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A Wittig Route to (Z)-13-Eicosen-10-one, the Pheromone of the Peach Fruit Moth, and Its Biological Activity Test

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(Z)-13-Eicosen-10-one, an active component of the sex pheromene of the peach fruit moth was synthesized from 4-oxo-tridecan-1-al and heptylidenetriphenylphosphonium ylide by Wittig reaction. The key intermediate, 4-oxo-tridecan-1-al, was synthesized by three different methods. The biological activity test of the synthetic pheromone as attractant for the male peach fruit moth was tested at several districts in Korea.

Introduction

(Z)-13-Eicosen-10-one, an active component of sex pheromone of the peach fruit moth, *Carposina niponensis* Walsingham, a major economic pest of apple, peach and other fruits was isolated by Tamaki[1] in 1977. Structurally, while most lepidopterous pheromones were characterized as unsaturated alcohols, acetates, or aldehydes of 12-, 14-, 16-, or 18-carbon chain length, the sex pheromone of the peach fruit moth is an exceptional unsaturated aliphatic ketone. Several syntheses of (Z)-13-eicosen-10-one have been reported[2]. In 1982, Yoshida[2e] reported the synthesis of (Z)-13-eicosen-10-one via salt-free Wittig reaction of heptylidenetriphenylphosphonium ylide and 4-oxo-tridecan-1-al(2). 4-Oxo-tridecan-1-al(2) was prepared from 1-(p-tolylsulfonyl) nonane and methyl 4,4-dimethoxybutanoate. Recently, 4-oxo-tridecan-1-al(2) was synthesized by Hernandez[2g] by addition of n-nonyllithium to γ-butyrolactone followed by PCC oxidation of the resulting alcohol in his synthesis of (Z)-13-eicosen-10-one(1). In 1981, Naoshima[2c] reported a synthesis of (Z)-13-eicosen-10-one[1] *via* the Wittig olefination of 4-oxo-tridecan-1-al(2) with heptylidenetriphenylphosphonium ylide in toluene in the presence of 12-crown-4-ether. In this report, 4-oxo-tridecan-1-al(2) was prepared from diethyl 2-oxo-glutarate in five steps.

Institute of Agricultural Sciences in Suwon, Korea needed a fair amount of the pheromone of the peach fruit moth to conduct field test experiments in Korea. We therefore undertook to develop some practical mothods for the synthesis of the pheromone of the peach fruit moth.

We wish to report a practical synthesis of (Z)-13-eicosen-10-one(1) via the Wittig olefination of 4-oxo-tridecan-1-al (2) with heptylidene-triphenylphosphonium ylide. The key intermediate, 4-oxo-tridecan-1-al(2) was prepared by three different synthetic mothods. Also we wish to report the results of the biological activity test as attractant for males of the peach fruit moth.

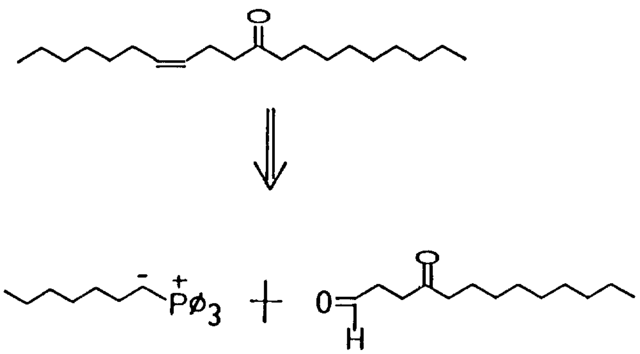
Results and Discussion

It has been well established that the Wittig reaction when carried out between aliphatic aldehyde and aliphatic non-stabilized triphenylphosphonium ylide in salt-free, nonpolar solvent or in polar aprotic solvents such as DMF, DMSO or HMPA gives Z-alkenes stereoselectively[3]. It has been known that only aldehyde reacts with phosphonium ylide in the presence of ketone[4]. A simple retrosynthetic analysis (Scheme 1) reveals that 4-oxo-tridecan-1-al(2) is the key intermediate.

