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Cycloadditions of Allyl Cations, 29[1]

Acid Catalyzed Reactions of 2,3-Dimethyl-3-penten-2-ol and Cyclopentadiene in Two Phases. Formation of Seven- and Five-membered Rings

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2,3-Dimethyl-3-penten-2-ol (**3**) and cyclopentadiene were stirred in dilute aqueous sulfonic acid/pentane, giving 2,3,4,4-tetramethylbicyclo[3.2.1]octa-2,6-diene (**4**), the epimeric 3-methylene isomers **5a, b** and, for the first time, also a five-membered ring, namely 2,3,4,4-tetramethylbicyclo[3.3.0]octa-2,6-diene (**6**) in 69 – 73% overall yield. The major bicyclic diene **4** was conveniently isolated as crystalline silver nitrate complex $(C_{12}H_{18})_2 \cdot AgNO_3$ (41 – 44%). In a modified approach the two phase reaction was carried out at 0 °C, the resulting alcohols were separated by chromatography and cyclized at 50 °C, giving an increased proportion of the thermodynamically more stable, novel [3.3.0] bicyclic isomer **6** (**4**:**6** = 2.6:1)

Cycloadditionen von Allyl-Kationen, 29[1]

Säurekatalysierte Reaktionen von 2,3-Dimethyl-3-penten-2-ol mit Cyclopentadien in zwei Phasen. Bildung von sieben- und fünfgliedrigen Ringen

2,3-Dimethyl-3-penten-2-ol (**3**) und Cyclopentadien wurden in verdünnter wäßriger Sulfonsäure/Pentan gerührt. Es bildeten sich 2,3,4,4-Tetramethylbicyclo[3.2.1]octa-2,6-dien (**4**), die epimeren 3-Methylen-Isomeren **5a, b** und zum ersten Mal auch ein fünfgliedriger Ring, nämlich 2,3,4,4-Tetramethylbicyclo[3.3.0]octa-2,6-dien (**6**) mit 69 – 73% Gesamtausbeute. Das bicyclische Dien **4** war Hauptprodukt und wurde leicht als kristallisierter Silbernitratkomplex $(C_{12}H_{18})_2 \cdot AgNO_3$ isoliert (41 – 44%). In einem modifizierten Verfahren wurde die Zweiphasenreaktion bei 0 °C ausgeführt. Anschließend wurden die resultierenden Alkohole chromatographisch abgetrennt und bei 50 °C cyclisiert. Diese Variante ergab einen höheren Anteil des thermodynamisch stabileren, neuartigen [3.3.0]-Bicyclus **6** (**4**:**6** = 2.6:1).

The synthesis of cyclohexenes[2] and bridged cyclohexenes[1,3] by acid promoted two phase reactions of allyl alcohols and conjugated dienes has been reported recently. This work complements and contrasts with another reaction mode of allyl cations, exemplified by the preparation of 3-methylbicyclo[3.2.1]octa-2,6-diene (**1**) and its isomer **2** from cyclopentadiene and 2-methylallyl cation[4] (Scheme 1). We now describe the reaction of 2,3-dimethyl-3-penten-2-ol (**3**) and cyclopentadiene, which yields seven- and, for the first time, also five-membered rings.

