Chem. Ber. 114, 1464 – 1475 (1981)

Cycloadditions of Allyl Cations, 26[1]

# Norbornene Derivatives from Cyclopentadiene and 2,4-Dimethyl-3-penten-2-ol in an Acidic Two Phase System. A Stepwise Diels-Alder-like Cyclization[2]

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Received September 1, 1980

2,4-Dimethyl-3-penten-2-ol (**1**) and cyclopentadiene react in an acidic two phase system at 0 – 25 °C in several steps yielding epimeric norbornenylcarbinols (*endo*-**4** and *exo*-**4**) and at least three isomeric allylcyclopentenols (**2a, b, c**), whereas allylcyclopentadienes (**3a, b**) and norbornene-type olefins (*endo*-**5**, *exo*-**5**, and **6**) are formed in traces under these conditions. All bicyclic products of this reaction were synthesized independently. On subjecting the pure product norbornenylcarbinols (*endo*-**4** and *exo*-**4**) to the acidic, two phase reaction conditions at slightly elevated temperature, i. e. 50 °C, some epimerization occurs and the norbornene-type olefins (*exo*-**5**, *endo*-**5**, and **6**) are mainly formed in addition to allylcyclopentadienes (**3a,b**), allylcyclopentenols (**2a, b, c**), nortricyclic alcohol **7**, and tricyclic ether **8**. Independently, the forward reaction was traced by subjecting the isomeric allylcyclopentenols **2b, c** to the acidic, two phase reaction conditions at 50 °C: once again, *endo/exo* bicyclization gave the olefins **5** and **6** as well as alcohols **4** and **7**. Hence, a stepwise Diels-Alder-like cyclization is proposed to account for the norbornene-type alcohols and bicyclic olefins, which are formed from the acid promoted reaction of cyclopentadiene and **1**.

**Cycloadditionen von Allyl-Kationen, 26[1]**

**Norbornenderivate aus Cyclopentadien und 2,4-Dimethyl-3-penten-2-ol in einem sauren Zweiphasensystem. Eine stufenweise Diels-Alder-ähnliche Cyclisierung[2]**

2,4-Dimethyl-3-penten-2-ol (**1**) und Cyclopentadien reagieren in einem sauren Zweiphasensystem bei 0 – 25 °C in mehreren Schritten unter Bildung epimerer Norbornenylcarbinole (*endo*-**4** und *exo*-**4**) sowie von mindestens drei isomeren Allylcyclopentenolen (**2a, b, c**). Allylcyclopentadiene (**3a, b**) und Olefine vom Norbornentyp (*endo*-**5**, *exo*-**5** und **6**) werden unter diesen Bedingungen in Spuren gebildet. Alle bicyclischen Produkte dieser Reaktion wurden unabhängig synthetisiert. Wenn die reinen Produkt-Norbornenylcarbinole (*endo*-**4** und *exo*-**4**) den sauren Zweiphasenbedingungen bei leicht erhöhter Temperatur, d.h. 50 °C, unterworfen werden, tritt teilweise Epimerisierung ein, und es bilden sich hauptsächlich Olefine vom Norbornentyp (*exo*-**5**, *endo*-**5** und **6**) neben Allylcyclopentadienen (**3a, b**) sowie Allylcyclopentenole (**2a, b, c**), Nortricyclylalkohol **7** und tricyclischer Ether **8**. Unabhängig wurde die Vorwärtsreaktion sichtbar gemacht, indem die isomeren Allylcyclopentenole **2b, c** den sauren Zweiphasenbedingungen bei 50 °C unterworfen

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wurden: *endo*- und *exo*-Bicyclisierung ergaben wiederum die Olefine **5** und **6** sowie die Alkohole **4** und **7**. Damit macht eine stufenweise Diels-Alder-ähnliche Cyclisierung die Bildung der Alkohole und Olefine vom Norbornentyp verständlich, welche aus der säure-induzierten Reaktion von Cyclopentadien und **1** entstehen.

The activation of allyl alcohols toward formation of allyl cations via low temperature trifluoroacetylation followed by zinc halide promoted alkyl-oxygen fission has been reported recently[3]. We now describe a still simpler method of activation which is applicable to allyl alcohols with a weak carbon-oxygen bond, i.e. allyl alcohols giving a comparatively stable allyl cation. The method will be exemplified by the acid induced two phase reaction of 2,4-dimethyl-3-penten-2-ol (**1**) and cyclopentadiene.

## Results

Although cyclopentadiene has long been known to be prone to dimerization and formation of deeply colored polymers under the influence of acids[4], we now show that it survives in an acidic two phase system to react with allyl alcohol **1**, giving mainly monocyclic allyl alcohols **2a, b, c** and epimeric norbornenylcarbinols *endo*-**4** and *exo*-**4** as well as some olefins. Chromatography of the more polar alcohols over silica gel for 1 week allowed us to separate various components (Tables 1 and 2). The cyclopentenols **2a – c** could easily be discerned by their pleasant odour.

Table 1. Products from the Reaction of Cyclopentadiene and 2,4-Dimethyl-3-penten-2-ol (**1**) in an Acidic Two Phase System[a]

| Reaction Time [h] | Reaction Temp. [°C] | % Alcohol[b] **2a, b, c** + **4** | [g] | Olefins[c] [g] |
|---|---|---|---|---|
| 1 | 0 | 31 | 1.40 | 0.36 |
| 1 | 0 | 31 | 1.40 | 0.43 |
| 7 | 0 | 33 | 1.48 | 0.64 |
| 7 | 0 | 37 | 1.65 | 0.66 |
| 24 | 0 | 35 | 1.57 | 0.79 |
| 1 | 25 | 29 | 1.32 | 0.42 |
| 1 | 25 | 36 | 1.63 | 0.69 |
| 1 | 25 | 38 | 1.73 | 0.65 |
| 4 | 25 | 33 | 1.48 | 0.70 |
| 4 | 25 | 37 | 1.65 | 0.75 |

[a] Alcohol (**1**) (2.85 g, 25 mmol) and cyclopentadiene (3.3 g, 50 mmol) in pentane (5 ml) were stirred with water (5 ml) containing *p*-toluenesulfonic acid (2.4 g, ca. 13 mmol). – [b] **2a, b, c**:**4** is ca. 2.4:1, 2.5:1. At least three isomeric allylcyclopentenols **2a, b, c** are formed (carbowax 20 M); (*endo*-**4**):(*exo*-**4**) = 2.5:1. Polymer residue from distillation: 0.13 – 0.20 g. – [c] Mainly dicyclopentadiene; **6** (ca. 1%) was isolated by preparative GC (6 m SE 30 column) and also synthesized independently (see text). Further olefin products: **5** (ca. 1%), two substituted cyclopentadienes **3a, b** (ca. 1%), dimeric diene $C_{14}H_{24}$ (2 – 3%). Higher boiling polymers: 0.10 – 0.30 g.

