INSECT PHEROMONES AND THEIR ANALOGS

I. SYNTHESIS OF THE SEX ATTRACTANT OF THE CODLING MOTH

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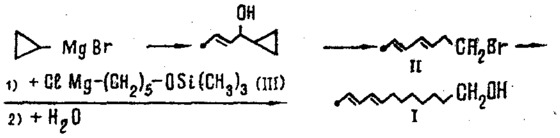
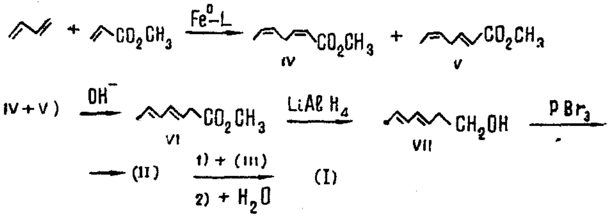
The study of copolymerization reactions of 1,3-dienes with acrylates catalyzed by transition metals is opening up new possibilities for the stereochemical synthesis of unsaturated compounds close in structure to insect sex attractants and juvenoids [1-5]. In the present paper we describe a simple method for the synthesis of the sex attractant of the codling moth Laspeyresia pomonella.

According to Descoins and Henrick [6], the synthesis of the attractant, which has the structure of dodeca-trans-8,trans-10-dien-1-ol (I) is formed by a " 7+5" scheme. Difficultly accessible cyclopropane derivatives are used to obtain the C_7 fragment. The concluding stage of the synthesis consists of the coupling of 1-bromohepta-3,5-diene (II) with the organomagnesium reagent (III), which is readily obtainable from tetrahydropyran. The whole scheme of synthesis appears as follows:



Scheme 1

We have developed a new scheme for the synthesis of the attractant which provides for the synthesis of the C_7 fragment from accessible compounds. As is well known [7, 3], the copolymerization of butadiene with methyl acrylate catalyzed by iron complexes permits the production of mixture of hepta-cis-2,cis-5-dienoic and hepta-cis-2,trans-5-dienoic acids (IV and V). Their isomerization with methanolic alkali or sodium methanolate gave methyl hepta-trans-3,trans-5-dienoate (VI), which was smoothly reduced by $LiAlH_4$ to hepta-trans-3,trans-5-dien-1-ol (VIII). The latter, by treatment with PBr_3 was converted into the bromide (II). To pass to the attractant, we used the condensation of the bromide with compound (III) described by Descoins and Henrick [6]. Thus, the method for the synthesis that we propose is based on the use of accessible initial substances and ensures a fairly high yield of attractant (not less than 60% calculated on the mixture of esters (IV) and (V)):



Scheme 2

EXPERIMENTAL

The methyl esters of hepta-cis-2,cis-5-, -trans-2,cis-5-, and -trans-3,-trans-5-dienoic acids (IV, V, and VI, respectively), and also hepta-trans-3,-trans-5-dieniol (VII) were obtained as described previously [7]. The PMR spectra were recorded on a Tesla BS-480 B instrument (internal standard hexamethyldisiloxane, solvent CCl_4). The IR spectra were recorded on a UR-20 spectrophotometer (film).

1-Bromohepta-trans-3,trans-5-diene (II). A solution of 4.5 g of hepta-trans-3,trans-5-dien-1-ol (VII) in 60 ml of benzene was treated with 3-4 drops of 48% HBr and, with stirring at 10°C, 5.5 g of PBr_3 was added

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over 1 h. The reaction mixture was left overnight at room temperature and was then washed with 10% $NaHCO_3$ solution and with water. The organic layer was dried with Na_2SO_4, the benzene was evaporated off, and the residue was distilled under a reduced pressure of argon. This gave 5.6 g of (II) (yields ~ 80%) with bp 34°C/1 mm, n_D^{20} 1.5200; UV spectrum: $\lambda_{max}^{ethanol}$ 321 nm, ε 1800; IR spectrum (ν, cm^{-1}): 1630, 1665 (C=C–C=C), 975 (trans-CH=CH); PMR spectrum (δ, ppm): 1.68 (CH_3–C=), 5.2-6.3 (CH=CH–CH=CH), 3.20 (–CH_2–Br); m/e 175.

Dodeca-trans-8,trans-10-dienol (I). Over two hours at –5 to 0°C, 4.4 g of 1-bromohepta-trans-3,trans-5-diene (II) was added to a solution of the Grignard reagent $ClMg-(CH_2)_5-OSi(CH_3)_3$ (III) in tetrahydrofuran (prepared from 0.61 g of Mg and 5 g of $Cl-(CH_2)_5-OSi(CH_3)_3$ by a known method [6]) and catalytic amounts of the complex $Li_2[CuCl_4]$ [8]. Then the reaction mixture was left at room temperature for 14-15 h, the precipitate that had deposited was filtered off, the tetrahydrofuran was evaporated off, and, without purification, the residue was boiled in aqueous ethanol for 2 h. After cooling, the product was extracted with ether, the extract was dried with Na_2SO_4, the ether was evaporated off, and the residue was distilled in vacuum. This gave 5.4 g of (I), yield 72%. bp 122°C/0.5 mm, mp 29-30°C (recrystallization from pentane). UV spectrum: $\lambda_{max}^{ethanol}$ 234 nm; IR spectrum (ν, cm^{-1}): 990, 1060, 3380; PMR spectrum (δ, ppm): 1.65 (CH_3–C=), 2.05 (–CH_2–C=), 3.63 (–CH_2–O–), 5.2-6.30 (CH=CH–CH=CH); m/e 182.

SUMMARY

The synthesis of the sex attractant of the codling moth *Laspeyresia pomonella* has been performed using as the initial compounds linear dimers of butadiene with methyl acrylate.

LITERATURE CITED

1. G. A. Tolstikov, U. M. Dzhemilev, and R. I. Khusnutdinov, Izv. Akad. Nauk SSSR, Ser. Khim., 1562 (1975).
2. G. A. Tolstikov, U. M. Dzhemilev, R. I. Khusnutdinov, and L. M. Zelenova, Zh. Org. Khim., 12, No. 2, 315 (1976).
3. H. Singer, U. Wilfried, and D. Manfred, Synthesis, 5, 265 (1971).
4. O. S. Vostrikova, U. M. Dzhemilev, G. A. Tolstikov, and L. M. Zelenova, Izv. Akad. Nauk SSSR, Ser. Khim., 2018 (1975).
5. E. Klein, F. Thömel, M. Struwe, P. Heimbach, and H. Schenkluhn, Ann. Chem., 352 (1976).
6. C. Descoins and C. A. Henrick, Tetrahedron Lett., No. 3, 2999 (1972).
7. G. A. Tolstikov, U. M. Dzhemilev, and R. I. Khusnutdinov, Zh. Obshch. Khim., 45, 1322 (1975).
8. M. Tamura and J. Kochi, J. Am. Chem. Soc., 93, 1485 (1971).