## A Convenient Synthesis of (*Z*)- and (*E*)-3-(1-Alkenyl)-cyclopentenes

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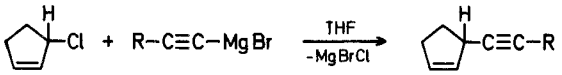
Cellular chemotaxis plays a decisive part in the pre-conjugational communication between female and male gametes of marine brown algae[1,2,3]. The molecular basis of these interactions are highly unsaturated hydrocarbons; in the case of the sea-weeds *Ectocarpus* and *Cutleria*, isomers of $C_{11}H_{16}$-trienes containing rings of different size (2-7 C-atoms) have been identified[4,5]. *Cutleria multifida*, a mediterranean species originally collected near Naples[5], releases three volatile olefinic compounds into the surrounding water. The major constituent (~ 70 %) and true active lure is *multifidene*, the structure of which was established as *cis*-3-(*cis*-1-butenyl)-4-vinylcyclopentene[6].

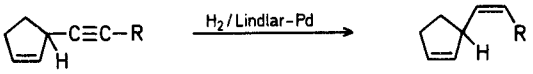
In connection with our work on the specificity of the plant receptor system, we wished to synthesize the natural product and its isosters[7] and, in particular, some simple monosubstituted 3-(1-alkenyl)-cyclopentenes of various chain lengths and unambiguous stereochemistry.

3-Vinylcyclopentene has previously been prepared by reaction of 3-chlorocyclopentene (**1**) with vinylmagnesium bromide[8]. However, extension of this reaction to the synthesis of higher 3-(1-alkenyl)-cyclopentenes (**3, 4**) was not promising because the isomerically pure (*Z*)- and (*E*)-1-bromo-1-alkenes needed as starting material are rather difficult to obtain. We therefore used the better available 1-alkynylmagnesium bromides as starting material. The 3-(1-alkynyl)-cyclopentenes (**2**) thus obtained[9] in fair to good yields could be reduced to both the *Z*- and *E*-isomers of the desired 3-(1-alkenyl)-cyclopentenes (Table 1).



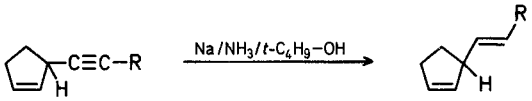

**1** **2**

Hydrogenation of compounds **2** over Lindlar catalyst in pentane at 0° afforded the (*Z*)-3-(1-alkenyl)-cyclopentenes **3** in high yield and high isomeric purity. The final purification of products **3** was easily achieved by preparative G.L.C. using SE 30 or PEG 4000 as liquid phase. The data of the compounds synthesized are compiled in Table 2.




**2** **3**

The attempted *trans* reduction of compounds **2** with sodium/ammonia failed completely; it afforded only products of over-reduction. Similar results have been reported for the sodium/ammonia reduction of 1,4-diynes[10]. However, it has recently been shown by Henrick[11] that in the reduction of alkynes with sodium/ammonia isomerization of the product alkenes followed by over-reduction can be avoided by adding an appropriate alcohol to the reaction mixture. In fact, the reduction of compounds **2** with sodium in liquid ammonia in the presence of 1 equiv *t*-butanol afforded the desired (*E*)-3-(1-alkenyl)-cyclopentenes **4** in high yield and 100 % isomeric purity. Not even traces of the *Z* isomers could be detected in the products as may be taken from Table 3.




**2** **4**

Thus, (*Z*)- (**3**) and (*E*)-3-(1-alkenyl)-cyclopentenes (**4**) which are useful starting materials for further syntheses (and which were the subject of comparative receptor studies with *Cutleria* and *Ectocarpus* androgametes[12]) can be prepared selectively by simple two-step methods starting from 3-halocyclopentenes and 1-alkynylmagnesium halides.

**3-(1-Alkynyl)-cyclopentenes (2); General Procedure:**
A solution of a 1-alkynylmagnesium bromide (0.2 mol) in tetrahydrofuran (150 ml) is added dropwise to a stirred solution of freshly

0039–7881/79/0232–0114 $ 03.00 

**Table 1.** 3-(1-Alkynyl)-cyclopentenes (**2**)

| 2 | R | Yield [%] | b.p./torr | $n_D^{25}$ | Molecular formula[a] | I.R. (KBr) $\nu_{max}$ [$cm^{-1}$] | $^1$H-N.M.R. ($CCl_4$) $\delta$ [ppm] |
|---|---|---|---|---|---|---|---|
| **a**[14] | H | 21 | 101°/760 | 1.4608 | $C_7H_8$ (92.1) | 3290, 3050, 2960, 2840, 2010, 720 | |
| **b** | $C_2H_5$ | 34 | 95°/100 | 1.4745 | $C_9H_{12}$ (120.2) | 3050, 2960, 2920, 2830, 720 | 1.1 (t, 3H); 1.48–2.60 (m, 6H); 3.35 (m, 1H); 5.65 (m, 2H) |
| **c** | *n*-$C_4H_9$ | 47 | 121°/80 | 1.4728 | $C_{11}H_{16}$ (148.2) | 3050, 2960, 2920, 2860, 720 | 0.9 (t, 3H); 1.15–2.65 (m, 10H); 3.30 (m, 1H); 5.65 (m, 2H) |
| **d** | *n*-$C_6H_{13}$ | 72 | 119°/17 | 1.4736 | $C_{13}H_{20}$ (176.3) | 3050, 2960, 2930, 2860, 720 | 0.93 (t, 3H); 1.15–2.60 (m, 14H); 3.35 (m, 1H); 5.65 (m, 2H) |

[a] All products gave satisfactory mass spectra and microanalyses: C, ±0.10; H, ±0.07; the microanalyses were performed by I. Beetz, D-3251 Kronach.