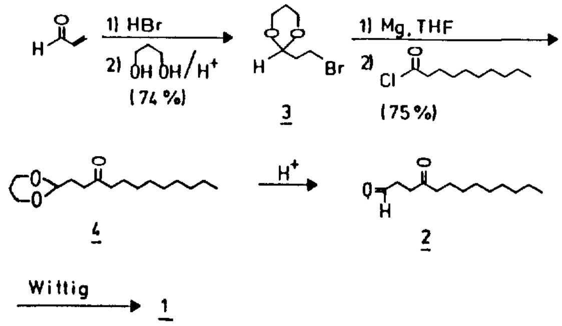
We have prepared 4-oxo-tridecan-1-al(2), the key intermediate by three different methods and synthesized the pheromone of the peach fruit moth by olefination reaction of 4-oxo-tridecan-1-al(2).

(*1*) *Grignard Route.* 4-Oxo-tridecan-1-al(2) was prepared from commercially available acrolein and decanoyl chloride (Scheme 2).

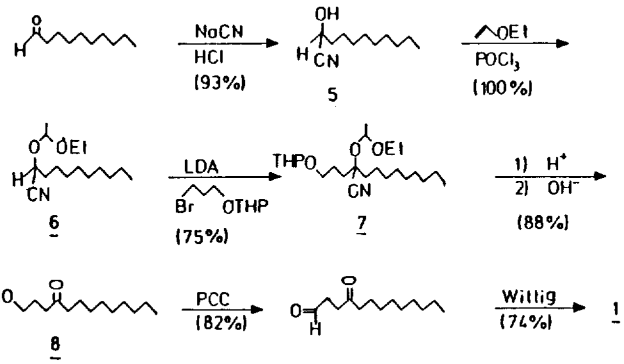
1,4-Addition of HBr to acrolein, followed by protection of the aldehyde portion with 1,3-propanediol afforded 2-(2-bromoethyl)-1,3-dioxane(3)[5]. Grignard reagent[6] from 2-(2-bromoethyl)-1,3-dioxane and Mg in THF was added to



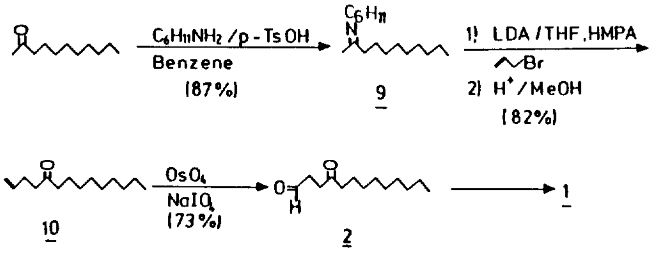
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

decanoyl chloride at dry ice temperature (−78 °C) gave 2-(3-oxodecanyl)-1,3-dioxane(4) with no more than a trace of tertiary alcohol. Deprotection of the ketone acetal(4) with oxalic acid and water gave 4-oxo-tridecan-1-al(2), which was converted to (Z)-13-eicosen-10-one(1).

(*2*) *Umpolung Route.* The key intermediate(2) could also be prepared from 1-decanal using alkylation reaction of the protected cyanohydrin by Umpolung (Scheme 3).

Decylcyanohydrin(5) from 1-decanal and HCN was allowed with ethyl vinyl ether under the catalysis of $POCl_3$, ethoxyethyl ether was afforded[7]. The carbanion of protected cyanohydrin generated by reacting with LDA in HMPA/THF was alkylated with 3-bromopropanol THF ether to produce the fully protected diol cyanide(7). Sequential treatment with acid (H_2SO_4/MeOH) and with base(0.5 *N* NaOH) gave 4-oxo-tridecan-1-ol(8), which was oxidized with PCC[8] to afford 4-oxo-tridecan-1-al(2).

