CONCLUSION

1. The synthesis of DL-4-amino-2-hydroxy-3,3-dimethylbutanoic acid has been performed, and it has been resolved into its stereoisomers.

2. D-, L-, and DL-N-(4-Amino-2-hydroxy-3,3-dimethylbutyryl)- β -alanines - amino analogs of pantothenic acid - have been obtained by the condensation of the N-hydroxysuccinimide esters of N-BOC-D-, -L-, and -DL-4-amino-2-hydroxy-3,3-dimethylbutanoic acids with β -alanine followed by the elimination of the protective group.

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PHEROMONES OF INSECTS AND THEIR ANALOGS.

V. A NEW APPROACH TO THE SYNTHESIS OF THE SEX PHEROMONES OF INSECTS OF THE ORDER Lepidoptera WHICH IS BASED ON THE SELECTIVE OZONOLYSIS OF 1-METHYLCYCLOOCTA-1Z,5Z-DIENE

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A new synthesis of l-acetoxyalk-Z-enes (sex pheromones of insects of the order *Lepidoptera*) has been developed which is based on the selective ozonolysis of l-methylcycloocta-1Z-5Z-diene — a cooligomer of isoprene and butadiene.

The synthesis of pheromones of *Lepidoptera*, which have the structure of acetates of alk-Z-en-1-ols, is usually performed via acetylene derivatives [1-4]. We have developed a new approach to the synthesis of the sex pheromones of this class which is based on the selective ozonolysis of the readily accessible 1-methylcycloocta-12,52-diene (I) — a cyclic codimer of isoprene and butadiene [5]. For the selective deoxygenation of the resulting non-42-ene-1,8-dione (II) at the keto group, the formyl group must be protected, for example, by reaction with methanol in the presence of ammonium chloride, which leads to 9,9-dimethoxynon-52-en-1,2-one (III) [5].

It has been found, however, that under the conditions of reducing the tosylhydrazone of the keto acetal (III) with sodium cyanotrihydroborate — an effective reducing agent for tosyl hydrazones [6] — the acetal protection is not retained, and instead of 1,1-dimethoxynon-4Z-ene a mixture of (3:5) of non-4Z-ene (IV) and nonane — the products of the reduction of both carbonyl groups and of the double bond — is obtained. The acetal group is retained if the tosyl-hydrazone of the keto acetal (III) is reduced with sodium tetrahydroborate by Caglioti's method [7], but in this case, in addition to the reduction of the keto group, the double bond also undergoes hydrogenation, which leads to a 46% yield of 1,1-dimethoxynonane (V).

The reduction of the keto group to a methylene group leading to the desired non-4Z-en-1ol (IX) [(X) is the acetate] was successfully achieved by the selective transformation of the keto aldehyde (II) into 9-hydroxynon-5Z-en-2-one (VI) [(VII) is the corresponding acetoxy

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derivative and (VIII) the 1-ethoxyethyl ether] by the action of potassium triacetoxyhydroborate [8] followed by the reduction of the tosylhydrazone of the hydroxy ketone (VI). When sodium cyanotrihydroborate or sodium tetrahydroborate was used, nonyl alcohol was the main product (about 65% and 100%, respectively).

If the hydroxy group were converted into an acetal group by the action of ethyl vinyl ether, the subsequent reduction of the tosylhydrazone of compound (VIII) by sodium cyanotrihydroborate led to a mixture of nonan-1-ol and nonen-1-ol (1:1, from the ratio of the intensities of the signals of the CH_2O and CH=CH groups in the PMR spectrum). The selective production of the tosylhydrazone of the hydroxyketone (VI) was successfully effected with the aid of sodium triacetoxyhydroborate. In this case, a mixture (1:2) of the alcohol (IX) and its acetate (X) was formed in 80% yield, and the hydrolysis of this mixture with aqueous ethanolic caustic soda gave the unsaturated alcohol (IX), while acylation gave the corresponding acetate (X). The bromination of the alcohol (IX) by the action of phosphorus tribromide led to 1-bromonon-4Z-ene (XI) — the key starting material for obtaining pheromones of the alk-Z-en-1-ol series and their acetates. The mass spectrum of compound (XI) contains the doublet of the molecular ion that is characteristic for bromides [9] (M⁺ 206 and 204).



