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Cycloadditions of Allyl Cations, 27[1)]

Dehydrative Cyclodimerization of 4-Methyl-3-penten-2-ol in Two Phases. One-Pot Preparation of Dimethylated Limonenes and α-Terpineol

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Cycloadditionen von Allyl-Kationen, 27[1)]

Dehydrative Cyclodimerisierung von 4-Methyl-3-penten-2-ol in zwei Phasen

Dehydrative Eintopfcyclodimerisierung von 4-Methyl-3-penten-2-ol (**1**) in einem Gemisch aus wäßriger Toluolsulfonsäure/Kohlenwasserstoff gibt dimethylierte Limonene **2a** und **c** sowie dimethyliertes α-Terpineol **3**.

In studying reactions of allyl alcohols in dilute aqueous sulfonic acid/hydrocarbon media we have noted earlier the formation of dimeric dienes. These dimers are olefinic hydrocarbons which arise by dehydrative dimerization of allyl alcohols. Dimeric dienes can be monocyclic dienes and also acyclic trienes depending on the experimental conditions. Sometimes their formation has competed with intended cross combinations of allyl cations and conjugated dienes, but dehydrative dimerization can also be put to good synthetic use, for example in the preparation of 3,3,5,5-tetramethyllimonene from 2,4-dimethyl-3-penten-2-ol[2)]. We here describe the dehydrative one-pot cyclodimerization of 4-methyl-3-penten-2-ol (**1**).

The experimental conditions were very simple: allyl alcohol **1** was stirred in a medium of dilute aqueous toluenesulfonic acid and hydrocarbon solvent at 0 and 25 °C (Table 1).

The reaction mixture was worked up by chromatography on silica gel, giving a nonpolar fraction of olefinic products and a more polar fraction containing alcohols as well as allyl ethers. The diastereoisomeric allyl ethers **4a**, **b** were formed mainly at 0 °C (entries 1 – 3). At room temperature the major fraction was nonpolar and consisted of a simple mixture of three dimeric dienes $C_{12}H_{20}$ in a ratio of **2a**:**2b**:**2c** = 17:9:74. The major isomer **2c** was identified by ^1H

Scheme 1. Acid Catalyzed Reactions of **1** in Aqueous Toluenesulfonic Acid/Light Petroleum

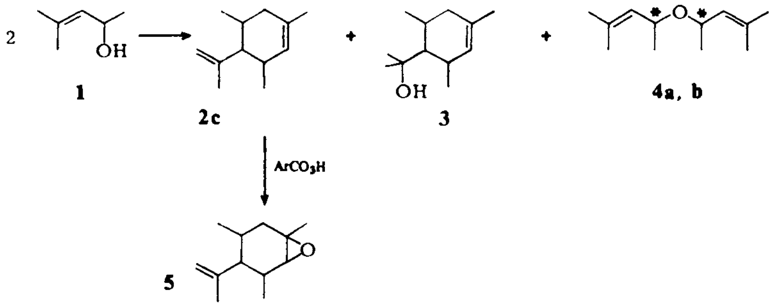

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Table 1. Dehydrative Dimerization of 4-Methyl-3-penten-2-ol (**1**) in Aqueous Toluenesulfonic Acid/Light Petroleum at 0 °C and Room Temperature (RT)

Entry	Educt **1** (g)	Temperature (°C)	Reaction time (h)	Dimeric dienes $C_{12}H_{20}$ (g)	(%)	Polar Products (g)	(%)
1	2.5	0	7	0.29	14	1.00	44[a]
2	2.5	0	1	0.26	13	1.00	44[a]
3	2.5	0	1	0.20	10	0.80	35[a]
4	5.0	RT	24	1.76	43	0.94	27[b]
5	5.0	RT	24	2.05	50	0.46	11[b]
6	5.0	RT	24	1.86	45	0.59	13[c]
7	2.5	60 – 70	3	1.32	64		
8	2.5	ca. 40	1	0.76	37	0.86	38

[a] Mainly allylic ether **4**. – [b] Mixture of products containing inter al. ether **4**, alcohol **3**. – [c] Complex mixture products (GC-MS) containing **3** and other alcohols (IR: OH band).

NMR, GC-MS, and microanalysis as 3,5-dimethyllimonene. GC-MS showed an almost identical mass spectrum (Table 2, below) for isomers **2a** and **2c**: the characteristic base peak at $M^+/2 = 82$ is due to a retro-Diels-Alder reaction and corresponds to the base peak of $M^+/2 = 96$ of 3,3,5,5-tetramethyllimonene[2]. Thus, **2a** and **c** can be assumed to have a very similar constitution and are probably diastereoisomers. The third and minor olefinic isomer **2b** (9% of nonpolar products) has the same GC retention time as the main product **2c** on a SE 30 column. Its structure is unknown at present. Epoxidation of **2c** to give **5** was faster and gave higher yields than that of 3,3,5,5-tetramethyllimonene[2] which has a more hindered trisubstituted double bond.

The mixture of alcohols in the polar fraction of the product was complex (GC). The dimethylated α-terpineol **3** was formed amongst a number of isomers. Apparently, these alcohols are formed preferentially in the temperature range of 25 – 35 °C by hydration of the olefins.

