PREPARATION OF PHEROMONE COMPONENTS BY COMETATHESIS REACTIONS IN THE PRESENCE OF $MoCl_5/SiO_2-R_4Sn$ CATALYST

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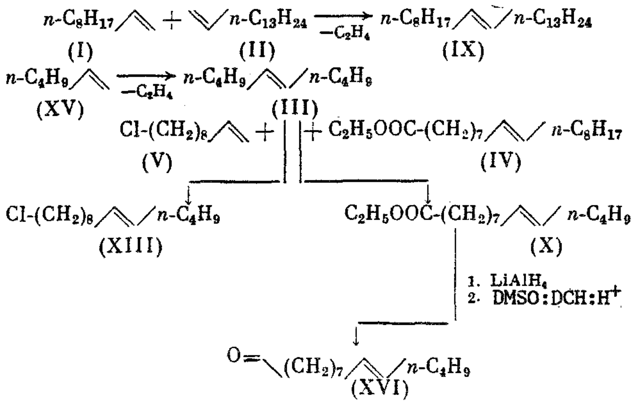
Cometathesis of olefins and their derivatives represents a promising approach to the synthesis of a variety of naturally occurring 1,5-dienes, terpenoids, fragrance components, and pheromones [1-6]. Syntheses have recently been reported of cis-9-tricosene, and housefly pheromone *(Musca Domestica)* [7, 8], cis-9-tetradecenal, the cotton moth (cutworm) *(Heliothis armigera)* [3, 9], and a mixture of geometric isomers of 9-tetradecenal, in the ratio cis/trans = 5/95, which is the pheromone of the leaf roller moth caterpillar, which is the pest which consumes spruce buds *(Choristoneura fumiferana)* [3, 10].

We have previously proposed a heterogeneous catalyst derived from $MoCl_5/SiO_2$ and Group IVB metal compounds [11], which is active in the metathesis of higher α-olefins and cometathesis involving alkenyl halides and unsaturated esters. It was therefore possible to use this catalyst for the synthesis of mixtures of cis and trans isomers of unsaturated long-chain structures, which are incorporated as components of various insects of their precursors.

Scheme 1



In Table 1 we have summarized the results of typical metathesis experiments, which reveal that it is possible to achieve satisfactory yields of desired products in a wide variety of cases. It is clear from the data reported in the Table that, just as has been described in the literature for many different catalytic systems [5, 12], cometathesis reactions involving functionalized olefin derivatives require harsher conditions and proceed at lower rates and smaller turnover numbers, than metathesis reactions involving simple olefins. This is probably due to interaction of the polar functional groups in these olefins with the active sites on the catalyst [12], as well as due to the presence of difficult-to-remove impurities, which act as catalyst poisons.

Compounds (IX), (XIII), and (X) were isolated from the catalysates as a mixture of geometric isomers, in the ratio cis/trans = 16-18/84-82. It should be noted that the stereoselectivity of this reaction is practically independent of the substrate structure or reaction temperature. It is apparent from Scheme 1 that (XVI) can be prepared either from 10-chlorodec-1-ene (V) or from ethyl oleate (IV), although the latter would appear to be the more promising approach, based on the ready availability of ethyl oleate compared to (V).

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TABLE 1. Metathesis and Cometathesis of 1-Decane (I), 1-Pentadecene (II), 5-Decene (III), Ethyl Oleate (IV), and 10-Chlorodec-1-ene (V) on $MoCl_5/SiO_2$–SnR_4*