 $R = H(v_1, x)$, $Ac(v_1, x)$, $CH(CH_3)OC_2H_5(v_1)$; $n = 3(x_1)$, $5(x_1v)$, $7(x_2v)$.

Scheme 1

The action of the Grignard reagent obtained from the bromide (XI) on the 1-ethoxyethyl ethers of the corresponding ω -bromo alcohols (3-bromopropan-1-ol, 5-bromopentan-1-ol, and 7-bromoheptan-1-ol) followed by acid hydrolysis and acylation led to the acetates of dodec-72-en-1-ol (XIII), tetradec-92-en-ol (XIV), and hexadec-112-en-ol (XV), which are the sex pheromones of the Lepidoptera Trichoplusiani, Spodoptera frugiperda [1], and Scotogramma trifoli [10]. The acetates (XIII)-(XV) were also obtained by the reaction of non-42-en-1-ylmagnesium bromide with bromoalkyl acetates. However, the yield of desired pheromones in this case fell from 60-80% to 40% because of the competing attack of the organomagnesium reagent on the ester group.

It has been reported that a considerable part of non-4Z-en-1-ylmagnesium bromide is consumed in self-condensation, leading to the formation of octadeca-5Z,13Z-diene (XVI). It is more desirable to generate the Grignard reagent from the more readily available w-bromo alcohols. In case of the Grignard reagent it is possible satisfactorily to use the corresponding dialkyllithium cuprate, and in place of the bromide (XI) 1-tosyloxynon-4Z-ene (XII), obtained by the reaction of the alcohol (IX) with tosyl chloride in pyridine solution.



The C₃ and C₅ ω -bromoalkan-l-ol derivatives required for the synthesis of the pheromones (XIII-XV) were obtained from propane-1, 3-diol [11] and tetrahydropyran [12], respectively. 7-Bromoheptan-1-ol (XXI) was synthesized by Scheme 2.

The pyrolysis of cyclooctene (XVII) [13] gave a 95% yield at 35% conversion of octa-1,7diene (XVIII). The selective hydroalumination of the latter with the aid of triisobutylaluminum and oxidation of the organoaluminum compound formed led with an 80% yield to oct-7-en-1-ol (XIX), bromination of which gave 8-bromooct-1-ene (XX). Ozonization of the latter in methanol followed by reduction of the peroxide products of ozonolosis with the aid of sodium tetrahydroborate led to 7-bromoheptan-1-ol (XXI).

EXPERIMENTAL

The PMR spectra of the substances were obtained on a Tesla BS-487B spectrometer with a working frequency of 80 MHz using CCl₄ as solvent, and the chemical shifts are given in the δ -scale relative to the signal of HMDS (internal standard). IR spectra were taken on a UR-20 spectrometer (in a film). GLC analysis was performed on a Chrom-41 instrument with the stationary phase SE-30 (5%) on Chromaton N-AW-DMCS (0.2-0.25 mm) at working temperatures at 50-300°C (14 deg/min) with helium as the carrier gas at the rate of 50 ml/min. The elementary compositions of the compounds obtained correspond to the calculated figures.

8-Oxonon-4Z-en-1-al (II) and its dimethyl acetyl (III) were obtained as described previously [5].