**Table 2.** (*Z*)-3-(1-Alkenyl)-cyclopentenes (**3**)

| 3 | H | Yield [%] | $n_D^{25}$ | *Z*/*E*-ratio [%] | Molecular formula[a] | I.R. (KBr) $\nu_{max}$ [$cm^{-1}$] | $^1$H-N.M.R. ($CCl_4$) $\delta$ [ppm] |
|---|---|---|---|---|---|---|---|
| **a**[15] | H | 92 | 1.4450 | — | $C_7H_{10}$ (94.2) | 3080, 3060, 2980, 990, 910, 725 | |
| **b** | $C_2H_5$ | 91 | 1.4596 | 97/3 | $C_9H_{14}$ (122.2) | 3050, 3000, 2960, 2850, 740, 720 | 0.96 (t, 3H); 1.20–2.50 (m, 6H); 3.55 (m, 1H); 5.0–5.83 (m, 4H) |
| **c** | *n*-$C_4H_9$ | 96 | 1.4626 | 99/1 | $C_{11}H_{18}$ (150.3) | 3050, 3000, 2960, 2850, 740, 720 | 0.96 (t, 3H); 1.10–2.60 (m, 12H); 3.55 (m, 1H); 5.02–5.83 (m, 4H) |
| **d** | *n*-$C_6H_{13}$ | 98 | 1.4687 | 96/4 | $C_{13}H_{22}$ (178.3) | 3050, 3000, 2920, 2840, 740, 720 | 0.94 (t, 3H); 1.10–2.48 (m, 16H); 3.55 (m, 1H); 5.00–5.85 (m, 4H) |

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.09; H, ±0.10.

**Table 3.** (*E*)-3-(1-Alkenyl)-cyclopentenes (**4**)

| 4 | R | Yield [%] | $n_D^{25}$ | *E*/*Z*-ratio [%] | Molecular formula[a] | I.R. (KBr) $\nu_{max}$ [$cm^{-1}$] | $^1$H-N.M.R. ($CCl_4$) $\delta$ [ppm] |
|---|---|---|---|---|---|---|---|
| **a** | $C_2H_5$ | 76 | 1.4594 | 100/0 | $C_9H_{14}$ (122.2) | 3040, 3010, 2950, 2840, 965, 720 | 0.96 (t, 3H); 1.25–2.55 (m, 6H); 3.20 (m, 1H); 5.10–5.85 (m, 4H) |
| **b** | *n*-$C_4H_9$ | 81 | 1.4608 | 100/0 | $C_{11}H_{18}$ (150.3) | 3040, 3010, 2950, 2830, 965, 720 | 0.96 (t, 3H); 1.00–2.50 (m, 12H); 3.20 (m, 1H); 5.10–5.80 (m, 4H) |
| **c** | *n*-$C_6H_{13}$ | 84 | 1.4629 | 100/0 | $C_{13}H_{22}$ (178.3) | 3040, 3010, 2960, 2855, 965, 720 | 0.96 (t, 3H); 1.05–2.50 (m, 16H); 3.20 (m, 1H); 5.15–5.85 (m, 4H) |

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.13; H, ±0.1.

distilled 3-chlorocyclopentene (**1**; 18.52 g, 0.2 mol) in tetrahydrofuran (70 ml). The temperature of the mixture is kept below 30° by occasional cooling while stirring is continued for a further 2 h. The solution is then poured into ice/ammonium chloride and the product extracted with ether (3 × 100 ml). The extract is washed with 2 normal hydrochloric acid (2 × 50 ml) and water (2 × 50 ml) and dried with magnesium sulfate. The ether is removed under reduced pressure and the resultant crude product purified by distillation over a short Vigreux column.

**(*Z*)-3-(1-Alkenyl)-cyclopentenes (3); General Procedure:**
Lindlar catalyst (Merck, Darmstadt; 100 mg) and quinoline (20 µl) are added to a solution of the 3-(1-alkynyl)-cyclopentene (**2**; 2.0 g) in pentane (50 ml). Hydrogen is then bubbled through the stirred mixture until G.L.C. analysis of a sample indicates complete conversion. The catalyst is removed by filtration, the solvent evaporated, and the crude product purified by preparative G.L.C. (chromosorb W 30/60, SE 30 or PEG 4000, 1.5 m × 0.5 cm).

**(*E*)-3-(1-Alkenyl)-cyclopentenes (4); General Procedure:**
A solution of the 3-(1-alkynyl)-cyclopentene (**2**; 0.03 mol) in dry tetrahydrofuran (25 ml) is added dropwise to a stirred solution of sodium (2.0 g, 0.09 g-atom) and *t*-butanol (7.6 g, 0.09 mol) in liquid ammonia (100 ml) and stirring is continued for 45 min at −34°. Excess sodium is then removed by the addition of ammonium chloride (3 g) and the ammonia is allowed to evaporate overnight. Water (70 ml) is added to the residue and the product is extracted with ether (3 × 50 ml). The extract is washed with 2 normal hydrochloric acid (2 × 50 ml) and water (2 × 50 ml) and dried with magnesium sulfate. The solvent is evaporated and the crude product purified by preparative G.L.C. (chromosorb, SE 30, 1.5 m × 0.5 cm).

*The authors thank the "Deutsche Forschungsgemeinschaft" and the "Fonds der Chemischen Industrie" for support of this work.*

Received: July 11, 1978

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