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Fulvenes acting as 4π Components in an Intramolecular [4+2] Cycloaddition Reaction: Entry into the Novel 6-Oxatricyclo[6.4.0.0^{2,10}]dodeca-2,11-diene Ring System

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Abstract: Intramolecular [4+2] cycloaddition of fulvenes **2a,b** gives 6-oxatricyclo[6.4.0.0^{2,10}]dodeca-2,11-diene-[4,5-a]naphtho-*endo* 9-carboxylic acid alkyl esters **3a,b**. Compounds **3a,b** are the first representatives of this bridged tricyclic ring system.

Theoretical and synthetic aspects of fulvenes are of considerable interest in view of the periselectivity of their reactions.[1] Fulvenes have found extensive use as key intermediates in the synthesis of hirsutene, capnellene, β-vetivone, viburtinal, hinesol, silphinene and longifolene.[2] The use of fulvenes as 6π components in many inter[3] and intramolecular[1] [6+4] cycloadditions is well documented. Many intermolecular [4+2] cycloaddition reactions involving fulvenes as 4π or 2π components have also been reported in literature.[4,5] An intramolecular [6+2] cycloaddition reaction involving a fulvene as a 6π component has been reported by Wu and Houk.[6] However, there appears to be no report of an intramolecular [4+2] cycloaddition involving a fulvene functioning as a 4π component. In continuation of our work in the area of cycloaddition reactions,[7] herein, we report one such interesting intramolecular [4 +2] cycloaddition reaction.

The fulvenes **2a,b** required for the reaction were prepared by treatment of the aldehydes **1a,b** with cyclopentadiene in the presence of diethylamine.[8] Fulvenes **2a,b** underwent intramolecular [4+2] cycloaddition using lithium perchlorate as a Lewis acid catalyst in refluxing nitromethane and provided the novel tricyclic endo adducts **3a,b** in 31% and 33% of yields, respectively.[9] (Scheme). Confirmatory evidence for the structures **3a,b** was available from IR, ^{1}H and ^{13}C NMR, mass spectra and elemental analyses.[10] Structure **3a** was further corroborated by ^{1}H – ^{1}H , ^{1}H – ^{13}C COSY data. The stereochemistry of the cycloadducts **3a,b** was

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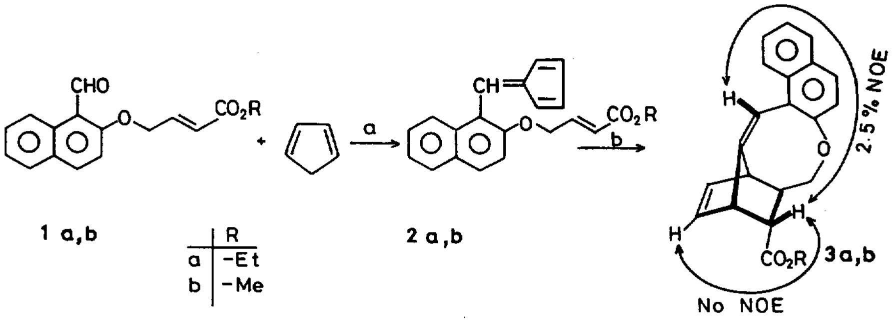
established by NOE studies. This reaction sequence constitutes the first recorded synthesis of the 6-oxatricyclo[6.4.0.0^{2,10}]dodeca-2,11-diene ring system.



^{a} Et_2NH, MeOH, rt, 8h (65% for **2a**, 62% for **2b**) ^{b}$LiClO_4$, CH_3NO_2, reflux ,12h (31% for **3a**, 33% for **3b**)

(SCHEME)

In conclusion, to the best of our knowledge, this is the first report of an intramolecular [4+2] cycloaddition involving fulvene as the 4π component to afford a novel 6-oxatricyclo[6.4.0.0^{2,10}]dodeca-2,11-diene ring system. Further work is in progress to evaluate the synthetic potential of this reaction.

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9. To a refluxing solution of fulvenes **2a,b** (5 mmol) in 20 ml of nitromethane under nitrogen, lithium perchlorate (5 mmol) was added. After 12h, work up and flash chromatography gave cycloadducts as colourless oils.
10. Data for compound **3a**: ^{1}H NMR 400 MHz ($CDCl_3$/TMS) δ 1.28 (t, J = 7.3Hz, 3H), 2.02(m, 1H), 2.69 (bs, 1H), 3.24 (t, J = 3.9Hz, 1H), 3.83(bs, 1H), 4.14 (q, J = 7.3Hz, 2H), 4.21 (dd, J = 12.7, 1.5Hz, 1H), 4.68 (dd, J = 12.7, 1.0Hz, 1H), 6.16(s, 1H), 6.20 (dd, J = 5.8, 3.4Hz, 1H), 6.30 (dd, J = 5.8, 3.4Hz, 1H), 7.28 – 7.87 (m, 6H). ^{13}C NMR (100.4 MHz) δ 14.30, 40.63, 48.15, 49.34, 49.41, 60.55, 75.51, 103.44, 122.40, 124.88, 125.79, 126.17, 127.79, 129.20, 130.42, 132.72, 132.95, 136.62, 155.83, 158.24, 173.00.