<u>Mixture of Non-4Z-ene (IV) and N-Nonane.</u> A mixture of 1.2 g (8.0 mmole) of the acetal (III), 1.42 g (7.5 mmole) of tosylhydrazine, 0.15 g of p-toluenesulfonic acid, and 5 ml of a mixture (1:1) of dimethylformamide, freshly distilled over calcium hydride, and sulfolane was heated to 100 °C and, in an atmosphere of argon, 1.51 g (24 mmole) of sodium cyanotrihydroborate [14] in 25 ml of a 1:1 mixture of dimethylformamide and sulfolane was added dropwise, and then 10 ml of cyclohexane, redistilled over sodium, was added and the mixture was boiled for 2 h. The cooled reaction mixture was extracted with pentane, and the extract was washed with water and dried over MgSO₄. Evaporation of the solvent yielded 0.3 g (40%) of a mixture [3:5, from the ratio of the intensities of the signals in the 1.95 or 5.3 ppm region (IV) and the 0.2 ppm region $(n-C_9H_{20})$] of non-4Z-ene (IV) and n-nonane.

<u>1,1-Dimethoxynonane (V).</u> A mixture of 2.0 g (10 mmole) of the acetal (III), 3.7 g (20 mmole) of tosylhydrazine, and 80 ml of absolute methanol was boiled for 2 h, and then, at 15-20°C, 3.8 g (100 mmole) of sodium tetrahydroborate was gradually added, after which the resulting mixture was boiled for another 4 h. This gave 1.3 g of a product which by chromatography on alumina with a mixture of heptane and diethyl ether (10:1) yielded 0.9 g (46%) of the acetal (V) with n_D^{20} 1.4310 [15]. IR spectrum, (v, cm⁻¹): 1065 s, 1080 s, 1130 s, 1380 s. PMR spectrum (δ , ppm): t 0.83 (3 H, CH₃, J = 6.5 Hz), m 1.23 (14 H, CH₂), s 3.13 (6 H, OCH₃), t 4.18 (H, OCHO, J = 3.5 Hz). Mass spectrum (m/z): 188 (M⁺).

<u>9-Hydroxynon-5Z-en-2-one (VI)</u>. With stirring (Ar, cooling with ice water), a mixture of 17 ml of glacial acetic acid and 10 ml of benzene was added to a suspension of 3.5 g (6.5 mmole) of potassium tetrahydroborate in 100 ml of absolute benzene, stirring was continued for another 15 min, and then a solution of 5 g (32.5 mmole) of the keto aldehyde (II) in benzene was added dropwise, after which the reaction mixture was stirred at 20°C for 5 h and was left for 12 h. Then 10 ml of water was added, the mixture was stirred for 0.5 h, the benzene was distilled off in vacuum (rotary evaporator). The residue was extracted with diethyl ether (3 × 100 ml), and the ethereal solution was washed with 10% NaHCO₃ and then with saturated NH₄Cl solution and was dried over MgSO₄ and evaporated.

This gave 3.8 g (75%) of the hydroxy ketone (VI) containing 10-15% of 4-methyloct-4Zene-1,8-diol (XXII). IR spectrum (v, cm⁻¹): 730 w, 1070 v.s, 1380, m, 1715 s, 3400 br.s. PMR spectra (δ , ppm): m 1.5 (2 H, C⁸H₂); s 1.61 [CH₃C=C, corresponding to 10-15% of the diol (XXII) as impurity]; s 2.05 (3 H, CH₃CO); m 2.05 (4 H, CH₂C=C); t 2.3 (2 H, CH₂CO, J = 4.5 Hz); t 3.48 (2 H, CH₂O, J = 6 Hz); t 5.25 (2 H, CH=CH, J = 4.5 Hz). The presence of the diol (XXII) as an impurity is due to the fact that the keto aldehyde (II) obtained by the given method [5] contains 10-15% of the product of the ozonolysis of the diene (I) at the disubstituted double bond and was used without purification.

