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SYNTHESIS OF *CIS* - 7,8 – EPOXY - OCTADECANE, SPECIES - SPECIFIC COMPONENT OF THE SEX PHEROMONE OF NUN MOTH *LYMANTRIA MONACHA* (LEPIDOPTERA, LIMANTRIIDAE)

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ABSTRACT. The synthesis of *cis*-7,8-epoxy-octadecane, species-specific component of the sex pheromone of nun moth *Lymantria monacha* was based on a $C_{10}+C_2=C_{12}$ and $C_{12}+C_6=C_{18}$ coupling scheme, by acetylenic route, starting from 1-bromo-decane. The second coupling reaction took place between di-n-dodecyne mercury and 1-bromo–hexane in a transmetallation reaction.

Keywords: nun moth, *Lymantria monacha*, *cis*-7,8-epoxy-octadecane

Introduction

Nun moth (NM), *Lymantria monacha*, in Europe and gypsy moth (GM) *Lymantria dispar*, in Europe and North America are most important defoliators of coniferous and deciduous forests, respectively.

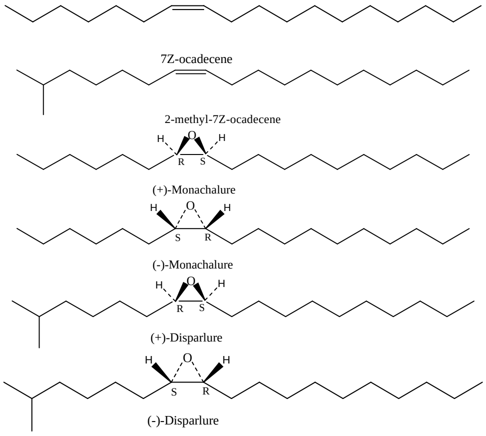

Figure 1

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For sexual communication GM and NM females produce the pheromone disparlure; NM and GM males respond to the (+) - disparlure enantiomer [(7R, 8S)-cis-7,8-epoxy-2- methyloctadecane] as a single attractive but unspecific pheromone component [1-29].

Three epoxies [(-) - disparlure, (+) - and – (-) - monachalure] and two hydrocarbon volatile components [2- methyl- Z7- octadecene and Z7-octadecene] [30] synergistically prevented cross-attraction of coseasonal GM males and imparted specificity to NM sexual communication. Fig.1

In the literature are not mentioned the synthesis of cis-7,8-epoxy-octadecane, species-specific component of the sex pheromone of nun moth *Lymantria monacha.*

The paper presents a route for the synthesis of *cis*-7,8-epoxy-octadecane.

Results and Discussion

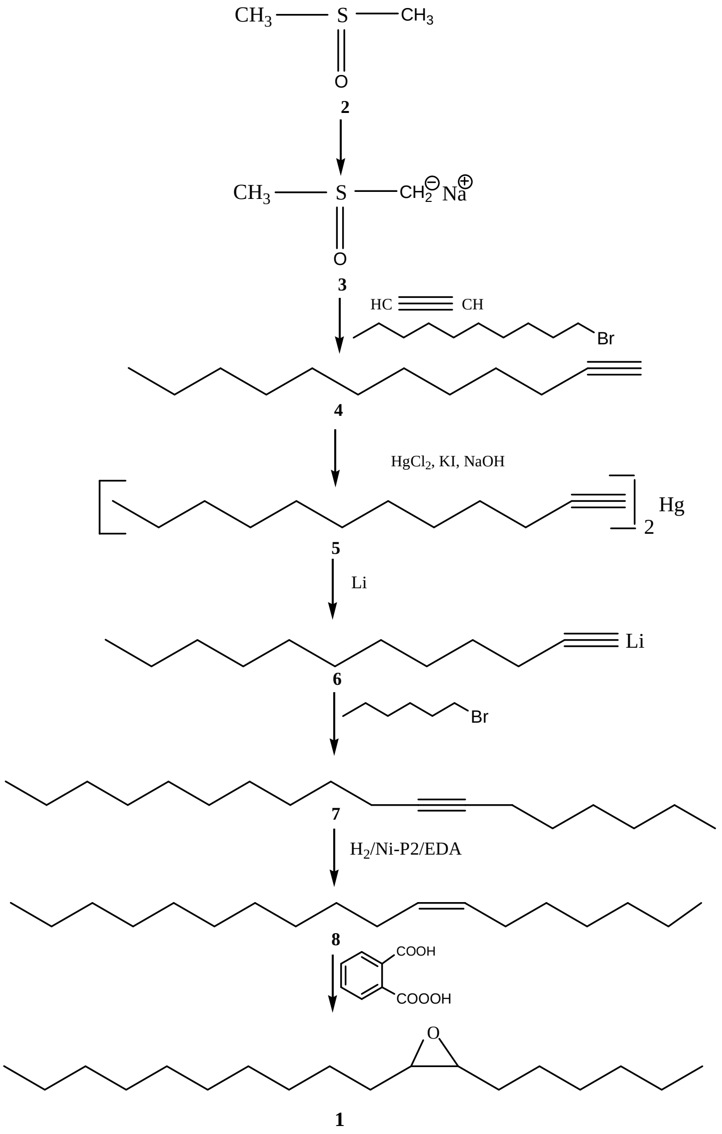
For the synthesis of *cis*-7,8-epoxy-octadecane (1) we explored the pathway outlined in Scheme 1, based on a $C_{10}+C_2=C_{12}$ and $C_{12}+C_6=C_{18}$ coupling scheme, by acetylenic route, starting from 1-bromo-decane.