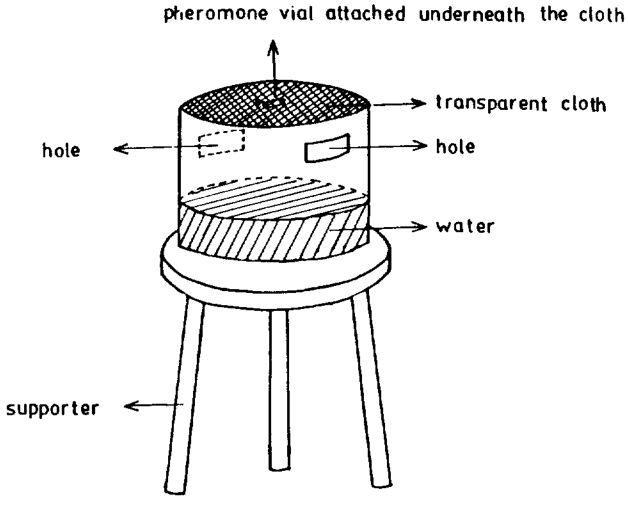


Figure 1. Water trap.

(*3*) *Imine Route.* The ketoaldehyde(2) was prepared from commercially available undecan2-one (Scheme 4).

2-Undecanone cyclohexylimine(9) was obtained by refluxing a solution of 2-undecanone, cyclohexylamine, and *p*-TsOH in dry benzene while trapping water with Dean-Stark water separator. The carbanion of 2-undecanone cyclohexylimine(9), generated upon treatment of the imine with 1 eqiv. of LDA was selectively alkylated at less hindered carbon with allyl bromide in HMPA/THF followed by acidic hydrolysis to give the keto olefin(10)[9]. The $OsO_4/NaIO_4$ cleavage of the keto olefin afforded 4-oxo-tridecan-1-al(2).

The above synthetic methods described were considered to be convenient and economic. Especially, Grignard route involves routine reaction conditions which are amenable to large-scale preparations.

Biological Activity

The biological activity test of the synthetic pheromone as attractant for the male peach fruit moth was conducted in 1983 at the Horticultural Experiment Station in Suwon, Korea. In this test, 18 pheromone vials at a concentration of 3 mg per polyethylene capsule were tested on 107 consecultive nights from June 1 to September 15 using water traps with covers (Figure 1). A total of 1873 male moths were caught in 18 traps (Table 1). Most of the male peach fruit moth were caught from June 26 to July 5 and from August 6 to August 31. From the above results, the synthetic pheromone was tested as active from males of the peach fruit moth.

The biological activity test of the synthetic pheromone as attractant for the male peach fruit moth was conducted in 1984 at several districts of Korea. From the Table 2, it could be concluded that the numbers of moths trapped were proportional to the percentage of the fruits damaged. In Suwon, Yesan, Naju, and Jinju, a total of 134, 11, 28, 453 male moths were

TABLE 1: The Attractant Effect of the Males of the Peach Fruit Moth for the Synthetic Pheromone