9-Acetoxynon-5Z-en-2-one (VII). A mixture of 5 g of the hydroxy ketone (VI) and 50 ml of a mixture of acetic anhydride and pyridine (2:3) was stirred and was then left at room temperature for 24 h. After this, 50 ml of methylene chloride was added to the reaction mix-

ture and it was washed with 10% HCl and then with 10% NaHCO₃ and with saturated NH₄Cl solution. After drying over MgSO₄, it was evaporated and chromatographed [Al₂O₃, pentane-diethyl ether (1:1)]. This yielded 5.08 g (80%) of the acetate (VII), $C_{11}H_{18}O_3$, $n_D^{2^{\circ}}$ 1.4590. IR spectra (v, cm⁻¹): 740 w, 1045 m, 1250 s, 1370 w, 1660 w, 1715 and 1735 s, 3015 w. PMR spectrum (ppm): m 1.61 (2 H, C⁸H₂); s 1.94 [3 H, CH₃C(0)O]; s 2.02 (3 H, CH₃CO) m 2.1 (4 H, CH₂C=C); t 2.5 (2 H, CH₂CO, J = 4.5 Hz); t 3.92 (2 H, CH₂O, J = 6.5 Hz); t 5.25 (2 H, CH=CH, J = 4.5 Hz). Mass spectrum, m/z (I, %): 198 (M⁺, 0.144), 153(0.19), 152(0.16), 138, (M⁺ - CH₃COOH, -6.88), 110(1.28), 109(1.04), 95(7.52), 80(13.12), 67(7.8), 43(100%).

<u>9-(1-Ethoxyethoxy)non-5Z-en-2-one (VIII)</u>. A mixture of 3.12 g (20 mmole) of the hydroxy ketone (VI), 2.16 g (30 mmole) of ethyl vinyl ether, 0.1 ml of trifluoroacetic acid, and 50 ml of tetrahydrofuran was stirred for 6 h and was then left for 15 h at room temperature. Then 200 ml of diethyl ether was added and the reaction mixture was washed with 10% NaHCO₃ solution, dried over MgSO₄, and evaporated, and the residue was distilled in vacuum. This gave 3.65 g (80%) of the acetal (VIII), $C_{13}H_{24}O_{3}$, bp 115°C (1.5 mm). IR spectrum (ν , cm⁻¹): 730 w, 1070, 1100, 1140 and 1170 s, 1370 m-s, 1715 s. PMR spectrum (ppm): d 1.01 (3 H, CH₃, J = 6 Hz), t 1.2, (3 H, CH₃, J = 6 Hz), t 1.2 (3 H, CH₃, J = 6 Hz), m 1.57 (2 H, C⁸H₂); s 2.0 (3 H, CH₃CO); m 2.0 (4 H, CH₂C=C); m 2.25 (2 H, CH₂CO); m 3.25-3.5 (4 H, CH₂O); q 4.5 (1 H, OCHO, J = 6 Hz); m 5.23 (2 H, CH=CH).

Acetate of Non-4Z-en-1-o1 (X). A mixture of 1.56 g (10 mmole) of the hydroxy ketone ĩ (VI), 2.05 g (11 mmole) of tosylhydrazine, and 50 ml of absolute ethanol was boiled (under argon) for 2 h. Then it was evaporated in vacuum, the residue was treated with 33 ml of glacial acetic acid, and then, at 15-20°C with stirring (under argon), 3.8 g (100 mmole) of sodium tetrahydroborate was added over 1 h and the mixture was stirred for another 1 h at room temperature and for 1.5 h at 70°C. Then 5 ml of water was added, the mixture was stirred for 30 min and evaporated, the residue was poured onto ice and was diluted with diethyl ether and neutralized with KOH, washed with saturated NH4Cl solution, and dried over MgSO4. Evaporation of the solvent left 1_{\circ} 05 g of a mixture (1:2 according to GLC) of the alcohol (IX) and its acetate (X); this was dissolved in 12 ml of a mixture of acetic anhydride and pyridine (2:3), and the solution was kept at room temperature for 24 h and was then diluted with 50 ml of methylene chloride, washed with dilute HC1 and then with 10% NaHCO₃ and saturated NH₄C1 solutions, dried over MgSO4, and evaporated, and, after chromatography [Al2O3, pentane-ether (10:1)], 1.1 g (60%) of the acetate (X) was obtained; $C_{11}H_{20}O_2$, n_D^{20} 1.4368. IR spectrum (v, cm⁻¹): 740 w, 1055 s, 1250 s, 1375 and 1390 m, 1665 w, 1750 s, 3020 w. PMR spectrum (ppm): 0.83 (3 H, CH_3 , J = 7 Hz); m 1.23 (6 H, CH_2); m 1.8-2.0.