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Experimental Part

Acid Catalyzed Dehydrative Dimerization of 4-Methyl-3-penten-2-ol (**1**) *in Two Phases:* A solution of **1**[3] (2.5 – 5.0 g, 25 – 50 mmol) in light petroleum (b.p. 40 – 60 °C, 5 ml) is stirred with a solution of toluenesulfonic acid (2.4 g, ca. 13 mmol) in water (5 ml) at 0 °C and room temperature. After the specified time (Table 1) the reaction mixture is worked up by neutralizing with a solution of aqueous $NaHCO_3$, separating the organic phase, and twice extracting the aqueous layer with light petroleum. The collected organic phase is washed with water, dried (Na_2SO_4), and the solvent is removed to leave an oil which is chromatographed on silica gel (20 g, 0.05 – 0.2 mm, Macherey-Nagel). Elution with pentane gave three isomeric $C_{12}H_{20}$ olefins **2a**, **b** and **c** in a ratio of 17 : 9 : 74, as determined by GC-MS (cf. Table 2). On a SE 30 column only two peaks for **2a** and **2b** + **2c** were discernible. The major isomer was:

4-Isopropenyl-1,3,5-trimethylcyclohexene (**2c**): 90 MHz ^1H NMR (CCl_4): δ = 0.80 (d, J = 7 Hz, 6 H), 1.60 (m, 3 H), 1.71 (m, 3 H), 1.60 – 2.40 (m, 5 H), 4.54 – 4.63 (m, 1 H), 4.82 – 4.93 (m, 1 H), 5.23 – 5.40 (m, 1 H).

$C_{12}H_{20}$ (164.3) Calcd. C 87.73 H 12.27 Found C 87.84 H 12.60

Table 2. GC-MS Spectra of Dimeric Dienes **2a, b, c**

Mass number	**2a**	**2b**	**2c**	Mass number	**2a**	**2b**	**2c**
	(17 :	9 :	74%)		(17 :	9 :	74%)
M^+ 164	15	16	10	93	–	30	–
149	8	13	8	91	13	26	10
135	3	9	3	82	100	50	100
121	39	100	35	81	–	44	–
107	24	73	18	79	10	18	8
105	9	18	4	77	8	18	8
96	–	34	–	67	60	78	68

Elution with pentane/ether (10 vol%) gave two diastereoisomeric allyl ethers (GC: APL column 1 : 1) (0.42 – 0.55 g, 18 – 24%, from 25 mmol experiments at room temperature and 0.80 – 1.00 g, 35 – 44%, from experiments at 0 °C), which were purified by distillation at the Kugelrohr.

Bis(1,3-dimethyl-2-butenyl) ether (**4a**): 90 MHz ^{1}H NMR (CCl_4): δ = 1.04 (d, J = 6.5 Hz, 6H), 1.56 (m, 6H), 1.71 (m, 6H), 4.10 (q, J = 6.5 Hz, 2H), 4.79 – 5.10 (m, 2H).

Diastereoisomer **4b**: 90 MHz ^{1}H NMR (CCl_4): δ = 1.06 (d, J = 6.5 Hz, 6H), 1.60 (m, 6H), 1.71 (m, 6H), 4.01 (q, J = 6.5 Hz, 2H), 4.79 – 5.10 (m, 2H). – MS (70 eV): *m/e* = 167 (4%, M^+ – 15), 99 (13), 83 (100).

$C_{12}H_{22}O$ (182.3) Calcd. C 79.06 H 12.16 Found C 79.05 H 12.12

Further chromatography and GC-MS showed a complex mixture of alcohols. – 90 MHz ^{1}H NMR (CCl_4): δ = 0.90 – 1.33 (12H), 1.56 – 1.72 (3H), 1.33 – 2.52 (5H), 4.78 – 5.50 (1H); the signals of the OH protons were obscured, but in solvent DMSO singlets at 3.85 (main product), and 3.96 ppm (ratio ca. 4 : 1) were observed. The major alcohol was

α,α,2,4,6-Pentamethyl-3-cyclohexene-1-methanol (**3**): 90 MHz ^{1}H NMR (CCl_4): inter al. δ = 0.94 (d, J = 7 Hz, 6H), 1.27 (s, 6H), 1.59 [m, 3H, $=C(CH_3)$], 5.17 – 5.31 (m, 1H). – MS (70 eV): *m/e* = 182 (1%, M^+), 167 (3), 164 (7), 121 (30), 109 (30), 105 (24), 91 (20), 85 (23), 83 (32), 82 (31), 41 (100).

$C_{12}H_{22}O$ (182.3) Calcd. C 79.06 H 12.16 Found C 78.98 H 12.39

4-Isopropenyl-1,3,5-trimethyl-7-oxabicyclo[4.1.0]heptane (**5**): A mixture of dimeric dienes **2a, b, c** (1.64 g, 10 mmol) was epoxidized as described previously[2], giving a colorless oil (1.66 – 1.74 g, 92 – 97%). – 90 MHz ^{1}H NMR (CCl_4): δ = 0.74 – 0.97 (several d, 6H), 1.26 (s, 3H), 1.64 – 1.78 (m, 3H), 1.52 – 2.32 (m, 5H), 2.56 – 2.87 (several d (?), 1H), 4.39 – 4.97 (m, 2H). – Chromatography gave a major isomer **5**: 90 MHz ^{1}H NMR (CCl_4): δ = 0.90 (d, J = 7 Hz, 6H), 1.26 (s, 3H), 1.71 (m, 3H), 1.52 – 2.32 (m, 5H), 2.77 (d, J = 2.5 Hz, 1H), 4.39 – 4.60 (m, 1H), 4.87 – 4.97 (m, 1H). – MS (70 eV): *m/e* = 180 (< 1%, M^+), 165 (13), 162 (3), 151 (20), 147 (14), 138 (23), 137 (35), 123 (36), 109 (34), 107 (70), 95 (68), 83 (32), 82 (32), 81 (47), 77 (94), 43 (100).

$C_{12}H_{20}O$ (180.3) Calcd. C 79.94 H 11.18 Found C 80.45 H 11.19

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[1] Part 26: *H. Vathke-Ernst* and *H. M. R. Hoffmann*, Chem. Ber. **114**, 1464 (1981).

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