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CONCERTED [4+2] AND STEPWISE [2+2] CYCLOADDITIONS OF THE TRIPHENYLALLENYL CATION WITH CYCLOPENTADIENE

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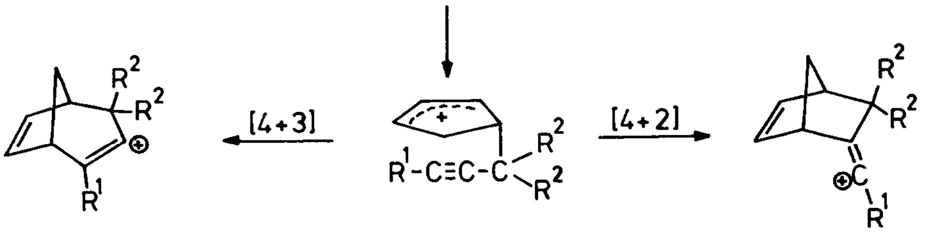
Summary. The triphenylallenyl cation (5), generated *in situ* under different conditions, reacts with cyclopentadiene *via* allyl cations 7 and 9. The exclusive formation of 7 from 12 and FSO_3H *proves* a concerted [4+2]cycloaddition leading to 9 and *suggests* a stepwise [2+2]cycloaddition reaction to give 7.

The differentiation between stepwise and concerted cycloaddition reactions is still a challenging problem in mechanistic chemistry.[1] Whereas stepwise processes can often be proven by lack of stereospecifity or by trapping intermediates,[2] it is generally difficult to find unequivocal evidence for concerted processes. Stepwise cycloadditions of neutral components proceed *via* dipolar or diradical intermediates, which can usually not be generated specifically. In ionic cycloadditions, however, possible intermediates are cations or anions, like the products and one of the cycloaddends. In these cases, an additional tool, the independent generation of the potential intermediates, is available for mechanistic studies. In this work we have used this tool to examine the mechanism of the title reaction.

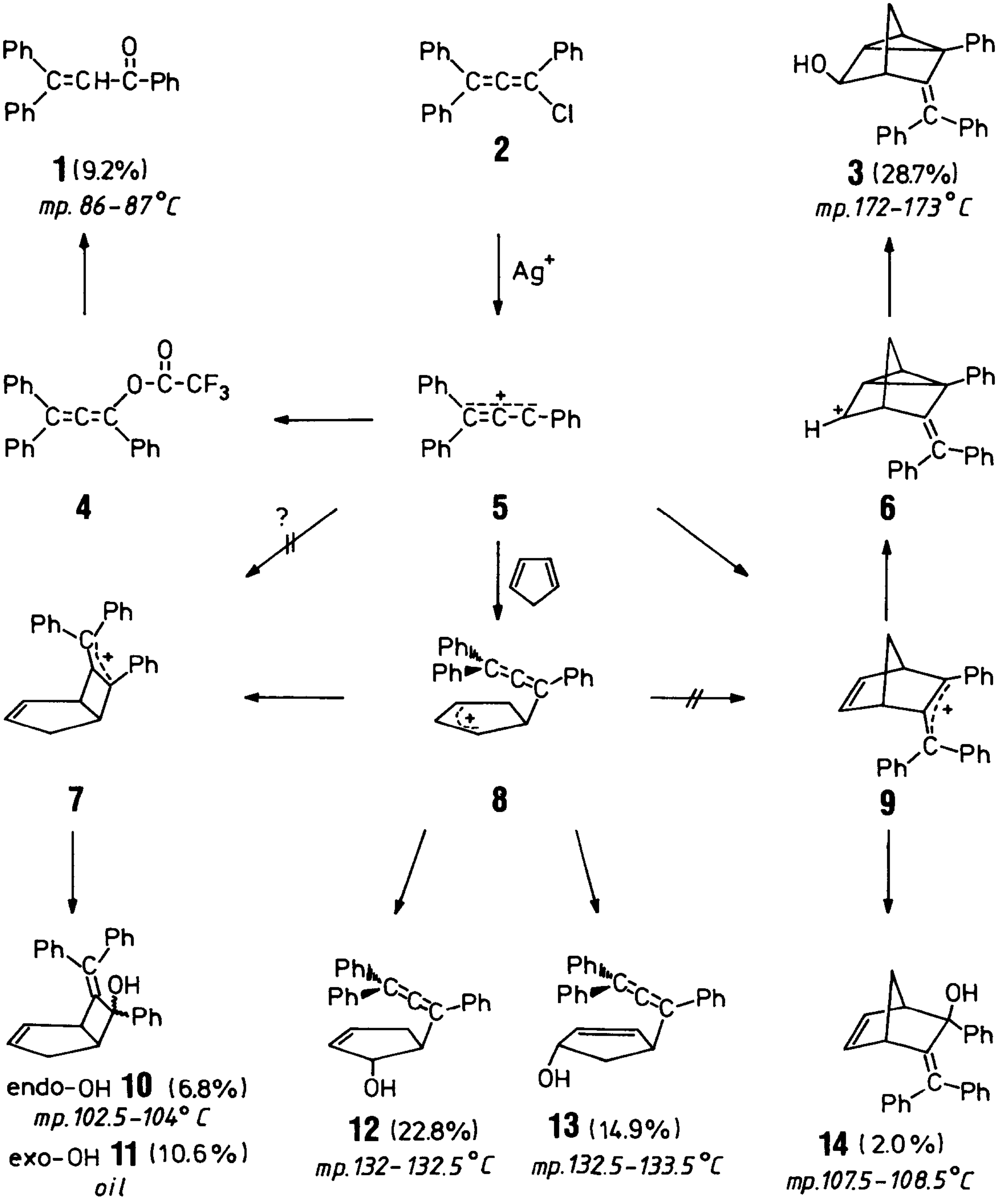
We previously reported that allenyl cations and cyclopentadiene predominantly undergo stepwise [4+3]and [4+2]cycloadditions to give vinyl cations (Scheme 1).[3]

