Atypical carbon–carbon bond scission and deoxygenation in the protonation of tungsten-η^1-oxabicyclic compounds

Lin-Hung Shiu, Hsin-Kuo Shu, Da-Hsin Cheng, Sue-Lein Wang and Rai-Shung Liu*

Department of Chemistry, National Tsing Hua University, Hsinchu, 30043, Taiwan, Republic of China

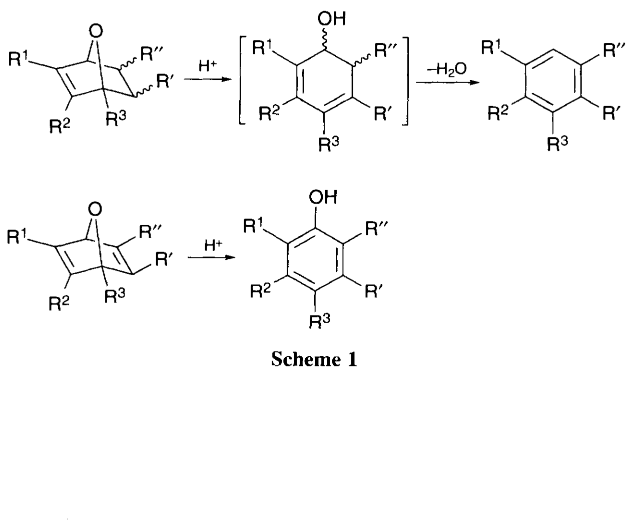
Treatment of tungsten-η^1-7-oxabicyclo[2.2.1]heptadiene and -η^1-7-oxabicyclo[2.2.1]heptene with CF_3SO_3H leads to atypical carbon–carbon bond scission and deoxygenation; the reaction intermediates in the bond scission involves a tungsten-η^1-2-hydrofurylium cation.

7-Oxabicyclo[2.2.1]heptene and 7-oxabicyclo[2.2.1]heptadiene are useful compounds in the syntheses of biologically active molecules. One important transformation in such syntheses involves the treatment of these compounds with a strong Brønsted acid to cleave the oxygen bridge, yielding functionalized benzenes and phenols respectively, Scheme 1. Such a pathway is typical in organic chemistry.[1–2] Here we report the protonation of tungsten-η^1-oxabicyclic complexes in which uncommon carbon–carbon scission and deoxygenation reactions are observed.

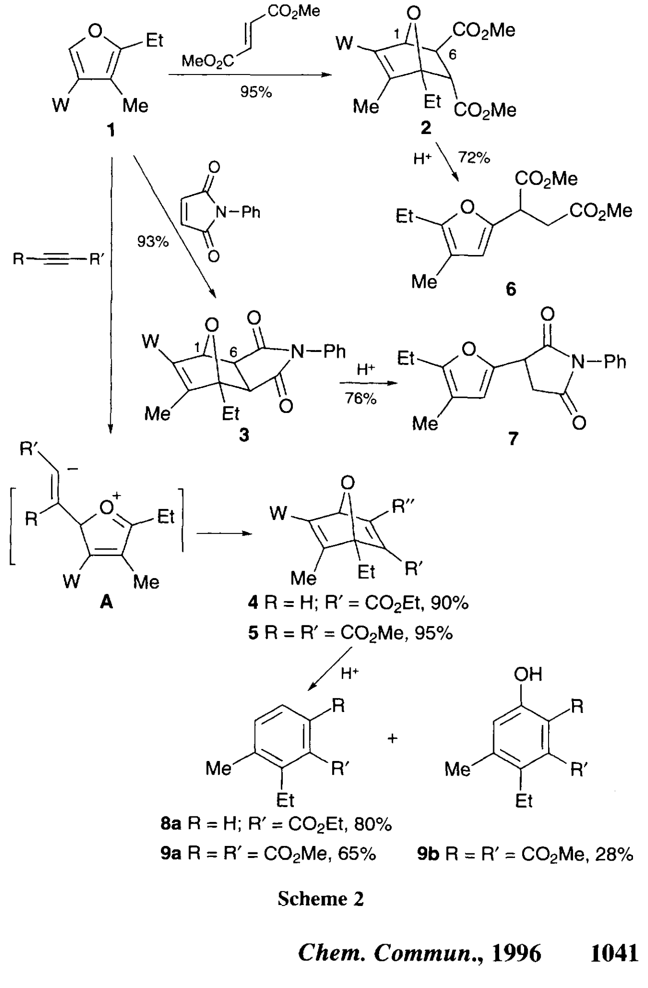
$C_5H_5W(CO)_3$ can be considered as an electron-donating group,[3–4] and it activates the furan ring towards [4+2] cycloadditions with a variety of electron-deficient alkenes and acetylenes. As shown in Scheme 2, treatment of **1**[4] with dimethyl fumarate, *N*-phenylmaleimide, ethyl propiolate and dimethyl acetylenedicarboxylate afforded **2–5** in excellent yields (>90%). The reaction was so highly stereoselective that only one isomer was found for **2–3** and **5**. The molecular structure of **5** was determined by X-ray diffraction.[†] The configurations of **2–3** were designated *exo* by the proton coupling constants J_{16} 0 Hz.[5] The structure of **4** was assigned by the proton coupling constants J_{16} 3.2 Hz; this regiochemistry suggested that the reaction intermediate possibly involves a zwitterion intermediate **A**. Protonation of **2–3** with CD_3SO_3H in cold CH_2Cl_2 (−40 °C), then warming the solution to 23 °C, yielded the 2-alkylated furans **6–7** in good yields (>72%). Protonation of **4–5** under the same conditions gave mainly the deoxygenated products **8a–9a** (65–80%); bipyroduct phenol **9b** (28%) was only observed in the demetalation of **5**. Generation of **8a–9a** from **4–5** is exceptional because deoxygenation of 7-oxabiclo[2.2.1]heptadiene to benzene can only be achieved with reactive low-valent metals.