Among the minor olefins, dicyclopentadiene predominated, whereas the norbornene-type Saytzeff olefin **6** and the epimeric Hofmann olefins *endo*-**5** and *exo*-**5** (cf.

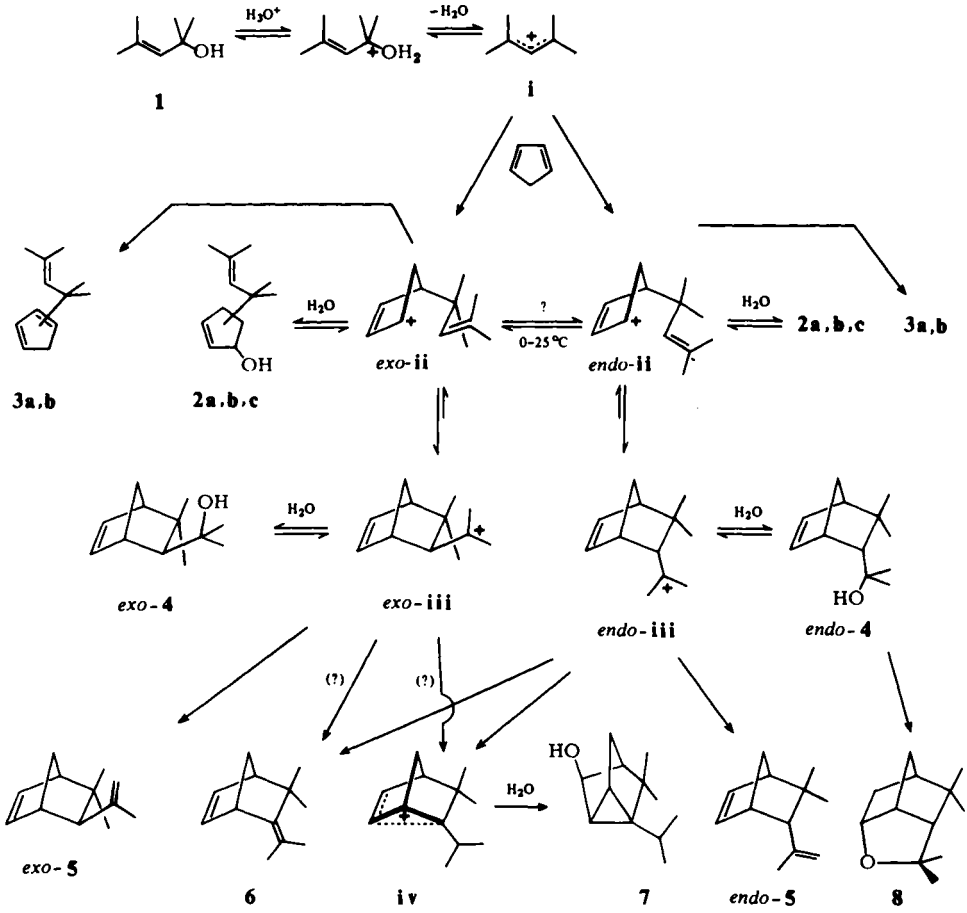
Table 2. Equilibration of Epimeric Norbornenylcarbinols **4** in Aqueous Toluenesulfonic Acid/Light Petroleum (bp. 60 – 70 °C) at 50 °C[a]

| Entry | Starting Alcohol (*endo*-**4**):(*exo*-**4**) initial | final[c] | % **3a,b** | % **5** | % **6** | % Olefins[b] | (*endo*-**5**):(*exo*-**5**) | Saytzeff:Hofmann **6**:**5** | % **2a,b,c** | % **4** | % **7** | % Alcohols[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ∞ | 1.8:1 | 7 | 11 | 30 | 48 | 1.4:1 | 2.7:1 | 6 | 15 | 20 | 41 |
| 2 | 2.4:1 | 1 :1.3 | 6 | 15 | 31 | 52 | 1 :2 | 2 :1 | 8 | 17 | 8 | 33 |
| 3 | 2.4:1[d] | 1 :1 | 4 | 9 | 21 | 34 | 1 :2.1 | 2.3:1 | 5 | 20 | 26 | 51 |
| 4 | 2 :1 | 1.3:1 | 11 | 15 | 29 | 55 | 1 :3 | 2 :1 | 4 | 9 | 16 | 29 |
| 5 | 1 :2.4 | 1 :1 | 7 | 18 | 23 | 48 | 1 :6.8 | 1.3:1 | 7 | 17 | 7 | 31 |
| 6 | 1 :2.4[d] | 1.3:1 | 8 | 19 | 22 | 49 | 1 :5.1 | 1.2:1 | 4 | 8 | 3 | 15 |
| 7[e] | 2.4:1 | – | 11 | 15 | 24 | 47 – 56 | 1 :2.3 | 1.7:1 | | | 23[f] | 21 – 25 |

[a] Alcohol **4** (1.80 g, 10 mmol or 4.5 g, 25 mmol) in light petroleum (10 ml) was stirred for 1 h at 50 °C with a solution of *p*-toluenesulfonic acid (2.4 g, ca. 13 mmol) in water (5 ml). Olefins **5** and **6** were stable to the equilibration conditions. Tricyclic ether **8** was formed in less than 2%. – [b] % Olefin: % alcohol determined by weighing after chromatography. The concentration of the individual products has been determined by integration of appropriate $^1$H NMR signals. – [c] Ratio approximate because of ill-resolved $^1$H NMR signals. – [d] Duplicate experiment with bigger sample of **4**. – [e] Heating at reflux temperature. – [f] (*exo*-**7**):(*endo*-**7**) = 6.1:1 at reflux temperature. At 50 °C *endo*-**7** is not discernible ($^1$H NMR).

