The synthesis of the *N*-ethoxycarbonyl derivative of 5-azabicyclo[2.1.0]-pent-2-ene (Dewar pyrrole)—The first member of the parent ring-system

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_N_-Ethoxycarbonyl Dewar pyrrole 9, the first member of the parent ring, is formed _via_ photofragmentation of 6 at −60 °C and trapped as its adduct with 1,3-diphenylisobenzofuran 11; above this temperature, 9 is unstable and isomerises to _N_-ethoxycarbonylpyrrole 10.

The Dewar form of the 5-membered heterocycles furan, thiophene and pyrrole are expected to be unstable species in view of the high ring-strain typical of Dewar valence-isomers and further as they are formally homo derivatives of cyclobutadiene, an archetypical anti-aromatic ring-system. While Dewar thiophene (5-thiabicyclo[2.1.0]pent-2-ene) has been formed by direct irradiation of thiophene,[1] the other parent 5-membered heterocycles have failed to yield to this photoisomerisation. We have previously demonstrated that Dewar furan (5-oxabicyclo[2.1.0]pent-2-ene) could be generated by an indirect photochemical approach, and while too unstable for direct isolation, it could be trapped as its isobenzofuran adduct.[2] Dewar pyrrole has remained an undetected species although some *C*-substituted derivatives are known.†

Here we report the Dewar pyrrole too has now been corralled and trapped in adduct form.

The method used for its production (Scheme 1) is again an indirect one and parallels the 1,2-photoaromatisation route[6] used in the generation of Dewar furan.[2] Access to photosubstrate **6** required initial production of Dewar azepine **4**, itself a high-energy species; this was achieved in two steps from the known bicyclo[2.2.0]hexene **1**.[2] Introduction of the aziridine ring was attained *via* carbomethoxy nitrene addition[7] to the π bond of **1**. Azepine **4** was generated *in situ* by Zn/Ag debromination of **3** in the presence of 2,5-diethyl-3,4-diphenylcyclopentadienone **5**[8]‡ and isolated as the adduct **6**.§ Irradiation of photosubstrate **6** in acetone at room temperature initially promoted decarbonylation to the cyclohexadiene **7** which underwent photofragmentation to form the phthalimide **8** and *N*-ethoxycarbonylpyrrole **10**. When this irradiation was conducted at low temperature (−60 °C) and in the presence of 1,3-diphenylisobenzofuran **11**, Dewar pyrrole **9** could be trapped as its adduct **12**; again significant production of *N*-ethoxycarbonyl pyrrole **10** is observed (**12**:**10** = *ca.* 1:1). The structure of adduct **12** was confirmed by separate synthesis from **13**[9] *via* cyclobutene **14** as outlined in Scheme 2.¶

Dewar pyrrole **9** differs significantly from its Dewar furan counterpart in two significant respects. First it is less stable (**9** is isomerised to **10** at −60 °C whereas Dewar furan is stable at −40 °C)[2] and Dewar pyrrole **9** rearranges to the 5-membered heterocycle **10** whereas Dewar furan is isomerised to cyclopropene-3-carbaldehyde.[2] This divergence of isomerisation pathways is currently being investigated using computational methods and will be reported at a later stage.

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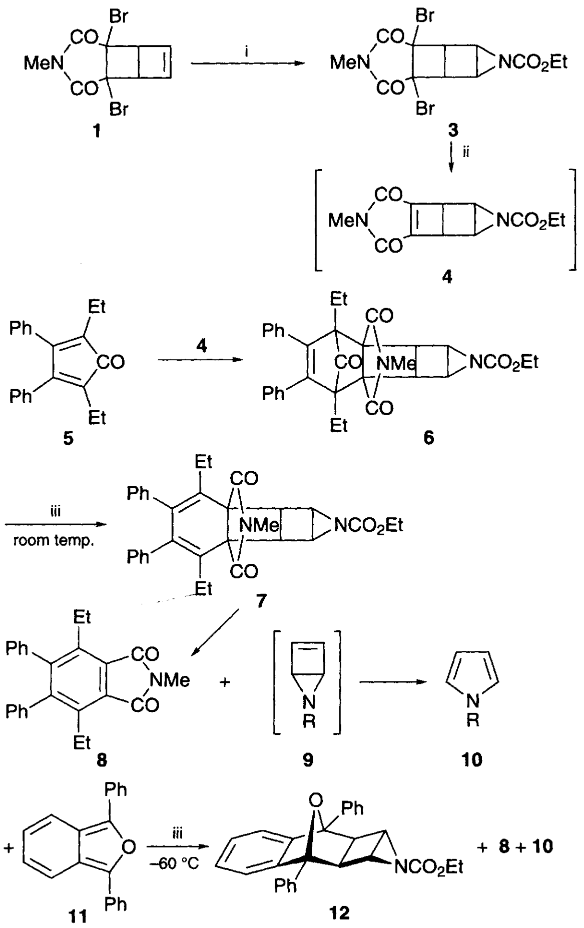
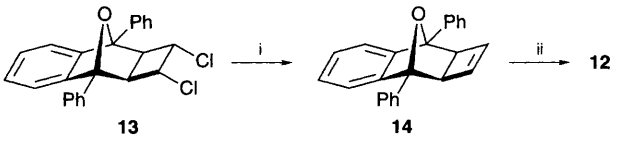


