3-Oxiranylprop-2-enals as Synthetic Building Blocks.[1] Easy and Stereoselective Synthesis of Naturally Occurring (*E*,*Z*)-1,3,5-Trienes and (*E*,*Z*)-2,4-Dienals, Pheromones and Flavour Components

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Wittig reactions of the title compound (**3**) lead in one step to the (*E*,*Z*)-alkadienyloxiranes (**6**) and (**7**), useful starting materials for the preparation of pheromones and flavour components.

Molecules with conjugated triene substructures are of great interest (*a*) due to their multitude of thermal and photochemical reactions and (*b*) as biologically active natural products (vitamin D, retinals, leukotrienes *etc.*). In connection with the synthesis of constituents from marine brown algae[2] we became interested in a simple and general method for stereoselective synthesis of oxiranylpropenals like (**1**) and (**2**) on a preparative scale.

(*E*,*Z*)-Octa-1,3,5-triene (**1**) (fucoserratene), a pheromone isolated in minute quantities from fertile eggs of *Fucus serratus*, displays interesting chemotactic properties.[3] However this material was only available *via* multi-step and non-stereoselective routes requiring tedious g.l.c. separations.[4] Equally difficultly accessible was (*E*,*Z*)-undeca-1,3,5-triene (**2**), a constituent of the essential oils of *Dictyopteris algae*[5,†] and *Ferula galbaniflua* (Umbelliferae).[6]

In contrast to its (*E*,*E*)-isomer, the triene (**2**) displays attractive and excellent olfactory properties and is therefore used in the perfume industry. While (*E*,*E*)-1,3,5-trienes are conveniently accessible *via* Wittig reactions from commercially available (*E*,*E*)-hexa-2,4- and -deca-2,4-dienals,[7] a simple and general route to compounds like (**1**) and (**2**) from readily available starting materials had to be developed.

Z-Stereoselective Wittig reactions (silazide method)[8] of (*E*)-3-oxiranylprop-2-enal (**3**)[1,9] with propylidene- and hexylidenetriphenylphosphoranes (**4**) and (**5**) produced the (*E*,*Z*)-hexa- and -nona-1,3-dienyloxiranes (**6**) (85%) and (**7**) (80%), respectively, with high isomeric purities (96 ± 2%).

Compounds (**6**) and (**7**) were simply deoxygenated in a quasi 'one-pot procedure' as follows: (*a*) conversion into the corresponding thiiranes (**8**) and (**9**) (sat. aqueous thiourea, $NaHCO_3$, room temp., 4 h >95%); (*b*) desulphurisation of crude (**8**) and (**9**) with Ph_3P (1.1 mol equiv. Ph_3P, Et_2O, room temp., 15 min, >95%, 85% after distillation).

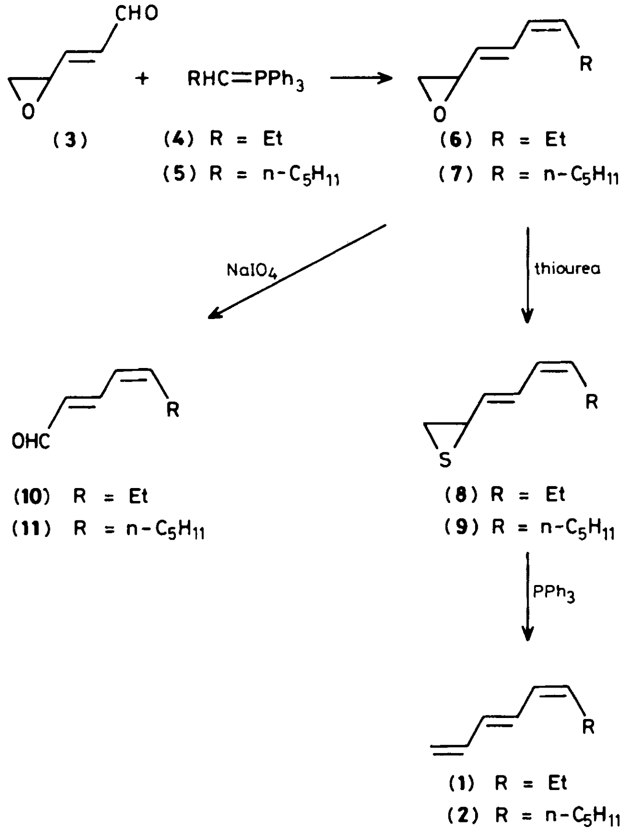
Compounds (**1**) and (**2**) are thus easily accessible in 10—20 g quantities in two simple steps with *ca.* 70% overall yield and isomeric purities of 96 ± 2%. Compound (**1**) was identical in all respects with natural fucoserratene, including its pheromone activity towards the spermatozoa of *Fucus serratus*.[‡]

Compound (**2**), again identical with the natural product isolated from *Dictyopteris algae* and *Ferula galbaniflua*, was tested organoleptically[§] and found to have excellent olfactory properties, in spite of the sulphur containing precursor (**9**).

[†] The biological function of (**2**) in dictyopteris is still somewhat obscure.

[‡] Compound (**1**) was identical with natural fucoserratene spectroscopically (^1H n.m.r., u.v.) and on two g.l.c. columns of different polarity. We are grateful to Professor Dr. D. G. Müller, University of Konstanz, for biological tests of our synthetic (**1**).

[§] G. Ohloff and W. Pickenhagen, Firmenich SA, Genève, Suisse.



Scheme 1

Surprisingly, (**9**), a stable compound, was also found to possess excellent olfactory properties after purification (SiO_2, CCl_4).

The oxiranes (**6**) and (**7**) are useful synthetic intermediates for the preparation of (*E*,*Z*)-hepta-2,4-dienal (**10**) and (*E*,*Z*)-deca-2,4-dienal (**11**), respectively.[11] Thus (**6**), by oxidation with $NaIO_4$ in H_2O/THF produces (**10**) (a tea[11] and tomato flavour[12] component), while (**7**) yields (**11**) (a flavour component of peanuts and carrot root[13]), both with 90% isomeric purity.[14] Compound (**7**) also closely resembles the 'lower portion' of the leukotrienes and can be considered as a building block for derivatives of leukotriene B.[15]

The described synthetic method is clearly generally applicable, allowing a convenient entry into a class of compounds which hitherto has been accessible only with difficulty.

We thank H. J. Bestmann (Erlangen), G. Gassmann (Helgoland), D. G. Müller (Konstanz), and G. Ohloff (Firmenich SA, Genève) for their kind contributions towards this project. We also thank the Deutsche Forschungsgesellschaft and the Fonds der chemischen Industrie for financial support.

Received, 8th May 1987; Com. 623

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