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Stereospecific Conversion of Diosgenin to α-Ecdysone

Sir:

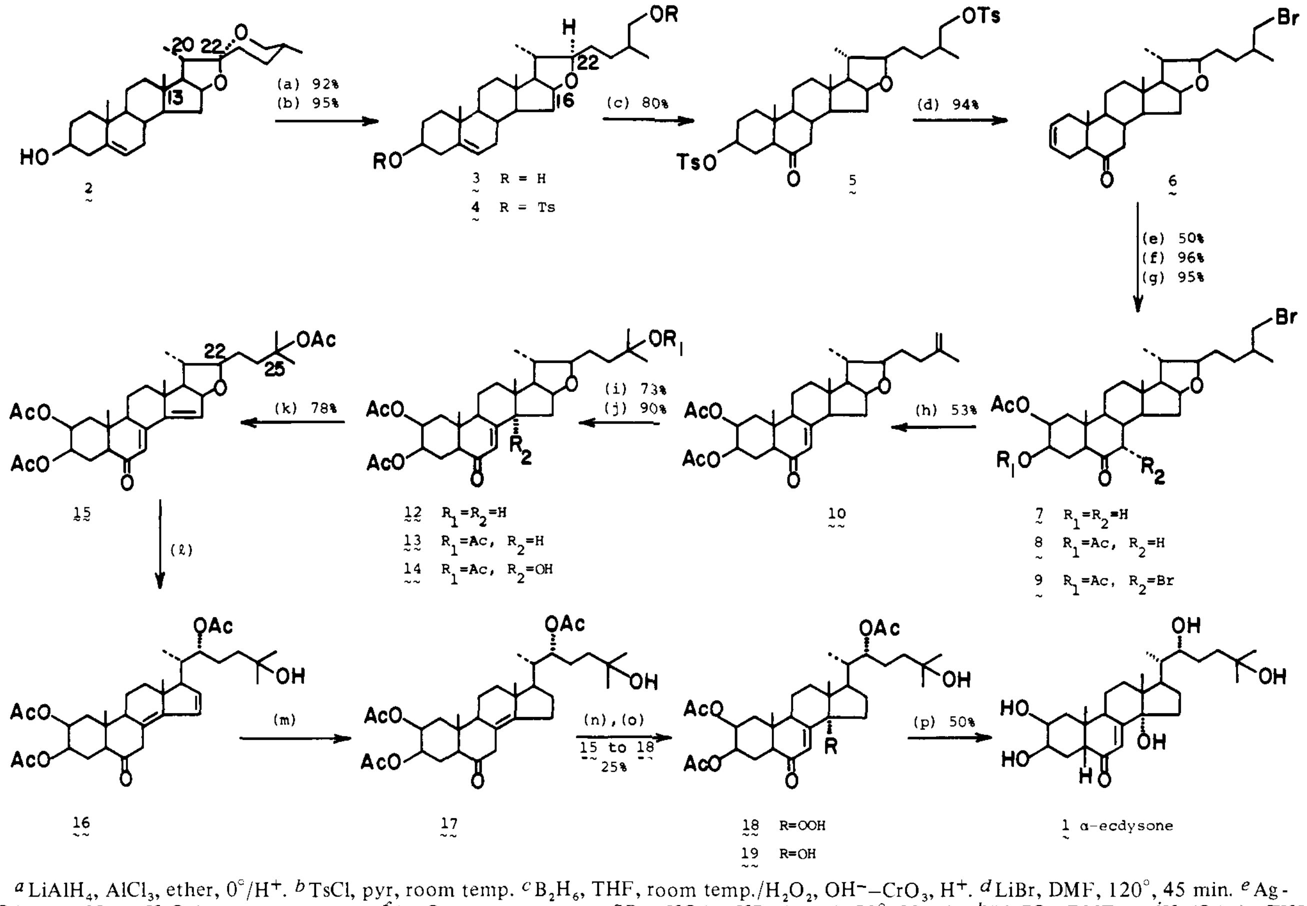
α-Ecdysone (**1**) was the first insect moulting hormone to be isolated,[1] characterized,[2] and synthesized.[3-6] In the following we report its synthesis from diosgenin (**2**), in which the correct configuration at C-22 is generated by stereospecific reduction of the diosgenin spiro-ketal group.