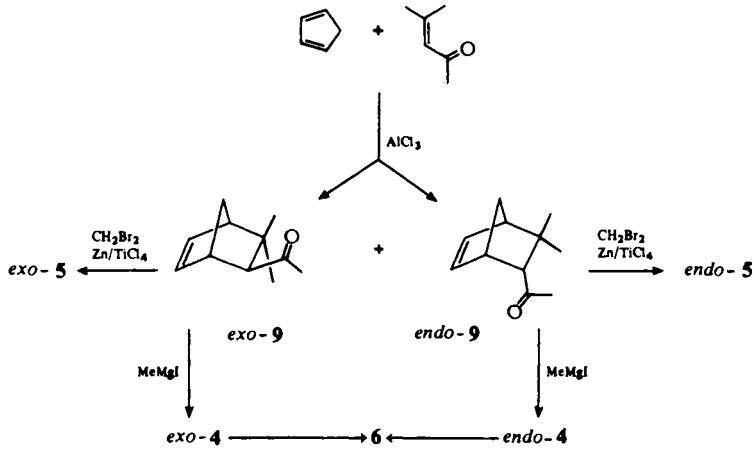
Scheme 1) were formed in traces (less than 1% each) at 0 and 25°C. We identified these minor, but mechanistically informative olefins by independent synthesis (Scheme 2): $AlCl_3$ promoted Diels-Alder addition of mesityl oxide to cyclopentadiene gave an epimeric mixture of adducts [(*endo*-**9**):(*exo*-**9**) = 2.4:1; cf. also Table 2, entries 2 and 3]. Base catalyzed equilibration allowed us to accumulate the more stable *exo*-epimer [(*endo*-**9**):(*exo*-**9**) = 1:2.4][5]. Methylenation[6] of ketone **9** gave the Hofmann olefins *endo*-**5** and *exo*-**5**, whilst methylation with Grignard reagent produced the norbornenylcarbinols *endo*-**4** and *exo*-**4**, which were dehydrated to Saytzeff olefin **6** in addition to other products (Table 2). 6-Isopropylidene-5,5-dimethyl-2-norbornene (**6**), which may also be regarded as the hypothetical Diels-Alder adduct of cyclopentadiene and tetramethylallene, was conveniently isolated and purified via its $AgNO_3$ complex (Table 4). Finally, the pure norbornenylcarbinols obtained as sketched in Scheme 2 were sub-

Scheme 1. Postulated Routes to **2** – **8** from Acid Catalyzed Two Phase Reaction of Allyl Alcohol **1** and Cyclopentadiene (**5**, **6**, and **7** are mainly formed at 50°C)

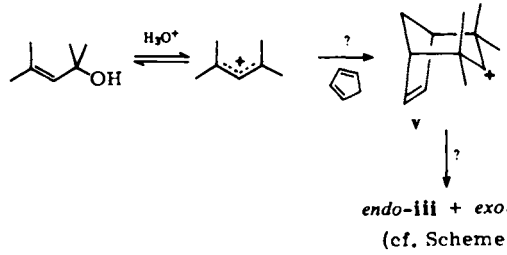


jected to the experimental conditions of the two phase system at slightly elevated temperature (50°C vs. 0–25°C). The results of these equilibration experiments are summarized in Table 2. Of course, the equilibrated system is not completely closed, but partially open in that, e.g. leakage into polymer formation is possible. Nonetheless, entries 1 – 5 show that the recovery of olefins + alcohols is 80% and higher, although mechanical losses on, e.g., distillation are inevitable. A major new compound formed at 50°C was a secondary alcohol [$^1$H NMR, $(CD_3)_2SO$ solvent; IR] of molecular weight $C_{12}H_{20}O$ which had no olefinic protons and was formulated as nortricyclic alcohol **7**. A minor $C_{12}H_{20}O$ product (< 2%) formed was tricyclic ether **8**.

Scheme 2. Independent Synthesis of Norbornene-Derived Products **4**, **5** and **6**




Scheme 3. Norbornenes via Rearrangement of [3.2.1] Bicyclics?




## Discussion

Once it has been shown that the reactions outlined in Table 1 are indeed feasible, the question arises as to how the various products are formed. It is a fortunate circumstance that the norbornenylcarbinols *endo*-**4** and *exo*-**4**, untrammelled by other products, can be subjected to the experimental conditions of running the cycloaddition

of **1** and cyclopentadiene in Table 1 (same pH, two phases, stirring) and that at the slightly higher temperature they enter into reactions which are not yet or hardly discernible at 25°C and below. Invoking the principle of microscopic reversibility we may assume that the products of equilibration (Table 2) are on the path of the acid promoted cycloaddition of cyclopentadiene and **1** (Table 1). Now the equilibration of the norbornenylcarbinols *endo*-**4** and *exo*-**4** can be seen to show up as a back reaction to monocyclic products **2a, b, c** and **3a, b** as well as a forward reaction to bicyclic olefins *exo*-**5**, *endo*-**5**, and **6**, and also tricyclic alcohol **7** and tricyclic ether **8**. Note that these bicyclic olefins and alcohol **7** (Table 2) are hardly or not at all formed from cyclopentadiene and **1** in the temperature range 0 – 25°C (Table 1). The results from the acid catalyzed equilibration can be summarized as follows (cf. also Scheme 1):

1) Alcohol *endo*-**4** reacts more readily than alcohol *exo*-**4**, consistent with the higher energy content of the *endo* epimer. Even if the initial *endo:exo* ratio is high or pure *endo*-**4** is equilibrated, the final (*endo*-**4**):(*exo*-**4**) ratio is about 1:1 within experimental error. Altogether, the *endo* series which has the further escape into tricyclic ether **8**, is more rapidly depleted than the *exo* series.

