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Cycloadditions of Allyl Cations, 28[1)]

Novel Diels-Alder Additions via Acid Catalyzed Reactions of 4-Methyl-3-penten-2-ol with Cyclopentadiene and Cyclohexadiene in Two Phases. Formation of Monocyclic, Bicyclic, and Tricyclic Adducts and Double Fragmentation of a Norbornenylcarbinol

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4-Methyl-3-penten-2-ol (**1**) and cyclopentadiene react in an acidic two phase system at 0 °C to form allylcyclopentenols **2** and norbornenylcarbinols **4**. At 50 °C and under similar conditions, **2** as well as **4** are equilibrated to allylcyclopentadienes **3**, bicyclic olefins **5** and **6**, and tricyclic ether **7**. With a comparatively reactive dehydrating agent ($SOCl_2$/pyridine), norbornenylcarbinol **4** suffers double fragmentation to give dimeric dienes $C_{12}H_{20}$, which were also obtained independently by acid catalyzed dehydrative dimerization of allyl alcohol **1**. – The *endo/exo* selectivity for the formation of epimeric norbornenylcarbinols **4** from cyclopentadiene and **1** is similar to that of the $AlCl_3$-catalyzed cycloaddition of methyl 2-butenoate und cyclopentadiene (13 : 1). The acid catalyzed two phase reaction of cyclohexadiene and **1** at room temperture gives the substituted bicyclo[2.2.2]octene *endo*-**13** in 19 – 23% yield.

Cycloadditionen von Allyl-Kationen, 28 [1)]

Neuartige Diels-Alder-Additionen: säurekatalysierte Reaktionen von 4-Methyl-3-penten-2-ol mit Cyclopentadien und Cyclohexadien im Zweiphasensystem. Bildung von monocyclischen, bicyclischen und tricyclischen Addukten und Doppelfragmentierung eines Norbornenylcarbinols

4-Methyl-3-penten-2-ol (**1**) und Cyclopentadien reagieren in einem sauren Zweiphasensystem bei 0 °C unter Bildung von Allylcyclopentenolen **2** und Norbornenylcarbinolen **4**. Bei 50 °C und unter ähnlichen Bedingungen werden **2** und **4** in Allylcyclopentadiene **3**, bicyclische Olefine **5** und **6** sowie in den tricyclischen Ether **7** umgewandelt. Mit einem vergleichsweise reaktiven Dehydratisierungsagens ($SOCl_2$/Pyridin) erleidet das Norbornenylcarbinol **4** eine doppelte Fragmentierung unter Bildung dimerer Diene $C_{12}H_{20}$, welche unabhängig durch säurekatalysierte dehydrative Dimerisierung des Allylalkohols **1** erhalten wurden. – Die *endo/exo*-Selektivität der Bildung der epimeren Norbornenylcarbinole **4** aus Cyclopentadien und **1** und die der $AlCl_3$-katalysierten Cycloaddition von 2-Butensäure-methylester und Cyclopentadien sind gleich (13 : 1). Die säurekatalysierte Zweiphasenreaktion von Cyclohexadien und **1** bei Raumtemperatur gibt das substituierte Bicyclo[2.2.2]octen *endo*-**13** mit 19 – 23% Ausbeute.