Okauchi et al.[7] reported that the cocoon spinning of a silk-worm colony can be synchronized when ecdysones are added to the diet (15 mg per 20 000 larvae) at a particular stage during the fifth instar. Extensive field tests carried out since have verified this, and further have shown that simultaneous application of lauryl alcohol repels larvae, automatically moving them towards the nesting area where spinning of high-quality cocoon is assured.[8] As far as we are aware, this is the first usage of ecdysones in insect control (in a positive sense).

The mixed hydride (LAH-$AlCl_3$) reduction of diosgenin is known to give dihydrodiosgenin (**3**) in excellent yield.[9] Examination of molecular models revealed that since the 13-Me would impose a greater steric hindrance than the 20-Me to a group approaching C-22, the dihydro-derivative **3** should possess the 22*R* configuration as shown.[10] A reductive cleavage of the C-16–O bond would then lead to a 22-OH having the same absolute configuration as that of the ecdysones,[2,11] a step which was achieved in transformation **15** → **16** (Scheme I).

Hydroboration-oxidation of dihydrodiosgenin ditosylate (**4**), mp 119.5–120.5 °C, gave 6-keto ditosylate (**5**), mp 133–134 °C, which when heated in DMF with LiBr produced **6**:[12] NMR δ 5.63, br s, 2-H, 3-H; 3.37, d, *J* = 5 Hz, 26-H; 0.83, s, 19-H; 0.73, s, 18-H. Prevost-Woodward hydroxylation[13] of **6** gave the 2-acetoxy-3-hydroxy derivative (**7**), mp 154–154.5 °C, which was acetylated to **8**, mp 147.5–148 °C. When crystalline **8** was treated with bromine under equilibrating conditions, 7α-bromo 6-ketone (**9**) was obtained in high yield as reported earlier for an analogous system.[13] Dehydrobromination of **9** in boiling DMF with Li_2CO_3 provided the 7,25-diene-6-one (**10**), mp 195.5–197 °C (NMR δ 5.72, distorted t, 7-H; 1.03, s, 19-H; 0.74, s, 18-H) in fair yield along with 4,25-dien-6-one (**11**),

Scheme I



[a] $LiAlH_4$, $AlCl_3$, ether, 0°/H^+. [b] TsCl, pyr, room temp. [c] B_2H_6, THF, room temp./H_2O_2, OH^-–CrO_3, H^+. [d] LiBr, DMF, 120°, 45 min. [e] AgOAc, I_2, HOAc, H_2O (trace), room temp. [f] Ac_2O, pyr, room temp. [g] Br_2, HOAc, HBr (trace), 70°, 90 min. [h] Li_2CO_3, DMF, Δ. [i] $Hg(OAc)_2$, THF, room temp./$NaBH_4$, OH^-, 0°/Ac_2O, CaH_2, 120°, 2 h. [j] SeO_2, dioxane, 80°, 30 min. [k] $(CF_3CO)_2O$, pyr, 0°, 20 min. [l] Zn, AcOH, Δ. [m] H_2, Pd(C), EtOAc, room temp. [n] O_2, rose bengal, MeOH, *hν*, room temp. [o] NaI, AcOH, MeOH, room temp. [p] K_2CO_3, MeOH, Δ.

