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A NOVEL SYNTHESIS OF LINEAR POLYENES VIA CONJUGATE ADDITION OF CUPRATES TO α,β-γ,δ-DIUNSATURATED SULFONES FOLLOWED BY SO_2 EXTRUSION

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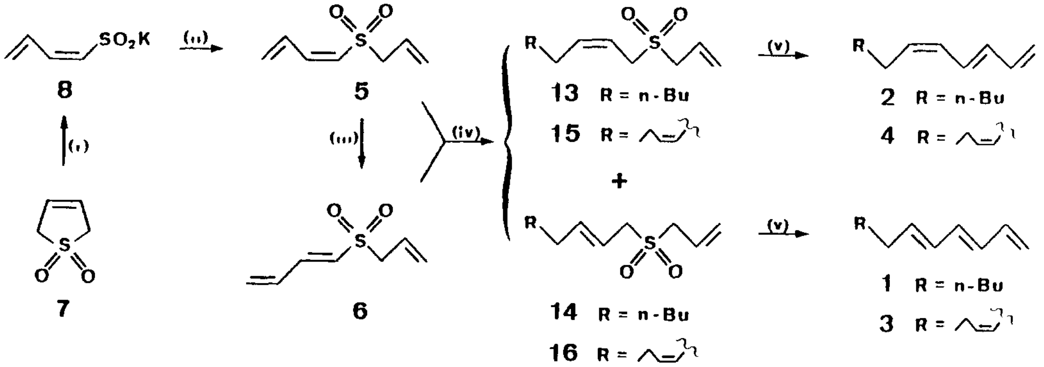
Summary - The two 1,3-butadienyl 2-propenyl sulfones 5 and 6, 1,3,5-heptatriene synthons, have been transformed into the tri- and tetraenes 1 - 4 by alkylcuprate addition and Ramberg-Backlund SO_2 extrusion The reaction stereochemistry is discussed

The undecatrienes 1 and 2, isolated from Galbanum[1,2], also occur, together with the undeca tetraenes 3 and 4, in the seaweeds *Dictyopteris plagiogramma* and *D australis*[4] Isomer 4 has been identified as a gamete secretion in *Spermatochnus paradoxus*[5,6]

The odors of the trienes 1 and 2 are highly appreciated in perfumery[7], and this induced us to develop a new convergent synthesis of 1 - 4 from the common intermediate 5 (and/or 6)[8]



Reagents
- (i) *t*-BuOK/DMSO
- (ii) Allyl bromide/DMSO
- (iii) I_2/heptane
- (iva) Lithium dibutylcuprate/ether
- (ivb) Lithium(*Z*)-di(1-butenyl)cuprate/ether
- (v) CCl_4/KOH/*t*-BuOH/H_2O

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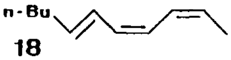

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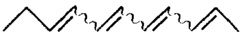

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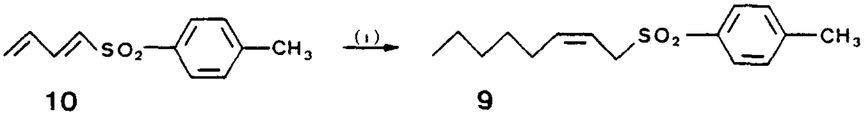
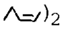
On treatment with strong bases sulfolane 7 undergoes chelotropic ring opening to 8[10,11] which can be alkylated at the sulfinate sulfur atom[11,12,13] We thus prepared a mixture of (*Z*)- and (*E*)-1,3-butadienyl propenyl sulfone 5 and 6, hoping to elaborate these into the polyenes 1 - 4 by a sequence of conjugate alkyl/alkenyl metal addition to the dienyl sulfone site[14] and Ramberg-Backlund sulfur dioxide extrusion[15,16] Although the alkylation step was expected to give only 5 rapid isomerization into 6 occurs under the reaction conditions, in our opinion via a radical process Pure 5 was stable towards bases such as LDA, potassium *t*-butoxide and sodium methylate in THF, DMF, DMSO at temperatures from -78° to $+50^{\circ}$, but was completely converted into 6 by I_2 in heptane (2 h/90°)[13]

Nothing about dialkylcuprate addition to α,β-γ,δ-diunsaturated sulfones was known at the outset of this work To our surprise, only (*Z*)-2-octenyl tosyl sulfone 9 was isolated when lithium dibutylcuprate[18] reacted with (*E*)-1,3-butadienyl tosyl sulfone (cf [19]) The butyl group was thus selectively added to the δ-position (1,6-addition) and the newly formed 2,3-double bond has exclusively (*Z*)-geometry[20] Lower (*Z*)-selectivity was obtained on reaction of substrate 6 (containing 5% 5) and 5 (containing 12% 6) with lithium dibutylcuprate or lithium (*Z*)-di(1-butenyl) cuprate[21] (cf *Table*, entries 2, 3, and 4)



(i) Lithium dibutylcuprate/ether

Organocuprate addition to α,β-γ,δ-diunsaturated sulfones[a]

Entry	Sulfones (ratio)	Cuprate	Products (% of mixture)	Yield (isolated)
1	10	Bu_2CuLi	9 (100%) + 11 (0%)[b]	21%
2	5 + 6 (88 : 12)[b]	Bu_2CuLi	13 (65%) + 14 (35%)[c]	60%
3	5 + 6 (5 : 95)[b]	Bu_2CuLi	13 (79%) + 14 (21%)[c]	46%
4	5 + 6 (21 : 79)[b]	)$_2$CuLi	15 (71%) + 16 (29%)	1.5%

[a] Conditions addition of sulfone to cuprate in ether at -40°, stirring at -40° (1 h) and 0° (2 h), decomposition at 0° by aq NH_4Cl

[b] Determined by GC and ^{1}H NMR

[c] Determined by HPLC and ^{1}H NMR

[d] Determined by ^{1}H NMR

The (*Z*)-geometry of the butenyl group was fully retained during the cuprate addition (cf other examples[14,21]) Owing to polymerization of 5 and 6, the yields of the addition reactions are moderate to low (reaction temperature +25° to -78°) The structures are in agreement with their ^{1}H NMR-data

When a mixture of 13 and 14 (79 21) was subjected to mild Ramberg-Backlund conditions (CCl_4/KOH/*t*-butanol/25° [22]) an undecatriene mixture (42% yield) of 2 (81%), 17 (14%), 1 (2%) and 18 (3%) was isolated[23] As expected, the double bonds already present in 13 and 14 preserved their configurations and the newly formed double bond in the Ramberg-Backlund step was mainly the (*E*)-configuration[15] Analogously, the mixture 15 + 16 (71 29) was transformed into an undecatetraene mixture (48% yield) containing 3 (14 5%), 4 (77 5%) and 19 (8%)[24]

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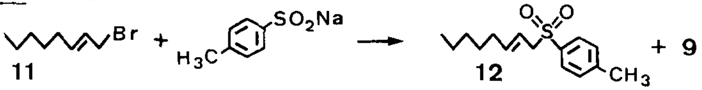

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23 Trienes 1, 2, 17 and 18 were identical in all respects (GC, ^{1}H NMR, MS, UV, IR) with the corresponding samples prepared earlier[3].

24 Tetraenes 3 and 4 were identical in all respects with the corresponding samples prepared by Wittig condensation of phosphorane 20[25] with (*E*)-2,4-pentadienal (21)[26] (inverse addition)

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