

Selective Hydrogen-atom Transfer–Rearrangement in the Norbornene System

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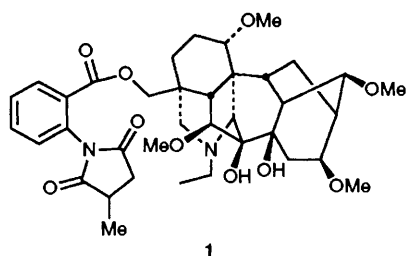
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The aryl radical derived from **3** undergoes hydrogen-atom transfer followed by rearrangement to **5** instead of cyclization to **2**; the crystal structure of **5** is determined.

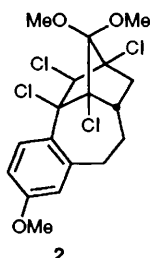
Although a variety of fused ring systems have been constructed using radical chemistry, comparatively few bridged systems have been prepared.¹ A recent notable exception is the elegant generation of the taxane ring system by Pattenden.² The challenging architecture plus the fascinating biolog-

ical activity of methyllycaconitine **1**³ prompted us to explore a direct synthetic route to ketal **2** based on an intramolecular radical cyclization.

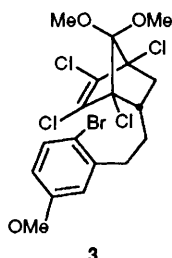
Bromide **3** was readily constructed in 98% yield by a Diels–Alder reaction between the dimethyl ketal of tetrachlo-



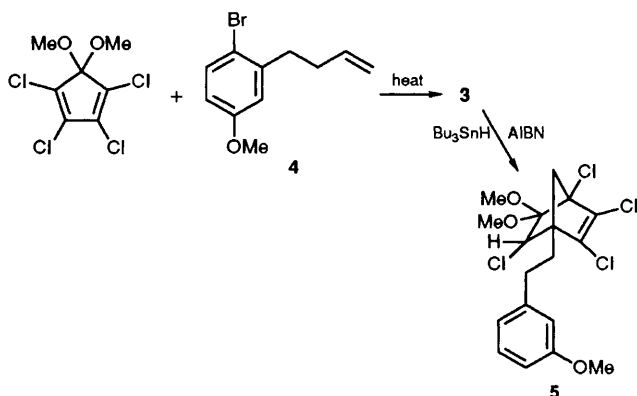
1



2

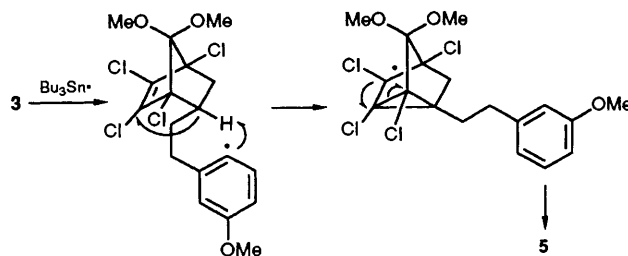


3



Scheme 1

rocyclopentadienone and bromide **4** (neat) at 150 °C for 10 h, Scheme 1. The *endo* stereochemistry of **3** was supported by COSY and NOESY 2D-NMR experiments. The reaction of **3** with tributyltin hydride and azoisobutyronitrile (AIBN) in hot toluene (12 h) appeared to form **2** in 55% yield. The assignment of structure was based on the ¹H NMR and mass spectrum. Since much of the structure could not be defined by NMR, we determined the structure by X-ray crystallography and to our surprise found that we had actually produced ketal



Scheme 2

5.† A tentative mechanism based on a selective intramolecular hydrogen-atom transfer reaction is illustrated in Scheme 2.

Aryl-radical-transfer reactions are becoming more widely utilized in organic chemistry.⁴ Although norbornene radicals are known to rearrange,⁵ the initiation of this rearrangement by an intramolecular radical-transfer reaction has no precedent. The overwhelming preference for hydrogen-atom transfer over the intramolecular radical addition to a strained alkene is particularly surprising.⁶

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References

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- 3 K. Wiesner *Experientia*, 1970, **26**, 471 and references cited therein. For reference to the biological activity of **1**, see: J. M. Ward, V. B. Cockcroft, G. G. Lunt, F. S. Smillie and S. Wonnacott *FEBS Lett.*, 1990, **270**, 45.
- 4 D. P. Curran, A. C. Abraham and H. Liu, *J. Org. Chem.*, 1991, **56**, 4335; V. Sniekus, J.-C. Cuevas, C. P. Sloan, H. Liu and D. P. Curran, *J. Am. Chem. Soc.*, 1990, **112**, 896; D. P. Curran and C. E. Schwartz, *J. Am. Chem. Soc.*, 1990, **112**, 9272.
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† *Crystal data*: colourless thin plates of C₁₈H₂₀O₃C₁₄; space group *P2₁/c* with *a* = 12.108(5), *b* = 11.370(2), *c* = 14.250(3) Å, α = 90.0, β = 94.09(2), γ = 90.0° at –50(1) °C with *Z* = 4 using Mo-Kα (λ = 0.71073 Å) monochromated incident beam. Number of unique data 1214 with *F_o²* > 2.5σ(*F_o²*) and 226 parameters yielded a final *R* = 0.047, *R_w* = 0.056. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.