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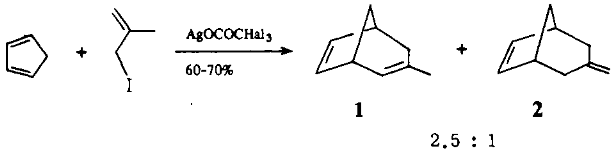
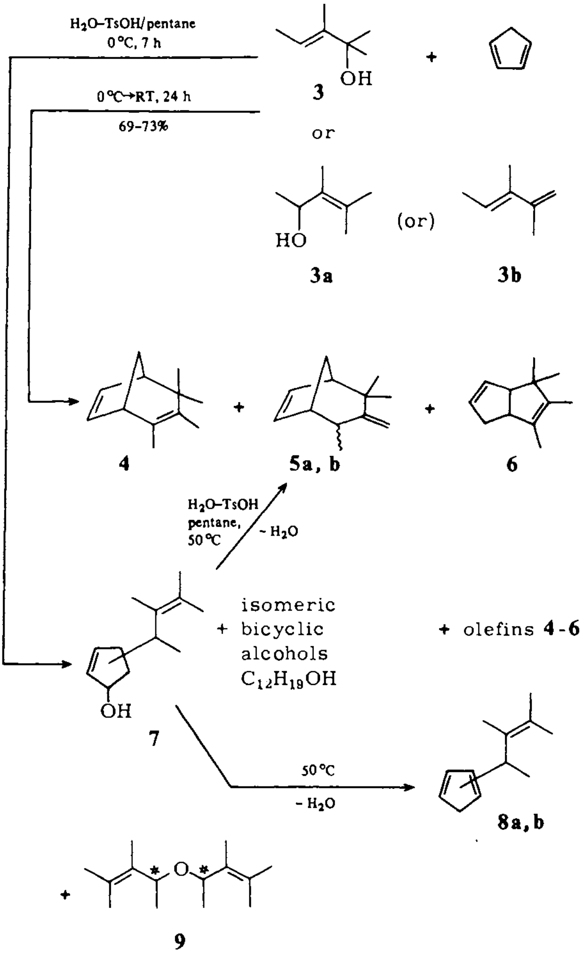
Scheme 1. The Silver Salt Route to Bicyclics **1** and **2**



Scheme 2. Products from the Two Phase Reaction of **3** and Cyclopentadiene



Results

A mixture of dilute aqueous sulfonic acid/pentane was used as a reaction medium and two sets of experimental conditions were chosen.

1) In the one-pot process the reaction was begun at 0°C, and continued at room temperature after 0.5 h. The mixture was worked up by complexation with aqueous silver

Table 1. Products (%) from the Acid Promoted Reaction of Cyclopentadiene and 3 in Two Phases

Reaction time (h)	Crude product[a] (g)	Distillate (g)	Distillate (%)	$AgNO_3$ Complex of **4** (g)	$AgNO_3$ Complex of **4** (%)	Remaining product[b] (g)	Remaining product[b] (%)	Polymer and byproducts (g)	Ratio of Olefins (GC-^{1}H NMR) **4**:**5**:**6**	Total Yield (%) **4** + **5** + **6**
4[c]	13.6			5.7	22	2.4	16	6.5	12:1:2	37
4[c]	13.7			5.9	23	3.0	14	5.7	11:1:2	38
24	20	10.7[d]	66	10.5	41	2.9	18	8.9	12:1:2	69
24	21.5	10.9[e]	67	[f]	44			7.6	10:1:2	73

[a] Before precipitation with $AgNO_3$ and before distillation. – [b] Olefins **4**, **5**, and **6** from final distillation after separation of **4a**. If the crude product was precipitated with $AgNO_3$, some dicyclopentadiene is also present. – [c] After 4 h, 2,3-dimethyl-1,3-pentadiene (1.05 – 1.20 g, 11 – 13%) was formed. – [d] Forerun contained another 3% of **4**, **5**, and **6**: total yield 69%. – [e] Forerun: 6% of **4**, **5**, and **6**. Total yield 73%. – [f] 5.80 g of the distillate were allowed to react with $AgNO_3$; 44% is the corrected value. Yields refer to 0.1 mol of **3**.

