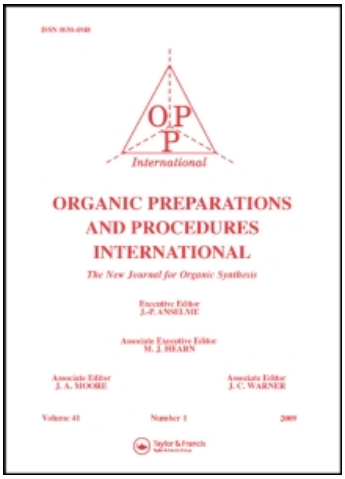

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A CONVENIENT SYNTHESIS OF (±)-10-METHYL-2-TRIDECANONE, THE PHEROMONE OF SOUTHERN CORN ROOTWORM

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gated C≡N), 3590 (OH) cm^{-1}. ^{1}HNMR ($CDCl_3$): δ 0.94 and 1.15 (2s, 18H); 1.55 (d, 1H, J = 8 Hz); 4.24 (d, 1H, J = 8 Hz); 4.30 (s, 1H, D_2O exchange); 6.98-7.30 (m, 5H).

Anal. Calcd. for $C_{21}H_{26}N_2O_2$: C, 74.52; H, 7.74 ; N, 8.28. Found: C, 74.77; H, 7.46; N, 8.02

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A CONVENIENT SYNTHESIS OF (±)-10-METHYL-2-TRIDECANONE, THE PHEROMONE OF SOUTHERN CORN ROOTWORM

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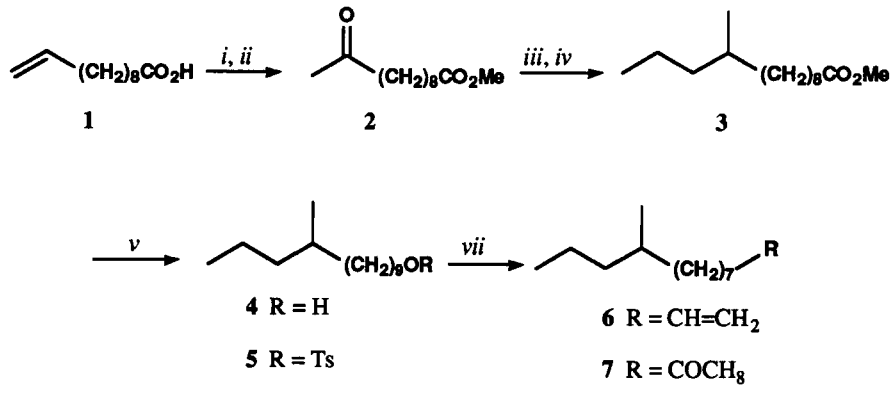
The pheromone secreted by the females of southern corn rootworm *Diabrotica undecimpunctata* has been identified[1] as (R)-10-methyltridecan-2-one (**7**). Effective control and eradication of this harmful pest *via* an integrated pest management program necessitated its pheromone be available in sufficient amount. In view of the non-detrimental effect exhibited[2] by its antipode, preparation and use of the pheromone in racemic form seemed to be economically appealing. We have formulated a simple strategy for the synthesis of (±) **7** utilizing the terminal bifunctionality of 10-undecenoic acid (**1**). This readily accessible acid (**1**) was used by us earlier for the synthesis of prostanoid synthons[3] and other bioactive compounds.[4,5] To the best of our knowledge this constitutes the first report of the synthesis of racemic 7, although chiral syntheses of 7 have been reported.[6-8]