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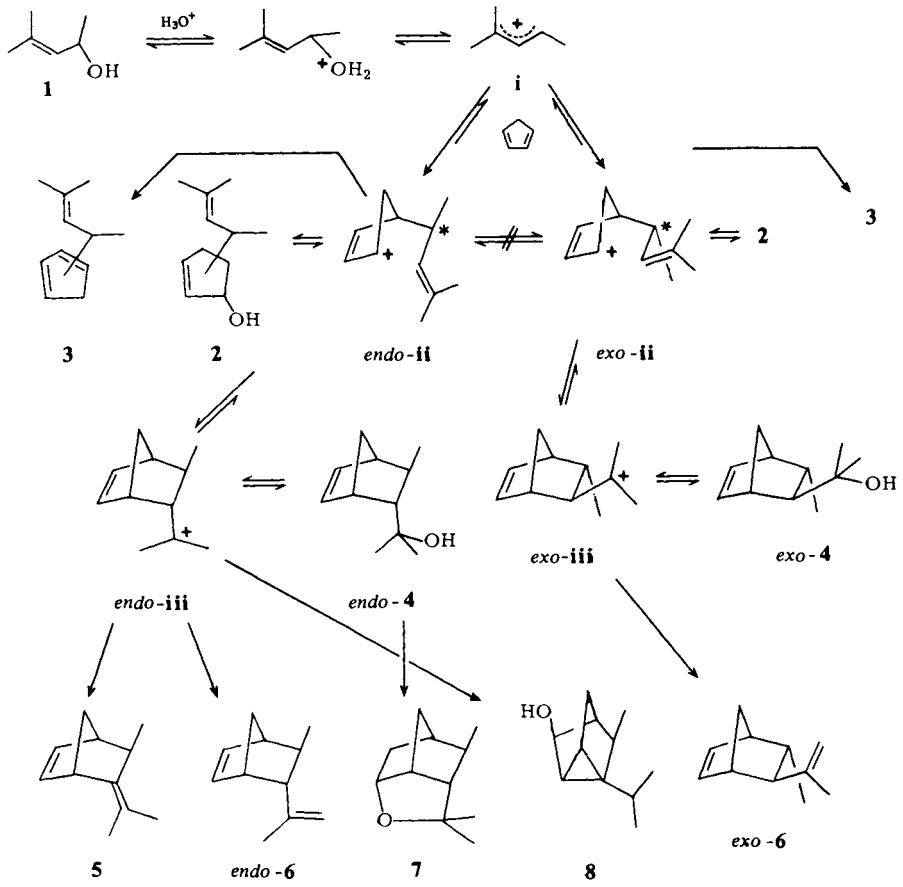
We have shown previously that allyl cations can be generated very simply from allyl alcohols in dilute aqueous acid/hydrocarbon mixtures, provided the cations are relatively stable[1-3]. In the presence of a conjugated diene a crossed combination of allyl cation and diene is feasible and the outcome of this reaction – which may involve an intricate chain of reversible steps as well as rearrangements – depends critically on the structure of both allyl cation and diene. We now report two phase reactions of 4-methyl-3-penten-2-ol (**1**) with cyclopentadiene and cyclohexadiene.

Results and Discussion

A solution of cyclopentadiene and allyl alcohol **1** (molar ratio 2:1) was dissolved in light petroleum or pentane and stirred with aqueous *p*-toluenesulfonic acid at 0°C. It was known that cyclopentadiene would not decompose in these conditions[2]. The products (cf. Table 1 and Scheme 1) were isolated by chromatography on silica gel –

Scheme 1. Postulated Acid Catalyzed Reactions of Cyclopentadiene and **1** at 0°C. (The formation of **5**, **6** and more than traces of **3** requires ca. 50°C; **7** is detected from ca. 30°C onwards)



which allowed the separation of the nonpolar olefins from the more polar ethers and alcohols – and were identified spectroscopically, especially by ^{1}H-NMR. Table 2 contains characteristic data for all new bicyclics and also for some substituted norbornenes which we had prepared earlier[2].

Table 1. Products from the Acid Catalyzed Reaction of Cyclopentadiene and **1** in Two Phases at 0 °C

Reaction time (h)	Alcohols **2** + **4** (g)	(%)[c]	Ratio **2**:**4**	Olefins[a] (g)	Allyl ether[b] (g)	(%)[c]
1[d]	2.16	52	2.4:1	0.58	0.15	7
1	2.26	54	2.5:1	0.40	0.14	6
1	2.32	56	2.6:1	0.32	0.11	5
7[e]	2.19	53	2 :1	0.73	0.10	4
7	2.28	55	2.2:1	0.70	0.14	6
7	2.29	55	2.4:1	0.78	0.11	5

[a] Mainly dicyclopentadiene, **5** (ca. 1–2%), **6** (ca. 0.5–1%) and olefin isomers **3** as well as dimeric dienes $C_{12}H_{20}$. – [b] A diastereoisomeric mixture of $(Me_2C=CH-CH(Me))_2O$ is formed. – [c] Yield with respect to **1** (2.5 g, 25 mmol). – [d] Polymers from olefin fraction: 0.09–0.11 g, from alcohol fraction: 0.07 g. – [e] Polymers from olefin fraction: 0.36–0.40 g, from alcohol fraction: 0.10–0.19 g.