Date	The numbers of males which were caught in 18 traps																		Total
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
6. 1-6. 5	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1
6. 6-6.10	0	0	3	0	0	0	0	0	1	1	0	1	2	2	0	0	1	1	12
6.11-6.15	4	2	2	3	1	1	0	0	0	1	4	1	3	5	3	2	1	3	36
6.16-6.20	0	3	0	1	3	1	0	0	1	1	0	0	4	7	2	0	2	2	27
6.21-6.25	3	0	0	0	1	0	2	1	1	3	1	0	4	6	6	0	3	4	35
6.26-6.30	3	3	5	1	1	1	1	1	2	3	5	2	12	19	13	4	6	10	92
7. -7. 5	15	6	3	3	6	6	3	2	2	4	2	1	9	13	16	3	0	2	96
7. 6-7.10	3	0	4	3	1	1	2	1	2	0	9	0	9	13	2	1	3	10	64
7.11-7.15	5	1	2	0	2	3	0	0	2	1	2	0	11	10	8	4	3	10	64
7.16-7.20	2	0	2	3	2	2	0	0	1	0	4	0	2	5	5	0	3	5	36
7.21-7.25	10	5	16	3	1	11	4	3	2	0	3	2	4	8	3	5	5	6	91
7.26-7.31	22	2	5	4	1	1	3	1	2	4	4	0	3	5	2	1	2	13	75
8. 1-8. 5	11	13	1	6	4	11	12	0	6	2	2	4	12	3	3	0	1	5	96
8. 6-8.10	16	7	12	15	6	14	11	5	17	7	15	2	14	21	18	6	17	13	216
8.16-8.20	44	4	11	9	6	19	22	1	12	0	20	5	52	60	10	9	33	19	336
8.21-8.25	32	8	3	6	2	7	15	2	1	4	4	6	22	22	5	4	14	5	162
8.26-8.31	19	1	5	1	1	12	13	1	11	5	18	2	10	11	3	3	8	14	138
9. 1-9. 5	7	9	11	6	6	6	6	0	0	2	4	4	7	9	0	0	15	10	102
9. 6-9.10	6	0	1	3	0	2	0	0	3	0	1	1	6	0	1	0	4	0	28
9.11-9.15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	1	0	0	3
Total																			1873

caught, respectively. In Chungju and Daegu, no male moth of the peach fruit moth was caught. This synthetic pheromone could be used not only as mass trapping of the peach fruit moth, but also as a tool for the forcasting the population of the peach fruit moth. After preliminary trapping of the male moths using this synthetic pheromone, pesticides can be appled to control the peach fruit moth in the field.

Experimental

Infrared spectra were recorded with Shimadzu IR-440 Spectrophotometer. Proton NMR were taken on a BRUKER WP 80 SY 80MHz NMR Spectrophotometer, using tetramethylsilane as an internal reference. All solvents and liquids were distilled before use.

2-(2-Bromoethyl)-1,3-dioxane (**3**). Bromine (9.81ml) was added dropwise to dry tetralin (3.01g) and swirled at room temperature from time to ensure a continuous evolution of hydrogen bromide. An excess of hydrogen bromide was bubbled into a solution of acrolein (2.00g) in dichloromethane (11.0ml) at room temperature. 1,3-Propandiol (2.71g) and *p*-toluenesulfonic acid hydrate (0.036g) were added to the crude 3-bromopropanal and the reaction mixture was stirred at room temperature for 8hr. The resulting solution was neutrallized with saturated sodium hydrogen carbonate, and washed with water. The organic layer was dried over anhydrous potassium carbonate, concentrated and the residual product was distilled in vacuo to afford 2-(2-bromoethyl)-1,3-dioxane (**2**) (5.08g, 74%): bp 68-70°C (3.0mmHg); IRcm^{-1}: 2950, 2850, 1140, 570; NMRδ: 1.30 (*m* lH), 2.10 (*m*, 3H), 3.36 (*t*, 2H), 3.90(*m*, 4H), 4.57 (*t*, 1H).

2-(3-Oxodecanyl)-1,3-dioxane (**4**). To a solution of thionyl chloride (1.43g) in dry benzene (1.0ml) was added decanoic acid (1.72g) in dry benzene (5.0ml). The reaction mixture was heated at reflux for 7h. The volatiles were evaporated and the residue was distilled on Kugelrohr (1.52g, 80%): bp 110-140°C (25mmHg); IR cm^{-1}: 2930, 2850, 1710, 1465; NMRδ: 0.90 (t, 3H), 1.10-1.90 (*m*, 14H), 2.86 (*t*, 2H).

