(η⁶-Naphthalene)tricarbonylchromium-mediated hydrogenation of 3,5-diene-1,7-diynes as a route to (*Z*,*Z*,*Z*)-1,4,7-trienes

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The hydrogenation of internal 3,5-diene-1,7-diynes over (η⁶-naphthalene)tricarbonylchromium affords homoconjugated (*Z*,*Z*,*Z*)-1,4,7-trienes as major products.

(η⁶-Arene)tricarbonylchromium complexes (ATCC) are known to catalyse 1,4-*cis*-hydrogenation of conjugated dienes[1,2] and 1,2-*syn*-hydrogenation of acetylenes,[2,3] which leads to (*Z*)-disubstituted olefins in both cases. Recently, ATCC were successfully used as catalysts for the simultaneous hydrogenation of both diene and acetylene groups in conjugated alkyl 2,4-diene-6-ynoates, which afforded the corresponding 'skipped' (*Z*,*Z*)-alka-3,6-dienoates.[4] The high selectivity of this process suggests that ATCC exhibit a higher affinity to the diene moiety than that to the triple bond.

Now, we have obtained conjugated enyne substrates of another type, where acetylenic groups are attached to the termini of an internal 1,3-diene system (compounds **1a**–**c**), and studied their ATCC-induced hydrogenation. Starting dienediynes **1a**,**b** were prepared by the Pd-promoted cross-coupling[5] of (*E*,*E*)-1,4-diiodobuta-1,3-diene **2**[6] (readily accessible *via* Pt-catalysed oxidative dimerization of acetylene in iodine-containing solutions) either with but-3-yn-1-ol **3a** alone or with undec-1-yne **3b** and **3a** consecutively (Scheme 1).

Pyrrolidine was found to be the best solvent for the cross-coupling of alkynes **3a**,**b** with diiodide **2** (see ref. 7 for an original procedure). Its advantage is that the reaction in this solvent needs no assistance of copper co-catalysts (since the latter can promote the unwanted dimerization of alkynes). Thus, when the traditional CuI–Et_3N combination in benzene[5] was tried, it brought about the accumulation of monosubstituted products along with unconverted **2** despite complete consumption (IR monitoring) of more than 2 equivalents of an aliphatic alkyne. By contrast, the reaction of **2** with alkynol **3a** (2 equivalents) in pyrrolidine led to symmetrical dienediyne **1a** in 81% yield. Attempts to prepare the monosubstituted iododienyne by condensing **2** with only 1 equivalent of **3a** were unsuccessful, because the selectivity of mono-alkylation was low. As the consequence, both simultaneous and consecutive addition of **3a** and **3b** (1 equivalent of each) to diiodide **2** invariably resulted in a mixture of three or more products.

Nevertheless, for the preparation of unsymmetric dienediynes, the use of two acetylenes of different polarity remains reasonable. In such a case, the target material can be readily separated from symmetric by-products by flash chromatography. In fact, the sequential cross-coupling of diiodide **2** with **3b** and **3a** (1.2 equivalents of each) followed by chromatography on SiO_2 afforded nonadeca-5,7-diene-3,9-diynol **1b** in 44% yield.† Symmetric diol **1a** was also isolated in this operation. To facilitate further manipulations, **1a** was converted into its diacetate **1c**.‡

For the planned transformation of diendiynes **1b**,**c** into skipped (*Z*,*Z*,*Z*)-trienes by ATCC-mediated hydrogenation (η⁶-naphthalene)tricarbonylchromium (NTCC) in THF was obviously the catalyst of choice because it is effective at temperatures as low as 45 °C.[2] Under these conditions, methylene-separated (*Z*,*Z*,*Z*)-trienes **4b**,**c** were obtained as the major products. Their ^{13}C NMR spectra displayed the signals (δ ~25 ppm) of methylene groups flanked by adjacent C=C bonds (=CH–CH_2–CH=), which were equally diagnostic for the *Z*-configured 'skipped' double bonds.[4(b),(c),8,§] Once again, the predominance of this molecular array corroborates a higher affinity of the '$Cr(CO)_3$' species[2] to 1,3-dienes with respect to triple bonds.