mp 125–131 °C (NMR δ 5.87, dd, J = 2.2 and 0.5 Hz, 4-H; 1.15, s, H-19; 0.83, s, 18-H) as a minor product (18% yield).[14] Oxymercuration–demercuration of **10** produced the tertiary alcohol **12,** mp 216–218 °C,[15] which was converted to the triacetate **13,** mp 199–201 °C, by Oppenauer's method.[16] Selenium dioxide in dioxane achieved a clean hydroxylation of **13** to yield the hydroxy enone (**14**) mp 196–197.5 °C: NMR δ 5.86, d, J = 2.5 Hz, 7-H. Dehydration to the 7,14-diene-6-one (**15**) (NMR δ 6.18, d, J = 2.5 Hz, 7-H; 5.84, d, J = 2.5 Hz, 15-H; uv (MeOH) 271 nm, ϵ 10 300) occurred readily when a dry pyridine solution of crude **14** was treated with trifluoroacetic anhydride at low temperature;[17,18] the hypsochromic uv shift of ca. 25 nm in **15** as compared to standard 7,14-dien-6-one values shows that the dienone chromophore is distorted, presumably by the fused tetrahydrofuran ring.

Cleavage of the C-16–O bond was accomplished when a pure sample of **15** was treated with excess zinc powder in vigorously stirred boiling acetic acid in the absence of oxygen to yield the desired 8(14),15-diene-6-one, (**16**) (NMR δ 6.32 (16-H) and 6.05 (17-H), ABq, J = 6 Hz; 3.30 and 2.90, ABq, J = 16 Hz, 7-H) a product of concomitant acetyl migration from 25-OH to 22-OH.[19] The crude product **16** was cleanly hydrogenated to the 6,8(14)-enone (**17**), (NMR δ 3.10 and 2.85, ABq, J = 16 Hz, 7-H) which was photooxygenated[20] to the hydroperoxy enone system (**18**) (NMR δ 5.90, d, J = 2 Hz, 7-H; 0.72, s, 18-H; 0.90, s, 21-H). Sodium iodide reduction afforded 5-epi-α-ecdysone 2,3,22-triacetate (**19**), mp 225 °C: NMR δ 5.89, d, J = 2 Hz, 7-H; 0.66, s, 18-H; 0.94, s, 21-H. α-Ecdysone (**1**), mp 170 °C (hydrate), was obtained after basic hydrolysis-epimerization[4b] in a total yield of 1% from diosgenin.[21]

We believe that the procedure described is adaptable to a number of interesting ecdysone analogues, some of which are now being bioassayed for ecdysone or antiecdysone activity, and to the large scale synthesis of α-ecdysone. Furthermore, the scheme allows an easy preparation of [15,16-$^3H_2$]-α-ecdysone, which should be valuable for metabolic studies of insect moulting hormones since the labels are located on unreactive nuclear positions. An alternative route via a 26,27-bisnor-25-methoxycarbonyl side chain which will afford [15,16-$^3H_2$, 26,27-$^{14}C_2$]-α-ecdysone has been completed with cold materials.[22]

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Visible Light to Electrical Energy Conversion. Stable Cadmium Sulfide and Cadmium Selenide Photoelectrodes in Aqueous Electrolytes

Sir:

We wish to report the first sustained conversion of low energy visible light (>1.7 eV) to electrical energy using wet photoelectrochemical cells where there are no net chemical changes in the system.

Irradiation of an n-type semiconductor electrode in a cell as depicted in Scheme I can result in a photocurrent.[1] Use of n-type CdS[2] or CdSe[3] results in photoanodic dissolution to yield Cd^{2+} ions and elemental S or Se. Such a result is typical for semiconductor photoelectrodes with the exception of TiO_2,[4-9] SnO_2,[10] $SrTiO_3$,[11] and $KTaO_3$.[12] Unfortunately, these oxides all have large band gaps (≥3.0 eV) and, consequently, do not respond to visible light. Both CdS (band gap 2.4 eV)[2] and CdSe (band gap ~1.7 eV)[2] respond to a major fraction of the visible spectrum, but the irreversible decomposition encountered in their use as photoelectrodes is a serious hurdle in practice.

An approach to "stabilization" of photoelectrodes is to employ an electrochemically active electrolyte such that its redox chemistry occurs at the expense of electrode decomposition. This approach has proven to yield mixed results. Oxidation of I^- occurs at an irradiated CdS anode, but the

Scheme I