To the magnesium turnings (0.13g) with catalytic amount of iodine in dry THF (4.0ml) under nitrogen atomsphere was added 2-(2-bromoethyl)-1,3-dioxane (**3**) (0.78g) in dry THF (1.0ml). The reaction mixture was heated at reflux until the magnesium turnings were dissolved. After cooling to room temperature, the solution was drawn up into a syringe, leaving the excess magnesium behind. At −78°C, the Grignard reagent solution prepared was added dropwise to a solution of decanoyl chloride (0.64g) in dry THF (4.0ml), and warmed to room temperature over 55min. The reaction mixture was quenched with ammonium chloride solution and then evaporated under reduced pressure. The residue was extracted with ether, washed with water and saturated sodium chloride solution. The organic layer was dried over anhydrous potassium carbonate and concentrated in vacuo. The residue was passed through a short column of silica gel eluting with 10% ethyl acetate in cyclohexane to afford 2-(3-oxodecanyl)-1,3-dioxane (**4**) (0.68g, 75%); IRcm^{-1}: 2900, 2850, 2710, 1140: NMRδ: 0.80∼2.20 (*m*, 21H), 2.50 (*m*, 4H), 2.90 (*m*, 4H), 4.55 (*t*, 1H).

4-Oxo-tridecan-1-al (**2**). To a 2-(3-oxodecanyl)-1,3-dioxane (0.12g) was added oxalic acid (0.067g) and water (2.0ml). The reaction mixture was vigorously heated at reflux for 6h. After cooling, the organic layer was extracted with ether, washed

TABLE 2: The Attractant Effect of the Males of the Peach Fruit Moth for the Synthetic Pheromone

Date	The numbers of males which were caught					
	Suwon	Chungju	Yesan	Naju	Daegu	Jinju
6. 1-6. 8	5	0	6	12	0	71
6. 9-6.15	4	0	2	7	0	84
6.16-6.22	2	0	1	5	0	57
6.23-6.29	5	0	0	2	0	53
6.30-7. 6	7	0	0	2	0	62
7. 7-7.13	5	0	2	0	0	53
7.14-7.20	0	0	0	0	0	16
7.21-7.27	33	0	0	0	0	36
7.28-8. 3	73	0	0	0	0	21
Total	134	0	11	28	0	453
Fruit	Apple Pear Peach	Apple	Apple Peach	Pear Peach	Apple	Peach
Fruit damaged (%)	64	0.0	0.0	0.0	0.5	90

In Suwon, two water traps were used, in the other districts, a stickly trap was used.

with water, aqueous sodium bicarbonate, and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated in cacuo. The residual oil was passed through a short column of silicagel using benzene-hexane (5:5) as eluent to give 4-oxo-tridecan-1-al (2) (0.074 g, 77 %); IR cm^{-1}: 2750, 1720, 1710; NMRδ: 0.90-1.85 (overlapping *m*'s, 17H), 2.40 (*m*, 9.80 (*s*, 1H).

Decylcyanohydrin (**5**). To a solution of decylaldehyde (5.28 g) in ether (10.0 m*l*) and water (16.5 m*l*) was added sodium cyanide (5.94 g). To the reaction mixture in an ice bath was slowly added concentrated hydrochloric acid (10.3 m*l*) over 1h. After the ice bath was removed, the reaction mixture was stirred at room temperature for 2h. The organic layer was extracted with ether and washed with 6*N* hydrochloric acid solution, water and saturated sodium chloride solution. The organic solution was dried over anhydrous magnesium sulfate and concentrated in vacuo to give decylcyanohydrin (**5**) (5.76 g, 93 %); IR cm^{-1}: 3450, 2930, 2225, 1450, 1025; NMRδ: 0.95 (3H), 1.10-1.95 (16H), 4.00 (1H), 4.35-4.60 (1H).

1-Cyano-decan-1-ol, Ethoxy Ethyl Ether (**6**). To the decylcyanohydrin (**5**) (1.84 g) was added ethyl vinyl ether (2.4 m*l*) under the catalytic amount of $POCl_3$. The reaction mixture was stirred at room temperature for 4h and neutralized with potassium carbonate (1.00 g). To the reaction mixture was added water (10.0 m*l*), extracted with ether, washed with water, saturated potasium carbonate solution, and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford 1-cyano-decan-1-ol, ethoxy ethyl ether (**6**) (2.50 g, 99 %); IR cm^{-1}: 2925, 2230, 1450, 1025; NMRδ: 0.90 (3H), 1.10-1.19 (22H), 3.30-3.85 (2H), 4.15-4.60 (1H), 4.75-5.15 (1H).