As expected, *endo*-substituents A appear upfield from *exo*-substituents B, owing to the anisotropic shielding of the norbornene double bond[4]. The same effect can be seen to influence the chemical shift of the OH proton (solvent DMSO) of the tertiary alcohols: the singlets due to the *endo*-**4** and *endo*-**11** alcohols are upfield from those of the *exo*-epimers. Finally, the signals of the bridgehead protons 1- and 4-H are generally well separated and can be located by decoupling of the olefinic protons 2- and 3-H. The adduct from cyclohexadiene and **1**, i.e. *endo*-**13**, was identified by spectral comparison with *endo*-**4**, which was the major bicyclic product from the reaction of cyclopentadi-

Scheme 2. Independent Synthesis of Norbornenylcarbinols *endo*-**4** and *exo*-**4**

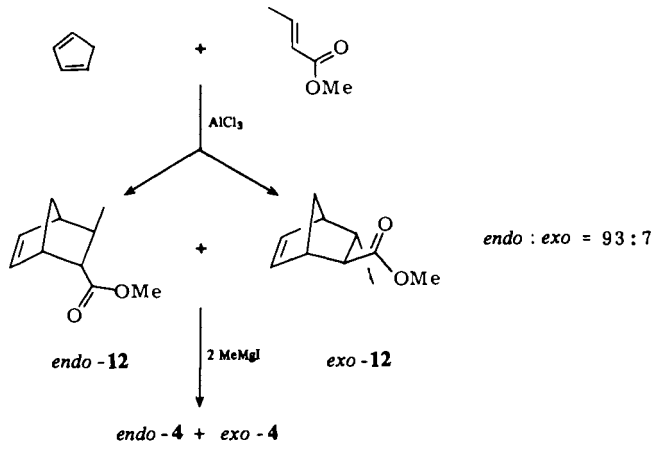
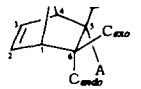
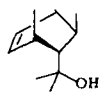


Table 2. Selected ^{1}H NMR Chemical Shifts of Norbornene Derivatives[a]



(C = substituent or H)



endo-13

	A	B	C_{endo}	C_{exo}	A	B	C_{endo}	C_{exo}	1-H	2-H	3-H	4-H	6-H	OH(DMSO)
endo-**9**	Me	Me	COMe	H	0.79	1.39	1.99		2.83	5.99 dd 6.29 dd (3, 5.5)		2.27	2.70 d(3)	
exo-**9**	Me	Me	H	COMe	1.03	1.08		2.07	2.73	6.13		2.27		
endo-**10**	Me	Me	$C(Me)=CH_2$	H	0.74	1.28	1.67		2.83	6.13		2.29	2.36 d(2.8)	
exo-**10**	Me	Me	H	$C(Me)=CH_2$	0.98	1.01		1.74	2.68	6.13		2.29		
endo-**11**	Me	Me	$C(OH)Me_2$	H	1.08	1.38	1.19 1.22		2.87	6.17		2.24	1.79 d(3)	3.65
exo-**11**	Me	Me	H	$C(OH)Me_2$	0.93	[1.34]		[1.30] [1.30]	2.64	6.18 dd	6.01 dd[b] (2.8, 5.5)	2.22[b]		4.04
endo-**12**	H	Me	CO_2Me	H	1.78 m	1.17 d(7)	3.57		3.05	5.91 dd 6.18 dd (2.9, 5.9)		2.42	2.27 dd (3.5, 4.5)	
exo-**12**	Me	H	H	CO_2Me	0.88 d(7)			3.63						
endo-**6**	H	Me	$C(Me)=CH_2$	H	2.02	1.12 d(6.5)	1.67		2.88[b]	5.81 dd[b]	6.11 dd (3, 5.5)	2.37		
endo-**4**	H	Me	$C(OH)Me_2$	H		1.17 d(6.5)	[1.08] [1.13]		2.84[b]	6.03 dd[b]	6.20 dd (3, 6)	2.34		3.59
exo-**4**	Me	H	H	$C(OH)Me_2$	0.86 d(6.8)				2.61					4.05
endo-**13**[c]	H[c]	Me[c]	$C(OH)Me_2$[c]	H[c]		1.10 d(6.5)	[1.11] [1.17]		2.61[b]	6.08[b] m	6.29 m	2.20		3.88
5	H	Me		$=CMe_2$		1.13 d(7)	1.67		3.29	5.99		2.51		
14	Me	Me		$=CMe_2$	1.04	1.30	1.68		3.47	6.03		2.33		