Protonation of tungsten η^1-oxabicyclic compounds **2–5** clearly proceeds in an atypical pathway. The reaction mechanism deserves further investigation. Treatment of **3** with $SnCl_4$ in CH_2Cl_2 at −78 °C, followed by reduction with $NaBH_3CN$, delivered an alkylated *cis*-2,5-dihydrofur-3-yl complex **10** (89%) of which the X-ray structure[†] is given in Fig. 1. This information indicates that $SnCl_4$ reacts with **3** to form a stable carbonium ion. Scheme 3 shows a plausible pathway in which $SnCl_4$ preferentially attacks at the carbonyl oxygen of **3** to build a positive charge at the C_α carbon, together with the electron-donating effect of $C_5H_5W(CO)_3$, leading to carbon–carbon cleavage to yield the carbenium cation **B**. Species **B** can also be represented by a 2-hydrofurylium structure analogous to that of species **A** Scheme 2. Further hydride addition at **B** preferentially proceeds opposite to the alkylated substituent to yield **10** with *cis*-configuration. Treatment of **3** with CF_3SO_3H in cold CH_2Cl_2 (−40 °C) immediately liberated **7**, indicating that the resulting intermediate **D** is unstable in solution. The instability of **D** may be attributed to the imide oxygen basicity of **D** which causes deprotonation to give furyl complex **E**; further proton cleavage[6,7] of the W–C sigma bond of **E** yields 2-alkylated furan **7**.

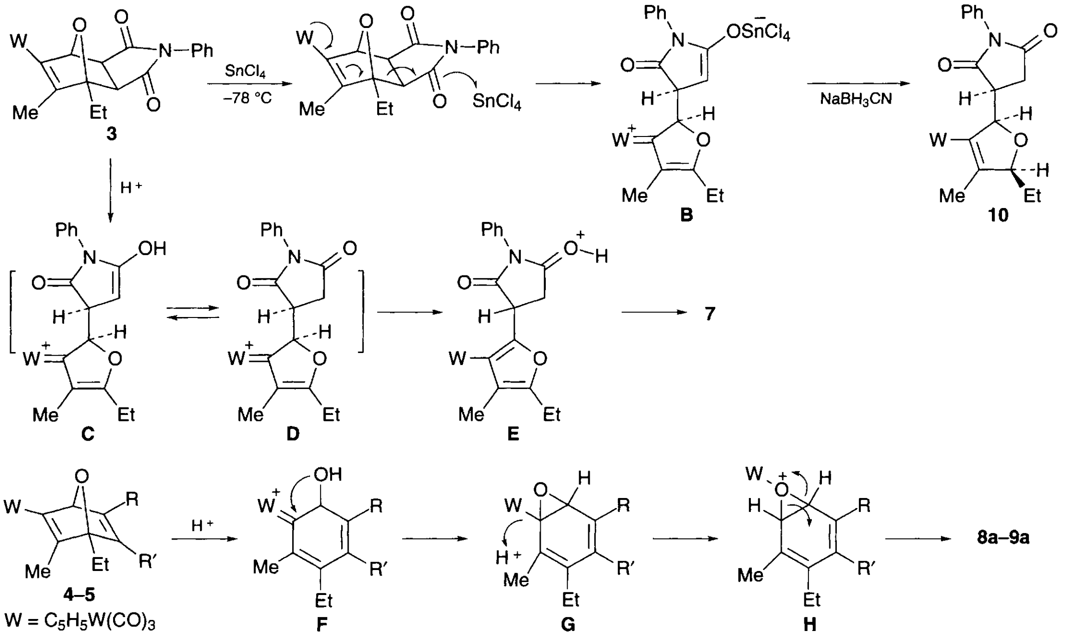
Treatment of **4–5** with $SnCl_4$ in cold CH_2Cl_2 (−78 °C) led to a reversible dissociation to **1** and acetylenes. To account for the deoxygenation, we propose a plausible mechanism which