Experiment No.	Substrates	Final products	T, °C	Ratio of (total substrate): molybdenum, mole/mole	Time	Conversion, wt. %	Selectivity, wt. %	Yield, mole %
1	1-Decene (I)	9-Octadecene (VI) Ethylene (VII)	20	420 : 1	8 min	68	90	60(VI)
2	1-Pentadecene (II)	14-Octacosene (VIII), (VII)	50	400 : 1	6 min	60	92	53(VIII)
3	(I) + (II)	9-Tricosene (IX), (VI), (VIII)	50	380 : 1	7 min	65	90	25(IX)
4	(I) + (II)	(IX), (VI), (VIII)	50	500 : 1	10 min	68(I) 90(II)	90	79(IX)
5	5-Decene (III) + Ethyl Oleate (IV)	Ethyl 9-Tetradecenoate (X), 5-Tetradecene (XI), and Diethyl 9-Octadecene-1,18-dioate (XII)	50	110 : 1	4 h	10	85	6(X)
6	(III) + (IV)	(X), (XI), (XII)	90	110 : 1	4 h	90	90	71(X)
7	(III) + (IV)	(X), (XI), (XII)	90	110 : 1	40 min	86	70	46(X)
8	(III) + (IV) **	(X), (XI), (XII)	90	110 : 1	1 h	90	40	22(X)
9	(III) + 10-Chloro-dec-1-ene (V)	1-Chloro-9-tetradecene (XIII), 1,18-Di-chloro-9-octadecene (XIV), 1-Hexene (XV)	90	110 : 1	4 h	92	90	93(XIII)

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*Either Me_4Sn or Et_4Sn (Experiment 7) were used as cocatalysts, at a Mo:R_4Sn ratio of 1:4 mole/mole.

**In this case the ethyl oleate sample came from the Khar'kov plant "Khimreacktiv"; in all other cases the oleate was prepared from olive oil.

EXPERIMENTAL

GLC analyses were carried out on an LKhM-8MD chromatograph equipped with FID and an ITs-26 integrator (25 m × 0.16 mm column filled with SE-30, with Ar as the carrier gas). PMR spectra were recorded on a Bruker WP-200 spectrometer (200.13 MHz) using 5% sample solutions in CCl_4, relative to TMS. IR spectra were recorded on a Specord IR-75 spectrophotometer, using thin sample films. Mass spectra were measured on an LKV-2091 spectrometer (at an ionization energy of 70 or 12 eV). Reaction products were isolated by fractional distillation or by preparative chromatography on a Pye Unicam chromatograph (2 m × 8 mm column filled with 10% SE-30). Ratios of cis and trans isomers were determined based on the results of IR, PMR, and GLC analyses. The error involved in these determinations of cis/trans ratios using PMR or GLC analysis was 2%. The starting materials were dried over Na, CaH_2, 5A molecular sieves, under an Ar atmosphere. The products (I), (II), (IV), and (XV) consisted of pure grade reagents.

Ethyl Oleate (IV). Prepared from olive oil according to [13]; from 300 g olive oil (0.34 mole) in a mixture with ethanol (500 ml, 8 moles), saponification with 20% KOH solution (56 g, 1 mole) at 50-70°C. After neutralization and crystallization of the precipitate at −60°C (acetone) and 10°C (ethanol) the yield of oleic acid was 60 g, bp 232°C (15 mm Hg), n_D^{20} 1.4580. Esterification of 42.7 g (0.15 mole) with ethanol (78.9 g, 1.6 mole) in the presence of concentrated H_2SO_4 at 80°C gave 33 g (70%) (IV), bp 150-155°C (1 mm Hg), n_D^{20} 1.4520, purity 92%.

10-Chlorodec-1-ene (V). Prepared in analogy with [14], by reaction of Mg (12 g, 0.5 mole) in THF at −20°C with α,ω-bromochloroheptane (107 g, 0.5 mole) and subsequent treatment of the Grignard reagent with allyl bromide (60.5 g, 0.5 mole) in THF at 20°C. Fractional distillation of the residue gave 90 g (51%) of (V), bp 65-70°C (3 mm Hg), n_D^{20} 1.4518, purity 96%.

5-Decene (III). To 0.5 g $MoCl_5/SiO_2$, prepared according to the method described in [7], at 50°C under Ar was added with stirring 5 ml of 1-hexene, containing 100 µl of dissolved Me_4Sn. The ethylene which was evolved was collected in a gas buret. The catalystate was separated from the catalyst and subjected to fractional distillation, which gave (III) in 99.6% purity [bp 170°C (760 mm Hg)] and in a cis/trans ratio of 16/84. Metathesis and cometathesis reactions involving (I) and (II), or (III) and (IV), or (III) and (V) were carried out in an analogous manner.