[a] For the sake of comparability the following numbering of the bicyclic skeleton has been adopted throughout: C-5 for the carbon bearing methyl (s) and C-6 for the carbon the substituent of which defines *endo*/*exo*-stereochemistry. The CA-IUPAC numbering may be different (see also experimental part). Coupling constants (Hz) are given in brackets. Chemical shifts δ (ppm), solvent CCl_4. The spectra of compounds **9** – **11** and **14** are given in full in ref.[2]. – [b] Decoupling experiments. – [c] Refers to bicyclo[2.2.2]octene skeleton, i.e. *endo*-**13** is α,α,3-trimethylbicyclo[2.2.2]oct-5-ene-2-methanol (solvent $CDCl_3$).

ene and **1** at 0 °C. The structure of **4** was also proven unambiguously through synthesis by another route: $AlCl_3$ catalyzed Diels-Alder reaction of cyclopentadiene and methyl crotonate gave preferentially *endo*-**12**[5], which was converted into *endo*-**4** on treatment with methylmagnesium iodide (Scheme 2).

The independent synthesis of *endo*-**4** is useful for acid catalyzed equilibration experiments. To this end, **4** (Table 3, entries 1 – 3, 6, 7) as well as allylcyclopentenol **2** (entries 4, 5), which had been obtained by chromatography from the reaction mixture, were each subjected to the reaction conditions, but at slightly elevated temperature. These conditions are still mild and allow S_N1 and E1 reactions with water acting as a nucleophile and base, and little if any deep-seated rearrangement. The new products thus formed (see also Scheme 1, bottom line) are thermodynamically more stable and they are hardly or not at all visible at 0 °C, i.e. the reaction temperature for the combination of **1** and cyclopentadiene. Thus, monocyclic olefins **3**, the bicyclic olefin **5**, *endo*- and *exo*-**6** as well as tricyclic ether **7** can now be isolated from the reaction mixture with little difficulty. At 50 °C the sum of the monocyclic products **2** + **3** is still greater than the amount of tricyclic product **7**, irrespective of whether bicyclic alcohol **4** (entries 1 – 3) or monocyclic alcohol **2** (entries 4, 5) has been used for equilibration. On the other hand, at reflux temperature (entries 6, 7) 2,4,4-trimethyl-5-oxatricyclo[4.2.1.$0^{3,7}$]-nonane (**7**) is the dominant consecutive product. Its preferred formation here contrasts with the minor amount (<2%) of its 2,2,4,4-tetramethyl analog, i.e. the tricyclic ether formed in the reaction of cyclopentadiene and 2,4-dimethyl-3-penten-2-ol[2]. Models show that the fourth methyl group, which must adopt an *endo*-position, clashes with one of the geminal methyl groups on the neighbouring carbon.

Table 3. Equilibration of Norbornenylcarbinol **4** and Allylcyclopentenol **2** in Aqueous *p*-Toluenesulfonic Acid/Light Petroleum (b.p. 60 – 70 °C) at 50 °C

Entry	Equilibrated Alcohol	% Olefins				% Alcohols and Ether				
		3	**5**	**6**		**2**	**4**	**7**	**8**	
1	**4**	14	9	3	26	7.5	48	7.5	–	63
2	**4**	11	9	4	24	8	35	8	–	51
3	**4**	8	8	3	19	10	52	8	–	70
4	**2**	10	3.6	1.4	15	8	42	8	–	58
5	**2**	11.5	6	1.5	19	10	41	8	–	59
6[a]	**4**	22	14	6	42	–	–	36	2	38
7[a]	**4**	16	15	6	37	–	–	33	2	35

[a] Equilibration at reflux temperature.

