

# Photospecific cleavage of one of the cyclopropyl $\sigma$ -bonds of vinylnorcaradienes

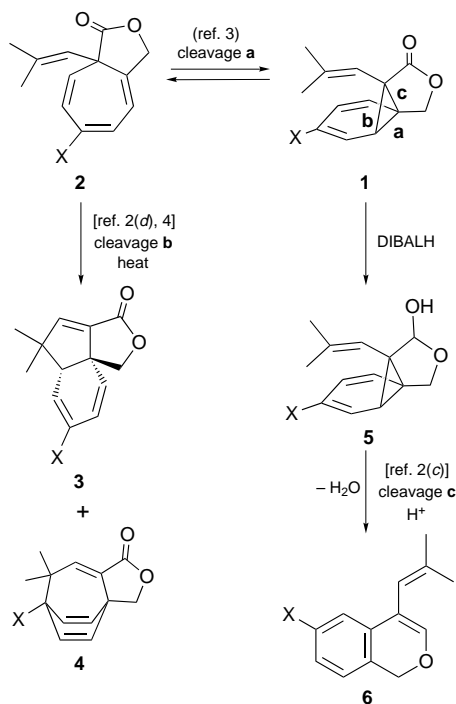
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The benzophenone sensitised photochemical reaction of vinylnorcaradiene derivatives **1**, 5-(2-methylprop-1-enyl)-3-oxatricyclo[4.4.0.0<sup>1,5</sup>]deca-7,9-dien-4-ones, resulted in the regioselective cleavage of one of the cyclopropyl  $\sigma$ -bonds to afford the isochroman-3-one derivatives **7**.

With the release of the large ring strain as a powerful driving force, the cleavage and ring expansion of the cyclopropyl ring has been intensively studied and demonstrated to be a useful synthetic tool.<sup>1</sup> The selective cleavage of one of the three cyclopropyl  $\sigma$ -bonds is an interesting subject from both mechanistic and synthetic view points. If the cleavage is perfectly controlled, then one of the three modes of rearrangement can be utilised at choice starting from the same compound. To the best of our knowledge, such a control has never been cited.

In our study of stable tricyclic vinylnorcaradienes **1**,<sup>2</sup> we have been interested in the photo- and thermo-specific, and regioselective cleavage of the cyclopropyl  $\sigma$ -bonds in the norcaradiene structure. The following three types of cleavage are possible (Scheme 1). The cleavage of bond **a** results in the formation of cycloheptatriene **2**, which corresponds to the norcaradiene–cycloheptatriene equilibrium.<sup>3</sup> The cleavage of the bond **b** has been reported in the thermal rearrangements of vinylnorcaradienes to afford vinylcyclopropane–cyclopentene and Cope rearrangement products, **3** and **4**, respectively.<sup>4</sup> The third type of cleavage, the cleavage of bond **c**, has been shown in the acid-catalysed dehydrative aromatisation of lactols **5**

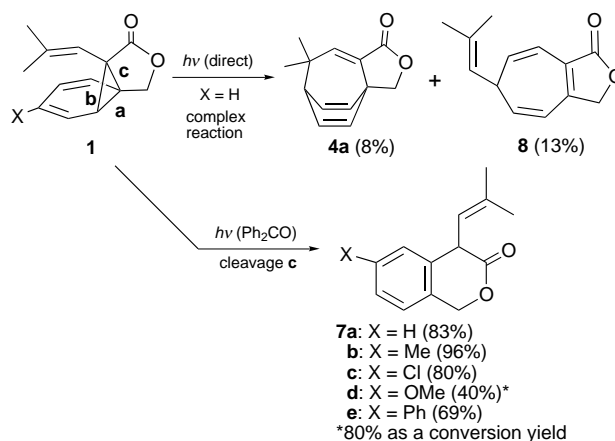


Scheme 1

derived from the reduction of **1** to afford **6**.<sup>2c</sup> Here we report on cleavage **c** of **1** which results in the formation of **7** directly.

Since the thermal reaction of **1** led to the cleavage of the cyclopropyl  $\sigma$ -bond **b**,<sup>2d,4</sup> we have investigated the photochemical reaction. In order to survey which part of the molecule, the diene or the carbonyl moiety, would act as the chromophore and be responsible for the photochemical reaction, a PM3 calculation of **1a** was carried out. The calculation showed that the lobe of the 1,3-diene moiety was much larger than the rest of the molecule in the LUMO of **1a**. The carbonyl moiety contributed to the excited state of **1a** in its next LUMO. The energy difference between the two states, the LUMO and the next LUMO, was large (0.94 eV). Therefore, the photochemical reaction of **1a** could possibly be initiated from the excited state of the 1,3-diene moiety.

