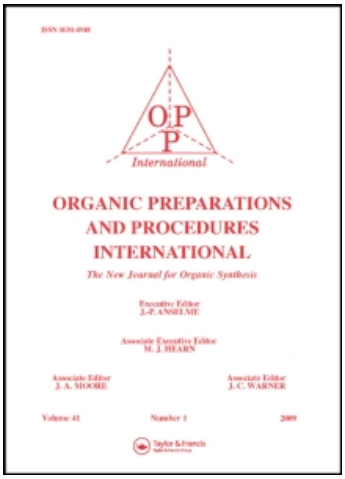

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A SIMPLE AND SHORT SYNTHESIS OF (Z)-13-EICOSEN-10-ONE, THE SEX PHEROMONE OF THE PEACH FRUIT MOTH

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To cite this Article Kang, Suk-Ku and Lee, Dong-Ha(1990) 'A SIMPLE AND SHORT SYNTHESIS OF (Z)-13-EICOSEN-10-ONE, THE SEX PHEROMONE OF THE PEACH FRUIT MOTH', Organic Preparations and Procedures International, 22: 1, 122 — 123
To link to this Article: DOI: 10.1080/00304949009356683
URL: http://dx.doi.org/10.1080/00304949009356683

A SIMPLE AND SHORT SYNTHESIS OF (Z)-13-EICOSEN-10-ONE, THE SEX PHEROMONE OF THE PEACH FRUIT MOTH

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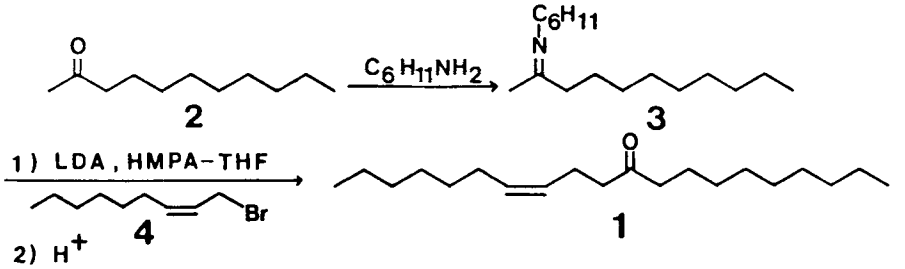
As a part of a program for improving the synthesis of insect sex pheromones, we have undertaken to synthesize the sex pheromone of the peach fruit moth, Carposina niponensis Walsingham, a major economic pest of apple, peach and other fruits in Japan[1] and Korea,[2] which was identified as (Z)-13-eicosen-10-one (1) and (Z)-12-nonadecen-9-one in the ratio of 20:1.[3] A number of syntheses of this pheromone have been reported,[4] many of which involved multi-step preparative strategies. We now report herein a short and simple synthesis of the aforementioned pheromone from 2-undecanone N-cyclohexylimine (3) which is easily obtained[5] in 87% yield by refluxing a solution of 2-undecanone (2), cyclohexylamine and p-toluenesulfonic acid in dry benzene using a Dean-Stark water separator.



The metalloenamine of N-cyclohexylketimine (3),[6] formed by regiospecific deprotonation of 3 with 3.0 equivalents of LDA in THF-HMPA, was monoalkylated at the less hindered carbon with (Z)-1-bromo-2-nonene (4)[7] followed by work-up to afford (Z)-13-eicosen-10-one (1) as the only isolated product in 73% yield. It was identical in all respects (TLC, IR, NMR, MS) with the compound reported in the literature.

EXPERIMENTAL SECTION

(Z)-13-Eicosen-10-one (1).- To a solution of dry THF (25 ml) and n-butyllithium (9.80 ml, 1.55 M in hexane) at -78°, was added diisopropylamine (1.52 ml, 15 mmol). To this LDA solution was slowly added 2-undecan-1-one cyclohexylimine (3) (1.20 g, 5.0 mmol) in HMPA (10 ml). The reaction mixture was stirred for 1 hr and then (Z)-1-bromo-2-nonene (1.00 g, 5.0 mmol) in HMPA (10 ml) was added. The reaction mixture was stirred at -78° for 2 hrs and then warmed to room temperature and stirred for 2 hrs. 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. The crude product was separated by column chromatography (silica gel, eluent: hexanes-ethyl acetate 7:1, $R_f \sim 0.64$) to afford pure (Z)-13-eicosen-10-one (1) (1.34 g, 73%). IR (neat): 3050, 1725, 1140, 1090, 730 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, 6H), 1.12-1.78 (m, 22H), 1.85-2.21 (m, 2H), 2.21-2.58 (m, 6H) 5.36 (m, 2H); ^{13}C NMR: 14.07, 21.81, 22.66, 23.91, 27.23, 28.99, 29.29, 29.45, 29.65, 31.80, 31.89, 42.68, 42.97, 127.86, 131.22, 210.74; MS (m/e): 294 (M^+, 11), 223 (9), 195 (9), 167 (9), 156 (11), 155 (100), 124 (20).

Anal. Calcd. for $C_{20}H_{38}O$: C, 81.56; H, 13.01. Found: C, 81.51; H, 13.06

Acknowledgement.- We thank the Korea Science and Engineering Foundation for financial support.

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