Scheme 1



These reactions, involving initial attack at the sp^2-carbon of the allenyl cation, are inhibited if R^2 = Ph, and the system is forced to undergo vinyl cation type cycloadditions.[4,5]

Scheme 2



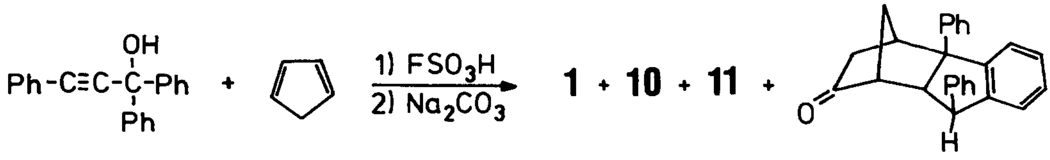
When a solution of chlorotriphenylallene **2**[6] and cyclopentadiene in pentane was treated with an equimolar amount of silver trifluoroacetate and worked up with KOH/C_2H_5OH, compounds **1**, **3** and **10** - **14** were isolated in 95 % total yield.[7] Scheme 2 shows that only 9 % of **5** are trapped by trifluoroacetate anion to give **4**, which hydrolyses to **1**. All other products arise from addition of **5** to cyclopentadiene.

Cyclopentenols **12** and **13** are derived from cyclopentenyl cation **8**, which is formed by attack of cyclopentadiene at the sp-terminus of **5**. While allyl cation **7** is trapped to give two diastereomeric alcohols **10** and **11**, **6** and **9** give only the exo-alcohols **3** and **14**, respectively. Since **14** rearranges to **3** on treatment with toluenesulfonic acid in dioxane at 70° C, **9** is considered to be a precursor of **6** and **3**.

Allyl cations **7** and **9** may either be formed by stepwise processes _via_ cation **8** or by concerted $_{\pi}2_{s}+_{\pi}2_{a}$ and $_{\pi}4_{s}+_{\pi}2_{s}$ mechanisms, respectively. In order to differentiate these possibilities, we treated **12** with 1.15 equivalents FSO_3H[8] in liquid SO_2 at -70° C. In the NMR spectra,[9] cation **7** was observed as the only species, indicating the cyclisation of **8** to **7**. Identical NMR spectra were obtained from **10** and FSO_3H. Quenching of these solutions with aqueous K_2CO_3 solution yielded **10** and **11** in 1:3.5 ratio.

Since **8** does not cyclise to give **9**, a concerted $_{\pi}4_{s}+_{\pi}2_{s}$ mechanism must be responsible for the formation of **9**. The observed rearrangement **8**→**7** furthermore suggests a stepwise [2+2]cycloaddition of **5** with cyclopentadiene, but cannot exclude the concerted $_{\pi}2_{s}+_{\pi}2_{a}$ process or a parallelism of stepwise and concerted mechanisms.

A weak point in our argumentation is the fact that the cycloaddition reactions and cyclisation experiments have been carried out under different conditions. Therefore, we added a mixture of triphenylpropargyl alcohol (**15**) and cyclopentadiene (1:1.3) to a solution of FSO_3H in SO_2 at -50° C. After alkaline workup **1**, **10**, **11** and **16** (25:47:20:9) were isolated in 33 % total yield.[7]



15

16
mp.154.5-155.5 °C

16 was formed in quantitative yield, when 14 was treated with FSO_3H at -78° C, and forms via electrocyclic ring closure of 9.[10] The low yield of quenching products in the latter cycloaddition reaction prevents a detailed interpretation. However, the mere fact that [2+2] and [4+2] addition products were obtained under the same conditions where 8 cyclised to 7 exclusively, proves the concerted [4+2] cycloaddition.

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7) Separation by column chromatography (silica gel, petroleum ether/dichloromethane). All compounds were structurally assigned by ^{1}H-NMR lanthanide shift experiments (EuFOD) and ^{13}C-NMR.
8) With a larger excess of acid, addition of FSO_3H to the cyclopentene double bond of 7 takes place.
9) ^{13}C-NMR of 7 ($CDCl_3$): δ = 37.3 (t), 49.8 (d), 55.8 (d), 127.8 - 139.9 (complex pattern), 152.1 (s), 182.7 (s), 210.0 (s).
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