J_{CH_3\text{-}CH_2}$ = 6.5), 1.27 (24H, br.s 12 CH_2), 2.26-2.48 [6H, m, 2-CH_2, 3-CH_2(IV), 2-CH_2(V)], 3.67 (6H, s, 2$COOCH_3$).

IR spectrum (ν_{max}, cm^{-1}): 1735 ($COOCH_3$), 1954 (C=C=C). Chromato-mass spectrum [130° (18 min) → 2°/min → 230°], m/z (%): (IV) 238 (M^+, 12.7), 140 (72.7), 98 (34.0), 97 (22.0), 95 (13.5), 93 (22.2), 84 (11.4), 82 (18.9), 81 (70.1), 80 (100), 79 (49.3), 77 (14.6), 74 (15.1), 67 (38.4), 59 (12.4), 57 (12.9), 55 (26.6), 54 (10.4); (V) 238 (M^+, 6.1), 140 (100), 123 (12.4), 108 (14.7), 107 (18.1), 98 (22.1), 97 (18.6), 95 (22.6), 93 (19.9), 82 (16.7), 81 (68.9), 80 (87.6), 79 (51.7), 77 (14.4), 74 (35.4), 69 (11.4), 67 (35.5), 59 (12.9), 55 (35.8).

Methyl (±)-Tetradeca-2E,4,5-trienoate (VI) and Methyl Tetradec-2E-en-5-ynoate (VII). To 8 ml of an 0.5 M solution of BuLi (4 mmoles) in hexane were added 5 ml of THF freshly distilled over Na and then 0.41 g (4 mmoles) of diisopropylamine. The reaction mixture was cooled to −78°C, and 0.47 g (2 mmoles) of the mixture of (IV) and (V) in 5 ml of THF was added dropwise. Stirring was continued for 30 min, and then 0.65 g (2 mmoles) of PhSeSePh in 5 ml of THF was added dropwise. The reaction mixture was kept at the given temperature for 1 h and was then warmed to 20°C, neutralized with saturated NH_4Cl solution, and extracted with ether.

The ethereal extract was washed with 10% sodium carbonate solution and was dried ($MgSO_4$). The ether was evaporated off in vacuum and the residue was chromatographed on silica gel (15 g) with elution by hexane and then by hexane—ether (9:1). This gave 190 mg of unchanged PhSeSePH and 350 mg (64.0%) of a mixture of isomeric selenoesters (69.5% conversion). The latter were dissolved in 10 ml of THF, and a solution of 0.75 g (3.5 mmoles) of $NaIO_4$ in 4 ml of hot H_2O was added. The reaction mixture was stirred at 20°C for 10 h, diluted with ether, washed with 10% sodium carbonate solution, and dried ($MgSO_4$), and the ether was evaporated off in vacuum. The residue was filtered through a layer of silica gel with petroleum ether as the eluent.

The ratio of (VI) to (VII) obtained by integrating the signals at 7.18 and 6.16 ppm, respectively, amounted to 74:26. PMR spectrum of compound (VII) determined from the spectrum of the mixture of (VI) and (VII): 0.88 (3H, t, CH_3, $J_{CH_3\text{-}CH_2}$ = 6.7), 1.27 (12H, br.s, 6CH_2), 2.19 (2H, t.t, 7-CH_2, $J_{7\text{-}CH_2\text{-}8\text{-}CH_2}$ = 7.0, $J_{7\text{-}CH_2\text{-}4\text{-}CH_2}$ = 2.4), 3.09 [2H, d.d.t (six lines), 4-CH_2, $J_{4\text{-}CH_2 3\text{-}H}$ = 5.0], 3.74 (3H, s, $COOCH_3$), 6.16 (1H, d.t, 2-H, $J_{2\text{-}H\text{-}3\text{-}H}$ = 15.6, $J_{2\text{-}H\text{-}4\text{-}CH_2}$ = 2.0, 6.93 (1H, d.t, 3-H).

The individual compounds were isolated by chromatography on silica gel (25 g) with petroleum ether as eluent. This gave 131 mg (62.4%) of (VI) and 50 mg (23.8%) of (VII). The overall yield of (VI) after two stages was 39.9%. TLC analysis (VI) R_f 0.42, (VII) [R_f 0.38 (hexane—ether (9:1)]. PMR spectrum (400 MHz): (VI) 0.88 (3H, t, CH_3, $J_{CH_3CH_2} = 6.7$), 1.27 (12H, br.s, $6CH_2$), 2.07 (2H, q.d, 7-CH_2, $J_{7\text{-}CH_2\text{-}8\text{-}CH_2(6\text{-}H)} = 7.5$), 3.73 (3H, s, $COOCH_3$), 5.44 (1H, t.d.d.d, 6H), 5.85 (1H, d.d.d, 2-H, $J_{2\text{-}H\text{-}3\text{-}H} = 15.45$, $J_{2\text{-}H\text{-}4\text{-}H} = 1.41$, $J_{2\text{-}H\text{-}6\text{-}H} = 0.71$), 5.85-5.92 (1H, d.d.t.d, $J_{4\text{-}H\text{-}6\text{-}H} = 6.14$, $J_{4\text{-}H\text{-}7\text{-}CH_2} = 2.86$), 7.18 (1H, d.d.d, 3-H, $J_{3\text{-}H\text{-}4\text{-}H} = 10.99$, $J_{3\text{-}H\text{-}6\text{-}H} = 0.97$). IR spectrum ($\nu_{max}$, cm^{-1}, $CDCl_3$): (VI) 1630 (C=C), 1710 ($COOCH_3$), 1945 (C=C=C).

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