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Phenanthro[2,3-*c*]furan—a stable benzologue of isobenzofuran with greater reactivity

Michelle E. Thibault, Laurie A. Pacarynuk, Taunia L. L. Closson and Peter W. Dibble*,†

Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, Alberta, Canada T1K 3M4

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Abstract—Phenanthro[2,3-*c*]furan, a benzologue of isobenzofuran has been isolated and found to be 15 times more reactive than isobenzofuran in agreement with extrapolated data of a linear Herndon relationship. © 2001 Elsevier Science Ltd. All rights reserved.

Isobenzofuran (IBF, **1**, Fig. 1), its benzologues and derivatives have been the subject of sustained interest.[1–5] IBF itself is a highly reactive polyene in Diels–Alder reactions and this reactivity has been exploited in many synthetic applications. Rickborn has referred to IBF as "the most reactive isolated diene for cycloaddition purposes".[2] Wege has reported[6,7] the second order rate constants of various benzologues of IBF (IBFs with differing ring fusion elements) and shown that they follow a linear Herndon relationship.[8,9] Based on extrapolation of this data we would expect phenanthro[2,3-*c*]furan, **2**, to be 12 times as reactive as IBF. We set out to prepare compound **2**, to see if it would prove stable enough to be characterized and to test whether its reactivity was indeed greater than IBF.

Wege's data relates a parameter known as the structure count ratio (SC_R) to the relative reactivities of IBF benzologues. The structure count ratio is simply the number of Kekulé structures of product (Diels–Alder addition product) plus the number of Kekulé structures of the reactant divided by the latter. Isobenzofuran has a single Kekulé structure while its adducts (Scheme 1) have the two Kekulé structures of the benzene ring. The SC_R of IBF is therefore 3. The SC_R is a comparison of the stability of product compared to reactant, stability being reflected by a greater number of resonance structures. The greater the value of the SC_R, the greater the stability of the product compared to the reactant. The Hammond postulate predicts that in the Diels–Alder reaction of IBF benzologues, more reactive examples will have transition state energies closer to the energy of the reactant molecule and lower activation barriers as a result. That there is a good linear relationship between the log of the second order rate constant and the log of the SC_R for many IBF benzologues suggests that this very simplistic model works well.

Higher SC_Rs suggest greater reactivity and associated difficulty in isolation. The SC_Rs of benzologues **2**, **3** and **4** are 3.5, 2.5 and 4, respectively. Accordingly, **3** is an isolable solid that melts without decomposition,[10] IBF is stable in solution but polymerizes at room tempera-

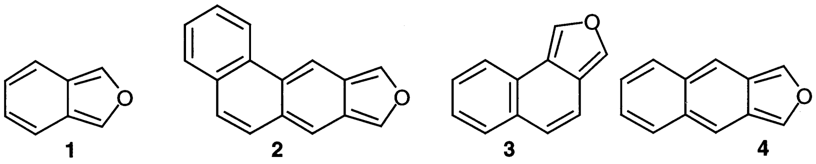

Figure 1.

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* Corresponding author.

[†] Visiting Professor at the Centre for Molecular Architecture, Central Queensland University, QLD, Australia.

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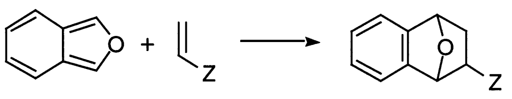

Scheme 1.

ture in the solid state[11] and linear benzologue **4** can be generated and trapped in situ, but has never been observed directly.[12] This is consistent with the known rate data for **1** and **3** and with the reactivities that are predicted by Wege's data. Previously unknown benzologue **2** has an SC_R that is intermediate between that of IBF and **4**. As such, Wege's model predicts that it should be more reactive than IBF but less reactive than **4**.

We synthesized **2** in five steps (Scheme 2) from known phenanthrene **5**[13] constructing the furan ring using our previous metallation strategy.[14] Formylation of alcohol **6** gave an equilibrium mixture of hydroxyaldehyde **7** and hemiacetal **8**.[15] Phenanthro[2,3-*c*]furan was formed from acetal **9** using Rickborn's base-induced method.[11] Examination of the reaction product showed ^{1}H NMR signals entirely consistent with that expected for **2**. Signals of **2** in $CDCl_3$ or CD_2Cl_2 survived for periods in excess of 10 hours with polymerization becoming increasingly apparent. Subsequent reaction with *N*-methylmaleimide (*N*-MeMI) gave *endo* adduct **10** with very high diastereoselectivity.[16] Compound **2** was further characterized by ^{13}C NMR and HRMS.

The proton NMR spectrum of **2**[17] says much about the character of this molecule. An early paper[18] suggests that **1** is best considered as furan with a butadiene fragment annelated onto the furan's c-face. The NMR spectrum of **2** is completely consistent with this picture, with H1–H3 couplings (1.6 Hz) very similar to that of furan and long range couplings to H4 and H11 (1.6 Hz) indicating polyene character for this part of the molecule. Protons 5 and 6 appear as an AB system with *J* values of 9 Hz. This coupling is comparable to that of cyclohexenes or that found in the 9–10 bond of phenanthrenes which have substantial double bond character.