Scheme 1 *Reagents and conditions*: i, excess **2**, CH_2Cl_2, 254 nm, 67%; ii, Zn/Ag couple, THF, **5**, 87% yield as **6**; iii, quartz, 254 nm, acetone



Scheme 2 *Reagents and conditions*: i, Zn, EtOH, reflux, 15 h, 74%; ii, 6 equiv. **2**, 254 nm, 56%

Footnotes

† All three Dewar isomers have been reported as their per(trifluoromethyl) derivatives;[3] notably the Dewar pyrrole is less stable than the others. The only other Dewar pyrrole reported was produced by ultra-violet irradiation of *N*-methyl 2-cyanopyrrole;[4] interestingly the product actually trapped is derived from the rearranged 2-cyanobicyclo[2.1.0]pent-2-ene rather than the first-formed 1-cyano isomer.[5]

‡ Dienone **5** has the advantage of existing as a monomer and is more soluble in organic solvents than its better known methyl analogue, hemicyclone which exists as a thermally reversible dimer. This is reflected in the improved trapping efficiency of **5**.[9]

§ All new compounds exhibited NMR data consistent with the assigned structures which were further supported by elemental analysis or mass spectral data. *Selected spectroscopic data* for **6**: mp 197–198 °C; ^{1}H NMR ($CDCl_3$) δ 0.78 (t, *J* 7.1 Hz, 6 H, 2 × CH_3), 1.31 (t, *J* 7.1 Hz, 319 H, CH_3), 2.10 (m, 4 H, 2 × CH_2), 2.89 (d, *J* 3.7 Hz, 2 H, H-2, H-6), 3.08 (s, 3 H, *N*-CH_3), 3.27 (d, *J* 3.7 Hz, 2 H, H-3, H-5), 4.24 (q, *J* 7.1 Hz, 2 H, OCH_2) and 6.80–7.20 (m, 10 H, 2 × Ph); ^{13}C NMR ($CDCl_3$) δ 9.26, 14.40, 15.41, 25.59, 37.75, 38.76, 53.23, 61.75, 62.94, 127.72, 128.26, 129.15, 133.58, 141.99, 159.07, 174.31 and 200.87; MS: *m/z* 536 (M^+). For **12**. mp 186–189 °C; ^{1}H NMR ($CDCl_3$) δ 1.31 (t, *J* 7.1 Hz, 3 H, CH_3), 3.01 (m, 2 H), 3.03 (m, 2 H), 4.23 (q, *J* 7.1 Hz, 2 H, OCH_2), 6.96 (m, 2 H), 7.12 (m, 2 H) and 7.45–7.73 (m, 10 H, 2 × Ph); ^{13}C NMR ($CDCl_3$) δ 14.48, 37.75, 38.55, 52.24, 62.38, 89.09, 119.22, 126.67, 127.12, 128.26, 128.73, 135.61, 147.75 and 160.99; MS: *m/z* 409 (14, M^+).

¶ The structure of **12** follows from the established stereochemistry of precursor cyclobutene **14** by X-ray[10] and its mode of formation. Comparison of splitting patterns of the cyclobutyl ring-protons in **12** with other known *anti*-cyclobutanes[11] confirms the stereochemical assignment. Semi-empirical methods (AM1) predict that isomer **12** is the favoured stereoisomer in the cycloaddition of **9** with **11** by about 4 kJ mol^{-1}.

‖ Calculations were performed for the reaction of **11** with the parent Dewar pyrrole. Different energies were found for the two tetrahedral conformation of the NH; that with the H *syn* with the cyclobutane ring being favoured.

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