2) Of the two olefinic types, Saytzeff and Hofmann, the Saytzeff olefin **6** always predominates, despite the statistical advantage of Hofmann olefin to exist as stereoisomeric *exo*-**5**/*endo*-**5** mixture. Further, Saytzeff olefin **6** is always the major product at 50°C, with the possible exception of entry 3, where the overall proportion of olefins compared with alcohols is low.

3) Of the epimeric norbornenylcarbinols, alcohol *endo*-**4** is more prone to give Saytzeff olefin **6** and, of course, tricyclic ether **8**. Conversely, an epimeric mixture rich in *exo*-**4** gives a comparatively high proportion of Hofmann olefin **5**, especially *exo*-**5** (entries 5 and 6). We suggest that loss of the tertiary proton from intermediate cation *exo*-**iii** with formation of **6** is difficult on stereoelectronic grounds in that the vacant carbenium carbon p orbital and the adjacent tertiary C – H bond in *exo*-**iii** are nearly orthogonal, whereas the dimethylcarbinyl side chain will be able to rotate more freely in *endo*-**iii** and hence gives rise to **6** more easily. Control experiments show that the bicyclic olefins **5** and **6** are stable to the equilibration conditions at 50°C.

4) The formation of nortricyclic alcohol **7** from norbornene precursors on equilibration with acid shows that the tricyclic system is comparatively stable, consistent with the equilibrium of the parent system which is on the side of the tricyclic isomer (norbornene:nortricyclene = 23:77[7]). We postulated above (cf. 3) that *endo*-**iii** is more likely to lose the tertiary proton and form **6** than *exo*-**iii**. On similar grounds, *endo*-**iii** should suffer 1,2 hydride shift to nortricyclic cation **iv** more readily than *exo*-**iii**. At reflux temperature leakage into another nortricyclic alcohol, presumably *endo*-**7** [(*exo*-**7**):(*endo*-**7**) = 6.1:1] is also observed (Table 2, entry 7).

5) Interestingly, our norbornenylcarbinols *endo*-**4** and *exo*-**4** must suffer some acid catalyzed epimerization at 50°C. Note that pure *endo*-**4** (entry 1) leaks into products of the *exo* series, i.e. alcohol *exo*-**4** and olefin *exo*-**5** (ca. 10%).

Thus, the formation of *exo* products is not just the consequence of a selective depopulation of the more reactive *endo* alcohol *endo*-**4**, but the result of a novel acid promoted *endo/exo* epimerization of a norbornene derivative which we formulate via

Table 3. Bicyclization via Equilibration of Isomeric Allylcyclopentenols **2** in Aqueous Toluenesulfonic Acid/Light Petroleum (bp. 60–70 °C) at 50 °C[a]

| Educt | (*endo*-**4**):(*exo*-**4**) initial | final | **3a,b** | **5** | **6** | % Olefins | (*endo*-**5**):(*exo*-**5**) | Saytzeff:Hofmann **6**:**5** | **2a,b,c** | **4** | **7** | % Alcohols[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **2b,c** | – | 1:1.3 | 14 | 8 | 28 | 50 | 1:2 | 3.4:1 | 3 | 5 | 12 | 21 |
| **2c** | – | 1:1.6 | 14 | 6 | 12 | 32 | 1:2.7 | 2 :1 | 4 | 7 | 15 | 26 |

[a] Cf. Table 2, footnotes a) and b) for experimental conditions and method of analysis. – [b] In addition 0.13 – 0.20 g of polymer and traces (ca. 5 %) of an unknown ketone ($C_{12}H_{18}O$) were formed. It is possible that this ketone was formed by aerial oxidation of **2a, b, c** and was present in the reaction mixture from the very beginning.

Table 4. Isolation and Purification of 6-Isopropylidene-5,5-dimethylbicyclo[2.2.1]hept-2-ene (**6**) via its $AgNO_3$ Complex

| Olefin mixture (g) | Educt **3a,b** | **5** | **6** | $AgNO_3$ Complex (crude) (g) | (%) | (g) | (%) | Aqueous phase (g) | (%) | Remaining Educt **3a, b**:**5**:**6** | Mother liquor (g) | (%) | **3a, b**:**5**:**6** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.95 | 12 | 24 | 64 | 2.60 | 78 | 2.14 | 71 | 0.07 | 4 | 1: 9.6:2 | 0.11 | 6 | 1 :8.2:4.7 |
| 1.76 | 31 | 26 | 44 | 1.74 | 64 | 1.40 | 52 | 0.24 | 14 | 1:20 :1 | 0.12 | 7 | 1.5:6.8:1 |
| 0.64 | 11 | 22[a] | 67 | 0.86 | 88 | | | 0.04 | 6[b] | | | | |

[a] (*endo*-**5**):(*exo*-**5**) = 1:1.9. In the aqueous phase, after precipitation with $AgNO_3$, the ratio is 1:3.8. – [b] Neither **3a, b** nor **6** are discernible by $^1H$ NMR.

fragmentative ring opening to allylcyclopentenyl cation **ii**. Presumably, **ii** exists in several conformations. An open conformation seems likely to react with an external nucleophile, i.e. water, to give **2a, b, c** or lose a proton to give **3a, b**, whereas compact conformations are required for *endo* and *exo* bicyclization.

6) As the norbornenylcarbinols *endo*-**4** and *exo*-**4** may revert to allylcyclopentenols **2a, b, c**, the key reaction in the forward cycloaddition is formulated as an electrophilic attack of cation **i**[*] on cyclopentadiene to give another allyl cation **ii**. We do not believe that the bicyclo [3.2.1] route is followed here which we first established, e.g. for the reaction of cyclopentadiene and the 2-methylallyl cation[8]. Formation of secondary cation **v** (Scheme 3) is thermodynamically unfavourable and subsequent ring contraction of **v** to norbornene derivatives, whilst feasible, requires more forcing conditions in this instance[9].