A solution of 1.0 g of the acetate (X) in 30 ml of methanol was treated with 5 ml of 1 M aqueous caustic potash solution and the mixture was kept at room temperature for 24 h, neutralized with dilute HCl, and extracted with ether, and the extract was washed with saturated NH₄Cl solution and dried over MgSO₄. Evaporation yielded 0.73 g (54%) of the alcohol (IX) [16].

<u>1-Bromonon-4Z-ene (XI)</u>. A solution of 0.35 g (5 mmole) of phosphorus tribromide in diethyl ether was added dropwise to a solution of 1.42 g (10 mmole) of the alcohol (IX) and 0.08 g (1 mmole) of pyridine in 20 ml of absolute ether at 5°C, and the mixture was stirred at 5°C for another 1 h and was left at room temperature for 12 h. Then 150 ml of diethyl ether was added and it was washed with saturated NaCl solution and dried over Na_2SO_4 . After evaporation, 1.65 g (80%) of the bromide (XI) [16] was obtained.

<u>1-Tosyloxynon-4Z-ene</u> (XII). At 0°C, 12.7 g (66 mole) of p-toluenesulfonyl chloride purified as described by Fieser and Fieser [17] was added in portions to a solution of 8.5 g (60 mmole) of non-4Z-en-1-ol (IX). The mixture was stirred at -5° C for 0.5 h and then at 0°C for 6 h and was poured onto ice and extracted with ethyl ether. The organic layer was washed with 10% HCl and then with cooled 10% NaHCO₃ and was dried over Na₂SO₄ and evaporated. This gave 16.9 g (95%) of the tosylate (XII). IR spectrum (ν , cm⁻¹): 740 m, 1465 m, 1600 m, 1650 w, 3080 w. PMR spectrum (δ , ppm): t 0.85 (3 H, CH₃, J = 7 Hz); m 1.0-1.3 (6 H, CH₂); m 1.85 (4 H, CH₂C=C); s 2.38 (3 H, CH₃-AR); t 3.93 (2 H, CH₂O, J = 6 Hz); m 5.28 (2 H, CH=CH); m 7.35 (2 H, H-Ar); m 7.75 (2 H, H-Ar).

Oct-7-en-ol (XIX). At 80° C with stirring, 15 g of octa-1,8-diene (XVIII) [13] was added to a solution of 9.8 g of triisobutylaluminum in 40 ml of absolute heptane, and then the reaction mixture was kept at 100°C for 6 h, by which time the distillation of isobutylene had ceased; it was then stirred at 80-90°C for another 2 h, after which it was cooled to 30°C 60 ml of diethyl ether was added, and oxidation was carried out with dry air for 2 h and then with oxygen for 3 h; after this the reaction mixture was cooled to 10°C and, with stirring, 60 ml of 10% HCl was added, and after another 0.5 h of stirring the organic layer was separated off, washed twice with saturated NaCl solution, and dried over MgSO₄. Evaporation yielded 14.0 g (80%) of the alcohol (XVII) with bp 64-66°C (7 mm) [18].

