A new Method for Conversion of *cis*-Vinyl Spirannic Ketones to the Corresponding *cis*-Dienones

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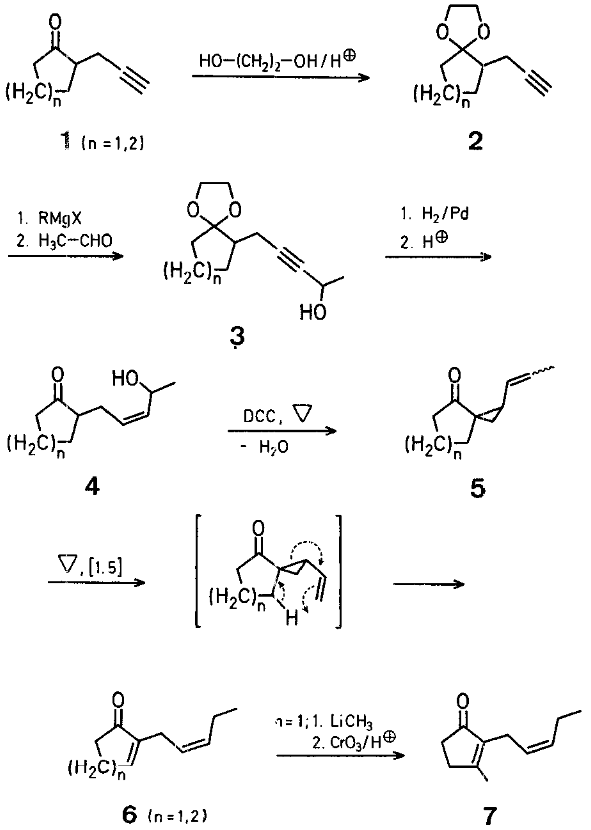
Thermic cyclodehydration of primary[1] and secondary[2] cyclanic ε-ketols gives, by a stereospecific reaction, *cis*-vinyl spirannic ketones. By heating this ketonic material, an epimerization and [1.5] sigmatropic rearrangement is observed to form *cis*-dienones which can be used for the synthesis of *cis*-jasmone[3,4].

The 2-propargylcyclanones **1** are easily obtained by reaction of propargyl bromide with the enamines of cyclopentanone (n = 1) or cyclohexanone (n = 2) following the known[5] procedure and compared with those already synthesized[6,7]. After protection of the carbonyl group with glycol, the condensation of the dioxolane **2** with ethanal gives the secondary



alcohol **3**. The *cis*-ketol **4** is obtained by hydrogenation on a Lindlar catalyst and the dioxolane group is removed by acidic treatment. This ketol **4** is heated under 200 °C following the procedure of Rouessac[8] for γ-ketols, with dicyclohexylcarbodiimide. The *cis*-spirannic ketones **5** are prepared in this way and the configuration is proved principally by N.M.R, using the rule of Conolly and McGrindle[9]. The pyrolysis of **5** at 240 °C quantitatively converts this spirannic *cis*-ketone to the *cis*-dienone **6** by an epimerization reaction and a [1.5] sigmatropic rearrangement.

In the case of **6** (n = 1), this dienone can be transformed into the *cis*-jasmone **7** by using the alkylation procedure with methyllithium and oxidation reaction described by Büchi[3]. This procedure of synthesis of jasmone complements the preceding ones recently reviewed[10].

The structure of the products (table) were confirmed by N.M.R. and elemental analyses.

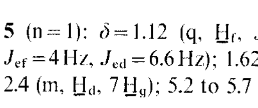
Table: Intermediates for the Synthesis of **5** and **6**

n	Compounds	Yield (%)	b.p/torr	n_D^{25}
1	**2**	85	101°/17	1.4772
2	**2**	85	120°/18	1.4835
1	**3**	70	140/1.5	1.4923
2	**3**	70	147/0.3	1.4990
1	**4**	76	[a]	—
2	**4**	78	135/0.6	1.4920

[a] Purification by preparative G.L.C. on a Carbowax 20 M (20%, 10′ × 1/4″, 200°) column.

