

A NOVEL STEREOSPECIFIC SYNTHESIS OF MUSCALURE,
THE SEX PHEROMONE OF HOUSE FLY (MUSCA DOMESTICA)

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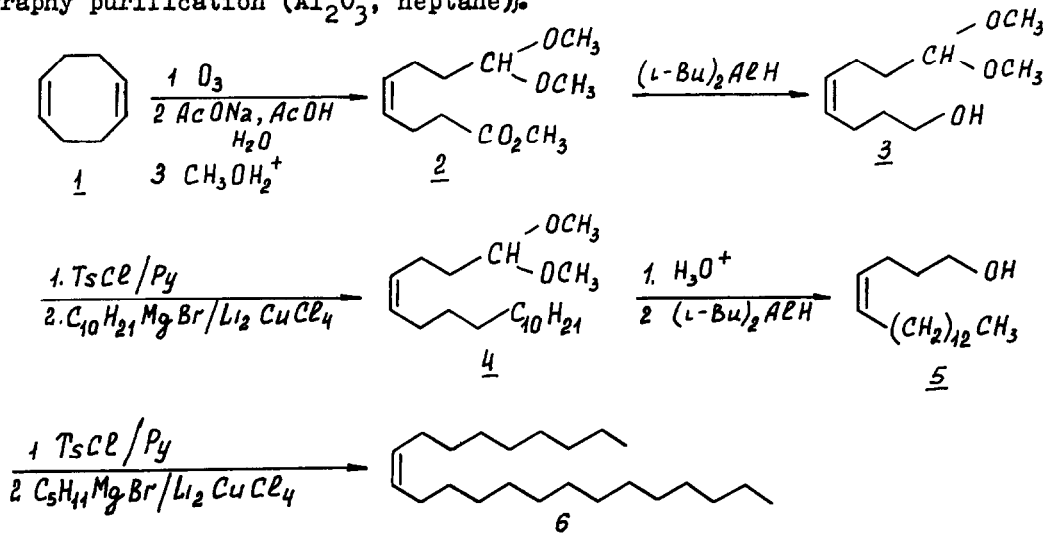
Abstracts. Partial ozonolysis of 1Z,5Z-cyclooctadiene followed by selective transformations of ester and acetal groups in methyl ester of 8,8-dimethoxy-4Z-octen-1-oic acid, and by a two step elongation of carbon chain of the latter by means of tosyloxy groups replacement under action of decyl- and pentyl magnesium bromides leads to muscalure - the sex pheromone of house fly.

Muscalure has the structure of 9Z-tricosene¹. A series of muscalure syntheses is known based on transformations of acetylene², oleic acid³, and olefins disproportionation⁴.

We have developed a novel approach to stereospecific synthesis of this pheromone based on partial ozonolysis of 1Z,5Z-cyclooctadiene (1)⁵ which furnished 8-oxo-4Z-octen-1-oic acid⁶. Treatment of the latter with mixture methanol/TsOH (100:0.5) at ambient temperature for 10 h gave methyl ester of 8,8-dimethoxy-4Z-octen-1-oic acid (2)⁷, n_D^{20} 1.4462, yield being 90% on diene (1). Reduction of compound (2) with diisobutyl aluminium hydride in mixture toluene/THF (1:1) at -10°C yielded 1,1-dimethoxy-8-hydroxy-4Z-octene (3)⁷ (98%) identified in the form of acetate (n_D^{20} 1.4430). The alcohol (3) has been converted to a corresponding tosylate by action of equimolar amount of tosyl chloride in pyridine at -10°C for 15 h. The tosylate has been introduced in interaction with 3 mol equiv. of decyl magnesium bromide and 0.5 mol equiv. of Li_2CuCl_4 ⁸ (solvent - ether/THF, 1:1, Ar, 2h at -78°C). The resulting mixture after column chromatography on alumina (hexane/ether, 20:1) gave 75% of 1,1-dimethoxy-4Z-octadecene (4), n_D^{20} 1.4430. Hydrolysis of acetal (4) in mixture of acetone and 5% aq. HCl (4:1, 25°C, 4h) and subsequent reduction of the aldehyde formed by action of 2.4 mol equiv. of diisobutyl aluminium hydride

in toluene/ether (1:1) (-10°C, 1.5 h; 25°C, 15h) gave 95% of 14Z-octadecene-1-ol (5)⁷ converted in the corresponding acetate ⁷ for identification.

Action of 3 mol equiv. of pentyl magnesium bromide and 0.5 mol equiv. of Li_2CuCl_4 ⁸ upon tosylate (5) in ether/THF (1:1, Ar, 2 h at -78°C) gave 9Z-tricosene⁷ - the sex pheromone of house fly (yield 95% after column chromatography purification (Al_2O_3 , heptane)).



Thus a novel stereospecific synthesis of muscalure has been developed, the total yield being 55% on the starting butadiene dimer.

REFERENCES AND FOOTNOTES

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