NOTES

Pyrolytic rearrangement of norbornene oxide[1]

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Norbornene oxide (4), stable to pyrolysis at 500°, rearranges at 550° to give Δ^3-cyclohexenylcarboxaldehyde (8), norcamphor (6), and Δ^2-cyclopentenone (7).

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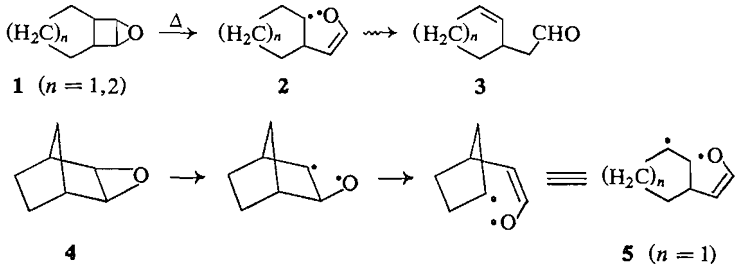
Introduction

The formation of cycloalkene acetaldehydes (**3**) from the pyrolysis of bridged cyclobutene epoxides (**1**) led to the consideration of a diradical intermediate **2** (1,2) (see Scheme 1). It appeared plausible that the pyrolysis of *exo*-2,3-epoxybicyclo[2.2.1]heptane (**4**, norbornene oxide) might give similar products via the closely related intermediate **5**. To examine this possibility, norbornene oxide was subjected to pyrolysis in a fashion similar to that reported for the pyrolysis of the cyclobutene epoxides (1).

Results

The solid epoxide (**4**) was added in small portions to a vertical pyrolysis column packed with glass helices under slow nitrogen flow. At temperatures up to 500°, the epoxide passed through the heated column unchanged but at 550° it was completely transformed into a large number of compounds. Analysis by vapor phase chromatography (v.p.c.) showed three major peaks whose ratios varied slightly from run to run. Samples of these three products were collected from the gas chromatograph and shown to be (in order of appearance) **7** (5–10%), **8** (62–67%), and **6** (5–10%) by spectral analysis and comparison with authentic samples. Percentage compositions refer to the relative areas observed for the different components in the chromatogram. A comparison of v.p.c. retention times showed that **3** (n = 1) was not present in the pyrolysate. These results are similar to those reported by Crandall for the acid catalyzed rearrangement of **4** which gives **6** and **8** (in approximately equal amounts) and nortricyclanol as primary products but no **7** (3). Norcamphor is not an intermediate in this reaction being stable to pyrolysis at 550°.



Scheme 1

Discussion

Schematically, intermediate **9** could account for the observed products (equation A, Scheme 2) but various mechanisms can be considered depicting either homonuclear or heteronuclear

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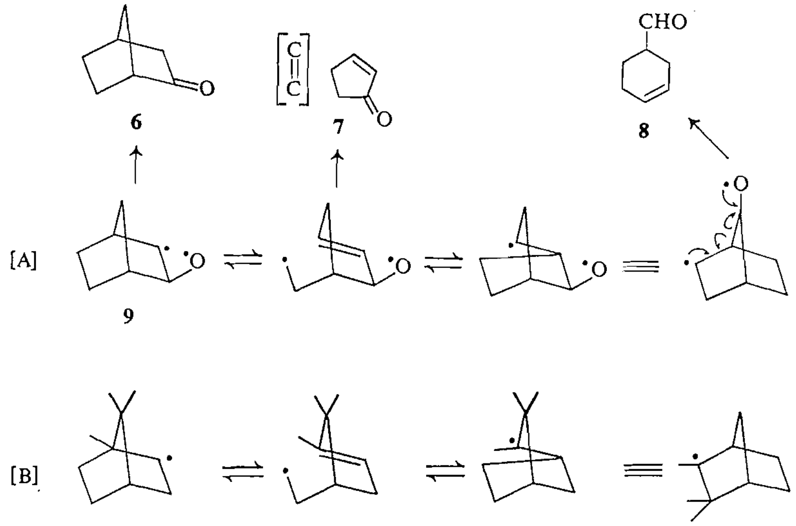

SCHEME 2

cleavage. (A referee has suggested the formation of **7** via a retro Diels–Alder reaction of the enol of norcamphor derived directly from **9**.) This intermediate (**9**) is analogous to that reported (4) for the rearrangement of the camphane radical (equation B, Scheme 2).

Experimental

Melting points and boiling points are uncorrected.

Norbornene Oxide (4)

Following the epoxidation procedure of Korach, Nielsen, and Rideout, norbornene (8.0 g, 0.085 mole) was reacted with 18 g of a 40% peracetic acid solution (FMC Corp., 0.095 mole) over 0.5 h, maintaining the temperature at 20° (5). The crude product was sublimed at atmospheric pressure using an oil bath at 130° to give 7.0 g (75%) of a white crystalline material m.p. 120–122° [lit. m.p. 118–119° (6) and 125–127° (7)]; infrared (i.r.) (CCl$_4$): 848 cm^{-1}. The peracid preparation of **4** is reported to give an isomeric composition that is 94% *exo* and 6% *endo* (8).

Pyrolysis of 4

Norbornene oxide, in *ca.* 50 mg portions, was manually dropped onto a vertical column of glass helices in a temperature control oven kept under continual nitrogen flow occasionally broken for 2–3 seconds for addition of the epoxide. Products were separated and collected by v.p.c. using a Perkin–Elmer RX column (two meter, 1/4" diameter column utilizing Ucon oil LB-550-X on diatomaceous earth) at 125°. The retention times for the products (in min) were 7.0 (**7**), 10.1 (**8**), and 13.2 (**6**).

Δ^2-Cyclopentenone (7)

The nuclear magnetic resonance (n.m.r.) spectrum of the unsaturated ketone, collected by preparative v.p.c. from the pyrolysis of **4**, was consistent with that reported (9). The 2,4-dinitrophenylhydrazone was deep red and had m.p. 165–166°; lit. m.p. 165–166° (10).

Δ^3-Cyclohexenylcarboxaldehyde (8)

The n.m.r. and i.r. spectra of the aldehyde from the pyrolysis of **4** was identical to that of an authentic sample of Δ^3-cyclohexenylcarboxaldehyde (kindly supplied by Dr. H. E. Hennis, Dow Chemical Co., Midland, Michigan). The 2,4-dinitrophenylhydrazone had m.p. 176–177°; lit. m.p. 176–177° (11).

Norcamphor (6)

The i.r. spectrum of the solid ketone was superimposable with that of an authentic sample (Aldrich Chemical Co., Inc.). The 2,4-dinitrophenylhydrazone had m.p. 131–131.7°; lit. m.p. 130–131.5° (12).

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