Formation of Azuleno[4,5-*c*]furan

Masaru Sato,[a] **Katsunori Tanaka,**[b] **Seiji Ebine,***[b] **and Kazuko Takahashi**[c]

[a] *Chemical Analysis Center, and* [b] *Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan*

[c] *Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Miyagi 980, Japan*

Azuleno[4,5-*c*]furan (**1**) was generated and trapped as its cycloadduct with maleic anhydride, the *exo*-isomer (**6**) predominating over the *endo*-isomer (**7**).

No azuleno[*c*]furan derivative, a new type of heterocyclic *o*-quinonoidal analogue, has been reported to date, whereas some azuleno[*b*]furan derivatives have been derived from natural products[1,2] and prepared.[3,4] We now report the generation of azuleno[4,5-*c*]furan (**1**) and its trapping as the cycloadduct with maleic anhydride.

Dimethyl azulene-4,5-dicarboxylate (**2**)[5] was reduced with di-isobutylaluminium hydride in benzene to give 1-hydroxy-1,3-dihydroazuleno[4,5-*c*]furan (**3**) [blue needles, m.p. 122.5—123.5 °C,† yield 97%, ^{1}H n.m.r. ($CDCl_3$) δ 8.27 (d, $J_{5,6}$ 9.5 Hz, 6-H), 7.91 (t, 8-H), 7.44 (d, $J_{8,9}$ 3.7 Hz, 9-H), 7.43 (d, $J_{4,5}$ 9.5 Hz, 4-H), 7.34 (d, $J_{7,8}$ 3.7 Hz, 7-H), 7.15 (t, 5-H), 6.85 (dd, $J_{1,3}$ 1.8 Hz, 1-H), 5.41 (br.d, 3-H), 5.11 (d, $J_{3,3}$ 13.0 Hz, 3-H), and 3.64 (d, J 7.2 Hz, OH)]. On addition of D_2O, the doublet at δ 3.64 disappeared and the doublet at δ 6.85 changed into a sharp singlet. To elucidate the position of the hydroxy group, (**3**) was oxidized with MnO_2 to give 1-oxo-1,3-dihydro-azuleno[4,5-*c*]furan (**4**) (blue green plates, m.p. 138.5—139 °C,† yield 90%). The ^{1}H n.m.r. spectrum ($CDCl_3$) of (**4**) showed a doublet due to 9-H at much lower field (δ 8.43) than the corresponding proton in azulene (δ 7.57), confirming that (**4**) is a 1-oxo compound and not a 3-oxo one. Thus, (**3**) was the 1-hydroxy compound rather than the 3-hydroxy isomer.

The alcohol (**3**) was treated with $BF_3{\cdot}OEt_2$ in methanol to give 1-methoxy-1,3-dihydroazuleno[4,5-*c*]furan (**5**) [blue plates, m.p. 63—64 °C, yield 70%, ^{1}H n.m.r. ($CDCl_3$) δ 3.51 (s, Me)]. An attempt to generate (**1**) with lithium di-isopropylamide in benzene[6] was unsuccessful. However, a solution of (**5**) in toluene was refluxed with maleic anhydride for 2 h to give two adducts: the *exo*-isomer, (**6**) (purple needles, m.p.

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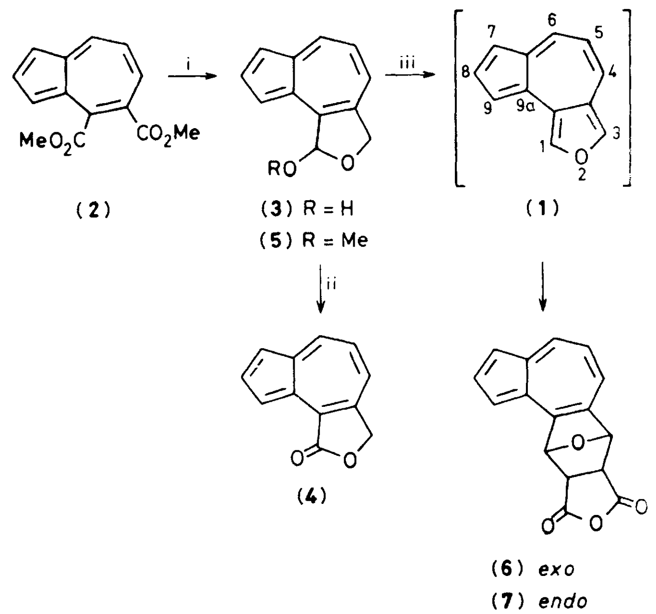
† All compounds have satisfactory microanalyses and show the corresponding molecular ions in their mass spectra.



(i) Di-isobutylaluminium hydride, C_6H_6, room temperature; (ii) MnO_2, $CHCl_3$; (iii) maleic anhydride, toluene, reflux.