Table 2. Two Phase Reaction of **3** and Cyclopentadiene at 0 °C

Reaction time [h]	Olefins[a] **4** – **6** [g]	Olefins[a] **4** – **6** [%]	Alcohols **7**[b,c] [g]	Alcohols **7**[b,c] [%]
1	1.02	<25	1.79	40
1	1.05	<26	1.86	41
7	1.46	<36	1.84	41

[a] Pentane eluate which contains also some dicyclopentadiene. After separation of the bulk of **4** with $AgNO_3$, GC-MS showed 8 olefins with $M^+ = 162$ (cf. **4**, **5a, b** and **6**; the remaining 2 olefins are probably the epimeric pair of Hofmann olefins related to **6** which on heating to ca. 35° were sometimes formed in 5% yield). – [b] Ether eluate contains also diallyl ether **9** (0.03 – 0.13 g, 1 – 5%). – [c] A mixture of alcohols (IR: OH band; $M^+ = m/e = 180$) is formed. ^{1}H NMR: the ratio of methyl groups attached to saturated carbon/methyl groups attached to unsaturated carbon is higher than it should be for monocyclic alcohols **7** (1:3). Hence, bicyclic alcohols must have also been formed (ratio 4:0). The observed ratio bicyclic alcohol/monocyclic alcohol **7** is ca. 2.3:1, 1.4:1

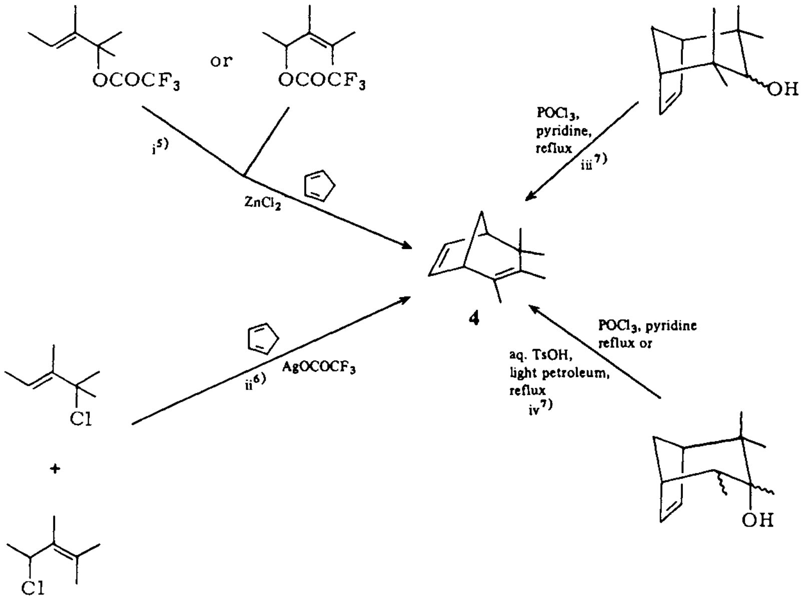
nitrate, which removed the major bicyclic diene **4** as crystalline complex **4a** (41 – 44% isolated). Two minor bicyclic dienes **5** and **6** were also obtained, the total yield of **4** – **6** being 69 – 73% (Table 1). There was no discernible difference in yields and product ratios when using a 0.25 – 1 molar equivalent (with respect to **3**) of the following sulfonic acids: methanesulfonic acid, *p*-toluenesulfonic acid and 2,4,6-trimethylbenzenesulfonic acid (Scheme 2). The allylically rearranged alcohol **3a** could also be used in place of **3** without change.

2) In the modified approach **3** and cyclopentadiene were allowed to react at 0°C for 1 and 7 h. Chromatography on silica gel gave a nonpolar olefinic fraction of **4** – **6** and a more polar major fraction of isomeric alcohols $C_{12}H_{19}OH$ including **7** and also some diallyl ether **9** (Table 2). After subjecting the $C_{12}H_{19}OH$ alcohols to the two phase conditions at 50°C we again obtained bicyclic dienes **4** – **6**, and also monocyclic isomers **8a, b** in a ratio of **4**:**5**:**6**:**8** = 9.8:1:3.8:4.