In our variant, the first coupling reaction was effected in order to obtain 1-dodecyne (4) by adding 1-bromo-decane to monosodate acetylene, obtained in situ from acetylene in DMSO with sodium hydride. 1-Dodecyne (4) with mercuric chloride in an aqueous solution containing potassium iodide and sodium hydroxide (Nessler's reagent [31]) was quantitatively precipitated as di-n-dodecynyl mercury (5).

The key step in our acetylenic route consisted in transmetallation of di-n-dodecynyl mercury (5), which was directly lithiated by heating with lithium metal in diglyme and then alkylated with 1-bromo-hexane obtaining 7-octadecyne (7).

Z-7-Octadecene (8) was prepared from 7-octadecyne (7) by hydrogenation using Ni-P2/EDA catalyst, obtained by reducing nickel acetate with sodium borohydride and subsequent poisoning with ethylenediamine [32]. Using NiP-2 catalyst, the hydrogenation takes place quantitatively and with a very high degree of stereoselectivity.

To prepare *cis*-7,8-epoxy-octadecane (1) the olefine 8 was epoxidated with monoperphtalic acid.



Scheme 1

Experimental

GC-MS analyses were performed on a Hewlett Packard GL-MSD 5890-5972 instrument, using a HP-5MS 30mX0.25mmX0.25µm capillary columm.

A Perkin Elmer Spectrometer Model 700 was used for IR spectra.

1-Dodecyne (4)

Aparatus: 1L reactor provided with a thermometer dipping into the liquid, a dropping funnel, a stirrer and a 20-30 cm long tube for preventing any splasting out of the reaction mixture.

All operations took place in inert atmosphere and under vigorous stirring.

4,41g (92 mmoles) of natrium hydride were added to 56 mL of dry DMSO. The temperature was risen up to 65^0-68^0. The conversion was finished when no more hydrogen was evolved.

Acetylene (freed from acetone) was introduced for 15 min. at a rate of about 2L/min with external cooling in order to moderate the reaction.

During this process the temperature is maintained between 20^0 and 30^0C.

28 mL of DMSO were added and afferwards, between 20^0-30^0, 8,17 g (37 mmoles) of 1-bromo-decane with external cooling.

The reaction was led to completion by stirring for 3 hours at room temperature. The reaction mixture was poured into 100 mL of ice-water and extracted with four portions of 100 mL petroleum ether.

The combined extract were washed with brine and dried over $MgSO_4$. A satisfactory purity could be achieved by vacuum distillation collecting the fraction at 92^0-94^0C/28 mmHg; yield: 6,14g (79%)

IR spectrum (film, cm^{-1}): 2160 s (-C≡C), 3280 vs (≡CH).

Mass spectrum (m/z; %): 151(<1), 137(<1), 123(1), 109(10), 95(40), 81(100), 67(77), 55(53), 41(85), 29(37).

Di-n-dodecynyl mercury (5)

18,4 g (110 mmoles) of 1-dodecyne (4) dissolved in 500 mL ethanol was added to a vigorous stirred solution of Nessler's reagent prepared according to the standard procedure [31].

The product 5 was obtained in yield of 93%, m.p.= 86^0-87^0.

7-Octadecyne (7)

16,33 g (30 mmoles) of di-n-dodecynyl mercury (5) in 84 mL diglyme was treated with 0,44 g of lithium under inert atmosphere at 100-110^0 for 2 hours.

11g (66 mmoles) of 1-bromo-hexane was added dropwise then the temperature raised to 120^0-130^0 under stirring for 6 hours. The mixture was left overnight, decanted, diluted with water and extracted with ethyl ether. The ethereal solution was washed to neutral and dried over $MgSO_4$.

After the removal of the solvent 12,1g (75%) of 7 were obtained, GC purity: 92%.

Mass spectrum (m/z; %): 250(<1), 235(<1), 221(<1), 207(<1), 180(1), 165(4), 152(2), 123(12), 109(29.9), 95(44.5), 81(53), 55(76.04), 67(54), 40(100), 29(24).

Z-7- Octadecene (8)

7-Octadecyne (7) was hydrogenated at Z-7-octadecene (8) in the presence of the NiP2/EDA catalyst, prepared in situ according to the standard procedure [32]. Z-7-octadecene (8) was obtained in yield of 93% , GC purity: 95%.

Mass spectrum (m/z, %): 252(10), 224(1), 196(<1), 182(<1), 168(1), 158(1.9), 125(11), 111(31.2), 97(59.8), 83(65.5), 69(73.4), 55(100), 41(99.5), 29(44.9).

Z-7,8-Epoxy-octadecane (1)

7,56g (30 mmoles) of Z-7-octadecene (8) was trated with 68 mL of ethereal solution of monoperphtalic acid (1 mL containing 93 mg of peracid) and kept at room temperature for 24 hours. The mixture was then filtered, the Synthesis of *cis* - 7,8 - epoxY- octadecane filtrate washed successively with 10% $NaHCO_3$, diluted NaOH and water. After drying over $MgSO_4$, the solvent was removed and the residium was **1**. Yield: 95%, GC purity: 95%.

Mass spectrum (m/z, %): M=268(<1), 252(<1), 225(<1), 211(<1), 197(<1), 183(12), 152(2.5), 141(<1), 127(15), 97(55.9), 83(40.9), 69(59), 55(100), 41(84), 29(45.5).

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