THE THERMAL REORGANIZATION OF 1,2-EPOXITROPYLIDENE

P.W. Schiess and M. Wisson

Institut für Organische Chemie, Universität Basel, Switzerland

The thermal reorganization of hetero-analogues of bicyclic vinyl cyclo-propanes has received considerable attention in recent years (1). In this communication we wish to report the synthesis and the facile thermal rearrangement of 1,2-epoxitropylidene $\underline{1}$, a heterocyclic counterpart of 1,2-homotropylidene (2).

Oxidation of tropylidene with one equivalent of peracetic acid in methylene chloride solution in the presence of potassium carbonate (3) leads to the 1,2-epoxide $\underline{1}$ which is obtained as a colourless oil (bp. 59.0 - 59.5° at 13 mm) in 25 % yield after separation from excess tropylidene and from minor byproducts by careful destillation through a 1 m spinning band column.

Compounds identified in the pyrolysis mixture obtained from 1,2-epoxi-tropylidene $\underline{1}$.

	yield	pyrolysis temperature	Reference
$CH_2=CH-(CH=CH)_2-CHO$ $\underline{2}$	36 %	270°	
$\underline{3}$ + $\underline{4}$	5 %	270°	(5)
$\underline{5}$	16 %	315°	(6)
-CHO $\underline{6}$	34 %	400°	(7)
-CHO $\underline{7}$	26 %	400°	(8)
benzylalcohol	2 %	450°	
benzaldehyde	11 %	450°	
o-cresol	7 %	450°	
benzene	40 %	600°	
1,3-cyclohexadiene	5 %	600°	
1,2-cyclopentadiene	2 %	600°	

Vapour phase pyrolysis of 1,2-epoxitropylidene $\underline{1}$ at 0.1 mm pressure between 200 and 500° (contact time: 0.1 to 0.2 sec.) leads in high yield to a mixture of isomeric compounds of formula C_7H_8O accompanied by benzaldehyde. After separation by glpc the known components of this mixture (rf. Table) have been identified

through their IR-, UV- and NMR-spectra and by their glpc-retention times. The **previously** unknown 2,4,6-heptatrienaldehyde 2 is formed as a mixture of its stereoisomers as could be inferred by the observation of four doublets (J = 7 cps) at 9.51, 9.56, 10.11 and 10.16 ppm in the NMR-spectrum of the crude product obtained upon pyrolysis between 200 and 300°. These signals are assigned the aldehyde proton in the 2-trans,4-trans-, 2-trans,4-cis-, 2-cis, 4-trans- and 2-cis,4-cis-isomer of 2 respectively (4). Upon treatment with dilute acid or upon attempted separation by preparative glcp this mixture is converted to the most stable trans,trans-isomer of 2 (bp. 60 - 70° at 12 mm; IR(film): 1680, 1613 cm^{-1}; UV(ether): 298 nm/31'000, 288 nm/32'500; NMR(CCl$_4$): 9.51 ppm doublet, J = 7 cps, -CH=O; Dinitrophenylhydrazone: red needles, mp. 140 - 141°).

Pyrolysis of 1 at 600° leads to the formation of volatile degradation products to a considerable extent. Among these benzene (40 %), 1,3-cyclo-hexadiene (5 %) and cyclopentadiene (2 %) have been positively identified. Furthermore a small amount of ketene is formed as indicated by the isolation of acetanilide(2 %) after addition of aniline to the volatile reaction product.
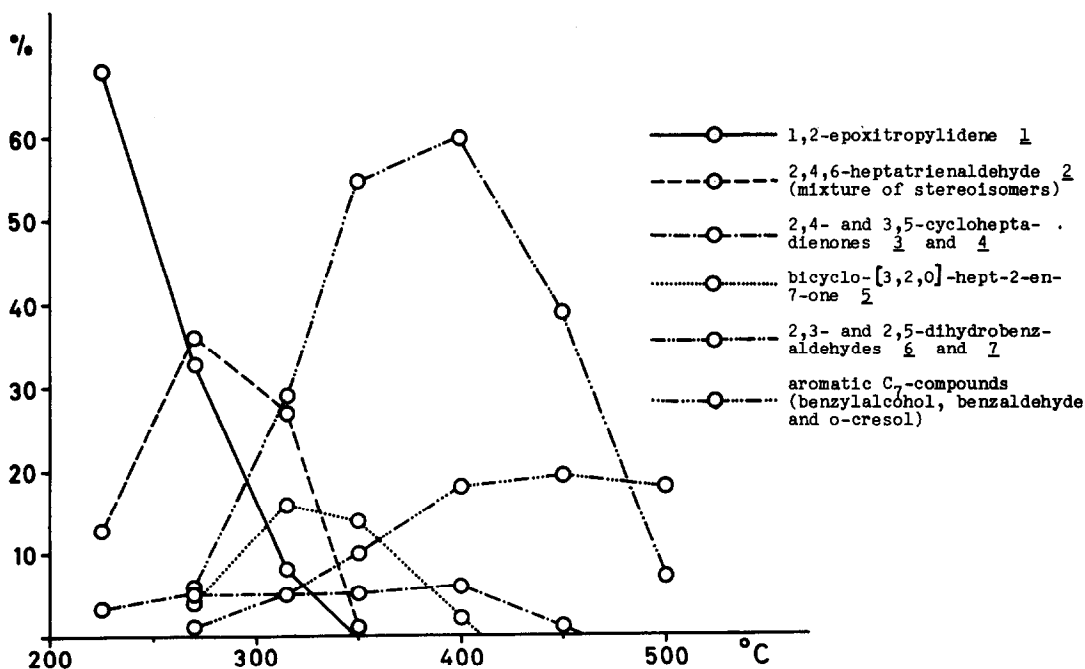

Yield of C$_7$-compounds obtained by vapour phase pyrolysis of 1,2-epoxi-tropylidene 1 as a function of temperature.