7) As a further check on Scheme 1, we have bicyclized the isomeric allylcyclopentenols **2b, c** under our general conditions, i.e. in the acidic water-hydrocarbon mixture at 50°C (Table 3). The product distribution is similar to that obtained from the norbornenylcarbinols **4**. If anything, the products of thermodynamic control, i.e. bicyclic olefin **6** (28%) and nortricyclic alcohol **7** (12%), are formed even more prominently here. Formally, the bicyclization of allylcyclopentenols **2b, c** represents a novel norbornene synthesis.

8) It is striking that the acid catalyzed two phase reaction of **1** and cyclopentadiene gives ratios of *endo/exo* products, i.e. (*endo*-**4**):(*exo*-**4**) = 2.5:1, which are comparable to the $AlCl_3$ catalyzed cycloaddition of mesityl oxide to cyclopentadiene [(*endo*-**9**):(*exo*-**9**) = 2.4:1, cf. Scheme 2]. Thus, the combination of cyclopentadiene and **i** has characteristics of the bona fide Diels-Alder reaction of cyclopentadiene and mesityl oxide/$AlCl_3$. Yet, as a major product, isomeric allylcyclopentenols **2a, b, c** are formed and one hesitates to regard an allyl cation as a classical dienophile, which enters into concerted [4 + 2] additions. A stepwise combination of cyclopentadiene and **i**, involving a *conformationally free* allylcyclopentenyl cation **ii** seems equally unsatisfactory, as we would expect *endo/exo* product ratios of thermodynamic control, with the more stable *exo* epimer dominating. It is for these reasons that two oriented ion pairs or π-complexes, i.e. *endo*-**ii** and *exo*-**ii**, have been postulated as precursors for the products of the *endo* and *exo* series in the temperature range 0 – 25°C (Scheme 1). The $AlCl_3$ catalyzed cycloaddition should be regarded as mechanistically related.

*Conclusions:* The reactions which we have described, by virtue of the two phase system and the chosen experimental conditions show the power of microscopic reversibility for tracing reaction paths and for making various intermediates visible. Our work also points to novel ways in which allyl cations can react with conjugated dienes. The reactions are preparatively useful as they can be scaled up, the starting materials being cheap and the reactions being easy to run. Finally, complexation by $AgNO_3$ appears to be the method of choice for handling 5-alkylidene-2-norbornenes as it is for bicyclo[3.2.1]octa-2,6-dienes[9].

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[*] For simplicity ion **i** is formulated as a symmetrical species, without regard to possible complications due to solvation and ion pairing.

We thank Drs. *E. J. Brunke* and *F. J. Hammerschmidt* of Dragoco for GC-MS measurements, *K. L. Loening* of Chemical Abstracts for help regarding nomenclature, and the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for support of our work.

## Experimental Part

IR spectra: Perkin-Elmer 457 and 590. – $^1$H NMR spectra: Bruker HX 90 and WH 90. – Mass spectra: Varian CH 5. – Gaschromatography: Varian 1400 FID, $N_2$ as carrier gas. – Preparative GC: Wilkens A 700 Autoprep.; thermal conductivity detector, $H_2$ as carrier gas, 6m 5% SE 30 column. – Chromatography: Silica gel 0.2 – 0.5 mm (technical) and 0.05 – 0.2 mm (Macherey-Nagel). – Microanalyses: Frau *E. Jirotka*, Institut für Organische Chemie, Universität Hannover.

*2,4-Dimethyl-3-penten-2-ol* (**1**) (cf. also ref.[10]): Magnesium turnings (36.5 g, 1.5 mol) in absol. ether (150 ml) are allowed to react with some methyl iodide [ca. 1/20 of 1.5 mol (10.7 g)]. After the reaction has started the remaining methyl iodide in ether (250 ml) is dropped in at a rate which sustains gentle boiling of the ether. The solution is refluxed for 0.5 – 1 h and cooled to 0 – 5 °C (ice water/NaCl). 4-Methyl-3-penten-2-one (mesityl oxide) (1.2 mol, 118 g) in absol. ether (250 ml) is dropped in over a period of 3 – 4 h. The reaction mixture is stirred for 1 h at 0°C, left overnight at room temperature and re-cooled to 0°C. Ice water (100 g) is carefully stirred into the solution during 2 – 3 h, the temperature being kept below 10°C. As soon as the evolution of gas has ceased and the temperature does not rise further, the mixture is efficiently stirred into a solution of ammonium chloride (85 g) in water (85 ml). After settling of the precipitate the clear ether solution is decanted (*Note 1*) and the precipitate digested with ether (3 ×). The combined organic phase is washed with water containing some $K_2CO_3$ (*Note 2*), washed and dried. After removal of the solvent the remaining oil is distilled at the Kugelrohr (water pump vacuum), the temperature not exceeding 80°C (*Note 3*), to give **1** (95 – 110 g, 70 – 80%). – 60 MHz $^1$H NMR ($CCl_4$): δ = 1.28 (s, 6H), 1.65 (m, 3H), 1.82 (m, 3H), 2.22 (s, 1H, OH), 5.27 (m, 1H).

*Note 1:* If the ether solution turns darker (orange-red-black), further work up should proceed as quickly as possible, otherwise substantial decomposition occurs. Darkred to black solutions contain hardly any product allyl alcohol, but mainly diene and polymers.

*Note 2:* Distilled water appears to promote decomposition.

*Note 3:* However, two samples were distilled at the Kugelrohr without noticeable decomposition at 100°C and higher pressure. The presence of some solid $K_2CO_3$ in the distillation flask seems advisable. The allyl alcohol is also oxygen sensitive, especially during work up.