4-Cyano-1.4-tridecanediol, 1-THP ETHER, 4-Ethoxyethyl ether (**7**). The lithium diisopropylamide was obtained by reacting disopropylamine (0.50 m*l*) in dry THF (2.0 m*l*) with 1.6*M* solution of *n*-butyllithium (2.50 m*l*) in hexane. To this solution was added 1-cyano-decan-1-ol, ethoxy ethyl ether (**6**) (0.85 g) in dry HMPA (1.0 m*l*), and stirred for 10 min, and then added 3-bromo-propan-1-ol THP ether (0.74 g) in dry THF (1.5 m*l*). The solution was stirred at −70 °C for 1h, warmed to room temperature, and stirred for 1h. THF was evaporated and the residue was extracted with ether, washed with water, and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo, and distilled on Kugelrohr to give 4-cyano-1.4-tridecanediol, 1-THP ether, 4-ethoxy ethylether (**7**), (0.99 g, 75 %): bp 200 °C (30 mmHg); IR CM^{-1}; 2920, 2230, 1020; NMRδ: 0.85-0.95 (3H), 1.10-2.50 (32H), 3.20-4.15(6H), 4.50-4.75 (1H), 4.85-5.30 (1H).

4-Oxo-tridencan-1-01 (**8**). To a solution of 4-cyano-1.4-tridencan ediol, 1-THP ether, 4-ethoxyethyl ether (**7**) (0.920 g) in methanol (25.0 m*l*) was added 5 % sulfuric acid (2.50 m*l*). The reaction mixture was stirred at 65 °C for 3h. After evaporation of the methanol, 0.5*N* sodium hydroxide solution was added to the residue. The reaction mixture was heated at reflux for 1h, extracted with ther, and washed with 6*N* hydrocholoric acid solutioon, water and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford 4-oxotridecan-1-ol (**8**) (0.40g, 80%); IR cm^{-1}: 3300, 2925, 1715, 1450, 1025; NMRδ: 0.90 (3H), 1.10-2.10 (16H), 2.25-2.75 (4H), 3.32 (1H), 3.50-3.80 (2H).

4-Oxo-tridecan-1-al (**2**). To a stirred solution of pyridinium chlorochromate (0.48 g) in dry dichloromethane (4.0 m*l*) was added in one portion, 4-oxo-tridecan-1-ol (**8**) (0.43 g) in dry dichloromethane (1.0 m*l*). The reaction mixture was stirred at room temperature for 3h. The reaction mixture was dissolved in ether and washed thoroughly from the black gum. Ether and dry dichloromethane were evaporated and the residue was extracted with ether and the extract was washed with saturated sodium bicarbonate solution, water and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo to give 4-oxo-tridencan-1-al (*2*) (0.32 g, 82 %): IR cm^{-1}; 2930, 2750, 1720, 1710, 1450; NMRδ: 0.90 (3H), 1.10-1.85 (14H), 2.20-2.65 (6H), 9.80 (1H).

(Z)-13-Eicosen-10one (**1**). To a suspension of hepthyltriphenylphosphonium bromide (0.45 g) in dry toluene (2.0 m*l*) 12-crown-4-ether (0.030 m*l*), 1.6*M* solution of *n*-butyllithium (1.00 m*l*) in hexane were added at room temperature under N_2. The reaction mixture was heated for 1h at 80-100 °C with stirring. The mixture was cooled to −35 °C to the mixture was slowly added a solution of 4-oxo-tridencan-1-al (0.19 g) in dry toluene (1.0 m*l*) and mixture was stirred at −35-30°C for 30min, at −5-0°C for 1h and at 10 °C overnight. The reaction mixture was evaporated in vacuo, and the residue was extracted with *n*-hexane, washed with dilute hydrochloric acid and saturated sodium chloride. The organic layer was dried over anhydrous magnesium sulfate and distilled off in vacuo to give a yellow viscous oil, which was purified by column chromatography with hexane-benzene (7:3) as eluent to afford pure (Z)-13-elcosen-10-one (**1**) (0.25 g, 74 %); IR