The composition of the pyrolysis product mixture is strongly dependent of the pyrolysis temperature (figure). It is evident that the cycloheptadienones 3 and 4 and the stereoisomeric aldehydes 2 are both primary reaction products, formed concurrently from epoxide 1.

The formation of the cyclic ketones 3 and 4 is inferred as proceeding by a heterolytic process catalyzed by active sites on the glass surface of the pyrolysis chamber or by trace impurities as has been suggested in related reactions (1a, 9). In a separate experiment it could be shown that 3 and 4 which rapidly interconvert above 200° (5) are the precursors of the 1,3-cyclohexadiene formed at 600°.

Heptatrienaldehyde 2 and bicyclo[3.2.0]hept-2-en-7-one 5 lead to the same product mixture upon pyrolysis at 400° as epoxide 1. They must therefore be intermediates in the main reaction path leading from 1 to thermally stable aromatic products. While there are several different mechanistic pathways for the formation of 2 from 1 which cannot be decided upon at the moment, this reaction finds its close analogy in the thermal rearrangement of 1,2-homo-tropylidene (2) and 2,3-homoazepine (1b) recently described. Electrocyclic ring closure of 2 is expected to lead to 1,6-dihydrobenzaldehyde 8 which constitutes a reasonable precursor of its conjugated isomers 6 and 7. The yield of benzyl-alcohol and benzaldehyde varies considerably from run to run. This indicates that these two compounds are formed at least partially after pyrolysis during workup and preparation of the samples for analysis (10).
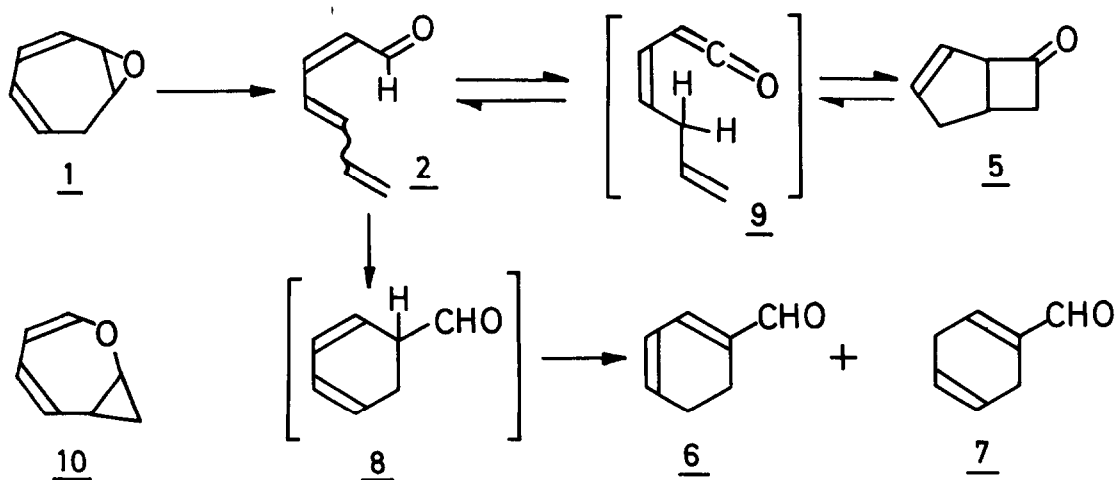
The isolation of bicyclic ketone 5 as product of thermolysis of 1 or 2 was unexpected. Its formation points to the occurrence of the unsaturated ketene 9 as an intermediate from which 5 could be formed through an intra-molecular cycloaddition reaction (11). Ketene 9 could be generated from one of the 2-cis-isomers of 2 by a novel 1,5-shift of the aldehyde hydrogen (12).

This 1,5-hydrogen shift must be a reversible process since the same product
mixture derived through cyclization of 2 is obtained on pyrolysis starting
with ketone 5 as with epoxide 1 or aldehyde 2. A fragmentation to cyclopenta-
diene and ketene does constitute at best a minor thermal reaction pathway
for 5.

Finally it should be emphasized that there is no indication of formation
of 2,3-homooxepine 10 from 1 in the course of the pyrolysis reaction. The
question whether a C_7H_8O-isomer of structure 10 is bypassed in the thermal
reorganization of 1 of whether 10 is actually formed as in the nitrogen
homomorphous system (1b) but rearranges at a rate faster than 1 is under active
investigation.

Footnotes and References

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(4) The stereochemical assignment rests i.a. on the chemical shift values for the
    formyl hydrogens. These hydrogens are expected to be more strongly deshielded
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(10) Benzaldehyde characteristically is the main monomer product formed at the
    exclusion of dihydrobenzaldehydes 7 or 8 if a solution of 1 in CCl_4 is
    heated at 175° for one hour.

(11) For a discussion of the two possible modes of intramolecular cycloaddition of
    a structurally similar ketene see: W.F. Erman, R.S. Treptow, P. Bakuzis and
    E. Wenkert, J. Amer. chem. Soc. 93, 657 (1971).

(12) Formation of a ketene from an unsaturated aldehyde by a 1,5-hydrogen shift
    has been observed upon irradiation in a related system: Chr. Suter and P.
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    A reversible intramolecular 1,5-shift of an aldehyde hydrogen to a ketene
    function has recently been evoked in the explanation of the thermal inter-
    conversion of 3- and 5-alkyl-2-pyrones by W.H. Pirkle, H. Seto and W.V.
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