In order to evaluate the relative reactivities of **1** and **2**, we used a competition experiment (Scheme 3) involving *N*-methylmaleimide as described by Rickborn.[19] Equimolar amounts of acetals **9** and **11** were cooled to 0°C and treated with excess LDA. LDA was destroyed with methanol and then *N*-methylmaleimide (0.8 equivalents) was added. The resulting reaction mixture contained adducts **10** and **12** in a ratio of 15:1 suggesting that under these conditions, **2** is 15 times as reactive as **1**. A substantial amount of unreacted **1** and a small amount of unreacted **2** were also present. Despite the differing reaction conditions, our result is remarkably close to the value of 12 predicted by Wege's data.

We have demonstrated that phenanthro[2,3-*c*]furan is a more reactive diene than isobenzofuran but is still sufficiently stable to be characterized in solution making it the most reactive isolable Diels–Alder diene reported. We are preparing further benzologues with SC_Rs intermediate between **2** and **4** in order to determine an upper limit of SC_R which will still allow product characterization.

Acknowledgements

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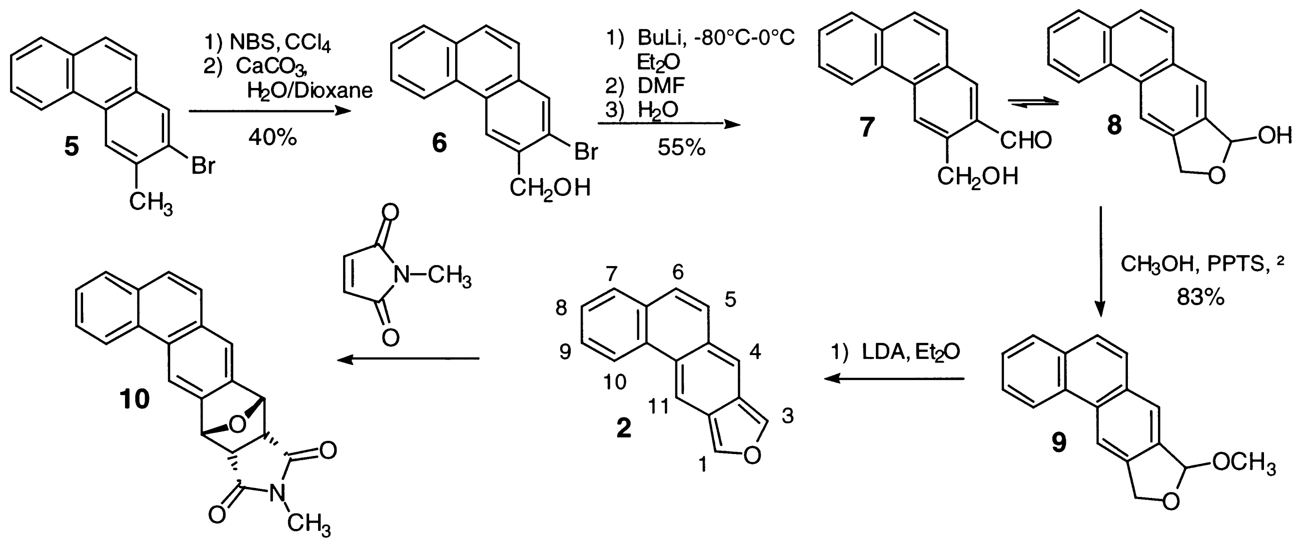
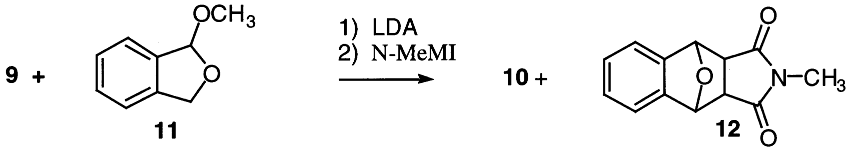


Scheme 2.



Scheme 3.

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16. Phenanthro[2,3-*c*]furan, *N*-methyl maleimide adduct. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (s, 3H), 3.84–3.91 (m, 2H), 5.86–5.97 (m, 2H), 7.48–7.86 (m, 5H), 7.91 (dd, $J=2$, 8 Hz, 1H), 8.56 (s, 1H), 8.65 (d, $J=8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.95, 49.46, 49.53, 80.56, 80.86, 115.04, 120.70, 123.25, 127.03, 127.23, 127.89, 128.86, 130.29, 130.48, 131.94, 132.57, 138.92, 139.12, 174.48, 174.60; MS (EI) *m*/*e* calcd for $C_{21}H_{15}NO_3$: 329.1052, found 329.1052; 329 (M+, 14), 219 (19), 218 (100), 190 (6), 189 (29), 109 (6).
17. Phenanthro[2,3-*c*]furan: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.09 and 7.23 (H5 and H6, ABq, $J=9$ Hz, 2H), 7.35–7.46 (H8 and H9, m, 2H), 7.50 (H7, dd, $J=2$, 7 Hz, 1H), 7.73 (H4, s, 1H), 8.24 (H1, t, $J=1.4$ Hz, 1H), 8.31 (H3, t, $J=1.6$ Hz, 1H), 8.37 (H10, dd, $J=1.3$, 7 Hz, 1H), 8.56 (H11, d, $J=1$ Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ CHs only, 112.66, 117.74, 123.38, 127.12, 127.84, 128.14, 129.10, 129.39, 135.76, 136.28; MS (EI) *m*/*e* calcd for $C_{16}H_{10}O$: 218.0732, found 218.0732; 218 (M+, 18), 191 (5), 190 (5), 189 (15).
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