cm^{-1}: 2960, 1715, 1450; NMRδ: 0.90 (6H), 1.15-1.50 (22H), 1.80-2.50 (8H), 5.20-5.50 (2H).

2-Undecan-1-one Cyclohexylimine (**9**). To a solution of 2-undecan-1-one (5.10 g) in dry bonzene (50.0ml) was added cyclohexylamine (4.95 g) and *p*-toluenesulfonic acid (20.0 mg). The reaction mixture heated at reflux for 3 days until the water (0.9 ml) was traped by the Dean-Stark apparatus. Benezene was evaporated and the crude ketimine was extracted with ether, washed with water and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo to afford 2-undecan-1-one, cyclohexylimine (**9**) (6.42 g, 87 %); IR cm^{-1}: 1680, 1620, NMRδ: 0.90 (3H), 1.10-1.65 (28H), 1,80 (3H), 2.15 (2H), 2.85 (1H).

1-Tetradecen-5-one (**10**). At -78 °C, to a solution of dry THF (5.0 ml) and *n*-butyllithium (0.67 ml) was added isopropylamine (1.54 ml). To this LDA solution was slowly added 2-undecan-1-one cyclohexylimine (**9**) (2.51 g) in HMPA (2.5 ml). The reaction mixture was stirred for 30 min and then added allyl bromide (1.20 g) in THF (1.2 ml). The reaction mixture was stirred at -78 °C for 2 h. It was warmed to room temperature and stirred for 1 h. The solution was evaporated under reduced pressure. The residue was extracted with ether, washed with water and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo to give 1-tetradecen-5-one, cyclohexylimine (3.39 g, 82 %); IR cm^{-1}: 1695, 1640; NMRδ: 0.90 (3H), 1.15-1.80 (24H), 4.78-5.15 (2H), 5.45-6.12 (1H), 3.00 (1H).

To a solution of 1-tetradecen-5-one, cyclohexylimine (0.22 g) in methanol (15 ml) was added hydrochloric acid (0.25 ml). The reaction mixture was heated at reflux for 3 h. Methanol was evaporated and the residue was extracted with ether and the extract was washed with 5 % sodium bicarbonate solution and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford 1-tetradecen-5-one (**10**) (0.17 g, 80 %); IR cm^{-1}: 1710, 1640, NMRδ: 0.90 (3H), 1.10-1.75 (14H), 2.35 (6H), 4.78-5.15 (2H), 5.45-6.12 (1H).

4-Oxo-tridecan-1-al (**2**). To a solution of THF (2.0 ml) and water (0.5 ml) was added 1-tetradecen-5-one (**10**) (0.10 g), and stirred at 0 °C for 15 min. To this solution was added dropwise osmiumtetraoxide (3.30 mg) in water (1.0 ml) under N_2. After cooling was continued for an additional 30min at 5 °C, finly powdered sodium metaperiodate (0.26 g) was added to the solution over an hour little by little and stirred for additional 4 h at room temperature. Sodium iodate was filtered off and the residual solution was extracted with ether and washed with a saturated aqueous solution of sodium sulfite, a saturated aqueous solution of sodium hydrogen carbonate, brine. The organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residual oil was passed through a short column of silica gel using benzene-hexane (5:5) as eluent to give 4-oxo-tridecan-1-al(**2**). (0.075 g, 73 %); IR cm^{-1}: 1720, 1710; NMRδ: 0.90 (3H), 1.10-1.85 (14H), 2.20-2.65 (6H), 9.80 (1H).

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