Discussion

Clearly, the formation of the major product **4** and that of **5** can be compared with that of **1** and **2** in the reaction of the simple 2-methylallyl cation. In the present instance, there is comparatively more tetrasubstituted olefin **4** (**4**:**5** = 11:1) than there is trisubstituted olefin **1** (**1**:**2** = 2.5:1) in the reaction reported earlier (Scheme 1). As the minor olefin of each isomeric pair is disubstituted, i.e. **5** and **2**, the olefin ratios are Saytzeff-controlled, as demanded for an E1-like elimination.

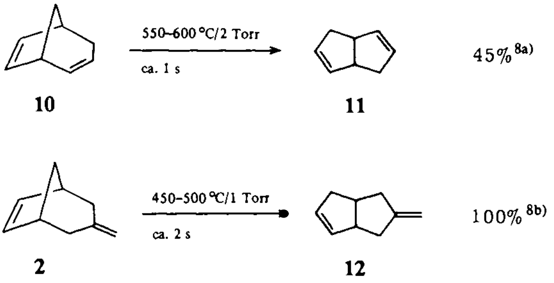
Scheme 3. Further Routes to 2,3,4,4-Tetramethylbicyclo[3.2.1]octa-2,6-diene (**4**). In Routes i and ii, Bicyclic Diene **6** is also formed



The bicyclo[3.2.1]octane carbon skeleton of **4** serves as model for many natural products. We have therefore prepared **4** by some other routes (Scheme 3), two of which (iii and iv) have been published. The other two (i and ii) are related to the approach described here. A type of product which has not yet been obtained in reactions of allyl cations with cyclopentadiene is the [3.3.0] bicyclic diene **6**. Unlike its isomer **4** which is sensitive to oxygen, diene **6** is more stable and does not form an $AgNO_3$ complex. **6** is also formed as a byproduct in routes i and ii (Scheme 3).

Although *Klumpp* has shown that a lower homologue of **4**, *i.e.* **10** rearranges to **11** on flash pyrolysis above 500°C[8a] and **2** rearranges somewhat more readily to **12**[8b] (Scheme 4), it seems clear that bicyclic diene **4** does not form **6** in our conditions, not even at 120°C.

Scheme 4. Thermal rearrangement of **10** and **2**



The ratio **4**:**6** = 5.5:1 obtained in the one-pot reaction is higher than in the two stage reaction which involves heating of allylcyclopentenols **7** and their bicyclic $C_{12}H_{19}OH$ isomers (obtained at 0°C) under acidic two phase conditions to 50°C (**4**:**6** = 2.6:1). More thermodynamic control at the higher temperature seems reasonable and is consistent with previous experience on acid induced consecutive reactions of other allyl cation precursors in the same medium and at the same temperature, i.e. aqueous *p*-toluenesulfonic acid/light petroleum (b.p. 60 – 70°C) at 50°C. The two stage variant for making **4** and **6** has the advantage that dicyclopentadiene need no longer be separated towards the end, having been removed easily from the alcohols after the first stage by chromatography. The experiment at 50°C suggests the possibility that some norbornenylcarbinol **17** is formed also (see experimental part).

Finally, we have used conjugated diene **3b** instead of allylic alcohols **3** or **3a** in two phase reactions with cyclopentadiene. However, the formation of cycloadducts was somewhat slower and yields were lower in this case (Table 3). Apparently, protonation of **3b** proceeds less readily than the combined protonation of the lone pair of either allylic alcohol and carbon-oxygen heterolysis.

In summary, our work shows that allylcyclopentenols are synthetically versatile, giving bicyclo[3.3.0], bicyclo[3.2.1], and norbornene systems[1,3)] under mild conditions. What type of cyclization takes places depends inter al. on the substitution pattern of the allyl side chain. The distribution of products is also sensitive to temperature. The formation of norbornene derivatives from cyclopentadiene and allyl cations is a stepwise Diels-Alder reaction[1,3)].