1-(*cis*-1-Propenyl)spiro[2,n + 3]alkan-4-ones (5, n = 1,2):
Following the known procedure[8], the compound **4** (0.006 mol) and dicyclohexylcarbodiimide (0.065 mol) in ether (100 ml) were heated for two days in the presence of traces of copper (I) chloride. The solid material was removed by filtration, and after evaporation of the solvent, the ketone **5** was obtained by heating the oily crude carbamidate derivative at 160° (n = 1) or 200° (n = 2) under reduced pressure. The crude ketone was dissolved again in ether, washed, dried, and distilled; yield = 25%; **5** (n = 1): b.p 60°/2.5 torr; **5** (n = 2): b.p 69–70°/0.7 torr.

^{1}H-N.M.R. (CCl_4):



5 (n = 1): $\delta = 1.12$ (q, $\underline{H}_f$, $J_{fe} = 4$ Hz, $J_{ed} = 8.5$ Hz); 1.25 (q, $\underline{H}_e$, $J_{ef} = 4$ Hz, $J_{ed} = 6.6$ Hz); 1.62 (d, 3$\underline{H}_a$, $J_{ab} = 5$ Hz, $J_{ac} = 2$ Hz); 1.7 to 2.4 (m, $\underline{H}_d$, 7$\underline{H}_g$); 5.2 to 5.7 ppm (m, $\underline{H}_b$, $\underline{H}_c$).

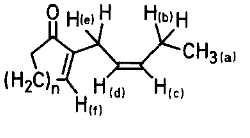
$\Delta\delta = (\delta_{CCl_4} - \delta_{C_6D_6})$ Hz: $\underline{H}_f$ (+0.1); $\underline{H}_e$ (−0.15); CH_3 (+0.05); $\underline{H}_b$, $\underline{H}_c$(−0.2).

5 (n = 2): $\delta = 0.65$ (q, $\underline{H}_f$, $J_{fe} = 7.5$ Hz, $J_{fd} = 11$ Hz); 1.63 (d, 3$\underline{H}_a$, $J_{ab} = 6.5$ Hz, $J_{ac} = 2$ Hz); 1.5 to 2.2 (m, $\underline{H}_d$, $\underline{H}_e$, 9$\underline{H}_g$); 4.9 (m, $\underline{H}_c$); 5.5 ppm (m, $\underline{H}_b$).

2-(*cis*-2-Pentenyl)-cyclo-2-alkenones (6, n = 1,2):
After heating of **5** (n = 1,2) in a sealed tube under 240° for 15 min and 30 min respectively, the dienones **6** were isolated by preparative G.L.C. on a silicone S.E. 52 (20%, 10′ × 1/4″, 140°) column, identified from spectroscopy and compared with those already described[3,4].

I.R. (neat): **6** (n = 1) $\nu_{max} = 1700, 1630, 730\ cm^{-1}$
6 (n = 2) $\nu_{max} = 1690, 1640, 710\ cm^{-1}$

^{1}H-NMR (CCl_4):



6 (n = 1): $\delta = 0.97$ (t, 3$\underline{H}_a$, $J = 7$ Hz); 1.85 to 2.8 (m, $\underline{H}_b$, 4$\underline{H}_g$); 2.85 (d, $\underline{H}_e$, $J = 5$ Hz); 5.4 (m, $\underline{H}_c$, $\underline{H}_d$); 7.5 ppm (m, $\underline{H}_f$).

6 (n = 2): $\delta = 0.97$ (t, 3H, $J = 7$ Hz); 1.5 to 2.5 (m, $\underline{H}_b$, 6$\underline{H}_g$); 2.88 (d, $\underline{H}_e$, $J = 5$ Hz); 5.38 (m, $\underline{H}_c$, $\underline{H}_d$); 6.66 (m, $\underline{H}_f$).

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