The methyl ester of **1** was converted[3] to the ketoester **2** by *in situ* oxidation of its mercurated intermediate. Wittig olefination of **2** with *n*-propyltriphenylphosphonium bromide followed by hydrogenation of the double bond of the resultant methyl (10-methyl)-10-tridecenoate gave an excellent yield of ester **3** which on subsequent reduction gave the alcohol **4**. After tosylation, the resultant tosylate **5** was subjected to base-catalyzed elimination to furnish **6** in 90% yield. Surprisingly, this simple



i) MeOH/H^+, *ii*) $Hg(OAc)_2$/THF/H_2O, Jones' reagent
iii) *n*-$C_3H_7PPh_3Br$/Dimsyl, *iv*) H_2/10% Pd-C, *v*) LAH
vi) *p*-TsCl/Py, *vii*) $KOBu^t$/DMSO/Δ

elimination protocol has hardly been exploited in the case of primary carbinols. Recently, Ley *et al.*[9] have used it for the generation of terminal olefins even at room temperature. However, in the present case the reaction failed under their conditions even after 24 hrs. The desired conversion could be effected cleanly in only 4 hrs at 70°. *In situ* oxidation of its mercurated derivative produced the target pheromone **7**. The physical and spectral data of **7** were identical with the reported values.[7]

EXPERIMENTAL SECTION

All bps are uncorrected. The IR spectra were recorded as film on Perkin Elmer spectrophotometer model 783 and only the pertinent bands(in cm^{-1}) are reported. The PMR (TMS as internal standard) spectra were scanned on a Varian EM 60 (60 MHz) instrument in $CDCl_3$. All reactions involving anhydrous media were performed under argon atmosphere. Unless otherwise mentioned, the organic extracts were dried over anhydrous Na_2SO_4.

Methyl 10-Methyltridecanoate (3).- To a solution of dimsyl anion [prepared from NaH (1.6 g, 50% emulsion in oil, 0.033 mol) and anhydrous DMSO (20 mL)] in THF (30 mL) was added *n*-propylphosphonium bromide (12.9 g, 0.033 mol) at ambient temperature. After stirring for 1 hr, compound (**2**)[3] (6g, 0.03 mol) in THF (20 mL) was added dropwise at -20°, It was stirred for an additional 3 hrs at the same temperature and then overnight at room temperature. The reaction mixture was poured in ice-water (500 mL) and the aqueous layer thoroughly extracted with *n*-hexane. The organic extract was washed with water, brine and dried. Removal of the solvent followed by purification by column chromatography (silica gel, 0-15% EtOAc in hexane) furnished 5.4 g (90%) of pure methyl (10-methyl)-10-tridecenoate, bp. 105°/0.1 mm. IR: 1760, 1480 and 1470. PMR: δ 0.88 (t, *J* = 6Hz, 3H), 1.3 (bs, 12H), 1.5 (s, 3H), 1.9-2.5 (m, 6H), 3.78 (s, 3H), 5.06 (1H, t, *J* = 6Hz).

Anal. Calcd. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.77; H, 11.98

The above unsaturated ester (3.9 g, 0.016 mol) was hydrogenated over 10% Pd-C in methanol

(30 mL). After completion of the reaction, solvent ether (60 mL) was added into the reaction mixture and the supernatant passed through a small pad of florisil. The precipitated catalyst was washed with ether and subjected to the same treatment. Removal of the solvent under reduced pressure gave 3.8 g (90%) of pure **3**, bp. 106-8°/0.1 mm. IR: 1740. PMR: δ 0.9-1.0 (t and d merged, 6H), 1.28 (bs, 22H), 1.7-2.3 (m, 3H), 3.81 (s, 3H).

Anal. Calcd. for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48. Found: C, 74.54; H, 12.69

10-Methyltridecanol (4).- Compound 3 (3.9g, 0.016 mol) was reduced with LAH (0.6 g, 0.012 mol) in anhydrous ether (50 mL). After completion of the reaction (cf. tlc), excess hydride was decomposed with saturated aqueous solution of Na_2SO_4. The clear supernatant was decanted and the remaining solid washed with ether. The combined organic extract was concentrated *in vacuo* to furnish 3.5 g (90%) of pure **4**, bp. 100-104°/2mm. IR: 3480. PMR: δ 0.9-1.0 (t and d merged, 6H), 1.32 (bs, 21H), 2.48 (s, 1H, D_2O exchangeable), 3.68 (t, 2H , J = 7Hz).