*Acid Catalyzed Two Phase Reaction of Cyclopentadiene and 2,4-Dimethyl-3-penten-2-ol* (**1**): **1** (2.85 g, 25 mmol) and cyclopentadiene (3.3 g, 50 mmol) in pentane (5 ml) were stirred with water (5 ml) containing *p*-toluenesulfonic acid (2.4 g, ca. 13 mmol) at 0 and 25°C as specified in Table 1. The reaction mixture was worked up by neutralizing with aqueous $NaHCO_3$, separating the organic phase and extracting the aqueous layer with three portions of pentane. The collected organic phase was washed with water, dried ($Na_2SO_4$), and the solvent removed at reduced pressure to leave an oil which was filtered over silica gel (25 g) with pentane (ca. 200 ml) as eluent. The less polar product olefins were collected. After elution with ether (100 – 150 ml) the alcoholic eluates were dried ($Na_2SO_4$), freed from solvent, and distilled at the Kugelrohr (cf. Table 1). Chromatography of the product alcohols (4.4 g) over silica gel (200 g) with light petroleum (bp. 40 – 60°C)/ether (10 vol%) gave 5 isomers in the sequence of increasing polarity (on silica gel and also on GC (CWAX 20M)): *endo*-**4** < *exo*-**4** < **2a** < **2b** < **2c**.

*α,α,3,3-Tetramethylbicyclo[2.2.1]hept-5-ene-2-methanol, endo epimer* (*endo*-**4**): 0.54 g, colorless solid at room temperature. – 90 MHz $^1$H NMR ($CCl_4$): δ = 0.95 (s, 1H), 1.08 (s, 3H), 1.19 (s, 3H), 1.22 (s, 3H), 1.38 (s, 3H), 1.32 [d ($J$ = 8 Hz) of t ($J$ = 1.7 Hz), 1H], 1.60 [d ($J$ = 8 Hz) of t ($J$ = 1.5 Hz), 1H], 1.79 (d, $J$ = 3 Hz, 1H), 2.17 – 2.31 (m, 1H), 2.80 – 2.95 (m, 1H), 6.07 – 6.28 (m, 2H). In $(CD_3)_2SO$ solvent the OH proton appeared as a singlet at 3.65 ppm. – MS (70 eV, room temperature): *m/e* = 180 (2%, $M^+$), 165 (2), 162 (3), 147 (3), 107 (11), 105 (8), 99 (76), 97 (71), 93 (9), 91 (9), 81 (17), 79 (24), 77 (13), 66 (100).

*α,α,3,3-Tetramethylbicyclo[2.2.1]hept-5-ene-2-methanol, exo epimer* (*exo*-**4**): 0.56 g, isolated as a colorless oil containing *endo*-**4**. Spectra were measured on the last fraction richest in *exo*-**4**. – 90 MHz $^1$H NMR ($CCl_4$): δ = 0.93 (s, 3H), 1.29 (s, 6H), 1.35 (s, 3H), 0.93 – 1.35 (m, 2H), 1.72 – 1.90 (m, 1H), 2.15 – 2.32 (m, 1H), 2.59 – 2.70 (m, 1H), 6.02 (dd, $J$ = 3 and 5.8 Hz, 1H), 6.16 (dd, $J$ = 3 and 5.8 Hz, 1H). In $(CD_3)_2SO$ solvent the OH proton appeared as a singlet at 4.04 ppm. – MS (70 eV): *m/e* = 180 (2%, $M^+$), 165 (2), 162 (3), 147 (5), 121 (4), 119 (5), 107 (11), 105 (9), 99 (100).

*Independent Synthesis of endo- and exo-***4**: Methyl iodide (14.2 g, 0.10 mol) in absol. ether (50 ml) was added dropwise to magnesium turnings (2.4 g, 0.10 mol) in absol. ether (50 ml), the reaction solution boiling gently and after complete addition, being refluxed for 1 h. Bicyclic ketone **9**[5] (9.84 g, 0.060 mol) in absol. ether (50 ml) was added dropwise at 0 – 5°C for 1 – 2h. After being stirred for 1 h at 0°C and 12 h at room temperature the solution was cooled to 0°C and worked up by carefully adding ice water (5 ml) such that the temperature did not exceed 10°C (the product alcohols being dehydrated easily). After addition of $NH_4Cl$ (5 g) the solution was decanted and the precipitate digested three times with ether. The combined ether layer was washed with water, dried ($Na_2SO_4$), and the solvent evaporated to leave a residue which was distilled at the Kugelrohr (80 – 100°C/ca. 1 Torr). Starting from **9** (*endo:exo* = 2.4:1) colorless alcohol **4** (9.63 – 9.85 g, 89 – 91%) was obtained, solid at room temperature. **9** (*endo:exo* = 1:2.4) gave **4** (9.70 – 9.85 g, 90 – 91%) as a colorless oil. The alcohols were separated by chromatography on silica gel and by GC (CWAX 20M) as described above.

$C_{12}H_{20}O$ (180.3) Calcd. C 79.94 H 11.18 Found C 79.80 H 11.02

*4- and 5-(1,1,3-Trimethyl-2-butenyl)-2-cyclopenten-1-ols* (**2a, b, c**): The least polar **2a** was a minor isomer and could not be isolated pure. Unlike *endo*-**4** and *exo*-**4** these cyclopentenols are pleasant smelling liquids. – 90 MHz $^1$H NMR ($CDCl_3$): inter al. δ = 1.12 (s, 3H), 1.16 (s, 3H), 1.69 (d, $J$ = 1.5 Hz, 3H), 1.76 (d, $J$ = 1.5 Hz, 3H), 5.66 – 5.96 (m, 2H). – GC-MS (70 eV, room temperature): *m/e* = 165 (1%, $M^+$ – 15), 162 (4), 147 (8), 123 (88), 119 (9), 109 (30), 107 (8), 105 (12), 99 (20), 97 (100), 95 (23), 91 (16), 83 (19), 82 (44), 81 (21), 79 (16), 77 (14), 69 (28), 67 (18), 65 (10), 57 (60), 55 (93), 53 (20).