Table 3. Reaction of 2,3-Dimethyl-1,3-pentadiene (**3b**) and Cyclopentadiene under Two Phase Conditions[a)]

p-Toluene-sulfonic acid [g]	Reaction time [h]	Distillate [g]	Yield[b)] [%]
2.4	1	0.74	18
2.4	4	1.25	32
3.0	1	0.82 – 1.48	20 – 35
5.9	4	1.63	40

[a)] **3b** (2.4 g, 25 mmol) and cyclopentadiene (3.3 g, 50 mmol) in pentane (5 ml) were stirred with 5 ml of aqueous sulfonic acid. – [b)] Refers to the total mixture of olefins **4**, **5a, b**, **6**.

We thank *M. R. Ashcroft, G. Grundke*, and *O. R. Lalko* for additional approaches to bicyclic dienes **4** and **6**, Dr. *F. J. Hammerschmidt* of Dragoco for GC-MS measurements and the *Deutsche Forschungsgemeinschaft* as well as the *Fonds der Chemischen Industrie* for support of our work.

Experimental Part

IR spectra: Perkin-Elmer 457 and 590. – ^{1}H NMR spectra: Varian EM 360 and HA 100; Bruker HX 90 and WH 90. – Mass spectra: Varian CH 5. – Gaschromatograph: Varian 1400 FID and N_2 as carrier gas. – Preparative gaschromatography: Wilkens A 700 Autoprep. Thermal conductivity detector and H_2 as carrier gas; 6 m of a 5% SE 30 column unless noted otherwise. – 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 der Universität Hannover.

2,3-Dimethyl-3-penten-2-ol (**3**)[9)]

a) *3-Methyl-3-penten-2-one:* 4-Hydroxy-3-methyl-2-pentanone (116 g, 1.0 mol), which had been obtained by a crossed aldol reaction of 2-butanone and acetaldehyde in 70% yield[10)], was heated to 180 °C together with 3 drops of aqueous HBr (54%) in a distillation flask attached to a Vigreux column (30 cm). The distillate contained the desired α,β-unsaturated enone and water, which was separated and extracted three times with a little ether. The combined organic phase was dried (Na_2SO_4). After removal of the ether at reduced pressure 3-methyl-3-penten-2-one (78.6 – 88.0 g, 80 – 90%), b.p. 62 – 64 °C/50 Torr, was obtained. – 60 MHz ^{1}H NMR (CCl_4): δ = 1.72 (m, 3H), 1.88 (m, 3H), 2.25 (s, 3H), 6.35 – 7.00 (m, 1H). The compound polymerizes on standing in a refrigerator.

b) Magnesium turnings (36.5 g, 1.5 mol) in absol. ether (150 ml) are treated with methyl iodide [ca. 1/20 of 1.5 mol (213 g)] to initiate the reaction. The bulk of the methyl iodide in absol. ether (250 ml) is then added at a rate which maintains gentle refluxing. After being heated for 0.5 h to 1 h under reflux, the solution is cooled to 0 °C. 3-Methyl-3-penten-2-one (98 g, 1.0 mol) in absol. ether (250 ml) is dropped in over a period of 3 – 4 h at 0 – 5 °C (ice water/NaCl). After being stirred for 1 h at 0 °C the mixture is left overnight at room temperature and re-cooled to 0 °C. Ice water (100 g) is carefully stirred into the solution below 10 °C during 2 – 3 h. When the evolution of gas has ceased and the temperature does not rise further, the mixture is efficiently stirred into a solution of NH_4Cl (85 g) in water (85 ml). After the precipitate has settled, the clear ether solution is decanted (Note 1) and the precipitate is treated with three portions of ether. The combined organic phase is washed with water containing some K_2CO_3 (Note 2) and dried. After removal of the solvent, the residue is distilled at the Kugelrohr (water pump vacuum) below 80 °C (Note 3), yielding 3 (80 – 91 g, 70 – 80%). – 60 MHz ^1H NMR (CCl_4): δ = 1.22 (s, 6H), 1.58 (m, 3H), 1.65 (m, 3H), 2.50 (s, 1H, OH), 5.30 – 5.70 (m, 1H). In solvent $(CD_3)_2SO$ the OH singlet appears at 4.30 ppm.

