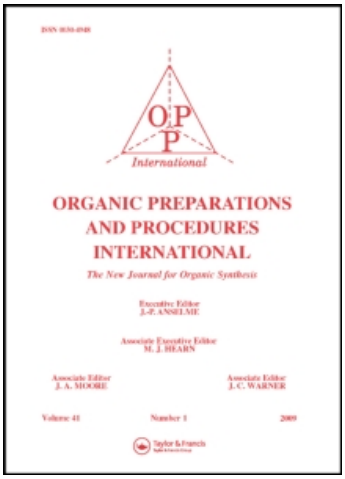

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NEW SIMPLE SYNTHESIS OF THE HOUSEFLY SEX ATTRACTANT

Yao-Pin Yen[a]; Fey-Long Wang[a]
[a] Department of Applied Chemistry, Providence University, Hsien, REPUBLIC OF CHINA

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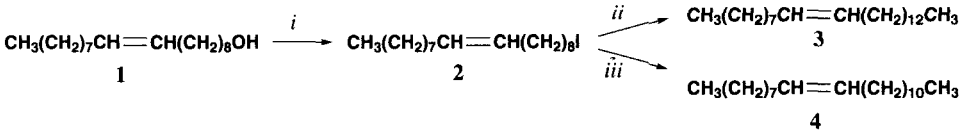
NEW SIMPLE SYNTHESIS OF THE HOUSEFLY SEX ATTRACTANT

Submitted by (11/18/96) Yao-Pin Yen* and Fey-Long Wang

Department of Applied Chemistry, Providence University, Shalu Taichung Hsien, Taiwan 43309, REPUBLIC OF CHINA

Muscalure [(Z)-9-tricosene, **3**], a sex attractant of the housefly (Musca domestica L.), has been prepared in a number of different ways, such as the transformations of acetylene,[1] oleic acid,[2] and olefin disproportionation.[3] Most of the chemical syntheses involve multistep processes.[4] We now describe a simple, convenient, and more efficient synthesis of muscalure proceeding *via* a cuprate-catalyzed Grignard coupling reaction as the key step.

As shown in Scheme 1, commercially available oleyl alcohol (**1**) was efficiently converted to oleyl iodide (**2**) by treament with triphenylphosphine, diethyl azodicarboxylate and lithium iodide.[5] The oleyl iodide was then coupled with pentylmagnesium bromide in the presence of dilithium trichlorocuprate (Li_2CuCl_3).[6,7] The reaction was complete in 4 h at room temperature to yield (Z)-9-tricosene. The product was purified by column chromatography to obtain pure (Z)-9-tricosene in 86% yield.



i) PPH_3, DEAD, LiI (91%) *ii*) $C_5H_{11}MgBr$, Li_2CuCl_3 (86%) *iii*) C_3H_7MgBr, Li_2CuCl_3 (87%)

In addition, Mansingh and coworkers[8] reported that a 7:3 mixture of (Z)-9-tricosene and (Z)-9-heneicosene (**4**) was a more potent attractant than muscalure. The lower homolog, (Z)-9-heneicosene, could also be synthesized by using the same methodology coupling of oleyl iodide and propylmagnesium bromide in the presence of Li_2CuCl_3 gave **4** in 87% yield.

EXPERIMENTAL SECTION

All reactions were carried out in flame-dried glassware under a N_2 atmosphere. Oleyl alcohol and Grignard reagents were obtained from Aldrich. THF was distilled from sodium benzophenone ketyl. Dilithium trichlorocuprate was prepared according to the procedure described in the literature.[6] The IR spectra were recorded on a Perkin-Elmer 2000 FT-IR. The ^1H NMR spectra were obtained on a Brucker AC-250 Spectrometer, and the mass spectra were recorded using an HP 5890 and HP 5971 MSD.

Li_2CuCl_3 was obtained by dissolving copper(I) chloride (0.146 g, 1.46 mmol) and lithium chloride (0.124 g, 2.92 mmol) in THF (6 mL).

Oleyl Iodide (2).- Diethyl azodicarboxylate (DEAD, 2.14 g, 12.3 mmole) was added dropwise with stirring to a 0° solution of triphenylphosphine (3.3g, 12.5 mmol) in anhydrous THF (10 ml) under nitrogen. After 20 min, lithium iodide (3.4 g, 25 mmol) was added to the solution, followed by oleyl alcohol (1.34 g, 5 mmol) in anhydrous THF (2 mL). The reaction mixture was maintained at 0° for 2 h. Upon evaporation of the solvent, the residue was poured into water and extracted with ether. The combined ethereal extracts were washed with brine, dried over anhydrous Na_2SO_4, and evaporated. Flash chromatography on silica gel with hexane as the eluant afforded (1.72 g, 91% yield) of **3**: IR (film): 3004, 2925, 2854, 1462, 722 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.91(t, 3H, J = 6.0 Hz,-CH_3), 1.20-1.49 (m, 24 H), 1.82 (m, 2 H), 2.02 (m, 2 H), 3.18 (t, 2H, J = 7.0 Hz, -CH_2-I), 5.30-5.45 (m, 2 H); MS m/z (%) 378 (M+, 7), 280 (10), 266 (11), 238 (11), 224 (18), 155 (37), 111 (31), 97 (84).

(Z)-9-Tricosene (1).- Freshly prepared Li_2CuCl_3 (0.25 M, 6 mL, 1.5 mmol) was added to oleyl iodide (0.6 g, 1.59 mmol) in THF (5 mL) at room temperature. Pentylmagnesium bromide (2.0 M in ether, 2.0 mL, 4.0 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 4 h and then quenched with saturated aq. NH_4Cl. The organic layer was collected and the aqueous layer was extracted with *n*-pentane. The combined organic solution washed with brine, dried, and concentrated *in vacuo*, Chromatography on silica gel eluting with *n*-hexane gave (0.44 g, 86 %) of pure **1**: IR (film): 3006, 2923, 2854, 1654, 1467, 1378, 721; ^1H NMR ($CDCl_3$): δ 0.88 (m, 6 H), 1.21-1.40 (m, 34 H), 1.90-2.10 (m, 4 H), 5.30-5.40 (m, 2 H); MS m/z (%): 322 (M+, 14), 168 (4), 139 (15), 125 (31), 111 (55), 97 (92).

(Z)-9-Heneicosene (4).- Li_2CuCl_3(0.25 M, 6.4 mL, 1.6 mmol) was added to the oleyl iodide (0.55 g, 1.45 mmol) in THF (5 mL) at room temperature. A solution of propylmagnesium bromide (1.4 M in THF, 2.1 mL, 2.9 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 4 h. Work up as previously described gave (0.37 g, 87 %) of **4**: IR (film): 3006, 2923, 2854, 1654,

1466, 1378, 721; ^{1}H NMR ($CDCl_3$): δ 0.88 (m, 6H), 1.11-1.43 (m, 30H), 1.92-2.10 (m, 4H), 5.30-5.48 (m, 2H); MS m/z (%): 294 (M+, 19), 154 (7), 140 (7), 125 (30), 111 (50), 97 (84).

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