Anal. Calcd. for $C_{14}H_{30}O$: C, 78.43; H, 14.11. Found: C, 78.41; H, 14.41

10-Methyltridecene (6).- *p*-TsCl (2.9 g, 0.015 mol) was added at 0° to a stirred mixture of **4** (2.14 g, 0.01 mol) and pyridine (1.5 mL, 0.02 mol) in CH_2Cl_2 (30 mL). After 24 hrs at 0° the reaction mixture was poured into ice-water (100 mL) and the lower organic layer separated. The aqueous portion was extracted with $CHCl_3$ (2x30 mL). The combined organic layers were successively washed with aq. 2N HCl, water, 10% aq. $NaHCO_3$, water, brine and dried. Evaporation of the solvent under reduced pressure gave a residue which was purified by column cbromatography (0-15% ethyl acetate in hexane) over silica gel to furnish 3.19 g (86%) of **5**. IR: 1640, 1180, 1020, 880.

To a solution of *t*-BuOK (0.009 mol) in DMSO (10 mL) was added 5 (2.87 g, 0.008 mol) at room temperature. After the addition, the mixture was heated at 70° for 4 hrs. It was cooled, poured into a large excess of water and extracted with hexane. Removal of the solvent followed by distillation furnished 1.37 g (90%) of pure **6**, bp. 100°/5mm; IR: 3005, 1640, 990, 910; PMR: δ 0.9-1.0 (t and d merged, 6H), 1.28 (bs, 16H), 1.9-2.3 (m, 3H), 4.8-6.2 (m, 3H).

10-Methyltridecanone (7).- Following our reported[3] procedure, compound **6** (1.4 g, 0.004mol) was converted to **7** using $Hg(OAc)_2$ (0.480 g, 1.5 mmol) in acetone (15 mL), water (0.5 mL) and excess Jones' reagent. Yield 0.88 g (91%); bp. 128° (bath)/5mm, lit.[6] bp. 105-115° (bath)/3mm; IR: 2980 and 1720; PMR: δ 0.9-1.0 (t and d merged, 6H), 1.38 (bs, 17H), 2.2 (s, 3H), 2.4 (t, J = 7Hz, 2H).

Anal. Calcd. for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 78.93; H, 13.48

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A SHORT SYNTHESIS OF (11Z,15Z)-EICOSADIENOIC ACID, A COMPOUND OF MARINE SPONGE ORIGIN

Submitted by (05/04/92)

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The chemical investigation of marine organisms has resulted in the isolation and characterization of a number of unusual compounds[1-3] of diverse biological activities. This has provided great impetus to the studies of their metabolism and biosynthesis. Their low natural abundance makes their syntheses of great importance. Among the various types of marine products, the ubiquitous phospholipids occupy an important position. Recently, Carballeira *et al.*[2] isolated a new compound, (11Z,15Z)-eicosadienoic acid (**1**) from Caribbean sponge, *Amphimedon complanata*. To the best of our knowledge, there is no report of its synthesis. We herein report a practical and stereoselective synthesis of this compound relying on the "building block" approach.

From a retrosynthetic perspective, the easily available acetylenic alcohol **2** seems to be ideally suited for its derivatization to the necessary 1,5-alkadienic unit present in **1**. The bifunctional alcohol was used earlier in the preparation[4] of other classes of active compounds *viz* pheromones, jasmonoids and a prostaglandin synthon. The other notable feature was utilization of yet another commercially available substance *viz*. 10-undecenoic acid (**3**) for the preparation of the C_{11}–synthon (**5**) required for the synthesis. Hydrogen bromide was added to **3** and the product was esterified.[5] Subsequent treatment of the resulting bromoester (**4**) with triphenylphosphine in refluxing acetonitrile afforded the