<u>1-Bromooct-7-ene (XX).</u> At 10°C with stirring, a solution of 22.6 g of phosphorus tribromide in 20 ml of benzene was added to a solution of 8 g of oct-7-en-1-ol (XIX) in 100 ml of absolute benzene, and then the mixture was heated and was kept at 80°C for 2 h. After cooling, 50 g of ice was added with stirring, and then 50 ml of diethyl ether. The organic layer was washed with 6% Na₂CO₃ solution and then with saturated NaCl solution and was dried over MgSO₄. The residue after evaporation was distilled in vacuum. This gave 9.5 g (80%) of the bromide (XX) with bp 80-83°C (7 mm), n_D^{21} 1.4692 [19]. IR spectrum (v, cm⁻¹): 557 m, 650 m, 730 m, 920 s, 1000 m, 1260 m, 1640 m, 3085 m. PMR spectrum (δ , ppm): m 1.23-1.34 (8 H, CH₂); m 1.53-2.1 (2 H, CH₂C=C); t 3.28 (2 H, CH₂Br, J = 7 Hz); m 4.7-5.0 (4.74, 4.89, 4.95) (2 H CH₂=C); m 5.4-5.8 (1 H, CH=C).

7-Bromoheptan-1-ol (XXI). The ozonization of 3 g (15.7 mmole) of 8-bromooct-1-ene (XX). in 70 ml of methanol was effected by passing a mixture of ozone and oxygen (5 wt. % of O_3) at the rate of 30 liters/h through the solution at -60°C until 0.68 g (15.6 mmole) of ozone has been absorbed. Then the reaction mixture was purged with nitrogen and, with stirring at 25°C, 0.42 g of sodium tetrahydroborate was added in portions, the mixture was kept for 1 h, 3 ml of water containing 0.1 ml of acetic acid was added, and after being stirred for 0.5 h it was evaporated in vacuum. The residue was treated with 60 ml of a mixture of diethyl ether and THF. The organic layer was washed with 10% Na₂CO₃ and saturated NH₄Cl solutions and then with saturated NaCl solution and was dried over Na₂SO₄ and evaporated. This gave 1.8 g (95%) of the hydroxy bromide (IV) bp 100-150°C (2 mm) [20]. IR spectrum (v, cm⁻¹): 557 m, 650 m, 730 m, 1060 s, 1125 m, 1260 m, 3400 br.s. PMR spectrum (δ , ppm): m 1.07-1.4 (10 H, CH₂); t 3.28 (2 H, CH₂Br, J = 7 Hz); t 3.35 (2 H, CH₂-O, J = 7 Hz).

 $\frac{1-\text{Acetoxy-7-bromoheptane.}}{\text{m, 1050 m, 1250 s, 1370 m, 1740 s.}} \text{ pMR spectrum (ω, ppm): m 1.14-1.35 (10 H, CH_2); s} \\ 1.9 (3 H, CH_3CO); t 3.27 (2 H, CH_2Br, J = 7 Hz); t 3.89 (2 H, CH_2O, J = 6 Hz). \end{cases}$

Acetate of Dodec-7Z-3n-1-o1 (XIII). At 10 °C, a solution of the Grignard reagent obtained from 10.5 g of the bromide (XI) and 1.22 g of Mg in 100 ml of absolute THF was added over 1 h to a solution of 8.84 g (40 mmole) of 3-bromo-1-(1-ethoxyethoxy)propane in 10 ml of absolute THF containing 1.6 ml of 0.5 M Li₂CuCl₄ in THF [22] under argon, and the mixture was stirred at 10-15°C for 4 h and was then left at room temperature for 12 h. Then 30 ml of 10% HCl was added, the mixture was stirred for 12 h, 500 ml of diethyl ether was added, and the organic layer was washed with 10% NaHCO₃ solution and then with saturated NaCl solution, dried over Na_2SO_4 , and evaporated. The residue was treated with a mixture of acetic anhydride and pyridine as described above for the acetate (VII). The yield of the acetate (XIII) after chromatography [Al₂O₃, pentane-diethyl ether (1:1)] was 5.7 g (60%), bp 90-92°C (0.1 mm) [23].