Note 1. If the ether solution turns darker (orange-red-black), it must be worked up as quickly as possible. Dark-red to black solutions contain hardly any **3**. Distillation gives pure 2,3-dimethyl-1,3-pentadiene in low yield and further decomposition products.

Note 2. Distilled water appears to promote decomposition.

Note 3. At 80 °C dehydration sets in. Some solid K_2CO_3 in the distillation flask is advisable. The allyl alcohol seems also oxygen sensitive, at least during work up.

Two Phase Method for the Reaction of 3 *and Cyclopentadiene. Work up and Purification by Silver Nitrate Complexation:* 3 (11.4 g, 0.10 mol) and freshly distilled cyclopentadiene (13.2 g, 0.20 mol for 4 h reaction; 19.8 g, 0.30 mol for 24 h reaction) were dissolved in pentane (20 ml) and a cooled solution of *p*-toluenesulfonic acid (7 g, ca. 30 mmol) in water (10 ml) was added at 0 °C (Note 1) under an atmosphere of nitrogen (Note 2). The mixture is stirred for 0.5 h at 0 °C, then 3.5 or 23.5 h at room temperature and neutralized with an aqueous solution of $NaHCO_3$. After separation of the organic layer, the aqueous phase is extracted 3 – 4 times with a little pentane. The collected organic phase is washed with water and dried (Na_2SO_4). After removal of the solvent (room temperature, water pump vacuum), the reaction mixture is added either immediately or after distillation (Note 3) to a solution of $AgNO_3$ (10 g, 59 mmol) in water (10 ml). The solution becomes warm. When using the distilled rather than the crude oil, a colorless paste is precipitated immediately. After 0.25 – 0.5 h the solution is cooled to 0 °C, the colorless or slightly yellowish paste is suction filtered and dried for 1 h at the water pump (Note 4). The paste is dissolved in a little methanol at 40 °C and the solution filtered (Note 5). On cooling, the colorless $AgNO_3$ complex crystallizes (Note 6). Having been kept for 12 h in the refrigerator, the complex is separated from the methanolic mother liquor, washed with a little methanol (Note 4) and dried by suction. The mother liquor is carefully concentrated at the water pump at room temperature (Note 7) until more complex is precipitated, which is redissolved on warming the mother liquor to 40 °C. On slow cooling, colorless complex comes down again, the procedure being repeated 3 – 4 times. The filtered aqueous phase and the methanolic mother liquor were worked up separately by adding water (10 ml) and extracting several times with pentane. The collected organic phase is washed with water and dried (Na_2SO_4). After evaporation of the solvent (room temperature, water pump) the resulting oil is distilled at the Kugelrohr (60 – 100 °C, water pump). The product ratio is determined by ^1H NMR and GC (cf. Table 1).

Note 1. Occasionally **3** is so reactive that the reaction mixture becomes warm on adding the solution of aqueous toluenesulfonic acid. In this case more byproducts and polymers are formed.

Note 2. After 2 h the reaction was continued under a stationary atmosphere of nitrogen. Bicyclic diene **6** forms an epoxide with atmospheric oxygen[7)].

Note 3. It is recommended that the reaction mixture be distilled before precipitation with aqueous $AgNO_3$. Dicyclopentadiene which also forms an $AgNO_3$ complex, and olefins **4**, **5**, and **6** can thus be separated without recourse to chromatography. The silver nitrate complex from the crude reaction mixture co-precipitates higher boiling products and can be recrystallized only with difficulty. In the presence of much polymer, the silver nitrate complex forms slowly on seeding and cooling to 0 °C.

Note 4. Ether and pentane partially decompose the $AgNO_3$ complex.

Note 5. The $AgNO_3$ complex of dicyclopentadiene is less soluble in methanol and can be separated almost completely.