9-Tricosene (IX). Prepared by cometathesis of (I) and (II) in an analogous manner (Table 1); isolated by fractional distillation [bp 210°C (1 mm Hg), n_D 1.4528] in 97% purity. PMR spectrum (δ, ppm): 0.85 m (6H, $2CH_3$), 1.25 br s (34H, $17CH_2$), 1.90 br s (4H, $2CH_2{-}\overset{|}{C}{=}$), 5.52 m (2H, 2CH), cis-CH (16%) 5.50, trans-CH (84%) 5.54.

Mass spectrum (m/z, I, %): M 322 (13), 140 (9), 126 (23), 102 (30), 98 (53), 83 (80), 69 (69), 57 (92), 58 (76), 43 (100), 41 (69). IR spectrum: trans-CH 970 cm^{-1}; cis-CH 730 cm^{-1}.

Ethyl 9-Tetradecenoate (X) (mixture of cis/trans isomers 18/82). Prepared by cometathesis of (III) and (IV); isolated by preparative chromatography, purity 96%. PMR spectrum (δ, ppm; J, Hz): 0.85 m (3H, CH_3), 1.25 m (15H, 3H, CH_3, 12H, $6CH_2$), 1.60 m (2H, $CH_2{-}C$), 1.90 br s (4H, $2CH_2{-}\overset{|}{C}{=}$), 2.15 t (2H, $CH_2{-}\overset{|}{C}{=}$, J = 7.0), 4.05 q (2H, $CH_2{-}O$, J = 7.1), 5.30 m (2H, 2CH=), cis-CH (18%) 5.27, trans-CH (82%) 5.31. Mass spectrum, 12 eV (m/z, I, %): M 254 (91), 208 (100), 167 (31), 124 (21), 111 (16), 110 (17), 98 (28), 97 (26), 96 (34), 88 (19), 84 (31), 83 (18). IR spectrum: trans-CH 950 cm^{-1}; cis-CH 710 cm^{-1}.

1-Chloro-9-tetradecene (XIII) (mixture of cis/trans isomers, 16/84). Prepared by cometathesis of (III) and (V); isolated by fractional distillation, bp 100°C (1 mm Hg), purity 98%. PMR spectrum (δ, ppm; J, Hz): 0.85 m (3H, CH_3), 1.25 m (14H, $7CH_2$), 1.71 m (2H, $CH_2{-}\overset{|}{\underset{|}{C}}Cl$), 1.90 s br (4H, $2CH_2{-}\overset{|}{C}{=}$), 3.41 t (2H, CH_2, J = 6.5), 5.27 m (2H, 2CH=), cis-CH (16%) 5.26, trans-CH (84%) 5.30. Mass spectrum (m/z, I, %): M 232 (36), 23 (10), 97 (18), 83 (29), 69 (42), 55 (100).

9-Tetradecenal (XVI) (mixture of cis/trans isomers, 18/82). Prepared according to [15, 16] by reduction of (X) (0.2 g, 0.79 mmole) with $LiAlH_4$ (0.045 g, 1.2 mmole) in ether. After evaporation of the ether solvent the residue was oxidized with DMSO and dicyclohexylcarbodiimide (DCH) (0.16 g, 0.79 mmole) in the presence of pyridinium trifluoroacetate (0.019 g, 0.079 mmole). After washing and solvent removal the yield of (XVI) was 0.1 g (60%), 90% purity. PMR spectrum (δ, ppm): 0.85 m (3H, CH_3), 1.25-2.65 m (20H, $10CH_2$), 5.30 m (2H, 2CH), 9.70 t (1H, CHO). Mass spectrum (m/z, I, %): M 210 (3), 193 (1), 181 (1), 166 (3), 149 (5), 135 (5), 126 (12), 98 (20), 83 (29), 69 (32), 55 (100), 41 (86).

CONCLUSIONS

1. The cometathesis of long-chain olefins and their functionalized derivatives has been carried out on a heterogeneous Mo catalyst, to give mixtures of geometric isomers of 9-tricosene and 9-tetradecenal, with cis/trans ratios of 16-18/84-82.

2. The rates of these cometathesis rections decrease in the transition from simple olefins to their functionalized derivatives.

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