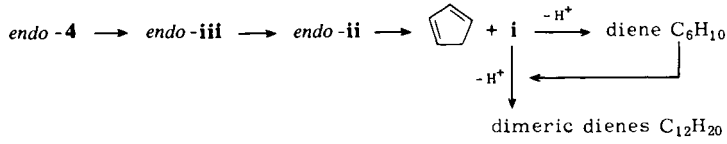
Using a comparatively reactive dehydrating agent ($SOCl_2$/pyridine) we have uncovered a further reaction mode of norbornenylcarbinol **4**. To our surprise, not only bicyclic Hofmann olefin **6** and very little Saytzeff olefin **5** were formed (**6**:**5** > 10:1), but also a substantial amount (39 – 45%) of dimeric dienes $C_{12}H_{20}$. At first sight, one might write these $C_{12}H_{20}$ isomers off as uninteresting and inevitable by-products. However, we were able to prepare them independently by a completely different route,

viz dehydrative dimerization of allyl alcohol **1** in aqueous toluenesulfonic acid/pentane, according to the equation[1)]

$$2\,C_6H_{11}OH \xrightarrow{-2H_2O} C_{12}H_{20}$$

Thus on dehydration, norbornenylcarbinol **4** and allyl alcohol **1** give an isomeric $C_{12}H_{20}$ mixture which is the same (GC – ^{1}H-NMR), irrespective of the precursor. The formation of dimeric dienes $C_{12}H_{20}$ from **4** is accomodated by retracing the appropriate arrows in Scheme 1 (cf. Scheme 3).

Scheme 3. Postulated Double Fragmentation of Norbornenylcarbinol **4** with $SOCl_2$/Pyridine (cf. also Scheme 1)



A double fragmentation of **4** generates allyl cation **i**, which is finally captured nucleophilically by its conjugate base C_6H_{10}.

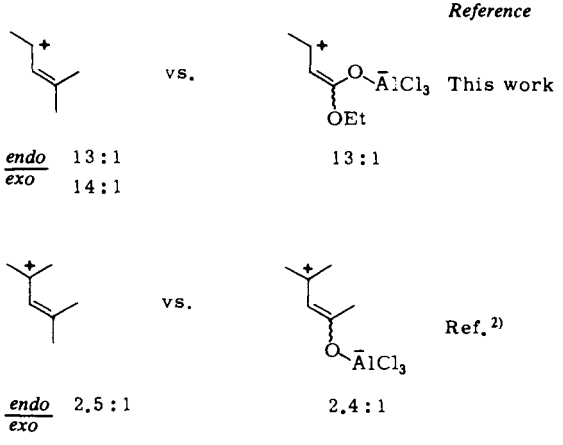
In judging our overall mechanistic scheme so far we may state that it has a high degree of probability, for several reasons. Scheme 1 has been entered at several points, i.e. from the reaction of **1** and cyclopentadiene, from the equilibration of **2** and of **4**: the reaction paths have been traced in both forward and backward directions with internally consistent results and as expected from the principle of microscopic reversibility.

Nonetheless, one should ask whether allyl cation **i** can be considered as a "dienophile", which enters into concerted, Diels-Alder-like reactions. A feature not expected for a concerted Diels-Alder reaction is the relatively large proportion of the product of electrophilic substitution, i.e. allylcyclopentenol **2**. Now, the other mechanistic extreme is a stepwise reaction involving a completely free allylcyclopentenyl cation **ii**. In our opinion, such a cation **ii** would not only collapse to **2** and perhaps cyclize to **4**, but would also suffer some loss of configuration, with formation of *cis-exo-* and *cis-endo-*epimers, which were not observed, at least not in the temperature range 0 – 25 °C. Of the various mechanistic possibilities we prefer a stepwise reaction of cyclopentadiene and **i** – implicit in Scheme 1 – giving two oriented π-complexes *endo*-**ii** and *exo*-**ii**, as intermediates on the way to *endo-* and *exo*-products. *endo*-**ii** and *exo*-**ii** have opposite chirality at the methyl bearing carbon and hence are not interconvertible by rotation about single bonds, even if free rotation without nucleophilic intervention of water were possible. Thus, the energy surfaces of the *endo-* and *exo*-reactions appear to be well separated.