Note 6. On slow recrystallization the dicyclopentadiene complex comes down first. Further precipitate contains very little dicyclopentadiene (ca. 1% by GC after decomposition of the complex).

Note 7. At higher temperature (30 – 40 °C) some of the cycloadduct is evaporated together with methanol (GC).

2,3,4,4-Tetramethylbicyclo[3.2.1]octa-2,6-diene (4): 90 MHz ^{1}H NMR (CCl_4): δ = 0.87 (s, 3 H), 1.13 (s, 3 H), 1.46 (m, ^5J = 1.2 Hz, 3 H), 1.65 (m, ^5J = 1.2 Hz, 3 H), 1.76 – 2.00 (m, 2 H), 2.22 – 2.40 (m, 2 H), 5.79 (dd, J = 3 Hz, 5.5 Hz, 1 H), 6.34 (dd, J = 3 Hz, 5.5 Hz, 1 H). – MS (70 eV): m/e = 162 (41%, M^+), 147 (100), 133 (12), 131 (9), 121 (20), 119 (45), 117 (12), 115 (13), 108 (14), 105 (35), 97 (34).

$C_{12}H_{18}$ (162.3) Calcd. C 88.82 H 11.18 Found C 88.32 H 11.20

Silver Nitrate Complex of **4**: m.p. 114 – 115 °C. – 90 MHz ^{1}H NMR (CD_3OD): δ = 0.89 (s, 3 H), 1.14 (s, 3 H), 1.44 (m, 3 H), 1.66 (m, J = 1 Hz, 3 H), 1.72 – 2.04 (m, 2 H), 2.37 – 2.56 (m, 2 H), 5.94 (dd, J = 5.5, J = 2.8 Hz, 1 H), 6.52 (dd, J = 5.5, J = 3 Hz, 1 H).

$(C_{12}H_{18})_2 \cdot AgNO_3$ Calcd. C 58.30 H 7.34 N 2.83 Found C 58.15 H 7.33 N 2.71

The recovery of **4** from its complex has been described, as has an independent synthesis of the epimeric 2,2,4-trimethyl-3-methylenebicyclo[3.2.1]oct-6-enes (**5a, b**)[7]. The minor bicyclic isomer **6** could not be separated from **4** by GC (SE 30, 4 m APL column). Its ^{1}H NMR spectrum was recorded on a sample which had been obtained by preparative GC and had been enriched in **6** by partial oxidation of **4** with air (**4**:**6** = 2:1).

2,3,4,4-Tetramethylbicyclo[3.3.0]octa-2,6-diene (**6**): 90 MHz ^{1}H NMR (CCl_4): inter al. δ = 0.98 (s, 3 H), 1.02 (s, 3 H), 1.46 (m, 3 H), 1.56 (m, 3 H), 2.17 – 2.39 (m, 2 H), 2.78 – 3.00 (m, 1 H), 3.00 – 3.28 (m, 1 H), 5.50 (br s, 2 H; in solvent $CDCl_3$, this singlet appears at 5.62 ppm)[11].

Two Phase Reaction at 0 °C: A solution of **3** (2.85 g, 25 mmol) and cyclopentadiene (3.3 g, 50 mmol) was stirred with water (5 ml) containing *p*-toluenesulfonic acid (2.4 g, ca. 13 mmol) for 1 h and 7 h (Table 2). The reaction mixture was neutralized with aqueous $NaHCO_3$, the organic layer separated, and the aqueous layer extracted 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 through a column of 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 pentane/ether (10 vol %) (100 – 150 ml) the more polar alcohols and allyl ether(s) **9** were obtained. The mixture of alcohols was analyzed.