Scheme 1



Scheme 2



Scheme 3

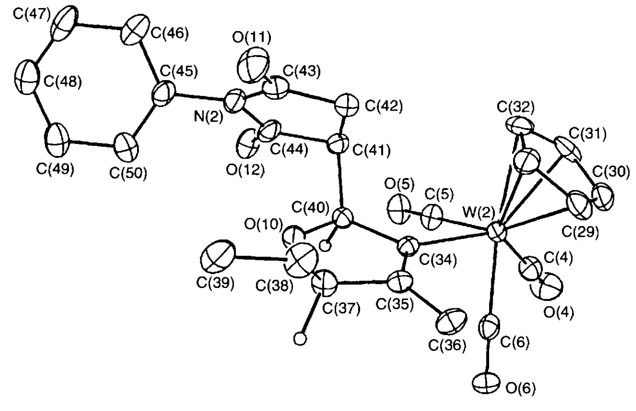


Fig. 1 ORTEP drawing of one independent molecule of **10**. Pertinent distances (Å): W(2)–C(34) 2.258(7), C(34)–C(35) 1.342(10), C(4)–O(10) 1.438(9), C(37)–O(10) 1.463(9).

involves cleavage of the bridging oxygen bond of **4–5** to yield a carbenium intermediate **F**, further yielding epoxide species **G** *via* an intramolecular oxygen attack at the W=C carbon. Proton cleavage of the W–C sigma bond of **G** yields η^1-(O)-epoxide **H**. Subsequent deoxygenation of **H** with $C_5H_5W(CO)_3$ fragment[8] gave arene compounds **8a–9a**.

Footnote

† *Crystal data* for **5**, monoclinic, space group $P2_{1/n}$, a = 10.452(4), b = 12.263(4), c = 19.916(5) Å, β = 90.28(3)°, V = 2552.9(13) Å^3, Z = 4. Each asymmetric unit contains two independent molecules. Data were collected on a Siemens R3m/V diffractometer, using Mo-Kα radiation. Final R = 0.0366, R_w = 0.0389 for 3204 reflections $>3.0\,\sigma(I)$ out of 4537 unique reflections. For **10**, monoclinic, space group $P2_{1/c}$, a = 13.295(2), b = 16.502(2), c = 21.717(2) Å, β = 97.82(2)°, V = 4710.9(10) Å^3, Z = 8. Each asymmetric unit contains two independent molecules. Data were collected on a Siemens R3m/V diffractometer, using Mo-Kα radiation. Final R = 0.0408, R_w = 0.0513 for 6673 reflections $>3.0\,\sigma(I)$ out of 8094 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/29.

References

1 N. N. C. Wong, T.-K. Ng, T.-Y. Wong and Y.-D. Xing, *Heterocycles*, 1984, **22**, 875; T. Suami, *Pure Appl. Chem.*, 1987, **59**, 1509.

2 H. Hart and G. Nwokogu, *J. Org. Chem.*, 1981, **46**, 1251.

3 M. J. Morris, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, vol. 5, p. 7, p. 393; S. A. Benyunes, M. Green and M. J. Grimshire, *Organometallics*, 1989, **8**, 2268; H. Adams, N. A. Bailey and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1984, 273.

4 For synthesis of compound **1**, see H.-G. Shu, L.-H. Shiu, S.-H. Wang, G.-H. Lee, S.-M. Peng and R.-S. Liu, *J. Am. Chem. Soc.*, 1996, in the press; S.-H. Wang, L.-H. Shiu, H.-G. Shu, Y.-L. Liao, S.-L. Wang, G.-H. Lee, S.-M. Peng and R.-S. Liu, *J. Am. Chem. Soc.*, 1994, **116**, 5967.

5 M. Tada, N. Mutoh and T. Shimizu, *J. Org. Chem.*, 1995, **60**, 550.

6 M. J. Robertson, C. J. White and R. J. Angelici, *J. Am. Chem. Soc.*, 1994, **116**, 5190.

7 L. Dong, S. B. Duckett, K. F. Ohman and W. D. Jones, *J. Am. Chem. Soc.*, 1992, **114**, 151.

8 Several tungsten(II) compounds were reactive toward to deoxydenation of epoxide to olefins, see K. A. Hall and J. M. Mayer, *J. Am. Chem. Soc.*, 1992, **114**, 10402.

Received, 17th January 1996; Com. 6/00391E