Having obtained clearly defined reaction paths and intermediates for the two phase reaction, we find it striking to compare the appropriate $AlCl_3$-catalyzed reactions (Scheme 4). The *endo*-selectivity is the same or fractionally greater in the two-phase reaction!

Both pairs of postulated intermediates (cf. Scheme 4) have an electrophilic spearhead (which has the greatest LUMO coefficient) with a similar structural environment and perhaps also with similar electric charge. We conclude that the two $AlCl_3$-catalyzed Diels-Alder reactions also proceed via oriented π-complexes, analogous to *endo*-**ii** and *exo*-**ii**.

Scheme 4. Postulated "Dienophiles" and *endo/exo*-Selectivities in Cycloadditions to Cyclopentadiene



Note added in proof (April 22, 1981): D. J. Bellville, D. D. Wirth and *N. L. Bauld,* J. Am. Chem. Soc. **103**, 718 (1981), have just reported Diels-Alder reactions, in which the dienophile is the radical-cation of a diene rather than the protonated diene, i. e. allyl cation. Apparently, radical-cation dienophiles are slightly more *endo*-selective than the corresponding neutral dienophiles, and retain their configuration, not unlike the allyl cations in our reactions (see also ref.[2]).

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for support of our work.

Experimental Part

4-Methyl-3-penten-2-ol (**1**)[6]: A solution of mesityl oxide (45 g, 0.50 mol) (containing ca. 9% deconjugated enone) in absol. ether (125 ml) is dropped into a solution of $LiAlH_4$ (6.0 g, 85%, 0.134 mol) in absol. ether (125 ml), the mixture boiling gently (1 – 2 h). After complete addition of the ketone, the mixture is stirred for 1 h at room temperature, cooled to 0 °C and carefully treated with ice water (50 g). The organic layer is separated after adding more water (200 g), and the aqueous layer is extracted with ether (3 ×). The combined ether phase is washed with a saturated aqueous solution of NaCl and dried (Na_2SO_4). After removal of the ether the residue is distilled, b.p. 44 – 46 °C/water pump vacuum. Yield 41 – 42 g (92 – 94%). – 60 MHz ^1H NMR ($CDCl_3$): δ = 1.15 (d, *J* = 6 Hz, 3H), 1.63 (m, 6H), 2.38 (1H, OH), 4.32 – 4.62 (m, 1H), 5.05 – 5.25 (m, 1H).

Acid Catalyzed Reaction of Cyclopentadiene and **1** *in Two Phases:* **1** (2.5 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 °C for 1 and 7 h, respectively (Table 1). The reaction

mixture was worked up by neutralization with aqueous $NaHCO_3$, separation of the organic phase, and extraction of the aqueous layer with pentane (3 ×). 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, 0.05 – 0.2 mm, Macherey-Nagel) with pentane (ca. 200 ml) as eluent. The less polar olefinic products were collected. After elution with light petroleum/ether (10 vol%) (100 – 150 ml) the more polar ether **7** and alcohols **4** and **2** were obtained. Sequence of polarities: **7** < **4** < **2**. Retention times (GC, SE 30 column): *exo*-**4** < *endo*-**4** < **2**. Alcohol **2** consisted of at least three isomers.

The olefins **3**, **5**, and **6** were separated by preparative GC (6 m SE 30 column) from dicyclopentadiene and dimeric dienes $C_{12}H_{20}$. Under these conditions the olefins **3** were partially decomposed, also on prolonged standing in the refrigerator and on treatment with aqueous $AgNO_3$ solution.

1- and 2-(1,3-Dimethyl-2-butenyl)-1,3-cyclopentadiene Isomers (**3**): 90 MHz ^{1}H NMR (CCl_4): δ = 1.16 (d, *J* = 6.8 Hz, 3H), 1.59 – 1.68 (6H), 3.22 – 3.34 (m, 1H), [(2.73 – 2.80, q) and (2.80 – 2.93, q), 2H], 5.60 – 6.44 (m, 3H), 4.93 – 5.16 (m, 1H).

5-Isopropylidene-6-methylbicyclo[2.2.1]hept-2-ene (**5**): 90 MHz ^{1}H NMR (CCl_4): δ = 1.13 (d, *J* = 7 Hz, 3H), 1.67 (m, 6H), 1.2 – 1.8 (m, 3H), 2.46 – 2.57 (m, 1H), 3.22 – 3.37 (m, 1H), 5.93 – 6.07 (m, 2H).