213—214 °C) and the *endo*-isomer, (**7**) (blue-purple needles, m.p. 168—169 °C) in 49 and 20% yields, respectively.‡ The ^1H n.m.r. spectrum of (**6**) showed two singlets at δ 5.89 and 6.29, assignable to the bridgehead protons, in addition to the signals corresponding to the dihydroazulenofuran structure [δ 8.31 (d, $J_{5,6}$ 9.4 Hz, 6-H), 7.97 (t, 8-H), 7.65 (d, $J_{4,5}$ 9.4 Hz, 4-H), 7.44 (d, $J_{7,8}$ and $J_{8,9}$ 3.6 Hz, 7-H and 9-H), 7.10 (t, 5-H), 6.29 (s, 1-H), and 5.89 (s, 3-H)], indicating that the two dihedral angles between the bridgehead and the neighbouring protons (1-H–10-H and 3-H–11-H) are both about 90°. The adduct (**6**), therefore, was confirmed to be the *exo*-isomer by consideration of molecular models. The ^1H n.m.r. spectrum ($CDCl_3$) of the other isomer (**7**) [δ 8.28 (d, $J_{5,6}$ 9.9 Hz, 6-H), 7.95 (t, 8-H), 7.54 (d, $J_{4,5}$ 9.9 Hz, 4-H), 7.41 (d, $J_{7,8}$ 3.6 Hz, 7-H), 7.37 (d, $J_{8,9}$ 3.6 Hz, 9-H), 7.05 (t, 5-H), 6.25 (m, 1-H), 5.08 (m, 3-H), and 4.20—4.12 (m, 2H)] was also in accord with the *endo* structure taking the two dihedral angles 1-H–10-H and 3-H–11-H into account. The production of the cycloadducts (**6**) and (**7**) implies the generation of (**1**) in the reaction described above. Moreover, the reaction of (**1**) with maleic anhydride showed an unusual preferential *exo*-addition. Thus, the ratio between the amount of *exo*- and *endo*-isomers formed [(**6**):(**7**)] was nearly constant (about 5:2) irrespective of the reaction time. When solutions of each cycloadduct in toluene were refluxed for 2 h in the presence of a large excess of maleic anhydride, (**6**) did not change at all, and (**7**) isomerized to give (**6**) in only about 15% yield along with 68% recovery of (**7**). This result indicates that (**6**) is formed more predominantly than (**7**) from the beginning of this reaction. Such an interesting predominance of an *exo*-isomer in cycloaddition is also known for reactions involving isobenzofuran,[7] in contrast to the preferred *endo*-addition of normal Diels–Alder reactions.

CNDO/2 calculations on (**1**) showed that the π-HOMO coefficients of the furan ring and the 5-membered carbocyclic ring resemble those of butadiene and fulvene, respectively (Figure 1). Consequently, (**1**) may undergo cycloaddition at both 1,3- and 7,9a-positions with electron-deficient dienophiles. The predominant cycloaddition at the 1,3-position would occur because of a preference for a transition state stabilized by the recovery of an aromatic azulene framework and also because the energy difference between the HOMO [diene part of (**1**)] and the LUMO (maleic anhydride) is smaller in 1,3- than in 7,9a-cycloaddition. The calculations also suggested higher charge densities on the 5-membered carbocyclic ring than on the remainder, resulting in a large dipole moment ($\mu_{\text{cal.}}$ = 3.6 Debye, Figure 1).

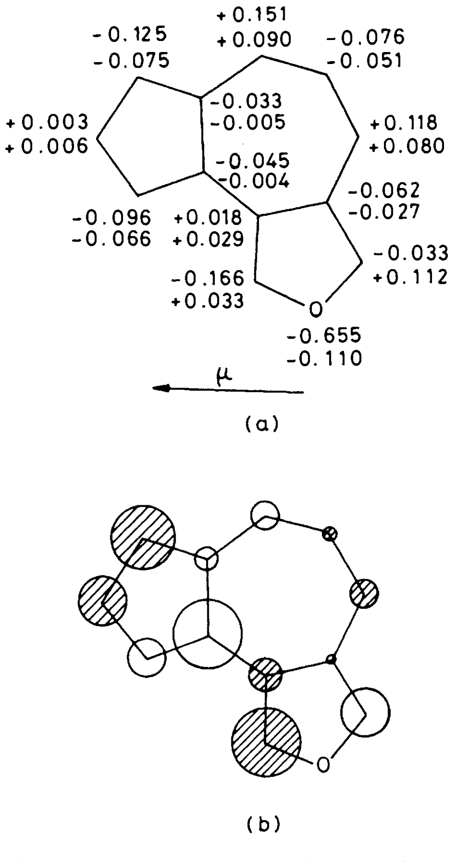


Figure 1. CNDO/2 calculation on azuleno[4,5-*c*]furan (**1**). (a) Total (lower figure) and π (upper figure) charge densities ($\mu_{\text{cal.}}$ = 3.607 Debye); (b) $2p\pi$ HOMO coefficients (ϕ_{31} = −9.108 eV).

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‡ *exo* and *endo* refer to the relative positions of the azulene nucleus and anhydride bridge.

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