Long-chain Enals *via* Carbonyl–Olefin Metathesis. An Application in Pheromone Synthesis

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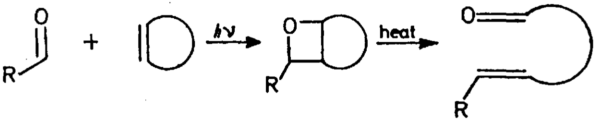
Summary 7-Phenylhept-6-enal and non-6-enal have been obtained from readily available materials through consecutive photochemical cycloaddition and selective thermal cycloreversion steps involving bicyclic oxetans as intermediates; subsequent reduction in one of the series produces *trans*-non-6-en-1-ol, an insect pheromone.

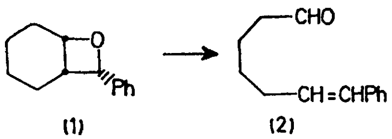
Recently we reported the potential synthetic utility of the photochemical Paterno-Buchi cycloaddition of carbonyl compounds and olefins in carbonyl-olefin metathesis, as shown for cyclic olefins in equation 1.[1] We now report two applications of this reaction to the preparation of long-chain enals, one of which leads to an important natural product.

Photolysis of benzaldehyde and cyclohexene[2] gave, after column chromatography, the bicyclic oxetan (**1**) (35%). The stereochemistry of the adduct was investigated (assuming the more likely *cis*-ring fusion) since careful examination of the oxetan chromatographic fraction revealed the presence of two isomers in a ratio of 8 : 1. The n.m.r. spectrum showed δ 5·81, [d, J 7 Hz, (major)] and 5·32, [d, J 5 Hz (minor)] assigned to benzylic hydrogens α to oxygen. The assignment of the *endo*-configuration to the major oxetan product follows from the n.m.r. data using the criteria of Barltrop[3] and Yang[4] (lower field and higher coupling constant for *cis* vicinal ring protons) and from the relative deshielding of aryl protons for the minor isomer on addition of Eu(fod)$_3$.

Cracking of (**1**) (predominantly *endo*-) proceeded under several sets of conditions with generally good yields and varied stereochemistry (Table).† The 7-phenylhept-6-enals (**2**) were identified by elemental analysis, i.r. and n.m.r. spectral data, and ozonolysis with oxidative workup to adipic and benzoic acids. Stereochemical assignments



(1)



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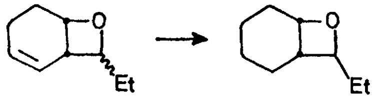

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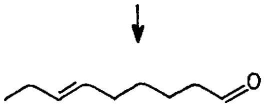

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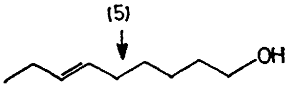

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† Mechanistic details will be subsequently reported.

were based on i.r. bands at 960 and 725 cm^{-1} assigned to *trans*- and *cis*-isomers, respectively[5]) and n.m.r. spectra (relative chemical shifts of C-6 protons[6] and vicinal vinylic coupling constants[7]).

Table

Products and conditions for cycloreversion of (**1**) to (**2**).

Reaction conditions	Yield/%	Stereochemistry of (**2**) (*cis* : *trans*)
G.l.c. injector port pyrolysis, 250°	—	2·6
Flow pyrolysis, 400°, 35 ml min^{-1}	23	2·6
Benzene–TsOH, 25°	94	0·41
Benzene–$[Rh(CO)_2Cl]_2$, 80°	70	0·31

Irradiation of propionaldehyde and cyclohexene did not produce the cycloadduct but led to products of the photoreduction type.[8] On the other hand, photolysis (450 W Hanovia immersion apparatus, Corex filter) of propionaldehyde and cyclohexa-1,3-diene[9] in acetonitrile gave (**3**) (80% *exo*-[9]) in 77% yield. Hydrogenation (PtO_2, EtOH, 1 atm.) proceeded quantitatively and pure (**4**) was conveniently obtained in 5—10 g quantities by preparative g.l.c. (FFAP, 140°). Pyrolysis of (**4**) in a packed Pyrex tube (nitrogen flow) at 270—340° gave (**5**) in fair yield. More conveniently (**5**), identified by i.r. and n.m.r. spectra and by mixed m.p. of its 2,4-dinitrophenylhydrazone derivative with that of authentic *trans*-non-6-enal,[10]‡ was obtained by treatment of (**4**) with $[Rh(CO)_2Cl]_2$ in benzene under reflux (89%). Further g.l.c. comparison of the product of rhodium catalysed cleavage with authentic *cis*-6-nonenal‡ revealed that cycloreversion was $> 95\%$ stereoselective.† Early examples here and elsewhere[11,12] of the thermal or catalysed decomposition of bicyclic oxetans indicate high regioselection in favour of metathesis products over regenerated carbonyl–olefin pairs. Thus long chain alcohols, aldehydes, acids, and esters could be synthesised using the photolysis-pyrolysis sequence.

Carbonyl–olefin metathesis can also be applied to the synthesis of insect pheromones, many of which have been identified as derivatives of long-chain unsaturated aldehydes.[13] We have synthesised *trans*-non-6-en-1-ol, a sex attractant of the Mediterranean fruit fly.[14] Obtained in virtually quantitative yield by $LiAlH_4$ reduction of (**5**), the alcohol (**6**), b.p. 83—87°, 0·25 mm Hg (lit.[15] b.p. 76—84°, 0·2 mm Hg), is identical with the authentic pheromone (i.r. and n.m.r. spectra and g.l.c. retention time).‡ The four-step stereoselective metathesis route from propionaldehyde and cyclohexa-1,3-diene (overall yield 40—50%) is a convenient alternative to the eight-step synthesis previously reported.[15]

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