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A Short Synthesis of (*Z*)-5-Undecen-2-one, a Ketone from the Pedal Gland of the Bontebok (*Damaliscus dorcas dorcas*)†

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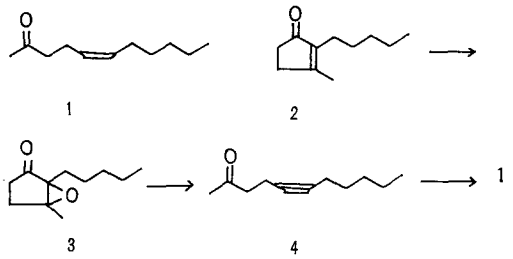
(*Z*)-5-Undecen-2-one (**1**) was isolated as the principal volatile component contained in the pedal gland exudate of the bontebok, *Damaliscus dorcas dorcas* by Burger *et al.*[1] The synthetic ketone (**1**) was subjected to the preliminary biological test as a mammalian pheromone of the bontebok and intense interest was shown by two captive animals.[1] Their synthesis of **1**, however, required six steps for completion. We here describe a three-step synthesis of **1** from readily available dihydrojasmone (**2**). This is a further illustration of synthesis of aliphatic pheromones from alicyclic starting materials.[2]

Dihydrojasmone (**2**) was epoxidized with basic hydrogen peroxide to give an epoxy ketone (**3**) after chromatographic purification. This was subjected to the Eschenmoser cleavage[3] via the corresponding tosylhydrazone to give an acetylenic ketone (**4**). The semi-hydrogenation of **4** gave the desired product (**1**). Its physical properties were in good accord with the published data.[1] The NMR spectrum of our ketone (**1**) was indeed identical with the published chart.



EXPERIMENTAL

All bps were uncorrected. IR spectra refer to films. NMR spectra were recorded as CCl_4 solution with TMS as an internal standard.

2, 3-Oxido-2-pentyl-3-methylcyclopentan-1-one (**3**)

Hydrogen peroxide (30%, 32 ml) was added dropwise to a stirred and ice-cooled solution of dihydrojasmone (**2**, 13.8 g) in methanol (80 ml) at 5~10°C. Subsequently 3 N-aqueous sodium hydroxide solution (13.5 ml) was added to the mixture during 10 min period. After stirring for 4 hr at 20°C, the mixture was poured into water and extracted with ether. The ether solution was washed with water and brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was chromatographed over silicic acid (200 g) and eluted with *n*-hexane–ether (20: 1) to give 4.6 g (34%) of **3**. This was distilled *in vacuo* to give 3.80 g of pure **3**, bp 110~112°C (11 mmHg), n_D^{22} 1.4513; IR ν_{max} cm^{-1}: 2920 (s), 2860 (m), 1740 (s), 1460 (m), 1410 (m), 1385 (m), 1070 (m), 1050 (m), 850 (m); NMR δ (60 MHz) 0.90 (3H, deformed t, J=7 Hz), 1.47 (3H, s). *Anal.* Found: C, 73.24; H, 10.26. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96%.

5-Undecyn-2-one (**4**)

p-Tosylhydrazide (3.2 g) was added in one portion to a stirred and ice-cooled solution of **3** (3.6 g) in methylene chloride (20 ml) and acetic acid (10 ml) at 0~5°C. The mixture was stirred for 3 hr at 0~5°C and for 16 hr at room temperature. Then it was poured into water and extracted with *n*-hexane. The *n*-hexane solution was washed with water, aqueous sodium bicarbonate solution and brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was chromatographed over silicic acid (50 g). Elution with *n*-hexane gave crude **4**. This was distilled *in vacuo* to give 1.94 g (59%) of pure **4**, bp 104~106°C (10 mmHg), n_D^{22} 1.4495; IR ν_{max} cm^{-1}: 2920 (s), 2860 (m), 1725 (s), 1460 (m), 1440 (m), 1370 (m), 1165 (m), 760 (w); NMR δ (60 MHz) 0.92 (3H, deformed t, J=7 Hz), 2.11 (3H, s); GLC, (column, 10% QF-1 at 130°C, Carrier gas, N_2, 0.85 kg/cm²): t_R 7.05 min (single peak). *Anal.* Found: C, 78.70; H, 10.87. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

(*Z*)-*5-Undecen-2-one* (**1**)

5% Palladium on barium sulfate (100 mg) and quinoline (two drops) were added to a solution of **4** (1 g) in methanol (20 ml) and the mixture was shaken under hydrogen atmosphere for about 1 hr at room temperature (156 ml uptake of hydrogen). The mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in ether. The ether solution was washed with dilute hydrochloric acid, aqueous sodium bicarbonate solution and brine, dried over magnesium sulfate and concentrated *in vacuo*. The

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residue was distilled to give 0.75 g (75%) of **1**, bp 97~99°C (12 mmHg), n_D^{22} 1.4420; IR ν_{max} cm^{-1}: 3010 (w), 2920 (s), 2860 (m), 1725 (s), 1470 (m), 1410 (m), 1365 (m), 1165 (m), 970 (w); NMR δ (100 MHz) 0.88 (3H, deformed t, J=7 Hz), ~1.08–~1.6 (6H, broad), 2.04 (3H, s), ~1.8– ~2.1 (2H), ~2.2– ~2.5 (4H, m), ~5.14– ~5.50 (2H, m); GLC (column, 10% QF-1 at 130°C, carrier gas, N_2, 0.85 kg/cm^2): t_R 6.1 min (93%), 9.6 min (7%). *Anal.* Found: C, 78.02; H, 11.93. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

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