5-Isopropenyl-6-methylbicyclo[2.2.1]hept-2-ene (**6**): 90 MHz ^{1}H NMR (CCl_4): δ = 1.12 (d, *J* = 6.5 Hz, 3H), 1.67 (m, 3H), 1.27 – 1.80 (m, 3H), 1.93 – 2.16 (m, 1H), 2.30 – 2.42 (m, 1H, 1-H after decoupling), 2.81 – 2.91 (m, 1H, 4-H after decoupling), 4.44 – 4.72 (m, 2H), 5.81 and 6.11 (dd, *J* = 3, 5.5 Hz, 2-, 3-H after decoupling). – MS (70 eV): *m/e* = 148 (19%, M^+), 82 (100), 66 (33).

*2,4,4-Trimethyl-5-oxatricyclo[4.2.1.0^{3,7}]nonane**) (**7**): 90 MHz ^{1}H NMR (CCl_4): δ = 0.92 (d, *J* = 7 Hz, 3H), 1.10 (s, 3H), 1.21 (s, 3H), 0.90 – 1.27 (m, 2H), 1.32 – 2.0 (m, 5H), 2.73 – 2.91 [m, (br, t centered on 2.81), 1H], 4.10 (dd, *J* = 5.5, 7 Hz, 1H).

$C_{11}H_{18}O$ (166.3) Calcd. C 79.47 H 10.91 Found C 79.55 H 10.93

α,α,3-Trimethylbicyclo[2.2.1]hept-5-ene-2-methanol (*endo*-**4**): 90 MHz ^{1}H NMR (CCl_4): δ = 1.07 (s, 3H), 1.12 (s, 3H), 1.16 (d, *J* = 7 Hz, 3H), 1.33 – 1.67 (m, 4H), 2.30 – 2.40 (m, 1H), 2.74 – 2.91 (m, 1H), 6.03 (dd, *J* = 5.5, 3 Hz, 1H), 6.19 (dd, *J* = 5.5, 3 Hz, 1H). – MS (70 eV): *m/e* = 166 (3%, M^+), 151 (6), 148 (5), 85 (26), 83 (70), 66 (100).

At room temperature the reaction of cyclopentadiene and **1** gave *endo*-**4**: *exo*-**4** = 13:1 and 14:1 (^{1}H NMR).

exo-**4**: 90 MHz ^{1}H NMR (CCl_4): inter al. δ = 0.86 (d, *J* = 6.8 Hz, 3H), 2.51 – 2.71 (m, 1H).

$C_{11}H_{18}O$ (166.3) Calcd. C 79.47 H 10.91 Found C 79.79 H 10.99

Independent Synthesis of endo-4 and exo-4: The Diels-Alder adduct of cyclopentadiene and methyl crotonate[5] (*endo*:*exo* = 13:1) (4.98 g, 30 mmol) (Scheme 2) was methylated with methylmagnesium iodide (cf. also preparation of α,α,3,3-tetramethylbicyclo[2.2.1]hept-5-ene-2-methanol[2]) yielding 4.48 – 4.73 g of **4** (90 – 95%).

4- and 5-(1,3-Dimethyl-2-butenyl)-2-cyclopenten-1-ol Isomers (**2**): At least three isomers were formed (GC: SE 30). – 90 MHz ^{1}H NMR (CCl_4): δ = 0.86 – 1.20 (6H), 1.50 – 1.70 (5H), 2.08 – 2.40 (2H), [4.30 – 4.48; 4.49 – 4.69; 4.76 – 5.00] (2H), 5.54 – 5.88 (m, 2H). – MS (70 eV): *m/e* = 166 (M^+).