Direct irradiation of a benzene solution of **1a** ( $X = H$ ,  $2.5 \times 10^{-2}$  M) in a Pyrex test-tube cooled in a water bath was carried out externally with a 400 W high pressure mercury lamp for 5 h through a Pyrex filter under argon bubbling. The photoreaction was complex and two products, **4a**<sup>2d</sup> ( $X = H$ , 8%) and **8** (13%) (Scheme 2),<sup>†</sup> were isolated in low yields by preparative HPLC purification together with 35% recovery of **1a**. The Cope rearrangement product **4a** was the result of the cleavage of bond **b** and **8a** was derived from the 1,5-shift of vinyl group from cycloheptatriene **2a**. The Cope rearrangement product **4a** can also be obtained thermally, however its formation requires heating at over 130 °C.<sup>2d</sup> Therefore, **4a** is almost certainly the photochemical product in the present case. No product corresponding to the rearrangement *via* the cleavage of bond **c** was found. However, when the reaction of **1a** ( $X = H$ , 0.12 mmol) was sensitised by the addition of benzophenone (1 equiv.) in benzene (10 ml) and irradiated with a 400 W high pressure mercury lamp for 70 min, **7a** ( $X = H$ ) was obtained in 83% yield as a sole product.<sup>†</sup> The triplet excited state of the 1,3-diene moiety is probably responsible for the photorearrangement. This benzophenone sensitised photorearrangement also worked well for other vinylnorcaradienes **1b** ( $X = Me$ ), **1c** ( $X = Cl$ ), **1d** ( $X = OMe$ ) and **1e** ( $X = Ph$ ) to give the



**7a**:  $X = H$  (83%)  
**b**:  $X = Me$  (96%)  
**c**:  $X = Cl$  (80%)  
**d**:  $X = OMe$  (40%)\*  
**e**:  $X = Ph$  (69%)  
\*80% as a conversion yield

Scheme 2

corresponding rearrangement products **7b–7e** in 96, 80, 40 (80% as a conversion yield) and 69% yields with irradiation times of 70, 80, 75, 60 and 720 min, respectively.† The reason for the relatively low photoreactivity of **1e** compared to the others is unclear. The phenyl substituent on the diene lowers the energy of the LUMO, from  $-0.31$  eV for **1a** to  $-0.66$  eV for **1e** as calculated by PM3, which might be responsible for inefficient energy transfer. The multiplicity dependent photochemical reaction of cyclohexa-1,3-diene derivatives has been reported.<sup>5</sup> In the present work, the selective cleavage of the cyclopropyl  $\sigma$ -bond **c** requires such a multiplicity dependent reaction of a cyclohexa-1,3-diene chromophore.

The results show a nice contrast to that of the reported thermolysis (cleavage of bond **b**) and provide useful information on the photochemistry of cyclopropane derivatives.<sup>6</sup>

## Footnotes and References

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† All photo-products gave satisfactory spectral data. Selected data for compound **7a**: mp 78.5–79.5 °C;  $\nu_{\max}$ (KBr)/ $\text{cm}^{-1}$  1730;  $\delta_{\text{H}}$ (270 MHz,  $\text{CDCl}_3$ ) 1.76 (3 H, d,  $J$  1.4 Hz), 1.93, (3 H, d,  $J$  1.4 Hz), 4.41 (1 H, d,  $J$  8.9 Hz), 5.31 (1 H, d,  $J$  13.9 Hz), 5.38 (1 H, d,  $J$  13.9 Hz), 5.45 (1 H, qd,  $J$  1.4, 1.4 and 8.9 Hz), 7.39–7.18 (m, 4 H);  $\delta_{\text{C}}$ (22.4 MHz,  $\text{CDCl}_3$ ) 18.29 (q), 25.74 (q), 44.66 (d), 69.21 (t), 116.95 (d), 124.68 (d), 125.90 (d), 127.12 (d),

128.70 (d), 131.57 (s), 134.49 (s), 138.34 (s), 171.97 (s) [Found:  $\text{MH}^+$ , 203.1065.  $\text{C}_{13}\text{H}_{15}\text{O}_2$  ( $\text{MH}^+$ ) requires 203.1072].

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