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Unusual Cope Rearrangement of Tricyclo[5.2.1.$0^{2,6}$]decadienone 2-carboxylic Ester on Acetalisation with Ethylene Glycol, PTSA:

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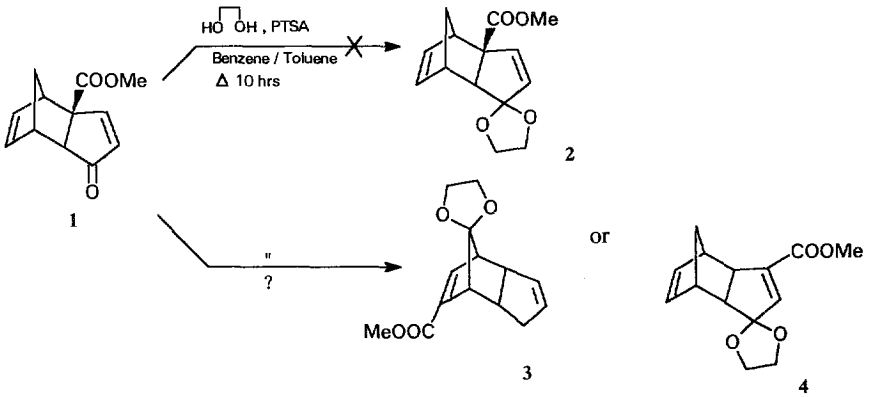
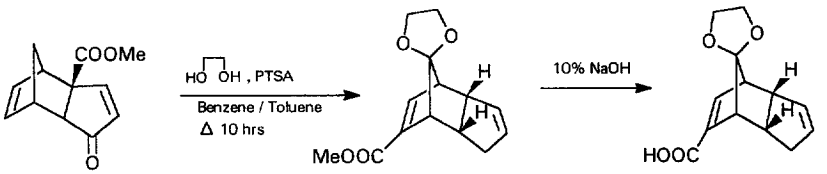
Abstract: *Protection of 2-exo-carbomethoxytricyclo[5.2.1.$0^{2,6}$] deca-3,8-dien-5-one with ethylene glycol, PTSA afforded the unexpected Cope rearranged product i.e. 1-carbomethoxy endo-dicyclopenta-1,4-diene-8-one 8-ethylene acetal, instead of protected acetal 2.*

Tricyclo[5.2.1.$0^{2,6}$] decadienones[1] are useful synthons for a variety of functionalised cyclopentenones, tricyclic systems are for the synthesis of cyclopentanoid natural products. During our synthetic strategy towards the synthesis of tricyclic systems using reductive cyclisation developed by us[2a] and others[2b], it was planned to synthesise compound **2** from the decadienone ester **1**.



Compound **1** was prepared by the procedure as reported in literature[3]. Following the reported procedure[4] protection of ketone carbonyl in decadienone ester **1** was carried out with ethylene glycol, PTSA in refluxing toluene for 10 hrs. It was surprising to note that the expected acetal **2** was not obtained, instead an unexpected isomeric product was obtained in 80% yield. Although the structure **3** was not totally unexpected based on the Cope rearrangement[5] of such systems, formation of isomeric compound **4** could be ruled out by spectral analysis[6] as well as chemical reactions. Attempts to deprotect the acetal under normal conditions proved to be difficult.

Even protection of compound **1** with ethylene glycol and PTSA in the presence of benzoquinone gave only the rearranged product **3**. No cross product nor dicyclopentadiene was obtained, hence ruling out the formation of compound **4**. Similarly protection of decadienone ester **1** in refluxing benzene for 10 hrs gave the same rearranged product **3** in 75% yield. Although the authors[4] report the protection of **1** under "careful ketalisation" conditions, it was observed that we could not under our conditions get **2**.



1 3 5

Reaction of compound **1** with BF_3Et_2O in CH_2Cl_2 or PTSA in benzene at room temperature led to the recovery of starting material. However on heating **1** with PTSA in benzene, intractable mixture was obtained which could not be characterised. In addition protection with 1,2-ethanedithiol and 2-mercaptoethanol with BF_3 Et_2O afforded complex mixture of compounds, which could not be separated by chromatography. Protection with PPTS as catalyst also gave the rearranged product **3** along with unreacted starting material. Finally the protected acetal was hydrolysed to the corresponding acid (85%) and the structure was confirmed to be **5** by single crystal X-ray analysis. From the above study it is likely that first, the acetalisation of **1** occurs to furnish **2** followed by Cope rearrangement under the conditions to furnish **3**. In view of the recent publication describing the utility of such systems for the synthesis of funtionalised hydrindanes[7a,b], we feel this observation would be of synthetic utility to synthetic organic chemists.

In conclusion, the protection of 2-exo-carbomethoxytricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene-5-one **1** gave the Cope rearranged product, 1-carbomethoxy endo-dicyclopenta-1,4-diene-8-one 8-ethylene acetal.

Procedure : 250mg (1.225 mmol) of compound **1** , 1.5 eq of ethylene glycol and 50 mg PTSA in 50 ml dry benzene / toluene refluxed for 10 hrs employing Dean-Stark apparatus. Reaction was monitored by TLC. Usual workup and chromatography (SiO_2) gave compound **3**.

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6. ^{1}H NMR (200 MHz) δ : 1.65-1.85 (m, 1H), 2.35 (m, 1H), 2.8-3.2 (m, 3H), 3.5- 3.6 (m, 1H), 3.75 (s, 3H), 3.8-4.0 (m, 4H), 5.4- 5.6 (m, 2H), 6.95 (m, 1H). ^{13}C NMR ppm: 34.08 (t), 37.8 (d), 50.9 (d), 51.29 (d), 51.35 (d), 51.76 (d), 64.29 (t), 64.95 (t), 126.75 (s), 129.29 (d), 134.14 (d), 135.61 (s), 144.9 (d), 164.86 (s). IR cm^{-1} (neat) : 1697, 1594.
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