*Isomer* **2b**: 90 MHz $^1$H NMR ($CCl_4$): δ = 1.05 (s, 3H), 1.07 (s, 3H), 1.0 – 1.44 (m, 1H), 1.67 (d, $J$ = 1.5 Hz, 3H), 1.71 (d, $J$ = 1.5 Hz, 3H), 1.9 – 2.67 (m, 2H), 1.44 (s, 1H (OH)), 4.54 – 4.76 (m, 1H), 5.01 – 5.14 (m, 1H), 5.74 (s, 2H) [in $CCl_4$ and $(CD_3)_2SO$ this signal appears as a singlet, in $CDCl_3$ as a multiplet]. – MS (70 eV): *m/e* = 180 (2%, $M^+$), 165 (3), 162 (2), 147 (5), 97 (100). – GC-MS: 162 (1%, $M^+$ – 18), 147 (1), 97 (100), 91 (3), 81 (3), 79 (3), 77 (3), 69 (14), 67 (3), 65 (3), 57 (9), 55 (53), 53 (7).

*Isomer* **2c**: 90 MHz $^1$H NMR ($CCl_4$): δ = 1.02 (s, 3H), 1.04 (s, 3H), 1.64 (m, $J$ = 1.5 Hz, 3H), 1.74 (m, 3H), 1.60 – 1.90 (m, 2H), 2.78 – 3.03 (m, 2H), 4.59 – 4.80 (m, 1H), 4.92 – 5.09 (m, 1H), 5.80 (s, 2H) [in $CCl_4$ and $(CD_3)_2SO$ this signal appears as a singlet, in $CDCl_3$ as a multiplet]. – MS (70 eV, room temperature): *m/e* = 180 (1%, $M^+$), 165 (2), 162 (3), 147 (8), 123 (8), 119 (5), 107 (5), 105 (5), 97 (100).

$C_{12}H_{20}O$ (180.3) Calcd. C 79.94 H 11.18 Found C 79.97 H 10.81

Traces of the three bicyclic olefins *endo*-**5**, *exo*-**5**, and **6** as well as **3a, b** were first of all isolated from the pentane eluates after preparative GC and identified by $^1$H NMR spectroscopy (Table 1). Their structures were confirmed by independent syntheses (cf. Scheme 2 and below).

The olefin fraction of the two phase equilibration at 50°C (Table 2) contained two isomeric 4- and 5-(1,1,3-trimethyl-2-butenyl)-1,3-cyclopentadienes in differing proportions (1.6:1 to 2.7:1). The following signals were assigned to isomer **3a**: 90 MHz $^1$H NMR ($CDCl_3$): δ = 1.29 (s, 6H), 1.69 (m(?), 6H), 2.82 – 2.90 (q, 2H), 5.22 – 5.40 (m, 1H), 5.94 – 6.55 (m, 3H). **3b**: 1.28 (s, 6H), 1.64 – 1.69 (6H), 2.90 – 2.98 (q, 2H), 5.22 – 5.44 (m, 1H), 5.94 – 6.55 (m, 3H).

*Independent Synthesis of 5,5-Dimethyl-6-(1-methylethenyl)bicyclo[2.2.1]hept-2-ene* (**5**) (*endo and exo epimer*): Following the methylenation method of *Nozaki* et al.[6] titanium tetrachloride (2.09 g, 11 mmol) followed by absol. dichloromethane (11 ml) were dropped into a suspension of zinc dust (2.95 g, 45 mmol) in dibromomethane (2.60 g, 15 mmol) and absol. tetrahydrofuran (50 ml) under nitrogen for ca. 15 min at room temperature. The solution warmed and turned dark brown. After a further 15 min bicyclic ketone **9**[5] (1.64 g, 10 mmol) in absol. tetrahydrofuran (10 ml) was added dropwise. The resulting suspension was stirred for 24h at room temperature and added to solid $NaHCO_3$ (3 g). After dropping in a little water the solution was decanted, the remaining precipitate being digested three times with dichloromethane. The combined organic phase was washed with water, dried ($MgSO_4$), and the solvent removed to leave an oily residue which was distilled at the Kugelrohr (80 – 100°C/water pump). Starting from **9** (*endo:exo* = 2.4:1) colorless **5** (1.50 g, 93%) was obtained. Similarly, **9** (*endo:exo* = 1:2.4) gave **5** (1.40 g, 86%).

*5,5-Dimethyl-6-(1-methylethenyl)bicyclo[2.2.1]hept-2-ene* (*endo*-**5**): 90 MHz $^1$H NMR ($CCl_4$): δ = 0.74 (s, 3H), 1.28 (s, 3H), 1.67 (m, *J* = 1 Hz, 3H), 1.28 – 1.81 (m, 2H), 2.21 – 2.44 (m, 2H), 2.74 – 2.91 (m, 1H), 4.55 – 4.70 (m, 2H), 6.0 – 6.27 (m, 2H). – MS (70 eV): *m/e* = 162 (5%, $M^+$), 147 (8), 119 (10), 106 (12), 97 (100), 92 (19), 82 (73). *exo*-**5**: 90 MHz $^1$H NMR ($CCl_4$): δ = 0.98 (s, 3H), 1.01 (s, 3H), 1.74 (m, *J* = 1 Hz, 3H), 1.28 – 1.90 (m, 3H), 2.23 – 2.34 (m, 1H), 2.62 – 2.74 (m, 1H), 4.58 – 4.71 (m, 1H), 4.71 – 4.80 (m, 1H), 6.0 – 6.27 (m, 2H). – MS (70 eV): *m/e* = 162 (5%, $M^+$), 147 (10), 119 (13), 105 (12), 96 (100), 91 (24), 81 (73).

$C_{12}H_{18}$ (162.3) Calcd. C 88.82 H 11.18 Found C 88.67 H 11.18

*6-Isopropylidene-5,5-dimethylbicyclo[2.2.1]hept-2-ene* (**6**) was obtained most conveniently via its $AgNO_3$ complex (cf. below). – 90 MHz $^1$H NMR ($CCl_4$): δ = 1.04 (s, 3H), 1.30 (s, 3H), 1.68 (s, 6H), 1.36 – 1.50 (m, 1H), 1.59 – 1.68 (m, 1H), 2.26 – 2.40 (m, 1H), 3.40 – 3.53 (m, 1H), 5.92 – 6.14 (m, 2H). – MS (70 eV): *m/e* = 162 (53%, $M^+$), 147 (61), 121 (32), 119 (33), 96 (75), 91 (49), 81 (100).

