A SIMPLE SYNTHESIS OF HENEICOS-6Z-EN-11-ONE – THE SEX PHEROMONE OF *Orgyia pseudotsugata*

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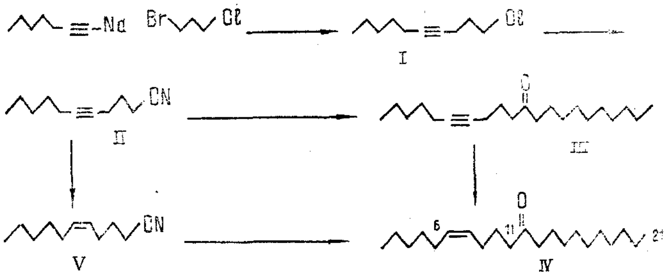
A method is proposed for synthesizing the insect sex pheromone heneicos-6Z-en-11-one and its homolog eicos-6Z-en-11-one.

Two syntheses of heneicos-6Z-en-11-one – the sex pheromone of *Orgyia pseudotsugata* – have been reported previously, starting from 1-chlorodec-4-yne and using the lithium derivatives of hept-1-yne [1] and of 2-decyl-1,3-dithiane [2]. We have obtained this pheromone by the following simpler scheme:



The action of 1-bromo-3-chloropropane on sodioheptyne in liquid NH_3 gave a good yield of 1-chlorodec-4-yne (I). On reaction with NaCN in DMSO solution at 100-110°C the later gave a quantitative yield of 1-cyanodec-4-yne (II) which was converted by two routes into heneicos-6Z-en-11-one (IV). According to the first route, compound (II) was treated with n-$C_{10}H_{21}MgCl$ in ether, followed by acid hydrolysis to give heneicos-6-yn-11-one (III). This acetylenic ketone was hydrogenated quantitatively in hexane at 20 °C over Lindlar catalyst to heneicos-6Z-en-11-one. On the second route, the order of the reactions was the opposite: compound (II) was first hydrogenated to 1-cyanodec-4Z-ene (V) which, on reaction with n-$C_{10}H_{21}MgCl$ in ether followed by hydrolysis was converted into the pheromone (IV). The yield of (IV) reckoned on the hept-1-yne was 45-50%.

The action of n-$C_9H_{19}MgCl$ in ether on 1-cyanodec-4Z-ene followed by hydrolysis gave a homolog of the pheromone (IV) – eicos-6Z-en-11-one.

A determination of the individuality of the pheromone (IV) by the method of Smith et al. [2] showed that it contained more than 98.5% of cis isomer.

EXPERIMENTAL

The purity of the products was determined by GLC in a Tsvet-4- chromatograph using a column 200 × 0.4 cm containing 15% of SE-30 on Celite-545 with helium as the carrier gas.

1-Chlorodec-4-yne (I). At −40°C, 35 g of 1-bromo-3-chloropropane was added to the sodioheptyne prepared from 19.2 g of hept-1-yne and $NaNH_2$ in 250 ml of liquid NH_3, and the mixture was stirred at this temperature for 2 h. Then water was carefully added and the organic layer that separated out was extracted with ether. The ethereal extract was washed with water and with dilute HCl and was dried over $CaCl_2$. Vacuum distillation gave 28 g (82%) of 1-chlorodec-4-yne with bp 95-97°C (10 mm). Found %: C 69.80; H 9.90; Cl 20.53; $C_{10}H_{17}Cl$. Calculated %: C 69.75; H 9.87; Cl 20.60.

1-Cyanodec-4-yne (II). A mixture of 17.2 g of 1-chlorodec-4-yne and 8 g of dry NaCN in 80 ml of DMSO was stirred at 100-110 °C for 5 h. Then it was cooled, diluted with water, and extracted with ether. The ethereal extract was dried over Na_2SO_4. Vacuum distillation yielded 15.5 g (95%) of 1-cyanodec-4-yne with bp 125-126°C (10 mm), n_D^{20} 1.4565. Found %: C 81.65; H 10.41. $C_{11}H_{17}N$. Calculated %: C 81.25; H 10.42.

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1-Cyanodec-4Z-ene (V). A solution of 8.1 g of (II) in 30 ml of hexane was hydrogenated at 20°C by the usual method over Lindlar catalyst [3]. This gave 8 g of (V) with bp 123-124°C (10 mm); n_D^{20} 1.4492. Found %: C 79.28; H 11.40; N 8.97; $C_{11}H_{19}N$. Calculated %: C 79.82; H 11.50; N 8.52.

Heneicos-6-yn-11-one (III). With stirring, 7.2 g of (II) in 15 ml of ether was added to a solution of n-$C_{10}H_{21}MgCl$ (from 12 g of n-$C_{10}H_{21}Cl$ and 3 g of Mg) in 50 ml of ether, and the mixture was boiled for 7 h. When the nitrile was added, a rise in temperature and the formation of a precipitate took place, and on heating the amount of precipitate increased. After cooling, 40 ml of water and then 10 ml of concentrated HCl were added and the mixture was boiled for 2 h. Then it was cooled, and the ethereal solution was separated off, washed with water, and dried over $MgSO_4$. Vacuum distillation gave 9.5 g (68%) of (III), bp 182-184°C (4 mm) of a wax-like substance. IR spectrum (CCl_4): $\nu_{C=O}$ 1718 cm^{-1}.

Heneicos-6Z-en-11-one (IV). A. A solution of 6 g of (III) in 25 ml of hexane was hydrogenated at 20°C by the usual method over Lindlar catalyst [3]. This gave 5.8 g of (IV) with bp 178-180 °C (4 mm); n_D^{20} 1.4567.

B. With stirring, 7.6 g of (V) in 15 ml of ether was added to a solution of n-$C_{10}H_{21}MgCl$ (from 12 g of n-$C_{10}H_{21}Cl$ and 3 g of Mg) in 50 ml of ether. Then a solution of 10 ml of concentrated HCl in 40 ml of water was added in the cold, and the mixture was boiled with stirring for 2.5 h. After the usual working up, 9.2 g (64%) of (IV) was obtained with bp 178-180°C (4 mm); n_D^{20} 1.4567. IR spectrum (CCl_4): $\nu_{C=O}$ 1718 cm^{-1}. According to the literature [2]: bp 150-152°C (0.01 mm); IR spectrum (CCl_4): $\nu_{C=O}$ 1718 cm^{-1}.

Eicos-6Z-en-11-one. With stirring, 3.7 g of (V) in 10 ml of ether was added to a solution of n-$C_9H_{19}MgCl$ (from 6 g of n-$C_9H_{19}Cl$ and 1.5 g of Mg) in 25 ml of ether, and the mixture was boiled for 7 h. After hydrolysis with hydrochloric acid, 4.9 g (75%) of eicos-6Z-en-11-one was obtained with bp 176-178°C (4 mm); n_D^{20} 1.4572. IR spectrum (CCl_4): $\nu_{C=O}$ 1718 cm^{-1}. Found %: C 81.45; H 12.96; $C_{20}H_{38}O$. Calculated %: C 81.56; H 12.96.

SUMMARY

Heneicos-6Z-en-11-one – a sex pheromone of Orgyia pseudotsugata – and its homolog eicos-6Z-11-one have been synthesized from hept-1-yne via 1-chlorodec-5-yne.

LITERATURE CITED

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