<u>Acetate of Tetradec-9Z-ene-1-ol (XIV)</u>. A. At 10°C, a solution of the Grignard reagent obtained from 14.6 g of 5-bromo-1-(1-ethoxyethoxy)pentane and 1.46 g of Mg in 80 ml of THF was added over 1 h to a solution of 8.7 g (42 mmole) of the bromide (IX) in 50 ml of absolute THF containing 1.7 ml of 0.5 m Li₂CuCl₄ in THF [22] under argon, and the mixture was stirred at 10-15° for 3 h and was left at room temperature for 15 h. Then it was worked up as in the preceding experiment. The yield of the acetate (XIV) after chromatography was 8.6 g (80%) bp 102-104°C (0.1 mm) [24].

B. Over 1 h at -10 to -15°C under argon, a solution of the Grignard reagent obtained from 10.5 g of the bromide (XI) and 1.22 g of Mg in 100 ml of absolute THF was added to a solution of 10.66 g (51 mmole) of 1-acetoxy-5-bromopentane in 100 ml of absolute THF containing 2 ml of 0.5 M Li₂CuCl₄ in THF [22] and the mixture was stirred for another 4 h, after which the temperature was raised to that of the room and 500 ml of diethyl ether was added, and it was washed with 50 ml of saturated NH₄Cl solution, dried over Na₂SO₄, and evaporated. The residue was chromatographed [Al₂O₃, pentane-ether (7:3)], giving 5.3 g (40%) of the acetate (XIV) identical (IR, PMR, and mass spectra) with the product obtained in the preceding experiment.

Acetate of Hexadec-11Z-en-1-ol (XV). A. At -70 °C, a solution of the Grignard reagent obtained from 40.9 (170 mmole) of 7-bromo-1-(1-ethoxyethoxy)heptane and 4.1 g (170 mmole) of Mg in 150 ml of absolute THF was added to a solution of 16.9 (57 mmole) of the tosylate (XII)

in 100 ml of absolute THF containing 3 ml of 0.5 M Li2CuCl4 in THF under argon and the mixture was stirred for 3 h, heated to room temperature, and left for 12 h, after which 30 ml of 10% HCl was added and the product was worked up as described above in the preparation of compound (XIII). After chromatography, 9.7 g (80%) of the acetate (XV) was obtained with bp 112-114°C (0.1 mm) [25].

B. With stirring at -15°C a solution of 5.54 g (22.8 mmole) of 7-bromo-1-(1-ethoxyethoxy) heptane in 50 ml of absolute THF (after the turbidity of the solution had disappeared the temperature was kept at -20 °C) was added to 3.19 g (45.6 mmole) of finely cut lithium in 150 ml of absolute diethyl ether under argon, and then the mixture was stirred at -10°C for another 2 h and was added to a suspension of 21.7 g (11.4 mmole) of CuI, purified by the method of Novak et al. [26], in 80 ml of absolute diethyl ether at -25° C, the resulting mixture was stirred for another 0.5 h, and then 40 ml of absolute THF was added; after 10 min a solution of 1.68 g (5.7 mmole) of the tosylate (XII) in 40 ml of absolute THF was gradually added and after two hours' stirring the temperature was raised to -10° C and the mixture was left for 12 h. Then it was treated with 30 ml of 100% HCl and the product was worked up as described above in the preparation of (XIII). After chromatography, 1.3 g (82%) of the acetate (XV), identical (IR, PMR, and mass spectra) with the product of the preceding experiment, was obtained.

CONCLUSION

A new synthesis of 1-acetoxyalk-Z-enes (sex pheromones of insects of the order Lepidoptera) has been developed which is based on the selective ozonolysis of 1-methylcycloocta-12, 5Z-diene - a cooligomer of isoprene and butadiene.

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