$C_{12}H_{18}$ (162.3) Calcd. C 88.82 H 11.18 Found C 88.28 H 11.18

*$AgNO_3$ complex of* **6**: A mixture of the olefins **3**, **5**, and **6** (ca. 2 g, cf. Table 4), which had been obtained from an equilibration experiment (Table 2), was dropped into a solution of silver nitrate (2 g) in distilled water (2 ml). The resulting mixture, which was shaken gently, became warm. After cooling to room temperature (0.5h) the lightcolored paste was suction filtered for 1h to achieve best possible drying. The aqueous phase and the collected mother liquor were diluted with water (5 ml each) and extracted three times with pentane. The combined extracts were washed with water and dried ($Na_2SO_4$). After evaporation of the solvent the remaining oil was distilled at the Kugelrohr (80 – 100°C/water pump) (cf. Table 4).

The complex was dissolved in methanol at 40°C and the resulting solution filtered. On cooling to room temperature the colorless complex was precipitated (see Note below), suction filtered, washed with a little methanol, and dried at the water pump, whilst the mother liquor was concentrated and recycled. (Note: The silver nitrate complex of 6 must be precipitated slowly, as bicyclic olefin **5** is co-precipitated otherwise). Complex m.p. 132.5°C. – 90 MHz $^1$H NMR

($CD_3CN$): δ = 1.05 (s, 3H), 1.30 (s, 3H), 1.68 (6H), 1.30 – 1.47 (m, 1H), 1.59 – 1.74 (m, 1H), 2.32 – 2.46 (m, 1H), 3.37 – 3.48 (m, 1H), 6.02 – 6.26 (m, 2H). A trace of *endo*-**5** was still present (cf. Table 4, footnote a and b).

$(C_{12}H_{18})_2 \cdot AgNO_3$ (332.2) Calcd. C 58.30 H 7.34 N 2.83 Found C 58.53 H 7.43 N 2.92

*Recovery of* **6** *by decomposition of its* $AgNO_3$ *complex:* The complex was dissolved in aqueous ammonia and the solution extracted three times with little pentane. The combined organic phase was washed with water and dried over magnesium sulfate. After removal of the solvent the remaining oil was distilled at the Kugelrohr, 0.70 g of the complex gave 0.32 g of olefin **6** (70%) and 1.14 g of the complex gave 0.53 g of **6** (71%).

A mixture (2.0 g) of alcohols **2a, b, c, 4, 7,** and tricyclic ether **8** from an equilibration experiment (Table 2) was chromatographed on silica gel (80 g) with light petroleum/ether (10 vol%) as eluent, the polarity increasing along the series **8** < *endo*-**4** < *exo*-**4** < **2a** < **2b** < *exo*-**7** < **2c**.

*2,2,4,4-Tetramethyl-5-oxatricyclo[4.2.1.0$^{3,7}$]nonane**) (**8**): 0.10 g (ca. 2%). – 90 MHz $^1$H NMR ($CDCl_3$): δ = 1.01 (s, 3H), 1.17 (s, 3H), 1.20 (s, 3H), 1.41 (s, 3H), 1.24 – 1.80 (m, 6H), 2.93 – 3.07 [m(br t centered on 3.00), 1H], 4.25 (dd, *J* = 7 Hz, 5 Hz, 1H).

*7,7-Dimethyl-1-(1-methylethyl)tricyclo[2.2.1.0$^{2,6}$]heptan-3-ol* (*exo*-**7**): 90 MHz $^1$H NMR ($CDCl_3$): δ = 0.84 (d, *J* = 7 Hz, decoupling expt., 6H), 0.92 (s, 3H), 0.98 (s, 3H), 1.07 – 1.76 (m, 5H), 1.94 (sept, *J* = 7 Hz, decoupling expt., 1H), 4.25 (t, *J* = 1.7 Hz, 1H). In $(CD_3)_2SO$: 0.81 (d, *J* = 7 Hz, 3H), 0.82 (d, *J* = 7 Hz, 3H), 0.87 (s, 3H), 0.93 (s, 3H), 0.98 – 1.80 (m, 5H), 1.90 (sept, *J* = 7 Hz, 1H), 4.00 – 4.11 (m, 1H), 4.23 (d, AB type, *J* = 4 Hz, 1H) (OH: exchange after addition of $CF_3CO_2H$). – MS (70 eV): *m/e* = 180 (28%, $M^+$), 165 (10), 162 (10), 147 (14), 137 (100), 122 (26), 121 (30), 119 (26), 109 (85), 107 (50), 105 (25), 97 (91), 95 (61), 93 (42), 91 (67).

$C_{12}H_{20}O$ (180.3) Calcd. C 79.94 H 11.18 Found C 80.02 H 10.65

Heating of the bicyclic alcohols **4** at reflux produced also an isomer (*endo*-**7**?) (Table 2, footnote f): $^1$H NMR ($CDCl_3$) inter al. 2.67 – 2.75 (m, 1H), 3.58 – 3.71 (m, 1H). In $(CD_3)_2SO$ solvent the OH proton appeared as a doublet at 4.52 (*J* = 4 Hz).

*Ketone* $C_{12}H_{18}O$: After bicyclization of the allylcyclopentenols **2a, b, c** (cf. Table 3, footnote b) a ketone (60 mg) was isolated by chromatography. – 90 MHz $^1$H NMR ($CDCl_3$): δ = 7.66 (dd, *J* = 2.3 Hz, 6 Hz, 1H), 6.11 (dd, *J* = 2.3 Hz, 6 Hz, 1H), 5.0 – 5.1 (m, 1H). – GC-MS (70 eV, room temperature): *m/e* = 178 (< 1%, $M^+$), 163 (< 1), 135 (< 1), 121 (1), 97 (100), 91 (3), 81 (4), 79 (5), 77 (5), 69 (18), 67 (4), 65 (3), 57 (11), 55 (68), 53 (18). – IR: 1714 $cm^{-1}$ (C=O).

*) Nomenclature of Chem. Abstr.: Hexahydro-2,2,7,7-tetramethyl-3,5-methano-2*H*-cyclopenta[*b*]furan.


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