In contrast to the clean transformation of alkyl alka-2,4-dien-6-ynoates into skipped (*Z*,*Z*)-dienes,[4] the selectivity of hydrogenation for dienediynes **1b** and **1c** was no higher than 75%. Both the ^1H NMR spectra at 300 MHz and mass spectra (electron ionization at 70 eV) (the $[M + 2]^+$ peak with I_{rel} = 15% in addition to the molecular ion of **4b** with I_{rel} = 8%) showed that the target trienes were contaminated by products with the same carbon skeleton, but with only two double bonds separated by two or more methylene groups. This result was not unprecedented, because chromium carbonyls are known to induce 1,3-hydrogen

† *(*E,E*)-Nonadeca-5,7-diene-3,9-diyn-1-ol* **1b**. Into a degassed solution of diiodide **2** (306 mg, 1 mmol), $PdCl_2 \cdot (PPh_3)_2$ (35 mg, 0.05 mmol) and PPh_3 (35 mg) in dry pyrrolidine (1.5 ml) undec-1-yne **3b** (183 mg, 1.2 mmol) and but-3-yn-1-ol **3a** (84 mg, 1.2 mmol) were consecutively injected within a 10 min interval with stirring, and the reaction was monitored by TLC. In 1 h the mixture was worked up as described earlier[7] and subjected to column chromatography on SiO_2 (eluents: 5, 10 and 20% EtOAc in hexane) to afford 120 mg (44%) of the title compound as white crystals, mp 59–60 °C. UV (EtOH, λ_{max}/nm): 292 and 310. ^1H NMR ($CDCl_3$) δ: 0.90 (t, 3H, *J* 7.2 Hz), 1.20–1.45 (m, 12H), 1.52 (quint., 2H, *J* 6.9 Hz), 1.84 (br. s, 1H), 2.32 (br. t, 2H, *J* 7.0 Hz), 2.61 (br. t, 2H, *J* 7.0 Hz), 3.72 (t, 2H, *J* 6.8 Hz), 5.60 (br. d, 1H, *J* 14.1 Hz), 5.67 (br. d, 1H, *J* 14.1 Hz), 6.43–6.60 (several peaks, 2H). ^{13}C NMR ($CDCl_3$) δ: 14.1 (Me), 19.8, 22.7, 24.1, 28.7, 28.9, 29.1, 29.3, 29.5, 31.9 and 61.1 (CH_2), 79.7, 81.7, 90.4 and 95.3 (C), 112.3, 114.0, 139.7 and 140.5 (CH).

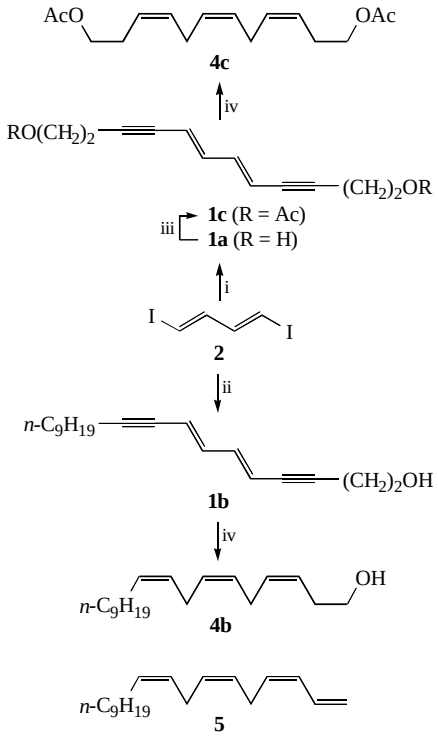
‡ *(*E,E*)-Dodeca-5,7-diene-3,9-diyne-1,12-diol* **1a** was prepared in a similar manner (yield 81%) by treating **2** with **3a** (2 equiv.). ^1H NMR ($CDCl_3$) δ: 1.75 (br. s, 2H), 2.75 (br. t, 4H, *J* 6.6 Hz), 3.75 (t, 4H, *J* 6.6 Hz), 5.26 (br. d, 2H, *J* 14.2 Hz), 6.60 (several peaks, 2H).

*(*E,E*)-1,12-Diacetoxydodeca-5,7-diene-3,9-diyne* **1c** was prepared conventionally (Ac_2O–Py) and isolated by column chromatography as white crystals (mp 69–70 °C). UV (EtOH, λ_{max}/nm): 292 and 308. ^1H NMR ($CDCl_3$) δ: 2.09 (s, 6H), 2.68 (br. t, 4H, *J* 6.6 Hz), 4.17 (t, 4H, *J* 6.6 Hz), 5.24 (br. d, 2H, *J* 15.4 Hz), 6.52 (several peaks, 2H). ^{13}C NMR ($CDCl_3$) δ: 20.1 (CH_2), 20.9 (Me), 62.2 (CH_2), 81.1 (C), 89.9(C), 113.1 (CH), 140.2 (CH), 170.8 (C=O).

§ Dienediynes **1b** or **1c** (0.1 g in 5 ml of THF in both cases) were hydrogenated over NTCC (0.1–0.15 g) in a 50 ml stainless-steel autoclave (50 atm of H_2, 45–60 °C, 2 h). The reaction mixtures were filtered, concentrated *in vacuo*, and subjected to column chromatography (hexane–benzene, 1:1; then hexane–EtOAc, 4:1) to afford compound **4b** (0.04 g, 40%) or **4c** (0.056 g, 56%) as yellowish oil contaminated with 25–30 mol% of the corresponding overhydrogenation products.