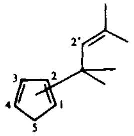
$C_{12}H_{20}O$ (180.3) Calcd. C 79.94 H 11.18 Found C 78.65 H 11.10

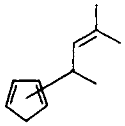
5- and 4-(1,2,3-Trimethyl-2-butenyl)-2-cyclopenten-1-ols (**7**): 90 MHz ^{1}H NMR ($CDCl_3$): inter al. δ = 0.77 – 1.29 (3 H), 1.47 – 1.74 (9 H), 4.68 – 5.06 (m, 1 H), 5.60 – 6.09 (m, 2 H). – MS (70 eV): m/e = 180 (M^+).

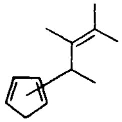
Trimethyl-2-butenyl ether(s) **9a, b**: 90 MHz ^{1}H NMR (CCl_4): **9a**: δ = 1.02 (d, J = 6.5 Hz, 6 H), 1.54 (m, 18 H), 4.06 (q, J = 6.5 Hz, 2 H), and **9b**: δ = 1.04 (d, J = 6.2 Hz, 6 H), 1.63 (m, 18 H), 4.25 (q, J = 6.2 Hz, 2 H). – MS (70 eV): m/e = 210 (M^+).

Two Phase Reaction at 50 °C of Isomeric $C_{12}H_{19}OH$ Alcohols Obtained by Two Phase Reaction at 0 °C: The isomeric $C_{12}H_{19}OH$ alcohols (2.4 g, ca. 13 mmol) obtained by chromatography after two phase reaction at 0 °C (Table 2) were dissolved in light petroleum (b.p. 60 to 70 °C, 10 ml) and stirred for 1 h at 50 °C with a solution of *p*-toluenesulfonic acid (2.4 g, ca. 13 mmol) in water (5 ml). After usual work up by chromatography an olefinic fraction (1.09 g, 55%) and a polar fraction (0.72 g, 30%) were isolated. The composition of olefins was determined by ^{1}H NMR-GC **4**:**5**:**6**:**8** = 9.8:1:3.8:4. Traces of a further olefin were formed [90 MHz ^{1}H NMR ($CDCl_3$): δ = 5.00 – 5.19]. 1- and 2-(1,2,3-Trimethyl-2-butenyl)-1,3-cyclopentadienes (**8a, b**) were identified by the characteristic signals and chemical shifts of the saturated protons attached to C-5 of the ring: 90 MHz ^{1}H NMR ($CDCl_3$): δ = 2.73 – 2.80 (q) and 2.80 – 2.93 (q) (cf. Scheme 5).

Scheme 5. Characteristic Chemical Shifts and Splitting Patterns of Allylcyclopentadienes



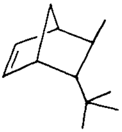
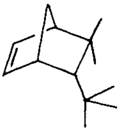
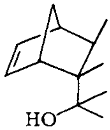




	13a, b[3]	**14a, b**[1]	**8a, b**
5-H$_2$	2.82-2.90 q	2.74-2.81 q	2.74-2.81 q
	2.90-2.98 q	2.81-2.93 q	2.81-2.93 q
2'-H	5.22-5.44	4.93-5.16	–

Bicyclic alcohol **17**: Tentative identification. The polar alcohol fraction from the reaction at 50 °C contained reproducible peaks of an alcohol with chemical shifts and line shapes characteristic for norbornenyl derivatives. 90 MHz ^{1}H NMR (CDCl$_3$): inter al. δ = 2.39, 2.87 (bridgehead protons). In solvent DMSO the olefinic protons of two alcohols (ratio 2.6: 1) were also discernible, the major alcohol **17** showing signals at 6.02, 6.22 ppm.

Scheme 6. Chemical Shifts of Bridgehead (1-H, 4-H) and Olefinic Protons (2-H, 3-H) in Norbornenylcarbinols (Solvent CCl$_4$)

Protons	Chemical Shift δ		
1-H, 4-H	2.84, 2.34	2.87, 2.24	2.87 2.39
2-H, 3-H	6.03, 6.20	6.17	6.02 6.22
			
	15[1]	**16**[3]	**17**

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[18/81]