$C_{11}H_{18}O$ (166.3) Calcd. C 79.47 H 10.91 Found C 79.68 H 10.88

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

Acid Catalyzed Equilibration of **4** *and* **2** *in Two Phases (cf. Table 3):* Standard conditions. Alcohol **4** (2.9 g, 17 mmol) in light petroleum (b.p. 60 – 70 °C) (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). The reaction mixture was worked up in the usual way and separated by chromatography into a nonpolar and a polar alcohol + ether fraction. Both fractions were weighed, giving olefins (0.76 g) and alcohols + ethers (1.82 g) in this instance. The concentration of the individual products was determined by integration of appropriate ^{1}H NMR signals. For the experiments in Table 3 (entries 4, 5) allylcyclopentenol **2** (1.16 g) was used.

Tricyclic alcohol (**8**?): Alcohol **4** (2.97 g, 18 mmol) was refluxed for 1 h as detailed above (see also Table 1). Chromatography of the polar fraction (1.09 g) and combined ^{1}H NMR-IR spectroscopy showed that a further alcohol which was assigned structure **8**, was formed in a small amount (**7**:**8**, ca. 15:1). – 90 MHz ^{1}H NMR ($CDCl_3$): inter al. δ = 0.68 (d, J = 7 Hz, 3H), 0.72 (d, J = 7 Hz, 6H). – IR (OH).

Dehydration of **4** *with Thionyl Chloride/Pyridine:* **4** (1.66 g, 10 mmol) was dissolved in absol. benzene (75 ml) and pyridine (10 ml). After cooling to 5 °C thionyl chloride (1.5 ml, ca. 21 mmol) in absol. benzene (20 ml) was dropped in. The reaction mixture was stirred for 0.5 h at room temperature and carefully poured onto ice (25 g). The aqueous phase was extracted with ether (3 ×), the collected organic phase washed with water, dried (Na_2SO_4), and the solvent removed leaving an oil which was distilled at the Kugelrohr to give a colorless oil (0.84 – 0.99 g). Preparative GC (6 m SE 30 column) gave **6** (0.47 – 0.67 g, 32 – 45%), very little **5** (**6**:**5** > 10:1), and dimeric dienes $C_{12}H_{20}$ (0.37 – 0.42 g, 39 – 45%). The composition of the dimeric dienes (two compounds in a ratio of 1:4 on a SE 30 column; three isomers by GC-MS) was the same as in the acid catalyzed dehydrative dimerization of 4-methyl-3-penten-2-ol studied previously[1].

α,α,3-Trimethylbicyclo[2.2.2]oct-5-ene-2-methanol (*endo*-**13**) *by Acid Promoted Two Phase Reaction of Cyclohexadiene and* **1**: 1,3-Cyclohexadiene (4.0 g, 50 mmol) and 4-methyl-3-penten-2-ol (**1**) (2.5 g, ca. 25 mmol) in pentane (5 ml) were added to water (5 ml) containing methanesulfonic acid (2.4 g, 25 mmol), and the mixture was stirred for 4 h at room temperature. [In other experiments methanesulfonic acid was replaced by toluenesulfonic acid (1/4 to 1 molar equivalent with respect to allyl alcohol **1**) and by 2,4,6-trimethylbenzenesulfonic acid (1/6 to 1 molar equivalent) with no apparent change]. Usual work up and chromatography on silica gel (20 g) gave a nonpolar fraction (0.87 – 1.33 g, colorless oil), which consisted of dimeric dienes $C_{12}H_{20}$ (0.47 – 0.73 g, 23 – 36%) and of diastereoisomeric allyl ethers $[Me_2C=CH-CH(Me)]_2O$ (0.40 – 0.60 g, 18 – 26%) (SE 30 column). Kugelrohr distillation (60 – 100 °C, 1 Torr) of the polar alcohol fraction gave *endo*-**13** as a colorless oil (0.85 – 1.03 g, 19 – 23%). – 90 MHz ^{1}H NMR ($CDCl_3$): δ = 1.10 (s, 3H), 1.11 (d, J = 6.5 Hz, 3H), 1.17 (s, 3H), 1.25 – 1.83 (m, 6H), 2.04 – 2.22 (m, 1H), 2.49 – 2.67 (m, 1H), 6.04 – 6.50 (m, 2H); the signal of the OH proton is obscured. – MS (70 eV): *m/e* = 180 (1%, M^+), 165 (2), 162 (4), 147 (6), 83 (100), 80 (71).

$C_{12}H_{20}O$ (180.3) Calcd. C 79.94 H 11.18 Found C 79.72 H 11.69

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