*(*Z,Z,Z*)-Nonadeca-3,6,9-trienol* **4b**: ^1H NMR ($CDCl_3$) spectrum is consistent with that reported earlier.[10] ^{13}C NMR ($CDCl_3$) δ: 14.1 (Me), 22.7 (CH_2), 25.6 (CH_2), 25.7 (CH_2), 27.2 (CH_2), 29.3 (CH_2), 29.5 (two peaks, CH_2), 29.6 (two peaks, CH_2), 30.8 (CH_2), 31.9 (CH_2), 62.2 (CH_2), 125.6 (CH), 127.5 (CH), 127.7 (CH), 128.6 (CH), 128.7 (CH), 130.5 (CH), 131.2 (CH), there is a good agreement with the data for the lower C_{12} and C_{15} homologues of **4b**.[8(b),(c)] EI MS, *m*/*z*: 278 ($[M_1]^+$, **4b**, $C_{19}H_{34}O$) and 280 ($[M_2]^+$, dihydro-**4b**, $C_{19}H_{36}O$).

*(*Z,Z,Z*)-1,12-Diacetoxydodeca-3,6,9-triene* **4c**: ^1H NMR ($CDCl_3$) δ: 2.01 (s, 6H), 2.40 (q, 4H, *J* 6.6 Hz), 2.82 (br. t, 4H, *J* 6.1 Hz), 4.09 (t, 4H, *J* 6.6 Hz), 5.30–5.55 (several peaks, 6H). ^{13}C NMR ($CDCl_3$) δ: 20.9 (Me), 25.7 (CH_2), 26.9 (CH_2), 63.7 (CH_2), 124.9 (CH), 128.2 (CH), 130.6 (CH), 170.9 (C=O).



Scheme 1 *Reagents and conditions*: i, $HOCH_2CH_2C{\equiv}CH$ (**3a**, 2 equiv.), $PdCl_2(PPh_3)_2$–PPh_3/pyrrolidine, room temperature, 1 h (81%); ii, *n*-C_9H_{19}-$C{\equiv}CH$ (**3b**, 1.2 equiv.), then **3a** (1.2 equiv.), $PdCl_2{\cdot}(PPh_3)_2$–PPh_3/pyrrolidine, room temperature, 1 h (44%); iii, Ac_2O–Py, room temperature, 1 h (95%); iv, H_2 (50 atm)–(η^6-naphthalene)$Cr(CO)_3$/THF, 45–60 °C, 2 h (*ca*. 56% for **4c** and 40% for **4b**, not optimised).

shifts in linear 1,4-dienes[2] and methyl linolenate,[9] a structurally related triene, which gives rise to a conjugated diene system. In an atmosphere of H_2, the latter undergoes 1,4-*cis*-hydrogenation to give an isolated C=C bond. The formation of diolefinic contaminants, 'dihydro-**4b**' and 'dihydro-**4c**', may be tentatively represented by Scheme 2.

Because the separation of triolefins **4** from their dihydro congeners is technically feasible, *e.g.*, by using silica gel impregnated with $AgNO_3$, and all the intermediates shown in Scheme 1 can be readily prepared from acetylene, the short route from diodide **2** to molecules like **4b** seems to be synthetically attractive. Actually, alcohol **4b** is a known intermediate for the synthesis of (*Z*,*Z*,*Z*)-nonadeca-1,3,6,9-tetraene **5**, the sex pheromone of the winter moth *Operophtera brumata*.[9] Our synthesis of homoconjugated (*Z*,*Z*,*Z*)-trienes represents a new approach to compounds of this chemotype, among which are eicosanoids and a number of lepidopteran insect pheromones (for earlier methodologies, see ref. 10).

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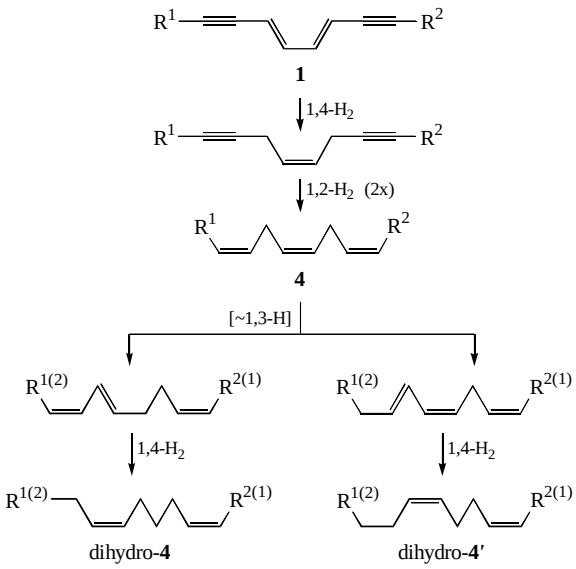

Scheme 2

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